Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

Laboratory Optimization Tests of Technetium Decontamination of Hanford Waste Treatment Plant Direct Feed Low Activity Waste Melter Off-Gas Condensate Simulant

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December 2015
SRNL-STI-2015-00677, Revision 0

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Printed in the United States of America

Prepared for
U.S. Department of Energy

Keywords: *decontamination, technetium, stannous chloride, DFLAW*

Retention: *Permanent*

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EXECUTIVE SUMMARY

The Hanford Waste Treatment and Immobilization Plant (WTP) Low Activity Waste (LAW) vitrification facility will generate an aqueous condensate recycle stream (LAW Off-Gas Condensate) from the off-gas system. The baseline plan for disposition of this stream is to send it to the WTP Pretreatment Facility, where it will be blended with LAW, concentrated by evaporation and recycled to the LAW vitrification facility. Alternate disposition of this stream would eliminate recycling of problematic components, and would enable less integrated operation of the LAW melter and the Pretreatment Facilities. Eliminating this stream from recycling within WTP would also decrease the LAW vitrification mission duration and quantity of glass waste.

This LAW Off-Gas Condensate stream will contain components that are volatile at melter temperatures and are problematic for the glass waste form, such as halides and sulfate. Because this stream will recycle within WTP, these components accumulate in the Condensate stream, exacerbating their impact on the number of LAW glass containers that must be produced. Diverting the stream reduces the halides and sulfate in the recycled Condensate and is a key outcome of this work. Additionally, under possible scenarios where the LAW vitrification facility commences operation prior to the WTP Pretreatment facility (a.k.a. Direct Feed LAW), identifying a disposition path becomes vitally important. This task examines the potential treatment of this stream to remove radionuclides and subsequently disposition the decontaminated stream elsewhere, such as the Effluent Treatment Facility (ETF), for example. The treatment process envisioned focuses on using mature radionuclide removal technologies that are also compatible with long-term tank storage and immobilization methods and builds on experience gained from the Actinide Removal Process (ARP) that has been operating for years at the Savannah River Site (SRS). For this new application, testing is needed to demonstrate acceptable precipitation agents and measure decontamination factors for Tc removal from this unique waste stream.

The origin of this LAW Off-Gas Condensate stream will be the liquids from the Submerged Bed Scrubber (SBS) and the Wet Electrostatic Precipitator (WESP) from the LAW melter off-gas system. The stream is expected to be a dilute salt solution with near neutral pH, and will likely contain some insoluble solids from melter carryover. The soluble components are expected to be mostly sodium and ammonium salts of nitrate, chloride, and fluoride. This stream has not been generated yet, but a simulant has been produced based on models, calculations, and comparison with pilot-scale tests. This work utilized the Direct Feed LAW (DFLAW) simulant, which is based on modeling of only the first several years of operation of the LAW melters prior to start-up of the entire WTP process. The waste feed composition to the LAW melters during DFLAW will differ from the baseline because the waste originates in fewer tanks, and the internal streams generated during processing within the WTP Pretreatment Facility such as sludge washing and leaching will not be included. Since the waste feed is different, the off-gas condensate will be different.

One of the radionuclides that is volatile and expected to be in greatest abundance in this DFLAW Off-Gas Condensate stream is Technetium-99 (^{99}Tc). Technetium will not be removed from the aqueous waste in the Hanford WTP, and will primarily end up immobilized in the LAW glass by repeated recycle of the off-gas condensate into the LAW melter. Other radionuclides that are expected to be in low but measurable concentration in the LAW Off-Gas Condensate are ^{129}I, ^{90}Sr, ^{137}Cs, ^{241}Pu, and ^{241}Am. These are present due to their partial volatility and some entrainment in the off-gas system.

Previous work has shown $SnCl_2$ to be an effective precipitation agent for the ^{99}Tc through reductive precipitation. This work focused on examining the pH range under which the $SnCl_2$ reductive precipitation is effective, examining the use of an alternate reductant, Fe(II), and examining the stability of the precipitate under alkaline conditions. The Condensate stream is expected to undergo concentration in the Effluent Management Facility (EMF) evaporator which will require pH adjustment prior to evaporation to reduce corrosion in the evaporator. Previous testing has shown the $SnCl_2$ precipitation to be effective at pH ~7; however, it is important to know the pH range that can be utilized for the Tc removal step to determine the sensitivity to pH control as well as to know if multiple pH adjustments will be needed. Therefore, testing was performed at pH 7, 10, and 12. The stability of the Sn precipitated slurry has previously been examined at neutral pH, and the Tc remained insoluble, but due to the EMF evaporator operating at higher pH, the stability of the Sn precipitated slurry was examined under alkaline conditions. Finally, prior work has shown that Fe(II) can also precipitate Tc, but not as well as Sn; however, most of the Sn is consumed by precipitation of Cr. Therefore, testing was performed to determine if Fe(II) can be used instead of or together with Sn to minimize Sn use.

Testing results confirmed that 1.5 equivalents of electrons from Sn(II) relative to those needed to reduce Cr(VI) and Tc(VII)[a] was effective at removing the ^{99}Tc to below the method detection limit (DF >497) in the neutral DFLAW simulant. However, the Sn(II) was found to be less effective under alkaline conditions, reaching DF values of only 6.1 and 2.6 in pH 10 and 12 simulants, respectively. Tests with Fe(II) showed that no Tc is removed from the neutral simulant; however, a small amount can be removed by adjusting the pH to 10 or 12. The highest Tc DF obtained was 14 with 4 equivalents of electrons from Fe(II) relative to those needed to reduce Cr(VI) and Tc(VII). The Fe(II) was more effective at precipitation of the Cr, however, removing Cr to below detection limits in several cases in the neutral and pH 10 simulants. The effectiveness of Fe(II) for Cr removal decreased at pH 12.

Stability testing in the DFLAW simulant after pH adjustment to 10 or 12 demonstrated that the precipitated solids are quickly reoxidized and dissolve after the pH is adjusted. The reoxidation rate increased as the pH increased from 10 to 12.

Further testing is needed to identify the larger scale conditions for the decontamination process. Once these conditions are established, follow-on tasks likely include evaluation and testing of applicable solid-liquid separation technologies, slurry rheology measurements, composition variability testing and evaluations, corrosion and erosion testing, slurry storage and immobilization investigations, and decontaminated DFLAW Off-Gas Condensate evaporation and solidification.

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[a] The 1.5 eq of Sn(II) is based on two electrons from Sn(II) to three electrons needed to reduce Cr(VI) and Tc(VII) to Cr(III) and Tc(IV), respectively. On a molar basis, this is equivalent to a ratio of 2.25:1.

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LIST OF ABBREVIATIONS

ARP	Actinide Removal Process
Avg	Average
DF	Decontamination Factor
DFLAW	Direct Feed Low-Activity Waste
DOE	Department of Energy
dpm	Disintegrations per minute
EMF	Effluent Management Facility
eq	Equivalents
ETF	Effluent Treatment Facility
g	Grams
GFC	Glass Forming Chemical
h	Hour
HLW	High-Level Waste
HTWOS	Hanford Tank Waste Operations Simulator
ICP-ES	Inductively Coupled Plasma – Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma – Mass Spectrometry
IDF	Integrated Disposal Facility
L	Liter
LAW	Low-Activity Waste
LERF	Liquid Effluent Retention Facility
mg	Milligram
mL	Milliliter
MST	Monosodium titanate
PA	Performance Assessment
PuTTA	Plutonium Thenoyltrifluoroacetone Extraction
SBS	Submerged Bed Scrubber
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
µg	Micrograms
WESP	Wet Electrostatic Precipitator
WG	Weapons Grade
WRPS	Washington River Protection Solutions
WTP	Waste Treatment Plant

1.0 Introduction

The Hanford LAW Off-Gas Condensate stream will be generated in the WTP by condensation and scrubbing of the LAW melter off-gas system by a SBS and WESP, as shown in Figure 1-1. This stream, which will contain substantial amounts of chloride, fluoride, ammonia, and sulfate ions, will get recycled within the WTP process by return to the Pretreatment Facility where it will be combined with LAW and evaporated. Although the SBS and WESP streams can be separately routed to different points in the WTP, they are combined for purposes of this study since they ultimately re-combine at some point within the process. The halide and sulfate components are only marginally soluble in glass, and often dictate the waste loading and thereby impact LAW waste glass volume. Additionally, long-lived ^{99}Tc and ^{129}I are volatile radionuclides that accumulate in the LAW system, and are challenging to incorporate in glass under the Hanford LAW melter operating conditions. Because ^{99}Tc has a very long half-life and is highly mobile, it is the largest dose contributor to the Performance Assessment (PA) of the Integrated Disposal Facility (IDF),[1] although the glass waste form has been shown to meet the leaching requirements of the IDF waste acceptance criteria. Diverting this LAW Off-Gas Condensate stream to an alternate disposal path would have substantial beneficial impacts on the cost, life cycle, and operational complexity of WTP.

