

**Evaluation of Waste Release Testing Results against
the Tank Farm Performance Assessment Waste
Release Model**

November 2018

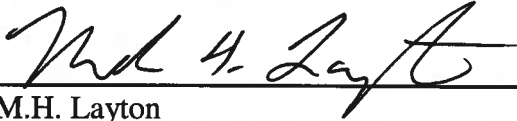
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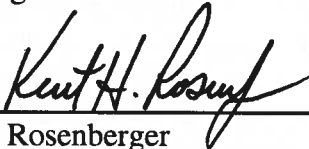
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EXECUTIVE SUMMARY

An experimental plan was developed in FY2013 to provide additional information regarding the residual waste solubility values documented in the Waste Release Model (WRM) supporting the F-Area Tank Farm (FTF) and H-Area Tank Farm (HTF) Performance Assessments (PA). The experiment, referred to as waste release testing, was performed in two parts. The first part of the waste release testing was the development of the test plan and analytic methods. These analytic methods would be used to test the solubility of various elements of interest under various simulated grouted waste tank chemistry conditions. The elements of interest for initial testing included plutonium (Pu), neptunium (Np), uranium (U), and technetium (Tc). The second part of the waste release testing was conducting the tests with residual waste simulants and actual residual waste samples. Through FY2018 waste testing has been performed on actual residual waste from Waste Tanks 18F and 12H.

The solubilities of Pu, Np, U, and Tc were tested under simulated waste tank chemistry conditions using Tank 18F and Tank 12H residual waste samples, with I also being tested using the Tank 12H residual waste samples. Data was collected via measured concentrations (or solubilities) over a multiple week testing period under different chemical conditions (pH and E_h were varied). The chemical conditions reflect a range of states such that the test results can be used to better understand the impact of transitory waste tank chemical conditions on solubility. The measured solubilities for the tested elements are consistent for the residuals from both Tanks 18F and 12H, with the Tank 12H solubilities tending to be less soluble. The experimental results indicate there may be some variance from the actual waste solubilities and the WRM assigned solubilities. For example, Np and I was in all cases more insoluble than assigned in the TF WRM. The results indicate that I-129 in the Tank 12H residual waste sample is relatively insoluble, under both reduced and oxidized conditions, compared to the WRM which conservatively assumed no solubility control for iodine. The other three elements – Pu, Tc and U - appeared in most instances to be potentially more soluble than was assumed in the WRM. For example, Pu was relatively insoluble when oxidized, but was still more soluble than calculated by the WRM. As demonstrated in Section 4, even if the experimental results were conservatively accepted into the PA WRM, the newly assigned solubilities would have a negligible impact on peak doses in 1,000 or 10,000 years. Because replacing the WRM values associated with Pu, Tc, U and Np does not significantly impact FTF and HTF PA conclusions, there is no immediate need to update the current model to incorporate the waste release testing data. If the Tank 12H derived iodine solubility values were used in the PA model the HTF peak dose within 10,000 years would decrease significantly. The new waste release data can be integrated into the next revision to the FTF and HTF PAs.

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ACRONYMS/ABBREVIATIONS

AD	Analytical Development
ADMP	Advanced Design Mixer Pump
CC	Calcium Carbonate
CFR	Code of Federal Regulations
CFS	Cement, Fly Ash, and Slag
CSR	Chemical Sludge Removal
CZ	Contamination Zone
DI	deionized
DOE	U.S. Department of Energy
DWPF	Defense Waste Processing Facility
ECC	Enhanced Chemical Cleaning
EPD	Electronic Personal Dosimeter
FTF	F-Area Tank Farm
FY	Fiscal Year
HM	H-Modified
HTF	H-Area Tank Farm
GSA	General Separations Area
GWB	Geochemist's Workbench
HHW	High Heat Waste
HLW	High Level Waste
I	Iodine
IC	Ion Chromatography
ICM	Integrated Conceptual Model
ICP-ES	Inductively Coupled Plasma Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma Mass Spectroscopy
IHI	Inadvertent Human Intruder
ID	inner diameter
LWTRSAPP	Liquid Waste Tank Residuals Sampling and Analysis Program Plan
MSR	Mechanical Sludge Removal
MOP	Member of Public
NA	not applicable
NDAA	Ronald W. Reagan National Defense Authorization Act for Fiscal Year 2005
NEA	Nuclear Energy Agency
Np	Neptunium
NRC	U.S. Nuclear Regulatory Commission
NSC	No solubility control
OA	Oxalic Acid

OD	outer diameter
ORII	Oxidized Region II
ORIII	Oxidized Region III
ORP	Oxidation-Reduction Potential
PA	Performance Assessment
Pu	Plutonium
PUREX	Plutonium Uranium Extraction
PVDF	polyvinylidifluoride
RRII	Reduced Region II
SA	Special Analysis
SIW	Synthetic Infiltration Water
SLDR	Sample Location Determination Report
SRNL	Savannah River National Laboratory
Tc	Technetium
TER	Technical Evaluation Report
TF	Tank Farm
TFA	Tanks Focus Area
THOREX	Thorium Extraction
TIC	Total Inorganic Carbon
TSAP	Tank-Specific Sampling and Analysis Plan
TTA	thenoyltrifluoroacetone
U	Uranium
WCS	Waste Characterization System
WRM	Waste Release Model

1.0 INTRODUCTION

The primary purpose for waste release testing is related to the ongoing assessment and enhancement of the F-Area Tank Farm (FTF) and H-Area Tank Farm (HTF) Performance Assessment (PA) per the requirements of U.S. Department of Energy (DOE) Manual 435.1-1, *Radioactive Waste Management Manual*. [DOE M 435.1-1] Testing of actual waste tank residuals provides data to strengthen the Tank Farm (TF) Waste Release Model (WRM). The WRM was originally created in support of the FTF PA (SRS-REG-2007-00002), as documented in the report *Conceptual Model of Waste Release from the Contaminated Zone of Closed Radioactive Waste Tanks* (WSRC-STI-2007-00544). The WRM was updated for the HTF PA (SRR-CWDA-2010-00128), as documented in the report *Evolution of Chemical Conditions and Estimated Solubility Controls on Radionuclides in the Residual Waste Layer during Post-Closure Aging of High-Level Waste Tanks* (SRNL-STI-2012-00404).

Obtaining experimental data in support of the TF WRM will help reduce the uncertainty associated with the WRM outputs (i.e., solubility values) utilized in the TF PA fate and transport modeling. In addition, waste release testing is relevant to key U.S. Nuclear Regulatory Commission (NRC) monitoring factors identified in the NRC Monitoring Plan and the FTF and HTF Technical Evaluation Reports (TERs). [ML15238A761, ML112371715, ML14094A496]

Through the Ronald W. Reagan National Defense Authorization Act for Fiscal Year 2005 (NDAA) Section 3116(a) (NDAA_3116) consultation process, the NRC observed that uncertainties associated with the FTF PA doses might prevent DOE from meeting performance objectives, particularly with regard to plutonium-related modeling assumptions. The NRC staff's primary concern was that the timing of the FTF PA peak dose (i.e., the groundwater pathway peak dose) could be shifted into their period of performance (10,000 years) if certain modeling assumptions were incorrect. The peak dose of concern was principally associated with the residual Pu-239 inventory in Tank 18F. The NRC's TER recommended that DOE provide additional experimental support for waste release modeling assumptions. The experimental support would reduce the uncertainty surrounding PA waste release modeling assumptions that, if found to be significantly non-conservative, could result in this peak dose shifting into a 10,000-year performance period. The TER designated the performance of waste release testing as a key monitoring factor and highlighted the need for continued research in this area. [NDAA-3116, ML112371715]

An experimental plan for waste release testing was developed in Fiscal Year (FY) 2013. The waste release testing would provide additional information regarding the residual waste solubility assumptions used in the FTF and HTF PA waste release models. The waste release testing was performed in two parts. The first part of the waste release testing was the development of the test plan and analytic methods. These analytic methods were used to test the solubility of plutonium (Pu), neptunium (Np), uranium (U), and technetium (Tc) under various simulated waste tank chemistry conditions. These four elements were tested because their associated peak dose (as modeled in the TF PAs) had been shown to have some uncertainty regarding solubility, were expected to be sensitive to solubility, and had the potential to impact overall peak doses. The second part of the waste release testing was conducting the tests with residual waste simulants/surrogates and actual residual waste samples. The first part of the waste release testing was completed in FY2013 and demonstrated that the proposed testing was feasible. [SRNL-RP-2013-00203]

Waste release testing using residual waste simulants (i.e., surrogates) was initiated in FY2014 and the results were documented in *Determining the Release of Radionuclides from Tank Waste Residual Solids* (SRNL-STI-2014-00456). Based on their findings, the authors recommended that leachate testing with non-radioactive surrogate residual materials be continued and finalized prior to initiating testing with actual residual waste samples, which would contain radioactive materials. Testing with actual waste tank residuals would be expected to provide additional information regarding the residual waste solubility assumptions used in the FTF and HTF PA waste release models.

Waste release testing was performed in FY2015 in the areas of grout pore water development and testing of surrogates for the waste tank residual solids. Grout pore water, or pore fluid, is defined as the infiltrating groundwater exposed to the reducing grout fill material and the residual waste solids layer within the closed waste tank environment. The FY2015 waste release testing provided a methodology for developing grout pore water that has certain chemical conditions (i.e., E_h and pH) representative of the local groundwater in the presence of grout. The three pore water chemical conditions are defined as Reduced Region II (RRII), Oxidized Region II (ORII), and Oxidized Region III (ORIII). The pore water development also included testing to understand and control the stabilities of ORII and ORIII. The surrogate solids testing looked at the concentration of elements in the leachate (the pore fluid that now contains dissolved solids) under the various pore fluid chemical conditions. The testing compared the measured element concentrations to predicted trends for the oxidized elemental concentrations. The surrogate residual solids testing used a controlled atmosphere with both zero-head space and open-head space with O_2 and CO_2 as purge air for ORII and ORIII chemical conditions. The results of the FY2015 waste release testing was documented in SRNL-STI-2015-00446, *Determining the Release of Radionuclides from Tank Waste Residual Solids: FY2015 Report*, in anticipation of waste release testing with actual residual waste samples in FY2016.

Testing of actual residual waste with a Tank 18F residual waste sample was performed in FY2016 using the methodologies developed in FY2015. The waste release testing used a continuous purge and controlled atmosphere for oxidized state testing using CO_2 -stripped air and air purges to achieve conditions similar to those observed with the surrogate residual solids. Since the FY2016 waste release testing used actual residual waste, final development and installation of test equipment in the Savannah River National Lab (SRNL) shielded cells was required before beginning any testing. The results of the FY2016 waste release testing are documented in *Determining the Release of Radionuclides from Tank Waste Residual Solids: FY2016 Report* (SRNL-STI-2016-00432).

Testing of a Tank 12H residual waste sample was performed in FY2018 using the same basic methodology used for the Tank 18F residual waste testing, with some minor changes made to incorporate lessons learned. The Tank 12H testing was expanded to include iodine (I) in addition to Pu, Np, U, and Tc, since the HTF PA peak dose in 10,000 years is driven by I-129. The test setup modifications and the Tank 12H waste release testing results are documented in *Determining the Release of Radionuclides from Tank 12H Waste Residual Solids Following Tank Closure* (SRNL-STI-2018-00484).

2.0 TANK CLOSURE WASTE RELEASE MODELING

As stated previously, the waste release testing was performed to provide additional information regarding the residual waste solubility values documented in the TF WRM, which is a fundamental part of the Integrated Conceptual Model (ICM) used in the FTF and HTF PAs. [SRS-REG-2007-00002, SRR-CWDA-2010-00128] The following sections provide more details on the WRM and its role in the ICM.

2.1 Waste Release Model Development

The FTF and HTF PA ICMs simulate radiological and chemical contaminant release from the waste tanks. An independent conceptual WRM was used to simulate stabilized contaminant release from the grouted waste tanks based on various chemical conditions in the waste tank which control solubility and thereby affect the timing and rate of release of contaminants from the residual waste layer (designated as the contamination zone (CZ) in the TF PA modeling). The current TF WRM is described throughout this section and is explained in detail in *Evolution of Chemical Conditions and Estimated Solubility Controls on Radionuclides in the Residual Waste Layer during Post-Closure Aging of High-Level Waste Tanks* (SRNL-STI-2012-00404).

2.2 Waste Release Model

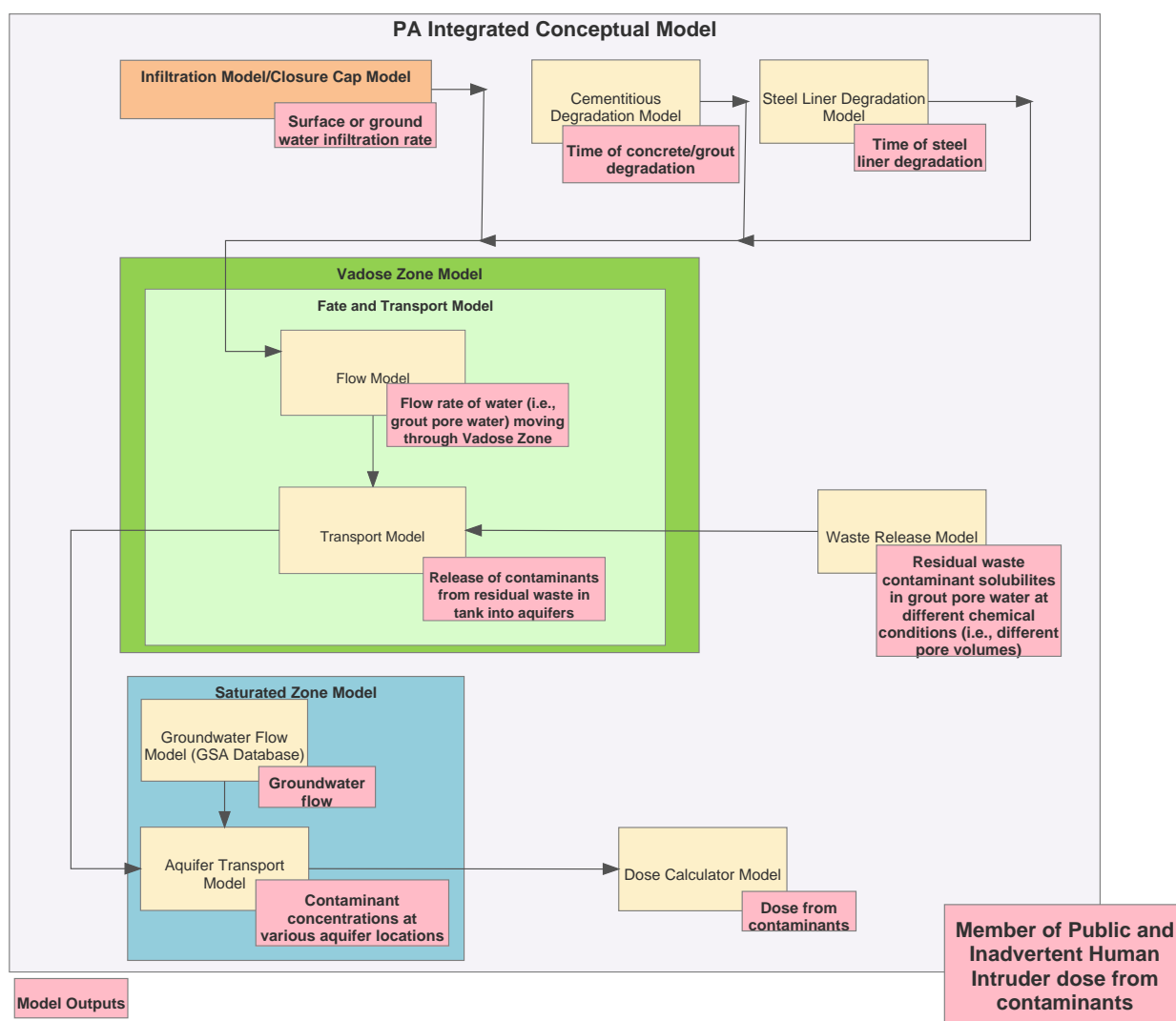
2.2.1 The Role of the Waste Release Model in the PA Integrated Conceptual Model

Release of contaminants from residual waste remaining in closed waste tanks will depend on the chemical composition of grout pore water (or pore fluids) passing through the residual waste layer. The composition of these fluids will vary, causing solubilities of key elements to vary, as infiltration water flows through the waste tank reducing grout. The WRM is a geochemical model that uses chemical thermodynamics and chemical kinetics to analyze the chemical reactions between the grout pore water and the residual waste layer. The WRM enables a fate and transport model with limited chemical capabilities to simulate these reactions. Figure 2.2-1 is a simplified diagram displaying how the WRM interacts with the other models in the ICM. The pink boxes indicate the various output data from each model. As seen on Figure 2.2-1, the WRM provides the residual waste layer contaminant solubilities (i.e., concentrations) in the grout pore water under different chemical conditions.

The simplifications that allow implementation of the WRM are documented and discussed in the TF PAs. In the most general sense, the WRM assumes that the residual waste remains as a discrete layer at the bottom of the waste tanks after they are filled with reducing grout. Water infiltration from the surface or groundwater that passes through the waste tanks interacts with the reducing grout driving changes to grout mineralogy and causing fluids (i.e., grout pore water) emerging from the grout into the residual waste layer to have a composition that reflects these interactions. Release of contaminants from the waste tanks is controlled primarily by solubility of assumed contaminant-bearing solid phases in the varying pore fluid composition. Hence, this WRM imposes chemical constraints on contaminant release that vary as the reducing grout changes over time (Note, these changes are typically referred to as “degradation” in this context). Varying physical controls such as hydraulic conductivity can be imposed by the fate and transport model that draws input from the WRM.

Development of the WRM was done in two stages, the modeling of the reducing grout degradation (utilizing the Cementitious Degradation Model which is also used as input to the fate and transport model) and the estimation of solubilities of 27 elements at various chemical conditions. Of the 27 elements, neptunium, plutonium, technetium, and uranium were initially considered the most likely to impose a risk to meeting Member Of Public (MOP) and Inadvertent Human Intruder (IHI) dose performance objectives based on process knowledge and previous PA modeling. These elements were given extra attention in the development of the WRM.

Figure 2.2-1: Simplified Diagram of PA ICM

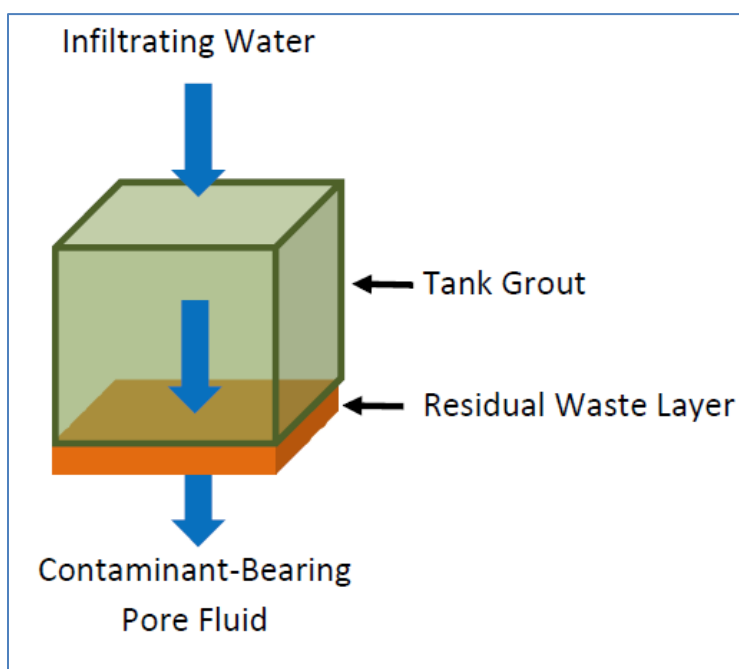


2.2.2 The PA Waste Release Model Description

As discussed previously, the current TF WRM is explained in detail in *Evolution of Chemical Conditions and Estimated Solubility Controls on Radionuclides in the Residual Waste Layer*

during *Post-Closure Aging of High-Level Waste Tanks* (SRNL-STI-2012-00404). Figure 2.2-2 shows a WRM diagram depicting the conceptual model of waste release from waste tanks. Water infiltrating through the cover system enters the reducing grout, reacts with grout minerals, and ultimately passes through the residual waste layer beneath the grout. As reactions in the grout progress and minerals dissolve or precipitate, the pore water chemistry exiting the grout changes. The changing pore water chemistry passing through the residual waste layer results in varying solubility limits of residual waste contaminants.

Figure 2.2-2: Conceptual Model of Pore Water Evolution and Contaminant Dissolution from the Residual Waste Layer



The conceptual model treats the waste tank reducing grout as a porous medium. It is recognized that fracturing could lead to heterogeneous flow patterns and that “fast” flow paths might occur within the waste tank. Yet, there is very little certainty about the nature and effects of fracturing over the thousands of years of waste tank aging. In particular, there is uncertainty surrounding the extent to which water passing through fractures interacts with the reducing grout and, importantly, how water that reaches the residual waste layer through a fracture interacts with that layer. The differing effects of fractures and fast flow paths are addressed in sensitivity analyses within the PA using information selected from the WRM and implemented with the fate and transport modeling.

The Geochemist’s Workbench (GWB) software was used for the WRM. The WRM simulates the major changes in pore fluid chemistry by modeling infiltrating fluid passing through a hypothetical 1 cubic meter block of waste tank grout. Each pore fluid volume that enters the grout block completely replaces the previous reacted pore fluid volume. This results in a reaction path model in which each pore fluid volume of reacting fluid changes the mineralogy of the grout. The changes are reflected in the chemical composition of the pore fluid exiting the grout. The nature of this type of modeling produces step changes in the major chemical

conditions of interest such as E_h and pH. These occur when a mineral that exerts the dominant control on a parameter is completely dissolved from the grout into the pore fluid. Minor changes in these parameters may occur when a previously stable mineral begins to dissolve or a mineral begins to precipitate.

Simulations of the evolution of the waste tank reducing grout chemical conditions (E_h and pH) were run and documented in the WRM technical report (SRNL-STI-2012-00404). Figures 2.2-3 and 2.2-4 show the evolution of E_h and pH in the pore fluids eluting from the waste tank reducing grout over 2,500 pore volumes. Figure 2.2-5 shows the evolution of the mineralogy of the reducing grout that dictates the pH and E_h transitions. A nomenclature modified to include redox aspects of the reducing grout is used to describe the chemical conditions of the waste tank reducing grout. The reducing grout evolves through three distinct regions beginning with RRII (Figure 2.2-3). [SRNL-STI-2012-00404]

Figure 2.2-3: E_h Evolution during Simulated Grout Aging

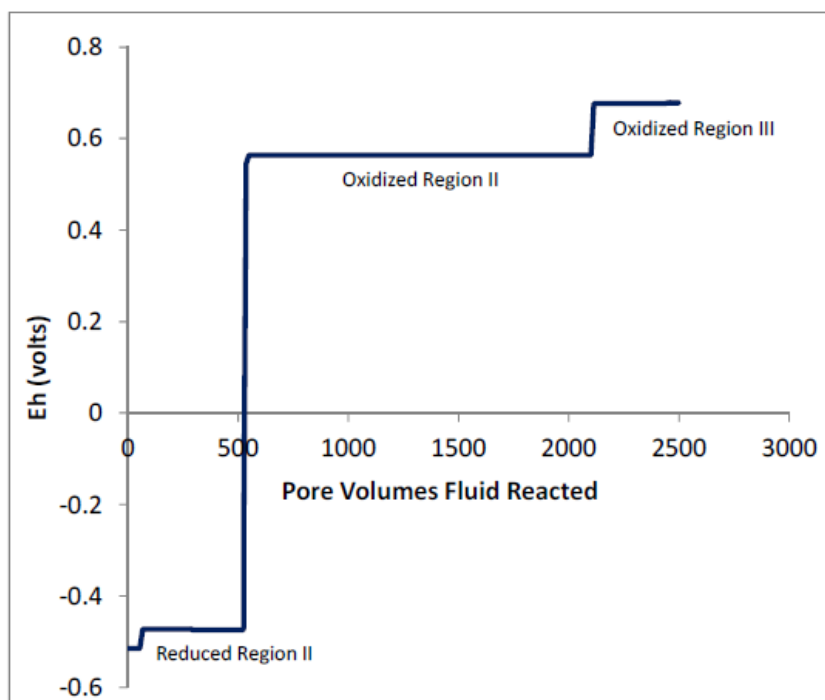


Figure 2.2-4: pH Evolution during Simulated Grout Aging

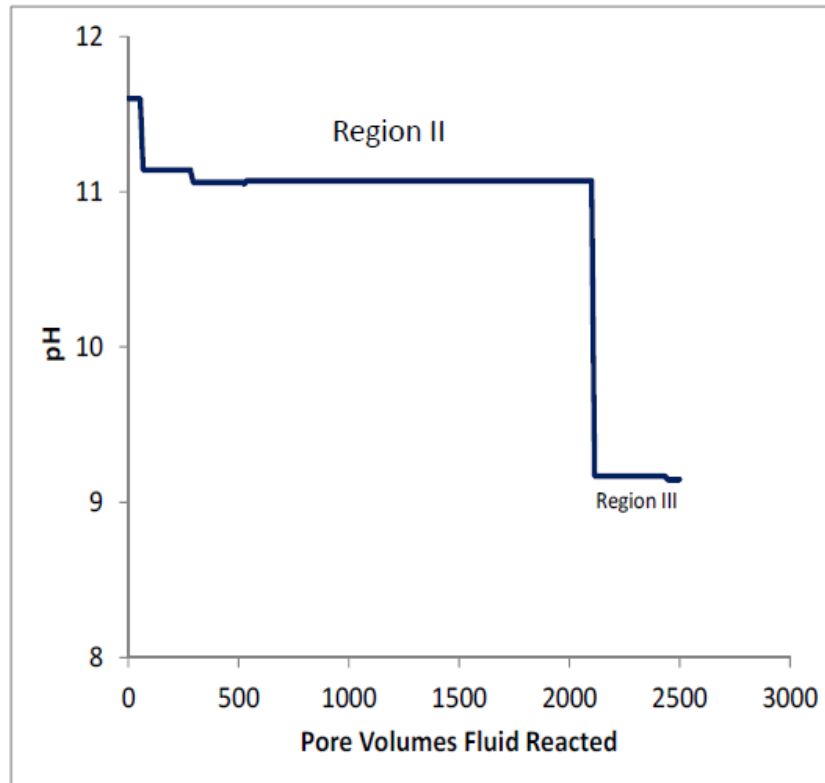
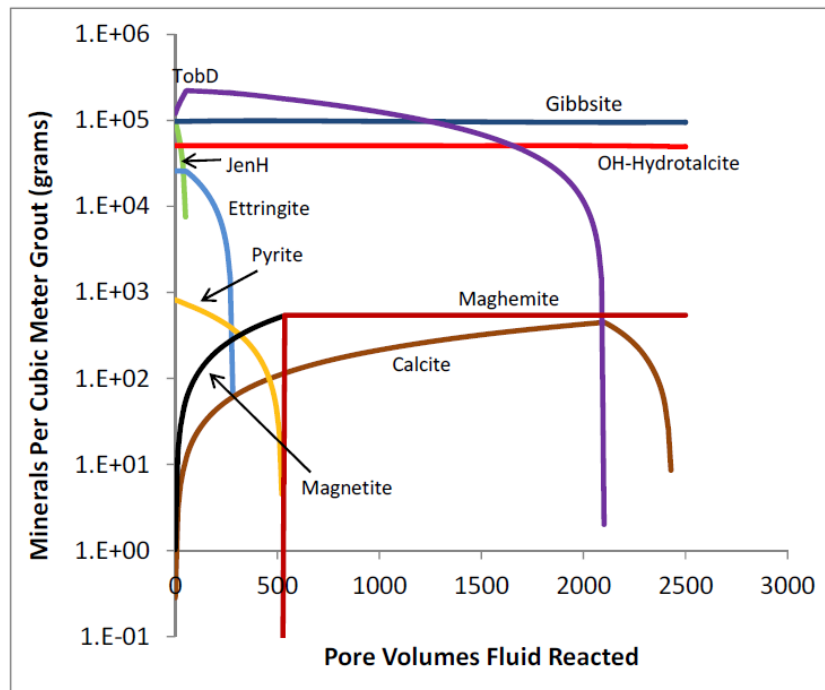


Figure 2.2-5: Simulated Evolution of Mineralogy in Waste Tank Grout



The simulation results provide the basis for choosing chemical conditions for calculating the solubility of various elements throughout the PA modeling period. These chemical conditions in the reducing grout pore water are shown in Table 2.2-1.

Table 2.2-1: Chemical Conditions of the Reducing Grout Pore Water

Chemical Condition	E_h (v)	pH	Calcium (molar)	Total Carbonate (molar)
Reduced Region II	-0.47	11.1	4.0E-03	6.7E-07
Oxidized Region II	+0.56	11.1	4.0E-03	6.9E-07
Oxidized Region III	+0.68	9.2	6.6E-05	7.5E-05

2.2.3 Solubility Estimates Used in the PA Modeling

As part of the WRM, solubility estimations were performed using GWB and documented in the WRM technical report (SRNL-STI-2012-00404). This involved selecting an appropriate thermodynamic database, selecting an appropriate solubility-controlling phase for each element, and then equilibrating these phase(s) with the applicable grout pore fluid compositions. [SRNL-STI-2012-00404]

For the elements americium, nickel, neptunium, plutonium, uranium, technetium, and thorium, thermodynamic data for aqueous hydroxyl and carbonate complexes, as well as appropriate solid phases, were obtained by direct download from the Nuclear Energy Agency (NEA). The NEA is part of the Organization for Economic Co-Operation and Development and has published several thorough reviews of thermodynamic data and compiled internally consistent traceable datasets. The data was converted to a format suitable for use by the GWB software using the Gibbs free energies of the solids and aqueous complexes of interest and their associated components to calculate LogK values for dissociation constants. These were entered into the “thermo_phreeqc” database available with GWB. For the other elements, the thermodynamic database available from the Japanese Atomic Energy Agency was used. It uses NEA data for some elements but includes many more elements than the Nuclear Energy Agency database. The Japanese Atomic Energy Agency database is also well reviewed, internally consistent, and traceable. For a few specific calculations, other sources of thermodynamic data were used and these are noted in the WRM Report as applicable. [SRNL-STI-2012-00404]

Selecting Solubility Controlling Phase

A fundamental part of establishing solubility controlled waste release concentrations is the selection of a solubility-controlling phase for each element. For some of the elements of interest there are studies in the literature that can guide selection of solubility controls. For other elements, selection of solubility controlling phases (i.e., chemical forms) was generally conservative, meaning that where multiple phases of an element were possible, selection was biased toward higher solubilities.

Two factors that determine the solubility of a phase are the composition and the structure of the phase. For phases with the same composition, amorphous forms usually have higher

solubilities than crystalline forms. Thus, where thermodynamic data existed, the amorphous forms were selected for solubility controls. For most, hydroxides were chosen over oxides because the hydroxide of an element usually has a higher solubility than the oxide. Carbonate phases were selected for strontium, calcium, and some trivalent species under relatively high carbonate conditions. Carbonate phases normally precipitate easily from solution and their occurrence in the grouted waste tanks was considered plausible.

The selection of solubility controlling phases followed a general process. For each element, the process began with an examination of the literature for occurrence of a stable phase with reliable thermodynamic data at conditions prevalent in the waste tanks or cementitious systems. If one was found, it was selected. If none was found, a list of other phases that contain components found in the waste tanks and having reliable thermodynamic data was assembled. The stability fields of these phases were examined and phases stable at conditions corresponding to those of the WRM were retained. If there were appropriate geologic or industrial process analogues cited in the literature, they were considered. Examples are radium sulfate and strontium carbonate. If there were no analogues cited in the literature, but the hydroxide was stable, it was retained. If reliable thermodynamic data was available for the amorphous hydroxide then it was selected. The process attempted to balance scientific knowledge with the need to be cautious and biased toward higher solubilities.

Solubility Estimation

As part of the WRM, solubility estimates for various elements were calculated by equilibrating a selected solubility-controlling phase with the composition of the grout pore fluid representing each chemical condition. For relatively soluble elements (i.e., greater than $1\text{E-}05$ mol/L), a different approach was used for calculating solubilities. Rather than equilibrating a solubility-controlling phase with a grout pore fluid composition, the element was added to the grout pore fluid composition until saturation with a controlling phase was reached. In the waste tank reducing grout chemical condition evolution simulations, the E_h at oxidizing conditions is controlled by equilibrium with the dissolved oxygen. Yet, E_h values of natural waters are rarely in equilibrium with dissolved oxygen despite being exposed to oxygenated groundwater for thousands of years. This may be due to predominantly slow reaction kinetics for oxidation by dissolved oxygen. E_h values of + 0.24 and + 0.29 volts were assumed for ORII and ORIII. [SRNL-STI-2012-00404]

Estimated Solubilities

Table 2.2-2 shows solubility values and controlling phases for all of the elements of interest at each of the reducing grout pore water chemical conditions defined in Table 2.2-1. The solubility values presented in Table 2.2-2 are those calculated by the WRM and are used as inputs in the PA fate and transport model. [SRNL-STI-2012-00404]

Table 2.2-2: Calculated Solubility and Controlling Phases for Elements of Interest

Element	Reduced Region II		Oxidized Region II		Oxidized Region III	
	Controlling Phase	Solubility (mol/L)	Controlling Phase	Solubility (mol/L)	Controlling Phase	Solubility (mol/L)
Ac	Ac(OH) ₃ (am)	1E-09	Ac(OH) ₃ (am)	1E-09	Ac(OH) ₃ (am)	6E-08
Am	Am(OH) ₃ (am)	1E-09	Am(OH) ₃ (am)	1E-09	AmCO ₃ OH·0.5H ₂ O	2E-09 ^c
Ba	BaSO ₄ (barite)	3E-05	BaSO ₄ (barite)	3E-05	BaSO ₄ (barite)	1E-05
Bk	Short half-life	-	Short half-life	-	Short half-life	-
C	CaCO ₃ (calcite)	2E-06	CaCO ₃ (calcite)	2E-06	CaCO ₃ (calcite)	1E-03
Cf	Small inventory	-	Small inventory	-	Small inventory	-
Cm	Cm(OH) ₃ (am)	1E-09	Cm(OH) ₃ (am)	1E-09	CmCO ₃ OH·0.5H ₂ O (c)	2E-09
Co	CoS (beta)	3E-02	No solubility control	-	No solubility control	-
Cs	No solubility control	-	No solubility control	-	No solubility control	-
Eu	Eu(OH) ₃ (am)	8E-07	Eu(OH) ₃ (am)	8E-07	EuOHCO ₃ (cr)	3E-08
I	No solubility control	-	No solubility control	-	No solubility control	-
Nb	No solubility control	-	No solubility control	-	No solubility control	-
Ni	NiS (c, alpha)	2E-09 ^a	Ni(OH) ₂ (beta)	1E-07	NiCO ₃ (c)	1E-05
Np	NpO ₂ (am, hyd)	1E-09	NpO ₂ (am, hyd)	3E-07	NpO ₂ (am, hyd)	2E-06
Pa	No solubility control	-	No solubility control	-	No solubility control	-
Pu	PuO ₂ (am, hyd)	3E-11	PuO ₂ (am, hyd)	3E-11	PuO ₂ (am, hyd)	3E-11
Ra	RaSO ₄	3E-05	RaSO ₄	3E-05	RaSO ₄	1E-05
Rh	Short half-life	-	Short half-life	-	Short half-life	-
Se	FeSe ₂ (cr)	2E-05	No solubility control	-	No solubility control	-
Sm	Sm(OH) ₃ (am)	1E-09	Sm(OH) ₃ (am)	1E-09	SmCO ₃ OH·0.5H ₂ O (c)	2E-09
Sn	SnO ₂ (am)	4E-04	SnO ₂ (am)	4E-04	SnO ₂ (am)	7E-07
Sr	SrCO ₃ (strontianite)	3E-03	SrCO ₃ (strontianite)	3E-03	SrCO ₃ (strontianite)	1E-04
Tc ^d	TcO ₂ 1.6H ₂ O	1E-08	No solubility control	-	No solubility control	-
Te	Short half-life	-	Short half-life	-	Short half-life	-
Th	ThO ₂ (am, hyd, aged)	1E-09	ThO ₂ (am, hyd, aged)	1E-09	ThO ₂ (am, hyd, aged)	1E-09
U	UO ₂ (am, hyd)	5E-09	UO ₃ ·2H ₂ O	5E-05	UO ₃ ·2H ₂ O	4E-06
Y	Y(OH) ₃ (c)	4E-13 ^b	Y(OH) ₃ (c)	4E-13 ^b	Y(OH) ₃ (c)	2E-09

a An alternate value is 1E-07 mol/L because NiS (alpha) is sensitive to Eh in Reduce Region II

b Note the Y-90 is the yttrium isotope of concern and its transport is controlled by the transport and decay of Sr-90

c An alternative value is 6E-08 mol/L for Am(OH)₃ (am) as the controlling phase

d For technetium, iron co-precipitated solubilities from Table 2.2-3 were used for deterministic modeling

Apparent Solubilities for Co-precipitated Elements

The term co-precipitated means that elements are bound in the crystal lattice of solid iron phases and mixed with iron phases such that the access of pore fluids to the element is occluded by the host phase. For example, technetium is believed to be very soluble at the conditions of waste tank washing; therefore, it is suspected that any technetium remaining in the residual waste after the washing process is co-precipitated with an iron phase. An apparent solubility of a co-precipitated element can be estimated if it is assumed that, as the host iron phase is dissolved, a co-precipitated element would be released at the same molar ratio at which it exists with the host iron phase. The molar ratios of neptunium, plutonium, technetium, and uranium with iron in the HTF waste tanks were calculated in the WRM report using the estimated final inventories. These ratios and the solubilities of an assumed host iron phase were used to estimate apparent solubilities for neptunium, plutonium, technetium, and uranium. Estimated solubilities for neptunium, plutonium, technetium, and uranium were calculated and are presented in Table 2.2-3. [SRNL-STI-2012-00404]

Table 2.2-3: Apparent Estimated Solubilities (mol/L) of Co-precipitated Elements at Pore Fluid Chemical Conditions

Chemical Condition	Pu	Np	U	Tc ^a
Reduced Region II	8E-13	5E-15	2E-12	1E-14
Oxidized Region II	7E-12	4E-14	2E-11	1E-13
Oxidized Region III	1E-13	9E-16	5E-13	2E-15

a Iron co-precipitated solubility for technetium used in deterministic modeling

Uncertainties in Solubility Estimates

Several sources contribute to uncertainty in the solubility estimates. Uncertainty in the thermodynamic data and the choice of the solubility controlling phase are inherent to any solubility estimate. Uncertainty in the solubility-controlling phase primarily reflects lack of available information on kinetics of nucleation and is the reason the estimates are mostly biased toward higher solubilities. The other sources of uncertainty are related to the chemical conditions of the pore fluid in which the solubility-controlling phase is dissolving.

Uncertainty in thermodynamic data is the product of uncertainty in experimental results from which the thermodynamic data is derived. In many cases equilibrium constants for aqueous species and solid phases are estimated from measurement of an equilibrium constant of a related entity. In these cases uncertainty is introduced by the estimation method. For the NEA database, uncertainties for all reactions were estimated from an evaluation of the experimental data by the NEA. There is also uncertainty associated with the composition of the pore fluids contacting the residual waste over time, which introduces uncertainty into the solubility estimates. Solubilities may be particularly sensitive to pH, E_h , dissolved inorganic carbon, and oxalate concentration.

Iodine Solubility Variability

Analyses of the residual waste sampled from the Tank 12H floor and cooling coils revealed higher than anticipated I-129 inventories (SRR-CWDA-2015-00166), suggesting that iodine release from waste tanks may be solubility-controlled. In the WRM, and correspondingly in the FTF and HTF PAs (SRS-REG-2007-00002, SRR-CWDA-2010-00128), it is assumed that there are no controls limiting the release of I-129 from residual waste once tank liners are breached. Yet, iodine can form solubility limiting solid phases with several metals that also occur in residual tank waste. SRNL report *Potential Solubility Controls for I-129 in Residual Tank Waste* (SRNL-STI-2015-00339) documented a scoping analysis of possible controls on the release of I-129 from Tank 12H residual waste.

Estimates of solubility controls on I-129 suggest the possibility that silver or mercury in the residual waste can limit the release of I-129 under certain conditions. Under various oxidizing conditions the calculated solubility of silver iodide (AgI) ranges from $9.8\text{E-}9$ to $2.7\text{E-}7$ moles/liter and the calculated solubility of mercury iodide (Hg_2I_2) ranges from $1.2\text{E-}7$ to $1.2\text{E-}4$ moles/liter. The lower solubilities in these ranges are associated with conditions for tanks in which the waste layer is below the water table. Under reducing conditions, the elemental forms of silver and mercury are stable, and no solubility limitations from AgI or Hg_2I_2 are applicable. [SRNL-STI-2015-00339] To study the potential impact that iodine solubility has on peak doses, sensitivity studies were performed using an HTF groundwater pathway dose model (the HTF GoldSim Model in deterministic mode). The various iodine solubility cases analyzed were based on the findings from SRNL report SRNL-STI-2015-00339, but did not mechanistically assume that iodine solubility controls were present in Reduced Region II and/or Submerged Region C. [SRR-CWDA-2016-00078]

The fact that all of the iodine in floor residual waste samples from Tank 12H was removed (during characterization) with a deionized (DI) water leach (SRNL-STI-2015-00241) is not inconsistent with active solubility controls on I-129 solubility. For the leaching test 0.5 grams of waste was leached with 30 ml of DI water. Essentially all of the iodine was removed and constituted an average of $2.7\text{E-}3$ wt.% of the sample. Thus, the average total iodine removed was $1.4\text{E-}5$ grams. This results in an average iodine concentration of $3.6\text{E-}6$ moles/L in 30 ml of water. This is within the range of solubility controlled by mercury iodide compounds.

3.0 WASTE RELEASE TESTING

The overall objective of the waste release testing was to provide additional information regarding the residual waste solubility assumptions used in the TF WRM by developing a series of analytic methods to be used to test the solubility of plutonium, neptunium, uranium, and technetium under various simulated waste tank chemistry conditions using actual waste tank residuals.

3.1 Waste Release Simulant Testing Development

The methodology for developing grout pour water that has certain chemical conditions (i.e., E_h and pH) representative of the local groundwater in the presence of grout has been ongoing for several years. Simulant testing done in FY2014 indicated that under oxidizing conditions (i.e., ORII and ORIII), the E_h shifted from oxidizing to reducing values over time using the zero head-

space methodology. As a result, for actual residual waste testing, continuous gas purge experiments were recommended as the preferred method to maintain the oxidizing conditions (ORII and ORIII) in the grout pore water. [SRNL-STI-2014-00456]

The primary goal for the FY2015 testing was the achievement of the target pH and E_h values for grout pore water solutions representative of local groundwater in the presence of grout or grout-representative (CaCO_3 or FeS) solids as well as residual waste surrogate solids representative of residual waste solids expected to be present in a closed waste tank. For oxidizing conditions representative of a closed waste tank after aging, a focus was placed on using solid phases believed to be controlling pH and E_h at equilibrium conditions. For all three pore water chemical conditions (RRII, ORII, and ORIII), the target pH values were achieved to within 0.5 pH units. Residual waste surrogate solids leaching studies were conducted over an E_h range of approximately 630 mV. Significantly higher E_h values were achieved for the oxidizing conditions (ORII and ORIII) than were previously observed. For the ORII chemical condition, the target E_h value was nearly achieved (within 50 mV). However, E_h values observed for the ORIII chemical condition were approximately 160 mV less positive than the target. E_h values observed for the RRII chemical condition were approximately 370 mV less negative than the target. Plutonium and uranium concentrations measured during the residual waste surrogate solids leaching studies under these conditions followed the general trends predicted for plutonium and uranium oxide phases, assuming equilibrium with dissolved oxygen. The highest plutonium and uranium concentrations were observed for the ORIII chemical condition and the lowest concentrations were observed for the RRII chemical condition. [SRNL-STI-2015-00446]

3.2 Waste Release Testing Equipment and Test Setup

The waste release testing involves interaction with actual residual waste and therefore requires use of the SRNL shielded cells facility (Figures 3.2-1 through 3.2-4), where the highly radioactive materials can be handled remotely.

Figure 3.2-1: SRNL Shielded Cell Exterior View

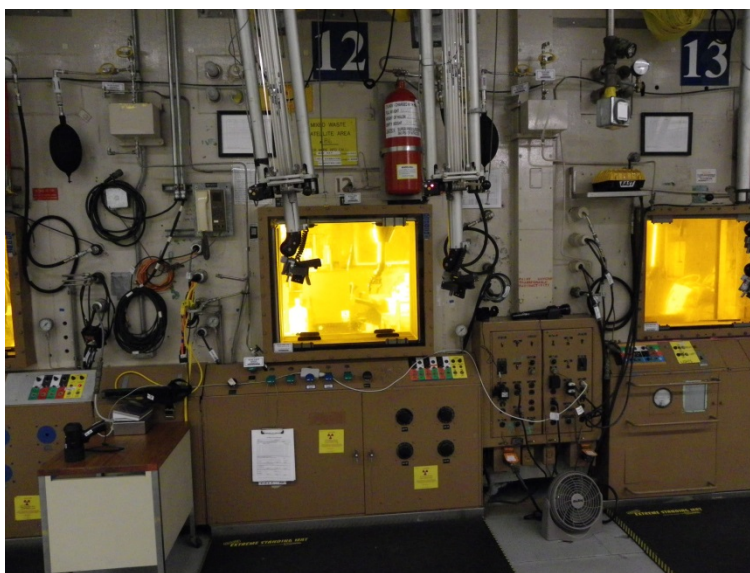


Figure 3.2-2: SRNL Shielded Cell Tank 18F Sample Testing Interior View

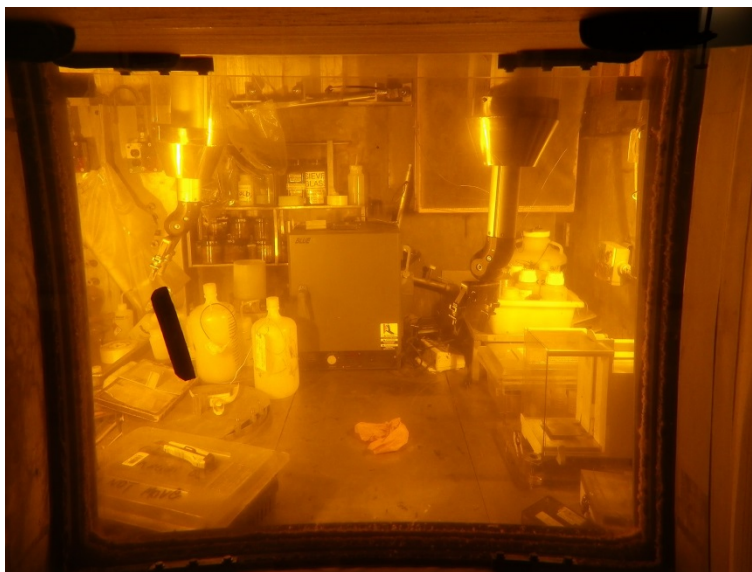
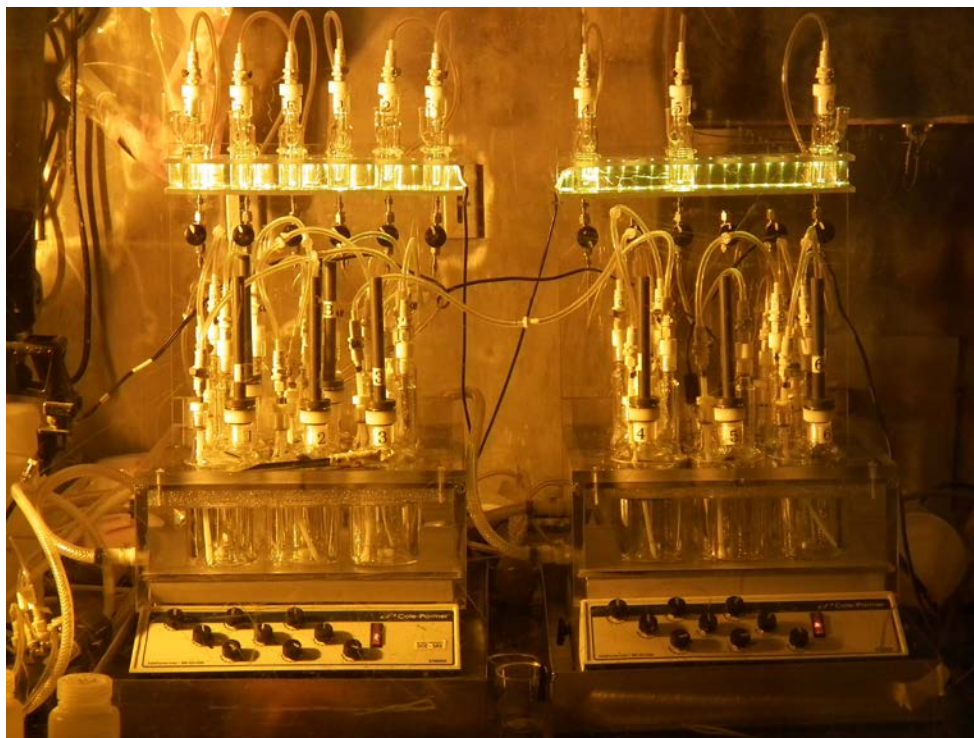


Figure 3.2-3: SRNL Shielded Cell Tank 12H Sample Testing Interior View



Figure 3.2-4: SRNL Shielded Cell Tank 12H Sample Test Equipment



SRNL researchers fabricated test vessels that could be used to conduct grout pore water leaching studies with surrogate waste residuals and grout pore water solutions expected to contact the residual waste solids following waste tank closure under reducing and oxidizing environments. The test vessels were equipped with agitation and probes to measure the solution pH, E_h , and temperature. The vessels were also designed to allow for repeated sampling of the liquid phase.

