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

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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 again. Alternate disposition of this stream would eliminate recycling of problematic components, and would enable simplified 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.

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 and will not be available until the WTP begins operation, but a simulant has been produced based on models, calculations, and comparison with pilot-scale tests.

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, 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 is very similar to that used for 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.

One of the radionuclides that is volatile and expected to be in greatest abundance in this LAW 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 determining the minimum amount of $SnCl_2$ required to effectively remove the ^{99}Tc, examining the use of an alternate reductant, Fe(II), and examining other variables that may impact the precipitation. Chromium is present in the stream as Cr(VI), and will consume some of the $SnCl_2$ added to reduce the Tc(VII); therefore testing was performed to examine the impact of varying Cr concentrations. The stream is also expected to contain insoluble glass formers. Previous testing had filtered the glass formers from the simulant prior to testing so as not to convolute the results; however, in the actual process it would be beneficial to perform the reductive precipitation with the glass formers present so only one filtration step is necessary. Therefore, testing was performed with simulant

containing the expected glass formers present. In addition, the resulting solids from the precipitation were characterized, and their stability in both the off-gas condensate stream and in a low activity waste (LAW) stream simulant was examined.

Testing results indicated 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. Tests with Fe(II) showed that the removal effectiveness of Fe(II) can be improved with the addition of sodium hydroxide to control the pH; however, the maximum decontamination factor (DF) obtained with Fe(II) under the conditions tested was only about 25, much lower than with Sn(II).

Test results indicated $SnCl_2$ was effective at removing ^{99}Tc at any of the Cr concentrations tested as long as the amount of Cr in the simulant was accounted for when determining the amount of $SnCl_2$ necessary. As little as 1.5 equivalents of $SnCl_2$ relative to the amount of Tc and Cr present has been shown to be sufficient (i.e., 1.5 equivalents of the two electrons from Sn(II) relative to the three electrons needed to reduce Cr(VI) to Cr(III)). In the case of simulant containing no Cr, it was found that 1.5 eq based on Tc alone was not sufficient, indicating another reaction was consuming the $SnCl_2$. The removal of Zn had been observed in other experiments; however the amount of Zn relative to Cr in the simulants containing Cr is relatively low, so the excess 0.5 eq of $SnCl_2$ was likely enough to account for this. However, in the 0 ppm Cr experiment, the Zn concentration is approximately 3x the amount of $SnCl_2$ added when based only on Tc. When 1.5 eq of $SnCl_2$ was added relative to the amount of Zn and Tc, successful removal of Tc was achieved. The presence of glass formers did not affect the reductive precipitation of ^{99}Tc. The testing was performed at room temperature under aerobic conditions, and the ^{99}Tc was removed to below detection within 1 hour in these experiments.

The digested and analyzed solids were found to be predominately Sn, as expected, making up 45 wt% of the solids. Chromium was also present at appreciable concentrations, representing 8.32 wt% of the solids. The precipitated ^{99}Tc accounted for 0.17 wt% of the solids. Mass balance calculations accounted for over 80% of the key elements between the solution and solids analyses.

Stability testing in the SBS/WESP simulant demonstrated that the precipitated solids are stable to reoxidation and dissolution for up to 72 hours, which indicates that a full-scale process could be developed with sufficient time for a solid-liquid separation. However, stability testing of the precipitated solids in LAW simulant showed that the precipitated solids containing the ^{99}Tc redissolve quickly once placed into the LAW simulant. Approximately 94 – 99% of the precipitated Tc had redissolved within one hour after mixing the LAW simulant with the precipitated solids. The precipitated Sn and U also followed a similar trend. The Cr that had precipitated also quickly redissolved (~90% at 1 hour); however, it then appeared that a small amount may have reprecipitated with time with only ~75% in solution after 72 hours.

Additional tasks needed to further develop this technology include examination of scale-up behavior, solid-liquid separation technologies, slurry rheology measurements, corrosion and erosion studies, and slurry storage and immobilization.