An alternate operating scenario is also under evaluation where tank supernate is decontaminated in another facility, called the LAW Pretreatment System, and sent directly to the LAW melter (a.k.a. Direct Feed LAW or DFLAW) without start-up of the Pretreatment Facility. This scenario would require alternate disposal of the Off-Gas Condensate stream because the Pretreatment Facility would not be available. Further, the DFLAW feed stream to the melter is likely to have a different chemical and radionuclide composition from the full WTP baseline operations feed stream, and thus will have a different Off-Gas Condensate composition.

This development task will evaluate the decontamination of this stream using sorbents and precipitation agents so that it can be diverted elsewhere (Figure 1-2). Although Figure 1-1 shows the baseline scenario where the stream is routed to the Pretreatment facility, the diversion point is the same for the DFLAW scenario. The process would be comparable to the ARP[b] at SRS that has been operating successfully for years, although that process treats tank waste, but demonstrates successful deployment of radionuclide sorption and filtration processes. The concept for this new process adapts the use of technically mature absorbents where feasible, such as Monosodium Titanate (MST), commercially available zeolites previously used in radioactive DOE applications, and common industrial chemicals. This task specifically examined removal of ^{99}Tc using reducing agents, but the other sorbents may be needed for the other radionuclides. Use of these inorganic materials is expected to simplify down-stream issues, such as storage and immobilization. Implementation would make available a short-term disposition path if the LAW facility commences operation prior to operation of the Pretreatment Facility and in the long term to divert the stream from recycling. Although Figure 1-2 indicates sending the decontaminated liquid to the ETF, other paths may also be identified. The ETF is used here as an example of a potential path that is used for an estimation of decontamination requirements.

The overall plan for technology development of the concentration option, and other options for disposal has been documented.[2] Preliminary testing of this process using the baseline simulant has also been documented.[3,4] Other alternative disposal paths could be considered as well, including tank farm storage options.

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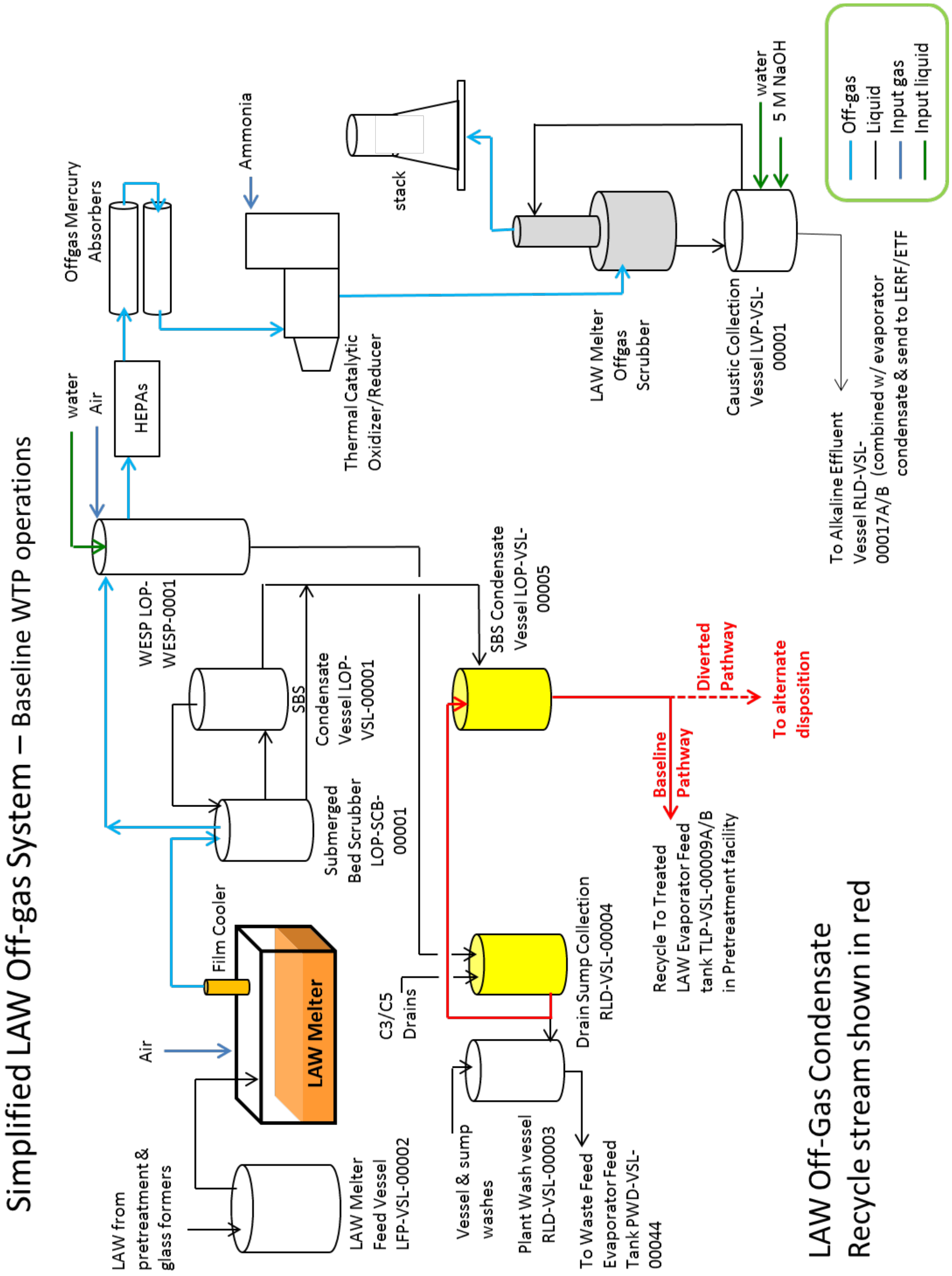
[b] The Actinide Removal Process (ARP) at SRS decontaminates ^{90}Sr and actinides from aqueous tank waste before it is further treated for ^{137}Cs removal by solvent extraction. In ARP, a small amount of Monosodium Titanate (MST) is added to a batch of decanted tank waste supernate and mixed for 6-12 hours, then filtered with a cross-flow stainless steel filter. The spent MST that is loaded with ^{90}Sr and actinides is washed with water, and sent for vitrification as HLW glass in the DWPF.



adapted from 24590-WTP-RPT-PT-02-005, Rev. 6; yellow indicates SBS/WESP LAW Off-Gas Condensate collection tanks, red lines indicate the collected off-gas condensate pathway

Figure 1-1. Simplified LAW Off-gas System

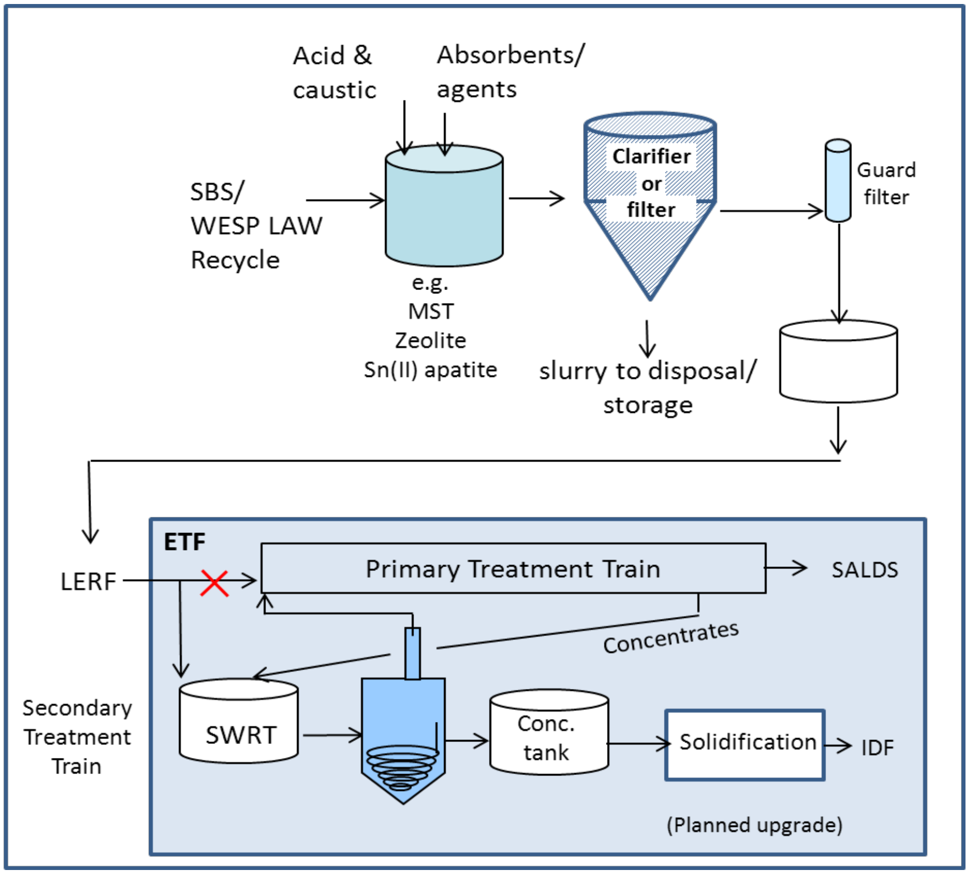


Figure 1-2. Schematic of a Proposed Decontamination Process and Disposition Path of LAW Off-Gas Condensate