3.2.1 Tank 18F Testing Equipment

Separate vessels were designed and prepared for Tank 18F residual waste testing (Figures 3.2-5 through 3.2-8). These vessels and associated equipment allowed for continuous gas purge, repeated sampling, and monitoring for pH and E_h . The system design included pre-humidification vessels to saturate the purge gases with water vapor and minimize sample evaporation. A diagram of the vessel layout utilized in the test apparatus is provided in Figure 3.2-6. Six leach tests were conducted (identified as samples A through F), two vessels for each sample type (RRII, ORII, and ORIII). As indicated in the figure, the gases were passed through a series of vessels for treatment to produce the desired conditions. The vessels in a given series were connected using tubing with quick-connect fittings on each end to allow for vessel detachment, removal, or reconfiguration during testing. The sample vessel gas outlet lines were connected to the bubbler system using the same tubing. Control vessels for each sample type (RRII, ORII, and ORIII) were also incorporated into the system in the locations shown. CO₂-stripped air was used as the baseline purge gas for the oxidizing samples (ORII and ORIII). During periods when carbon dioxide was needed to lower the pH, the caustic scrubber was removed from the sequence of vessels that the air was passed through until the target pH was reached. Ultra-high purity nitrogen gas (supplied by cylinder through front wall penetrations) was used as the purge gas for the reducing samples (RRII) throughout testing. [SRNL-STI-2016-00432]

Figure 3.2-5: Water Bath Stirrer for Controlled Atmosphere Testing

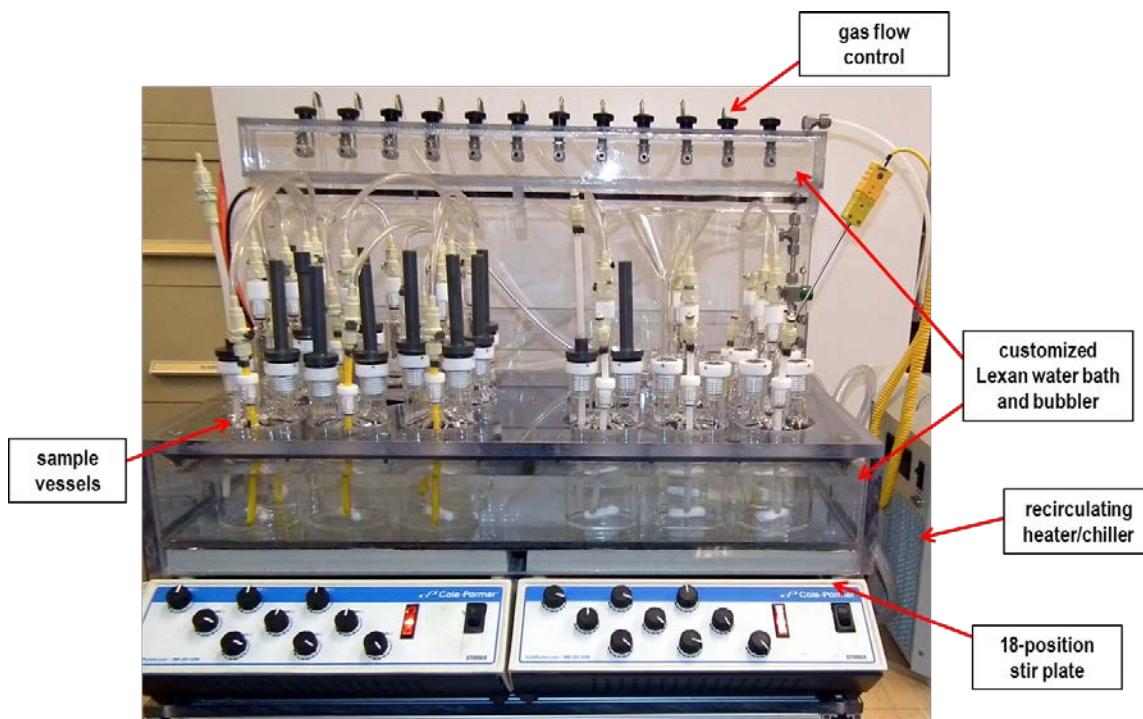


Figure 3.2-6: Sample and Gas Pretreatment Vessel Layout

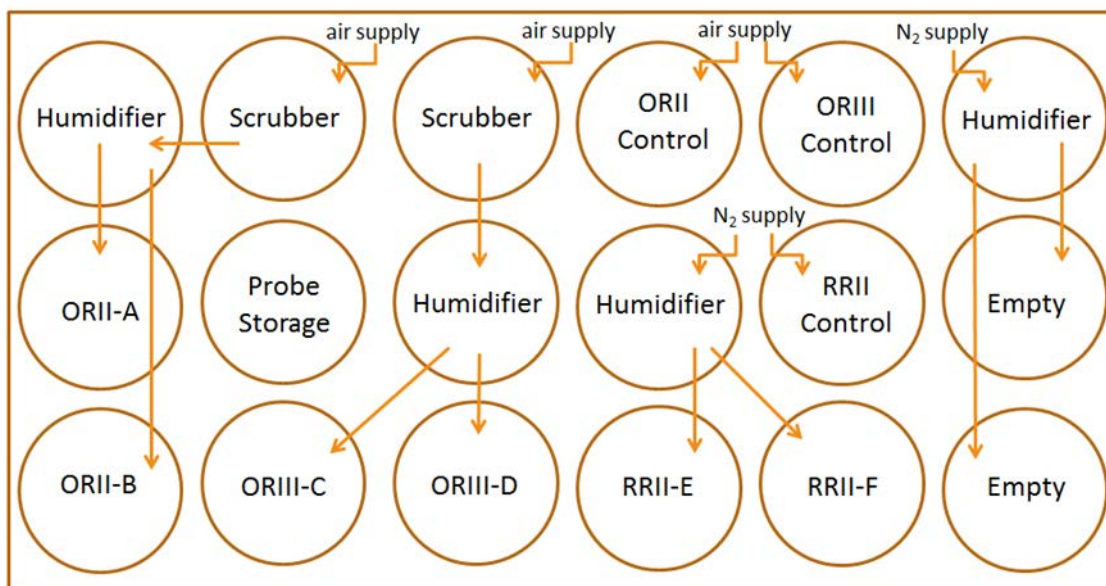


Figure 3.2-7: Leachate Test Sample Vessel Details

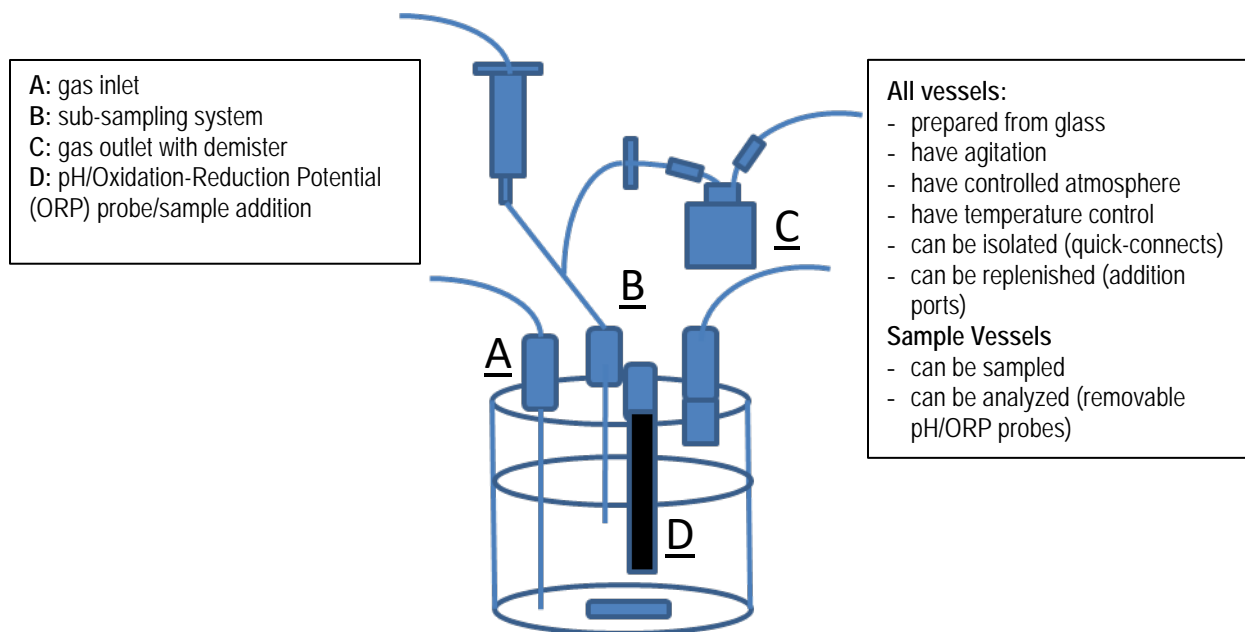
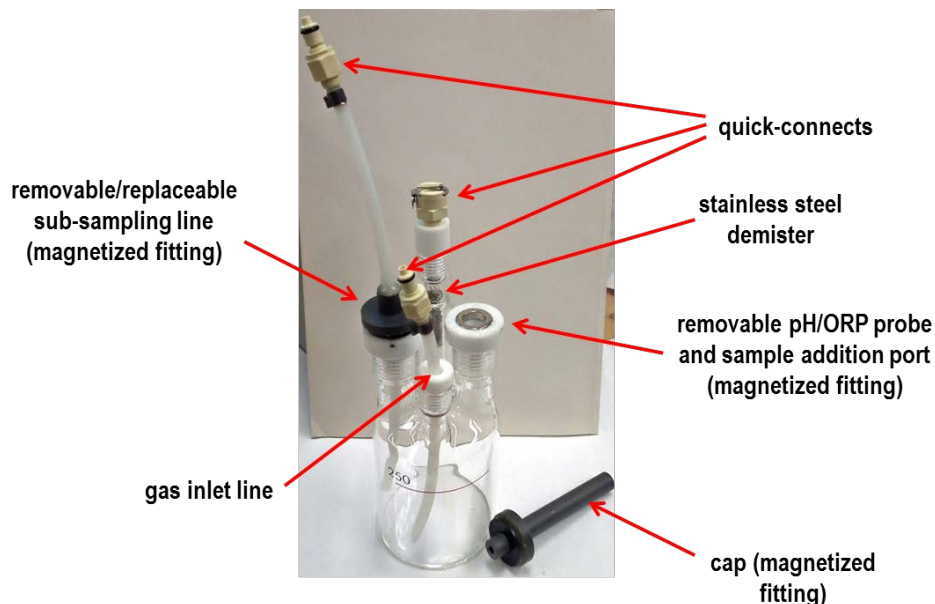


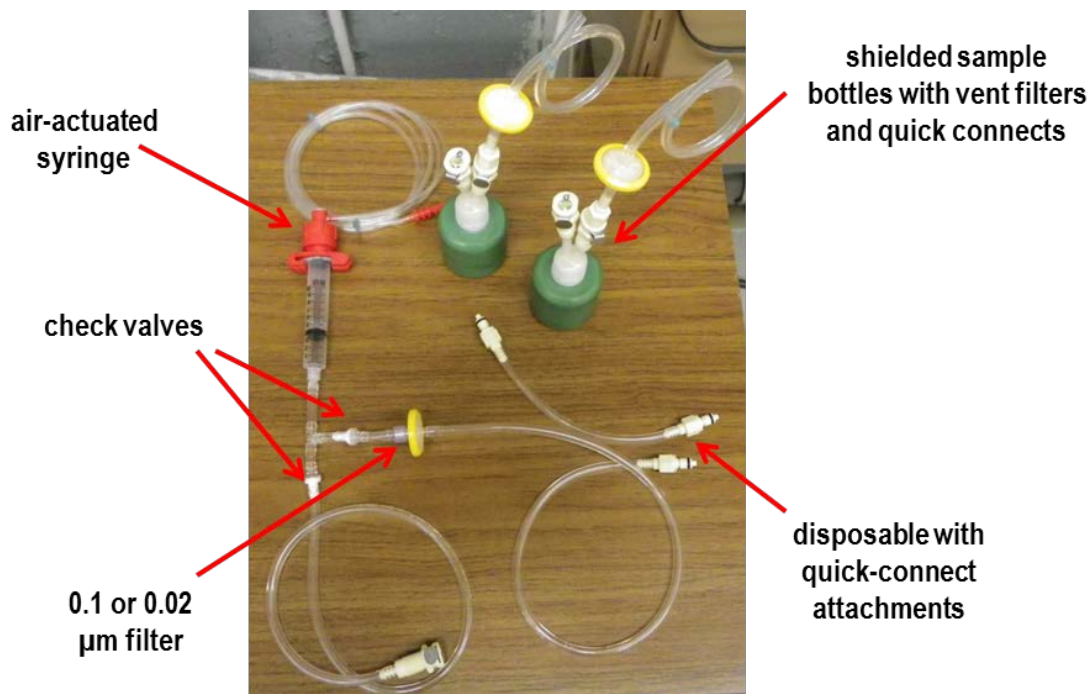
Figure 3.2-8: Leachate Test Sample Vessel



Based on the simulant studies and the expected solubilities of most of the metals, it was anticipated that very low solubilities near analysis detection limits would be observed. The need to measure very low concentrations was especially problematic for plutonium, since plutonium contamination of samples in the cells is known due to high background plutonium levels present in the facility. As a result, a sub-sampling system and methodology were developed to allow for the isolation of

filtered samples in the analysis bottles. The initial sub-sampling system used is shown in Figure 3.2-9. The system involved modified, shielded analysis bottles with caps containing polyethylene tubing and quick-connect attachments. As testing continued, the sampling system was simplified due to concerns regarding the volume of sample lost in the transfer lines and inconsistencies in the sample volumes collected. The modified system included a simple syringe with a directly-attached filter. Tubing was attached to the downstream side of the filter with a male quick-connect fitting attached to the other end of the tubing. [SRNL-STI-2016-00432]

Figure 3.2-9: Initial Leachate Test Sub-Sampling System



3.2.2 Tank 12H Testing Equipment

Based on lessons learned from Tank 18F waste release testing, modifications were made to the waste release testing setup and equipment in support of Tank 12H waste release testing. The Tank 12H test apparatus was designed and constructed to simultaneously maintain numerous actual radioactive samples under either oxidizing or reducing conditions with continuous agitation and gas purge and at constant temperature. A photograph of the test apparatus prior to transfer into the shielded cells is provided in Figure 3.2-10. Magnetic stir bars and multi-position stir plates were included to promote sample agitation. Glass test vessels were constructed in the SRNL glass shop for controlled-atmosphere testing that would accommodate periodic sub-sampling. [SRNL-STI-2018-00484]

Figure 3.2-10: Tank 12H Testing Equipment Prior to Installation into the Shielded Cells



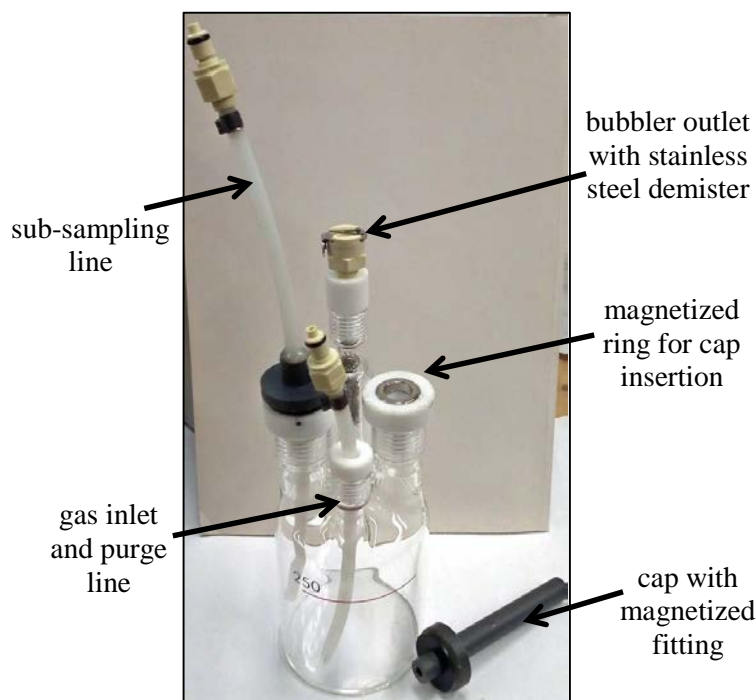
A customized water bath was constructed from ½" thick Lexan sheets to fit over two adjacent stir plates and maintain all samples at the target temperature. The glass test vessels were immersed in the water by placing the vessels through fitted slots in the top of the bath which were directly above the sample positions on the stir plates. A rubber gasket was positioned between two Lexan plates on the top of the water bath which resulted in a close fit for the glass test vessels and helped to insulate the bath from the cell environment. The water bath was attached to a temperature-controlled water recirculator. The recirculator set temperature was maintained at 22.0 °C throughout testing. The recirculator temperature varied little during testing ranging from 21.9 to 22.0 °C. [SRNL-STI-2018-00484]

A customized water bubbler manifold was constructed and attached to the back of the water baths to monitor and control gas flow through each individual vessel during testing. Low gas supply pressures (typically <5 PSI) were utilized during testing to purge the vessels. Gas flow control through the vessels was accomplished on the downstream side of each sample gas line by the adjustment of stainless steel Swagelok needle valves. Because the gas outlet lines for each sample were open to the bubbler, the gas pressures in the samples were slightly above atmospheric pressure during leach testing. [SRNL-STI-2018-00484]

Customized glass vessels of various types were prepared for testing (see example leach test vessel in Figure 3.2-11). All test vessels were made of 70.2 mm ID tubing and the main (straight) portion of the vessels (excluding the tops) were ~8 cm tall. The vessels would contain ≤300 mL of

solution. The vessels fit snugly into the sample slots in the top of the customized water bath. Four types of vessels were prepared for testing including: caustic scrubber, humidifier, leach sample, and probe storage vessels. Upper vessel attachments were made from #7 and #15 internal glass screw threads. Threaded Teflon fittings for the screw threads were modified to accommodate the various needed connections. Each vessel top included three to four screw thread fittings. [SRNL-STI-2018-00484]

Figure 3.2-11: Leach Testing Sample Vessel



The purpose of the caustic scrubber vessels was to remove carbon dioxide gas from the air supply lines through gas contact with 5 M NaOH solution. Carbon dioxide removal was required to avoid impacting the test slurry pH during air gas purging. Each scrubber vessel included a single gas supply line consisting of a 12 mm OD fritted glass gas dispersion tube to promote the formation of numerous gas bubbles to enhance gas/liquid contact. A second port with a quick connect fitting was included in the scrubber vessel top for the addition of the sodium hydroxide reagent. The third and final scrubber vessel attachment included a stainless-steel demister suspended within a short glass column for the removal of entrained solution from the outlet gas. When utilized, the caustic scrubbers were the first vessels that the air was passed through and the gas was then transferred to a humidifier vessel. [SRNL-STI-2018-00484]

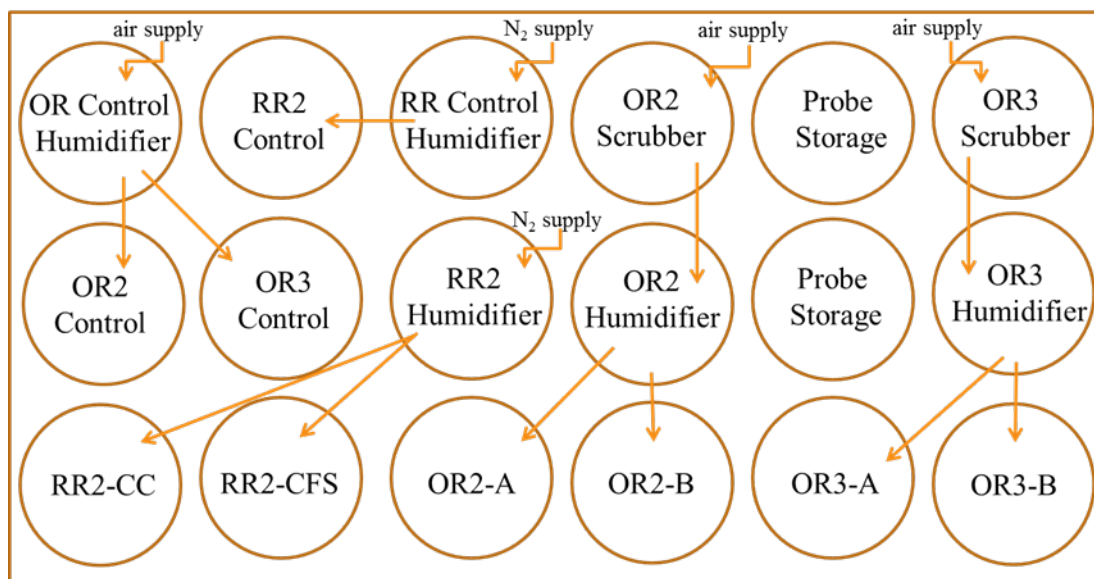
The humidifier vessels were filled with deionized water. The purpose of the humidifier vessels was to saturate the supply gas with water vapor at the sample temperature and minimize leach sample evaporation during testing. For oxidizing conditions, the humidifier vessels also served to isolate the leach test samples from the caustic scrubber solution. A single humidifier vessel was utilized to treat the supply gas for each sample type (RRII, ORII, and ORIII) with the water-

saturated gas stream then being split between two leach test vessels. Each humidifier vessel included a single gas supply line consisting of 1/4" diameter thin wall polyethylene tubing which had been heat-sealed at the end. Multiple 1/64" holes were drilled into the sides of the tubing near the bottom to produce bubbles and promote gas-liquid contact. The humidifier vessels also included a water addition port with a quick connect fitting and two gas outlet lines containing demisters. The outlet lines led to the leach test vessels. [SRNL-STI-2018-00484]

The glass leach sample vessels (example shown in Figure 3.2-9) included a gas supply port, a sample/reagent addition/collection port (magnetized cap), and a single gas outlet connection identical in design to the humidifier vessels. The sample addition port was also used to insert the pH and Oxidation-Reduction Potential (ORP) probes. The probe storage vessels were designed similarly to the other vessels but included open glass screw threads with no plastic fittings. Probes were immersed in water in these vessels when not in use. Reagents and samples were added to the various vessels using glass funnels or customized plastic funnels with an attached quick-connect fitting. [SRNL-STI-2018-00484]

A diagram of the vessel layout utilized in the Tank 12H test apparatus is provided in Figure 3.2-12. Six leach tests were conducted, two vessels for each sample type (RRII, ORII, and ORIII). As indicated in the figure, the gases were passed through a series of vessels for treatment to produce the desired conditions. The vessels in a given series were connected using 1/8" ID Tygon tubing with medical-grade check valves in the middle and quick-connect fittings (Colder Product Company PMC12 polypropylene fittings with 1/8" nominal flow) on each end to allow for vessel detachment, removal, or reconfiguration during testing. The sample vessel gas outlet lines were connected to the bubbler system using the same tubing with check valves included in each line. Blank control vessels for each sample type (RRII, ORII, and ORIII) were also incorporated into the system in the locations shown. CO₂-stripped air was used as the baseline purge gas for the oxidizing samples (ORII and ORIII). During periods when carbon dioxide was needed to lower the pH, the caustic scrubber was removed from the sequence of vessels that the air was passed through until the target pH was reached. Ultra-high purity nitrogen gas (supplied by cylinder through front wall penetrations) was used as the purge gas for the reducing samples (RRII) throughout testing. [SRNL-STI-2018-00484]

Figure 3.2-12: Vessel and Plumbing Layout for SRNL Shielded Cells Testing



It was anticipated that very low solubilities near analysis detection limits would be observed during leach testing. As a result, a sub-sampling system and methodology were developed to allow for the isolation of filtered samples in the analysis bottles. The sampling system included a simple 10 mL syringe with a directly-attached filter (see Figure 3.2-13). Tubing (1/8" ID) was attached to the downstream side of the filter with a male quick-connect fitting attached to the other end of the tubing. The system also included modified, shielded analysis bottles with caps containing 1/4" OD polyethylene tubing and quick-connect fittings for attachment to the syringe (see Figure 3.2-14). The analysis bottle required venting during sample collection via another quick-connect fitting with attached tubing and a second filter to isolate the sample from contamination on the downstream side. After sample collection, the vent line and the sub-sampling lines were removed from the analysis bottles by depressing the release tabs on the quick-connect fittings. The samples were transferred into fitted foam holders to maintain a vertical orientation during transport to analytical sample receiving. In analytical, care was taken not to contaminate the samples from personnel contact with the bottle exterior surfaces. The sample bottle caps were carefully removed with gloves following general radiological procedures. Then the analyst's gloves were changed and the sample was removed from the bottle with a pipet without touching the exterior bottle surface. Using this method, the analytical bottles were never opened inside the shielded cells environment and contamination from the bottle surfaces in the Analytical Development (AD) department was minimized or eliminated. [SRNL-STI-2018-00484]

Figure 3.2-13: Sub-Sampling System



Figure 3.2-14: Sub-Sampling System and Analysis Sample Vessels with Attached Vent Lines



During sub-sampling, the filter end of the syringe was covered with a small plastic bag to minimize the possibility of post-filtration contamination in the cell (see Figure 3.2-13). The bag was removed just prior to sampling and the syringe filter unit was attached directly to the analytical bottle via the quick-connect fitting. Using this system, the analysis sub-samples were removed from the leach test vessels and transferred into the top of the syringe barrel after removing the plunger. Prior to all sub-sampling events, disposable cloth wipes were laid down on the cell floor to minimize contamination. Prior to testing, and periodically during testing, the cell floors and manipulator fingers were wiped clean to remove contamination. [SRNL-STI-2018-00484]

3.3 Pore Water Simulant Preparation

Waste release testing requires preparation of the pore water simulant to be used in the actual waste testing. A Synthetic Infiltration Water (SIW) concentrated stock solution was prepared based on the average composition observed for groundwater from non-impacted wells within the SRS water table aquifer. For the waste release testing, grout pore water simulants were prepared for each condition in Table 2.2-1 based on simulant modeling and previously conducted recipe development. RRII and ORII solutions were prepared from the diluted SIW by the addition of approximately 0.1-0.2 g CaCO_3/L and ≥ 0.05 g $\text{Ca}(\text{OH})_2/\text{L}$ to achieve a pH near 11. The resulting solution contained a trace of CaCO_3 solids (assumed composition based on modeling predictions). The RRII and ORII pore water simulants had the same chemical composition and differed only in the gaseous atmosphere ultimately used to adjust the solution E_h values. ORIII simulant was prepared by the addition of 0.1 g CaCO_3/L . This resulted in a solution containing trace amounts of CaCO_3 solids with a pH near 10. Subsequent, brief (approximately 15 minutes) purging of the solution with air resulted in the absorption of CO_2 and a reduction in the solution pH to near 9. All of the as-prepared simulants had solution E_h values near +500 mV. Purging the RRII simulant with nitrogen gas overnight resulted in a solution E_h value near -100 mV. Subsequent addition of reagent grade ferrous sulfide (FeS) solids while continuously purging the solution resulted in solution E_h values near -200 mV (FeS not added in this study until test samples were prepared in the shielded cells facility). The final step in the preparation of grout pore water simulants and test samples was the transfer of additional calcium carbonate, actual grout solids, or FeS (reducing samples only) to the solution in the shielded cells environment prior to actual waste leach testing. Calcium carbonate reagent was utilized as a grout-representative phase in all ORII and ORIII tests and in one RRII test to simplify the system and allow for better control of the solution pH and E_h . Cement, fly ash, and slag (CFS) grout solids were utilized in the remaining RRII tests. [SRNL-STI-2016-00432, SRNL-STI-2018-00484]

3.4 Residual Waste Sample Preparation

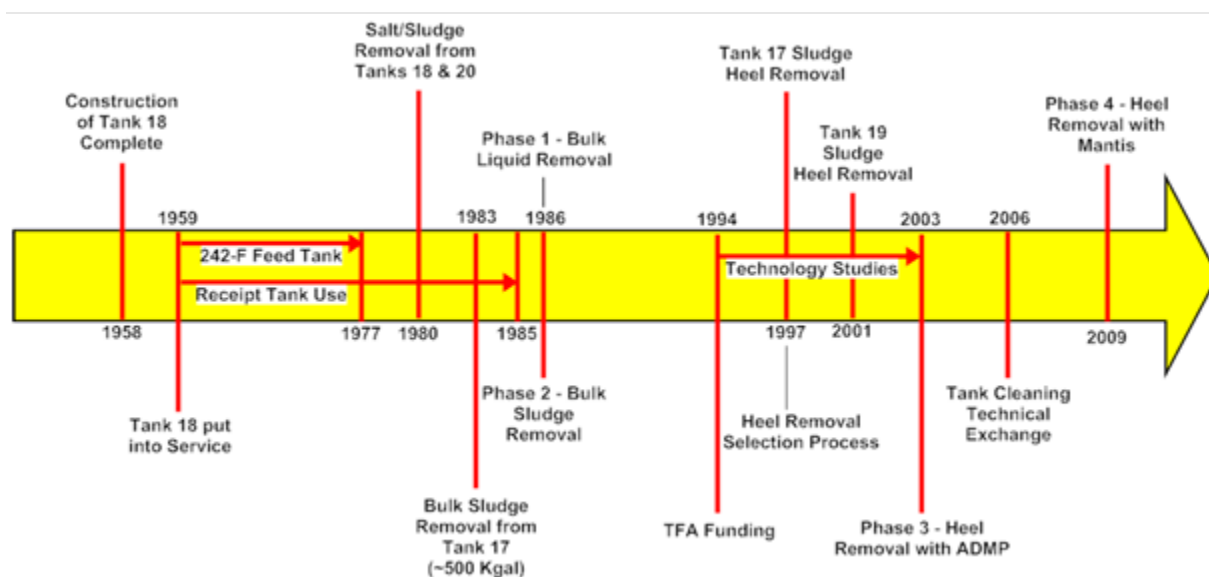
3.4.1 Tank 18F Sample Preparation

3.4.1.1 *Tank 18F Residuals Background*

Tank 18F is located in the FTF and was constructed between 1956 and 1958. From July 1959 to August 1987, Tank 18F received Plutonium Uranium Extraction (PUREX) and non-canyon waste. Because of the acidic characteristics of the PUREX waste when it leaves the F-Canyon processing vessels, the waste had to be neutralized to protect the FTF carbon steel tank liners. This waste stream contained sludge solids, insoluble salts, and other inert materials that settled to the bottom of Tank 18F. Because of its processing history, Tank 18F was known as a “sludge bearing” tank. The non-canyon waste sources were the 242-F Evaporator system, sludge removal from Tanks 17F, 20F and 19F, and heel removal from Tanks 19F. The 242-F Evaporator system concentrated the PUREX liquid waste, forming saltcake and concentrated liquid in three receipt tanks (Tanks 17F, 19F, and 20F). The concentrated PUREX liquid waste was subsequently transferred back (recycled) to Tank 18F for further processing. Settled sludge and insoluble solids from the PUREX process were transferred to Tank 18F via waste removal activity from Tanks 17F, 19F, and 20F. Approximately 560,000 gal of settled sludge was moved into and out of Tank 18F over its service life. Tank 18F was designed to be the only conventional transfer route out of the Tank 17F through Tank 20F area and, therefore, received essentially all of the sludge transferred into this area.

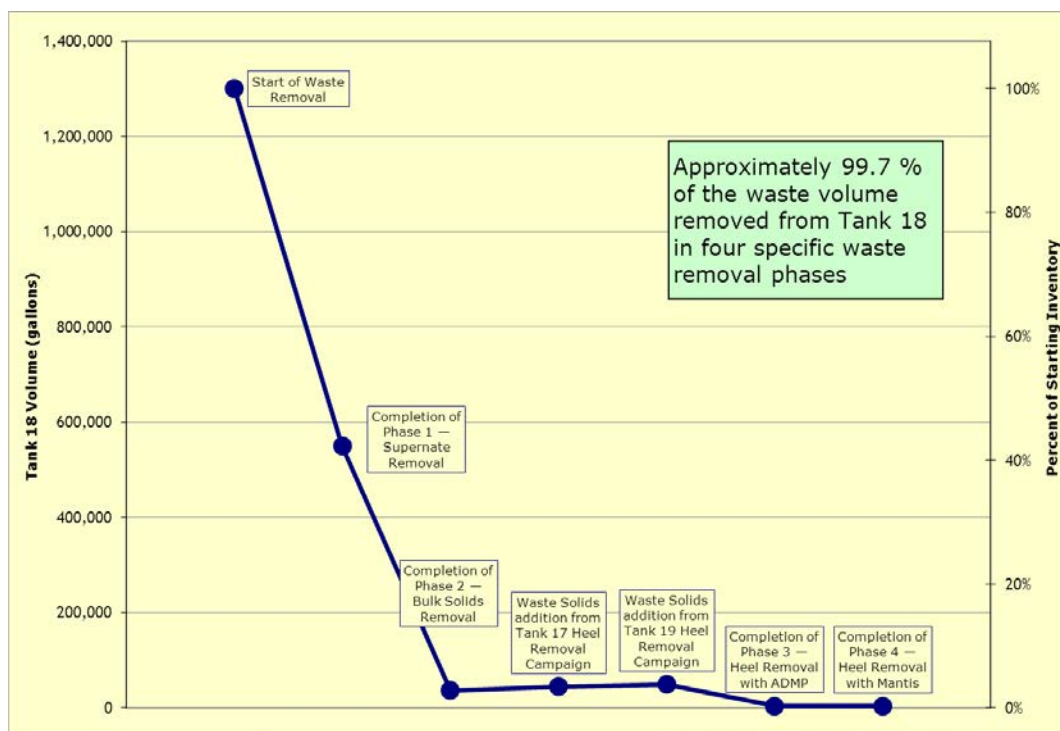
The Tank 18F historical timeline, including the four phases of Tank 18F waste removal (Phase 1: Bulk Liquid Waste Removal, Phase 2: Bulk Sludge Waste Removal, Phase 3: Heel Removal with the Advanced Design Mixer Pump (ADMP), Phase 4: Heel Removal with Mantis), are detailed in Figure 3.4.1-1. The key activities (including the definition of associated terms and phrases) on this timeline are described in the Industrial Wastewater Closure Module for the Liquid Waste Tanks 18 and 19 F-Area Tank Farm, Savannah River Site (SRR-CWDA-2010-00003).

Figure 3.4.1-1: Tank 18F Historical Timeline



Bulk sludge waste removal operations in Tank 18F (Phase 2) began in April 1986 using three standard slurry pumps. The last of seventeen sludge transfers from Tank 18F of this waste removal campaign occurred in August 1987 with the material being transferred to Tank 51H. This series of transfers made up the initial sludge batch which provided startup feed for the Defense Waste Processing Facility (DWPF). There was approximately 37,000 gallons of solids left in Tank 18F. In 1997 and 2001, Tanks 17F and 19F, respectively, underwent their final heel removal campaigns and added about 10,000 gallons of insoluble solids and 2,500 gallons of zeolite to the Tank 18F inventory. This brought the Tank 18F inventory to approximately 50,000 gallons of insoluble solids including zeolite. The Phase 3 heel removal campaign reduced the wet solids volume in Tank 18F from approximately 49,500 (37,000 gallons remaining after Phase 2 plus 12,500 gallons of solids that had been transferred from Tank 17F and Tank 19F heel removal) to a then-estimated 4,300 gallons. The heel removal process in Tank 18F (Phase 4) continued until March 13, 2009, when removal effectiveness had diminished. The determination was based on visual observation and by monitoring diminished Electronic Personal Dosimeter (EPD) readings from the transfer line radiation monitoring system. Figure 3.4.1-2 depicts the overall waste removal effectiveness for Tank 18F. Mantis operations reduced the volume of residual solids to approximately 4,000 gallons in Tank 18F. [DOE/SRS-WD-2014-001]

Figure 3.4.1-2: Tank 18F Waste Removal



3.4.1.2 Tank 18F Residual Waste Sample Selection, Compositing, and Pretreatment

Actual Tank 18F residual waste solid samples archived in the SRNL shielded cells were evaluated based on available characterization data, sampling location, sample size and history in order to select samples to use for leachate testing. Multiple Tank 18F residual waste samples were taken during Tank 18F operational closure for use in tank characterization. [SRNL-STI-2010-00386] The various samples were analyzed with respect to radiological and chemical composition as part of Tank 18F closure. Sample FTF-1 was chosen for independent waste release testing rather than compositing the sample with other Tank 18F samples. Using sample FTF-1 provided confidence that elements of interest will be detected, given that sample FTF-1 has the highest Fe, Mg, Ca, U, Np, Pu, Am, and oxalate concentrations compared to other Tank 18F samples (Tables 3.4-1 through 3.4-3). During sample selection, an emphasis was placed on using samples containing relatively high plutonium. Compositing would by definition dilute the higher concentration sample. While there is some variability in concentrations from sample to sample, a statistical study of the sampling results was performed and demonstrated the ability to characterize the waste tank as one population. [SRNL-STI-2010-00401] The study showed that a comparison of the range of relative standard deviations to the mean fell within a three sigma limit.

Table 3.4-1: Tank 18F Residual Waste Samples Radionuclide Concentrations (μCi/g)

	T18 Sample FTF-1	T18 Sample FTF-2	T18 Sample FTF-3	T18 Sample FTF-4	T18 Sample FTF-5	T18 Sample FTF-8 old	Average
Tc-99	2.69E-02	3.25E-02	3.21E-02	4.48E-02	4.48E-02	3.62E-02	3.6E-02
Th-229	1.91E-05	< 7.38E-05	2.33E-05	2.23E-05	< 6.93E-06	< 5.27E-06	2.5E-05
Th-230	1.40E-04	< 1.18E-04	< 3.08E-05	3.16E-05	2.99E-05	5.50E-05	6.8E-05
U-233	1.17E-03	1.37E-03	5.95E-04	< 8.24E-04	< 3.46E-04	9.69E-04	8.8E-04
U-234	2.04E-02	1.13E-02	4.36E-03	3.51E-03	2.22E-03	5.95E-03	8.0E-03
U-238	2.00E-02	1.13E-02	4.31E-03	3.43E-03	2.11E-03	6.08E-03	7.9E-03
Np-237	9.12E-03	5.24E-03	3.26E-03	3.77E-03	4.69E-03	2.65E-03	4.8E-03
Pu-238	5.72	3.57	2.67	3.32	3.38	3.85	3.8E+00
Pu-239	16.1	8.99	6.58	6.75	7.6	7.92	9.0E+00
Pu-240	3.62	2.09	1.53	1.6	1.75	1.8	2.1E+00
Pu-241	15.8	9.08	7.6	7.91	8.69	8.59	9.6E+00
Am-241	7.51	3.77	3.02	3.97	4.65	4.1	4.5E+00
Cm-244	1.17E-01	1.20E-01	1.29E+01	2.47E-01	2.25E-01	2.24E-01	2.3E+00

[SRNL-STI-2010-00386]

Table 3.4-2: Tank 18F Residual Waste Samples Elemental Wt%

	T18 Sample FTF-1	T18 Sample FTF-2	T18 Sample FTF-3	T18 Sample FTF-4	T18 Sample FTF-5	T18 Sample FTF-8 old
Al	11.00	13.90	16.60	17.00	16.40	13.90
Ca	2.93	2.13	1.93	2.29	2.73	2.60
Fe	9.76	6.96	7.29	7.45	8.81	8.47
Mg	3.76	1.78	2.09	1.49	2.19	1.84
Mn	1.04	0.83	0.79	0.97	1.09	1.21
Si	2.16	2.95	2.22	3.75	3.49	3.67
U	6.29	3.66	1.55	1.24	0.83	2.14
Total	36.94	32.21	32.47	34.19	35.54	33.83

[SRNL-STI-2010-00386]

Table 3.4-3: Tank 18F Residual Waste Samples Oxalate Concentrations (mg/g)

T18 Sample FTF-1	T18 Sample FTF-2	T18 Sample FTF-3	T18 Sample FTF-4	T18 Sample FTF-5	T18 Sample FTF-8 old
5.83	1.78	0.431	0.287	0.315	0.385

[SRNL-STI-2010-00386]

Scoping studies were conducted to determine washing requirements for the Tank 18F residual waste solids prior to the initiation of leaching studies and characterization. The ORIII condition required sample washing to remove residual, soluble caustic and attain the target solution pH. The RRII and ORII samples also required some level of sample washing. In order to avoid diluting the pore water solutions with additional water, the samples were washed with portions of the appropriate pore water solutions prior to longer term leachate testing. If washing resulted in the formation of peptized solids that did not settle within 24 to 48 hours, it was necessary to filter the

residual solids to remove the wash liquid. Filtration was conducted as needed using a 0.45 µm Nalgene Nylon filter unit. The sample material was recovered from the filter and used in subsequent pore water leaching studies (e.g., losses to tank wash studies).

3.4.2 Tank 12H Sample Preparation

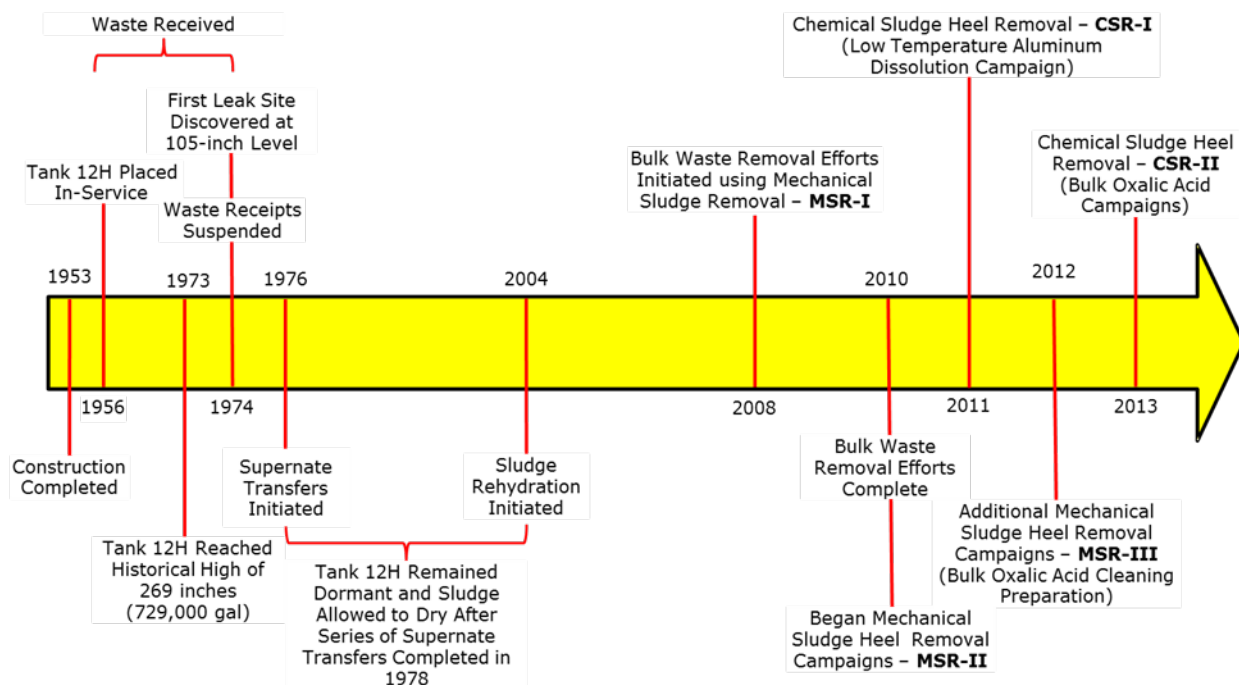
3.4.2.1 Tank 12H Residuals Background

In September 1956, Tank 12H was placed in service to receive periodic transfers of fresh high heat waste (HHW) from the PUREX process in H-Canyon. As of August 1957, Tank 12H had a sludge depth of 48 inches of PUREX waste (DPSP-57-1258). When the volume of waste in the tank neared operational capacity, additional receipts were suspended. Insoluble solids were allowed to settle, forming a sludge layer on the bottom of the tank. The waste was then allowed to cool and decay until aged supernatant liquid met acceptance criteria for transfer to an evaporator system for volume reduction purposes. In 1963, Tank 12H began receiving transfers from the enriched uranium process in H-Canyon. From August 1963 through December 1974, the process of filling Tank 12H with fresh HHW and decanting the supernate was performed five times. Comprised of settled solids and interstitial liquid, the sludge layer at the bottom of the tank grew larger after each decant. The largest volume of waste stored in Tank 12H was approximately 736,000 gallons. [DPSPU 78-11-9]

Tank 12H received HHW from the following three chemical separations processes: 1) PUREX, which was associated with recovery of weapons grade plutonium and uranium from natural and depleted uranium targets, 2) H-Modified (HM), which was associated with recovery of highly enriched uranium from spent uranium fuel and neptunium targets, and 3) Thorium Extraction (THOREX), which was associated with the recovery of U-233 from thorium targets. The HM and THOREX processes yielded waste streams with a high aluminum concentration, which affected the rheological properties of the sludge and later contributed to difficulty during waste removal. [SRR-CWDA-2014-00086]

The Tank 12H historical timeline, including the three phases of Tank 12H waste removal (Phase 1: Bulk Liquid Waste Removal, Phase 2: Bulk Sludge Waste Removal, Phase 3: Heel Removal), are detailed in Figure 3.4.2-1. The key activities (including the definition of associated terms and phrases) on this timeline are described in greater detail in the *Industrial Wastewater Closure Module for Liquid Waste Tank 12H H-Area Tank Farm Savannah River Site*. [SRR-CWDA-2014-00086]

Figure 3.4.2-1: Tank 12H Historical Timeline

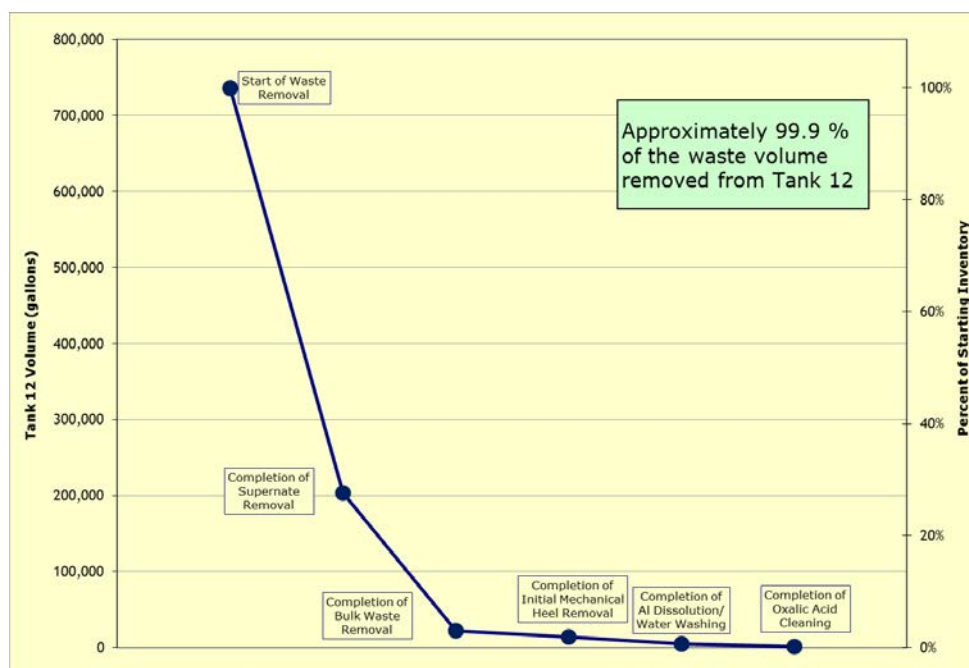


Tank 12H was taken out of operational service in 1974 after minor leakage into the annulus was discovered. Soon thereafter, planning was initiated to remove the bulk of the supernate (i.e., freestanding liquid) waste from the primary tank. The intent was to remove enough liquid that the remainder of waste in Tank 12H would reside safely below the leak site located 105 inches above the tank floor. In March 1976, transfers of supernate from Tank 12H began and a series of three liquid waste transfers were completed by August 1978.

Bulk sludge waste removal (Phase 2) was achieved through a series of campaigns using technologies categorized as either mechanical sludge removal (MSR) or chemical sludge removal (CSR). Although both MSR and CSR employ mechanical mixing to suspend settleable solids in liquid slurry, MSR typically uses supernate decants to supply the liquid slurry medium, where CSR involves the addition of chemicals that react with the solids to improve removal efficiency. Design and installation of bulk sludge removal equipment began in 2003 and resulted in the installation of four slurry pumps to provide mechanical mixing of the sludge. Bulk waste removal efforts resumed in 2009, were completed in 2010 and involved multiple mixing and transfer sludge removal campaigns. The total volume of solids at the beginning of these campaigns was estimated to be approximately 203,000 gallons. From 2009 through 2011, three mechanical sludge removal campaigns were conducted in Tank 12H to support sludge batch preparation for DWPF. The solids remaining in the waste tank at the conclusion of the mechanical sludge removal campaigns was estimated to be 13,700 gallons. A chemical cleaning campaign using Low Temperature Aluminum Dissolution, completed in 2011, reduced the residual solids volume to approximately 7,800 gallons. Additional mechanical sludge removal performed in 2012, following Low Temperature Aluminum Dissolution, further reduced the residual solids volume to approximately 4,400 gallons. A second chemical cleaning campaign, using oxalic acid, was performed in 2013. Prior to executing the oxalic acid cleaning, the Tank 12H flowsheet was revised to incorporate lessons

learned from previous chemical cleaning campaigns (e.g., Tanks 5, 6, and 16). The improvement to the flowsheet included such things as washing the Tank 12H material prior to cleaning to reduce the sodium concentration, modifying the mixing strategy to improve the contact rate of the acid with the material, monitoring pH of the solution and maintaining the temperature of the material at the maximum level allowed taking into consideration tank corrosion chemistry requirements. Overall, the Tank 12H oxalic acid cleaning campaign reduced the residual material volume by greater than 75 %. [SRR-CWDA-2014-00003] Figure 3.4.2-2 depicts the overall waste removal effectiveness for Tank 12. The volume of the residuals in the primary tank at the conclusion of heel removal operations was estimated to be approximately 1,400 gallons based on preliminary volume estimates. [DOE/SRS-WD-2014-001]

Figure 3.4.2-2: Tank 12H Waste Removal



3.4.2.2 Tank 12H Historical Waste Tank Sample Analyses

Throughout the history of the Tank Farms, sludge sampling activities have been carried out for various reasons, with some of these tasks associated with Tank 12H. Empirical concentration data from Tank 12H tank sludge sampling tasks (DP-1441, DPST-77-425, DPSP-76-1-7, WSRC-TR-2004-00180, SRNL-STI-2010-00223 and SRNL-STI-2011-00360) has been captured in Table 3.4.2-1. [N-ESR-H-00040]

Table 3.4.2-1: Tank 12H Sludge Samples (wt%)

Date	Material	Reference	Al	Fe	Mn	Hg	Ni	Th	U	S	Si	Na
1/1/2012	WCS	SRNL-STI-2012-00479 (c)	14	9	8	3	1	6	1	(d)	(d)	(d)
9/1/1975	Washed Sludge (a)	DPST-77-425, DP-1441	30.2	4.5	1.7	1.1	0.5	(d)	(b)	(d)	(d)	1
9/12/1975	Unwashed Sludge (a)	DPST-77-425	8	8	5	0.5	2	0.2	≤ 0.1	0.5	0.3	69
9/16/1975	Unwashed Sludge (a)	DPST-77-425	8	8	7	0.1	2	0.2	≤ 0.1	0.2	0.3	69
2004	Unwashed Sludge	WSRC-TR-2004-00180	34.2	4.3	2	(d)	1.2	(d)	(d)	(d)	0.2	1.3
2004	Washed Sludge	WSRC-TR-2004-00180	33	4.5	2.6	(d)	1.5	(d)	(d)	(d)	0.7	1.1
2004	Leached Sludge (e)	WSRC-TR-2004-00180	11	7.3	5.4	(d)	1.5	(d)	(d)	(d)	0.4	2.4
2/9/2010	Slurry	SRNL-STI-2010-00223	7.8	1.4	0.9	0.8	0.1	0.6	0.3	0.4	0.2	31.1
2009-10 (f)	Washed Sludge	SRNL-STI-2011-00360	26	4.5	2.8	1.9	0.5	1.6	0.6	(d)	0.3	4.2
2009-10 (f)	Treated Sludge	SRNL-STI-2011-00360	52	3.7	0.1	≤ 0.1	0.5	3.8	≤ 0.1	(d)	≤ 0.1	≤ 0.1
Sample 1	Residuals	SRNL-STI-2015-00241	6	32	1	19	1	3	0	<0.4	0.1	0.5
Sample 2	Residuals	SRNL-STI-2015-00241	9	22	2	12	1	8	0	<0.4	0.2	0.7
Sample 3	Residuals	SRNL-STI-2015-00241	6	36	1	16	1	3	0	<0.4	0.2	0.4

(a) C, N, O are not included in calculations of wt%.