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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
DOE	Department of Energy
dpm	Disintegrations per minute
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
NM	Not Measured
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.

The objective of this development task is to evaluate decontamination of this stream using sorbents and precipitation agents so that it can be diverted elsewhere (Figure 1-2). 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 both 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] The preliminary testing of this process has also been documented.[3,4] Other alternative disposal paths could be considered as well, including tank farm storage options.

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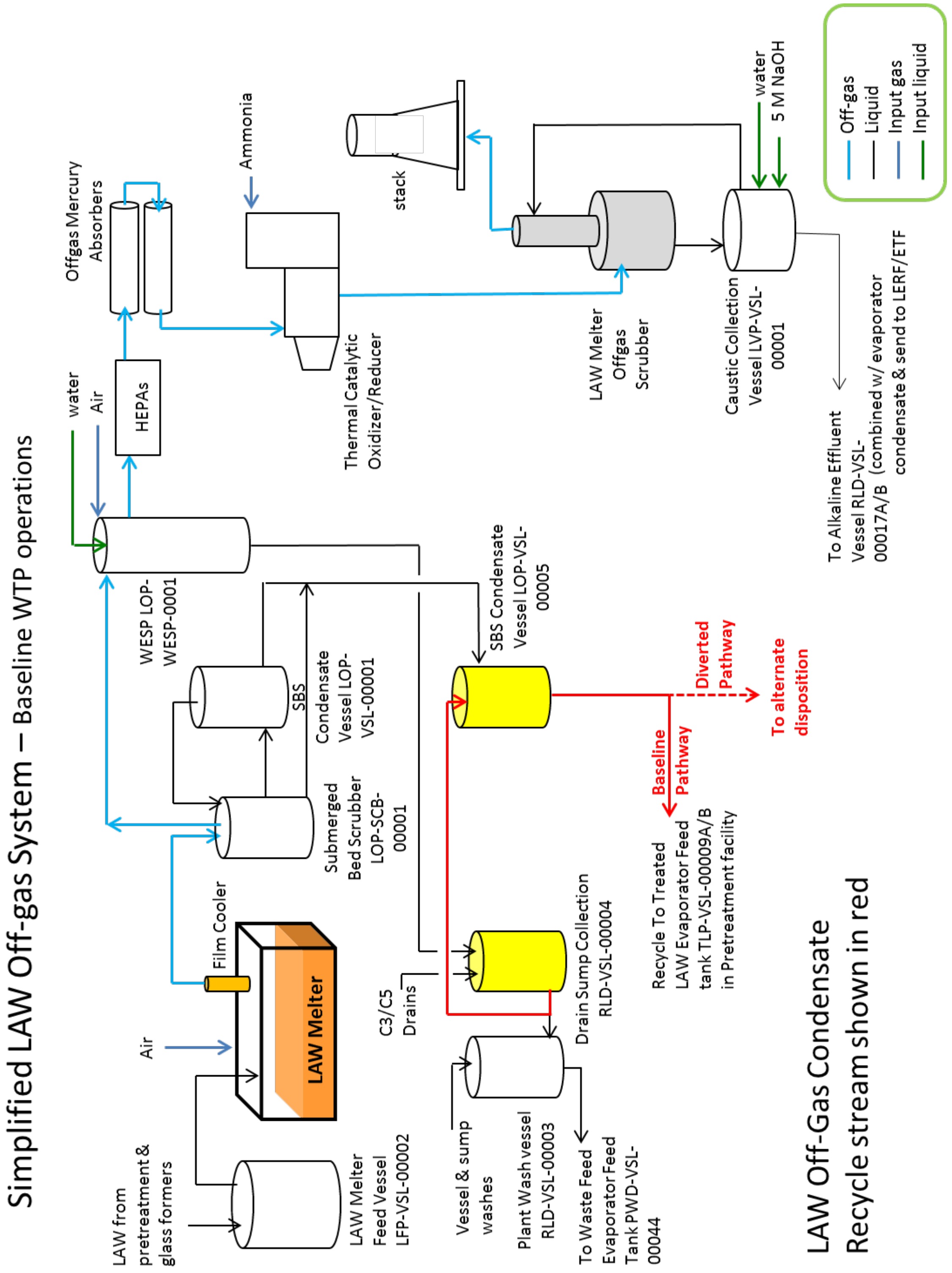
[b] The Actinide Removal Process (ARP) at SRS decontaminates ^{90}Sr and actinides from aqueous tank waste before it is further treated for ^{137}Cs removal by solvent extraction. In ARP, a small amount of Monosodium Titanate (MST) is added to a batch of decanted tank waste supernate and mixed for 6-12 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