1.1 Simulant Formulation Basis

Because the Off-Gas Condensate stream is not yet available for characterization, the simulant formulation was based on input from two sources. The projected solution chemistry and radionuclide content were based on version 7.4 of the Hanford Tank Waste Operations Simulator (HTWOS) modeling of the flow sheet[5] performed by WRPS.[6] Insoluble solids composition was primarily based on analysis of LAW Off-Gas Condensate obtained from pilot-scale simulant melter testing.[7] More detail on the basis for and synthesis of the simulant has been documented.[8,9]

1.2 Decontamination Process

One option that has been previously evaluated is disposal of the LAW Off-Gas Condensate stream directly to the ETF, however, this option has a number of consequences to ETF including increases in waste volume, halide levels, and radioactivity.[10,11]

The LAW Off-Gas Condensate stream is expected to contain ^{99}Tc due to its volatility at melter temperatures. The only chemical form of ^{99}Tc expected in the stream is pertechnetate anion (TcO_4^-) with a +7 technetium oxidation state. Although some fraction of the ^{99}Tc is present in the initial LAW stream as a soluble "non-pertechnetate" species, the LAW melter is expected to convert it to the same volatile species formed by vitrifying the pertechnetate form. The volatile species then becomes pertechnetate ion again when it contacts the water in the SBS and WESP. (Note that this has not been demonstrated.)

The current WTP baseline assumption is that technetium will not be removed from the aqueous waste in the WTP, and will primarily end up immobilized in the LAW glass waste form after several recycle passes to improve retention.[12] The LAW glass will be disposed in the IDF. Because ^{99}Tc has a very long half-life and is highly mobile,[13,14] it is the major dose contributor to the Performance Assessment (PA) of the IDF,[1] even though it is largely retained by the glass. Due to the high water solubility, high volatility during vitrification, and potential for impact to the PA, effective management of ^{99}Tc is important to the overall success of the River Protection Project mission. If a process was implemented that allowed disposal of the radionuclides offsite (e.g. by incorporation into HLW glass instead, for example), the amount of ^{99}Tc disposed in LAW glass at the IDF would decrease substantially.

For this proposed alternative treatment process, separation of the ^{99}Tc is accomplished by precipitation with chemical reagents, and settling and/or filtration, similar to the SRS ARP. For the Condensate stream, emphasis was on using entirely inorganic materials to enable easier storage and disposal as immobilized waste. For technetium removal, these materials included reducing agents (e.g. Sn(II) or Fe(II) compounds). Sn(II) with hydroxyapatite and oxalate have previously been found effective for precipitating Tc from water samples;[15] however, previous work has shown Sn(II) alone without an absorbent is sufficient for precipitation of the ^{99}Tc.

For this proposed alternative treatment process, disposal of the aqueous decontaminated Condensate stream at ETF is used as an example pathway. The basis for the target decontamination factors (DF) for the radionuclides was described previously.[3] The target DF for ^{99}Tc based on the current established LERF/ETF limits is only 2, but a DF of 100 was arbitrarily selected to minimize the impact of the final disposed waste form from ETF, which is disposed in IDF.

The DF is defined as the initial concentration (C_0) divided by the concentration at time *t* (C_t) (Equation 1). This is normally $\geq$1, but, if none of the species is removed, sampling and analytical analysis variability can occasionally cause it to be reported as <1.

$$DF = \frac{C_0}{C_t} \tag{1}$$

The precipitate slurry containing the radionuclides will be characterized in a future phase, and its potential disposition pathways will be evaluated. Immobilization testing will be in a subsequent phase of this program, once the slurry composition and quantities are defined.

2.0 Experimental Procedure

2.1 Simulant Preparation

Detail on the basis and synthesis of the simulant has been documented.[8] The target concentrations of chemicals and radionuclides were derived from the output from the HTWOS calculation, documented in SVF-3002, Rev. 1.[6] Two batches of identical simulant were prepared and used for the tests discussed in this report. The aqueous phase was prepared from dissolution of laboratory chemicals, as shown in Table 2-1. The first batch was previously prepared and characterized (i.d.: DFLAW 2014).[8] A second batch of 1.0 L of simulant was prepared and used for this testing. Because the HTWOS model is not constrained to generate a charge-balanced composition, no formulation can match all component concentrations simultaneously, and the chemical formulation must balance between cations and anions to create a mixture that can actually be prepared. Minor adjustments (5%) were made to some components versus the targets to account for this and to use readily available chemicals, and sodium and nitrate were adjusted by 25%. Note that the information in Table 2-1 does not necessarily reflect the final composition of the aqueous phase because it is impacted by precipitation and reaction with the glass forming chemicals (GFC), and with the nitric acid added during pH adjustment. Two 250-mL aliquots were removed from the 1-L batch of simulant prior to adding the GFCs. The GFCs were then added as shown in Table 2-2. The pH of each aliquot was then adjusted using either nitric acid or sodium hydroxide to reach target pH values of 7.3 (500-mL aliquot), 10 and 12 (250-mL aliquots). After pH adjustment the mixtures were stirred for five days at ambient temperature. After mixing, the solutions were re-adjusted as necessary back to the target pH values of 7.3, 10, and 12. See Table 2-3 for summary of pH adjustment steps. After the pH adjustment, the mixtures were stirred for over one hour, and were then filtered with a 0.45-µm Nalgene® filter.

Table 2-1. Aqueous Simulant Formulation Targets

Chemical	**Formula**	**Target Mass (g)/L simulant**	**Target Molarity**
Aluminum nitrate nonahydrate	$Al(NO_3)_3{\cdot}9H_2O$	0.12	0.00032
Sodium chromate	Na_2CrO_4	0.093	0.00058
Potassium chloride	KCl	0.456	0.0061
Sodium chloride	NaCl	2.05	0.0351
Sodium fluoride	NaF	1.23	0.0293
Ammonium nitrate	NH_4NO_3	3.05	0.0381
Sodium nitrate	$NaNO_3$	4.6	0.054
Sodium nitrite	$NaNO_2$	0.0094	0.00014
Ammonium sulfate	$(NH_4)_2SO_4$	1.8	0.0136
Dibasic sodium phosphate dihydrate	$Na_2HPO_4{\cdot}2H_2O$	0.086	0.00048

Table 2-2. Target Glass Forming Chemical Quantities

Mineral	**Formula**	**Mass (g)/L simulant**
kyanite	Al_2SiO_5	0.745
borax	$Na_2B_4O_7{\cdot}10H_2O$	0.0123
boric acid	H_3BO_3	1.430
wollastonite	$CaSiO_3$	0.772
iron oxide (hematite)	Fe_2O_3	0.430
lithium carbonate	Li_2CO_3	0.392
forsterite olivine	Mg_2SiO_4-Fe_2SiO_4	0.257
sodium carbonate	Na_2CO_3	0.003
silica	SiO_2	2.857
rutile	TiO_2	0.114
zinc oxide	ZnO	0.286
zircon	$ZrSiO_4$	0.372
sucrose	$C_{12}H_{22}O_{11}$	0
	Total	7.67

Table 2-3. pH Adjustment of 2015 Simulants

	500-mL pH 7.3 aliquot	**250-mL pH 10 aliquot**	**250-mL pH 12 aliquot**
Initial pH	8.03	7.99	7.99
pH after Adjustment	7.20	10.01	11.99
Conc. Of HNO_3/NaOH used	15.8 M HNO_3	50 wt% NaOH	50 wt% NaOH
Amt. of HNO_3/NaOH Added	0.256 g	1.424 g	2.294 g
pH after 5 days of stirring	7.40	9.85	11.38
Final pH after Adjustment	7.23	10.02	12.00
Conc. Of HNO_3/NaOH used	15.8 M HNO_3	50 wt% NaOH	50 wt% NaOH
Amt. of HNO_3/NaOH Added	0.0584 g	0.1179 g	0.4915 g