(b) None detected.

(c) Concentrations estimated using the data from Tables 3-1 to 3-4 of SRNL-STI-2012-00479.

(d) None recorded.

(e) Sludge leached for 48 hours with 8 mL of 50 wt % caustic solution (0.02 moles) and 5 mL of inhibited water (i.e., 0.01 M NaOH and 0.001 M NaNO₂ in water).

(f) A combination of several samples from Tank 12H taken from 2008 through 2010. Through waste removal activities, it was noted that the Tank 12H sludge was layered, with uranium enrichment and thorium content varying as layers were encountered. Because this Tank 12H material is a composite of several samples taken at different stages of waste removal, it is a blend of layers and does not represent any individual layer.

3.4.2.3 *Tank 12H Residual Waste Sample Selection, Compositing, and Pretreatment*

Using the methodology described in the Liquid Waste Tank Residuals Sampling and Analysis Program Plan (LWTRSAPP) and the primary tank preliminary volume estimate, a Sample Location Determination Report (SLDR) was written to support the residual material characterization in the Tank 12H primary tank. [SRR-CWDA-2014-00036] The Tank 12H Tank-Specific Sampling and Analysis Plan (TSAP) was then written to provide guidance for the actual sampling of the tank floor, mound, and cooling coils. [SRR-LWE-2014-00074]

Tank 12H floor and mound residuals sampling was performed using robotic crawlers. Tank 12H contained three distinct residual material segments for sampling and characterization; an undisturbed mound of material behind the valve house cooling coil piping, material on the tank floor, and material encrusting the cooling coils. Using measurements made during the waste additions and drying and rewetting of Tank 12H, the mound behind the valve house was believed to be layered. [SRR-CWDA-2014-00103] Using the residual material (solids) distribution maps generated during the waste removal campaigns, the material on the waste tank floor was considered to be well-mixed. [SRR-CWDA-2014-00056] Five of the six planned floor samples for

compositing were collected, and the final tank floor sampling locations are documented in SRR-CWDA-2015-00074.

Actual Tank 12H residual waste solid samples archived in the SRNL shielded cells were evaluated based on available characterization data, sampling location, sample size and history in order to select samples to use for leachate testing. Multiple Tank 12H residual waste samples were taken during Tank 12H operational closure for use in tank characterization (SRR-LWE-2014-00074). A Tank 12H Sample Compositing Determination was prepared to document the reasoning and calculation behind the Tank 12H residual material compositing. This determination was based on the final primary tank volume determination (i.e., sample locations) and the sample material densities. [SRR-CWDA-2014-00103]

SRNL performed an analysis of Tank 12H final characterization samples in 2015. Eleven Tank 12H floor and undisturbed mound residual material samples and three cooling coil scrape samples were collected and delivered to SRNL between May and August of 2014 (the sample weights (dry) and bulk densities are presented in Table 3.4.2-2). The eleven floor and mound samples were homogenized and combined into three composite samples based on a proportional compositing scheme and the resulting composite samples were analyzed for an extensive suite of radiological and elemental components. The construction of the Tank 12H composite samples (i.e., the four samples selected for each composite sample) are presented in Table 3.4.2-3. [SRR-CWDA-2014-00103]

Additional measurements performed on the Tank 12H composite samples included bulk densities, weight percent solids, and water leaching of the solids to determine water soluble components. In general, these analyses were performed and reported in triplicate, where possible. Where analytical methods yielded additional analytes other than those requested by the customer, the results were also reported. The cooling coil scrape samples and the combined liquid fraction separated from the floor samples were characterized for a limited suite of analytes. These Tank 12H analyses were used to adjust the residual tank inventories as part of tank closure. The Tank 12H final characterization results from the three composite samples are provided in Tables 3.4.2-4 and 3.4.2-5 for the radionuclides of interest. [SRNL-STI-2015-00241]

The Tank 12H sample material was re-packaged by SRNL in 2016 and retained for potential future use in the SRNL shielded cells (SRR-CWDA-2016-00105). Approximately 36 grams of floor residual sample solids was retained from the Tank 12H samples by compositing material from sample F-1R, F-3R, F-4, and F-5 into one container. Approximately 178 grams of primary mound residual sample solids was retained from the Tank 12H samples by compositing material from Tank 12H samples M-L-1, M-L-2, M-L-3 and samples M-H-1, M-H-2, M-H-3 into one container. The sample compositing was performed per the residual sample material disposition plan (SRR-CWDA-2016-00049) to the extent practical given the amounts of uncompromised material that were still available and the constraints affecting operations in the cells at the time of re-packaging.

Table 3.4.2-2: Tank 12H Sample Weights (dry) and Bulk Densities

Sample	Weight (grams)	Bulk Density (grams/ml)
F-1	No appreciable material recovered	NA
F-2	No appreciable material recovered	NA
F-3	No appreciable material recovered	NA
F-4	130 ^a	1.62±0.06 ^a
F-5	170 ^a	1.97±0.07 ^a
F-6	No appreciable material recovered	NA
F-1R	148 ^a	1.68±0.05 ^a
F-2R	20 ^a	0.93±0.01 ^a
F-3R	68 ^a	1.11±0.09 ^a
M-L-1	55 ^b	0.54±0.09 ^c
M-L-2	53 ^b	0.58±0.05 ^c
M-L-3	70 ^b	0.62±0.06 ^c
M-H-1	79 ^b	0.71±0.06 ^c
M-H-2	97 ^b	0.68±0.07 ^c
M-H-3	88 ^b	0.75±0.08 ^c

Note: F = Floor samples, M = Mound samples, L= Low sample, H = High sample,
R = Resample

^a Measurement made after air-drying for 146 hours

^b Sample weight after air-drying for 150 hours

^c Measurement made after air-drying for 24 hours

Table 3.4.2-3: Tank 12H Composite Sample Construction

Material Segment	Composite No. 1	Composite No. 2	Composite No. 3
Mound	M-L-1	M-L-2	M-L-3
Mound	M-H-1	M-H-2	M-H-3
Floor	F-4	F-2R	F-1R
Floor	F-5	F-3R	F-4

Table 3.4.2-4: Tank 12H Residual Waste Samples – Average Radionuclide Concentrations

	T12 Composite Sample 1 (μCi/g)	T12 Composite Sample 2 (μCi/g)	T12 Composite Sample 3 (μCi/g)	Average (μCi/g)
Tc-99	4.09E-03	4.40E-03	3.86E-03	4.12E-03
I-129	4.75E-03	5.03E-03	3.87E-03	4.55E-03
U-233	<3.56E-02	<7.94E-02	<3.33E-02	4.94E-02
U-234	4.41E-03	7.75E-03	4.95E-03	5.70E-03
U-238	2.27E-04	7.77E-04	3.22E-04	4.42E-04
Np-237	8.39E-03	2.12E-02	8.01E-03	1.25E-02
Pu-238	6.74E+01	1.35E+02	6.65E+01	8.96E+01
Pu-239	2.91E+00	5.77E+00	2.71E+00	3.80E+00
Pu-240	1.02E+00	2.13E+00	9.71E-01	1.37E+00
Pu-241	1.43E+01	3.20E+01	1.54E+01	2.06E+01

[SRNL-STI-2015-00241]

Table 3.4.2-5: Tank 12H Residual Waste Samples Elemental Wt% (a)

	T12 Composite Sample 1	T12 Composite Sample 2	T12 Composite Sample 3
Al	5.88	9.49	5.89
Ca	0.11	0.11	0.12
Fe	32.4	22.1	35.7
Mg	0.01	<0.01	0.02
Mn	1.18	1.58	1.33
Na	0.53	0.65	0.42
Ni	0.73	1.03	0.56
Si	0.13	0.15	0.18
U	0.04	0.15	0.07
Th	3.44	8.18	3.26
Hg	19.4	11.7	15.7
Total	63.85	55.14	63.25

[SRNL-STI-2015-00241]

(a) C, N, O are not included in calculations of wt%.

3.5 Residual Waste Samples Leachate Testing

3.5.1 Tank 18F Residual Waste Sample Leachate Testing

Leaching tests were conducted with Tank 18F residual waste solids. The dissolution of Pu, U, Tc, and Np present in Tank 18F residual solids mixed with calcium carbonate (CC) (also written as CaCO₃ throughout this document) or CFS solids and, for reducing cases, ferrous sulfide solids were evaluated in the grout pore water simulant solutions. CFS and calcium carbonate solids were added to each test sample at a concentration of 16.7±0.1 g/L. Tank 18F solids were added to each test sample at a concentration of 30.1±0.2 g/L. This phase ratio was selected based on a combination of solubility and analytical limit of detection considerations and not the actual condition in a grout-filled waste tank. A goal in selecting the phase ratio was ensuring that key dose contributors were not removed to any appreciable extent by the pore water flow prior to

reaching the ORIII condition. FeS solid was added to RRII samples at a concentration of 3.1-3.2 g/L. Slurry volumes ranged from 200-250 mL. Test samples were prepared by the addition of various solid reagents and simulant solutions (Table 3.4-1) to the test vessels after equipment installation in the shielded cells. The A and B leach samples were replicate samples for the ORII condition. The C and D samples were also initially replicate samples for the ORIII condition, until the D sample was compromised during testing (see discussion below). The E and F samples were both intended to represent the RRII condition, but with different grout-representative phases (calcium carbonate for Sample E; CFS solids for sample F). In addition to the reagents listed in Table 3.5.1-1, calcium hydroxide was added as needed to raise the pH of the ORII and RRII samples to near the target values. An air purge (without CO₂ removed) was utilized to lower the pH of the oxidizing samples (ORIII in particular), as needed. [SRNL-STI-2016-00432]

Table 3.5.1-1: Tank 18F Test Sample and Reagent Masses and Solution Volumes

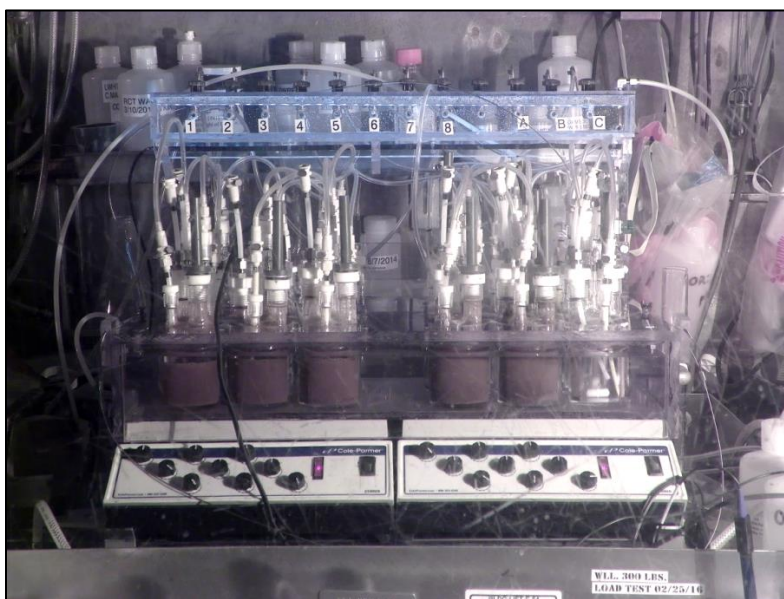
Sample ID	Tank18F Residual (g)	CaCO₃ (g)	FeS (g)	CFS (g)	Simulant Type	Simulant Volume (mL)
ORII-A	6.016	3.332	---	---	ORII/RRII	200
ORII-B	6.068	3.346	---	---	ORII/RRII	200
ORIII-C	6.013	3.352	---	---	ORIII	200
ORIII-D	6.034	3.341	---	---	ORIII	200
RRII-E	7.482	4.191	0.763	---	ORII/RRII	250
RRII-F	7.559	---	0.794	4.175	ORII/RRII	250

Initial sample preparations and conditioning were conducted 2 to 3 weeks prior to the test start date. Soon after contacting the RRII samples with pore water simulant solutions, the vessels were placed under nitrogen to avoid exposing the samples to ambient oxidizing conditions. Since the ORII and ORIII sample types represent the latter grout aging stages where many volumes of pore water have passed through the system, samples A through D were washed with two portions of the appropriate simulant solutions prior to the initiation of leaching studies. Scoping studies indicated that the wash volumes used would decrease the soluble sodium concentration to near that of the as-prepared simulant composition. The RRII samples (E and F) were not washed initially, since this condition represents the early portion of grout aging. After approximately three weeks of leach testing and sub-sampling, the liquid was decanted from each of the RRII samples and fresh simulant was added. As a result, RRII testing was conducted in two phases with the second testing phase involving lower ionic strength solution. Leach test samples were monitored during testing to evaluate whether evaporative or entrainment sample losses associated with continuous sample gas purging were an issue. After three weeks of testing, the liquid heights of selected samples were measured and it was confirmed that sample losses were minimal. During the entire course of the leaching studies, 30 to 50 volume percent of the initial sample slurries was consumed due to sub-sampling. [SRNL-STI-2016-00432]

The waste testing apparatus was installed in the SRNL shielded cells facility (Figure 3.5.1-1) for the actual leachate testing. The leach test slurries included grout-representative solids (CFS or calcium carbonate), Tank 18F residual solids, and ferrous sulfide solids (for reducing samples only). Two liquid simulants were used for testing with calcium carbonate reagent added to each simulant to just beyond saturation (dusting of solids observed in each simulant). Ca(OH)₂ was

added to one simulant sample to produce a solution pH of 11.1 and the resulting simulant was utilized for ORII and RRII testing. Air sparging of a second simulant sample resulted in a solution pH near 9.2 and this simulant was utilized for ORIII testing. Residual soluble salts in the actual Tank 18F solids resulted in elevated pH and elevated sodium levels relative to the initial SIW composition. As a result, except for selected tests it was necessary to wash the solids with simulant to remove the residual soluble salts. Sample washing was conducted for samples A through D (test conditions ORII and ORIII) prior to leach testing. Wash solutions were in contact with the test samples for several days prior to removal from the vessels. Sample washing was not conducted for samples E and F (RRII conditions) until after the completion of three weeks of leach testing. This two-phased approach was expected to be representative of the earlier and latter portions of the RRII phase of aging. As needed, calcium hydroxide reagent and air sparging were also used during testing to make any additional pH adjustments. During leach studies the test samples were continuously agitated with magnetic stir bars and purged with nitrogen, air, or CO₂-stripped air. Testing was conducted at 21-22 °C over a period of approximately two months with samples being collected approximately weekly. [SRNL-STI-2016-00432]

Figure 3.5.1-1: Testing Equipment after Installation in the SRNL Shielded Cells and After Sample Addition/Preparation



More details regarding the actual waste release testing are provided in the SRNL waste release testing report (SRNL-STI-2016-00432).

3.5.2 Tank 12H Residual Waste Sample Leachate Testing

Leaching tests were conducted with Tank 12H residual waste solids. Waste release test samples were prepared by mixing portions of the archived Tank 12H composite mound and composite floor residual materials in the shielded cells at an approximate 78:22 mass ratio ($3.5 \pm 0.1:1$) of floor:mound material. Exact reagent and sample masses used for the preparation of the individual test slurries are provided in Table 3.5.2-1. Test samples contained 7.5 ± 0.025 g of Tank 12H residual solids floor/mound composite. Approximately 4.2 g of CaCO₃ or CFS solids were added

to each test sample as indicated in Table 3.5.2-1. Approximately 0.8 g of FeS solids were initially added to each of the RRII test vessels. Another portion (~0.25 g) of FeS solids was added to each of the samples after the sampling event 6. The initial volume of each leachate slurry sample was 250 mL. [SRNL-STI-2018-00484]

Table 3.5.2-1: Tank 12H Test Sample and Reagent Masses

Sample Identifier	Tank 12H Floor (g)	Tank 12H Mound (g)	Floor: Mound (g:g)	CaCO₃ (g)	CFS (g)	FeS (g)	Porewater Simulant Type^a
RRII-1/ RRII-CC	5.857	1.648	3.4:1	4.171	---	1.048 ^b	RRII
RRII-2/ RRII-CFS	5.849	1.658	3.5:1	---	4.142	1.063 ^b	RRII
ORII-3/ ORII-A	5.867	1.657	3.5:1	4.160	---	---	ORII
ORII-4/ ORII-B	5.842	1.659	3.5:1	4.155	---	---	ORII
ORII-5/ ORIII-A	5.865	1.656	3.5:1	4.195	---	---	ORIII
ORII-6/ ORIII-B	5.839	1.644	3.6:1	4.175	---	---	ORIII

^a 250 mL of simulant solution was initially added to each sample vessel

^b ~0.8 g FeS added initially and another ~0.25 g added after sample event 6

^c Ca(OH)₂ also added to all samples except RRII-CFS as needed to achieve the target pH values

Analysis of similar floor/mound composite samples (mass ratio 3.5:1) was conducted using two different digestion methods (aqua regia and peroxide fusion). Results are provided in Table 3.5.2-2 along with previously reported results for the composite samples with floor:mound ratios most similar to the leach test samples. Aluminum, iron, thorium, and mercury are the primary waste components, as was the case for the characterized composite samples. Generally good agreement was observed between the two dissolution methods. However, the sub-sample composite used for leach testing contained considerably more Al (19 wt. %) than the samples analyzed previously (<10 wt. %). In addition, the leach test samples contained less Fe (17 wt%) than the previous composites used for characterization (20-35 wt. %). Mercury, thorium, and miscellaneous actinide levels (U, Np, Pu) were comparable to previous results. [SRNL-STI-2018-00484]

Insufficient floor sample was available for I-129 analysis. Therefore, a mound sample (no floor component) and a residual leachate test sample (RRII-CFS after leaching with porewater solution) were analyzed for I-129 to ensure that iodine levels were still comparable to previous results. A special I-129 analysis method was used for this characterization involving contact of the solid samples with concentrated nitric acid. Iodine analysis results are provided in Table 3.5.2-2. The mound sample contained I-129 at levels comparable to the Composite 3 sample reported in SRNL-STI-2015-00241. Correction of the I-129 concentration reported for the RRII-CFS sample to a Tank 12H solids only mass basis gives 2.0 E-3 µCi/g sludge. [SRNL-STI-2018-00484]

Table 3.5.2-2: Tank 12H Composite Leach Test Sample Selected Elemental and Radionuclide Concentrations Versus Previous Characterization Samples

Analyte	Aqua Regia ^a	Peroxide Fusion ^a	Average	%RSD	Composite 2 ^b	Composite 3 ^b
Weight %						
Al	19.1	18.4	18.8	3	9.5	5.9
Fe	15.7	19.0	17.4	13	22.1	35.7
Hg	11.3	5.8	8.6	45	11.7	15.7
Th	6.2	5.8	6.0	5	8.2	3.3
Mn	1.0	1.1	1.0	10	1.6	1.3
Na	0.64	---	0.64	---	0.65	0.42
Ni	0.45	0.56	0.51	16	1.03	0.56
Ca	0.12	0.41	0.27	76	0.11	0.12
Si	0.11	0.16	0.13	22	0.15	0.18
Zr	0.10	---	0.10	---	0.15	0.10
U ^c	0.19	0.19	0.19	2	0.15	0.07
uCi/g						
Tc-99					4.4E-03 ^d	3.9E-03 ^d
Np-237	1.0E-03	1.1E-03	1.1E-03	4	3.0E-03 ^d	1.1E-03 ^d
Pu-238	69.8	68.0	68.9	2	135.0	66.5
I-129	3.8E-03 ^e	1.3E-03 ^f			5.0E-03	3.9E-03
Floor:Mound (mass ratio)	3.5:1		---	---	1.9:1	4.4:1

^a Sludge residual dissolution method.

^b As reported in SRNL-STI-2015-00241.

^c Total uranium reported as sum of U-233, U-234, U-235, U-236, and U-238 isotopes.

^d Calculated from the values reported in SRNL-STI-2015-00241.

^e Composite mound residual solids not exposed to porewater leach solutions.

^f Leachate residual solids including both floor and mound composite materials and CFS solids following contact with porewater leach solutions.

The dissolution of Tc-99, I-129, U (sum of selected isotopes), Np-237, and Pu (sum of selected isotopes) present in Tank 12H residual solids mixed with calcium carbonate or CFS solids and, for reducing cases, ferrous sulfide solids were evaluated in the grout pore water simulant solutions. CFS and calcium carbonate solids were added to each test sample at a concentration of 16.7±0.1 g/L slurry. Tank 12H solids were added to each test sample at a concentration of 30.0±0.1 g/L slurry. This phase ratio was selected based on a combination of solubility and analytical limit of detection considerations and not the actual condition in a grout-filled tank. A goal in selecting the phase ratio was ensuring that key dose contributors were not removed to any appreciable extent by the pore water flow prior to reaching the ORIII condition. FeS solid was added to RRII samples at a cumulative concentration of 4.2±0.03 g/L slurry. Initial FeS concentrations were near 3.2 g/L and additional FeS was added after 81 contact days. All test sample initial slurry volumes were 250 mL. The sample volumes decreased during testing due to the removal of primarily liquid from the samples for analysis. [SRNL-STI-2018-00484]

The ORII-A and -B leach samples were replicates for the ORII condition. The ORIII-A and -B samples were also initially replicate samples for the ORIII condition, until the -B sample was compromised during testing (see discussion below). The RRII-CC and RRII-CFS samples were both intended to represent the RRII condition, but with different grout-representative phases (calcium carbonate and Cement Flyash and Slag solids as indicated in the sample names). [SRNL-STI-2018-00484]

As shown in Table 3.5.2-3, sample washing was conducted for the oxidizing samples (ORII and ORIII) prior to leach testing. Wash solutions were in contact with the test samples for several hours (5-12 hr) while the solids settled prior to removal from the vessels. Sample washing was not conducted for the reducing samples (RRII-CC and RRII-CFS) until after 62 days of contact. At this point the remaining free liquid simulant was removed from each leach test sample and additional simulant was added under a nitrogen gas purge to give a final slurry volume of 250 mL. This two-phased leach testing approach was intended to be representative of the earlier and later portions of the RRII phase of aging. [SRNL-STI-2018-00484]

Table 3.5.2-3 Test Sample Initial Wash Decant Volumes.

Test Sample	Volume (mL)	Comments
RRII-CC	0	No wash prior to initial leach testing; after 62 contact days the remaining free liquid was removed and fresh simulant was added to the test vessels to give a final slurry volume of 250 mL
RRII-CFS	0	
ORII-A	250	ORII wash samples composited into single bottle
ORII-B	250	
ORIII-A	250	ORIII wash samples composited into single bottle; after 69 contact days the ORIII sample leach test vessel broke and the sample was exposed to approximately 8.5 liters of liquid at pH 12 for several days
ORIII-B	250	

In addition to the reagents listed in Table 3.5.2-1, calcium hydroxide was added as needed to raise the pH of the ORII and RRII-CC samples to near the target values during testing (cumulative addition of 0.35-0.55 total g per sample typically added in 0.02 g portions). Considerably less calcium hydroxide (cumulative addition of ~0.1 total g) was added to the ORIII samples to raise the pH. An air purge (without CO₂ removed) was also utilized to lower the pH of the ORIII samples, as needed. The RRII-CFS sample did not require Ca(OH)₂ addition during testing. Sample liquid level heights were visually monitored during testing to confirm that liquid losses to evaporation were minimal. Gas flow rates were maintained at minimum levels and liquid levels in the demister vessels were maintained at sufficient heights to minimize sample evaporation. During the entire course of the leaching studies, ≤50 volume percent of the initial sample slurries was consumed due to sub-sampling. [SRNL-STI-2018-00484]

The dates of sample preparations and sub-sampling and comments regarding the testing are provided in Table 3.5.2-4. Prior to collection of the first analysis sample, an SRNL safety pause was initiated which delayed both sample pH adjustments and sub-sampling for almost a month. Therefore, the first analysis sub-samples were collected after 42 days of total contact. [SRNL-STI-2018-00484]

**Table 3.5.2-4 Test Sample Preparation and Sub-Sampling Timeline and Comments
(all activities conducted in 2018)**

Date	Activity	Contact Days	Comments
4/12	sample preparation	0	leach test samples prepared; oxidizing samples washed; target pH achieved
4/17	pH adjustment	5	discovered base consumption by samples and began pH adjustments
4/18		6	continued pH adjustment with calcium hydroxide
4/19		7	
SRNL Safety Pause			
5/15	pH adjustment	33	resumed pH adjustment with calcium hydroxide
5/16		34	continued pH adjustment with calcium hydroxide
5/17		35	
5/21		39	
5/24	1 st sub-sampling	42	
5/29	pH adjustment	47	continued pH adjustment with calcium hydroxide
5/30		48	
6/1	2 nd sub-sampling	50	
6/5	pH adjustment	54	continued pH adjustment with calcium hydroxide
6/7	3 rd sub-sampling	56	
6/11	pH adjustment	60	continued pH adjustment with calcium hydroxide
6/12		61	
6/13	4 th sub-sampling	62	removed free liquid from RRII samples and added fresh simulant
6/20	pH adjustment	69	continued pH adjustment with calcium hydroxide; ORIII-B leach test vessel broke but sample recovered
6/26	pH adjustment	75	continued pH adjustment with calcium hydroxide; ORIII-B to new vessel, re-established conditions
6/27		76	
6/28	5 th sub-sampling	77	
7/2	6 th sub-sampling	81	
7/3	pH adjustment	82	continued pH adjustment with calcium hydroxide
7/9		88	
7/11	7 th sub-sampling	90	
7/13	pH adjustment	92	continued pH adjustment with calcium hydroxide
7/16	8 th sub-sampling	95	
7/19	9 th sub-sampling	98	only sub-sampled reducing samples

Sample pH adjustments were required throughout most of the testing for the RRII-CC, ORII-A, and ORII-B samples due to base consumption by the samples. After the 4th sub-sampling event, remaining free liquid was removed from the RRII samples and fresh porewater simulant was added. Also, after the 4th sub-sampling event, the ORIII-B sample vessel and the ORIII caustic scrubber vessel broke resulting in the loss of the caustic reagent and sample into the water bath solution. The solids were recovered from the solution to give a final slurry with a pH near 12. The solids were subsequently washed with fresh porewater simulant and transferred to a new test vessel and the target conditions were re-created. The ORIII-B sample recovery liquid and subsequent wash solutions were analyzed to calculate radionuclide losses resulting from contact of the ORIII-B sample solids with these liquids. Sub-sampling of the ORIII-B sample was then resumed. This sample was subsequently considered to represent a highly-washed residual sludge sample, although the pH of the contact liquid was higher than any of the target conditions. [SRNL-STI-2018-00484]

ORP measurements on the reducing samples were much higher than the target values for most of the testing. After the 6th sub-sampling event, additional FeS reagent was added to each of these samples to attempt to lower the measured ORP values. These final additions resulted in significant reductions in the measured ORP values. As a result, the later sub-samples collected from the RRII samples are closer to the target E_h values than earlier sub-samples. One additional sub-sampling event (9th sub-sampling event) was conducted for the reducing samples due to the achievement of lower E_h values toward the end of testing. [SRNL-STI-2018-00484]

Sample aliquot volumes of 5-12 mL (depending on the volume needed for analysis) were collected from the leach test vessels for analysis after the measurement of the solution pH and E_h at approximately weekly intervals. Nine sampling events (eight for oxidizing samples) were conducted over a period of nearly two months (sub-sample collection sludge:simulant contact days: 42, 50, 56, 62, 77, 81, 95, and 98). Sub-sample aliquots were filtered as described above through 0.1- μ m polyvinylidene fluoride (PVDF) syringe filter units without opening the bottle caps. Identically-prepared blank samples were typically collected for analysis along with the leachate test samples. 5 M nitric acid volumes of 0.9-1.8 mL (adjusted for the target sample volume to give a sample:acid volume phase ratio near 6) were placed in the analysis bottles prior to cell entry to acidify the samples and avoid post-filtration precipitation of the dissolved radionuclides and metals. The isolated samples were manually shaken to promote mixing of the porewater filtrate and the diluent acid. [SRNL-STI-2018-00484]

The acidified sub-samples were analyzed for plutonium by alpha spectroscopy following separation using thenoyltrifluoroacetone (TTA) and for uranium, technetium, and neptunium by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Reported plutonium concentrations are based on the sum of the measured Pu-238 and Pu-239/240 concentrations in dpm/mL converted to molar concentrations. For the reducing samples, plutonium concentrations were typically below detectable limits. Quantification of the total plutonium detection limits on a molar basis for the reducing samples was conducted by adjustment of the Pu-238 detection limit to total Pu based on the known isotopic ratios for this sample. Total uranium concentrations were calculated as the sum of the U-235 and U-238 isotopes since sample characterization confirmed negligibly small contributions from other uranium isotopes (U-233, -234, and -236) on a molar basis. Neptunium was calculated from the reported concentration of mass Np-237. Technetium was calculated from the reported concentration of mass Tc-99. I-129 was analyzed by radiocounting techniques.

Other analyses were conducted on selected samples including: Inductively Coupled Plasma Emission Spectroscopy (ICP-ES), Ion Chromatography (IC), and Total Inorganic Carbon (TIC). Separate solid sub-samples were digested in acid (aqua regia and sodium peroxide fusion) to determine the elemental composition by ICP-MS, ICP-ES, beta scintillation counting (for Tc-99), and cold vapor atomic absorption for Hg. All sample chemical and physical analyses (excluding pH and ORP) were conducted by the SRNL AD department.

4.0 WASTE RELEASE TESTING DATA AND ANALYSIS

The purpose of this section is to document the results of the waste release testing and compare the results to the residual waste solubility assumptions used in the FTF and HTF PA WRMs.

4.1 Tank 18F Waste Release Testing Results

During the waste release testing, an attempt was made to drive the test conditions (i.e., pH, E_h) of each sample to the target chemical condition/region in the waste release test apparatus. The residual waste samples were driven towards target chemical conditions through various methods (i.e., FeS addition, controlling atmosphere, and washing). The chemical conditions achieved during each of the seven sample sets are presented in Table 4.1-1. The relative success in meeting the target pH and E_h conditions through five samples sets is displayed on Figures 4.1-1 and 4.1-2. [SRNL-STI-2016-00432] The target pH values were achieved to within 0.5 pH units for all samples. Leaching studies were conducted over an E_h range of approximately 0.7 V. However, the highest and lowest E_h values achieved of approximately +0.5 V and approximately -0.2 V were significantly less positive and less negative, respectively, than the target values. These experimental limitations are attributed to the presence of multiple solid phases and the relatively slow reaction kinetics for the conversion of solid phases under the tests conditions. As previously reported with simulated tank waste solids, more positive and more negative E_h values required the addition of non-representative oxidants and reductants, respectively. As was the case during simulant testing, the highest E_h values were observed for the ORIII test samples and the lowest values were observed for the RRII samples. Higher E_h values were observed for the early RRII samples prior to sample washing which was conducted between the third and fourth testing sampling events. Presumably, the higher E_h values are associated with the higher ionic strength of the samples prior to washing.

Overall, the test conditions achieved are reasonable and reflect a range of conditions such that the test results can be used to display the impact of transitory waste tank chemical conditions on solubility. The target pH values were met with a high degree of success. Achieving the extreme E_h target conditions used in solubility modeling continues to be a challenge (as it was in simulant testing) providing support to the supposition that extreme E_h values most likely would not occur under actual waste tank conditions.

Table 4.1-1: Tank 18F Waste Release Test Conditions

Test Number	ORII Sampling pH and E_h (mV)	ORIII Sampling pH and E_h (mV)	RRII Sampling pH and E_h (mV)
Target Conditions	11.1 / 560	9.2 / 680	11.1 / -470
Sample Event 1	(A) 11.4 / 330 (B) 11.0 / 311	(C) 9.6 / 354 (D) 9.8 / 348	(E) 11.0 / 59 (F) 11.7 / -29
Sample Event 2	(A) 11.3 / 391 (B) 11.0 / 291	(C) 9.6 / 304 No sample	(E) 10.9 / -159 (F) 11.7 / -321
Sample Event 3	(A) 11.4 / 356 (B) 10.9 / 407	(C) 9.5 / 520 (D) 9.0 / 520	(E) 10.9 / -43 (F) 11.7 / -174
Sample Event 4	(A) 11.4 / 402 (B) 10.9 / 342	(C) 9.2 / 522 (D) 9.0 / 472	(E) 10.9 / -174 (F) 11.3 / -199
Sample Event 5	(A) 11.2 / 324 (B) 11.0 / 309	(C) 9.2 / 474 (D) 9.1 / 511	(E) 10.9 / -244 (F) 11.4 / -249
Sample Event 6	(A) 11.2 / 320 (B) 10.8 / 317	(C) 9.5 / 536 (D) 9.5 / 516	(E) 10.9 / -262 (F) 11.4 / -202
Sample Event 7	(A) 11.1 / 358 (B) 10.6 / 343	(C) 9.7 / 549 (D) 9.5 / 472	(E) 10.9 / -153 (F) 11.4 / -135

Figure 4.1-1: Tank 18F Waste Release Test pH

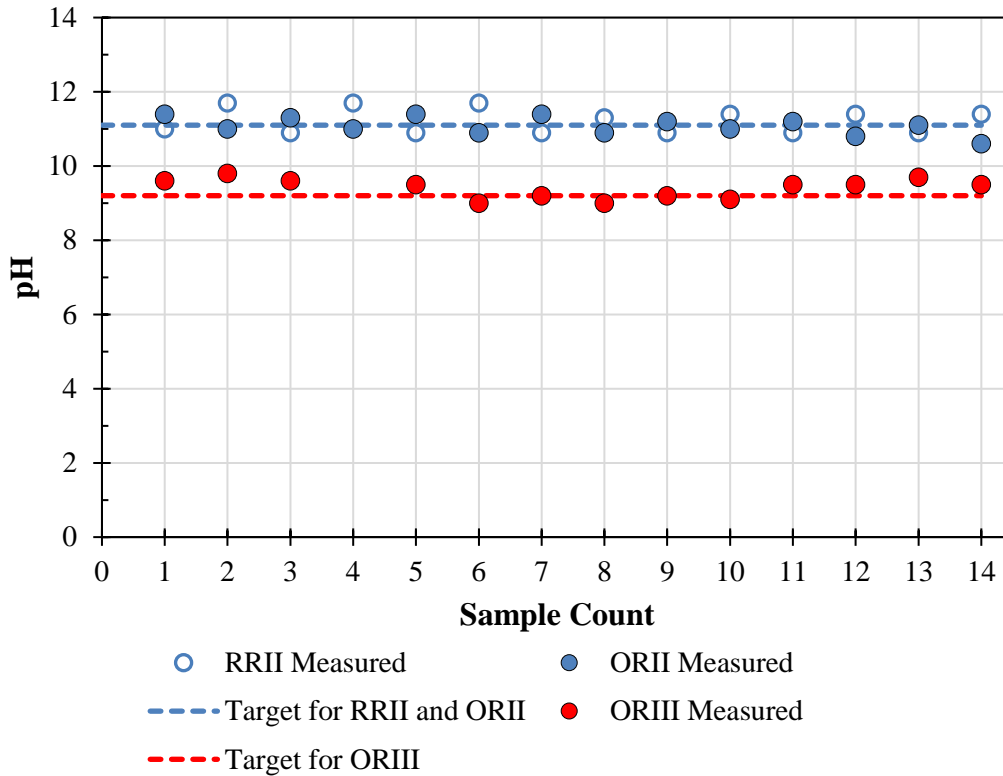
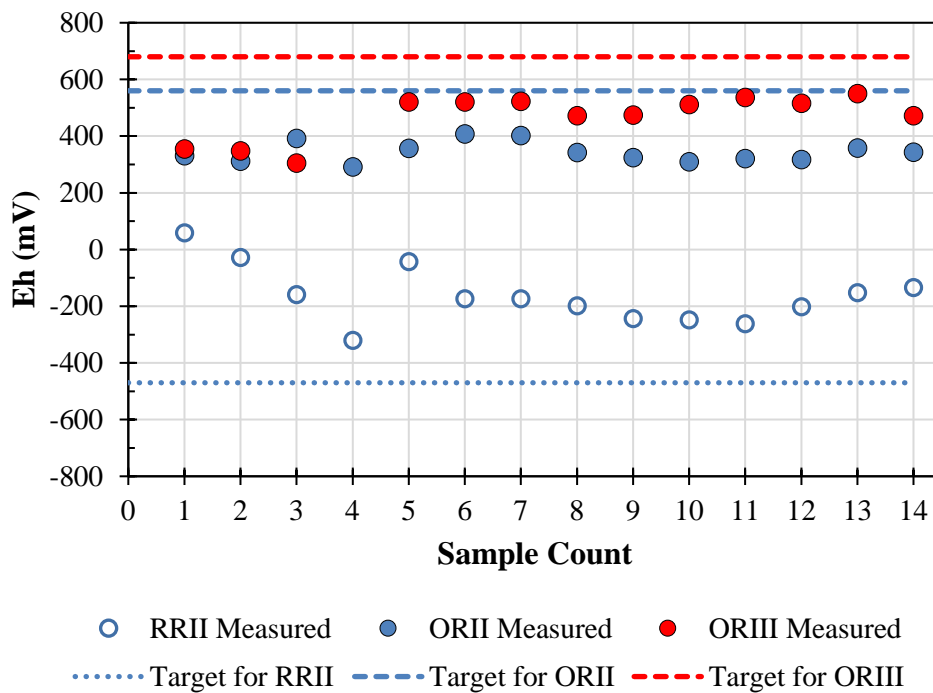


Figure 4.1-2: Tank 18F Waste Release Test E_h



The waste release testing results (in mol/L) for the four elements of interest for each of the filtered samples (seven sample sets) are presented in Table 4.1-2. The values calculated in the current TF WRM (SRNL-STI-2012-00404) for the target chemical conditions and for the various elemental solubilities are also listed in Table 4.1-2. The data values in Table 4.1-2 with a yellow highlight are minimum detection limits (versus measured values). The actual concentrations of the associated elements in the sample may be lower than the number shown. Missing data (an entry in Table 4.1-2 where the data cell is filled with a dash instead of a value) for some samples during the first three sampling events was the result of sample or sub-sampling issues during testing. A discussion of the various concentration results for plutonium, neptunium, technetium, and uranium is provided in Section 4.2.

Only one Pu control sample (44 days) contained plutonium above detectable limits, and this sample contained plutonium at levels just above detection and well below most leach test sample results. This observation provides confidence that the test methodology and sample design successfully eliminated plutonium contamination and the plutonium concentrations observed for the samples can be attributed to the metal leaching from the Tank 18F residual solids. The U control sample analysis indicated that uranium contamination occurred for the later control samples. However, the highest uranium concentration in the control samples of 1E-7 M is significantly lower than all leach test sample concentrations observed. No detectable neptunium or technetium was observed for any of the respective Np and Tc control samples. [SRNL-STI-2016-00432]

Conservatively estimated (maximum) losses of the various metals of interest to the wash solutions based on the wash volumes and assuming the maximum observed metal concentrations during leach testing are provided in Table 4.1-3. As shown in the table, the estimated loss to the wash solutions was greatest across the board for the D sample due to the larger wash volume for this sample. However, the estimated fraction removed was still small for Pu (<0.5%) and Np (<1.5%), meaning that the wash did not significantly impact the concentration results. The effects of washing are discussed further in Section 4.2.

Table 4.1-2: Tank 18F Waste Release Testing Results ^a

Sample	Event	pH	E _h (mV)	Event	Pu (M)	U (M)	Tc (M)	Np (M)
WRM Value		11.1	-470		3.00E-11	5.00E-09	1.00E-14	1.00E-09
RRII-E	1	11.0	59	1	---	---	---	---
	2	10.9	-159	2	7.80E-10	6.50E-04	1.70E-09	8.50E-10
	3	10.9	-43	3	7.40E-10	5.90E-04	2.90E-09	1.20E-09
	4	10.9	-174	4	7.70E-10	1.10E-06	5.70E-09	2.40E-09
	5	10.9	-244	5	4.50E-09	1.70E-06	5.70E-10	2.40E-10
	6	10.9	-262	6	2.80E-09	2.80E-06	5.60E-10	2.40E-10
	7	10.9	-153	7	1.80E-09	2.70E-06	5.70E-10	2.40E-10
RRII-F (CFS)	1	11.7	-29	1	2.50E-12	1.30E-05	1.10E-08	2.30E-09
	2	11.7	-321	2	1.40E-11	1.10E-05	3.00E-09	2.40E-10
	3	11.7	-174	3	1.40E-10	1.10E-05	2.90E-09	1.20E-09
	4	11.3	-199	4	1.10E-10	2.20E-06	5.80E-09	2.40E-09
	5	11.4	-249	5	4.50E-11	1.90E-06	5.70E-10	2.40E-10
	6	11.4	-202	6	9.10E-11	1.60E-06	5.60E-10	2.30E-10
	7	11.4	-135	7	3.30E-11	1.50E-06	5.70E-10	2.40E-10
WRM Value		11.1	560		3.00E-11	5.00E-05	1.00E-13	3.00E-07
ORII-A	1	11.4	330	1	6.00E-11	1.80E-06	5.40E-09	2.30E-09
	2	11.3	391	2	1.20E-10	2.60E-06	3.34E-09	2.40E-10
	3	11.4	356	3	9.30E-11	---	---	---
	4	11.4	402	4	1.70E-10	3.20E-06	7.70E-09	2.40E-09
	5	11.2	324	5	4.00E-10	4.30E-06	9.50E-09	2.40E-10
	6	11.2	320	6	4.70E-10	4.30E-06	1.10E-08	2.40E-10
	7	11.1	358	7	5.70E-10	3.60E-06	1.30E-08	2.40E-10
ORII-B	1	11.0	311	1	8.20E-10	2.90E-06	5.50E-09	2.30E-09
	2	11.0	291	2	2.60E-09	3.80E-06	6.60E-09	2.40E-10
	3	10.9	407	3	3.00E-09	3.50E-06	8.10E-09	1.20E-09
	4	10.9	342	4	4.20E-09	4.00E-06	8.80E-09	2.40E-09
	5	11.0	309	5	5.00E-09	6.80E-06	9.20E-09	2.40E-10
	6	10.8	317	6	5.00E-09	1.60E-05	1.10E-08	2.70E-10
	7	10.6	343	7	8.50E-09	4.20E-05	1.30E-08	3.40E-10
WRM Value		9.2	680		3.00E-11	4.00E-06	2.00E-15	2.00E-06
ORIII-C	1	9.6	354	1	1.00E-08	2.30E-04	5.50E-09	4.50E-09
	2	9.6	304	2	1.60E-08	2.70E-04	4.80E-09	4.20E-09
	3	9.5	520	3	1.70E-08	2.60E-04	7.80E-09	4.60E-09
	4	9.2	522	4	1.10E-08	3.70E-04	8.00E-09	4.20E-09
	5	9.2	474	5	1.20E-08	4.20E-04	8.50E-09	4.80E-09
	6	9.5	536	6	9.80E-09	3.90E-04	1.10E-08	3.20E-09
	7	9.7	549	7	7.90E-09	3.30E-04	1.20E-08	3.00E-09
ORIII-D	1	9.8	348	1	2.00E-08	1.60E-04	5.50E-09	7.90E-09
	2	---	---	2	---	---	---	---
	3	9.0	520	3	3.20E-09	5.00E-06	2.90E-09	1.40E-09
	4	9.0	472	4	7.60E-09	9.50E-05	5.70E-09	2.40E-09
	5	9.1	511	5	8.60E-09	6.50E-05	4.40E-09	1.50E-09
	6	9.5	516	6	4.80E-09	6.20E-05	6.30E-09	1.20E-09
	7	9.5	472	7	4.50E-09	4.70E-05	6.30E-09	1.30E-09

^a Values that are minimum detection limits versus actual measured values are highlighted in yellow.

**Table 4.1-3: Estimated Maximum Metal Losses to Tank 18F Residual Washes
Prior to Leach Testing ^a**

Maximum Total Losses to Wash (%)				
Sample	Pu	U	Np	Tc
ORII-A	0.18	16	0.57	6.5
ORII-B	0.18	16	0.57	6.4
ORIII-C	0.17	15	0.55	6.2
ORIII-D	0.46	40	1.5	17
RRII-E	0.14	12	0.44	5.0
RRII-F	0.11	10	0.36	4.1

^a calculated losses based on wash volumes and assuming maximum observed concentrations during leach testing

4.2 Tank 12H Waste Release Testing Results

The Tank 12H test apparatus was used in Spring/Summer 2018 in the SRNL shielded cells facility to determine the leaching characteristics of actual radioactive Tank 12H residual solids under conditions believed to be representative of a closed waste tank during three different aging periods after tank closure. The leach test slurries included grout-representative solids (CFS or calcium carbonate), Tank 12H residual solids, and ferrous sulfide solids (for reducing samples only). Two liquid simulants were used for testing based on the SIW composition with calcium carbonate reagent added to each simulant during initial preparations to just beyond saturation (dusting of solids observed in each simulant). $\text{Ca}(\text{OH})_2$ was added to one simulant sample to produce a solution pH of 11.1 and the resulting simulant was utilized for ORII and RRII testing. A second simulant sample was prepared without $\text{Ca}(\text{OH})_2$ addition resulting in a solution pH near 9 and this simulant was utilized for ORIII testing. Tank 12H residual sub-samples and added solids were contacted with these simulants in the leach test vessels inside the shielded cells environment. As needed, calcium hydroxide reagent and air gas sparging (without CO_2 scrubbing) were also used during testing to make any additional pH adjustments. Air gas sparging without CO_2 was only used for ORIII samples.

Sample agitation during leach studies could not be accomplished using magnetic stir bars. Stirring could not even be accomplished when the vessels were taken out of the water bath using various stir bar types and sizes. The inability to stir was apparently due to some unexpected sample characteristic, since water could be easily and vigorously stirred in these vessels using this equipment. Therefore, the samples were agitated daily by briefly lifting the vessels from the water bath and stirring manually. Continuous gas purging served to mix the samples throughout testing as well. Testing was conducted at 22 °C over a period of approximately two months (after the Safety Pause) with sub-samples being collected periodically (approximately weekly, but varying considerably depending upon shielded cell technician availability).