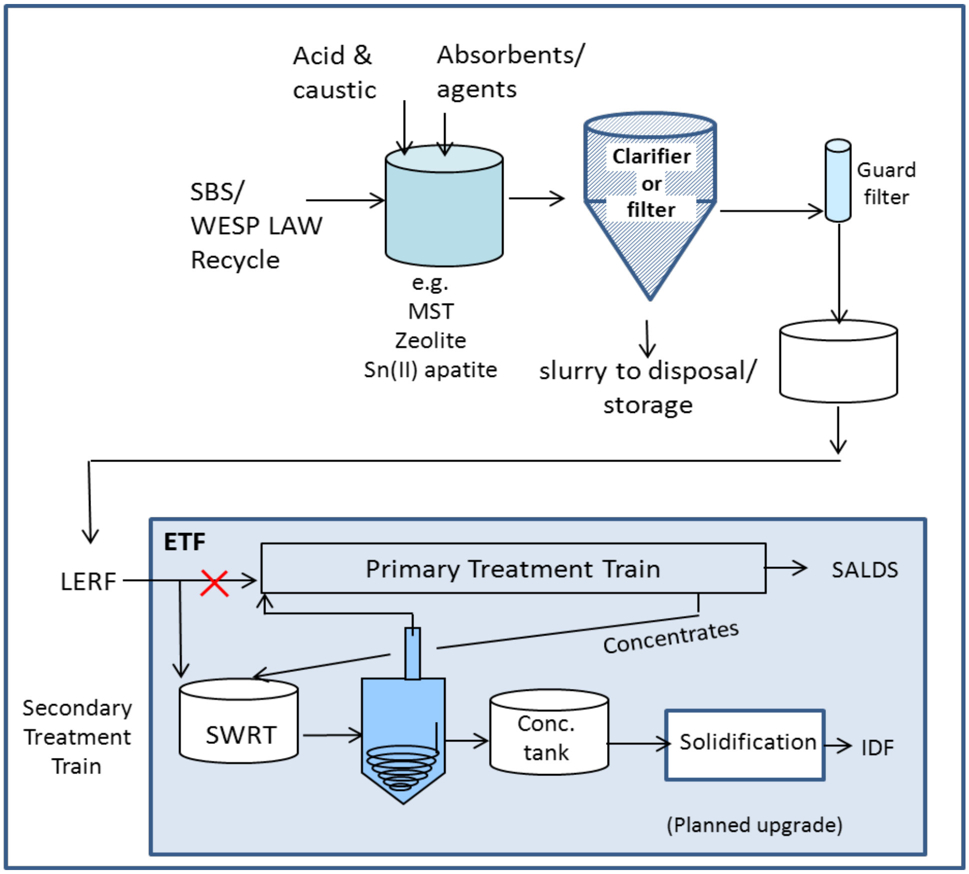


Figure 1-2. Schematic of a Proposed Decontamination Process and Disposition Path of LAW Off-Gas Condensate