2.2 Simulant Spiking with Radionuclides

The prepared simulants were then spiked with the radiotracer solutions shown in Table 2-4. The DFLAW 2014 simulant had been previously spiked and results of those analyses previously documented;[8] however, additional ^{241}Am, $^{239/240}$Pu, ^{99}Tc, and ^{85}Sr were added to increase the activities closer to the target values. Previous attempts to spike this and other similar simulants have shown the $^{239/240}$Pu and ^{241}Am to not be soluble. In an attempt to ensure that the actinides were at their actual solubility limits the solutions were mixed at 50 °C for 48 hours after spiking. This temperature is comparable to the expected operating condition of the SBS and WESP in WTP. The testing was designed to show that if these actinides were carried into the melter off-gas and were under these conditions they would be removable simply by filtration, rather than needing a sorbent, and that their minimal solubility was less influenced by the simulant preparation method. After the 48 hours of heating, the solutions were stirred at ambient temperature for an additional week. Samples were removed and filtered 24 hours and 5 days after heating ceased. The previous ^{99}Tc activity was only about 72% of the target and therefore additional ^{99}Tc was added, along with ^{85}Sr which had decayed since the original spiking due to the relatively short half-life of 64 days. The DFLAW 2015 simulant was stirred at room temperature overnight after spiking, prior to removing samples for analysis. The filtrates were analyzed for radionuclide contents. Analysis methods included Inductively Coupled Plasma – Mass Spectroscopy (ICP-MS) (^{99}Tc, ^{238}U), gamma spectroscopy (^{85}Sr, ^{137}Cs, ^{241}Am), and alpha pulse height analysis after an extraction with thenoyltrifluoroacetone (PuTTA) ($^{239/240}$Pu). Results are summarized in Section 3 and detailed in Appendix A.

Table 2-4. Radiotracer Solutions added to Simulants

Isotope	**Matrix**	**Target concentration (dpm/mL)**
^{137}Cs	^{137}Cs in 0.1 M HCl	1.12E4
^{238}U	$UO_2(NO_3)_2 \cdot 6H_2O$ aqueous solution (5 mg/mL U)	8.59E-2
$^{239/240}$Pu	1.5 g/L WG Pu in 0.45 M HNO_3	8.42E1
^{85}Sr	^{85}Sr radionuclide in 0.5 M HCl	2.58E3
^{99}Tc	Ammonium pertechnetate solution	2.29E5
^{241}Am	^{241}Am aqueous stock solution	5.15E2

2.3 Precipitation Testing

In general, tests were performed by adding a small amount of each reagent to separate poly bottles, followed by the addition of 19 mL of the radioactive simulant solution to each. The bottles were then agitated in a shaker oven at ~25 ˚C for the specified time. Each sample was then filtered through a 0.1-µm filter. The filtrate was then analyzed by ICP-MS for ^{99}Tc and U and by inductively coupled plasma – emission spectroscopy (ICP-ES) for Cr. Results are summarized in Section 3, with details in Appendix A.

Precipitation tests were performed with both ferrous sulfate and stannous chloride serving as the reducing agents. Previous work has shown that Fe(II) can remove some Tc through reductive precipitation; however, it does not perform as well as Sn(II). During the reductive precipitation, the majority of the reducing agent is consumed by reaction with the Cr(VI). Therefore, testing was performed to determine if Fe(II) can be used instead of Sn(II) or together with Sn(II) to minimize Sn use. Testing was performed in both neutral and pH 10 and 12 simulants with Fe(II) ratios of 2:1, 3:1, and 4:1. The ratio represents the moles of reductant (i.e. Fe(II)) versus the moles of electrons needed to reduce the Cr(VI) to Cr(III) and the Tc(VII) to Tc(IV). On a molar ratio, a "2:1 ratio" is equivalent to 6 moles of Fe(II) to 1 mole of Cr(VI) + Tc(VII). Testing was also performed to examine the performance of Sn(II) for ^{99}Tc removal from the DFLAW simulant at neutral, pH 10, and pH 12 conditions. These tests all used a Sn(II) ratio of 1.5:1, which has previously been shown to be sufficient in the baseline SBS/WESP simulant. Tests with Fe(II) used the 2014 batch of DFLAW, while the Sn(II) tests used the 2015 batch.

2.4 Stability of Precipitated Solids to Reoxidation

After the successful removal of ^{99}Tc through the reductive precipitation with Sn(II) had been demonstrated, testing was performed to examine the stability of the reduced ^{99}Tc to reoxidation and redissolution. Previous work with the baseline SBS/WESP simulant has shown the ^{99}Tc to be stable to reoxidation and redissolution for at least 72 hours under neutral conditions. Since pH adjustment of the stream may be necessary after the precipitation prior to evaporation to concentrate the stream, stability testing was performed at pH 10 and 12. Stannous chloride (1.5 eq) was added to 40 mL aliquots of the pH 7.3 2015 batch of DFLAW simulant, and the samples were mixed at ~25 °C in a shaker oven. The tests were carried out in 125-mL poly bottles to ensure sufficient excess of oxygen, and the bottles were opened twice per day to replenish the air. After allowing 1 hour for the precipitation reaction to complete, a sample was removed, and the pH was then adjusted to either pH 10 or 12. After adjusting the pH, the bottles continued mixing for a total of 72 hours, with samples being removed after 6, 24, 48, and 72 hours after the initial $SnCl_2$ addition. At each sampling event, the bottle was manually shaken to ensure the solids were well mixed and approximately 4 mL of sample was then filtered through a 0.1-µm syringe filter. The filtered samples were submitted for ICP-MS analysis. Results are summarized in Section 3, with details in Appendix A.

2.5 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2. Results are recorded in Electronic Laboratory Notebook #E7518-00159.

3.0 Results and Discussion

3.1 Simulant Compositions

3.1.1 DFLAW 2014 Simulant

(Note: chemical composition results were previously reported,[8] but are included here for completeness)

Chemical analysis results of a sample of the neutralized and filtered simulant is shown in Table 3-1. These match the target compositions reasonably well. Although boron, lithium, silicon, zinc, and carbonate were not in the aqueous simulant preparation, they are present in the solution due to addition of the glass forming chemicals and their subsequent dissolution. It appears that all of the lithium carbonate and boric acid dissolved, but only a small amount of a silicon mineral and a small amount of the zinc oxide dissolved; which is expected due to their relative solubilities. Additionally, the analyzed soluble fluoride in the simulant was about 50 mg/L lower than the target, and the phosphate was much lower than the target. Presumably, both fluoride and phosphate precipitate from the solution. The target concentration for soluble aluminum was 8.7 mg/L, based on computer modeling; however, consistent with prior results, the aluminum is not sufficiently soluble.

Table 3-1. DFLAW 2014 Simulant Filtrate Chemical Composition

Component	DFLAW Simulant Concentration (mg/L)	Method uncertainty (% RSD)	HTWOS projection Adjusted (avg. SVF-3002, R. 1) (mg/L)
Al	<0.309	n/a	8.7
B	243	10	GFC# (251 mg added as GFC)
Ca	3.67	10	GFC# (266 mg added as GFC)
Cr	28.4	10	30
Fe	<0.07	n/a	GFC# (385 mg added as GFC)
K	242	10	239
Li	72	10	GFC# (73.6 mg added as Li_2CO_3)
Mg	1.01	n/a	GFC# (36 mg added as GFC)
Na	2.66E3	10	2.78E3
P	4.38	11.8	15 (added as PO_4^{3-})
S	465	10.3	435 (added as SO_4^{2-})
Si	37.9	10	GFC# (1752 mg added as GFC)
Ti	<0.047	n/a	GFC# (68 mg added as GFC)
Zn	4.8	10	GFC# (230 mg added as GFC)
Zr	<0.031	n/a	GFC# (185 mg added as GFC)
F^-	511	10	559
Cl^-	1.45E3	10	1.46E3
NO_2^-	<10	n/a	6.3
NO_3^-	5.90E3	10	5.78E3
SO_4^{2-}	1.29E3	10	1.31E3
PO_4^{3-}	<20	n/a	46
CO_3^{2-}	319 (63.4 as TIC)	10	GFC# (318 mg added as Li_2CO_3)
NH_4^+	1.14E3	10	1.18E3

#Glass Forming chemical; minimal HTWOS projected concentration

This simulant was originally spiked in 2014; however, was respiked in 2015 just prior to this testing. Respiking was performed in an attempt to bring the ^{241}Am, $^{239/240}$Pu, and ^{99}Tc activities closer to the targets, and also to bring the ^{85}Sr activity back up to the target activity after decaying. In an attempt to increase the solubilities of the ^{241}Am and $^{239/240}$Pu, the simulant was heated to 50 °C for 48 hours after spiking. Samples were then removed and analyzed 24 hours (all) and 5 days (gamma and PuTTA) after heating ceased. Table 3-2 provides the measured radionuclide activities after 24 hours. There was little change between the 24 hour and 5 day samples, and the 5 day results are included in Appendix A. The Tc and U analyses are from ICP-MS as mg/L, and the dpm/mL are calculated from a specific activity of 0.0170 Ci/g and 3.36E-7 Ci/g, respectively. Despite the heating, the ^{241}Am and $^{239/240}$Pu remain insoluble in these simulants. The other radionuclides were reasonably close to the target values.