The chemical conditions achieved during each of the sample sets are presented in Table 4.2-1. The relative success in meeting the target pH and E_h conditions through eight samples sets (sixteen sample counts) is displayed on Figures 4.2-1 and 4.2-2. The Tank 12H waste release testing results (in mol/L) for the five elements of interest for each of the filtered samples (up to nine sample sets)

are presented in Table 4.2-2 (a ninth sample event was carried out only for the reducing condition with only the concentrations measured). The values calculated in the current TF WRM (SRNL-STI-2012-00404) for the target chemical conditions and for the various elemental solubilities are also listed in Table 4.2-2. The data values in Table 4.2-2 with a yellow highlight are minimum detection limits (versus measured values). The actual concentrations of the associated elements in the sample may be lower than the number shown. Missing data (an entry in Table 4.2-2 where the data cell is filled with a dash instead of a value) for some samples was the result of sample or sub-sampling issues during testing. A discussion of the various sample concentration results for iodine, plutonium, neptunium, technetium, and uranium is provided in Section 4.2. [SRNL-STI-2018-00484]

Table 4.2-1: Tank 12H Waste Release Test Conditions

Test Number	ORII Sampling pH and E_h (mV)	ORIII Sampling pH and E_h (mV)	RRII Sampling pH and E_h (mV)
Target Conditions	11.1 / 560	9.2 / 680	11.1 / -470
Sample Event 1 (42 days)	(A) 10.7 / 293 (B) 10.7 / 292	(A) 9.0 / 389 (B) 8.8 / 411	(CC) 10.3 / 227 (CFS) 11.5 / 151
Sample Event 2 (50 days)	(A) 10.3 / 388 (B) 10.4 / 397	(A) 9.2 / 401 (B) 9.2 / 417	(CC) 10.9 / 201 (CFS) 11.5 / 147
Sample Event 3 (56 days)	(A) 10.3 / 366 (B) 10.2 / 371	(A) 9.4 / 397 (B) 9.4 / 389	(CC) 11.1 / 188 (CFS) 11.5 / 136
Sample Event 4 (62 days)	(A) 10.2 / --- (B) 10.3 / ---	(A) 9.1 / --- (B) 9.3 / ---	(CC) 11.0 / --- (CFS) 11.6 / ---
Sample Event 5 (77 days)	(A) 10.5 / 366 (B) 10.6 / 355	(A) 9.4 / --- (B) --- / ---	(CC) 10.8 / 212 (CFS) 11.4 / 155
Sample Event 6 (81 days)	(A) 10.6 / --- (B) 10.8 / ---	(A) 9.3 / --- (B) 9.1 / ---	(CC) 11.1 / 216 (CFS) 11.4 / 141
Sample Event 7 (90 days)	(A) 11.0 / 295 (B) 10.8 / 311	(A) 9.2 / 410 (B) 9.0 / 404	(CC) 11.0 / -79 (CFS) 11.2 / -56
Sample Event 8 (95 days)	(A) 10.8 / 333 (B) 11.0 / 322	(A) 9.3 / 421 (B) 9.3 / 416	(CC) 10.9 / -50 (CFS) 11.3 / -87

Figure 4.2-1: Tank 12H Waste Release Test pH

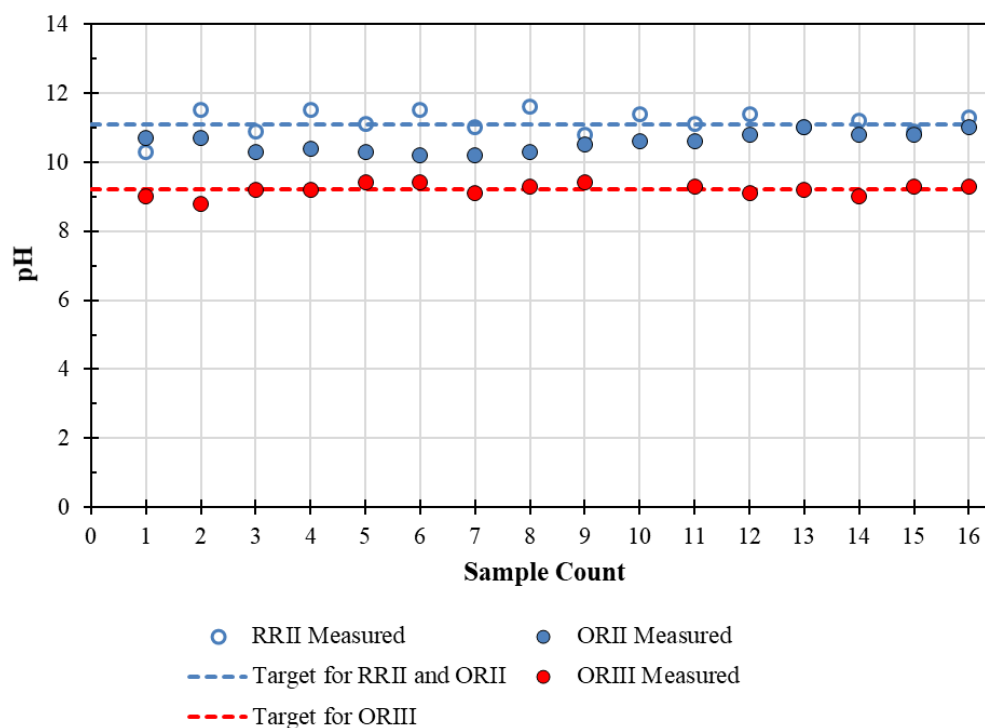


Figure 4.2-2: Tank 12H Waste Release Test E_h

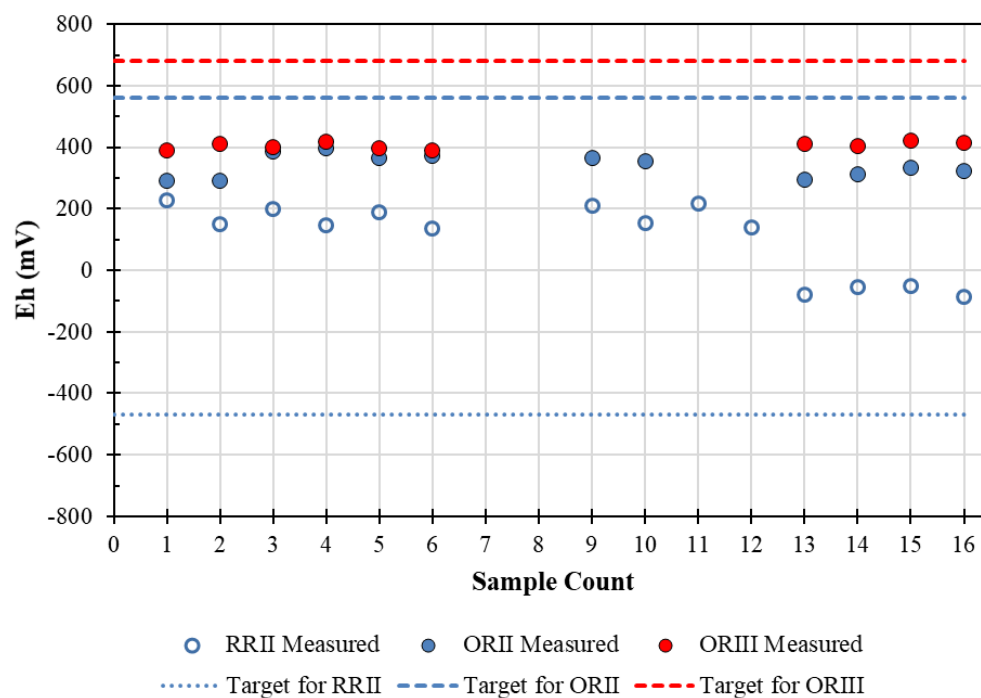


Table 4.2-2: Tank 12H Waste Release Testing Results ^a

Sample	Event	pH	E _h (mV)	I (M)	Pu (M)	U (M)	Tc (M)	Np (M)
WRM Value		11.1	-470	NSC	3.00E-11	5.00E-09	1.00E-14	1.00E-09
RRII-C	1	10.3	227	2.00E-07	3.00E-11	6.00E-08	4.00E-09	6.00E-11
	2	10.9	201	3.00E-07	5.00E-11	4.00E-08	4.00E-09	5.00E-11
	3	11.1	188	7.00E-07	3.00E-12	3.00E-08	2.00E-09	5.00E-11
	4	11.0	---	7.00E-07	6.00E-13	3.00E-08	2.00E-09	5.00E-11
	5	10.8	212	3.00E-07	2.00E-12	9.00E-09	1.00E-09	5.00E-11
	6	11.1	216	3.00E-07	6.00E-13	9.00E-09	1.00E-09	5.00E-11
	7	11.0	-79	4.00E-07	2.00E-12	9.00E-09	1.00E-10	5.00E-11
	8	10.9	-50	2.00E-07	4.00E-12	8.00E-09	1.00E-10	5.00E-11
	9	---	---	3.00E-07	7.00E-12	7.00E-09	3.00E-10	5.00E-11
RRII-(CFS)	1	11.5	151	2.00E-07	4.00E-13	4.00E-08	1.00E-08	4.00E-11
	2	11.5	147	6.00E-08	4.00E-11	3.00E-08	1.00E-08	5.00E-11
	3	11.5	136	1.00E-07	1.00E-12	3.00E-08	1.00E-08	5.00E-11
	4	11.6	---	5.00E-07	8.00E-13	3.00E-08	9.00E-09	5.00E-11
	5	11.4	155	2.00E-07	2.00E-12	1.00E-08	2.00E-09	5.00E-11
	6	11.4	141	2.00E-07	8.00E-13	1.00E-08	2.00E-09	5.00E-11
	7	11.2	-56	4.00E-08	3.00E-13	1.00E-08	1.00E-09	5.00E-11
	8	11.3	-87	2.00E-08	2.00E-12	2.00E-08	4.00E-10	5.00E-11
	9	---	---	1.00E-07	9.00E-13	2.00E-08	1.00E-09	5.00E-11
WRM Value		11.1	560	NSC	3.00E-11	5.00E-05	1.00E-13	3.00E-07
ORII-a	1	10.7	293	8.00E-08	2.00E-11	3.00E-08	8.00E-09	4.00E-11
	2	10.3	388	4.00E-08	1.00E-10	6.00E-07	8.00E-09	3.00E-10
	3	10.3	366	3.00E-08	1.00E-10	5.00E-07	8.00E-09	3.00E-10
	4	10.2	---	3.00E-08	8.00E-11	5.00E-08	9.00E-09	7.00E-11
	5	10.5	366	1.00E-08	4.00E-10	6.00E-07	1.00E-08	3.00E-10
	6	10.6	---	1.00E-08	7.00E-11	2.00E-07	1.00E-08	1.00E-10
	7	11.0	295	5.00E-08	1.00E-10	2.00E-07	9.00E-09	2.00E-10
	8	10.8	333	1.00E-08	1.00E-10	3.00E-07	1.00E-08	2.00E-10
ORII-b	1	10.7	292	1.00E-07	5.00E-11	3.00E-08	8.00E-09	4.00E-11
	2	10.4	397	2.00E-07	1.00E-10	6.00E-07	8.00E-09	3.00E-10
	3	10.2	371	7.00E-08	1.00E-10	5.00E-07	9.00E-09	2.00E-10
	4	10.3	---	1.00E-07	2.00E-10	6.00E-08	9.00E-09	1.00E-10
	5	10.6	355	6.00E-08	5.00E-11	9.00E-08	9.00E-09	8.00E-11
	6	10.8	---	6.00E-08	3.00E-11	4.00E-08	9.00E-09	5.00E-11
	7	10.8	311	5.00E-07	2.00E-11	2.00E-08	7.00E-09	5.00E-11
	8	11.0	322	2.00E-08	6.00E-11	4.00E-08	7.00E-09	6.00E-11
WRM Value		9.2	680	NSC	3.00E-11	4.00E-06	2.00E-15	2.00E-06
ORIII-a	1	9.0	389	1.00E-07	6.00E-11	1.00E-06	5.00E-09	1.00E-09
	2	9.2	401	1.00E-07	1.00E-10	2.00E-06	6.00E-09	1.00E-09
	3	9.4	397	2.00E-07	1.00E-10	2.00E-06	6.00E-09	9.00E-10
	4	9.1	---	2.00E-07	2.00E-10	2.00E-06	7.00E-09	9.00E-10
	5	9.4	---	1.00E-07	1.00E-10	2.00E-06	8.00E-09	8.00E-10
	6	9.3	---	1.00E-07	9.00E-11	1.00E-06	7.00E-09	7.00E-10
	7	9.2	410	5.00E-08	1.00E-10	1.00E-06	6.00E-09	7.00E-10
	8	9.3	421	4.00E-08	1.00E-10	1.00E-06	6.00E-09	7.00E-10
ORIII-b	1	8.8	411	2.00E-08	4.00E-11	2.00E-06	5.00E-09	1.00E-09
	2	9.2	417	2.00E-08	7.00E-11	2.00E-06	5.00E-09	1.00E-09
	3	9.4	389	2.00E-07	8.00E-11	2.00E-06	7.00E-09	9.00E-10
	4	9.3	---	3.00E-07	2.00E-10	2.00E-06	7.00E-09	9.00E-10
	5	---	---	5.00E-08	6.00E-11	6.00E-09	2.00E-10	7.00E-11
	6	9.1	---	7.00E-08	4.00E-11	2.00E-08	4.00E-10	3.00E-10
	7	9.0	404	2.00E-07	3.00E-11	3.00E-08	1.00E-10	3.00E-10
	8	9.3	416	2.00E-07	1.00E-10	4.00E-08	1.00E-10	3.00E-10

^a Values that are minimum detection limits versus actual measured values are highlighted in yellow.

NSC = No solubility control

Total uranium concentrations in Table 4.2-2 correspond to the sum of the measured U-235 and U-238 concentrations. For reducing samples, detection limits for total plutonium correspond to the reported values for Pu-238 corrected for the contribution from Pu-239/-240 based on the known isotopic ratios. The pH data values presented reflect average pH values measured for the samples during testing. Slurry pH values varied considerably during testing due to base consumption by the samples. Base consumption was likely the result of the dissolution of insoluble metals (such as aluminum) from the residual sludge to form soluble hydroxy complexes, with a high degree of variability in the slurry pH values during testing. The highest E_h values were observed for the ORIII samples and the lowest values were observed for the RRII samples, with the ORII samples having intermediate E_h values. The dramatic decrease in the E_h values for the reducing samples after contact day 81 is evident following sample washing and the addition of a second portion of FeS reagent to each bottle. [SRNL-STI-2018-00484]

Blank control samples were maintained under the same conditions as the leachate samples throughout the testing with sub-samples being collected periodically for analysis. The concentrations of Tc-99, I-129, Np-237, and Pu were generally below detectable limits for all control samples. For technetium, the detection limit was 1-2 orders of magnitude below the concentrations observed for most samples. The exception being the highly washed ORIII-B samples toward the end of testing for which the measured technetium concentrations were near the detection limit. Almost all leachate samples contained I-129 concentrations below detectable limits, as was the case for the control samples. For neptunium, control sample detection limits were generally 1-2 orders of magnitude lower than the Np-237 concentrations observed for the oxidizing samples (reducing samples typically contained less than detectable concentrations of Np-237). Detection limits for plutonium were generally 2-3 orders of magnitude lower than the Pu concentrations observed for the oxidizing samples (reducing samples typically contained less than detectable concentrations of Pu). Detectable U-238 contamination was observed for all control samples. The detection limits were corrected to total uranium based on the known isotopic ratios of the uranium isotopes in the Tank 12H solids. The corrected total uranium detection limits were typically an order of magnitude lower than the concentrations observed for reducing test sub-samples and 2-4 orders of magnitude lower than the uranium concentrations observed for oxidizing test sub-samples. Based on these observations, sub-sample contamination is not believed to have compromised the test results for most samples, although background uranium contamination could have influenced some of the results for the reducing samples. [SRNL-STI-2018-00484]

The leach sample wash solutions were analyzed to calculate radionuclide losses to the wash. Wash solution analysis results are provided in Table 4.2-3. The initial ORII and ORIII wash solutions correspond to 410 and 450 mL of composite wash solution, respectively, from the combined washes of the duplicate ORII and duplicate ORIII samples prior to leach testing initiation. Except for the neptunium concentration for the ORIII wash, the radionuclide concentrations in these wash solutions were comparable to those observed for the leachate samples. The neptunium concentration in the ORIII wash solution of $3\text{E-}08\text{ M}$ was nearly an order of magnitude higher than the most concentrated leachate sample ($1\text{E-}9\text{ M}$). Additional wash solutions were isolated from the ORIII-B sample after the test vessel broke following contact day 62 when the solution was exposed to a large volume (8.75 L) of caustic-contaminated (pH 12) water bath solution. The solids were subsequently washed with 1.05 L of simulant to restore the sample to the target

condition. The radionuclide concentrations in the ORIII-B water bath recovery solution (>8 L) and the ORIII-B sample second wash after recovery (>1 L) are also provided in Table 4.2-3. The radionuclide concentrations for these solutions were in the ranges observed for the leachate samples. Estimated radionuclide losses to the four wash solutions are provided in Table 4.2-4. Losses of the radionuclides of interest (Tc-99, I-129, U, Np-237, and Pu) to the initial ORII and ORIII wash solutions were minimal (<2.5%) and were greatest for Np-237. Losses to the wash for the RRII leachate samples following contact day 62 are represented by the leachate concentrations for the first four sub-sampling events. Significant material losses were observed for the ORIII-B sample after exposure to the water bath solution. These losses were primarily due to the large volumes of the wash solutions. Total material losses for the ORIII-B sample following exposure to the water bath solution were greatest for Tc-99 (49%) and lowest for Np-237 (3%). [SRNL-STI-2018-00484]

Table 4.2-3: Radionuclide Concentrations in Tank 12H Residual Wash Solutions

Wash Sample	Molarity				
	Tc-99	I-129	U	Np-237	Pu
Initial ORII Composite Wash	1E-09	<1E-07	3E-08	1E-09	1E-10
Initial ORIII Composite Wash	1E-09	1E-08	2E-06	3E-08	1E-10
ORIII-B Sample Water Bath Recovery Solution	9E-10	<4E-08	2E-06	4E-10	1E-10
ORIII-B Sample Second Wash After Recovery	5E-10	7E-09	2E-07	1E-10	5E-11

Table 4.2-4: Estimated Losses to Tank 12H Residual Wash Solutions

Wash Sample	Mass Percent (%)				
	Tc-99	I-129	U	Np-237	Pu
Initial ORII Wash	1.6	1.9	0.01	0.08	0.0012
Initial ORIII Wash	1.2	0.21	0.82	2.1	0.0015
ORIII-B Sample Water Bath Recovery Solution	44.3	<25.5	34.1	0.99	0.069
ORIII-B Sample Second Wash After Recovery	3.1	0.5	0.41	0.03	0.0035
ORIII-B Wash Composite	48.6	≤26.2	35.3	3.1	0.0073

Short-term leaching tests were conducted using distilled water during Tank 12H characterization studies conducted by Oji (SRNL-STI-2015-00241). Approximately 0.5 g of composite Tank 12H solids were contacted with 30 g of de-ionized water (1.7 g sludge per L of water slurry versus 30 g sludge/L of simulant slurry for Tank 12H testing) with periodic agitation. The residual sludge composite samples characterized in SRNL-STI-2015-00241 contained Tank 12H floor:mound mass ratios ranging from 1.9 to 5.6 versus the Tank 12H leachate samples which had a floor:mound ratio of 3.5. The water slurries were filtered and analyzed by Oji and the reported I-129 concentrations ranged from 2.2E-03 to 2.9E-03 wt. %. In addition, a composite liquid fraction was isolated from Tank 12H floor residuals which contained 20 dpm/mL of I-129. The Tank 12H leachate sub-samples isolated during porewater leaching studies typically contained below

detectable concentrations of I-129 (<9 dpm/mL average value). Four Tank 12H leachate and wash samples contained values above detectable amounts ranging from 0.3 to 1.0 dpm/mL. An I-129 concentration of 1 dpm/mL in the leachate corresponds to an iodine concentration of 4E-06 to 9E-06 wt. % in the original solid (depending on slurry volume) assuming that all I-129 leached from the sample. The measured I-129 concentrations from the current leaching studies were 3 orders of magnitude lower than those reported by Oji for water washes even though the sludge concentration in the leach test slurries was much higher (30 g/L versus 2 g/L for the SRNL-STI-2015-00241 characterization studies).

Solution pH differences in the leachate solutions used in these two studies (pH 5-6 in the water leachates used by Oji and pH 9-11 in the porewater leachates used in this study) should impact the I-129 solubility, but a solubility difference exceeding 3 orders of magnitude was unexpected. Other differences in the Tank 12H leaching studies and those conducted by Oji include the addition of grout or grout-representative phases and the manipulation of the ORP with the Tank 12H samples. Prior to analysis of the mound and leach sample solids it was postulated that the drying of the Tank 12H residual samples during interim storage may have resulted in the loss of iodine vapor from the samples. However, the analytical results on the mound composite and residual test sample indicate that iodine levels comparable to previous results remain in the samples. Apparently the different conditions used in these studies (discussed above) resulted in the dramatic differences in I-129 solubility. [SRNL-STI-2018-00484]

4.3 Comparison of Test Results to Waste Release Model

Measurement of element solubility provides data for evaluation versus the WRM solubility values used in the TF PA fate and transport models. Elements that are in the form of insoluble compounds, and/or have a high affinity to solid surface adsorption, exhibit lower transport rates from waste tanks into the surrounding environment. The waste release testing allows for a comparison of the TF WRM solubility assumptions versus the Tank 18F and Tank 12H residual waste solubility testing results. The individual elemental solubility testing results as well as a comparison to the TF WRM solubility values are discussed throughout Section 4.3.

Solubility testing results after sampling event four were typically given more weight since these testing results generally represented steady state conditions and the residual waste samples were generally closer to the target chemical conditions (Figures 4.1-1, 4.1-2, 4.2-1 and 4.2-2) after completion of washing.

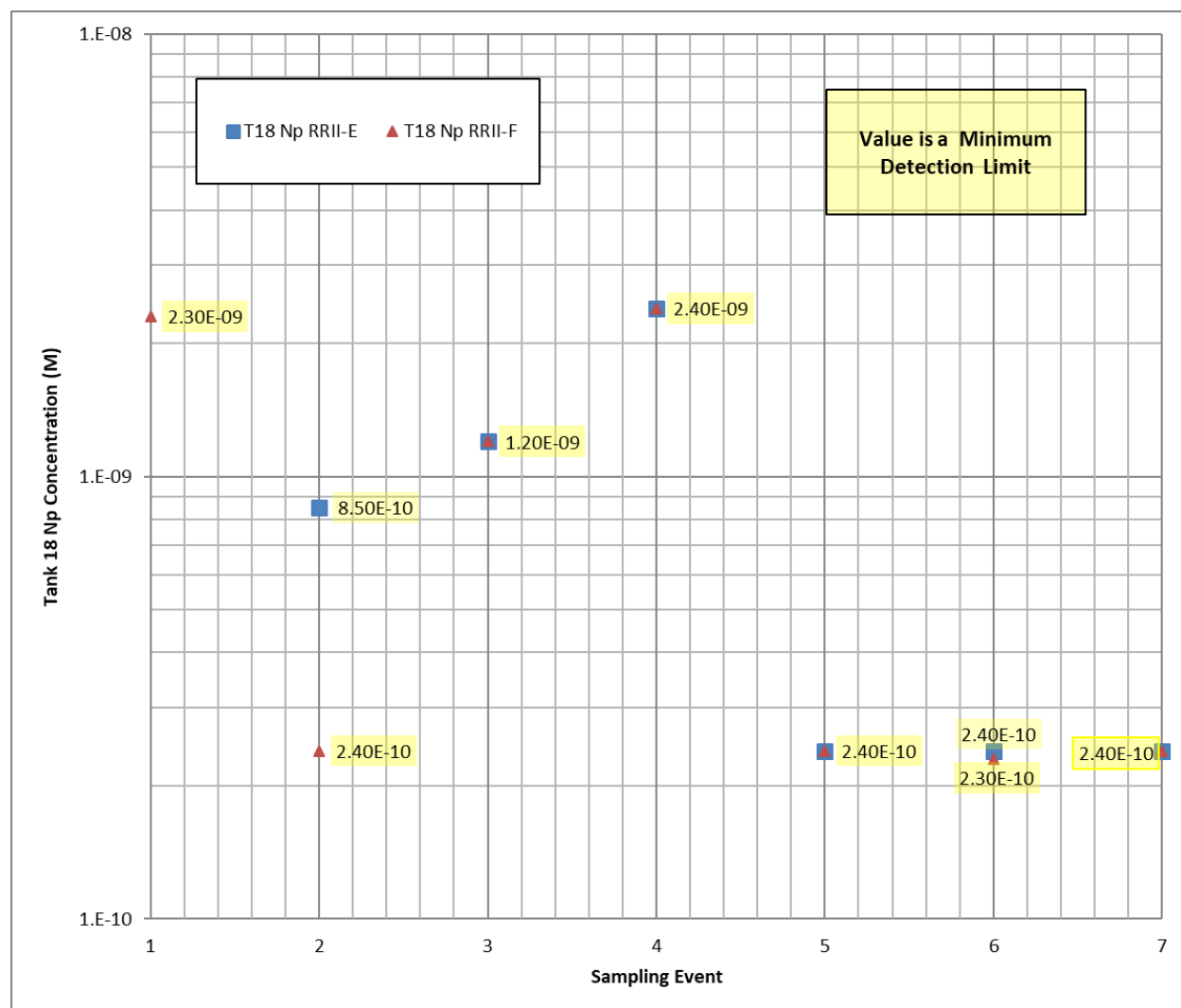
4.3.1 Neptunium Analysis

4.3.1.1 *Neptunium Reduced Region II*

Tank 18F Neptunium Reduced Region II Results

Figure 4.3.1-1 shows a plot of the Tank 18F waste release testing results (Table 4.1-2) over the testing period for Np with the sample subjected to RR2 chemical conditions (i.e., target pH of 11.1 and target E_h of -470 mV). All of the Np solubilities (solubility is also referred to as a concentration because the units are in mass per unit volume) included in this figure are minimum detection limits (versus measured values), so the actual Np concentrations/solubilities may be lower than those shown.

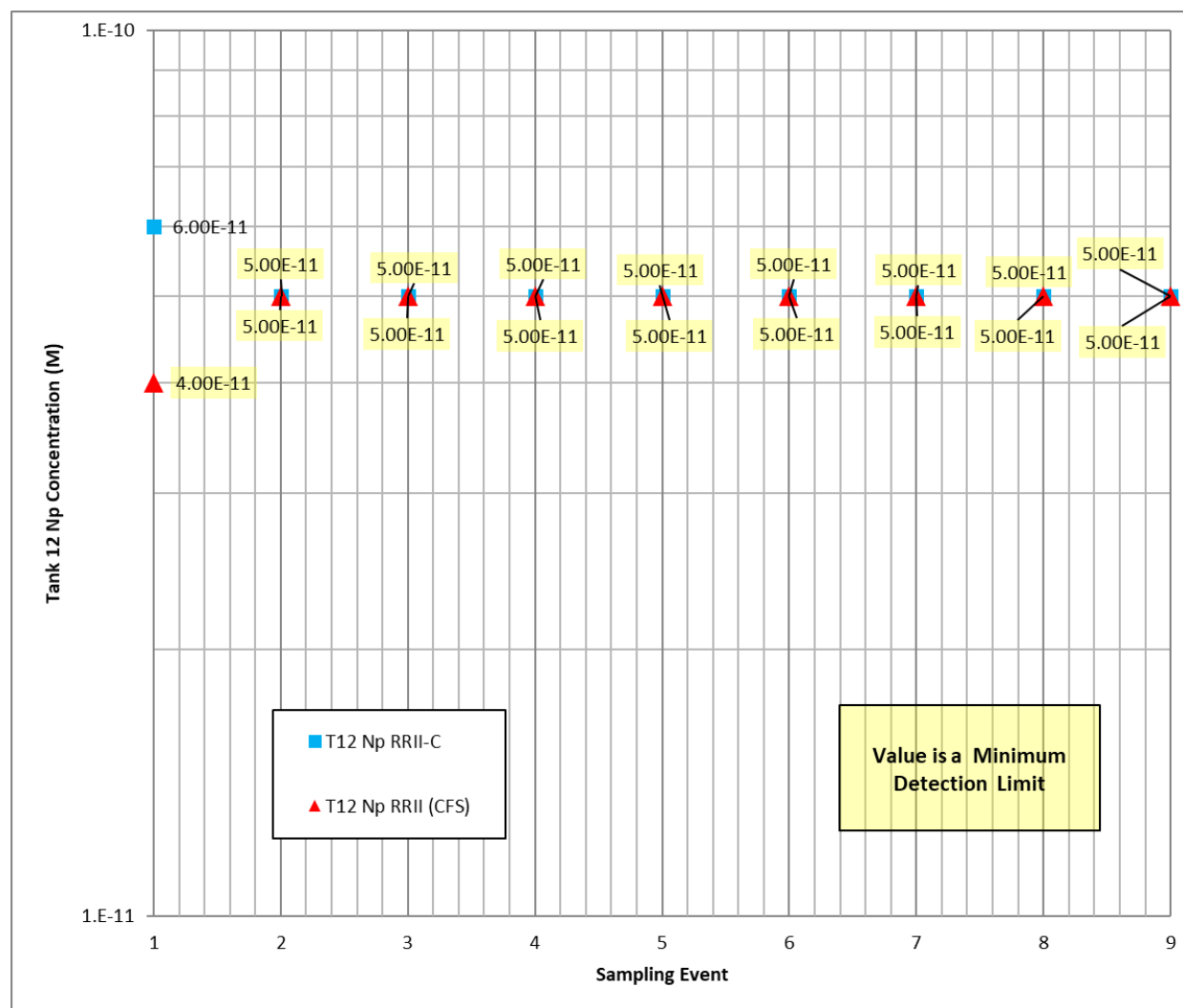
Figure 4.3.1-1: Tank 18F Np Concentrations under RRII Chemical Conditions



Tank 12H Neptunium Reduced Region II Results

Figure 4.3.1-2 shows a plot of the Tank 12H waste release testing results (Table 4.2-2) over the testing period for Np with the sample subjected to RRII chemical conditions (i.e., target pH of 11.1 and target E_h of -470 mV). Nearly all of the Np solubilities (solubility is also referred to as a concentration because the units are in mass per unit volume) included in this figure are minimum detection limits (versus measured values), so the actual Np concentrations/solubilities are lower than those shown. Nearly all reducing sub-samples (RRII-CC and RRII-CFS) contained below detectable concentrations of neptunium (typically $<5E-11$ M). [SRNL-STI-2018-00484]

Figure 4.3.1-2: Tank 12H Np Concentrations under RRII Chemical Conditions



Review of Neptunium Solubility Assumptions versus Reduced Region II Testing Results

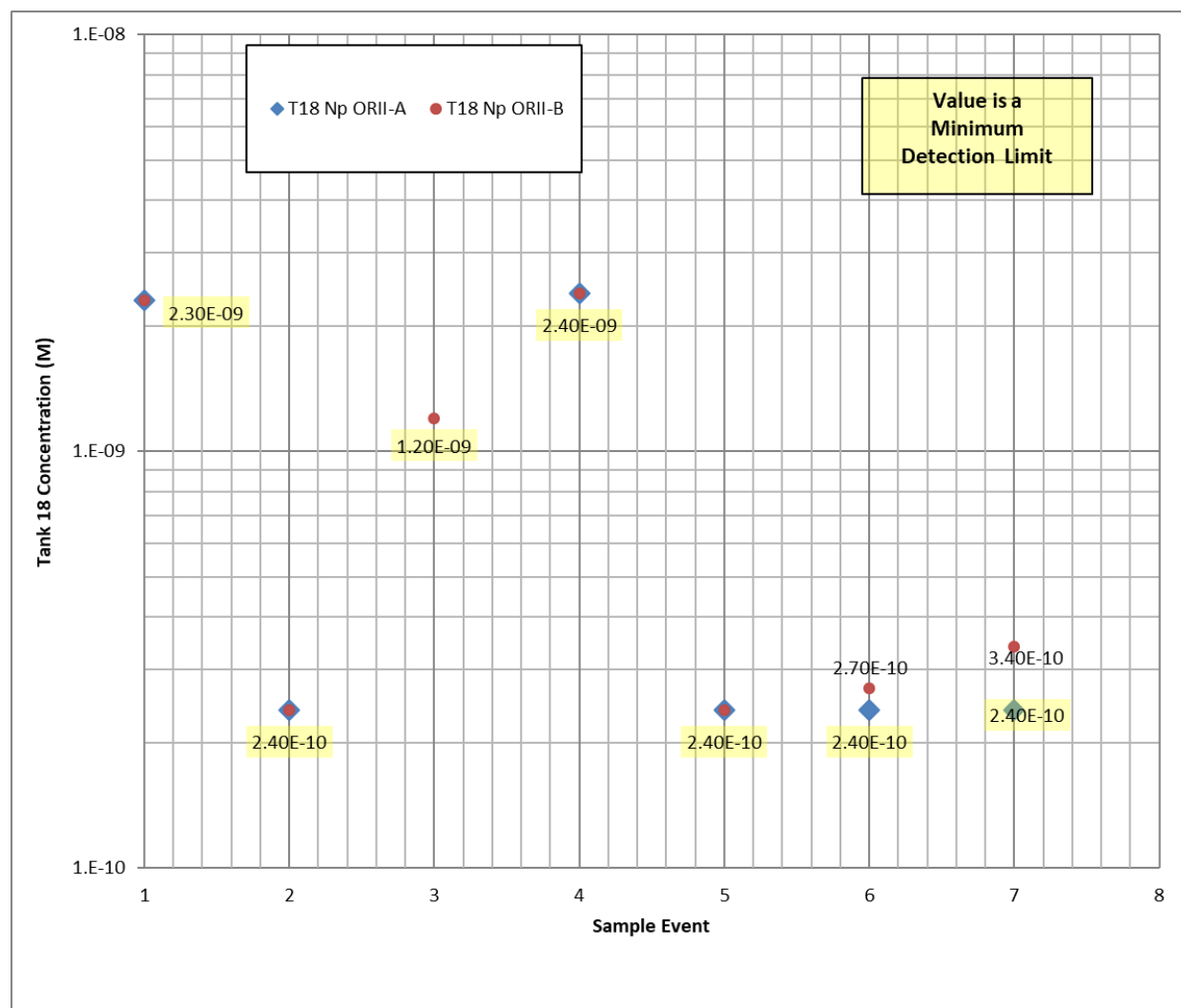
The TF WRM assigned Np a solubility of $1\text{E-}09$ M when subjected to RRII pore water. This modeling assumption is reasonable based on the fact that there were no observed Np concentrations under RRII chemical conditions above $1\text{E-}09$ M. In fact, multiple samples had non-detectable concentration with detection limits well below $1\text{E-}09$ M.

4.3.1.2 *Neptunium Oxidized Region II*

Tank 18F Neptunium Oxidized Region II Results

Figure 4.3.1-3 shows a plot of the Tank 18F waste release testing results (Table 4.1-2) over the testing period for Np with the sample subjected to ORII chemical conditions (i.e., target pH of 11.1 and target E_h of 560 mV). Most of the Np concentrations included in this figure are minimum detection limits (versus measured values), so the actual Np concentrations may be lower than those shown.

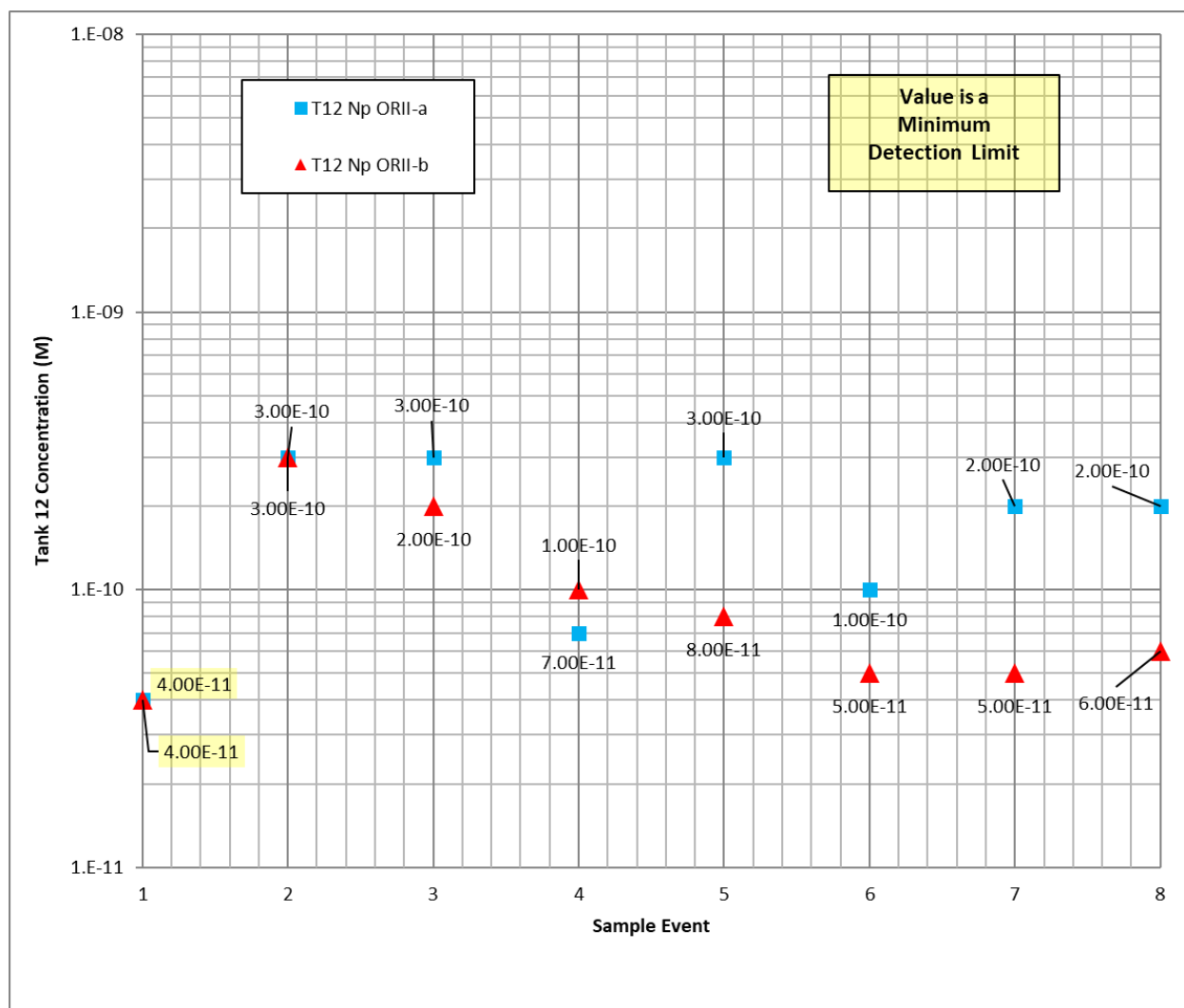
Figure 4.3.1-3: Tank 18F Np Concentrations under ORII Chemical Conditions



Tank 12H Neptunium Oxidized Region II Results

Figure 4.3.1-4 shows a plot of the Tank 12H waste release testing results (Table 4.2-2) over the testing period for Np with the sample subjected to ORII chemical conditions (i.e., target pH of 11.1 and target E_h of 560 mV). Most of the Np concentrations included in this figure are measured values (versus minimum detection limits). The average neptunium concentrations observed for the ORII-A and ORII-B sub-samples ranged from $<1\text{E-}10$ to $2\text{E-}10$ M. [SRNL-STI-2018-00484]

Figure 4.3.1-4: Tank 12H Np Concentrations under ORII Chemical Conditions



Review of Neptunium Solubility Assumptions versus Oxidized Region II Testing Results

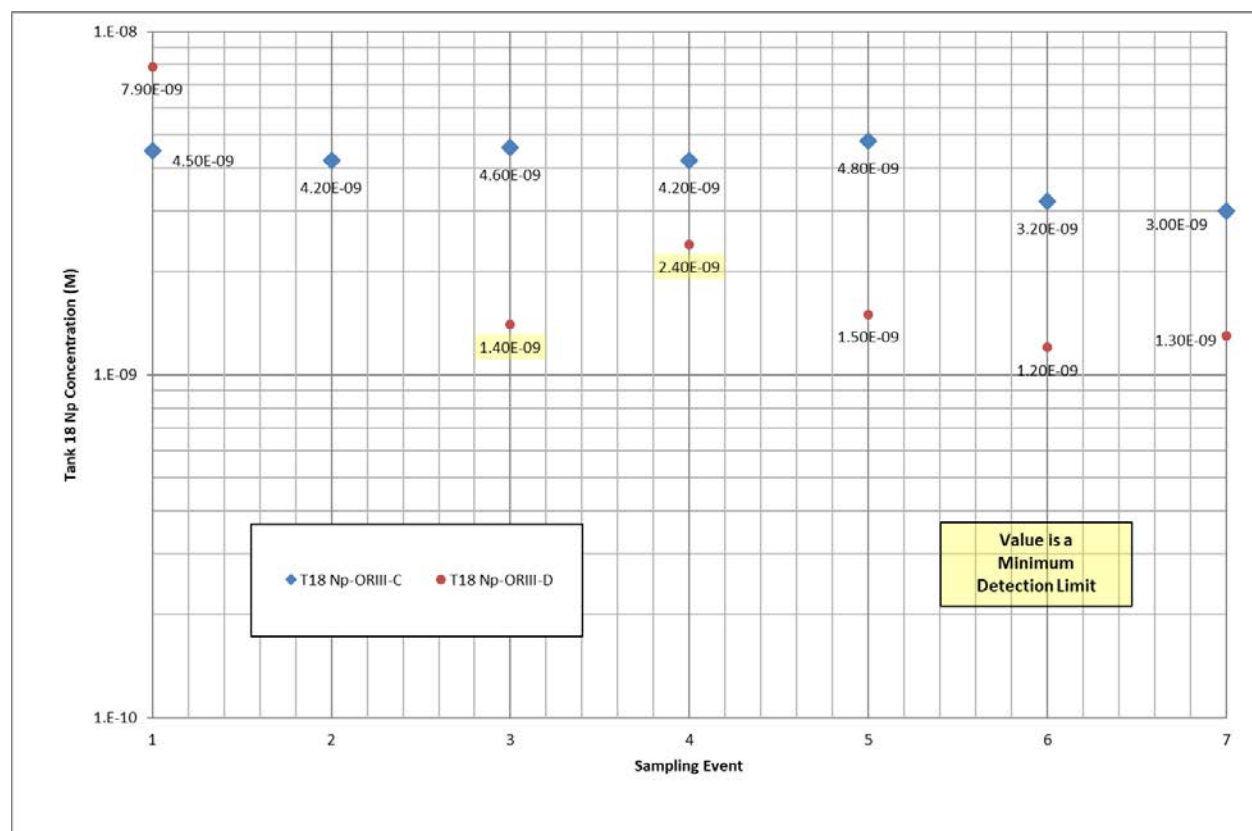
The TF WRM assigned Np a solubility of $3\text{E-}07$ M when subjected to ORII pore water. This modeling assumption is reasonable based on the fact that there were no observed Np concentrations under ORII chemical conditions above $2\text{E-}9$ M.

4.3.1.3 *Neptunium Oxidized Region III*

Tank 18F Neptunium Oxidized Region III Results

Figure 4.3.1-5 shows a plot of the waste release testing results (Table 4.1-2) over the testing period for Np with the sample subjected to ORIII chemical conditions (i.e., target pH of 9.2 and target E_h of 680 mV). Most of the Np concentrations included in this figure are measured values (versus minimum detection limits).

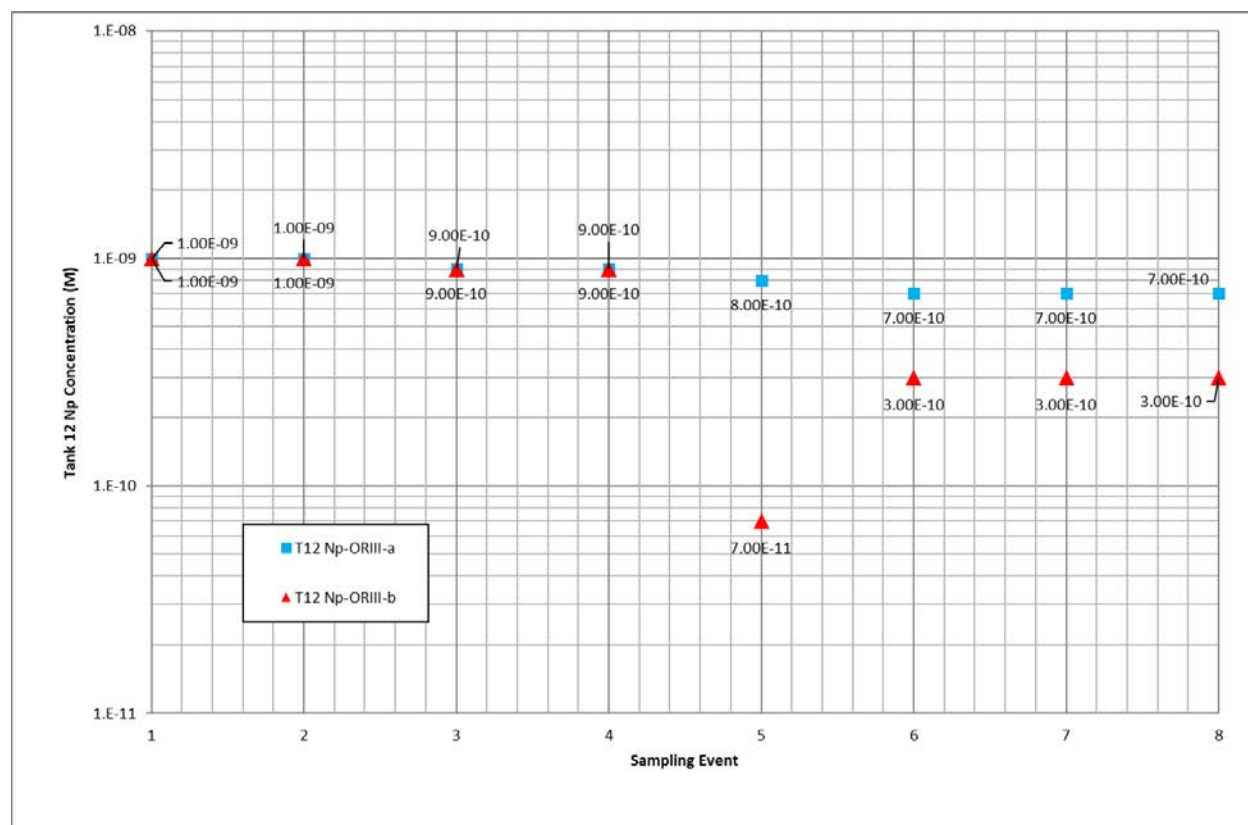
Figure 4.3.1-5: Tank 18F Np Concentrations under ORIII Chemical Conditions



Tank 12H Neptunium Oxidized Region III Results

Figure 4.3.1-6 shows a plot of the waste release testing results (Table 4.2-2) over the testing period for Np with the sample subjected to ORIII chemical conditions (i.e., target pH of 9.2 and target E_h of 680 mV). All of the Np concentrations included in this figure are measured values (versus minimum detection limits). Of all the Np test results, the highest neptunium concentrations were observed for the ORIII sub-samples. The average neptunium concentration for the ORIII-A sub-sample during the entire 95-day test duration was 9E-10 M. The average neptunium concentration for the ORIII-B sample over the first 62 days of testing was 1E-09 M. Following extensive washing, the average ORIII-B leachate sub-sample neptunium concentration was 3E-10 M, indicating that significant soluble neptunium was lost to the wash. [SRNL-STI-2018-00484]

Figure 4.3.1-6: Tank 12H Np Concentrations under ORIII Chemical Conditions



Review of Neptunium Solubility Assumptions versus Oxidized Region III Testing Results

The TF WRM assigned Np a solubility of $2\text{E-}06$ M when subjected to ORIII pore water. This modeling assumption is reasonable since there were no observed Np concentrations under ORIII chemical conditions above $1\text{E-}08$ M.

4.3.1.4 *Neptunium Analysis Conclusions*

The highest neptunium concentrations were typically observed for the low pH (i.e., ORIII) samples, while the concentrations for most of the higher pH samples (i.e., RRII and ORII) were significantly lower. The estimated losses to the washes for the Np samples were minimal (less than 1.5% for the Tank 18F samples and less than 3.1% for the Tank 12H samples). No measurable neptunium was observed for nearly all of the reducing samples, even with relatively low detection limits ($2\text{E-}10$ M for Tank 18F solids and $5\text{E-}11$ M for Tank 12H solids). Under oxidizing conditions (ORII and ORIII), Np-237 solubilities observed for Tank 18F residuals ($<2\text{E-}10$ to $4\text{E-}09$ M) were comparable to the solubilities observed with Tank 12H solids ($5\text{E-}11$ to $1\text{E-}09$ M).

Overall, the solubility testing results for RRII, ORII, and ORIII indicate that Np is less soluble than assumed in the TF WRM. Under reducing conditions (RRII), observed neptunium concentrations were below detectable concentration limits ($<5\text{E-}11$ M) and the detection limit was intermediate between the predicted solubilities for pure-phase NpO_2 and the co-precipitate phase which ranged from $5\text{E-}15$ to $1\text{E-}09$ M. The TF WRM predicted that neptunium solubility would increase significantly due to speciation changes from the hydrated NpO_2 phase to the Np(V)

species ($\text{NpO}_2(\text{OH})$), but the test results did not show a significant solubility change when transitioning to oxidizing conditions. The solubility values used in HTF (SRR-CWDA-2010-00128) and FTF (SRS-REG-2007-00002) PA modeling are presented in Table 4.3.1-1, along with “conservative case” values based upon a considered evaluation of the data presented in Figure 4.3.1-7. The WRM calculated the solubility for *reduced* $\text{NpO}_2(\text{am,hyd})$ to be $1\text{E-}09\text{ M}$ (Table 2.2-2), which is above all of the RR-II and OR-II detected concentration values and is reasonably close to the OR-III detected concentration values. The TF WRM characterized residual Np as being relatively soluble, especially under oxidized conditions. The waste release testing results suggest that Np in the Tank 18F and Tank 12H residual waste sample is reduced in the waste to a form that resists re-oxidation and is relatively insoluble, even under oxidized conditions. The waste release testing results would not affect any Np related TF WRM based conclusions, since dose associated with Np would only be further mitigated by assuming the Np was less soluble.

Figure 4.3.1-7: Np Concentration Data (Tanks 18F and 12H)

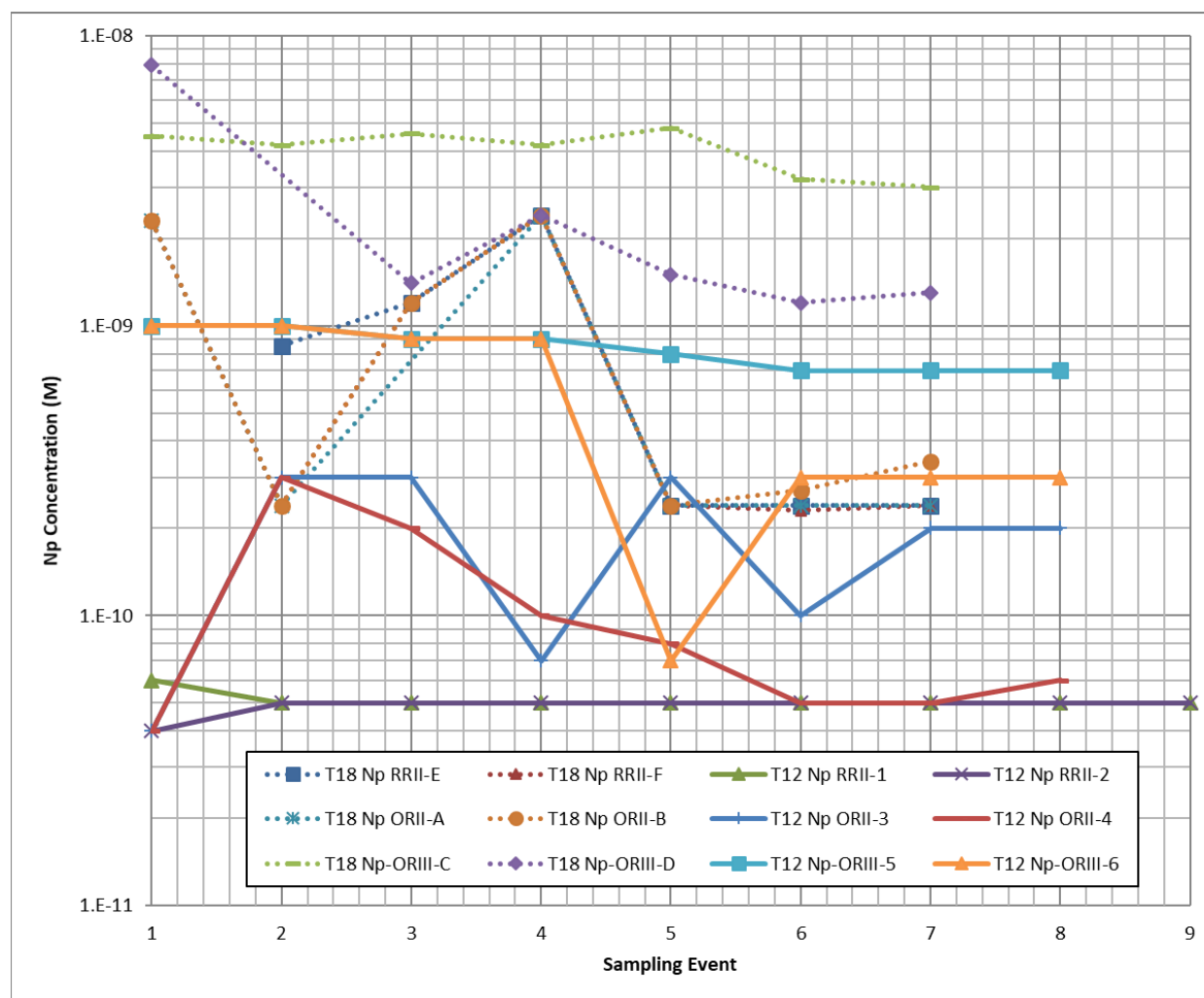


Table 4.3.1-1: Neptunium Solubility

	RRII (mol/L)	ORII (mol/L)	ORIII (mol/L)
FTF PA	2E-09	2E-05	1E-04
HTF PA / WRM	1E-09	3E-07	2E-06
Tank 18F Conservative Case	2E-10	3E-09	5E-09
Tank 12H Conservative Case	6E-11	1E-10	1E-09
Tank Farm Conservative Case	2E-10	3E-09	5E-09

Figures 4.3.1-8 and 4.3.1-9 show a plot of all of the measured Tank 18F and Tank 12H Np concentrations (Tables 4.1-2 and 4.2-2) versus pH and E_h . From these figures it appears Np concentrations are more sensitive to pH changes than to E_h changes. Figure 4.3.1-8 presents a noticeable trend in the Np concentration as the pH is increased, however in Figure 4.3.1-9 there is no trend in Np concentration changes as there is an increase in E_h values.