1.1 Simulant Formulation Basis

Because this stream is not yet available for characterization, the simulant formulation was based on input from two sources. The projected solution chemistry and radionuclide content was based on version 7.4 of the Hanford Tank Waste Operations Simulator (HTWOS) modeling of the flow sheet[5] performed by WRPS.[6] This model run was for the average composition of this stream for the entire WTP mission (all 177 tanks) and with full integration of all WTP pretreatment processes, such as caustic leaching, oxidative leaching, and cesium ion exchange. More detail on the basis for and synthesis of the simulant has been documented.[3,4,7]

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.[8,9]

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.[10] The LAW glass will be disposed in the IDF. Because ^{99}Tc has a very long half-life and is highly mobile,[11,12] 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 has previously been found effective for precipitating Tc from water samples;[13] 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 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).

$$DF = \frac{C_0}{C_t} \qquad (1)$$

Immobilization and potential disposition pathways will be evaluated 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 elsewhere.[7] The target concentrations of chemicals and radionuclides were derived from the output from the HTWOS calculation, documented in SVF-2732.[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.: SBS/WESP 2014).[4] A second batch of 2 L of simulant (i.d.: SBS/WESP 2015) was also prepared using the amounts shown in Table 2-1. 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 synthesized. 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 formers, and with the nitric acid added during pH adjustment. A 500 mL aliquot (i.d.: SBS/WESP – No Cr) was then removed from the 2 L batch prior to adding the sodium chromate to the remaining 1.5 L. This 500 mL was later subdivided to prepare simulants with 3 different Cr concentrations (0, 30, and 140 ppm). An additional 200 mL aliquot was also removed from the remaining 1.5 L batch after Cr addition to prepare simulant that would not have the glass formers filtered out (i.d.: SBS/WESP w/GFC). The glass formers (Table 2-2) were then added to all three aliquots, and mixed for five days at ambient temperature. These were derived from the overall mission average quantity.[14] Sucrose was excluded because it is destroyed in the melter. The pH of all three solutions was measured to be 8.0 after the 5 days of mixing. The pH of each bottle was then adjusted to approximately 7.3 with the addition of concentrated nitric acid. See Table 2-3 for final pH and amounts of acid used. After pH adjustment, the glass formers were filtered from the 1.3-L and 500-mL aliquots, but were left in the 200-mL aliquot. Samples were analyzed for elemental composition by Inductively Coupled Plasma – Emission Spectroscopy (ICP-ES), anions and ammonium by Ion Chromatography.

Table 2-1. Aqueous Simulant Formulation Targets

Chemical	Formula	Target Mass (g)/L simulant	Target Molarity
Aluminum nitrate nonahydrate	$Al(NO_3)_3{\cdot}9H_2O$	0.400	0.0011
Potassium chloride	KCl	0.219	0.0029
Sodium chloride	NaCl	1.395	0.0239
Sodium fluoride	NaF	3.209	0.0764
Ammonium nitrate	NH_4NO_3	2.820	0.0352
Sodium nitrate	$NaNO_3$	0	0*
Sodium nitrite	$NaNO_2$	0.016	0.0002
Ammonium sulfate	$(NH_4)_2SO_4$	3.220	0.0244
Dibasic sodium phosphate dihydrate	$Na_2HPO_4{\cdot}2H_2O$	0.040	0.0002
Sodium chromate	Na_2CrO_4	0.283[#]	0.0017[#]

*note that nitrate ion is added later as nitric acid during pH adjustment
[#]Sodium chromate added after removal of a 500 mL aliquot

Table 2-2. Target Glass Former 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 Adjustments of Simulants

	SBS/WESP 2015	SBS/WESP – No Cr	SBS/WESP w/GFC
Initial pH	7.97	7.98	8.04
pH after Adjustment	7.23	7.22	7.22
Amt. of HNO_3 Added	0.6308 g	0.2374 g	0.0870 g