Table 3-2. DFLAW 2014 Radionuclide Composition

Isotope	Activity (dpm/mL)	Reported Method Uncertainty	% of Target Activity
^{85}Sr	2.43×10^{3}	5.0%	94
^{99}Tc	1.99×10^{5} (5.26 mg/L)	20%	87
^{137}Cs	1.03×10^{4}	5.0%	92
^{238}U	0.094 (0.126 mg/L)	20%	111
$^{239/240}$Pu	< 20.4	mda	< 24
^{241}Am	< 40.9	mda	< 7.9

mda = minimum detectable activity

3.1.2 DFLAW 2015 Simulant

Results of the average and standard deviation of the duplicate chemical analysis of the neutralized, filtered simulants prepared in 2015 are shown in Table 3-3 (see Section 2.1 for a description of the simulant preparations). All three simulants are relatively good matches versus the accuracy and range of the projected composition, and the small variations are not expected to impact results obtained here. The silicon solubility varied considerably as a function of pH, with higher concentrations present in the pH 12 simulant. The Na^+ concentration increased with increasing pH due to the addition of NaOH to prepare the pH 10 and 12 simulants. The target concentration for soluble aluminum was 8.7 mg/L, based on computer modeling. However, consistent with prior results, the aluminum is not sufficiently soluble. The ammonium concentration decreases as the pH increases, which is expected as the ammonium converts to ammonia at higher pH values.

The radionuclide activities in the spiked simulants are provided in Table 3-4. The Tc and U analyses are from ICP-MS as mg/L, and the dpm/mL are calculated from a specific activity of 0.0170 Ci/g and 3.36E-7 Ci/g, respectively. Consistent with previous spiking attempts for similar simulants, the Am and Pu were not soluble, although an ^{241}Am activity slightly above the detection limit was reported for the pH 10 simulant. The other radionuclides were reasonably close to the target values; with the exception of ^{137}Cs which was ~35-40% below the target indicating the activity of the stock was likely lower than expected. The ^{99}Tc appeared to decrease in solubility as the pH increased; however, the three values were all within analytical uncertainty, so this may not be a true effect.

Table 3-3. DFLAW 2015 Simulant Filtrate Compositions

Component	pH 7.3 Aliquot Avg. (mg/L)	SD	pH 10 Aliquot Avg. (mg/L)	SD	pH 12 Aliquot Avg. (mg/L)	SD		HTWOS projection (avg. SVF-3002, R.1) (mg/L)
Al	< 0.500	n/a	< 0.500	n/a	0.652	0.004		8.7
B	169	2.83	167	2.12	161	1.41		GFC$^{\#}$ (251 mg added as GFC)
Ca	2.65	0.007	4.91	0.163	1.10	0.014		GFC$^{\#}$ (266 mg added as GFC)
Cr	29.3	0.212	31.2	0.212	29.7	0.071		30
Fe	<0.100	n/a	<0.100	n/a	<0.100	n/a		GFC$^{\#}$ (385 mg added as GFC)
K	239	16.3	228	0.707	229	4.24		239
Li	76.8	0.495	77.4	0.141	75.4	1.34		GFC$^{\#}$ (73.6 mg added as Li_2CO_3)
Mg	<0.100	n/a	<0.100	n/a	<0.100	n/a		GFC$^{\#}$ (36 mg added as GFC)
Na	2255	91.9	4125	63.6	5495	106		2.78E3
P	1.11	0.064	16.2	0.071	16.6	0.071		15 (added as PO_4^{3-})
S	457	2.12	462	0.707	457	0^{*}		435 (added as SO_4^{2-})
Si	48.3	0.495	109	0.707	598	0^{*}		GFC$^{\#}$ (1752 mg added as GFC)
Ti	<0.100	n/a	<0.100	n/a	<0.100	n/a		GFC$^{\#}$ (68 mg added as GFC)
Zn	18.8	0.141	0.490	0.003	8.04	0.078		GFC$^{\#}$ (230 mg added as GFC)
Zr	<0.500	n/a	<0.500	n/a	<0.500	n/a		GFC$^{\#}$ (185 mg added as GFC)
F^-	517	0.707	522	5.66	525	2.83		559
Cl^-	1455	7.07	1445	21.2	1440	0^{*}		1.46E3
NO_2^-	<100	n/a	<100	n/a	<100	n/a		6.3
NO_3^-	6200	240	5550	99.0	5535	7.07		5.78E3
SO_4^{2-}	1385	120	1360	56.6	1335	49.5		1.31E3
PO_4^{3-}	<100	n/a	<100	n/a	<100	n/a		46
NH_4^+	1080^{**}	n/a	903^{**}	n/a	845^{**}	n/a		1.18E3

*Standard Deviation of zero indicates the two analysis results were identical

**analysis of a single sample

#Glass Forming Chemical; minimal HTWOS projected concentration

Table 3-4. DFLAW 2015 Radionuclide Simulant Compositions

pH 7.3 Simulant			
Isotope	**Activity (dpm/mL)**	**Reported Method Uncertainty**	**% of Target Activity**
^{85}Sr	2.97 x 10^3	5.0%	115
^{99}Tc	1.83 x 10^5 (4.85 mg/L)	20%	80
^{137}Cs	6.68 x 10^3	5.0%	59
^{238}U	0.099 (0.133 mg/L)	20%	117
$^{239/240}$Pu	< 9.97	mda	< 12
^{241}Am	< 37.4	mda	< 7.3
pH 10 Simulant			
Isotope	**Activity (dpm/mL)**	**Reported Method Uncertainty**	**% of Target Activity**
^{85}Sr	3.14 x 10^3	5.0%	122
^{99}Tc	1.69 x 10^5 (4.49 mg/L)	20%	74
^{137}Cs	7.24 x 10^3	5.0%	64
^{238}U	0.082 (0.110 mg/L)	20%	97
$^{239/240}$Pu	< 4.84	mda	< 5.8
^{241}Am	84.3	13.1%	16
pH 12 Simulant			
Isotope	**Activity (dpm/mL)**	**Reported Method Uncertainty**	**% of Target Activity**
^{85}Sr	2.64 x 10^3	5.0%	103
^{99}Tc	1.62 x 10^5 (4.28 mg/L)	20%	71
^{137}Cs	7.31 x 10^3	5.0%	65
^{238}U	0.086 (0.115 mg/L)	20%	101
$^{239/240}$Pu	< 3.33	mda	< 4.0
^{241}Am	< 37.1	mda	< 7.2

mda = minimum detectable activity

3.2 Precipitation Testing

Results of the precipitation tests are shown in Tables 3-5 and 3-6. Details of the test results can be found in Appendix A. Analysis of the Tc and U were done by ICP-MS and Cr was done by ICP-ES.

The Fe(II) was most effective at removal of Tc at pH 10, where a maximum DF of 14 was obtained at the highest Fe(II) concentration tested (4:1). In all cases, however, the Tc appeared to quickly reoxidize as DF values were consistently lower at 24 hours when compared to 6 hours. The Fe(II) was effective at removing all of the Cr to below detection limit with the lowest Fe(II) ratio tested (2:1). No reoxidation was observed between 6 and 24 hours. The higher Fe(II) ratios were less effective possibly due to the drop in pH caused by the addition of the $FeSO_4$. The final pH values of the test bottles were 6.26, 5.24, and 4.93 for the 2:1, 3:1, and 4:1 tests, respectively, compared to an average pH value of 7.68 for the control sample.

In the pH 10 simulant, results indicated that all ratios of Fe(II) tested were effective at removing all of the Cr to below detection limits within 6 hours. However, the 24-hour results indicated some possible reoxidation of the Cr back into solution with the lower Fe(II) ratios tested (2:1 and 3:1). The 4:1 samples remained below detection limit for Cr concentration after 24 hours. The concentrations of Cr observed in solution for the 24-hour samples with 2:1 and 3:1 Fe(II) were still very low, and resulted in DF values near 500. The measured Cr concentrations in those samples ranged from ~10% to ~35% higher than the reported Cr detection limit. The $FeSO_4$ had less of an impact on the pH value of the simulant than in the case of the neutral simulant. At the highest Fe(II) ratio tested, the pH dropped less than 0.5 pH units compared to the control simulant (pH 9.58 vs 9.96).