Figure 4.3.1-8: Np Concentrations vs. pH

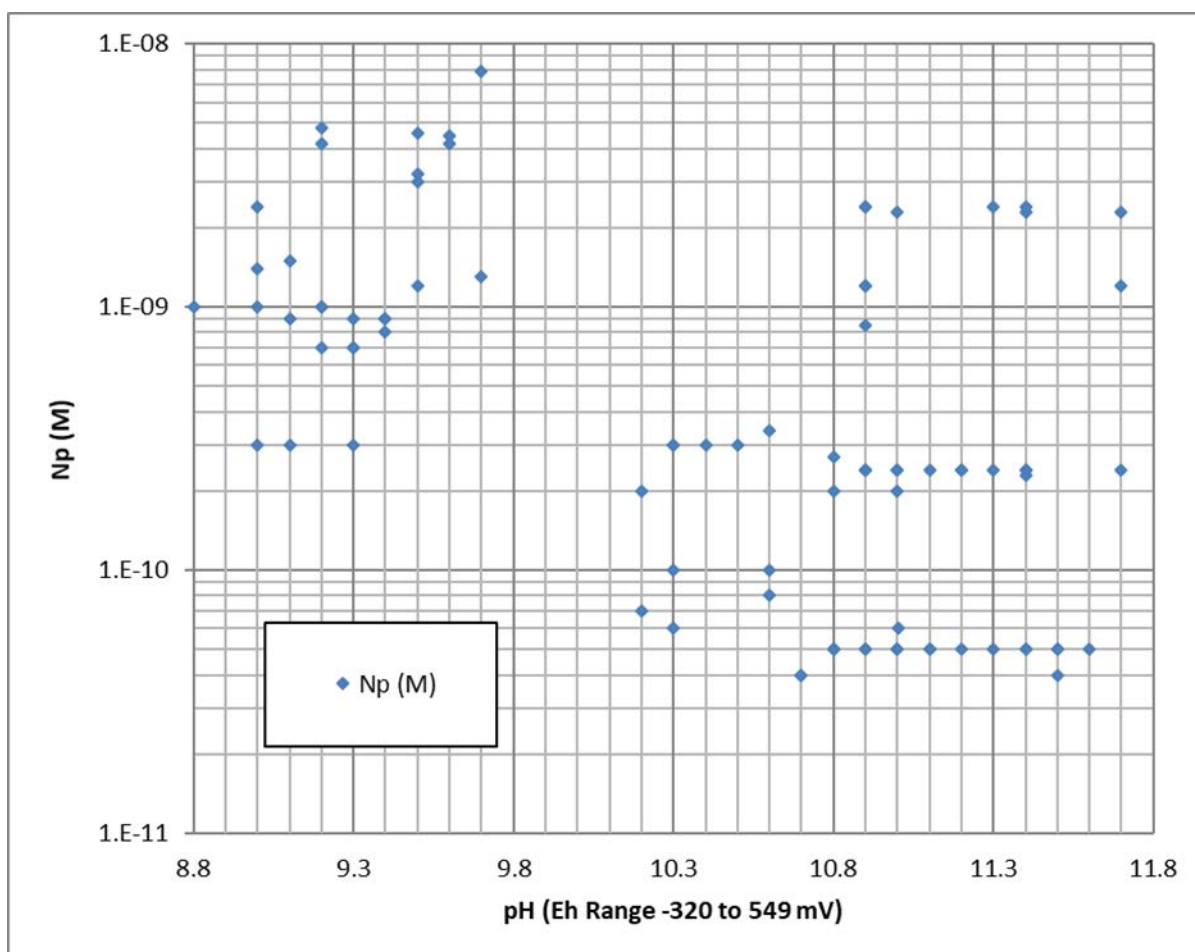
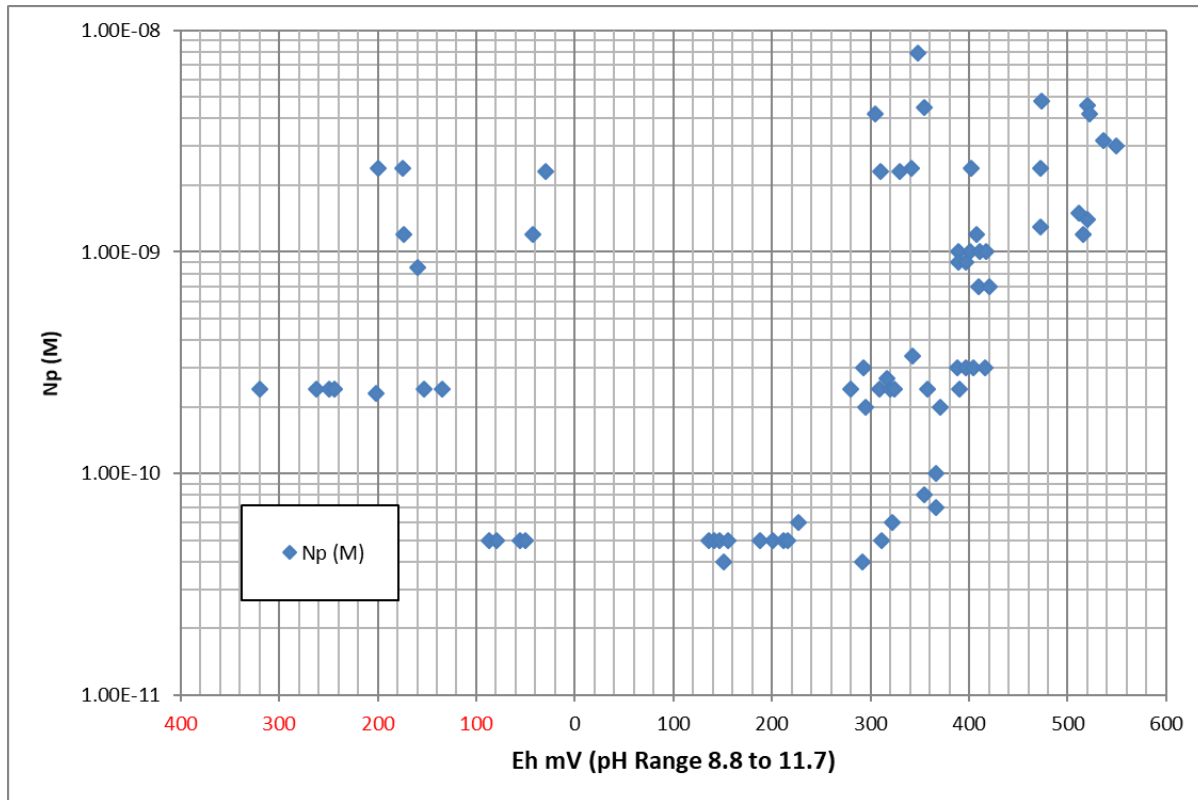


Figure 4.3.1-9: Np Concentrations vs. E_h



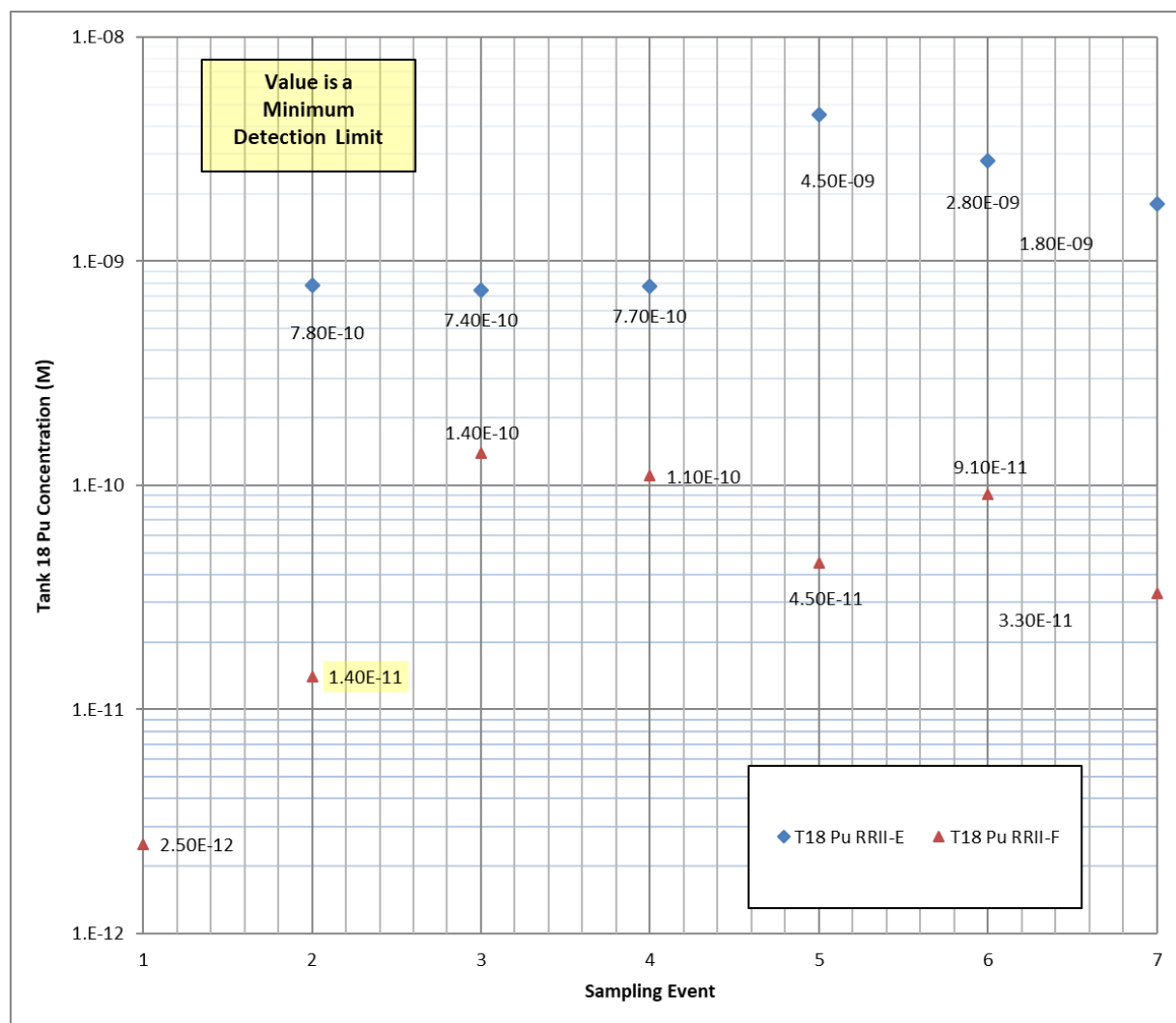
4.3.2 Plutonium Analysis

4.3.2.1 *Plutonium Reduced Region II*

Tank 18F Plutonium Reduced Region II Results

Figure 4.3.2-1 shows a plot of the waste release testing results (Table 4.1-2) over the testing period for Pu with the samples subjected to RRII chemical conditions (i.e., target pH of 11.1 and target E_h of -470 mV). All but one of the Pu concentrations included in this figure are measured values (versus minimum detection limits).

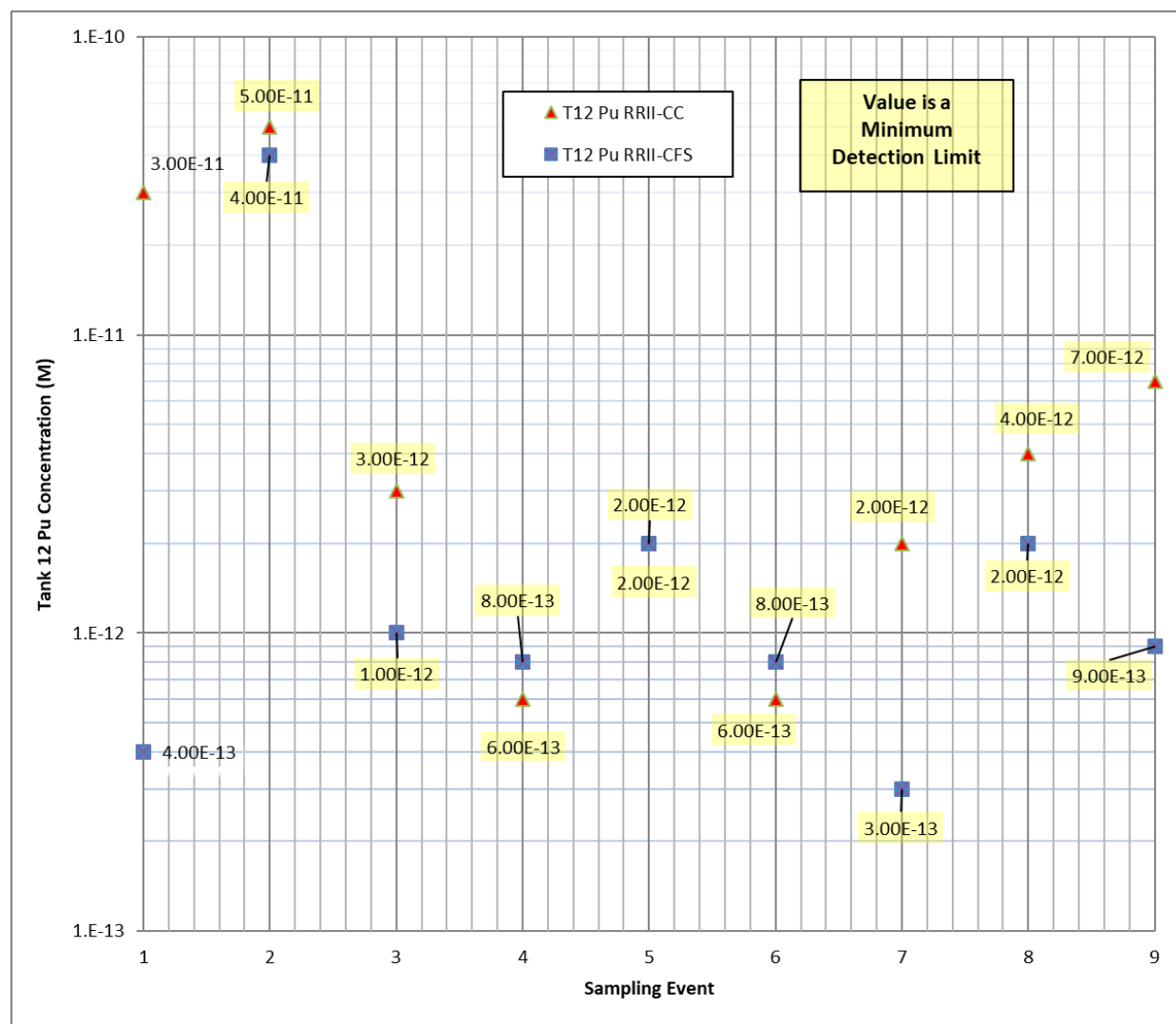
Figure 4.3.2-1: Tank 18F Pu Concentrations under RRII Chemical Conditions



Tank 12H Plutonium Reduced Region II Results

Figure 4.3.2-2 shows a plot of the waste release testing results (Table 4.2-2) over the testing period for Pu with the samples subjected to RRII chemical conditions (i.e., target pH of 11.1 and target E_h of -470 mV). Plutonium concentrations for almost all of the reducing test samples (RRII-CC and RRII-CFS) were below detectable limits. Observed detection limits for the initial 62 days of testing using unwashed Tank 12H sludge were near 1E-12 M. Detection limits for contact days 77-95 using washed Tank 12H sludge with reducing test samples at lower E_h values were near 2E-13 M. Overall the results indicate that very little plutonium should leach from Tank 12H during the early tank aging stages under reducing conditions. [SRNL-STI-2018-00484]

Figure 4.3.2-2: Tank 12H Pu Concentrations under RRII Chemical Conditions



Review of Plutonium Solubility Assumptions versus Reduced Region II Testing Results

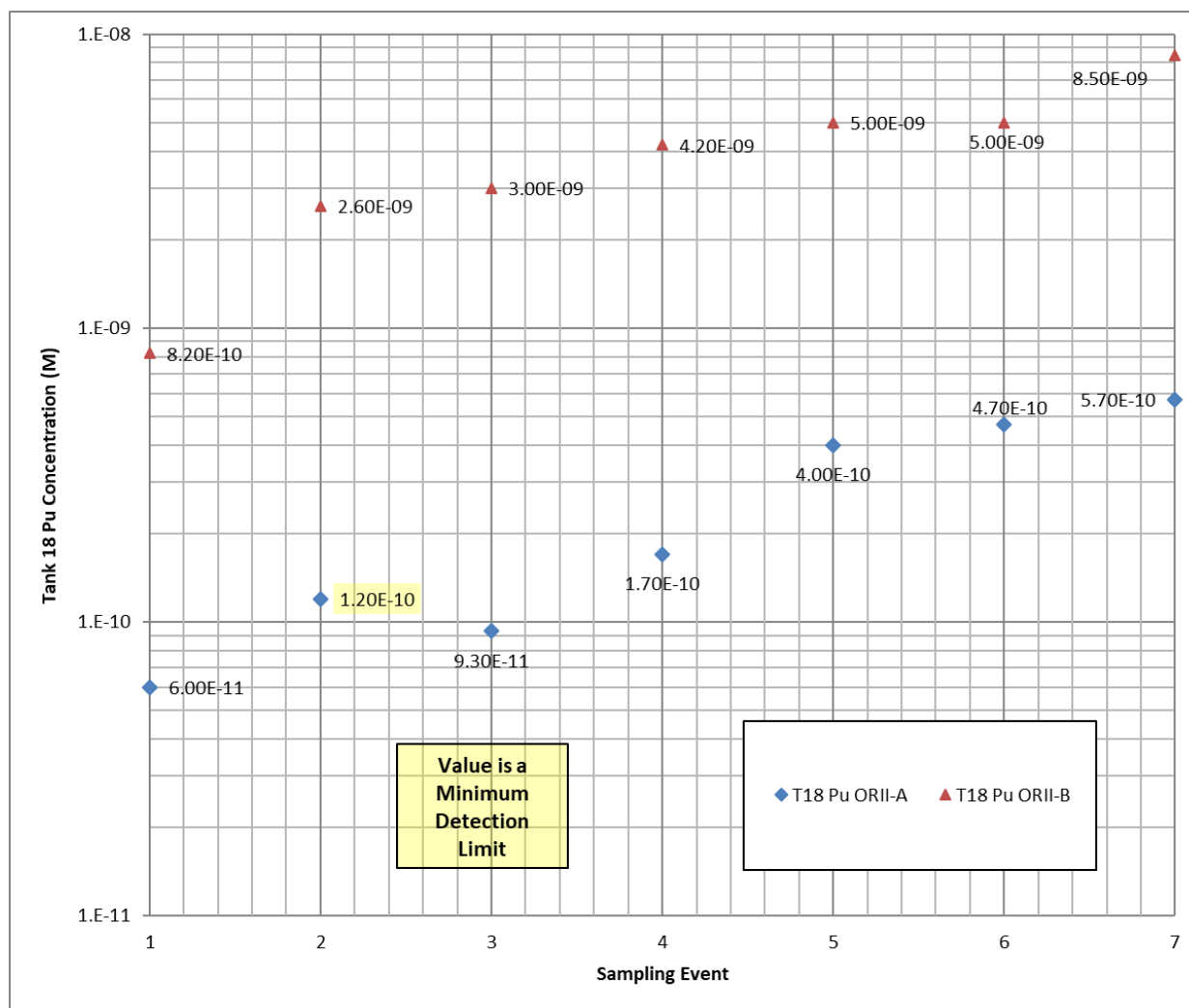
The TF WRM assigned Pu a solubility of $3\text{E-}11$ M when subjected to RRII pore water. The observed experimental Pu concentrations under RRII chemical conditions indicate that the Pu in the Tank 12H waste residuals under RRII chemical conditions is potentially more soluble than assumed in the TF WRM.

4.3.2.2 *Plutonium Oxidized Region II*

Tank 18F Plutonium Oxidized Region II Results

Figure 4.3.2-3 shows a plot of the waste release testing results (Table 4.1-2) over the testing period for Pu with the sample subjected to ORII chemical conditions (i.e., target pH of 11.1 and target E_h of 560 mV). All but one of the Pu concentrations included in this figure are measured values (versus minimum detection limits).

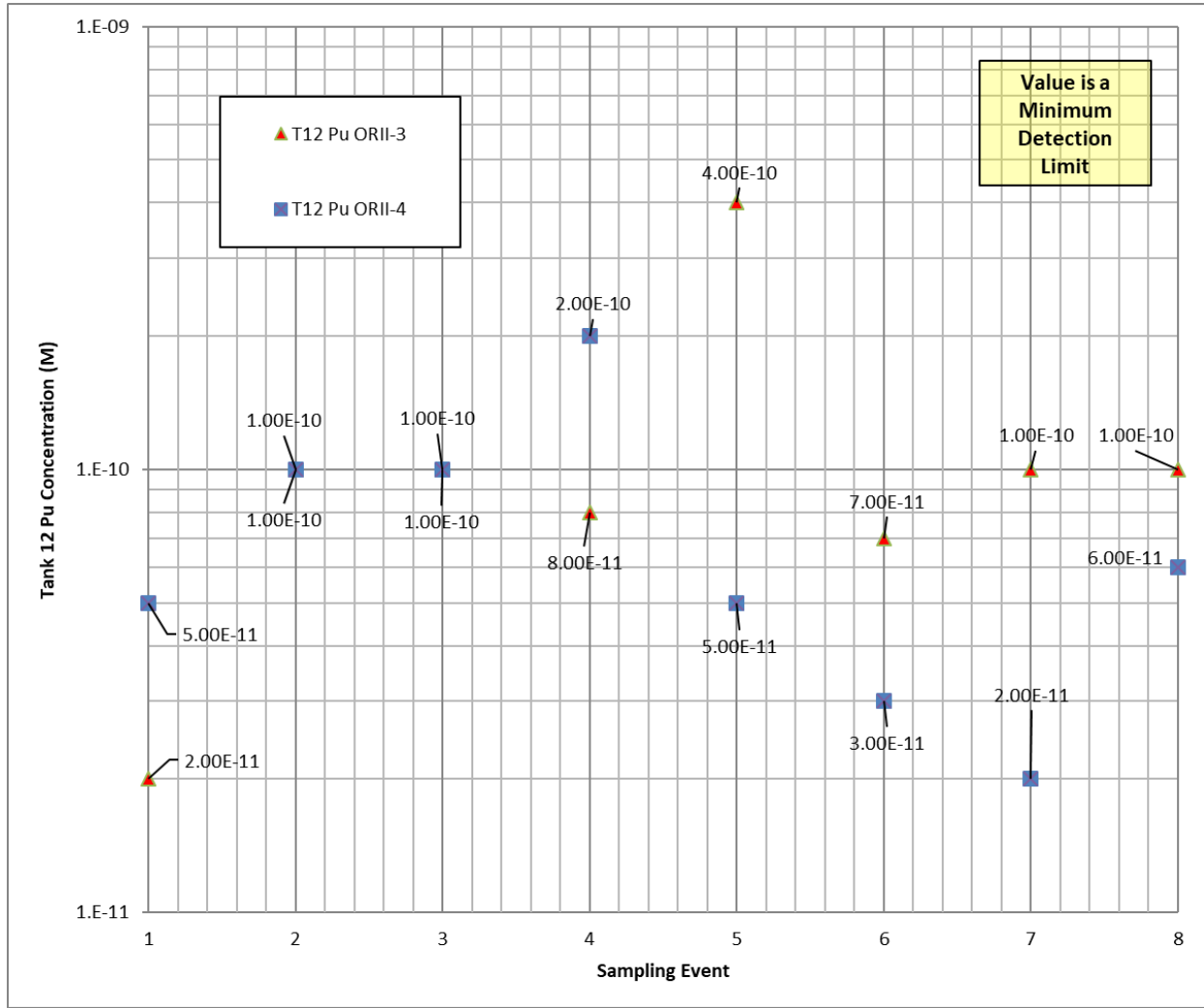
Figure 4.3.2-3: Tank 18F Pu Concentrations under ORII Chemical Conditions



Tank 12H Plutonium Oxidized Region II Results

Figure 4.3.2-4 shows a plot of the waste release testing results (Table 4.2-2) over the testing period for Pu with the sample subjected to ORII chemical conditions (i.e., target pH of 11.1 and target E_h of 560 mV). Plutonium concentrations observed for all oxidizing samples ranged from 2E-11 to 4E-10 M. The cause of the lower plutonium concentration variability observed for the ORII-4 (ORII-B) sub-samples from sampling events 5-8 is not understood. [SRNL-STI-2018-00484]

Figure 4.3.2-4: Tank 12H Pu Concentrations under ORII Chemical Conditions



Review of Plutonium Solubility Assumptions versus Oxidized Region II Testing Results

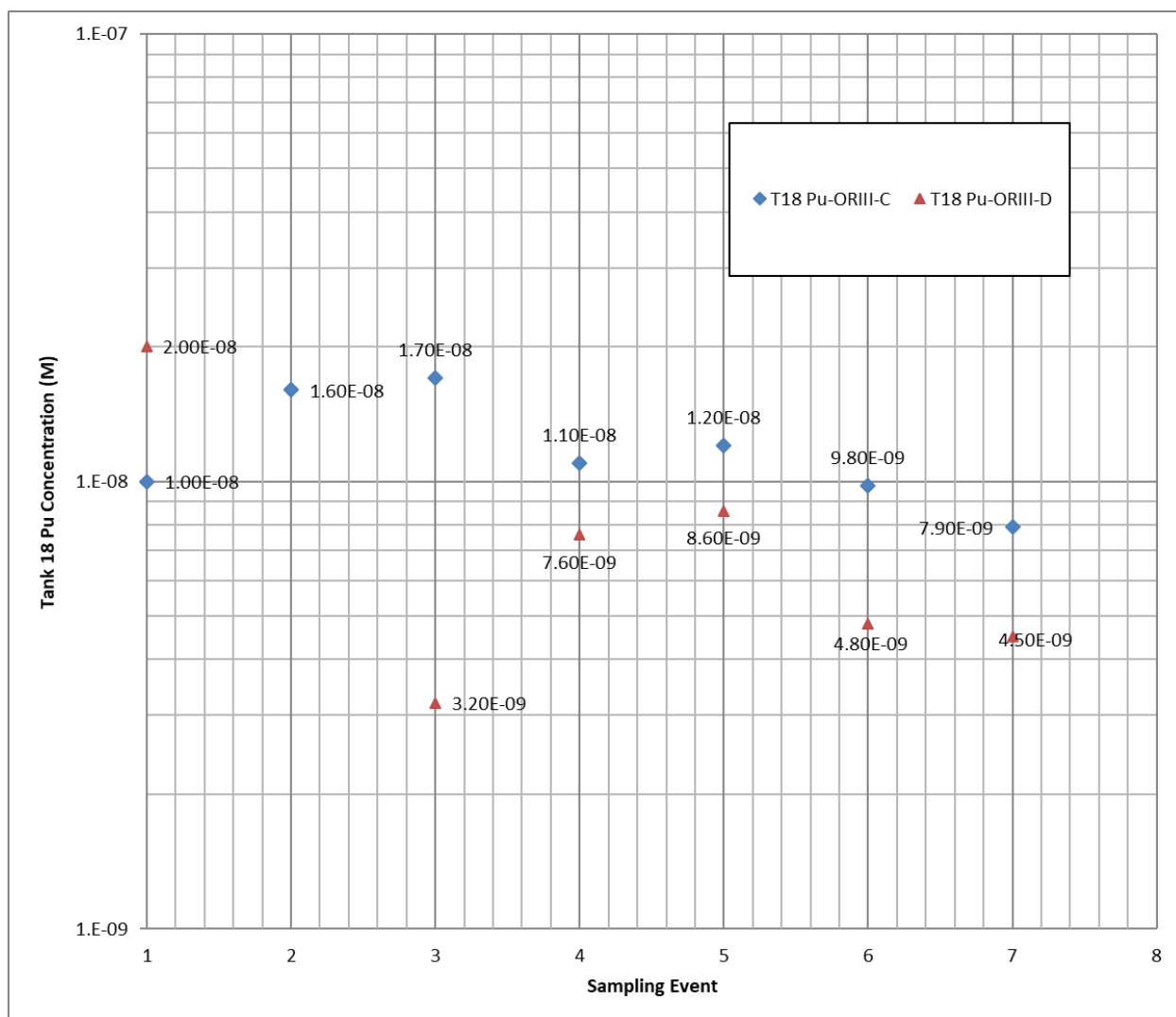
The TF WRM assigned Pu a solubility of 3E-11 M when subjected to ORII pore water. The observed experimental Pu concentrations under ORII chemical conditions indicate that the Pu in the Tank 18F and Tank 12H waste residuals under ORII chemical conditions is potentially more soluble than assumed in the TF WRM.

4.3.2.3 *Plutonium Oxidized Region III*

Tank 18F Plutonium Oxidized Region III Results

Figure 4.3.2-5 shows a plot of the waste release testing results (Table 4.1-2) over the testing period for Pu with the sample subjected to ORIII chemical conditions (i.e., target pH of 9.2 and target E_h of 680 mV).

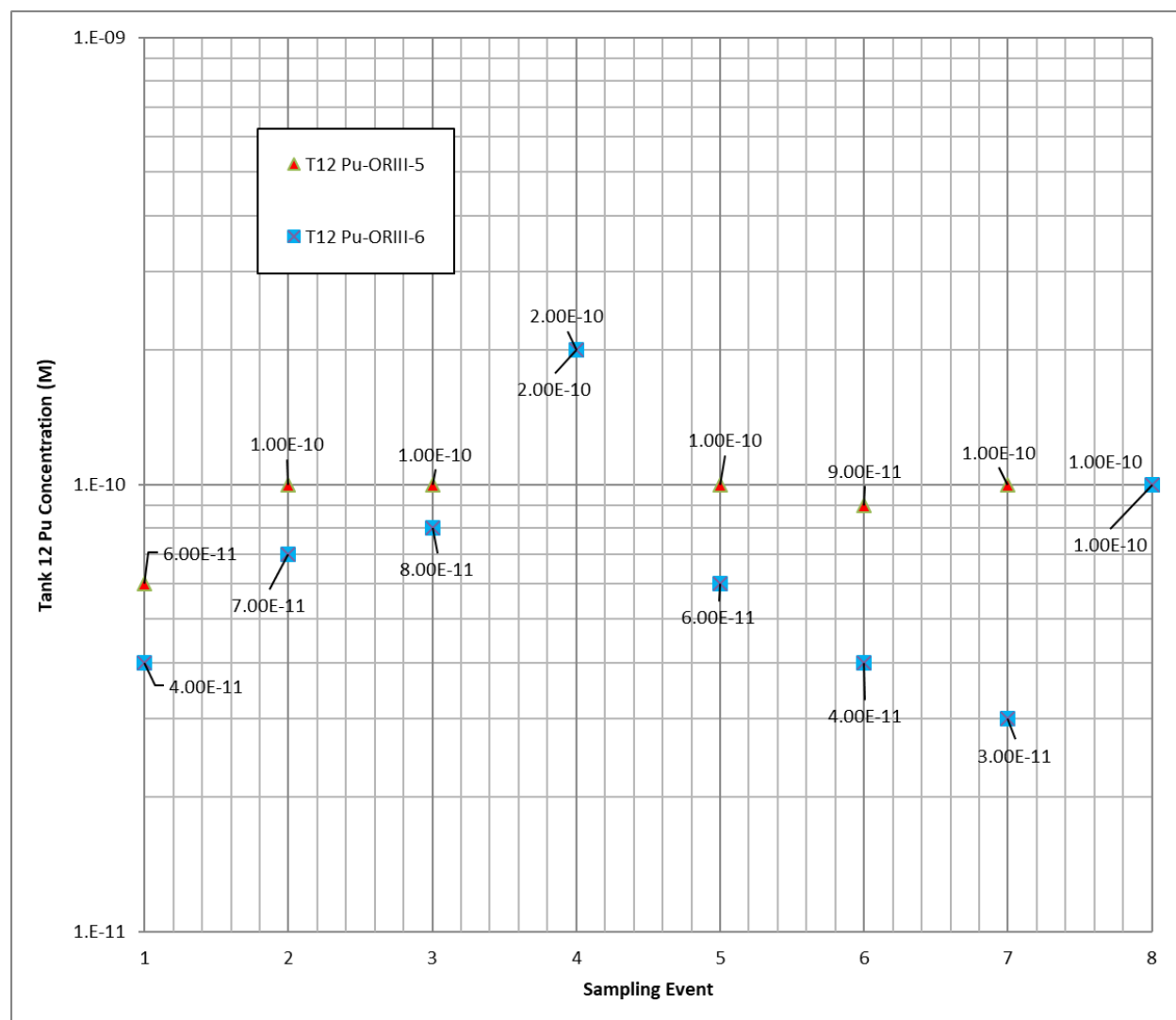
Figure 4.3.2-5: Tank 18F Pu Concentrations under ORIII Chemical Conditions



Tank 12H Plutonium Oxidized Region III Results

Figure 4.3.2-6 shows a plot of the waste release testing results (Table 4.2-2) over the testing period for Pu with the sample subjected to ORIII chemical conditions (i.e., target pH of 9.2 and target E_h of 680 mV). The average plutonium concentration for the ORIII-B sample during the first 62 days of testing was similar to the other oxidizing samples ($9\text{E-}11$ M). The average concentration for the ORIII-B sample from sampling events 5-8 was lower, presumably due to the extensive sample washing that occurred with this sample following test vessel rupture after contact day 69. The plutonium concentration for the final ORIII-B sub-sample increased to $1\text{E-}10$ M, indicating that extensive washing did not greatly change the equilibrium plutonium concentration for this sample. [SRNL-STI-2018-00484]

Figure 4.3.2-6: Tank 12H Pu Concentrations under ORIII Chemical Conditions



Review of Plutonium Solubility Assumptions versus Oxidized Region III Testing Results

The TF WRM assigned Pu a solubility of $3\text{E-}11$ M when subjected to ORIII pore water. The observed experimental Pu concentrations under ORIII chemical conditions indicate that the Pu in the Tank 18F and Tank 12H waste residuals under ORIII chemical conditions is potentially more soluble than assumed in the TF WRM.

4.3.2.4 Plutonium Analysis Conclusions

The Tank 18F RRII-F Pu sample concentrations were consistently lower than the Tank 18F RRII-E samples by about an order of magnitude, possibly due the presence of the CFS solids in the Tank 18F RRII-F sample. Lower plutonium concentrations were also observed for simulant samples containing CFS solids in previous testing. Early Tank 18F samples exhibited a rapid increase in plutonium concentration each sampling event. After Tank 18F sample washing (i.e., starting with sampling event 4), the Pu concentrations for the Tank 18F RRII-F samples stabilized near $1\text{E-}10$ M. The Pu concentrations for the Tank 18F RRII-E samples ranged from $1\text{E-}9$ to $5\text{E-}9$ M.

throughout the testing period. The Tank 12H RR2 Pu sample concentrations (based almost entirely on non-detect values) were orders of magnitude less soluble than the Tank 18F RR2 sample concentrations, with the Pu concentrations for the Tank 12H RR2 samples fluctuating below $1\text{E-}11$ M after stabilizing (starting with the sampling event 3 testing). The presence of the CFS solids in the Tank 12H RR2-CFS sample did not appear to consistently impact the Pu concentrations for the Tank 12H samples, but this conclusion is uncertain since the data basis is non-detect values.

A gradual increase in Pu concentration was observed for both Tank 18F OR2 test samples versus time, and it is uncertain based on the data whether saturation and equilibrium were achieved during the testing period. In addition, the Pu concentrations observed for the Tank 18F OR2-A sample were consistently an order of magnitude lower than the Tank 18F OR2-B samples. This difference is not understood, since nearly identical sample preparation methods and amounts were used for each sample. A gradual increase in Pu concentration was also observed for the Tank 12H OR2 test samples versus time for the first 4 to 5 samples, but Pu concentrations either stabilized (OR2-3) or tended to decrease (OR2-4), suggesting equilibrium was achieved during the testing period. In addition, while the Pu concentrations observed for the Tank 12H OR2-3 sample held steady around $1\text{E-}10$ M over sampling events 6 through 8, the Tank 12H OR2-4 samples fluctuated around $3\text{E-}11$ M over sampling events 5 through 8.

Plutonium concentrations observed for the Tank 18F OR3 test samples (Tank 18F C and Tank 18F D) were more stable and were typically the highest values observed (near $1\text{E-}8$ M) of any samples tested. Due to the gradual increases observed for the Tank 18F OR2-B samples, the final sample analyzed was also near $1\text{E-}8$ M. Plutonium concentrations observed for the Tank 12H OR3 test samples (Tank 12H OR3-5 and Tank 12H OR3-6) were also relatively stable. A gradual increase in Pu concentration was observed for the Tank 12H OR3 test samples versus time for the first 3 to 4 samples, but Pu concentrations either stabilized (OR3-5) or tended to decrease (OR3-6), suggesting equilibrium was achieved during the testing period. In addition, while the Pu concentrations observed for the Tank 12H OR3-5 sample held steady around $1\text{E-}10$ M over sampling events 3 through 8, the Tank 12H OR3-6 samples fluctuated around a $4\text{E-}11$ M over sampling events 5 through 8.

The Pu concentration results exhibit a significant level of uncertainty, and indicate a complexity not easily captured in a model using a single solubility value to represent the CZ at each time step. The Pu results likely reflect the possibility that residual samples from different tanks may contain different plutonium forms with differing solubilities, or that a residual sample from a single tank includes two or more types of plutonium with differing solubilities. The different solubilities could be associated with oxidation state, chemical speciation, or matrix differences. For example, a significant fraction of the plutonium in a single tank sample could be co-precipitated with other metals present in the residual solids or imbedded deep within the solid matrix. [SRNL-STI-2016-00432]

Under reducing conditions (RR2), plutonium solubilities observed for Tank 18F residuals ($7\text{E-}11$ to $2\text{E-}09$ M) exceeded those observed with Tank 12H solids ($<3\text{E-}13$ to $<2\text{E-}11$ M) by at least 1-2 orders of magnitude (Pu concentrations observed for Tank 12H residuals were below detectable limits) even though more reducing conditions were observed with the Tank 18F solids. Under oxidizing conditions (OR2 and OR3), plutonium solubilities observed for Tank 18F residuals ($4\text{E-}10$ to $1\text{E-}08$ M) were also 1-2 orders of magnitude higher than the solubilities observed with

Tank 12H solids (1E-11 to 4E-10 M). Overall, the solubility testing results for RR2, OR2, and OR3 indicate that the Pu in Tank 18F is orders of magnitude more soluble than the Pu in Tank 12H. This stark difference could be associated with either the varied waste forms present in the residuals (HTF Tank 12H versus FTF Tank 18F) or with the differing cleaning techniques (Tank 12H was acid cleaned while Tank 18F was mechanical cleaned). The Waste Tank Residuals Properties document (N-ESR-H-00040) describes the differences between the different tank farm waste contents (Section 2.1 of N-ESR-H-00040) and the various waste removal techniques used in the tank farms (Section 2.2 of N-ESR-H-00040).

The solubility testing results for RR2, OR2, and OR3 also indicate that the waste tank Pu residuals might not be as insoluble as assumed in the WRM, especially with respect to Tank 18F. However, the waste release testing does seem to demonstrate that the worst case (i.e., Tank 18F) solubility of Pu in OR2 and OR3 chemical conditions will not exceed the values calculated for the Pu phase in equilibrium with dissolved oxygen. The solubility of the Pu phase in equilibrium with dissolved oxygen ($\text{PuO}_2(\text{am,hyd})$) is 5E-8 moles/liter for OR2 and 8E-8 moles/liter for OR3, per Table 12 of SRNL-STI-2012-00404. Prior to residual waste testing there was a concern that Pu might exist in a much more soluble phase, as may be the case if the Pu existed in the residual waste as a carbonate phase. The solubility of the Pu carbonate phase ($\text{Pu}(\text{OH})_2\text{CO}_3$) in OR2 chemical conditions was calculated to be 4.8E-5 moles/liter in *Form and Aging of Plutonium in Savannah River Site Waste Tank 18F* (SRNL-STI-2012-00106). The solubilities seen during the waste release testing are higher than the $\text{PuO}_2(\text{am,hyd})$ solubility calculated for and documented in the TF WRM, more so in the case of the Tank 18F testing results. However, the solubility testing results for Tanks 18F and 12H are all at least 4-5 orders of magnitude lower than the $\text{Pu}(\text{OH})_2\text{CO}_3$ solubility of 4.8E-5 moles/liter.

While Pu might not be quite as insoluble as assumed in the TF WRM, it is still relatively insoluble and would therefore not be expected to contribute to the TF peak doses within 10,000 years. To confirm this hypothesis, new HTF and FTF Base Case model runs were carried out with higher solubility values using the HTF and FTF GoldSim models in a deterministic mode (SRR-CWDA-2018-00075). The Tank Farm solubility values used in these new base case model runs are presented in Table 4.3.2-1, along with the solubility values used in HTF (SRR-CWDA-2010-00128) and FTF (SRS-REG-2007-00002) PA modeling. The “Tank Farm conservative case” and “Tank Farm nominal case” values presented in Table 4.3.2-1 are based upon a considered evaluation (by the author) of the data presented in Figure 4.3.2-7, not statistical calculations.

Figure 4.3.2-7: Pu Concentration Data (Tanks 18F and 12H)

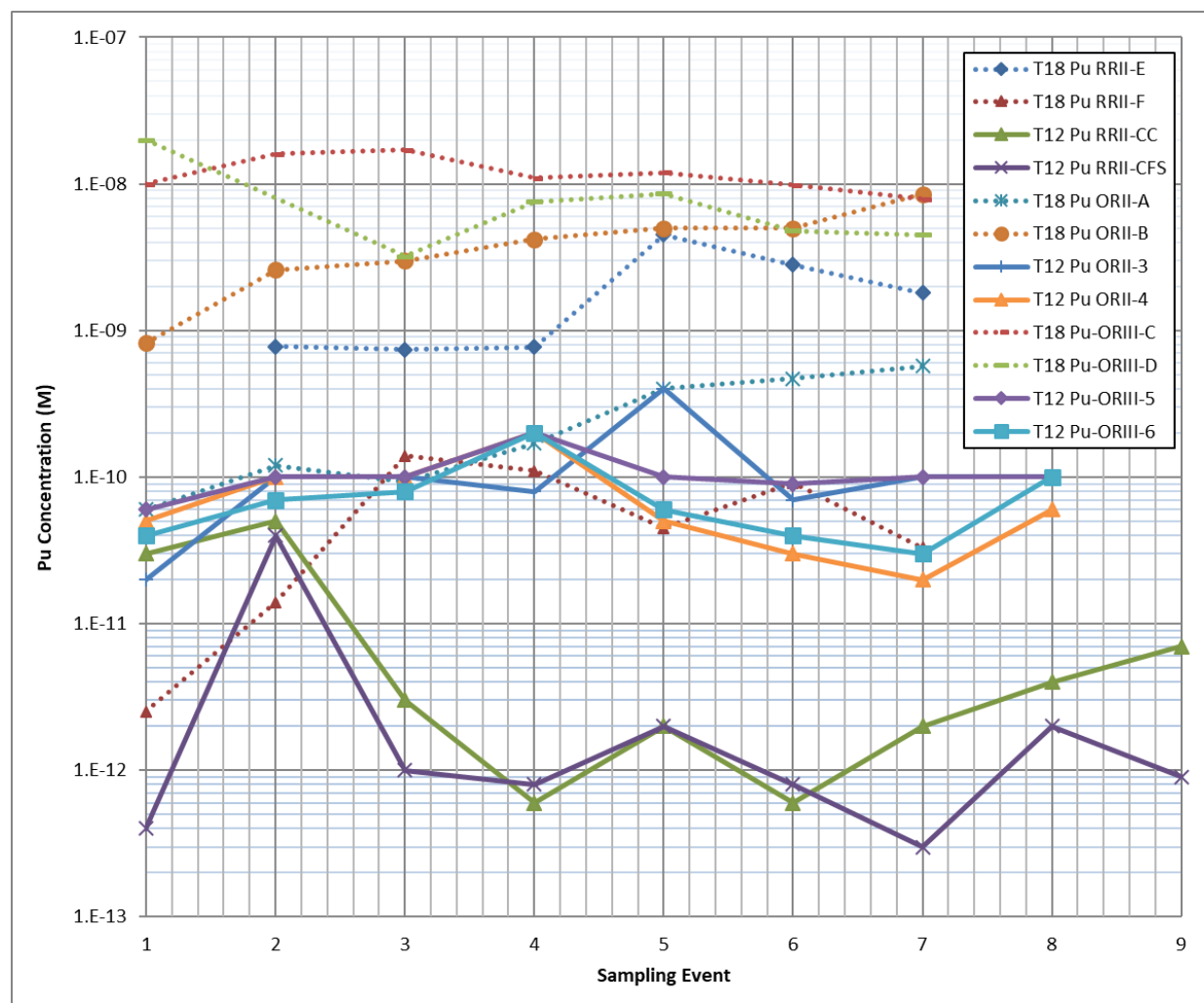


Table 4.3.2-1: Plutonium Solubility

	RRII (mol/L)	ORII (mol/L)	ORIII (mol/L)
FTF PA	4E-12	4E-14	6E-05
HTF PA / WRM	3E-11	3E-11	3E-11
Tank 18F Conservative Case	5E-09	1E-08	2E-08
Tank 18F Nominal Case	1E-09	1E-09	1E-08
Tank 12H Conservative Case	5E-11	4E-10	2E-10
Tank 12H Nominal Case	5E-12	1E-10	1E-10
Tank Farm Conservative Case	5E-09	1E-08	2E-08
Tank Farm Nominal Case	1E-09	1E-09	1E-08

As seen in Figure 4.3.2-8 and Figure 4.3.2-9, even assuming higher Pu solubility values (i.e., using the Pu solubility values from Table 4.3.2-1) there is no significant impact on the peak dose (accounting for all sources and all radionuclides) within 10,000 years for either HTF or FTF.