2.2 Simulant Spiking with Radionuclides

The prepared simulants were then spiked with the radiotracer solutions shown in Table 2-4. Two aliquots of SBS/WESP 2014 had been previously spiked and results of those analyses previously documented.[4,15] Previous attempts to spike this simulant have shown the $^{239/240}$Pu and ^{241}Am to not be soluble. In an attempt to increase the solubility of these actinides in the SBS/WESP 2015 simulants, the solutions were mixed at 50 °C for 48 hours after spiking. After the 48 hours of heating, the solutions were stirred at ambient temperature for an additional week. Samples were removed and filtered 24 hours, 4 days, and 1 week after heating ceased. 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). Non-radioactive constituents were analyzed as described above. 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	1.16E4
^{238}U	$UO_2(NO_3)_2 \cdot 6H_2O$ aqueous solution (5 mg/mL U)	6.24E-1
$^{239/240}$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	5.79E4
^{99}Tc	Ammonium pertechnetate solution	9.21E4
^{241}Am	^{241}Am aqueous stock solution	5.15E2

2.3 Precipitation Tests – Phases 3 and 4

In general, tests were performed by adding a small amount of each reagent to separate poly bottles, followed by 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. Select optimized samples were also analyzed for Cr, Cs, Sr, and actinides to determine the impact of the Tc-removal process on their solubility. Results are summarized in Section 3, with details in Appendix A.

Tables 2-5 and 2-6 show the test matrix for reagent addition for Phases 3 and 4, respectively. The "phase ratio" indicates the moles of reductant versus the moles of electrons needed to reduce the Cr(VI) to Cr(III). Because Cr(VI) is highly oxidizing, sufficient reductant may be needed to reduce all of the Cr(VI) before it is available to reduce the Tc. Phase 3 tests were designed to test the lower threshold of sufficient Sn(II) for the removal of all ^{99}Tc, and to also examine the effectiveness of ferrous to reduce the ^{99}Tc with the addition of sodium hydroxide to mitigate the drop in pH from the addition of ferrous sulfate. These experiments included tests to determine if the sequence of addition of ferrous or caustic affects the result. Phase 4 tests further increased the amount of sodium hydroxide and also examined a "double strike" of ferrous, i.e., where ferrous is added in two separate aliquots to determine if it affects the result.

Table 2-5. Reagent Test Matrix for Phase 3

Molar Phase Ratio (moles reductant electons:moles oxidizer electrons)	Reagent Quantity	Target Duration (hours)
Sn(II)		
1.5:1	0.8 g/L $SnCl_2$	1
Fe(II)		
2:1	0.61 g/L Fe(II)	6, 24
2:1 + 1 X caustic (Fe(II) first)	0.61 g/L Fe(II) 0.021 M NaOH	6, 24
2:1 + 1 X caustic (caustic first)	0.61 g/L Fe(II) 0.021 M NaOH	6, 24
2:1 + 1.5 X caustic (Fe(II) first)	0.61 g/L Fe(II) 0.032 M NaOH	6, 24

Table 2-6. Reagent Test Matrix for Phase 4

Molar Phase Ratio (moles reductant electons:moles oxidizer electrons)	Reagent Quantity	Target Duration (hours)
Fe(II)		
2:1 + 2 X caustic	0.61 g/L Fe(II) 0.044 M NaOH	6, 24
3:1 + 2 X caustic	0.91 g/L Fe(II) 0.066 M NaOH	6, 24
2:1 + 3 X caustic	0.61 g/L Fe(II) 0.066 M NaOH	6, 24
Double Strike 2:1 followed by 1:1 after 1 h 2 X caustic (based on total Fe(II) to be added, all NaOH added at once)	0.61 g/L Fe(II) 0.31 g/L Fe(II) 0.066 M NaOH	6, 24

2.4 Precipitation Tests – Impact of Cr Concentration

2.4.1 Preparation of Simulant

The baseline SBS/WESP simulant formulation includes 91 ppm Cr, which represents the average value from the projected composition based on version 7.4 of the HTWOS modeling of the flowsheet[5] performed by WRPS;[6] however, this projection also includes a minimum of 34 ppm and a maximum of 139 ppm Cr. Since it is known that the Sn(II) reductant is also consumed by Cr, a series of experiments were performed with simulants targeting 0 ppm, 30 ppm, and 140 ppm Cr.