Testing in pH 12 adjusted DFLAW simulant showed the Fe(II) to be much less effective at removing Cr, than at neutral or pH 10. In the pH 12 simulant, the highest Cr DF (41.6) was obtained after 24 hours with the highest Fe(II) ratio tested, 4:1. The Cr removal appeared to be continuing with time, as the DFs increased for all samples from 6 to 24 hours. The addition of $FeSO_4$ had no measurable effect on the pH value of the simulant. The pH averaged ~11.9 for all samples, including the controls.

Small amounts of U were also removed under all conditions tested, with the exception of 3:1 and 4:1 Fe(II) in the neutral simulant. In general the U removal appeared to increase with increasing pH and with increasing amounts of Fe(II). The highest U removal was observed in the pH 12 simulant with 4:1 equivalents of Fe(II), reaching a DF of 4.0 after 24 hours.

Table 3-5. Average Decontamination Factors for Fe(II) Precipitations in Variable pH Simulants

	Neutral Simulant			**pH 10**			**pH 12**		
Fe(II) ratio	2:1	3:1	4:1	2:1	3:1	4:1	2:1	3:1	4:1
6 h Tc DF	1.00 (0.00)	n/a[#]	n/a[#]	1.95 (0.08)	4.43 (1.71)	14.0 (4.42)	2.22 (0.07)	2.92 (0.01)	5.11 (0.97)
6 h U DF	1.32 (0.05)	n/a[#]	n/a[#]	2.48 (0.00)	2.49 (0.26)	2.34 (0.25)	1.99 (0.29)	2.59 (0.51)	3.78 (0.13)
6 h Cr DF	> 609 (0)	n/a[#]	n/a[#]	> 611 (0)	> 611 (0)	> 611 (0)	2.82 (0.49)	4.40 (0.95)	10.9 (0.09)
24 h Tc DF	1.01 (0.00)	1.00 (0.00)	1.01 (0.00)	1.67 (0.04)	2.50 (0.25)	4.08 (0.00)	2.09 (0.11)	2.99 (0.13)	4.69 (0.21)
24 h U DF	1.54 (0.01)	1.05 (0.00)	1.03 (0.00)	2.56 (0.06)	2.38 (0.06)	2.18 (0.04)	2.35 (0.16)	3.07 (0.32)	4.00 (0.06)
24 h Cr DF	> 614 (0)	22.2 (1.21)	17.4 (0.22)	460 (21.3)	502 (66.3)	> 602 (0)	3.97 (0.47)	9.99 (2.20)	41.6 (1.59)
Final pH	*6.26* *(0.11)*	*5.24* *(0.04)*	*4.93* *(0.04)*	*9.76* *(0.01)*	*9.66* *(0.01)*	*9.58* *(0.01)*	*11.89* *(0.02)*	*11.89* *(0.00)*	*11.86* *(0.00)*

Value in parentheses indicates standard deviation of replicate trials.

[#] After standing overnight the filtrates from the 3:1 and 4:1 6 h samples in the neutral simulant had formed a precipitate, indicating the reaction was not complete at the time of sampling, and therefore these samples were not submitted for analysis.

Results from testing with stannous chloride confirmed the effectiveness of 1.5 eq of $SnCl_2$ at quantitatively removing the Tc from DFLAW simulant at near neutral pH. Experiments in the as-prepared simulant (with no pH adjustment) showed removal of Tc to below detection limits. There was some discrepancy between the duplicate trials, as one achieved a DF of only 18 at 1 hour, while the other reached a DF of >480 at 1 hour. By 24 hours both duplicates had removed Tc to below the detection limit, achieving a DF of >497. The $SnCl_2$ was not as effective at higher pH values. In the pH 10 simulant, the maximum DF reached was 6.14 after 1 hour. The DF remained essentially unchanged between 1 and 24 hours. In the pH 12 simulant, the maximum DF reached was 2.59 after 24 hours. The Tc DFs did appear to increase slightly from 1 to 24 hours.

The Sn solubility at the end of the experiment tracked with the observed Tc DF values. In the neutral simulant, essentially all of the Sn added was precipitated by 1 hour. In the pH 10 simulant the percent of Sn added that remained soluble was ~16% after 1 hour (duplicates about the same), but ranged from ~5-35% after 24 hours. In the pH 12 simulant, the amount of Sn that remained soluble ranged from ~75-100% of the amount added.

The $SnCl_2$ also appeared to be somewhat effective at removing the U from the simulant in all three cases, although it was by far most effective at pH 12, reaching an average DF of 9.24 after 24 hours.

Table 3-6. Average Decontamination Factors for Sn(II) Precipitations in Variable pH Simulants

1.5 eq. Sn(II)	Neutral Simulant	pH 10	pH 12
1 h Tc DF	249 (327) #	3.76 (3.37)	1.08 (0.08)
1 h U DF	1.68 (0.21)	1.17 (0.06)	1.46 (0.26)
% Added Sn in Solution at 1 h	< 0.01%	16.1% (0.41%)	93.7% (26.9%)
24 h Tc DF	> 497 (0)	3.58 (3.22)	1.85 (1.05)
24 h U DF	1.85 (0.04)	1.17 (0.11)	9.24 (3.20)
% Added Sn in Solution at 24 h	0.04% (0.01%)	19.7% (21.3%)	86.8% (20.2%)
Final pH	*7.19 (0.04)*	*10.05 (0.18)*	*12.06 (0.06)*

Value in parentheses indicates standard deviation of replicate trials.
#Replicate trials had very different values, DF values of 18.0 and >480.

3.3 Stability of Precipitated Solids to Reoxidation

Results from the stability testing at variable pH are shown in Table 3-7. For these experiments the ^{99}Tc was precipitated upon the addition of 1.5 eq of $SnCl_2$ in the as-prepared (i.e., neutral) simulant. After precipitation was complete (1 h), the pH of the test bottles was adjusted to either pH 10 or 12 with the addition of sodium hydroxide and samples were removed over a period of 72 hours. The replicate trials at pH 10 were fairly consistent, and therefore, the table contains the average results of the two trials. There was some discrepancy between the two replicate experiments at pH 12, and therefore, the individual trial data is presented.

In the pH 10 and one of the pH 12 trials, the $SnCl_2$ effectively removed Tc to below detection limit (DF >501), as expected. In the second pH 12 trial only a small amount of Tc was removed, resulting in a DF of 2.11. In all cases, however, the Tc began to reoxidize and dissolve after the pH was increased. In the case of the pH 10 adjustment, the DF dropped from >501 to 174 from the 1 to 6 hour sampling events. The DF then continued to decrease over the remainder of the experiment, reaching a final value of 57 after 72 hours. The oxidation and dissolution happened more quickly in the pH 12 tests, with the DF dropping from >501 to only 3.23 between the 1 and 6 hour sampling events. The DF continued to drop, reaching 1.57 after 72 hours in trial 1. The second trial which did not show much Tc removal initially followed the same trend, with the Tc DF continually decreasing after the pH was adjusted to 12.

The measured amount of soluble Sn was below the detection limit in all 4 experiments after the initial Tc precipitation at neutral pH. After pH adjustment to 10, the soluble Sn increased to ~1.2% of the amount added, and then began to reprecipitate at later time points, dropping to 0.14% soluble at the end of the experiment. In the pH 12 experiments a large portion of the Sn redissolved after the pH adjustment, reaching solubility levels between 55 and 74% of the initial amount of Sn added. This observation seems to point to a possible explanation for the different results in the Trial 1 and Trial 2 Tc DF after one hour (i.e., DF = >501 vs 2.11). It is speculated that perhaps the amount of $SnCl_2$ added to the second pH 12 trial was lower than intended, which would explain the incomplete precipitation of Tc initially (DF = 2.11), and the lower percentages of soluble Sn after pH adjustment (since the percentage is based on the calculated intended amount added).

The $SnCl_2$ was also somewhat effective at removing the U, and the U removal increased with increasing pH. The initial U DF at 1 h (neutral simulant) ranged from about 1.6 – 2.2. After adjusting the pH to 10, the U DF increased to an average of about 2.7 after 6 hours and continued to increase with time, reaching a final value about 3.4. An even higher amount of U removal was observed after adjusting the pH to 12, with some discrepancy between the two trials. After increasing the pH to 12, the DF increased to 9.29 in trial 1 and 5.23 in trial 2 at the 6 hour sampling time. The DF remained fairly constant (within analytical error) for the remainder of the test.