Figure 4.3.2-8: FTF Peak MOP Doses for Various Pu Solubility Values – 20K & 100K Years

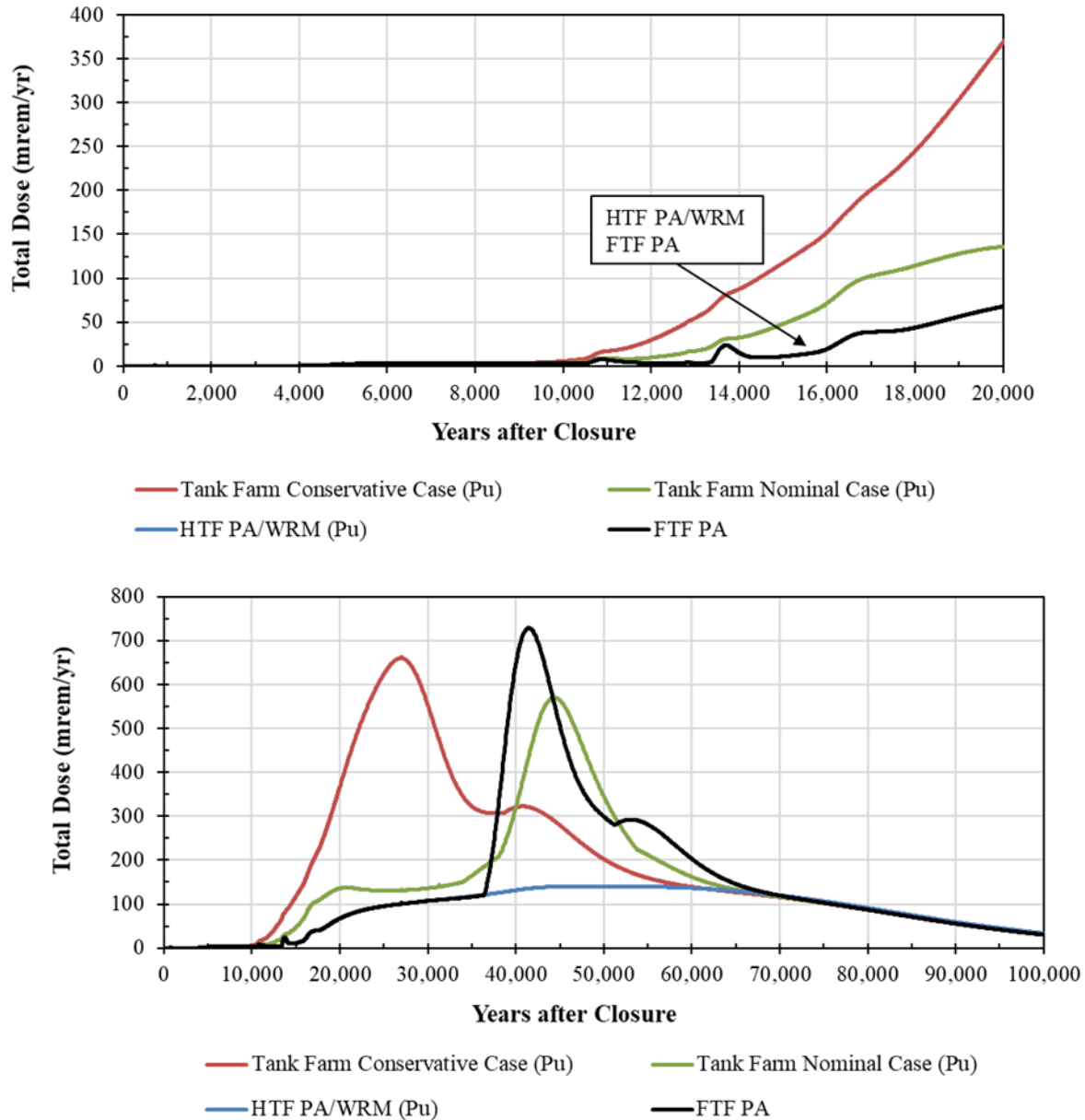
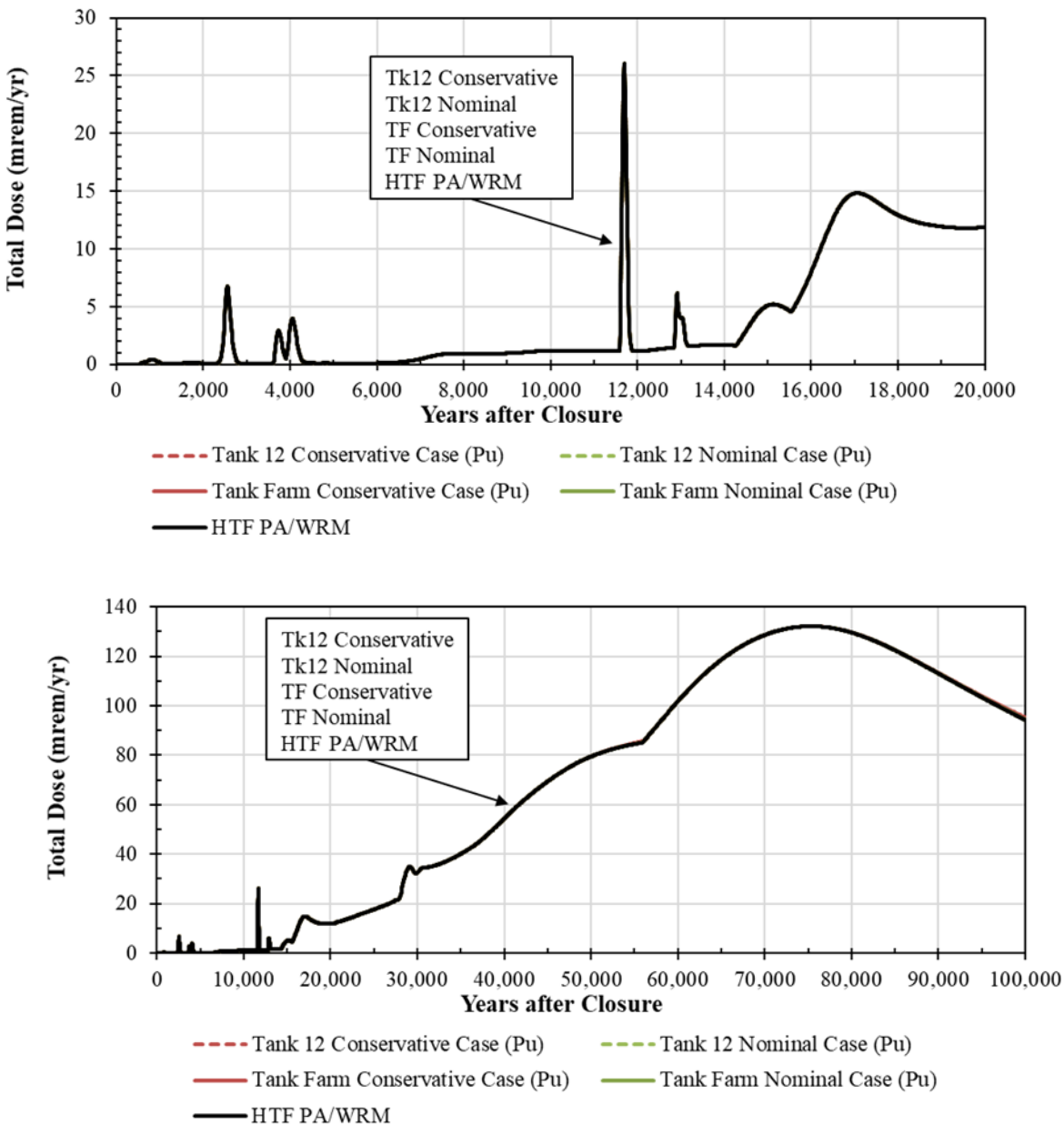


Figure 4.3.2-9: HTF Peak MOP Doses for Various Pu Solubility Values – 20K & 100K Years



To further clarify the impact higher Pu solubility values (i.e., using the Pu solubility values from Table 4.3.2-1) would have on the FTF peak dose, the Deterministic Model Composite Sensitivity Analyses from the Tank 18/19 Special Analysis (SA) (SRR-CWDA-2010-00124) was updated to include updated plutonium (Pu) sensitivity inputs. [SRR-CWDA-2017-00035] To evaluate the impact of uncertainty surrounding Pu solubility and sandy soil Kd values simultaneously, the Tank 18/19 SA included several PORFLOW sensitivity analyses that were performed substituting variable Pu solubility and Pu sandy soil Kd values into the FTF PA Base Case. After the initial Deterministic Model Composite Sensitivity Analyses was performed, new information became

available regarding the Pu solubility and soil Kd values used in the FTF PA modeling, as documented in SRR-CWDA-2017-00035 (Tables 1 and 2).

To assess the impact that the updated input values might have on dose, GoldSim model simulations were conducted using the most current version of the FTF GoldSim model (i.e., SRS FTF v3.0 Deterministic.gsm for FTF). The Base Case from the Tanks 5 and 6 Special Analysis for the Performance Assessment for the F-Area Tank Farm at the Savannah River Site (SRR-CWDA-2012-00106, herein referred to as the Tanks 5 & 6 SA), was utilized for the modeling simulations. The new Pu solubility and soil Kd data (from SRR-CWDA-2017-00035 Tables 1 and 2) was used to run twelve different sensitivity cases (displayed in Table 4.3.2-2).

Table 4.3.2-2: Composite Sensitivity Analyses Cases

Case	Pu Solubility (a)	Pu Sandy Soil Kas (b)
1	FTF PA	270/NA
2	Fe co-precipitation	270/NA
3	PuO _{2(am,hyd)} conservative E _h (Tank 18/19 SA)	270/NA
4	PuO _{2(am,hyd)} realistic E _h (Tank 18/19 SA)	270/NA
5	Waste Release Testing Conservative Case	270/NA
6	Waste Release Testing Nominal Case	270/NA
7	FTF PA	650/1,000
8	Fe co-precipitation	650/1,000
9	PuO _{2(am,hyd)} conservative E _h (Tank 18/19 SA)	650/1,000
10	PuO _{2(am,hyd)} realistic E _h (Tank 18/19 SA)	650/1,000
11	Waste Release Testing Conservative Case	650/1,000
12	Waste Release Testing Nominal Case	650/1,000

(a) SRR-CWDA-2017-00035, Table 1

(b) SRR-CWDA-2017-00035, Table 2

As shown in Figures 4.3.2-10 through 4.3.2-13, the FTF peak doses associated with Pu-239 can vary greatly in timing and magnitude depending on the Pu solubility limits assumed, with the peak doses occurring later for cases with lower solubility limits (the HTF peak doses are not sensitive to Pu solubility). In no case is there an appreciable FTF peak dose within 10,000 years, and for Cases 7 – 12 (using the updated Kd values) the peak doses within 20,000 years are less than 3 mrem/year regardless of the solubility case assumed. These figures highlight the fact that the peak dose associated with Pu-239 occurs well beyond the 10,000-year performance period for all of the sensitivity case studies performed, and in many cases, the peak dose occurs much later, and is significantly attenuated, when compared to the FTF modeling Base Case results. These sensitivity analyses confirm the uncertainty surrounding the doses associated with Tank 18F Pu-239 is reasonably bounded, and even after incorporating the new waste release testing data, there is confidence that the peak doses associated with Pu-239 in Tank 18F will not move forward in time into the 10,000-year performance period.

Figure 4.3.2-10: Sensitivity Cases 1 – 6, Sensitivity of Pu-239 Dose to Solubility with 270 ml/g Pu Sandy Soil Kds (0 - 20,000 Years)

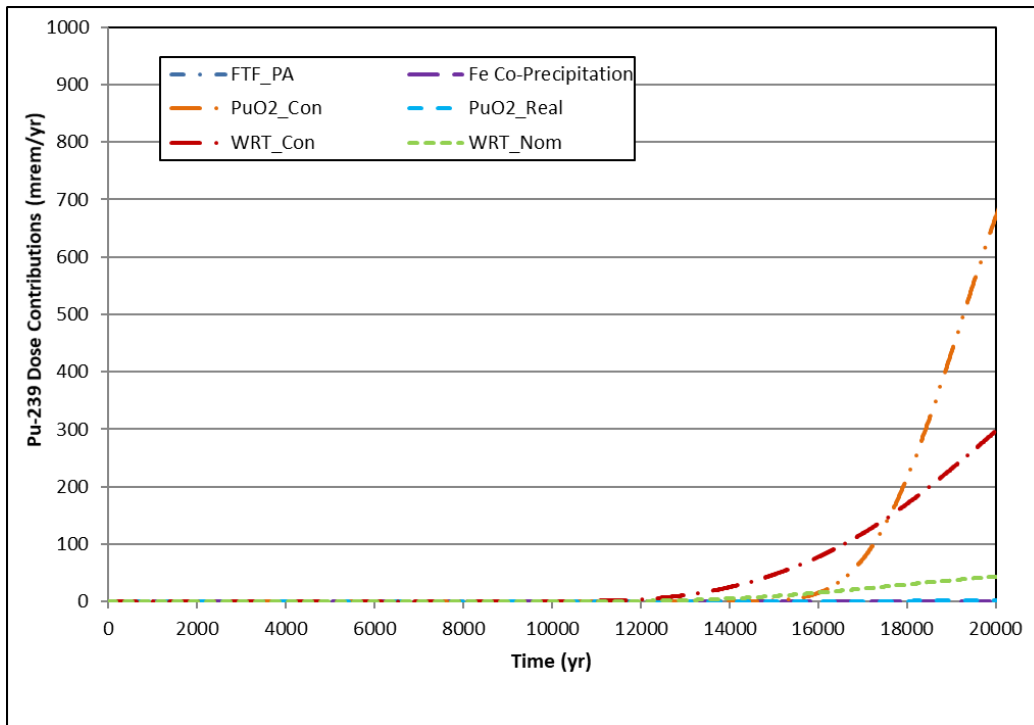


Figure 4.3.2-11: Sensitivity Cases 7 – 12, Sensitivity of Pu-239 Dose to Solubility with 650/1000 ml/g Pu Sandy Soil Kds (0 - 20,000 Years)

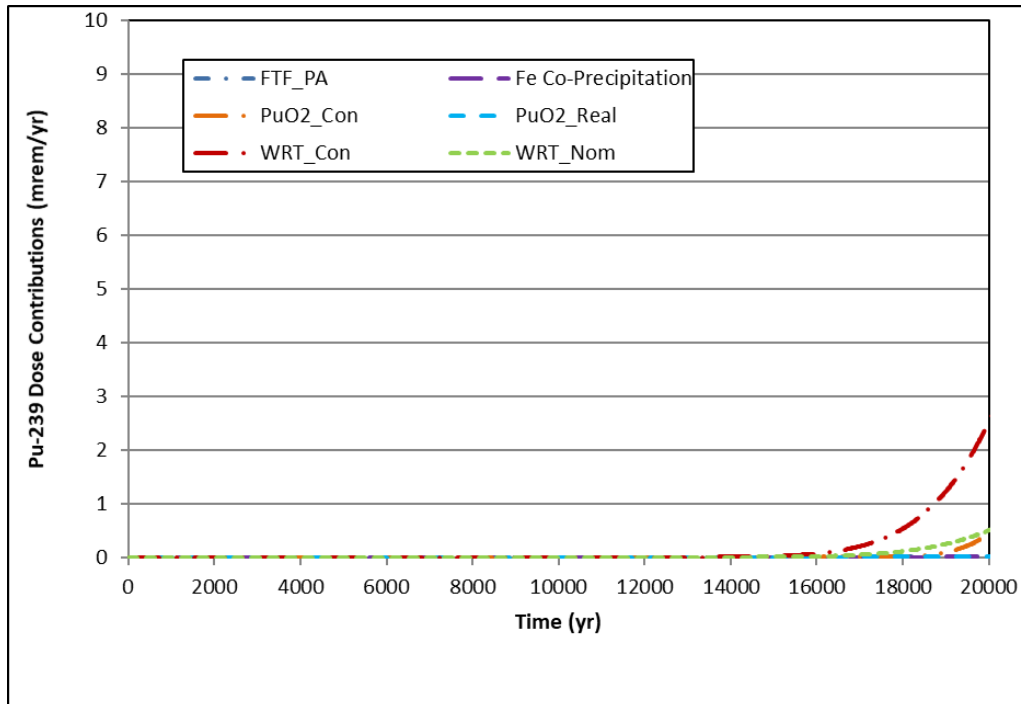


Figure 4.3.2-12: Sensitivity Cases 1 – 6, Sensitivity of Pu-239 Dose to Solubility with 270 ml/g Pu Sandy Soil Kds (0 - 100,000 Years)

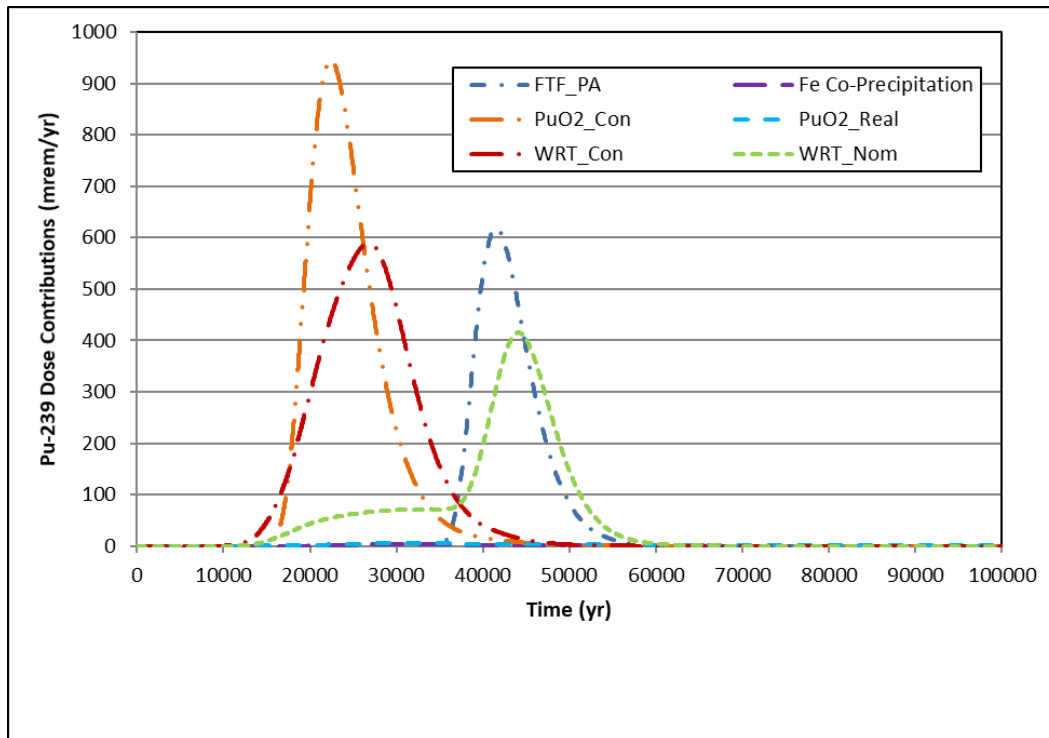
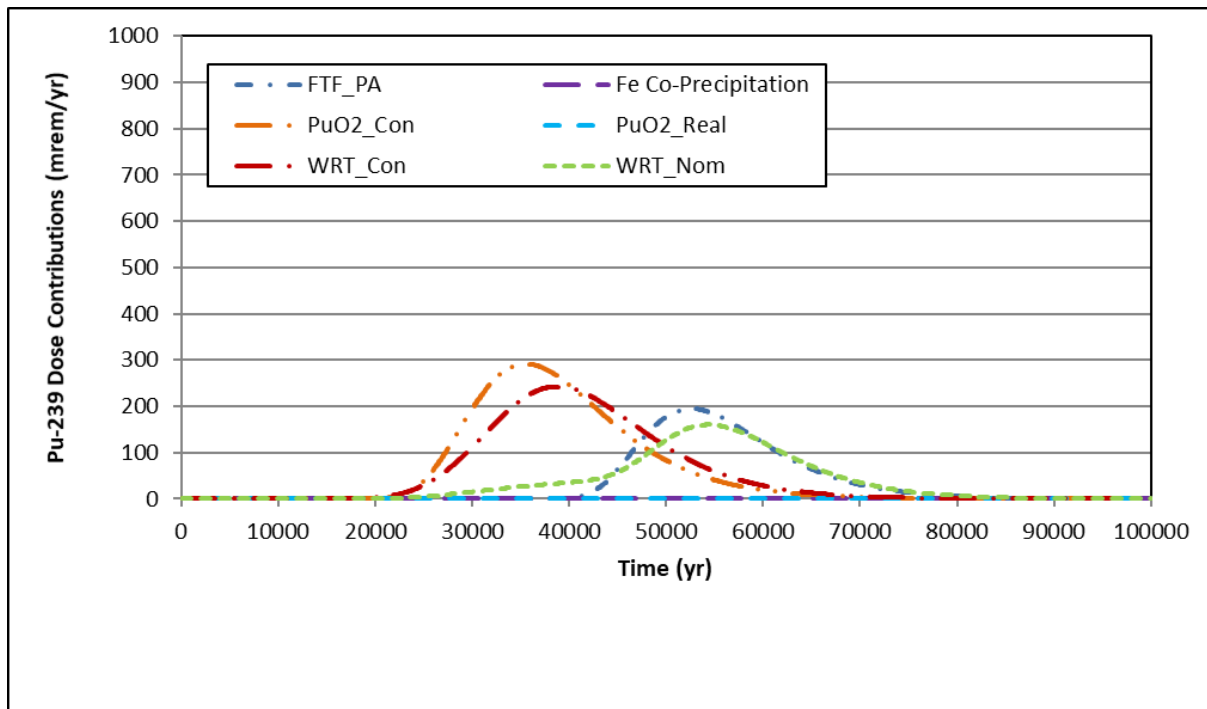


Figure 4.3.2-13: Sensitivity Cases 7 – 12, Sensitivity of Pu-239 Dose to Solubility with 650/1000 ml/g Pu Sandy Soil Kds (0 - 100,000 Years)



Figures 4.3.2-14 and 4.3.2-15 show a plot of the measured Pu concentrations over the testing period (Tables 4.1-2 and 4.2-2) versus pH and E_h . From these figures it appears Pu concentrations are more sensitive to pH changes than to E_h changes. Figure 4.3.2-14 presents a noticeable trend in the Pu concentration as the pH is increased, however in Figure 4.3.2-15 there is no trend in Pu concentration changes as there is an increase in E_h values.

Figure 4.3.2-14: Pu Concentrations vs. pH

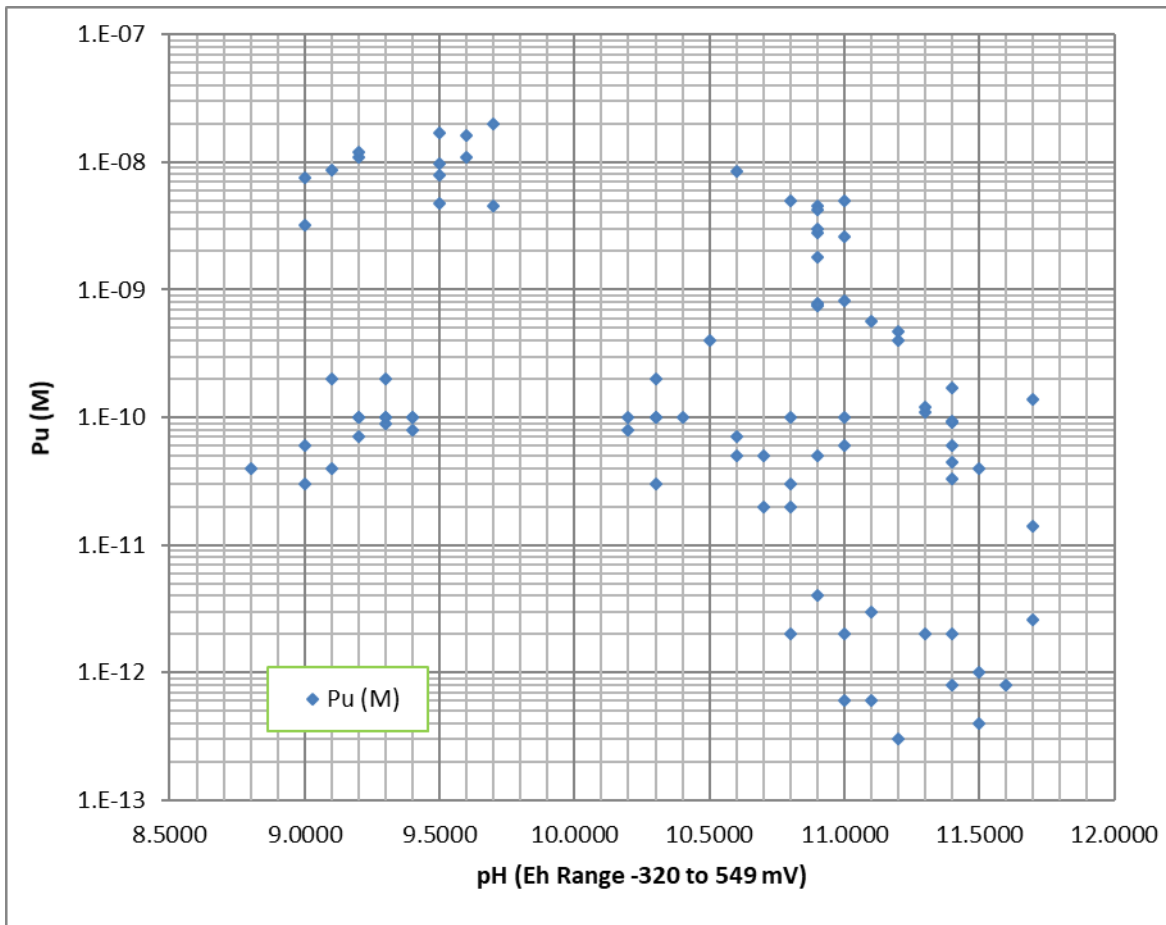
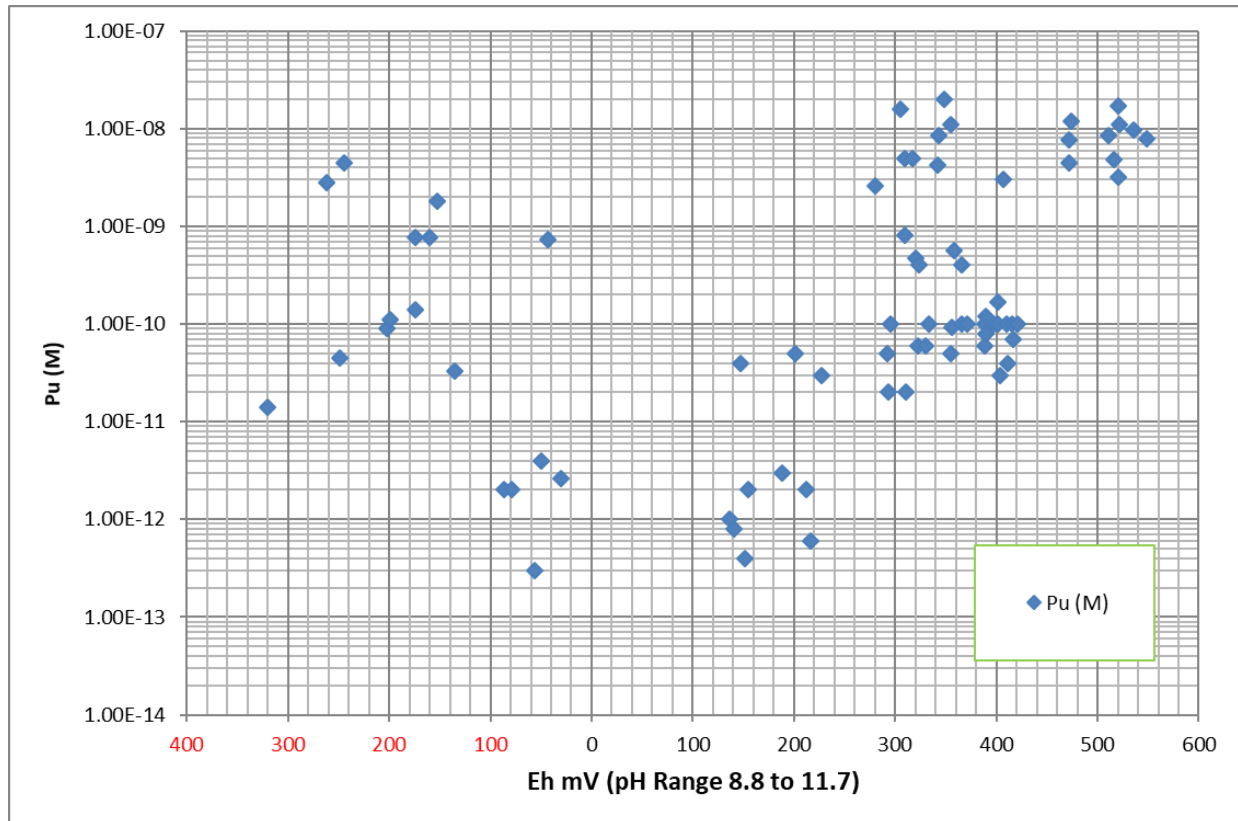


Figure 4.3.2-15: Pu Concentrations vs. E_h



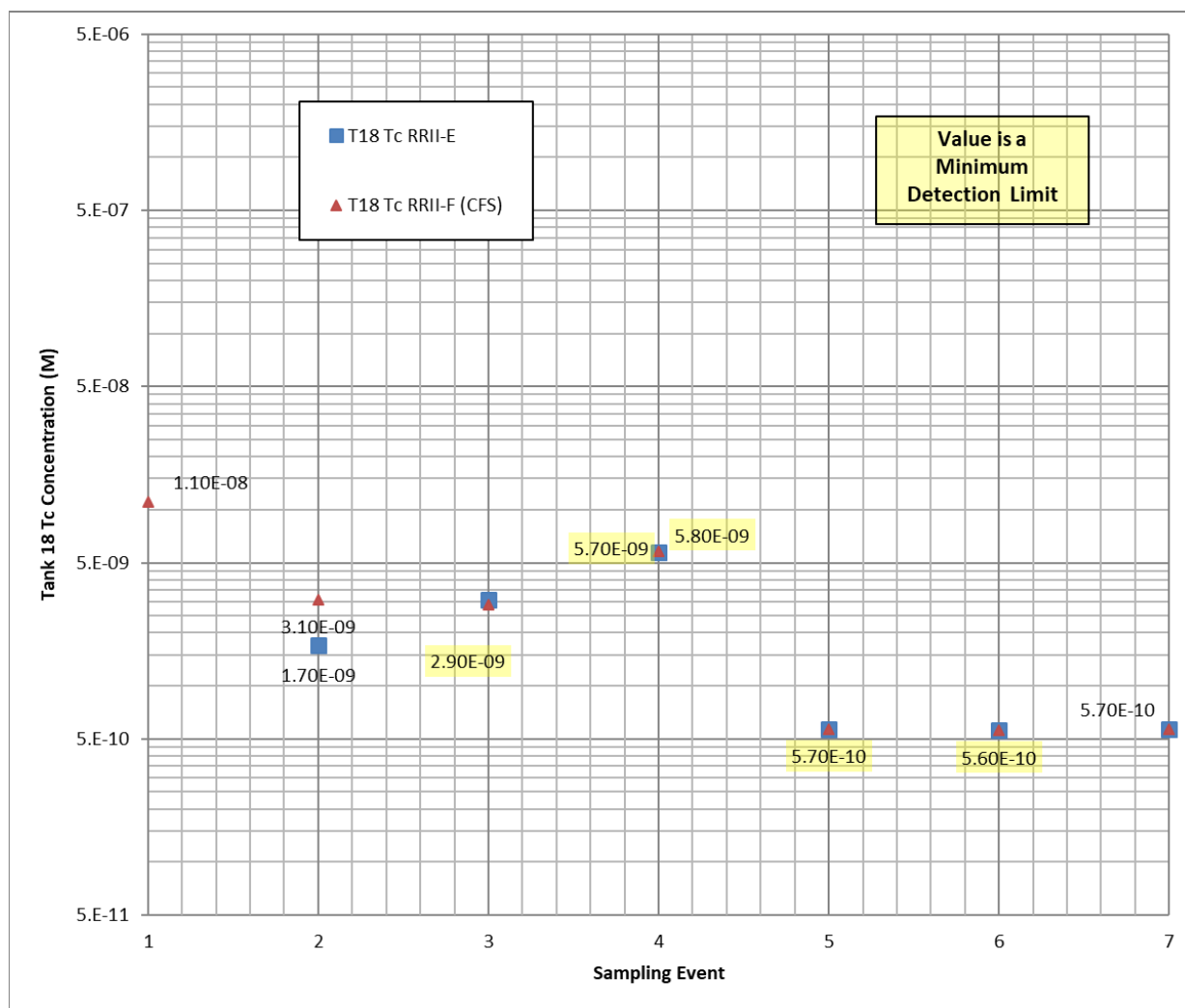
4.3.3 Technetium Analysis

4.3.3.1 *Technetium Reduced Region II*

Tank 18F Technetium Reduced Region II Results

Figure 4.3.3-1 shows a plot of the waste release testing results (Table 4.1-2) over the testing period for Tc with the sample subjected to RRII chemical conditions (i.e., target pH of 11.1 and target E_h of -470 mV). Many of the Tc concentrations included in this figure are minimum detection limits (versus measured values), so the actual Tc concentrations may be lower than those shown. Samples from the first two sampling events provided measured concentration values, but these samples were prior to completion of all sample washing and the samples were not as close to the target chemical conditions as desired. The sampling event four through seven samples (i.e., after washing) are believed to be more representative of steady state RRII chemical conditions since they were closer to the target chemical conditions.

Figure 4.3.3-1: Tank 18F Tc Concentrations under RRII Chemical Conditions

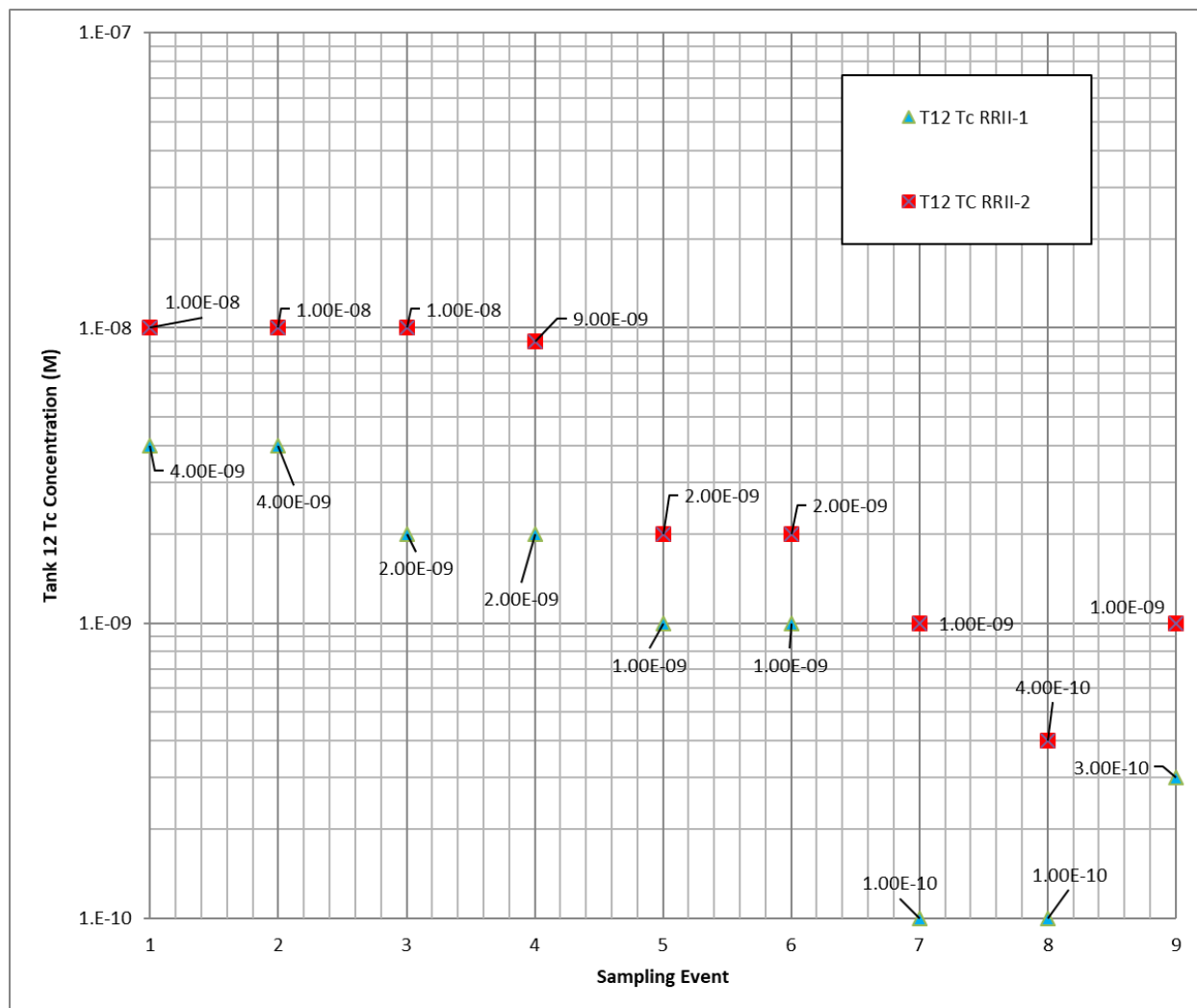


Tank 12H Technetium Reduced Region II Results

Figure 4.3.3-2 shows a plot of the waste release testing results (Table 4.2-2) over the testing period for Tc with the sample subjected to RRII chemical conditions (i.e., target pH of 11.1 and target E_h of -470 mV). None of the Tc concentrations included in this figure are minimum detection limits (versus measured values). The average technetium concentration for the unwashed reducing samples containing calcium carbonate solids (RRII-CC) during the first 62 contact days (sampling events 1-4) was 3E-09 M. The average technetium concentration for the unwashed reducing samples containing CFS solids (RRII-CFS) during the first 62 contact days (sampling events 1-4) of 1E-08 M was significantly higher than the RRII-CC sub-sample average and was similar to the oxidizing sub-sample concentrations. Following sample washing, the technetium concentrations of both reducing samples decreased with the CC sub-samples containing lower technetium concentrations than the CFS sub-samples during each sub-sampling event. The technetium concentrations appeared to decrease as the E_h values for the reducing samples decreased toward the end of testing. The average technetium concentrations observed for contact days 77 through

98 (sampling events 5-9) ranged from 6E-10 to 2E-09 M for the reducing samples. Overall, the results indicate that technetium concentrations in porewater leachates from Tank 12H residuals during the early tank aging stages under reducing conditions may be near 2E-09 M after significant porewater volumes have passed through the system. [SRNL-STI-2018-00484]

Figure 4.3.3-2: Tank 12H Tc Concentrations under RRII Chemical Conditions



Review of Technetium Solubility Assumptions versus Reduced Region II Testing Results

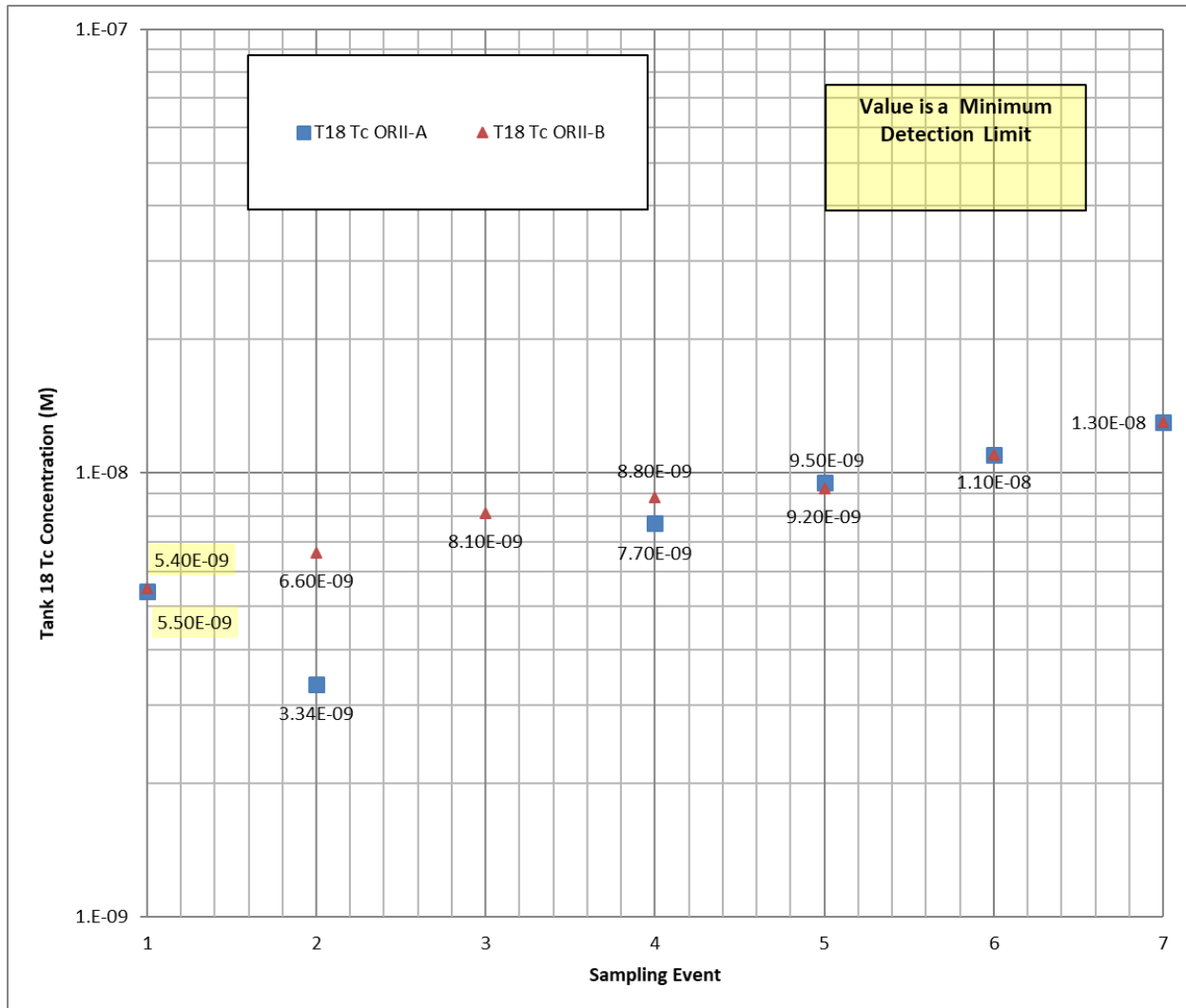
The TF WRM assigned Tc a solubility of 1E-14 M when subjected to RRII pore water. The observed experimental Tc concentrations under RRII chemical conditions indicate that the Tc in the Tank 18F and Tank 12H waste residuals under RRII chemical conditions is potentially more soluble than assumed in the TF WRM.

4.3.3.2 *Technetium Oxidized Region II*

Tank 18F Technetium Oxidized Region II Results

Figure 4.3.3-3 shows a plot of the waste release testing results (Table 4.1-2) over the testing period for Tc with the sample subjected to ORII chemical conditions (i.e., target pH of 11.1 and target E_h of 560 mV). Most of the Tc concentrations included in this figure are measured values (versus minimum detection limits).

Figure 4.3.3-3: Tank 18F Tc Concentrations under ORII Chemical Conditions

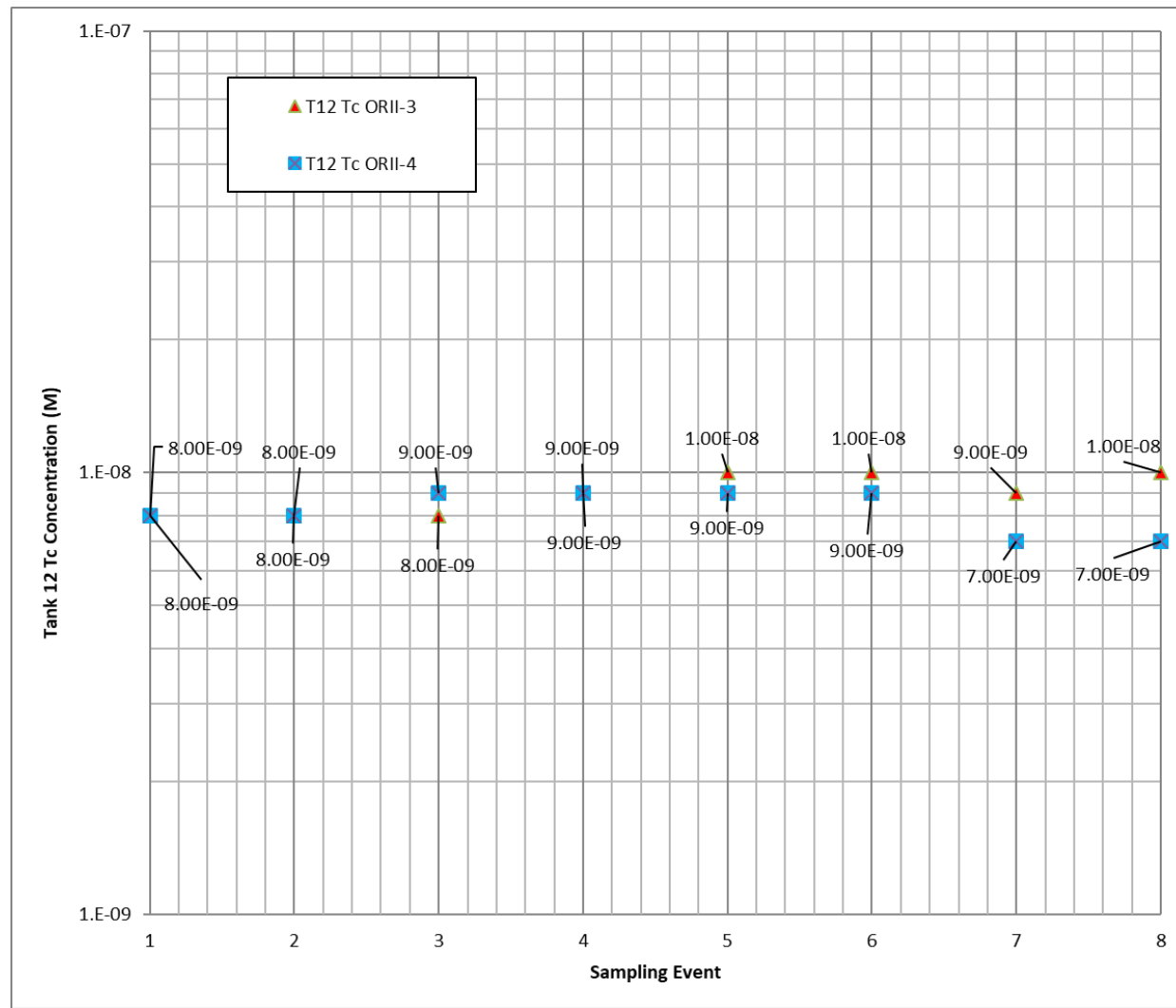


Tank 12H Technetium Oxidized Region II Results

Figure 4.3.3-4 shows a plot of the waste release testing results (Table 4.2-2) over the testing period for Tc with the sample subjected to ORII chemical conditions (i.e., target pH of 11.1 and target E_h of 560 mV). All of the Tc concentrations included in this figure are measured values (versus minimum detection limits). Technetium concentrations observed for the ORII-A and ORII-B test

sub-samples ranged only from 7E-09 to 1E-08 M across the entire testing period. [SRNL-STI-2018-00484]

Figure 4.3.3-4: Tank 12H Tc Concentrations under ORII Chemical Conditions



Review of Technetium Solubility Assumptions versus Oxidized Region II Testing Results

The TF WRM assigned Tc a solubility of 1E-13 M when subjected to ORII pore water. Nearly all of the Tc concentrations captured in the ORII testing are measured values (versus minimum detection limits). The observed experimental Tc concentrations indicate that the Tc in the Tank 18F and Tank 12H waste residuals under ORII chemical conditions is potentially more soluble than assumed in the WRM.

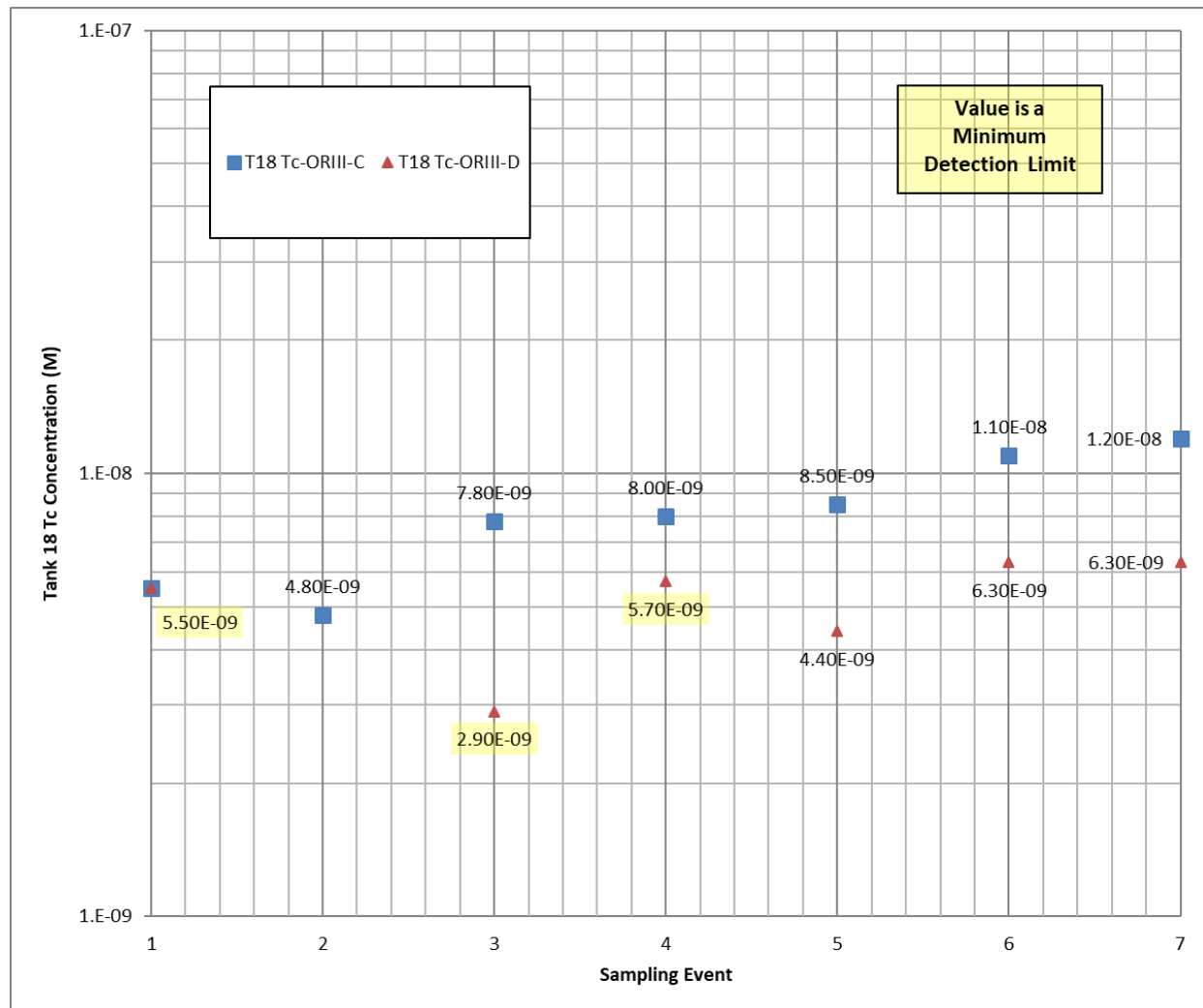
4.3.3.3 Technetium Oxidized Region III

Tank 18F Technetium Oxidized Region III Results

Figure 4.3.3-5 shows a plot of the waste release testing results (Table 4.1-2) over the testing period for Tc with the sample subjected to ORIII chemical conditions (i.e., Target pH of 9.2 and target E_h

of 680 mV). Most of the Tc concentrations included in this figure are measured values (versus minimum detection limits)

Figure 4.3.3-5: Tank 18F Tc Concentrations under ORIII Chemical Conditions

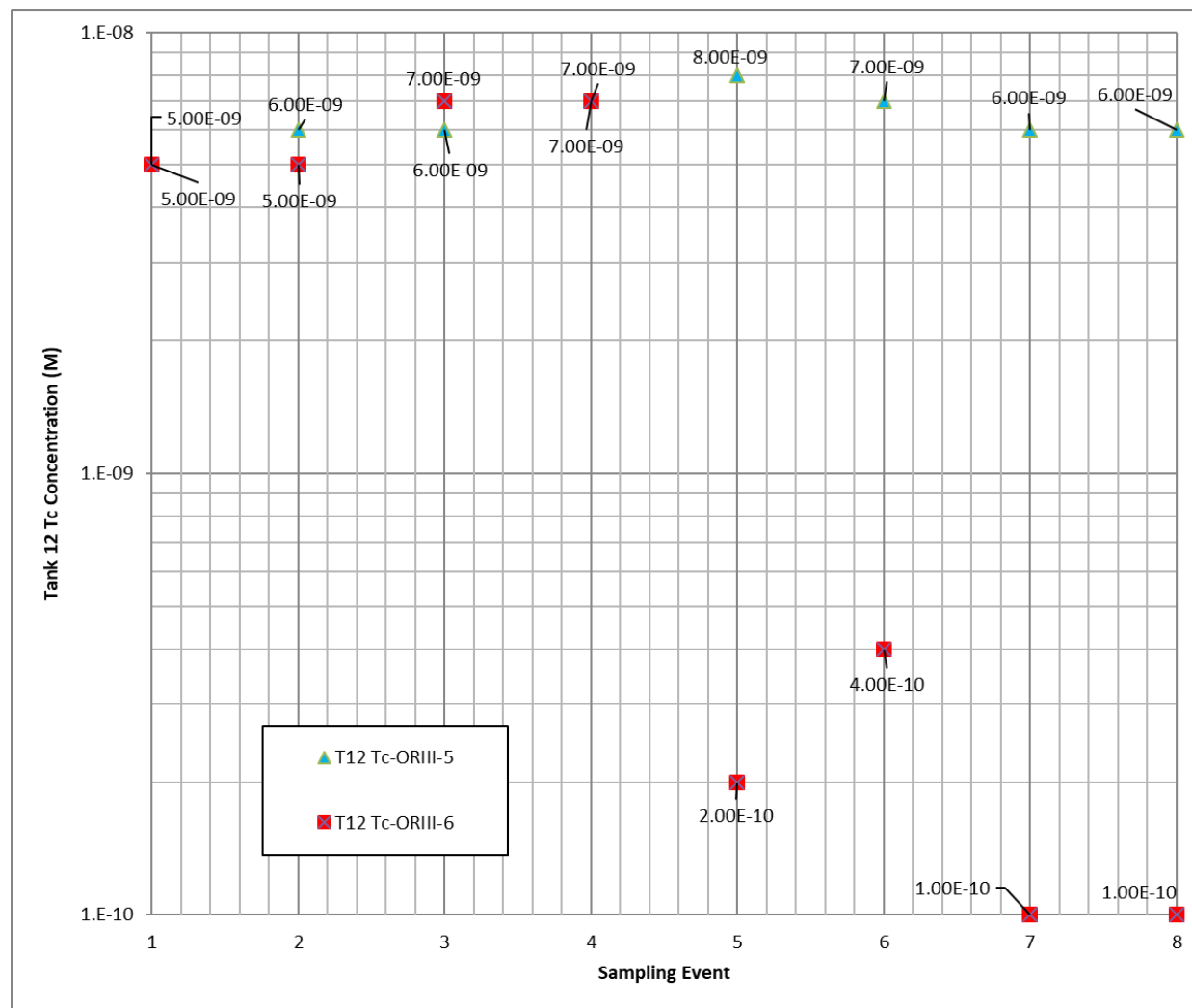


Tank 12H Technetium Oxidized Region III Results

Figure 4.3.3-6 shows a plot of the waste release testing results (Table 4.2-2) over the testing period for Tc with the sample subjected to ORIII chemical conditions (i.e., Target pH of 9.2 and target E_h of 680 mV). All of the Tc concentrations included in this figure are measured values (versus minimum detection limits). Technetium concentrations observed for the ORIII-A test sub-samples ranged from 5E-09 to 8E-09 M across the entire testing period. During the first 62 contact days (sample events 1-4), the average technetium concentration in the ORIII-B sub-samples of approximately 6E-09 M was similar to the other oxidizing samples. After exposure to significant wash volumes following the 62-day (sample events 1-4) sub-sampling event, the average technetium concentration in the ORIII-B sub-samples decreased to 2E-10 M (contact days 77-95,

sample events 5-8) presumably due to removal of significant amounts of soluble technetium during extensive washing. [SRNL-STI-2018-00484]

Figure 4.3.3-6: Tank 12H Tc Concentrations under ORIII Chemical Conditions



Review of Technetium Solubility Assumptions versus Oxidized Region III Testing Results

The TF WRM assigned Tc a solubility of $2\text{E-}15$ M when subjected to ORIII pore water. The observed experimental Tc concentrations indicate that the Tc in the Tank 18F and Tank 12H waste residuals under ORIII chemical conditions is potentially more soluble than assumed in the TF WRM.