The SBS/WESP – No Cr simulant described above was used for these experiments. Two 100-mL aliquots of this simulant were spiked with 30 and 140 ppm of Cr by the addition of 0.0096 g and 0.044 g of sodium chromate, respectively. After addition of the sodium chromate the bottles were stirred at ambient temperature overnight. A sample of each solution was then filtered and analyzed by ICP-ES to determine the final Cr concentration.

2.4.2 Precipitation Tests

Precipitation tests were performed by adding the appropriate amount of $SnCl_2{\cdot}2H_2O$ to separate poly bottles, followed by the addition of 19 mL of the appropriate radioactive simulant solution to each. The bottles were then agitated in a shaker oven at ~25 ˚C for the specified time (samples were removed after 1 and 6 hours; however, only the 1 hour samples were analyzed). Each sample was then filtered through a

0.1-µm filter. The filtrate was then analyzed by ICP-MS for ^{99}Tc and ICP-ES for Cr. Results are summarized in Section 3, with details in Appendix A.

Previous testing had shown 1.5 eq of Sn(II) added relative to the amount of Cr and ^{99}Tc to be sufficient to remove essentially all of the ^{99}Tc; therefore that ratio was used for these tests. This ratio is based on the moles of reductant (i.e. Sn(II)) versus the moles of electrons needed to reduce the Cr(VI) to Cr(III) and the Tc(VII) to Tc(IV). Based on insufficient removal of ^{99}Tc in the 0 ppm Cr simulant, an additional experiment was performed using a higher concentration of Sn(II). This higher amount was calculated to provide 1.5 eq of Sn(II) based on the concentrations of ^{99}Tc and Zn. For this calculation it was assumed the Zn could undergo a 2 electron reduction from Zn(II) to Zn(0).

2.5 Precipitation Tests – Impact of Glass Formers

Previous testing has shown the effectiveness of $SnCl_2$ reductive precipitation for the quantitative removal of ^{99}Tc from SBS/WESP simulant; however, all previous testing was performed using simulant that had the glass formers filtered out prior to testing so as not to convolute the results. However, in the actual process, it would be beneficial to perform the $SnCl_2$ reductive precipitation with the glass formers still present, so that only one filtration has to be performed (removing both glass formers and precipitated Tc). These experiments examined the effectiveness of the reductive precipitation in the presence of the glass formers.

Precipitation tests were performed by adding the appropriate amount of $SnCl_2 \cdot 2H_2O$ to separate poly bottles, followed by the addition of 19 mL of the SBS/WESP w/GFC simulant to each. The bottles were then agitated in a shaker oven at ~25 ˚C for the specified time (samples were removed after 1 and 6 hours; however, only the 1 hour samples were analyzed because the reaction was complete). Each sample was then filtered through a 0.1-µm filter. The filtrate was then analyzed by ICP-MS, ICP-ES, gamma spectroscopy, and PuTTA. In addition to the filtered samples, unfiltered samples from the control experiments were also submitted for gamma spectroscopy to determine the amount of ^{85}Sr removed by the glass formers. Results are summarized in Section 3, with details in Appendix A.