However, the removal of U may or may not be due to reduction by Sn, and could have instead been influenced by a combination of the pH adjustment and coprecipitation with another precipitate. The control sample was also pH adjusted and did not exhibit U removal, but no other solids formed in the control sample, since Sn(II) was not added to it.

Table 3-7. Results of Precipitate Stability Testing

	Tc DF			**U DF**			**% Added Sn in Solution**		
	pH 10	**pH 12**		**pH 10**	**pH 12**		**pH 10**	**pH 12**	
		Trial 1	**Trial 2**		**Trial 1**	**Trial 2**		**Trial 1**	**Trial 2**
1 h (neutral)	> 501 (0)	> 501	2.11	1.92 (0.36)	2.02	1.55	< 0.01% (0)	< 0.01%	< 0.01%
6 h	174 (7.18)	3.23	1.35	2.66 (0.27)	9.29	5.23	1.16% (0.06%)	64.7%	50.6%
24 h	106 (8.09)	1.89	1.21	3.27 (0.37)	8.81	5.31	0.50% (0.15%)	72.0%	55.4%
48 h	69.9 (12.4)	1.64	1.17	2.97 (0.89)	8.68	5.37	0.27% (0.07%)	73.5%	57.7%
72 h	57.1 (13.7)	1.57	1.15	3.39 (0.41)	8.46	5.33	0.14% (0.01%)	73.9%	54.6%

4.0 Conclusions

Tests were performed to ensure maximum solubility of ^{241}Am and $^{239/240}$Pu by heating the mixtures to 50 °C. Regardless of the preparation method, these actinides remained insoluble in the DFLAW off-gas condensate simulant. Other radionuclides were successfully spiked to the target concentrations. This indicates that even if these actinides partition into the off-gas condensate, they could be removed by filtration and do not need additional sorbents or reactants to remove them from the stream.

Testing results confirmed that 1.5 eq. of electrons from Sn(II) relative to those needed to reduce Cr(VI) and Tc(VII) was effective at removing the ^{99}Tc to below the method detection limit (DF >497) in the neutral DFLAW simulant. However, the Sn(II) was found to be less effective under alkaline conditions, reaching DF values of only 6.1 and 2.6 in pH 10 and 12 simulants, respectively. Tests with Fe(II) showed that no Tc is removed from the neutral simulant; however, a small amount can be removed by adjusting the pH to 10 or 12. The highest Tc DF obtained was 14 with 4 eq. of electrons from Fe(II) relative to those needed to reduce Cr(VI) and Tc(VII). The Fe(II) was more effective at precipitation of the Cr, however, removing Cr to below detection limits in several cases in the neutral and pH 10 simulants. The effectiveness of Fe(II) for Cr removal decreased at pH 12.

Stability testing in the DFLAW simulant after pH adjustment to 10 or 12 demonstrated that the precipitated solids are quickly reoxidized and dissolve after the pH is adjusted. The reoxidation rate increased as the pH increased from 10 to 12.

5.0 Future Work

Further testing is needed to identify the larger scale conditions for the decontamination process. Once these conditions are established, follow-on tasks likely include evaluation and testing of applicable solid-liquid separation technologies, slurry rheology measurements, composition variability testing and evaluations, corrosion and erosion testing, slurry storage and immobilization investigations, impact of Sn on immobilized waste formulations, and decontaminated DFLAW Off-Gas Condensate evaporation and solidification.

6.0 References

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Appendix A. Detailed Results

Table A-1. Measured Radionuclide Compositions for DFLAW 2014 Simulant – After respiking and heating.

Time since heating	24 h	5 day
^{85}Sr (dpm/mL)	2.43E+03 (5.0%)	2.23E+03 (5.0%)
^{99}Tc (µg/L)	5.26E+03 (20%)	NM
^{137}Cs (dpm/mL)	1.03E+04 (5.0%)	1.01E+04 (5.0%)
^{238}U (µg/L)	1.26E+02 (20%)	NM
$^{239/240}$Pu (dpm/mL)	< 20.4	< 13.2
^{241}Am (dpm/mL)	< 40.9	< 40.7

NM = not measured

Table A-2. Summary of Concentration Data from Fe(II) Precipitations in Neutral pH DFLAW

Test ID	DFLAW-127	DFLAW-128	DFLAW-129	DFLAW-130	DFLAW-131	DFLAW-132	DFLAW-133	DFLAW-134
Precip. Agent	None (Control)	None (Control)	Fe(II) (2:1)	Fe(II) (2:1)	Fe(II) (3:1)	Fe(II) (3:1)	Fe(II) (4:1)	Fe(II) (4:1)
Precip. Agent Conc. (g/L)#	n/a	n/a	0.54	0.55	0.81	0.81	1.08	1.09
Contact Time (h)	6.07	6.08	6.12	6.13	6.13	6.15	6.17	6.18
^{99}Tc (µg/L)	5.34E+03	5.33E+03	5.35E+03	5.36E+03	NM	NM	NM	NM
^{238}U (µg/L)	1.26E+02	1.27E+02	9.32E+01	9.88E+01	NM	NM	NM	NM
Cr (mg/L)	28.4	28.2	< 0.0465	< 0.0465	NM	NM	NM	NM
Zn (mg/L)	2.04	2.26	1.43	1.67	NM	NM	NM	NM
Contact Time (h)	24.03	24.05	24.07	24.08	24.08	24.10	24.12	24.13
^{99}Tc (µg/L)	5.41E+03	5.43E+03	5.38E+03	5.35E+03	5.38E+03	5.40E+03	5.35E+03	5.36E+03
^{238}U (µg/L)	1.27E+02	1.25E+02	8.16E+01	8.22E+01	1.21E+02	1.20E+02	1.22E+02	1.22E+02
Cr (mg/L)	28.6	28.5	< 0.0465	< 0.0465	1.24	1.34	1.63	1.66
Zn (mg/L)	1.76	1.77	1.06	1.36	2.96	3.00	3.39	3.27

#Concentration of $FeSO_4$.
NM = not measured

Table A-3. Summary of Concentration Data from Fe(II) Precipitations in pH 10 DFLAW

Test ID	**DFLAW-135**	**DFLAW-136**	**DFLAW-137**	**DFLAW-138**	**DFLAW-139**	**DFLAW-140**	**DFLAW-141**	**DFLAW-142**
Precip. Agent	None (Control)	None (Control)	Fe(II) (2:1)	Fe(II) (2:1)	Fe(II) (3:1)	Fe(II) (3:1)	Fe(II) (4:1)	Fe(II) (4:1)
Precip. Agent Conc. (g/L)[#]	n/a	n/a	0.54	0.55	0.81	0.81	1.09	1.08
Contact Time (h)	6.00	6.00	6.00	6.02	6.03	6.05	6.07	6.08
^{99}Tc (µg/L)	5.47E+03	5.43E+03	2.71E+03	2.88E+03	1.69E+03	9.68E+02	3.18E+02	5.01E+02
^{238}U (µg/L)	1.28E+02	1.25E+02	5.10E+01	5.09E+01	5.50E+01	4.73E+01	5.02E+01	5.85E+01
Cr (mg/L)	28.4	28.4	< 0.0465	< 0.0465	< 0.0465	< 0.0465	< 0.0465	< 0.0465
Zn (mg/L)	2.85	2.47	0.0865	0.0885	0.0925	0.0895	0.0840	0.0895
Contact Time (h)	25.03	25.03	25.03	25.05	25.07	25.08	25.08	25.10
^{99}Tc (µg/L)	5.51E+03	5.46E+03	3.24E+03	3.34E+03	2.36E+03	2.04E+03	1.34E+03	1.34E+03
^{238}U (µg/L)	1.28E+02	1.25E+02	5.03E+01	4.87E+01	5.41E+01	5.22E+01	5.88E+01	5.73E+01
Cr (mg/L)	28	28	0.059	0.063	0.0615	0.051	< 0.0465	< 0.0465
Zn (mg/L)	2.81	2.79	0.084	0.0885	0.0855	0.096	0.097	0.096

[#] Concentration of $FeSO_4$.