4.3.3.4 *Technetium Analysis Conclusions*

No measurable technetium was observed for any of the Tank 18F reducing samples (RRII-E and RRII-F concentrations $<6\text{E-}10$ M). Very similar results were observed for the Tank 18F A, B, and C Tc samples, while lower concentrations were observed for the Tank 18F D samples, presumably due to the fact that 17% of the Tank 18F sample technetium may have been lost from this sample

during washing (Table 4.1-3). The data trends in the Tank 18F technetium concentrations indicate that the technetium concentration did not stabilize during testing but continued to slowly increase.

Measurable technetium was observed for all of the Tank 12H samples and minimal Tank 12H sample technetium was lost during washing (Table 4.2-4). The data trends in the Tank 12H technetium concentrations are either stable or decreasing, suggesting that the Tank 12H technetium concentrations stabilized during testing. The average technetium solubilities under reducing conditions (RRII) ranged from $3\text{E-}09$ to $1\text{E-}08$ M for unwashed Tank 12H residual samples and from $6\text{E-}10$ to $2\text{E-}09$ M for washed samples. Higher technetium concentrations may have been associated with the fact that much higher E_h values were observed for the reducing Tank 12H samples during most of the leach testing. Under oxidizing conditions (ORII and ORIII), Tc-99 solubilities observed for Tank 12H solids ($2\text{E-}10$ to $1\text{E-}08$ M) were comparable to the solubilities observed with Tank 18F residuals ($6\text{E-}09$ to $1\text{E-}08$ M).

Overall, the Tank 18F and Tank 12H solubility testing results for RRII, ORII, and ORIII indicate that Tc might not be quite as insoluble as assumed in the WRM and in the TF PAs. The WRM and TF PAs assumed that Tc would either be co-precipitated with Fe, making it very insoluble, or would be instantaneously soluble. The WRM assumed Tc was co-precipitated with the iron phases based on the assumption that the Tc had to be in a low solubility form to remain in the residual waste after tank washing. The Tc was not assumed to exist in a reduced form that resisted oxidation due to the high solubilities of oxidized forms of technetium such as TcO_4^- . However, only a portion of the Tc-99 was removed from the Tank 12H residual samples during washing, indicating that Tc dissolution is solubility-controlled under the test conditions.

Many of the waste release testing results (under all chemical conditions) are very close to the solubility calculated for *reduced* Tc ($\text{TcO}_2 \cdot 1.6\text{H}_2\text{O}$) which is $1\text{E-}8$ moles/liter (Table 11 from SRNL-STI-2012-00404). Studies have suggested that Tc(VI) reduced by Fe(II) in the presence of Fe(III) solids forms a solid Tc(IV) phase at the surface of the Fe(III) solid and the Tc(IV) solid resists re-oxidation and has (in one study) an apparent solubility very near that of $\text{TcO}_2 \cdot 1.6\text{H}_2\text{O}$. [LBNL-5595E, Geochimica et Cosmochimica Acta 71 (2007) 2137–2157] The reduction of Tc by Fe(II) may have occurred in Tanks 18F and 12H (and in other waste tanks) causing much of the Tc in the sludge to be reduced. Therefore, the experimental results may indicate that Tc is reduced in the residual waste and resists reoxidation when exposed to ORII and ORIII chemical conditions.

If Tc is not radically affected by oxidizing conditions (as the waste release testing suggests), Tc would not be expected to contribute to the TF peak doses within 10,000 years in the relatively small inventories (e.g., approximately one curie of Tc-99 per waste tank) anticipated based on closure history to date. To confirm this hypothesis, new HTF and FTF Base Case model runs were carried out with higher solubility values using the HTF and FTF GoldSim models in a deterministic mode (SRR-CWDA-2018-00075). The Tank Farm solubility values used in these new base case model runs are presented in Table 4.3-3-1, along with the solubility values used in HTF (SRR-CWDA-2010-00128) and FTF (SRS-REG-2007-00002) PA modeling. The “Tank Farm conservative case” and “Tank Farm nominal case” values presented in Table 4.3.3-1 are based upon a considered evaluation of the data presented in Figure 4.3.3-7, not statistical calculations. The Table 4.3.3-1 “Tank Farm conservative case” and “Tank Farm nominal case” values are also based on the assumption that the later samples (i.e., after sampling events four or five) are more representative of steady state chemical conditions since the samples were closer to the target chemical conditions. As seen in Figures 4.3.3-8 and 4.3.3-9, even assuming larger Tc solubility

values (i.e., using the Tc solubility values from Table 4.3.3-1) has no significant impact on the peak dose (accounting for all sources and all radionuclides) within 10,000 years for either HTF or FTF.

Figure 4.3.3-7: Tc Concentration Data (Tanks 18F and 12H)

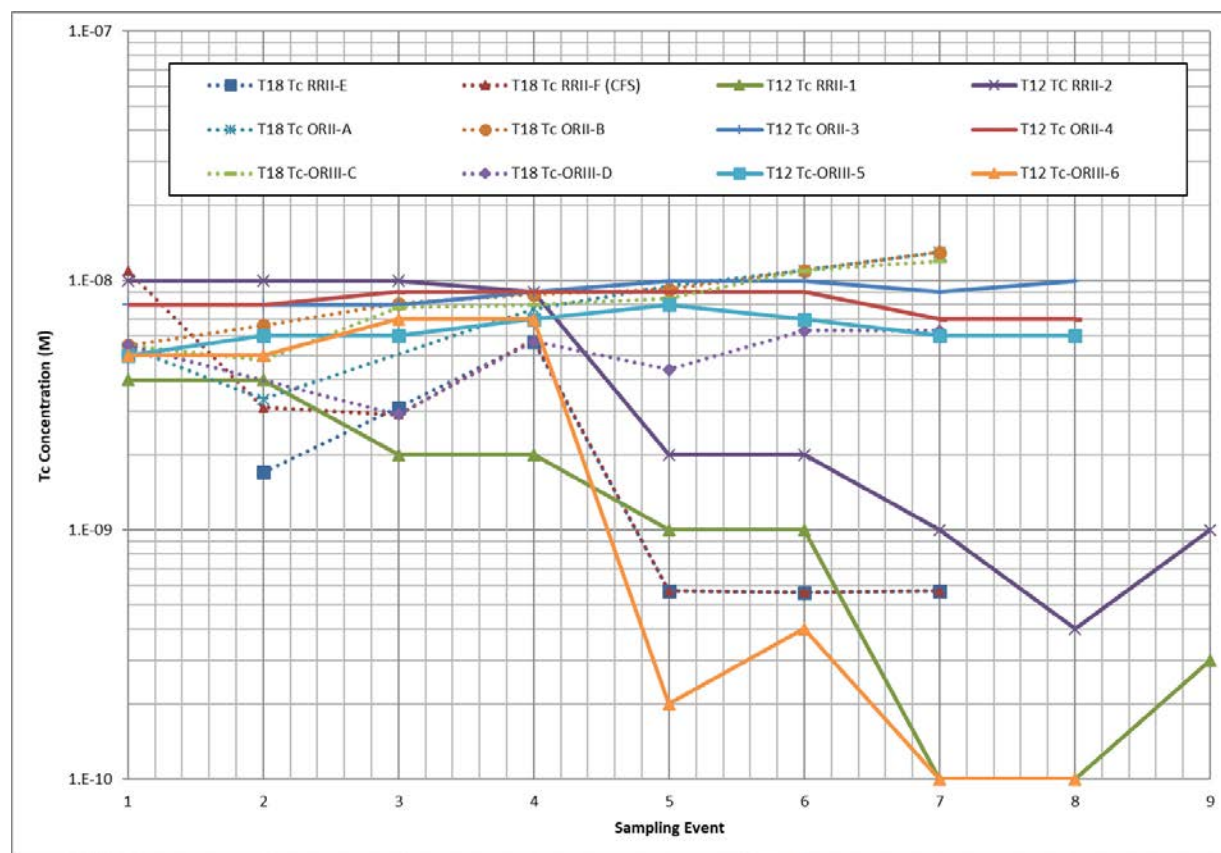


Table 4.3.3-1: Technetium Solubility

	RRII (mol/L)	ORII (mol/L)	ORIII (mol/L)
FTF PA	3E-11	3E-13	NA (no solubility control)
HTF PA / WRM	1E-14	1E-13	2E-15
Tank 18F Conservative Case	3E-09	2E-08	2E-08
Tank 18F Nominal Case	6E-10	1E-08	1E-08
Tank 12H Conservative Case	2E-09	1E-08	8E-09
Tank 12H Nominal Case	1E-09	1E-08	8E-09
Tank Farm Conservative Case	3E-09	2E-08	2E-08
Tank Farm Nominal Case	1E-09	1E-08	1E-08

**Figure 4.3.3-8: FTF Peak MOP Doses for Various Tc Solubility Values –
20K & 100K Years**

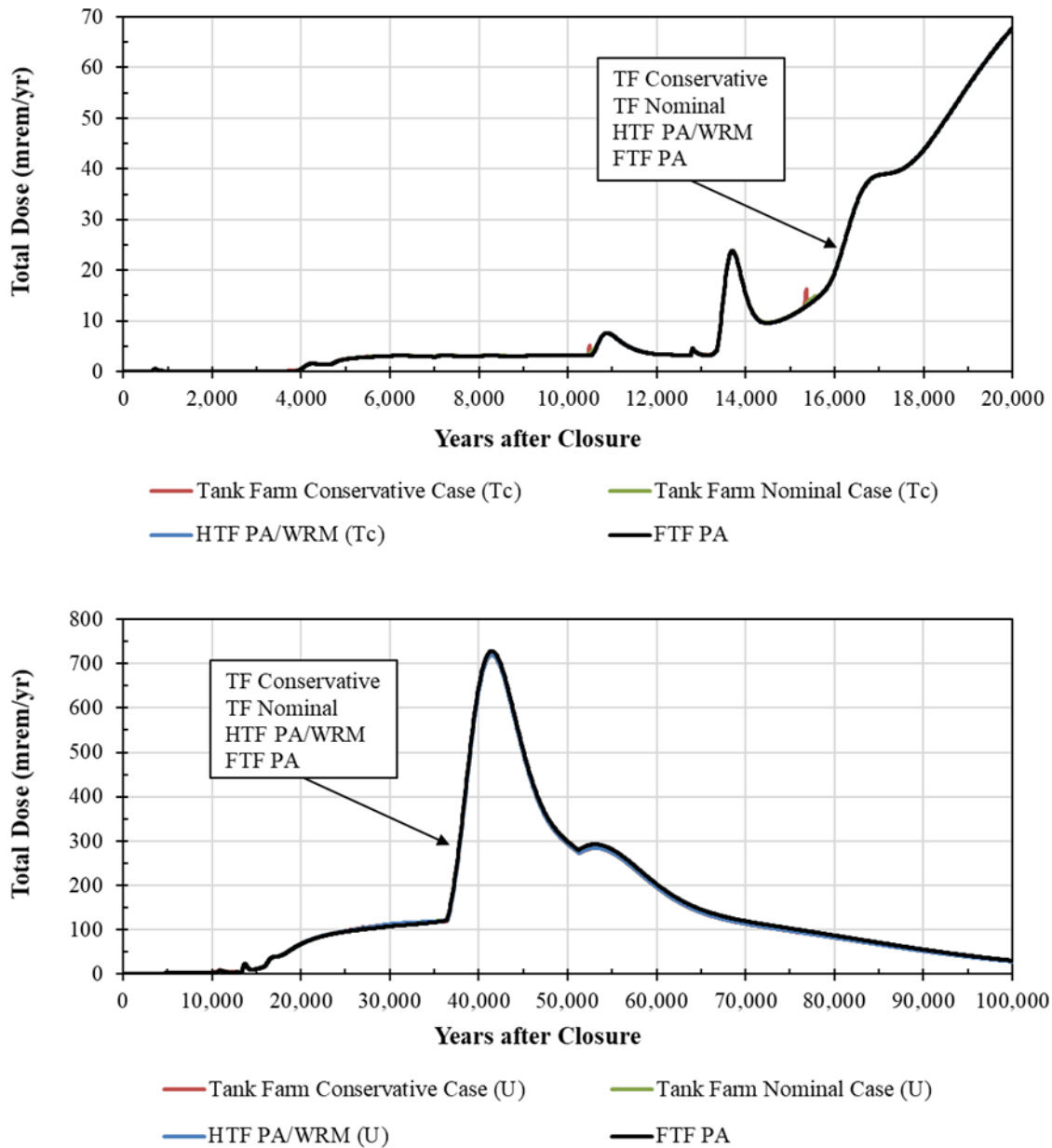
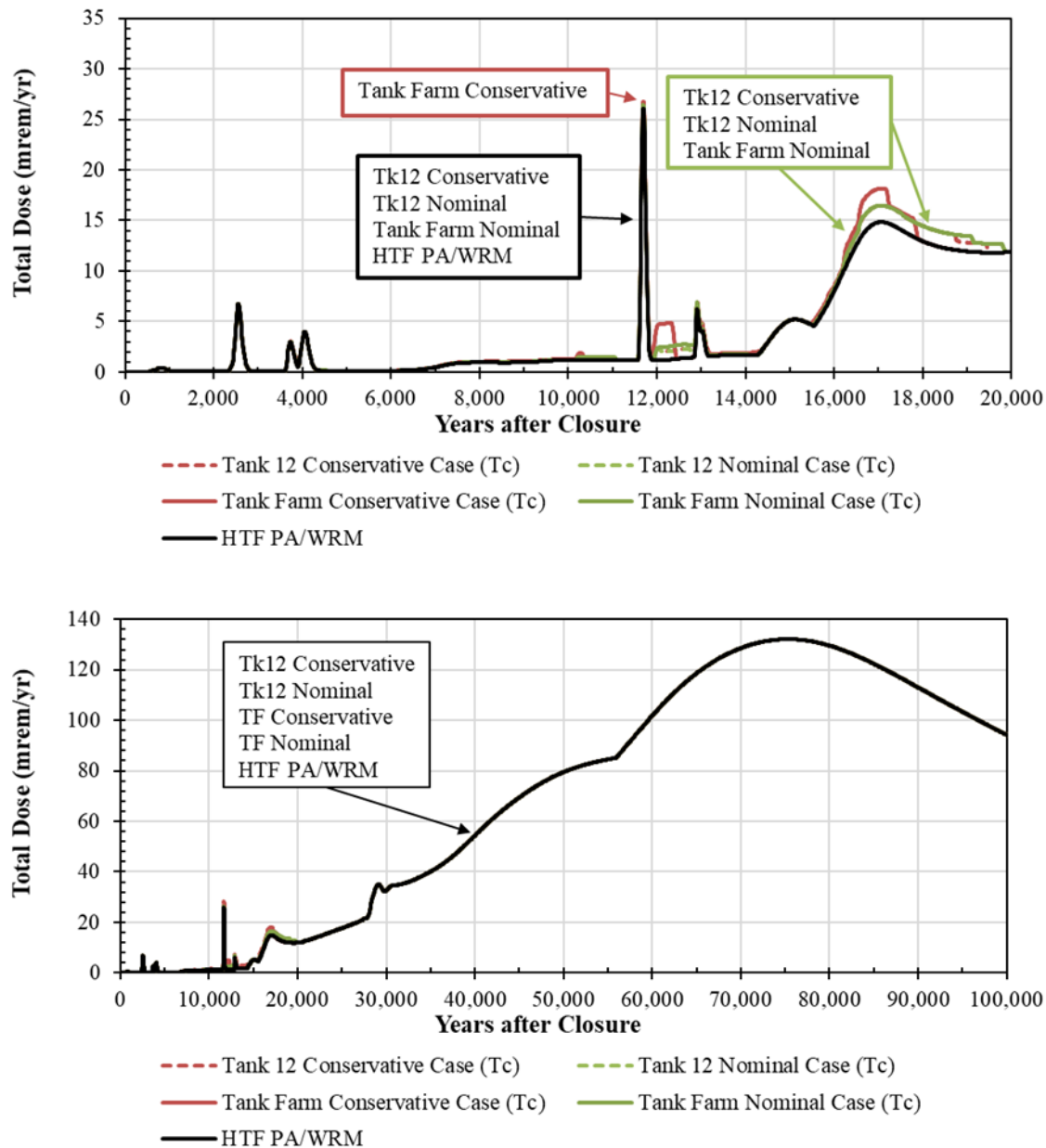


Figure 4.3.3-9: HTF Peak MOP Doses for Various Tc Solubility Values – 20K & 100K Years



Figures 4.3.3-10 and 4.3.3-11 show a plot of the measured Tc concentrations over the testing period (Tables 4.1-2 and 4.2-2) versus pH and E_h . From these figures it appears Tc concentrations are more sensitive to E_h changes than to pH changes. Figure 4.3.3-10 presents a noticeable trend in the Pu concentration as the E_h is increased, however in Figure 4.3.3-11 there is no trend in Pu concentration changes as there is an increase in pH values.

Figure 4.3.3-10: Tc Concentrations vs. pH

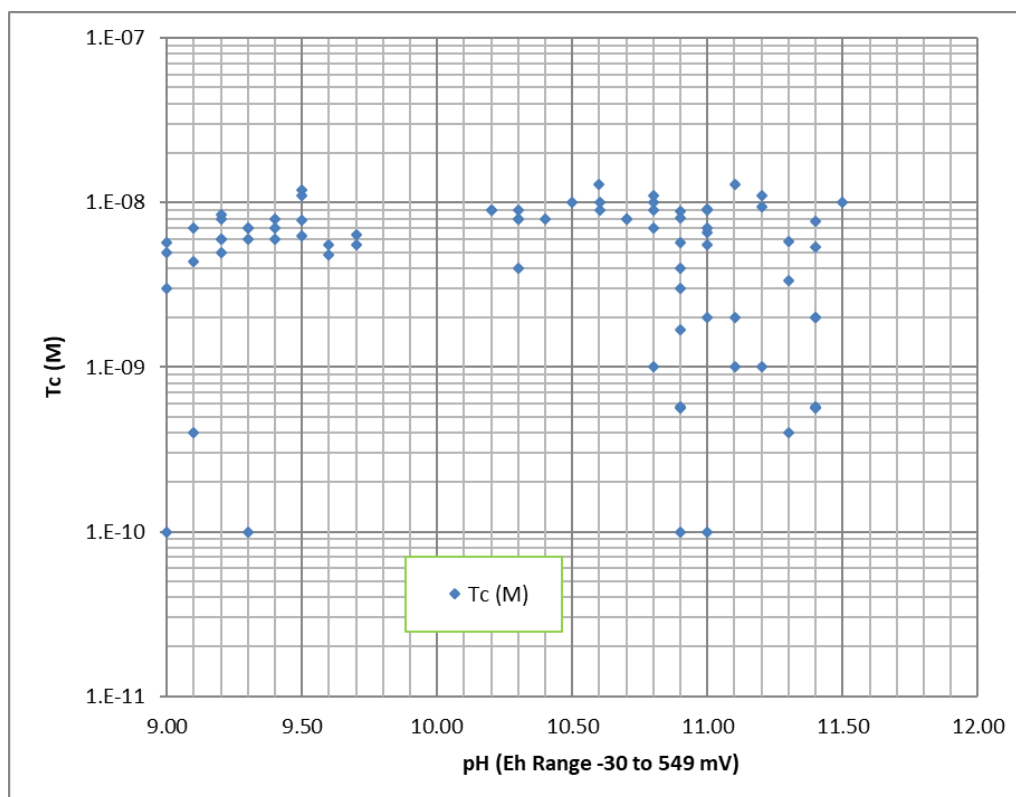
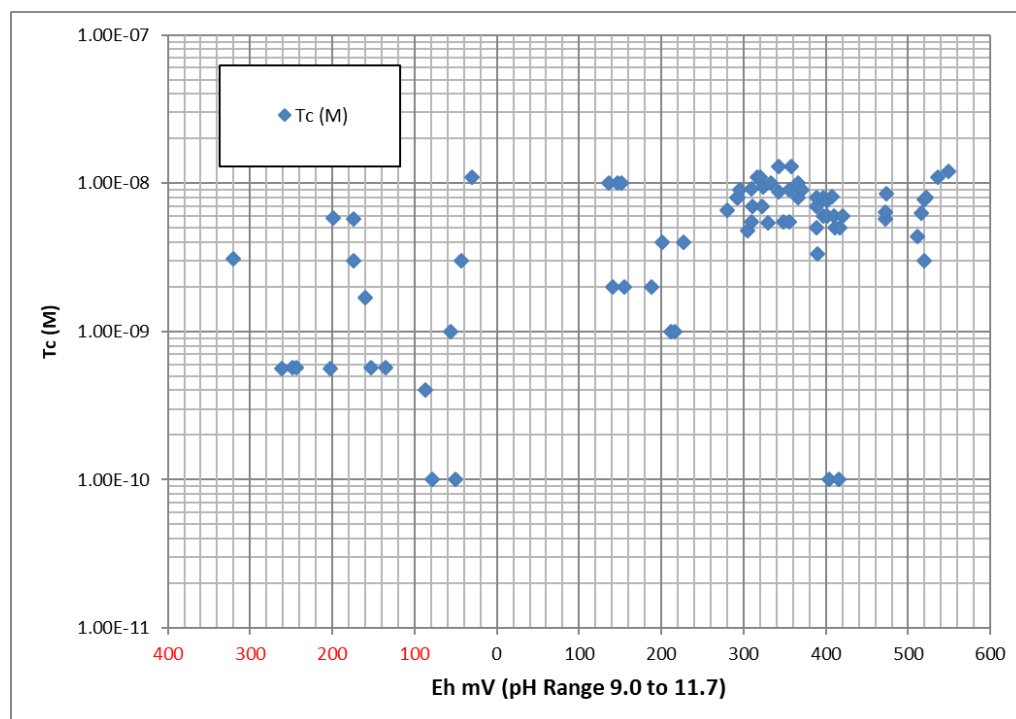


Figure 4.3.3-11: Tc Concentrations vs. E_h



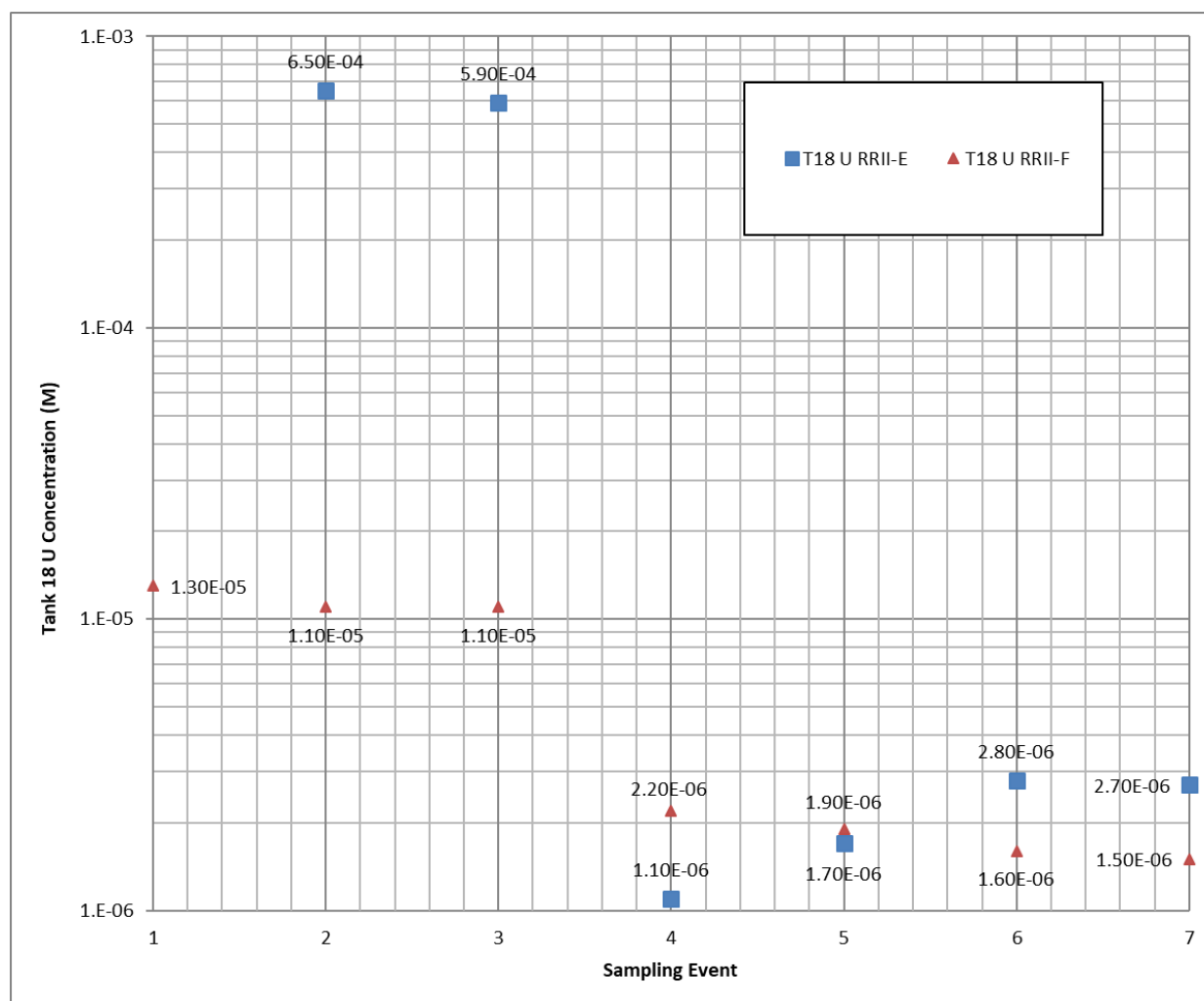
4.3.4 Uranium Analysis

4.3.4.1 *Uranium Reduced Region II*

Tank 18F Uranium Reduced Region II Results

Figure 4.3.4-1 shows a plot of the waste release testing results (Table 4.1-2) over the testing period for U with the sample subjected to RRII chemical conditions (i.e., target pH of 11.1 and target E_h of -470 mV). None of the U concentrations included in this figure are minimum detection limits (versus measured values). Samples from the first three sampling events are measured values, but these samples were prior to completion of all sample washing and the samples were not as close to the target chemical conditions as desired. The sampling event four through seven samples are believed to be more representative of steady state RRII chemical conditions since they were closer to the target chemical conditions.

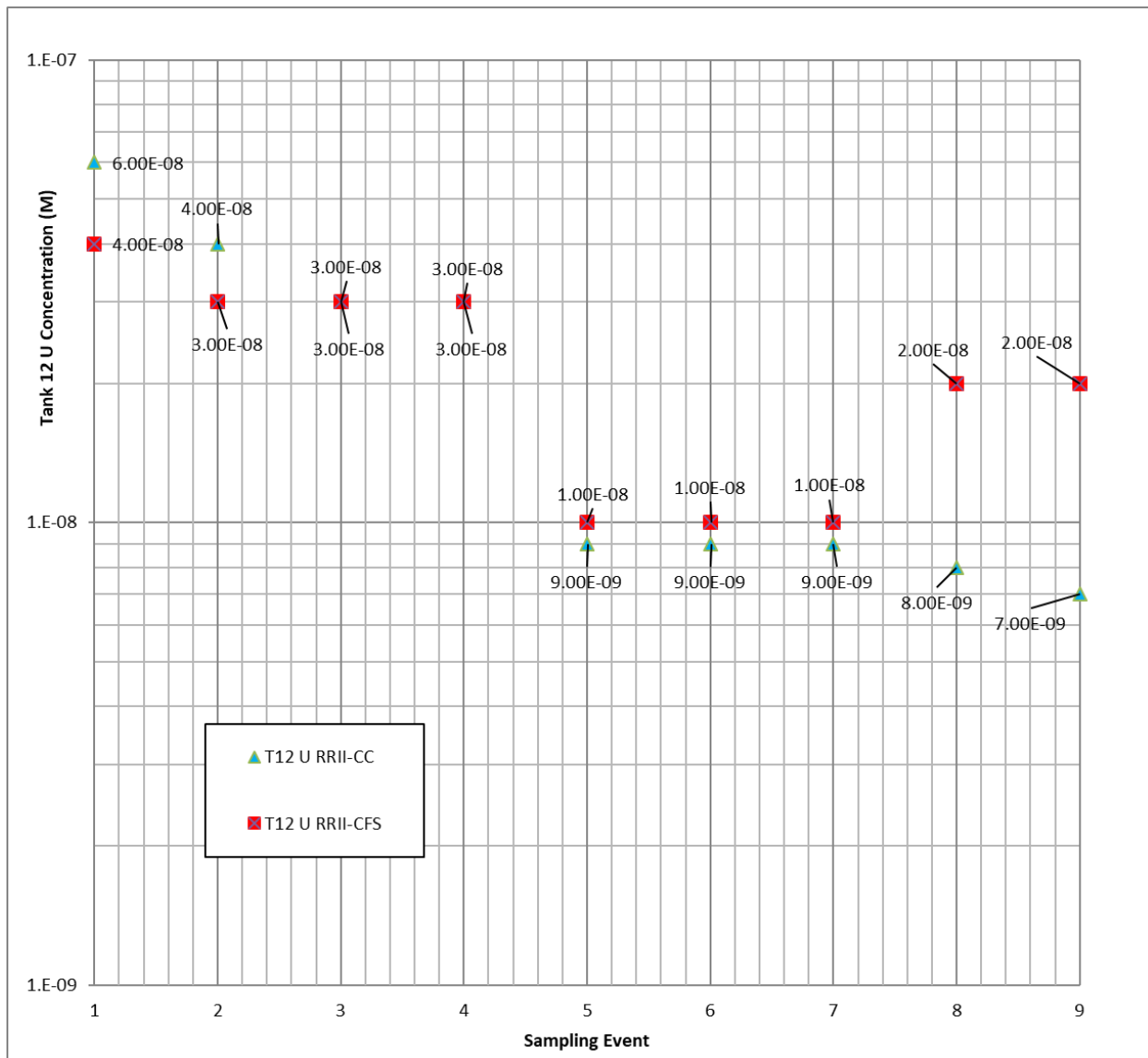
Figure 4.3.4-1: Tank 18F U Concentrations under RRII Chemical Conditions



Tank 12H Uranium Reduced Region II Results

Figure 4.3.4-2 shows a plot of the waste release testing results (Table 4.2-2) over the testing period for U with the sample subjected to RRII chemical conditions (i.e., target pH of 11.1 and target E_h of -470 mV). The average uranium concentrations observed for the reducing samples (RRII-CC and RRII-CFS) ranged from 3E-08 to 4E-08 M during the first 62 days of contact. Following washing and after decreasing the E_h values for the samples during contact days 77 through 98, the average uranium concentrations for the reducing samples decreased slightly and ranged from 1E-08 to 2E-08 M. Overall, the results indicate that uranium concentrations in porewater leachates from Tank 12H residuals during the early tank aging stages under reducing conditions should be near 4E-08 M. [SRNL-STI-2018-00484]

Figure 4.3.4-2: Tank 12H U Concentrations under RRII Chemical Conditions



Review of Uranium Solubility Assumptions versus Reduced Region II Testing Results

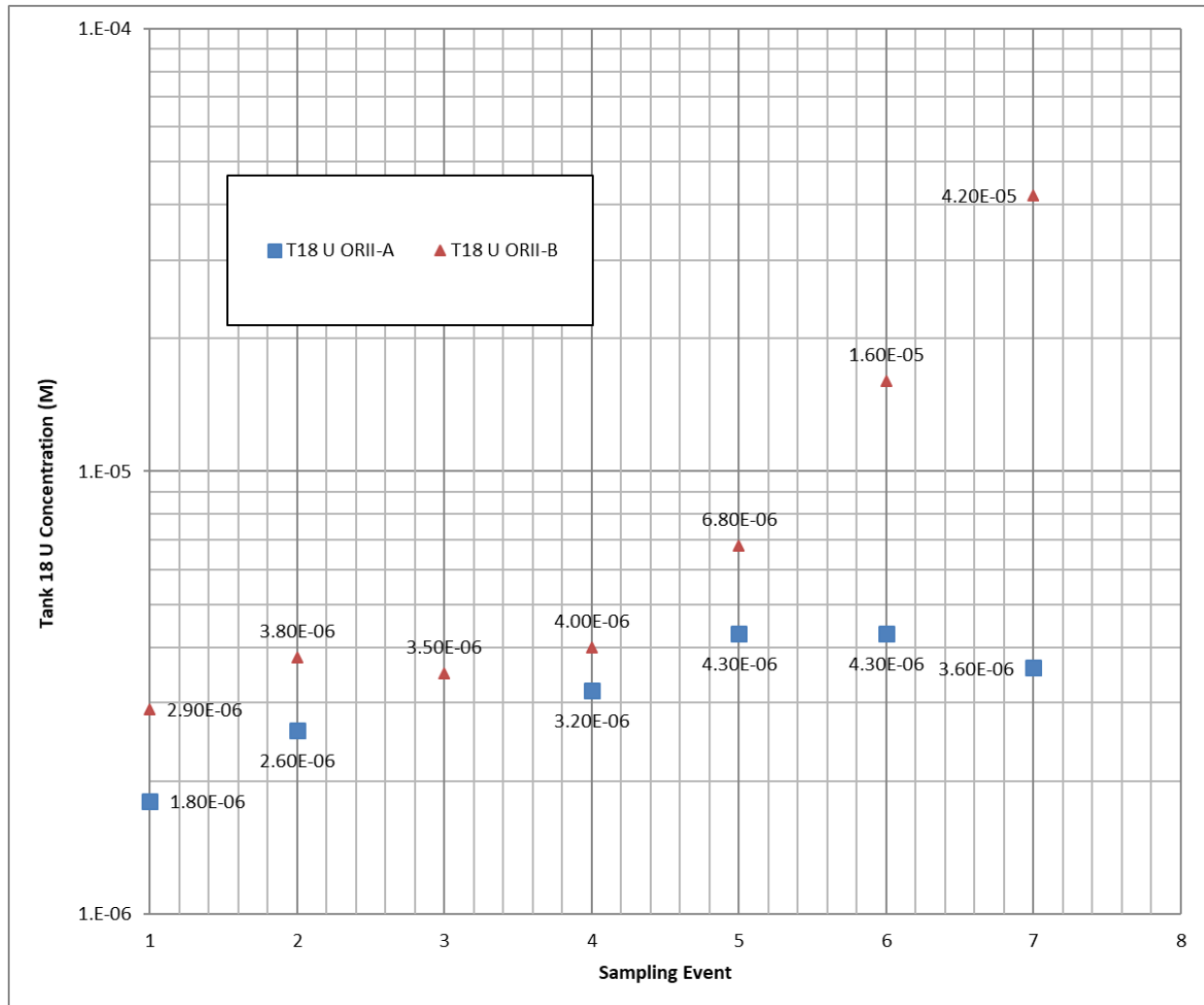
The TF WRM assigned U a solubility of $5\text{E-}9$ M when subjected to RRII pore water. The observed experimental U concentrations under RRII chemical conditions indicate that the U in the Tank 18F and Tank 12H waste residuals under RRII chemical conditions is potentially more soluble than assumed in the TF WRM, albeit with the Tank 12H testing results (ranging from $6\text{E-}8$ M to $9\text{E-}9$ M) occurring much closer to the assigned U solubility.

4.3.4.2 *Uranium Oxidized Region II*

Tank 18F Uranium Oxidized Region II Results

Figure 4.3.4-3 shows a plot of the waste release testing results (Table 4.1-2) over the testing period for U with the sample subjected to ORII chemical conditions (i.e., target pH of 11.1 and target E_h of 560 mV). The U concentrations included in this figure are all measured values (versus minimum detection limits).

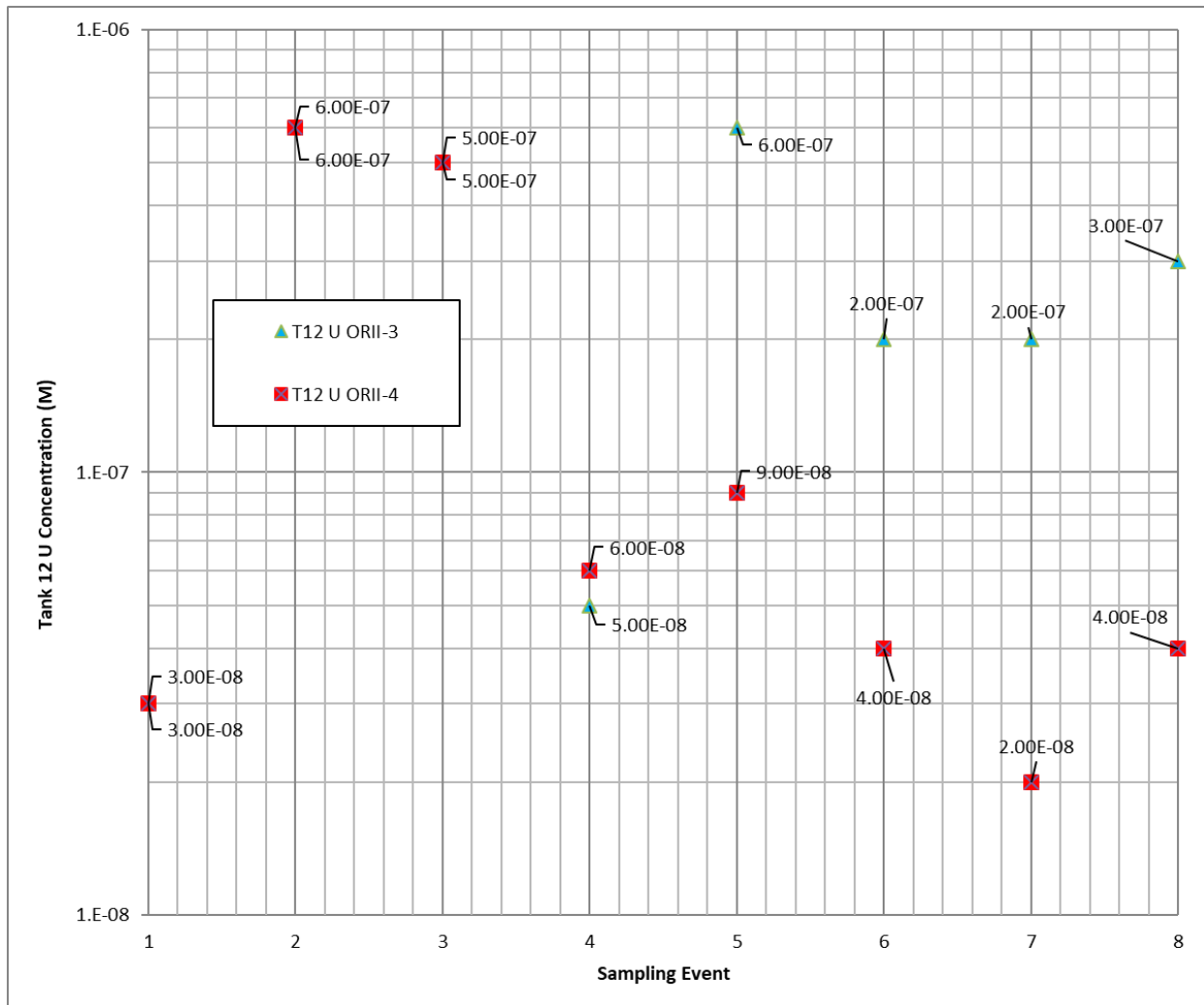
Figure 4.3.4-3: Tank 18F U Concentrations under ORII Chemical Conditions



Tank 12H Uranium Oxidized Region II Results

Figure 4.3.4-4 shows a plot of the waste release testing results (Table 4.2-2) over the testing period for U with the sample subjected to ORII chemical conditions (i.e., target pH of 11.1 and target E_h of 560 mV). The U concentrations included in this figure are all measured values (versus minimum detection limits). The average uranium concentrations observed for both the ORII-3 and ORII-4 sub-samples over the entire 95-day test period was $2\text{E-}07$ M, although the concentrations observed for the two samples were notably different from each other during contact days 62-98 (samples 4-8). [SRNL-STI-2018-00484]

Figure 4.3.4-4: Tank 12H U Concentrations under ORII Chemical Conditions



Review of Uranium Solubility Assumptions versus Oxidized Region II Testing Results

The TF WRM assigned U a solubility of $5\text{E-}05$ M when subjected to ORII pore water. The observed experimental U concentrations indicate that the U solubility in the Tank 18F waste residuals is similar to that assumed in the TF WRM when subjected to ORII pore water. The waste

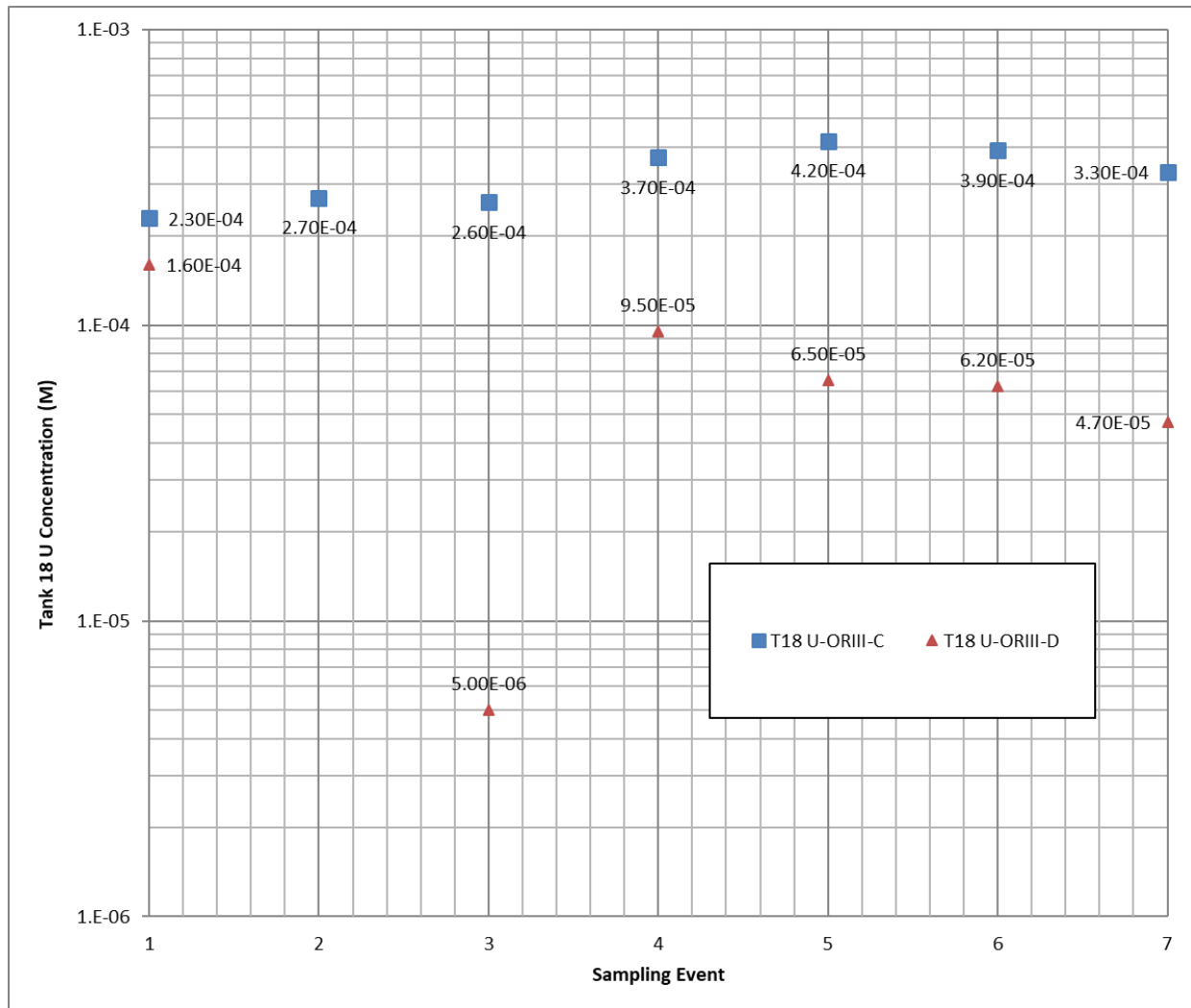
testing results indicate that the Tank 12H waste residuals are less soluble than assumed in the TF WRM when subjected to ORII pore water.

4.3.4.3 *Uranium Oxidized Region III*

Tank 18F Uranium Oxidized Region III Results

Figure 4.3.4-5 shows a plot of the waste release testing results (Table 4.1-2) over the testing period for U with the sample subjected to ORIII chemical conditions (i.e., target pH of 9.2 and target E_h of 680 mV). The U concentrations included in this figure are all measured values (versus minimum detection limits).