2.6 Characterization of Solids

The addition of $SnCl_2$ results in the reductive precipitation of both ^{99}Tc and Cr. In order to characterize the resultant precipitate, a larger scale precipitation reaction was performed and the solids were collected for analysis. For this experiment 1.5 eq (based on Tc and Cr) of $SnCl_2$ was added to 800 mL of the SBS/WESP 2015 simulant described above. After the $SnCl_2$ was added, the mixture was stirred at ambient temperature for 2 hours. After stirring, the contents of the bottle were filtered through a 0.45-µm Nylon filter to collect the solids. A sample of the filtrate was removed for ICP-MS, ICP-ES, and gamma spectroscopy analyses. The solids were then briefly washed with a small volume of water and left to air dry for several days. The air-dried solids were oven dried to a constant weight. The oven-dried solids were then dissolved by hot aqua regia digestion followed by ICP-MS, ICP-ES, gamma spectroscopy and PuTTA analyses. Results are summarized in Section 3, with details in Appendix A.

2.7 Stability of Precipitated Solids to Reoxidation

The successful removal of ^{99}Tc through the reductive precipitation with Sn(II) has been demonstrated. Testing was then performed to examine the stability of the reduced ^{99}Tc to reoxidaiton and redissolution under several conditions. The first set of tests were design to determine the stability of the stream to reoxidation to determine if sufficient time is available to filter or settle the solids prior to redissolution of Tc. The second set of tests determined the stability of the precipitated solids in a simulant of the low activity waste stream to simulate return of the solids to the tank farms as a possible disposal path. For both set of experiments, the solids were prepared by the addition of 1.5 eq of $SnCl_2$ to 40 mL aliquots (duplicate experiments) of the SBS/WESP simulant. The first set of tests used the SBS/WESP 2014 batch of simulant, while the second set used the 2015 batch.

In the first set of tests, after addition of the Sn(II) the bottles were mixed in a 25 °C shaker oven for 72 hours. 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. Samples were removed after 1, 6, 24, 48, and 72 hours. 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 and ICP-ES analyses.

For the second set of tests, after mixing for 1 hour at ~25 °C, the mixtures were transferred to centrifuge tubes and the solids allowed to settle for 1 week. After settling, the supernatant was carefully removed and was replaced with 40 mL of LAW simulant, and the mixtures transferred to 125-mL poly bottles. The composition of the LAW simulant is provided in Table 2-7. The bottles were then mixed in a 25 °C shaker oven and were sampled after 1, 6, 24, 48, and 72 hours of mixing. At each sampling event the bottle was manually shaken to ensure the solids were well mixed. Approximately 4 mL of sample was then filtered through a 0.1-µm syringe filter. An aliquot (3 mL) of the filtrate was then acidified with an equal volume of 5 M HNO_3. The acidified samples were then submitted for ICP-MS, ICP-ES, gamma spectroscopy, and PuTTA analyses.

Results from both sets of tests are summarized in Section 3, with details in Appendix A.

Table 2-7. Composition of LAW Simulant

Constituent	Molarity
Na^+	7.8
K^+	0.051
Al^{3+}	0.48
Cl^-	0.066
F^-	0.049
SO_4^{2-}	0.13
PO_4^{2-}	0.076
NO_2^-	0.88
NO_3^-	2.53
CO_3^{2-}	0.43
OH^-	2.43
TOC Total (acetate)	0.12 (0.060)

2.8 Quality Assurance

This test program is described in the Task Technical and Quality Assurance Plan for Developing a Flowsheet for Off-Gas Process Liquids from the Hanford Low Activity Waste Vitrification Process.[16] 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 SBS/WESP 2014 Simulant

(Note: results were previously reported,[4] but are included here for completeness)

Results of the average and standard deviation of the duplicate chemical analysis of the neutralized, filtered SBS/WESP 2014 simulant are shown in Table 3-1. These match the target compositions reasonably well, with the exception of nitrate which was low. The small variations are not expected to impact results obtained here. (The component expected to most influence these test results is chromium, since it would oxidize the reductant, preventing its reaction to remove technetium.) Note that the HTWOS model output is not charge balanced, so it is not possible to create an identical solution. Although boron, lithium, silicon, and zinc were not in the aqueous simulant preparation, they are present in the solution due to addition of the glass former solids and their subsequent dissolution. The sulfur analysis by ICP-ES indicated higher than expected, but the sulfate analysis by IC indicated it is close to the target. The target concentration for soluble aluminum was ~28 mg/L, based on computer modeling and comparison to the pilot scale melter off-gas condensate sample analyses.[17] However, attempts to dissolve the aluminum (added as 0.4 g/L aluminum nitrate nonahydrate) by manipulation of the sequence of chemical addition and temperature were unsuccessful.