Table A-4. Summary of Concentration Data from Fe(II) Precipitations in pH 12 DFLAW

Test ID	**DFLAW-143**	**DFLAW-144**	**DFLAW-145**	**DFLAW-146**	**DFLAW-147**	**DFLAW-148**	**DFLAW-149**	**DFLAW-150**
Precip. Agent	None (Control)	None (Control)	Fe(II) (2:1)	Fe(II) (2:1)	Fe(II) (3:1)	Fe(II) (3:1)	Fe(II) (4:1)	Fe(II) (4:1)
Precip. Agent Conc. (g/L)[#]	n/a	n/a	0.54	0.54	0.81	0.81	1.09	1.09
Contact Time (h)	5.98	6.00	6.02	6.02	6.02	6.03	6.05	6.07
^{99}Tc (µg/L)	5.41E+03	5.43E+03	2.39E+03	2.49E+03	1.85E+03	1.86E+03	9.34E+02	1.22E+03
^{238}U (µg/L)	1.19E+02	1.20E+02	5.44E+01	6.69E+01	4.05E+01	5.35E+01	3.08E+01	3.24E+01
Cr (mg/L)	27.7	27.8	8.75	11.2	5.47	7.45	2.55	2.52
Zn (mg/L)	3.44	3.49	0.168	0.471	0.0925	0.218	0.0995	0.0585
Contact Time (h)	25.02	25.02	25.03	25.05	25.05	25.07	25.08	25.10
^{99}Tc (µg/L)	5.46E+03	5.46E+03	2.71E+03	2.51E+03	1.77E+03	1.88E+03	1.20E+03	1.13E+03
^{238}U (µg/L)	1.21E+02	1.19E+02	4.86E+01	5.36E+01	3.64E+01	4.21E+01	2.97E+01	3.03E+01
Cr (mg/L)	27.7	27.5	6.42	7.58	2.39	3.27	0.646	0.682
Zn (mg/L)	3.46	3.48	0.103	0.168	0.047	0.0895	0.047	0.0355

[#] Concentration of $FeSO_4$.

Table A-5. Summary of Concentration Data from Sn(II) Precipitations in pH 7, 10, and 12 DFLAW

Test ID	**DFLAW-157**	**DFLAW-158**	**DFLAW-159**	**DFLAW-160**	**DFLAW-161**	**DFLAW-162**	**DFLAW-163**	**DFLAW-164**	**DFLAW-165**
Simulant	**pH 7 DFLAW**			**pH 10 DFLAW**			**pH 12 DFLAW**		
Precip. Agent	None (Control)	Sn(II) (1.5:1)	Sn(II) (1.5:1)	None (Control)	Sn(II) (1.5:1)	Sn(II) (1.5:1)	None (Control)	Sn(II) (1.5:1)	Sn(II) (1.5:1)
Precip. Agent Conc. (g/L)[#]	n/a	0.263	0.265	n/a	0.272	0.280	n/a	0.267	0.267
Contact Time (h)	1.12	1.07	1.07	1.10	1.10	0.92	1.12	1.13	1.13
^{99}Tc (µg/L)	4.80E+03	2.67E+02	<10	4.42E+03	3.21E+03	7.20E+02	4.27E+03	4.16E+03	3.74E+03
^{238}U (µg/L)	1.37E+02	8.99E+01	7.52E+01	1.19E+02	9.87E+01	1.06E+02	1.20E+02	7.31E+01	9.39E+01
Sn (µg/L)	< 10	< 10	< 10	< 10	2.68E+04	2.86E+04	< 10	1.25E+05	1.88E+05
Contact Time (h)	24.12	24.08	24.08	24.08	24.08	23.82	24.12	24.13	24.13
^{99}Tc (µg/L)	4.80E+03	2.67E+02	<10	4.42E+03	3.21E+03	7.20E+02	4.27E+03	4.16E+03	3.74E+03
^{238}U (µg/L)	1.37E+02	8.99E+01	7.52E+01	1.19E+02	9.87E+01	1.06E+02	1.20E+02	7.31E+01	9.39E+01
Sn (µg/L)	< 10	< 10	< 10	< 10	2.68E+04	2.86E+04	< 10	1.25E+05	1.88E+05

[#] Concentration of $SnCl_2$.

Table A-6. Summary of Concentration Data from Stability Testing in pH 10 and 12 DFLAW

Test ID	**DFLAW-151**	**DFLAW-152**	**DFLAW-153**	**DFLAW-154**	**DFLAW-155**	**DFLAW-156**
Precip. Agent	None (Control)	Sn(II) (1.5:1)	Sn(II) (1.5:1)	None (Control)	Sn(II) (1.5:1)	Sn(II) (1.5:1)
Precip. Agent Conc. (g/L)[#]	n/a	0.271	0.271	n/a	0.266	0.268
Initial pH	7.57	7.01	6.97	7.59	7.14	7.22
Final pH (adjusted after 1 h sample)	10.08	9.94	9.94	11.96	12.04	12.11
Contact Time (h)	1.07	1.07	1.07	1.07	1.05	1.07
^{99}Tc (µg/L)	5.01E+03	<10	<10	5.01E+03	<10	2.38E+03
^{238}U (µg/L)	1.33E+02	8.00E+01	6.14E+01	1.32E+02	6.55E+01	8.53E+01
Sn (µg/L)	< 10	< 10	< 10	< 10	< 10	< 10
Contact Time (h)	5.95	5.95	5.95	5.95	5.93	5.93
^{99}Tc (µg/L)	4.93E+03	2.75E+01	2.92E+01	4.89E+03	1.52E+03	3.62E+03
^{238}U (µg/L)	1.29E+02	5.21E+01	4.52E+01	1.33E+02	1.44E+01	2.55E+01
Sn (µg/L)	< 10	1.90E+03	2.03E+03	2.47E+01	1.08E+05	8.48E+04
Contact Time (h)	24.00	24.00	24.02	24.02	24.00	24.00
^{99}Tc (µg/L)	4.87E+03	4.38E+01	4.88E+01	4.89E+03	2.59E+03	4.04E+03
^{238}U (µg/L)	1.32E+02	4.40E+01	3.75E+01	1.34E+02	1.52E+01	2.53E+01
Sn (µg/L)	< 10	6.60E+02	1.02E+03	1.84E+01	1.20E+05	9.28E+04
Contact Time (h)	48.40	48.40	48.42	48.42	48.40	48.40
^{99}Tc (µg/L)	4.85E+03	6.16E+01	7.93E+01	4.90E+03	2.99E+03	4.18E+03
^{238}U (µg/L)	1.28E+02	5.48E+01	3.57E+01	1.37E+02	1.58E+01	2.55E+01
Sn (µg/L)	< 10	3.67E+02	5.43E+02	1.57E+01	1.23E+05	9.67E+04
Contact Time (h)	71.35	71.35	71.35	71.35	71.35	71.35
^{99}Tc (µg/L)	4.83E+03	7.24E+01	1.02E+02	4.98E+03	3.18E+03	4.34E+03
^{238}U (µg/L)	1.28E+02	4.14E+01	3.49E+01	1.34E+02	1.58E+01	2.52E+01
Sn (µg/L)	< 10	2.50E+02	2.18E+02	2.43E+01	1.23E+05	9.15E+04

[#]Concentration of $SnCl_2$.

Distribution:

T. B. Brown, 773-A
M. E. Cercy, 773-42A
D. A. Crowley, 773-43A
D. E. Dooley, 773-A
A. P. Fellinger. 773-42A
S. D. Fink, 773-A
C. C. Herman, 773-A
D. T. Hobbs, 773-A
E. N. Hoffman, 999-W
J. E. Hyatt, 773-A
K. M. Kostelnik, 773-42A
B. B. Looney, 773-42A
D. A. McGuire, 773-42A
T. O. Oliver, 773-42A
F. M. Pennebaker, 773-42A
G. N. Smoland, 773-42A
M. E. Stone, 999-W
A. L. Washington, II, 773-42A
W. R. Wilmarth, 773-A
Records Administration (EDWS)
E. N. Diaz. DOE-ORP
L. Holton, DOE-ORP
W. F. Hamel, DOE-ORP
T. W. Fletcher, DOE-ORP
B. J. Harp, DOE-ORP
B. M. Mauss, DOE-ORP
S. T. Arm, WRPS
P. A. Cavanah, WRPS
T. W. Crawford, WRPS
W. G. Ramsey, WRPS
D. J. Swanberg, WRPS
N. P. Machara, DOE-EM
J. A. Poppiti, DOE-EM
D. J. Koutsandreas, DOE-EM
R. A. Gilbert, DOE-ORP
R. H. Spires, WRPS
M. R. Thorson, WRPS
R. B. Mabrouki, WRPS
V. Jain, 766-H
R. E. Edwards, 766-H
E. J. Freed, 704-S
J. M. Bricker, 704-S
J. S. Contardi, 704-56H
T. L. Fellinger, 766-H
R. T. McNew, 766-H
H. H. Burns, 773-41A
A. D. Cozzi, 999-W
K. M. Fox, 999-W
E. K. Hansen, 999-W
M. R. Poirier, 773-42A
R. R. Seitz, 773-42A
G. P. Flach, 773-42A
K. W. Burnett, DOE-ORP
W. R. Wrzesinski, DOE-ORP