Figure 4.3.4-5: Tank 18F U Concentrations under ORIII Chemical Conditions

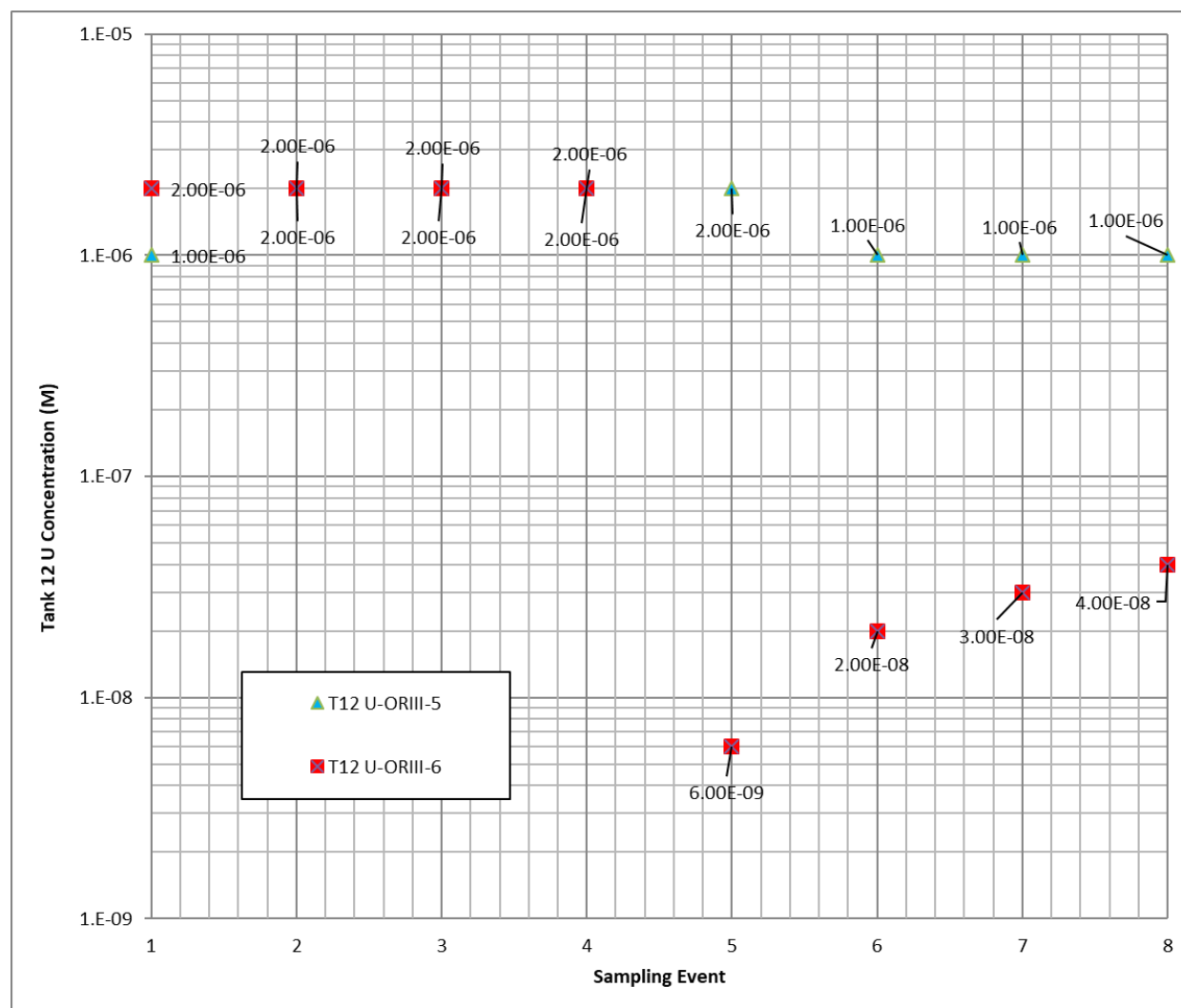


Tank 12H Uranium Oxidized Region III Results

Figure 4.3.4-6 shows a plot of the waste release testing results (Table 4.2-2) over the testing period for U with the sample subjected to ORIII chemical conditions (i.e., target pH of 9.2 and target E_h of 680 mV). The U concentrations included in this figure are all measured values (versus minimum

detection limits). The uranium concentrations for all test samples were generally higher than the concentrations observed for the other radionuclides, with the highest uranium concentrations observed for the ORIII condition. The average uranium concentration observed for the ORIII-5 sub-samples over the entire 95-day test period was $1\text{E-}06\text{ M}$. The average uranium concentration observed for the ORIII-6 sub-samples over the first 62 days of $2\text{E-}06\text{ M}$ was similar to the average observed for ORIII-5 sub-samples. Following extensive washing and exposure to pH 12 solution on contact day 69 the ORIII-6 sub-sample concentrations decreased significantly to approximately $3\text{E-}08\text{ M}$ (over sample events 7-8). [SRNL-STI-2018-00484]

Figure 4.3.4-6: Tank 12H U Concentrations under ORIII Chemical Conditions



Review of Uranium Solubility Assumptions versus Oxidized Region III Testing Results

The TF WRM assigned U a solubility of $4\text{E-}06\text{ M}$ when subjected to ORIII pore water. The observed experimental U concentrations indicate that the U solubility in the Tank 18F and Tank 12H waste residuals is potentially more soluble than the assumed solubility in the TF WRM when subjected to ORIII pore water.

4.3.4.4 *Uranium Analysis Conclusions*

The uranium concentrations for all test samples were generally much higher than the concentrations observed for the other elements.

The highest uranium concentration was observed for the Tank 18F ORIII-C sample where the uranium ranged from $2\text{E-}4$ M to $5\text{E-}4$ M. The Tank 18F ORIII-D samples contained significantly lower uranium concentrations than the C samples in all cases. This is believed to be due to the additional washing of the D sample. As shown in Table 4.1-3, as much as 40% of the total uranium present in the Tank 18F residual sample may have dissolved during sample washing. Uranium leaching from sludge samples is often observed during waste tank washing operations. The Tank 18F ORII-A and Tank 18F ORII-B samples contained significantly lower uranium concentrations than the Tank 18F ORIII-C sample. The A and B samples were quite similar during the first four sampling events and appeared to be stable. After sampling event four, the uranium concentrations in the B samples increased significantly while the concentrations for the A samples were more constant. The differences between the A and B samples are not understood. For the reduced samples (Tank 18F RRII-E and Tank 18F RRII-F), dramatic differences were observed in the uranium concentrations before and after sample washing (between sampling events three and four), with the concentrations after washing being one to two orders of magnitude lower than the concentrations before washing. The sampling event two and three uranium concentrations for the RRII-E sample were higher than the concentrations observed for any other samples, including the ORIII samples. Subsequent analysis of selected wash samples provided some insight into the higher elevated uranium concentrations for these samples. The concentrations observed for the “before washing samples” revealed that the Tank 18F RRII-F-1 sample concentrations were much lower than the Tank 18F RRII-E-1 sample concentrations, presumably due to the presence of the CFS solids. [SRNL-STI-2016-00432]

Despite the fact that the uranium solubilities reported for Tank 18F residual solids were compromised (due to most of the uranium in the samples being lost to the wash solution prior to testing), the stable uranium solubilities observed for Tank 18F residuals under reducing conditions ($2\text{E-}06$ M) exceeded those observed with Tank 12H solids ($7\text{E-}09$ to $6\text{E-}08$ M) by 2 orders of magnitude, even though more reducing conditions were observed with the Tank 18F solids than the Tank 12H solids (~ 200 mV vs ~ 100 mV with Tank 12H solids). Under oxidizing conditions (ORII and ORIII), uranium solubilities observed for Tank 18F residuals ($4\text{E-}06$ to $4\text{E-}04$ M) were higher than the solubilities observed with Tank 12H solids ($2\text{E-}08$ to $2\text{E-}06$ M), even though significant uranium was removed from the Tank 18F leach test samples during preliminary washing. In general, the Tank 12H results indicate that uranium might not be as soluble as indicated by the Tank 18F testing results.

The overall solubility testing results for RRII and ORIII indicate that U might not be quite as insoluble as assumed in the WRM and in the TF PAs, with the Tank 12H solubility testing results being more in line with the WRM and TF PAs assumptions. The ORII waste release testing concentration results for U are similar to (Tank 18F) or less than (Tank 12H) the solubility values assumed in the WRM and in the TF PAs when subjected to ORII pore water. Even if U were slightly more soluble than assumed in the TF WRM, U would not be expected to contribute to the TF peak doses within 10,000 years. To confirm this hypothesis, new HTF and FTF Base Case model runs were carried out with higher solubility values using the HTF and FTF GoldSim models in a deterministic mode (SRR-CWDA-2018-00075). The solubility values used in these new base

case model runs are presented in Table 4.3.4-1, along with the solubility values used in HTF (SRR-CWDA-2010-00128) and FTF (SRS-REG-2007-00002) PA modeling. The Tank Farm “conservative case” and Tank Farm “nominal case” values presented in Table 4.3.4-1 are based upon a considered evaluation of the data presented in Figure 4.3.4-7, not statistical calculations. The Table 4.3.4-1 “conservative case” and “nominal case” values are also based on the assumption that the sampling event four through seven samples are more representative of steady state chemical conditions since these samples were closer to the target chemical conditions. As seen in Figures 4.3.4-8 and 4.3.4-9, even assuming larger U solubility values (i.e., using the U solubility values from Table 4.2-4) has no significant impact on the peak dose (accounting for all sources and all radionuclides) within 10,000 years for either HTF or FTF (using the Tank 12H U solubility values does slightly decrease the peak doses).

Figure 4.3.4-7: U Concentration Data (Tanks 18F and 12H)

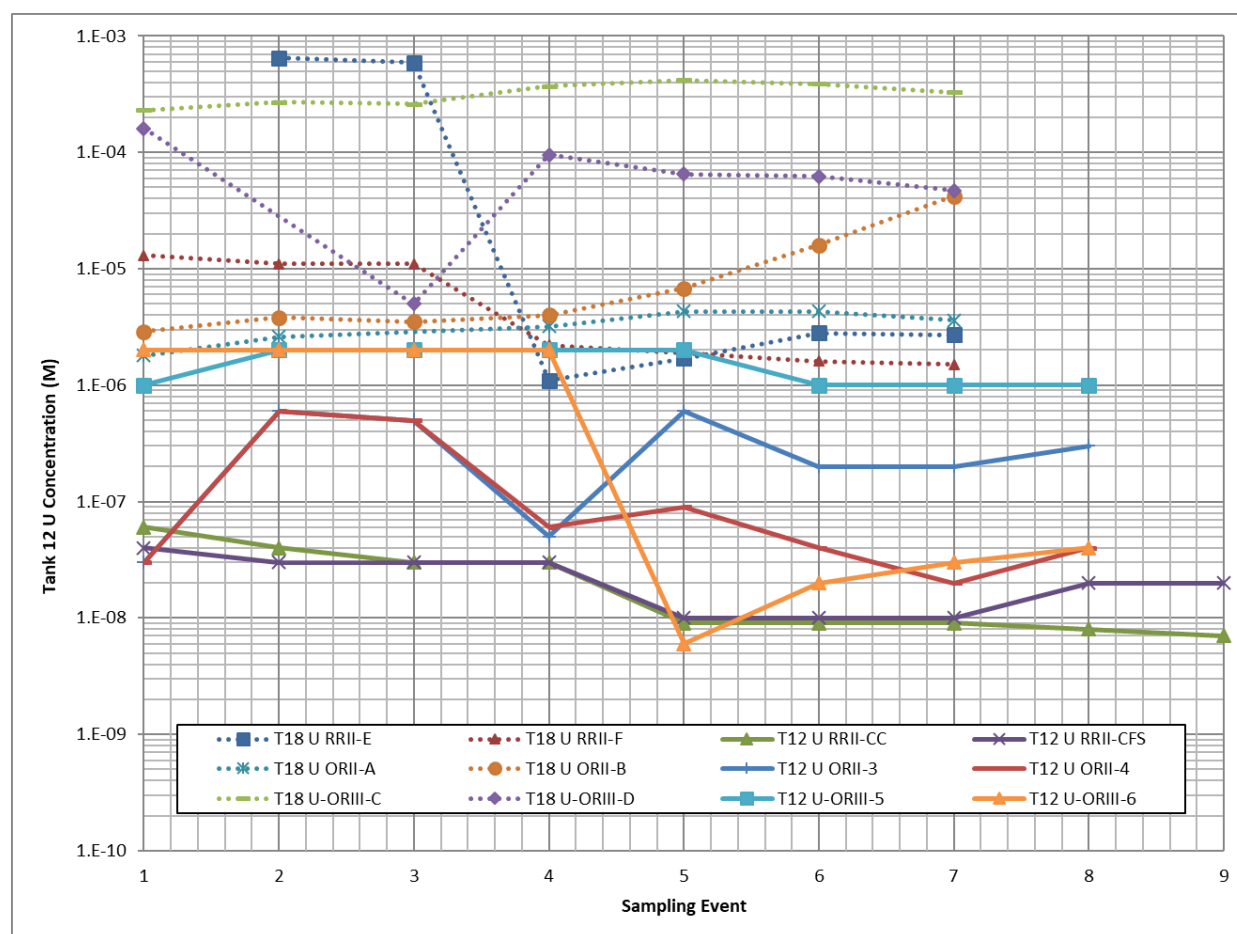


Table 4.3.4-1: Uranium Solubility

	RRII (mol/L)	ORII (mol/L)	ORIII (mol/L)
FTF PA	2E-09	2E-11	3E-05
HTF PA / WRM	5E-09	5E-05	4E-06
Tank 18F Conservative Case	1E-03	5E-05	5E-04
Tank 18F Nominal Case	2E-06	4E-06	1E-04
Tank 12H Conservative Case	6E-08	6E-07	2E-06
Tank 12H Nominal Case	3E-08	2E-07	1E-06
Tank Farm Conservative Case	1E-03	5E-05	5E-04
Tank Farm Nominal Case	2E-06	4E-06	1E-04

Figure 4.3.4-8: FTF Peak MOP Doses for Various U Solubility Values – 20K & 100K
Years

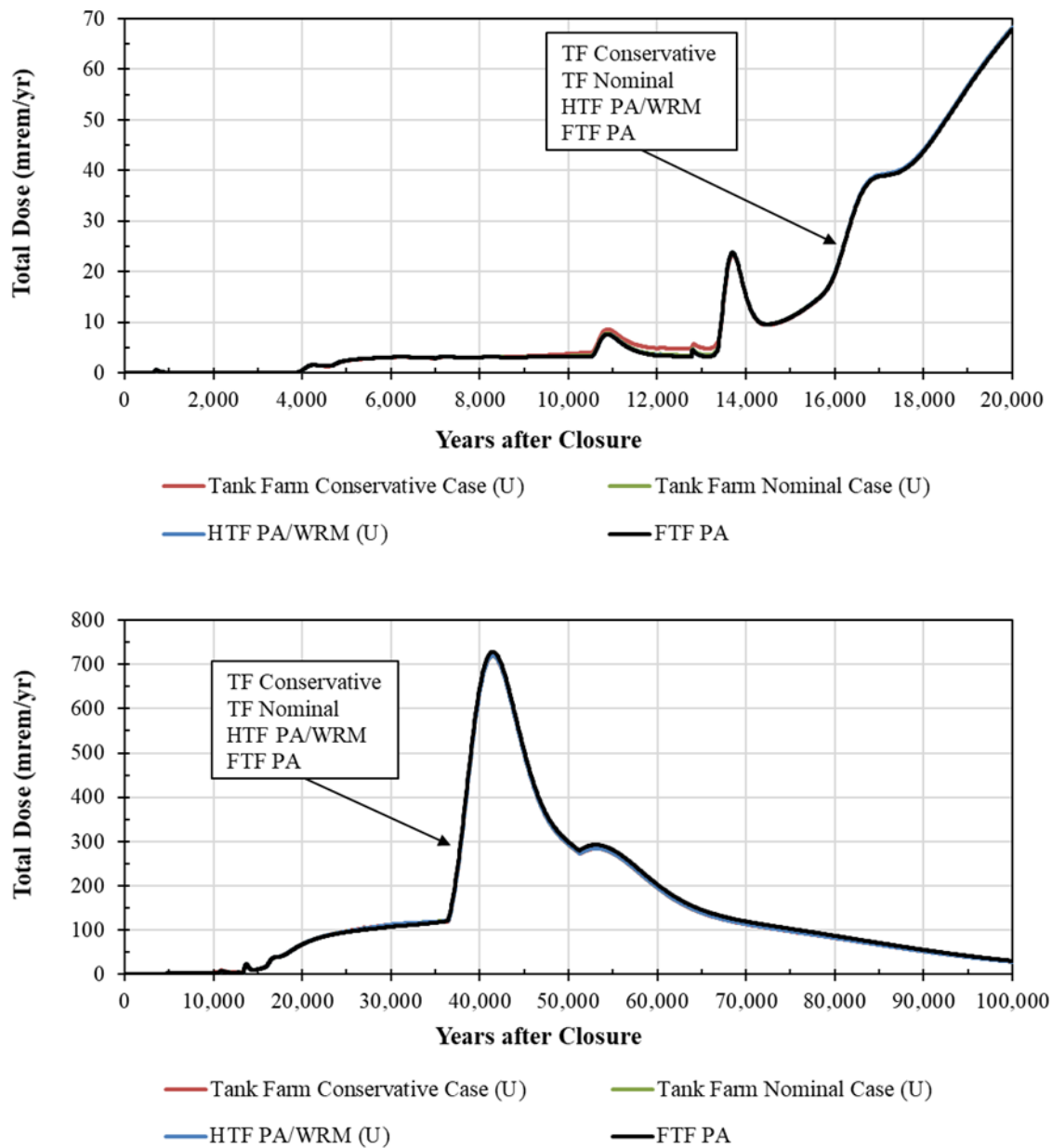
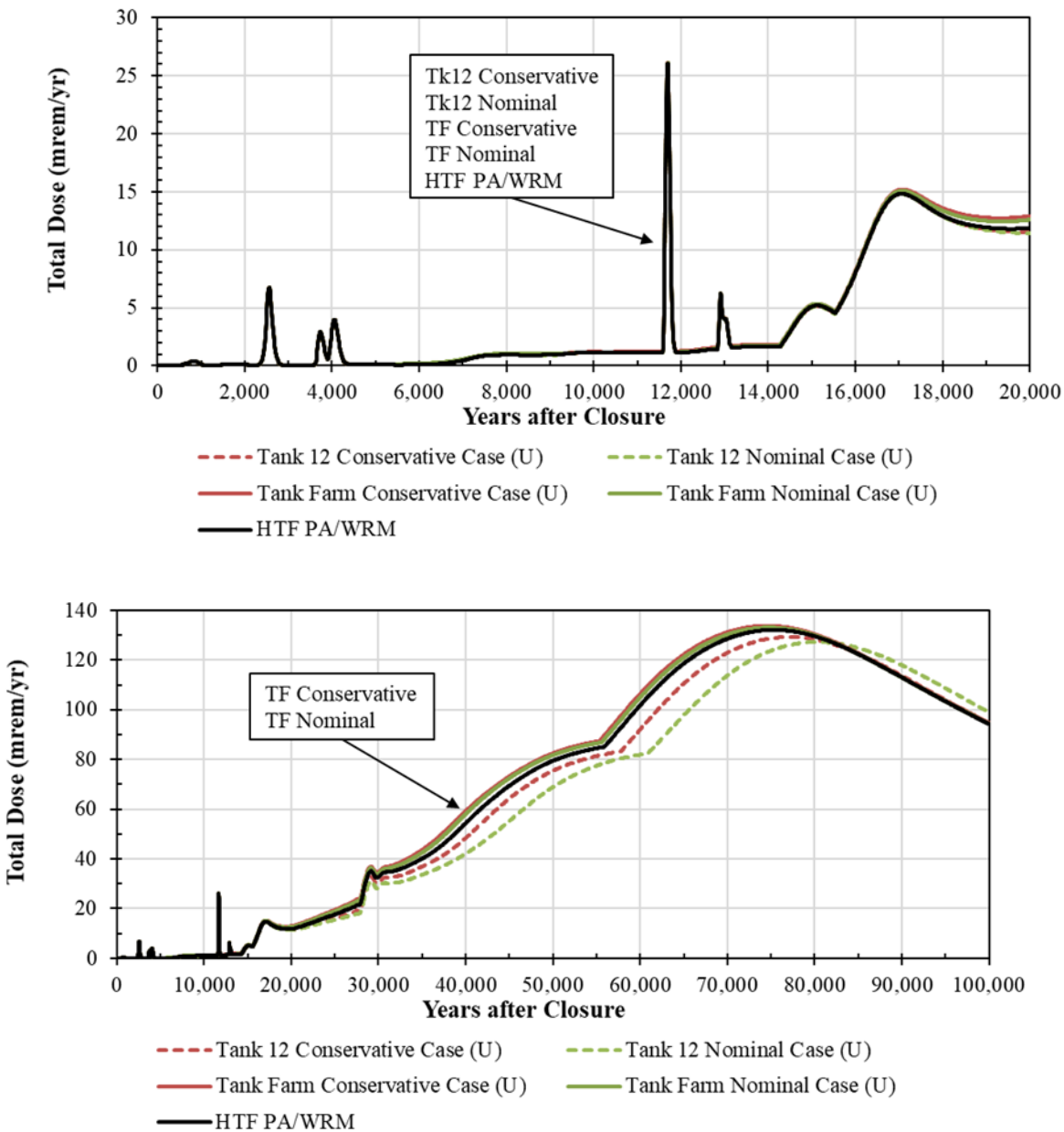


Figure 4.3.4-9: HTF Peak MOP Doses for Various U Solubility Values – 20K & 100K Years



Figures 4.3.4-10 and 4.3.4-11 show a plot of the measured Tank 18F and Tank 12H U concentrations over the entire testing periods (from Tables 4.1-2 and 4.2-2) versus pH and E_h . From these figures it appears U concentrations are more sensitive to pH changes than to E_h changes. Figure 4.3.4-10 presents a noticeable trend in the U concentration as the pH is increased, however in Figure 4.3.4-11 there is no trend in U concentration changes as there is an increase in E_h .

Figure 4.3.4-10: U Concentrations vs. pH

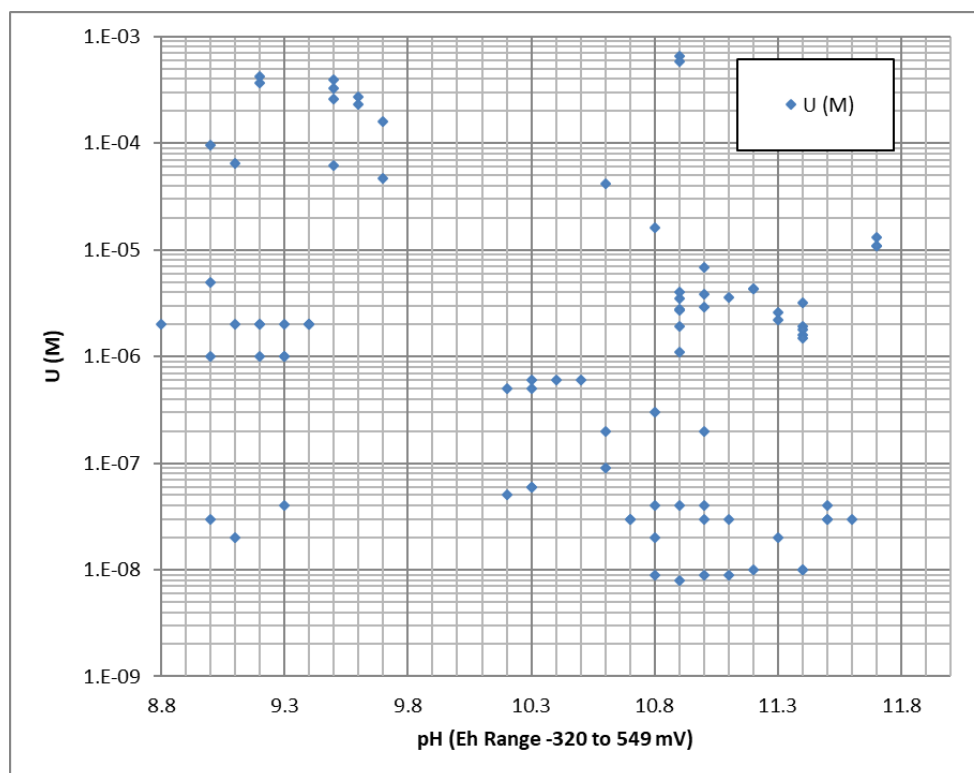
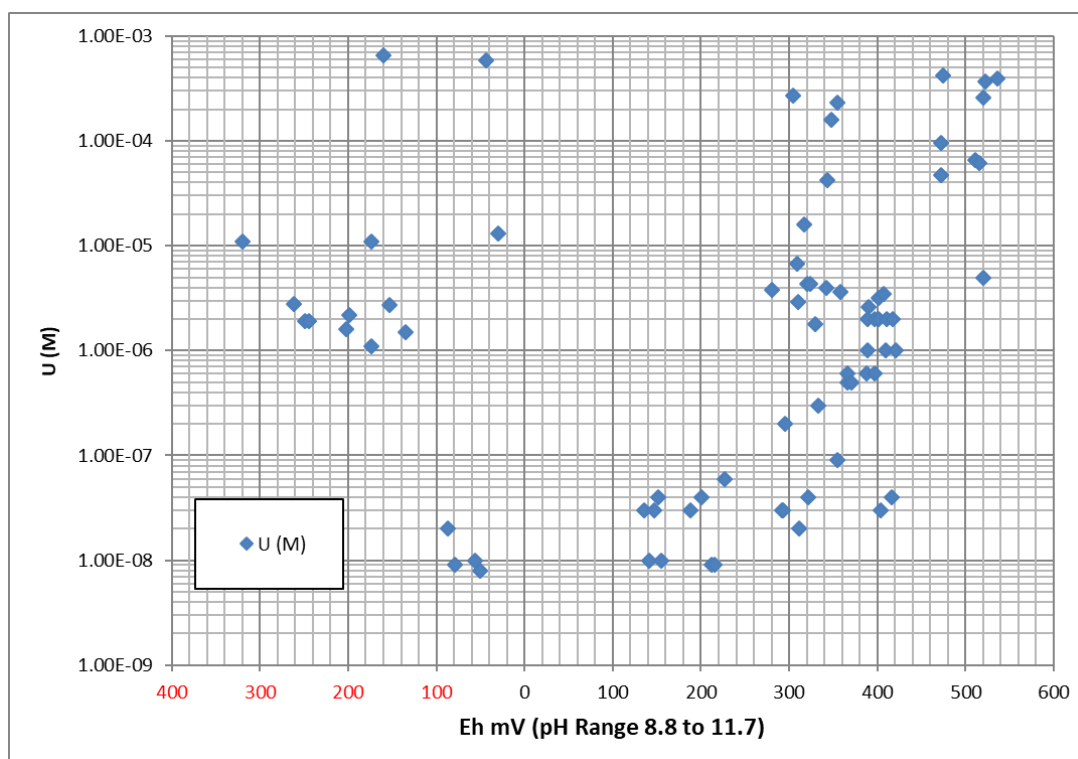


Figure 4.3.4-11: U Concentrations vs. E_h



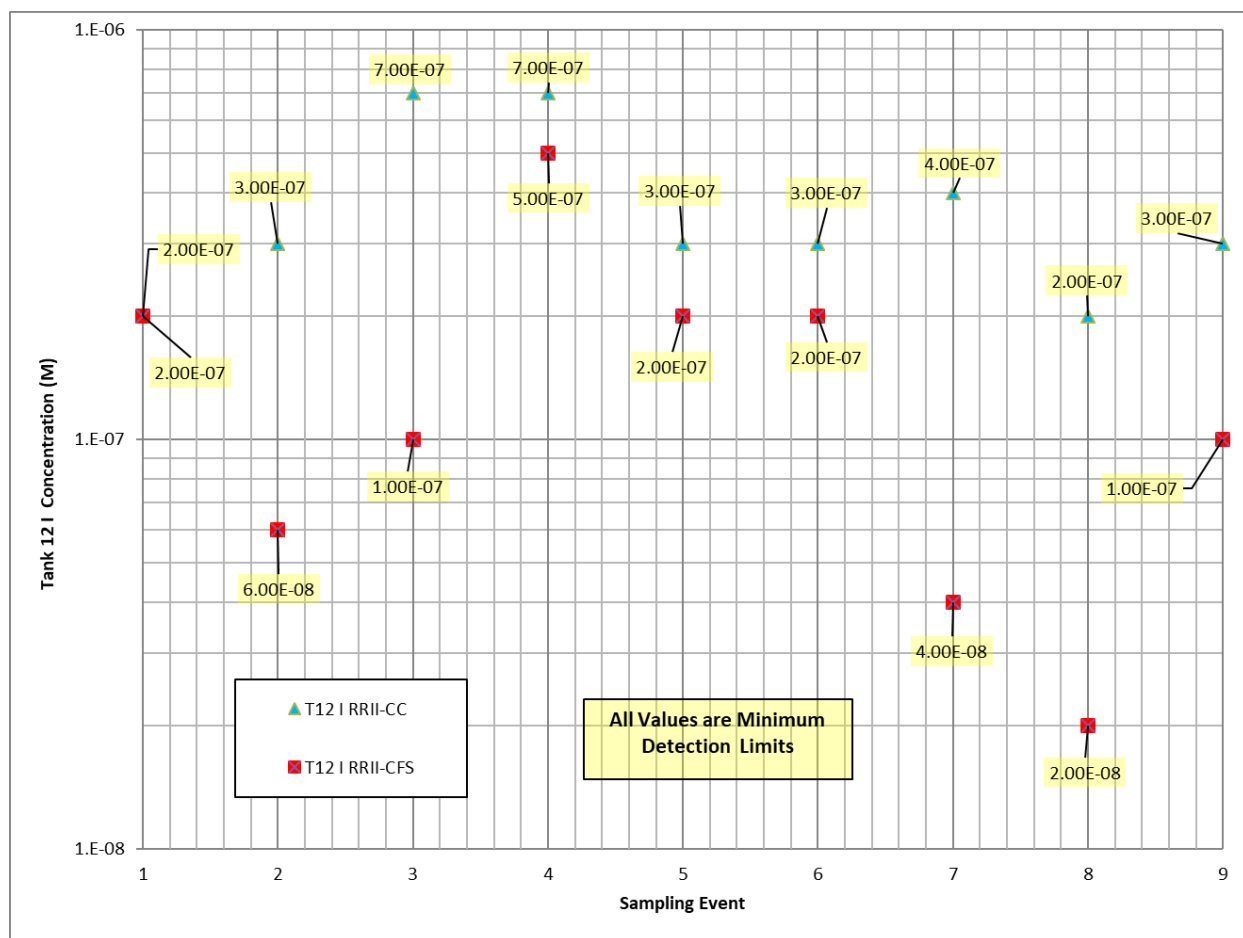
4.3.5 Iodine Analysis

4.3.5.1 Iodine Reduced Region II

Tank 12H Iodine Reduced Region II Results

Figure 4.3.5-1 shows a plot of the Tank 12H waste release testing results (Table 4.2-2) over the testing period for I with the sample subjected to RRII chemical conditions (i.e., target pH of 11.1 and target E_h of -470 mV). All of the I concentrations included in this figure are minimum detection limits (versus measured values), so the actual I concentrations/solubilities are likely lower than those shown in many instances.

Figure 4.3.5-1: Tank 12H I Concentrations under RRII Chemical Conditions



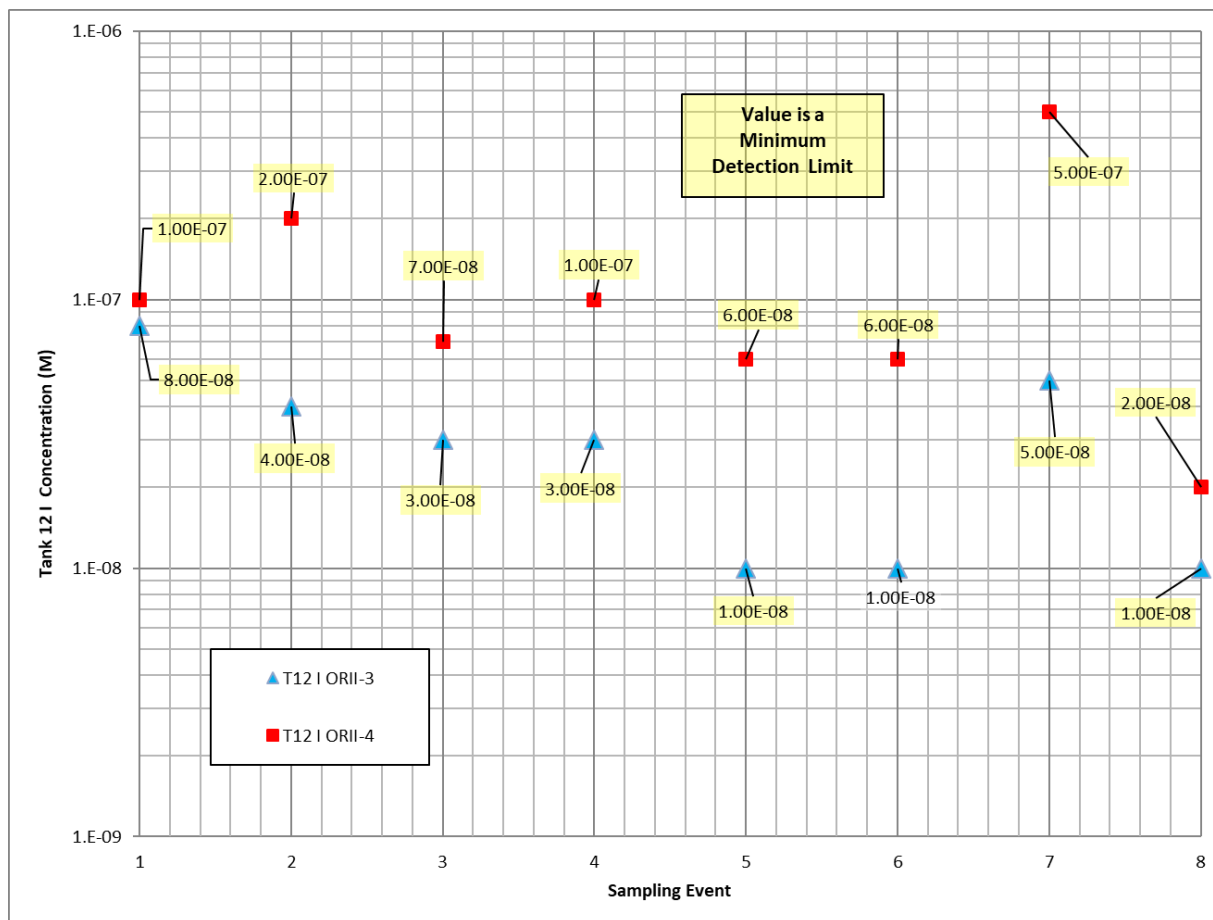
The TF WRM assigned no solubility control for I when subjected to RRII pore water. The observed experimental I concentrations (i.e., non-detects) under RRII chemical conditions indicate that the I in the Tank 12H waste residuals under RRII chemical conditions is less soluble than assumed in the TF WRM.

4.3.5.2 Iodine Oxidized Region II

Tank 12H Iodine Oxidized Region II Results

Figure 4.3.5-2 shows a plot of the waste release testing results (Table 4.2-2) over the testing period for I with the sample subjected to ORII chemical conditions (i.e., target pH of 11.1 and target E_h of 560 mV). The I concentrations included in this figure are all minimum detection limits except for one measured value (1.0E-08 M during the sixth sampling event).

Figure 4.3.5-2: Tank 12H I Concentrations under ORII Chemical Conditions



The TF WRM assigned no solubility control for I when subjected to ORII pore water. The observed experimental I concentrations (i.e., non-detects) under ORII chemical conditions indicate that the I in the Tank 12H waste residuals under ORII chemical conditions is less soluble than assumed in the TF WRM.

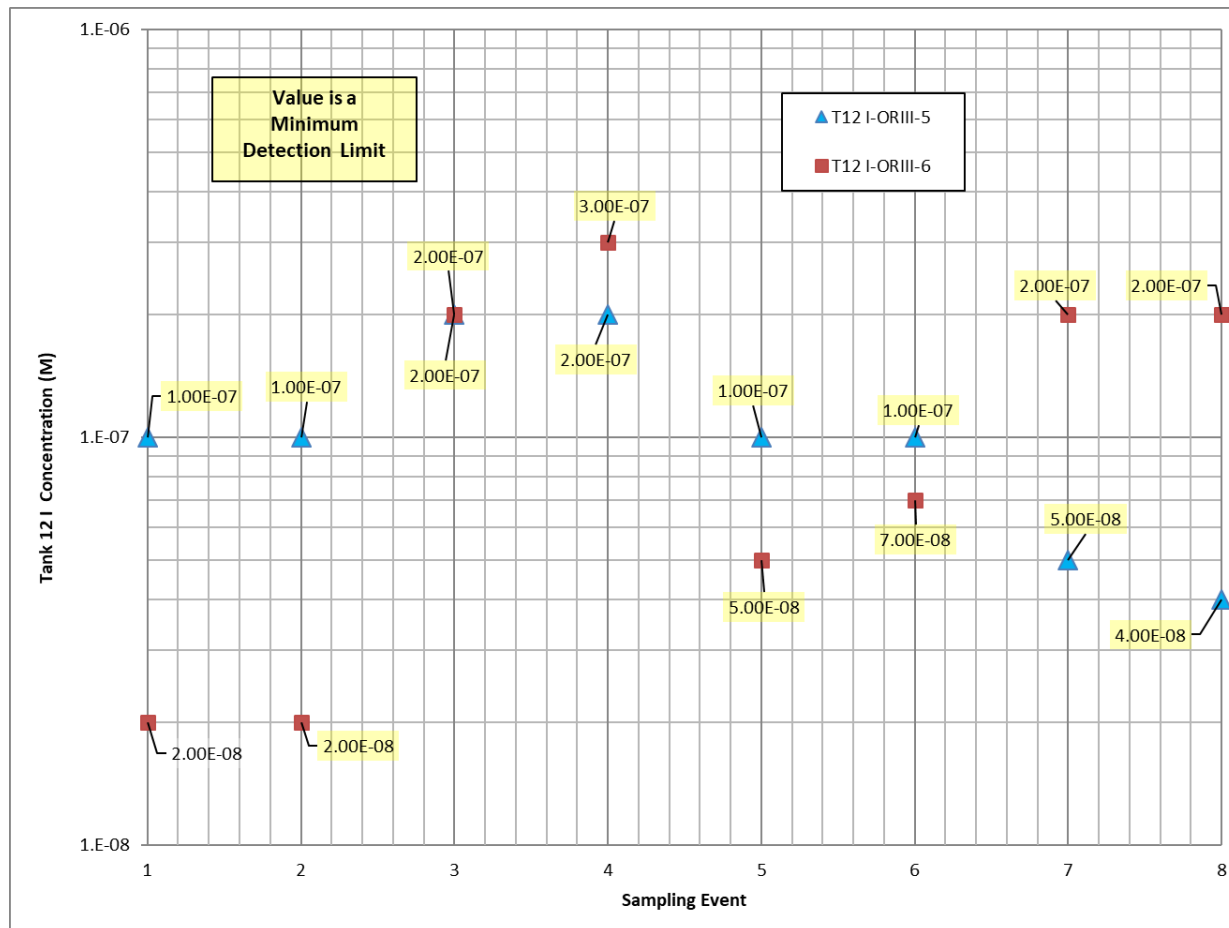
4.3.5.3 Iodine Oxidized Region III

Tank 12H Iodine Oxidized Region III Results

Figure 4.3.5-3 shows a plot of the waste release testing results (Table 4.2-2) over the testing period for I with the sample subjected to ORIII chemical conditions (i.e., target pH of 9.2 and target E_h

of 680 mV). The I concentrations included in this figure are all minimum detection limits except for one measured value ($2.0\text{E-}08$ M during the first sampling event).

Figure 4.3.5-3: Tank 12H I Concentrations under ORIII Chemical Conditions



The TF WRM assigned no solubility control for I when subjected to ORIII pore water. The observed experimental I concentrations (i.e., non-detects) under ORIII chemical conditions indicate that the I in the Tank 12H waste residuals under ORIII chemical conditions is less soluble than assumed in the TF WRM.

4.3.5.4 Iodine Analysis Conclusions

I-129 solubilities with Tank 12H residual solids in grout porewater simulants were generally below detectable concentration limits ($<6\text{E-}07$ M). No measurable iodine was observed for any of the reducing samples (RRII-CC and RRII-CFS), and iodine was detected only twice in the oxidizing samples (one for sample ORII-3 and one for sample ORIII-6). As discussed in the Section 2.2.3 (Iodine Solubility Variability), iodine can form solubility-limiting solid phases with several metals that are present in residual tank waste. While the I-129 results for nearly all samples were below detectable concentration limits, two oxidizing samples were observed to contain I-129 above the limits (concentrations ranging from $1\text{E-}08$ M to $2\text{E-}08$ M). These concentrations are below the predicted solubility for Hg_2I_2 .

Overall, the solubility testing results for RRII, ORII, and ORIII indicate I is much less soluble than assumed in the TF WRM. The solubility values used in HTF (SRR-CWDA-2010-00128) and FTF (SRS-REG-2007-00002) PA modeling are presented in Table 4.3.5-1, along with “conservative case” and “nominal case” values based upon a considered evaluation of the data presented in Figure 4.3.5-4. New HTF Base Case model runs were carried out with the “conservative case” and “nominal case” solubility values derived from the waste release testing using the HTF GoldSim models in a deterministic mode (SRR-CWDA-2018-00075). The AgI and Hg₂I₂ iodine solubility cases were based on the findings from SRNL report SRNL-STI-2015-00339, but did not mechanistically assume that iodine solubility controls were present in Reduced Region II and/or Submerged Region C (SRR-CWDA-2016-00078). As seen in Figure 4.3.5-5, assuming the Tank 12H derived I solubility values (i.e., using the I solubility values from Table 4.3.5-1) decreases the peak dose (accounting for all sources and all radionuclides) within 10,000 years for HTF.

The WRM assumed no solubility control for iodine, which is countered by the fact that the sampling data (detected concentration values and the detection limits that were not exceeded) show that the iodine present in the waste does appear to be solubility controlled. The waste release testing results suggest that I in the Tank 12H residual waste sample is relatively insoluble, even under both reduced and oxidized conditions. The waste release testing results would not negatively affect any I related TF WRM based conclusions, since dose associated with I would only be further mitigated by assuming the I was less soluble.

Figure 4.3.5-4: I Concentration Data (Tank 12H)

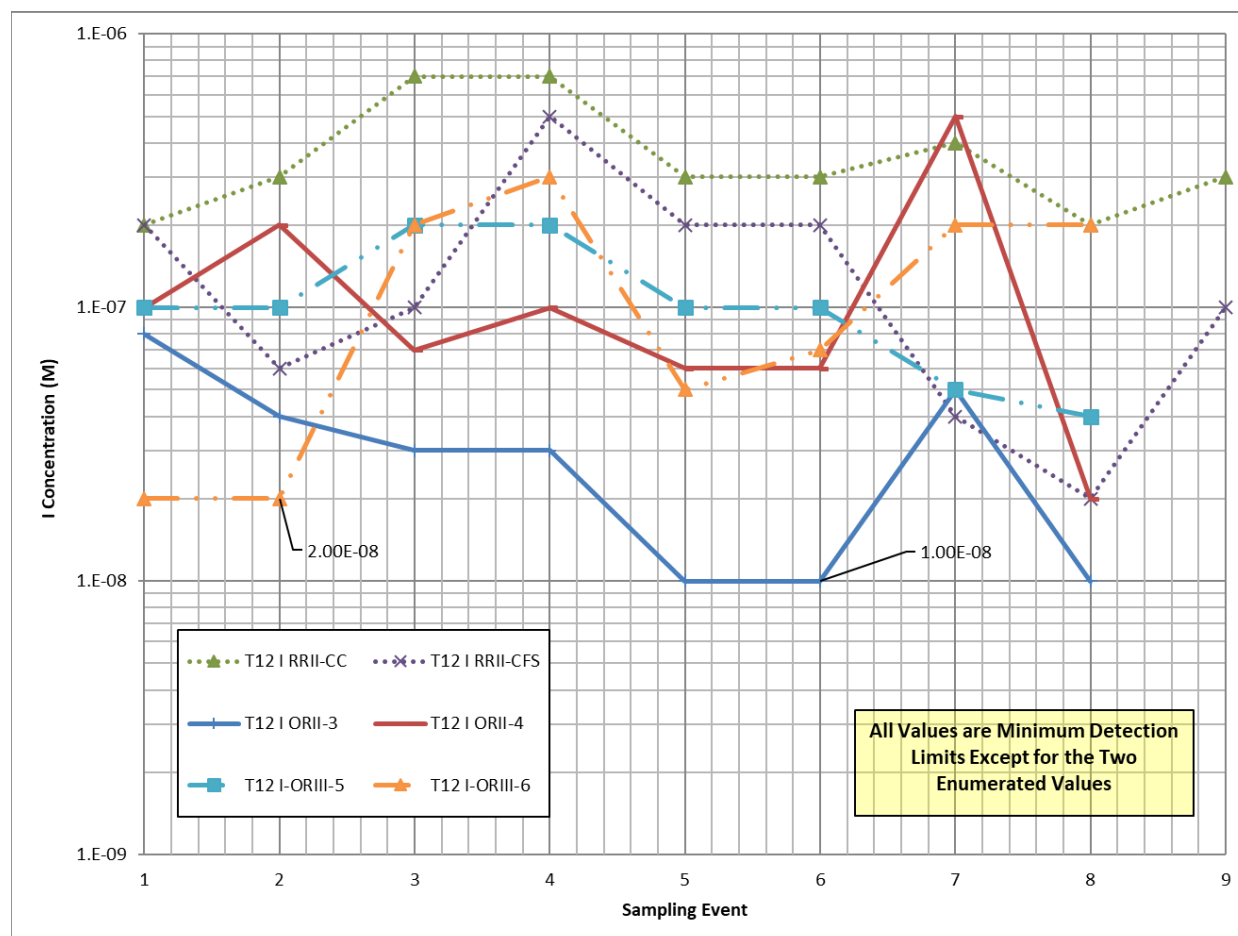
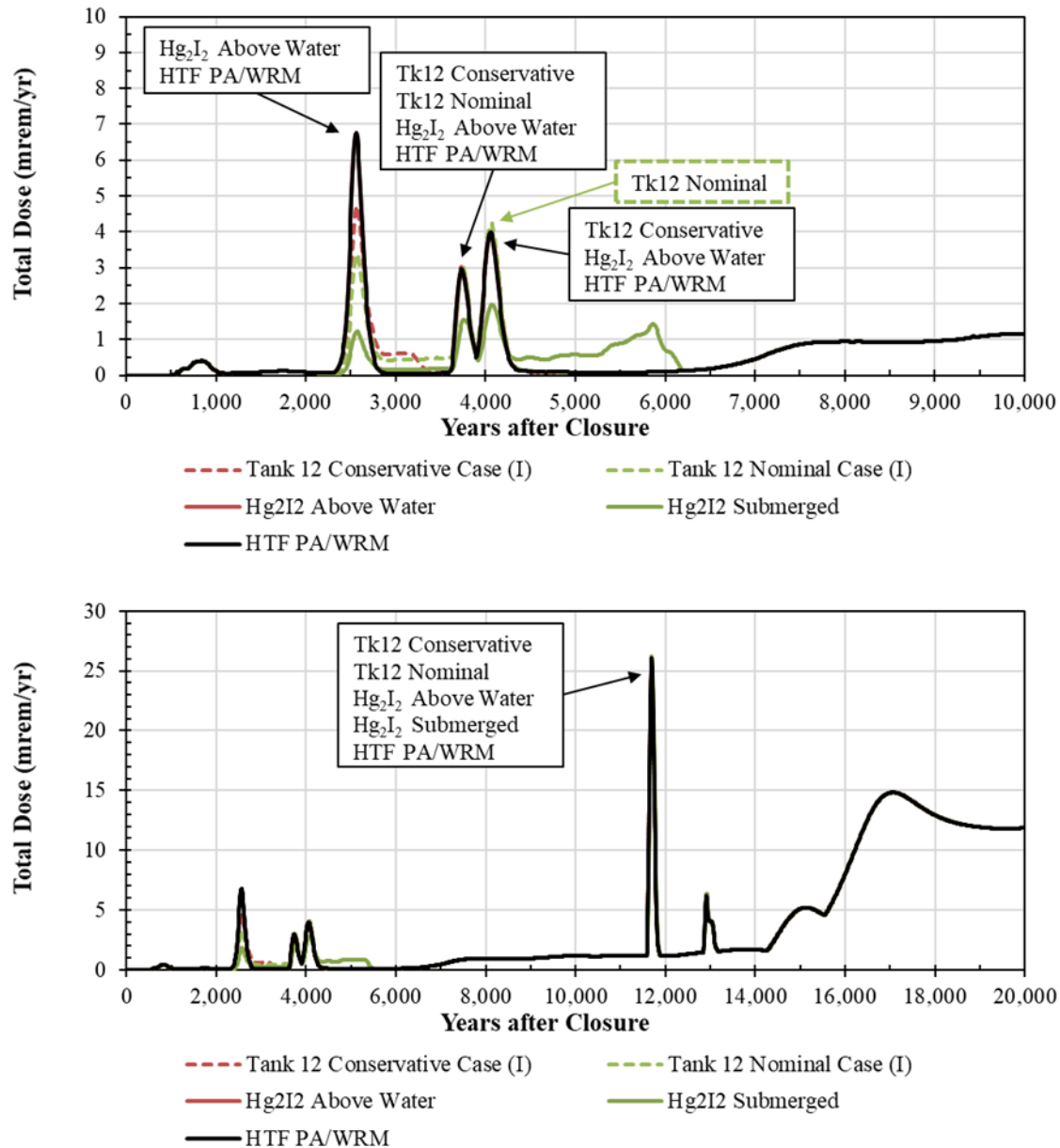


Table 4.3.5-1: Iodine Solubility

	RRII (mol/L)	ORII (mol/L)	ORIII (mol/L)
FTF PA /HTF PA /WRM	NSC	NSC	NSC
AgI Above Water	2.7E-07	2.7E-07	3.8E-08
AgI Submerged	9.8E-09	9.8E-09	3.8E-08
Hg ₂ I ₂ Above Water	2.0E-05	2.0E-05	1.2E-04
Hg ₂ I ₂ Submerged	1.8E-07	1.8E-07	1.8E-07
Tank 12H Conservative Case	7.0E-07	5.0E-07	2.0E-07
Tank 12H Nominal Case	5.0E-07	5.0E-08	5.0E-08

NSC = No solubility control

Figure 4.3.5-5: HTF Peak MOP Doses for Various I Solubility Values – 10K & 20K Years



5.0 CONCLUSION

Approximately six years have been dedicated to waste release testing. The objectives of this endeavor were to provide additional information regarding the residual waste solubility assumptions used in the FTF and HTF PA WRMs. The waste release testing was performed in two parts, the first part being the development of the test plan and methods and the second part being conducting the testing with residual waste surrogates and actual residual waste samples (material from Tank 18F and Tank 12H).

Using residual waste samples from Tank 18F and Tank 12H, the solubilities of Pu, Np, U, Tc, and I (Tank 12H only) were tested under simulated waste tank chemistry conditions. Data was collected via measured concentrations (or solubilities) over a multi-week testing period under different chemical conditions (pH and E_h were varied). The chemical conditions reflect a range of states such that the test results can be used to better understand the impact of transitory waste tank chemical conditions on solubility. The measured solubilities for the tested elements are consistent for the residuals from both Tanks 18F and 12H, with the Tank 12H solubilities tending to be less soluble. The experimental results indicate there may be some variance between the actual waste solubilities and the WRM assigned solubilities. For example, Np and I were in all cases more insoluble than assigned in the TF WRM. The results indicate that I-129 in the Tank 12H residual waste sample is relatively insoluble, under both reduced and oxidized conditions, compared to the WRM which conservatively assumed no solubility control for iodine. The other elements – Pu, Tc and U – appeared in most instances to be potentially more soluble than was assumed in the WRM. For example, Pu was relatively insoluble when oxidized, but was still more soluble than calculated by the WRM. As demonstrated in Section 4, even if the experimental results were conservatively accepted into the PA WRM, the newly assigned solubilities would have a negligible impact on peak doses in 1,000 or 10,000 years. Because replacing the WRM values associated with Pu, Tc, U, Np, and I does not significantly impact FTF and HTF PA conclusions, there is no immediate need to update the current model to incorporate the waste release testing data. If the Tank 12 derived iodine solubility values were used in the PA model the HTF peak dose within 10,000 years would decrease significantly. The new waste release data can be integrated into the next revision to the FTF and HTF PAs.

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