Table 3-1. Neutralized SBS/WESP 2014 Simulant Filtrate Composition

Component	Avg. Concentration (mg/L)	Std. Dev.	HTWOS projection (avg. SVF-2732) (mg/ L)
Al	<1.0		28
B	242	8.8	GFC[#]
Ca	1.1	0.014	GFC[#]
Cr	89.9	0.86	91
Fe	<1.0		GFC[#]
K	103	0.54	115
Li	80.9	0.80	GFC[#]
Mg	<1.0		GFC[#]
Na	2.28E3	14	2.29E3
P	<1.0		7 (as PO_4^{3-})
S	1.26E3	15	780 (as SO_4^{2-})
Si	55.0	0.42	GFC[#]
Ti	<1.0		GFC[#]
Zn	14.6	0.15	GFC[#]
Zr	<1.0		GFC[#]
F^-	1.41E3	0*	1.45E3
Cl^-	945	1.4	950
NO_2^-	<500		10.7
NO_3^-	3.20E3	57	5.53E3
SO_4^{2-}	2.23E3	14	2.34E3
PO_4^{3-}	<31 (based on P)		21.5
NH_4^+	1.54E3**		1.51E3

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

**analysis of a single sample

[#] Glass Forming chemical; minimal HTWOS projected concentration

3.1.2 SBS/WESP 2015 Simulants

Results of the average and standard deviation of the duplicate chemical analysis of the neutralized, filtered simulants prepared in 2015 are shown in Table 3-2 (see Section 2.1 for a description of the simulant preparations and identities). 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 Na^+ concentration in the simulants was ~20% below the target, and the F^- was approximately 10% low. The nitrate concentration in each of the simulants is only about half of the HTWOS projected concentration, but that target is unrealistic because of the charge imbalance. Sodium nitrate was not added to this optimized formulation, and instead comes mainly from the nitric acid added during pH adjustment. The nitrate concentration is slightly lower than the SBS/WESP 2014 simulant. Similar to the SBS/WESP 2014 simulant, the Al failed to reach the target concentration. None of these differences are expected to impact the test outcome because even these concentrations greatly exceed those of the redox-active species (Cr, Sn, Tc). Therefore, if any of these did interfere with the reaction, their concentrations are more than adequate to identify the interference.

Table 3-2. Neutralized Simulant Filtrate Compositions

Component	SBS/WESP 2015 Avg. (mg/L)	SD	SBS/WESP – No Cr Avg. (mg/L)	SD	SBS/WESP w/GFC Avg. (mg/L)	SD		HTWOS projection (avg. SVF-2732) (mg/L)
Al	< 0.500	n/a	< 0.500	n/a	< 0.500	n/a		28
B	158	2.1	164	0.71	165	3.5		GFC$^{\#}$
Ca	0.970	0.009	0.932	0.012	0.914	0.012		GFC$^{\#}$
Cr	93.3	2.7	<0.100	n/a	95.7	0.71		91
Fe	<0.100	n/a	<0.100	n/a	<0.100	n/a		GFC$^{\#}$
K	121	0.71	122	6.4	118	0*		115
Li	75.6	0.64	77.0	2.6	83.3	0.14		GFC$^{\#}$
Mg	<0.100	n/a	<0.100	n/a	<0.100	n/a		GFC$^{\#}$
Na	1780	0*	1775	35.4	1815	21.2		2.29E3
P	2.00	0*	1.19	0.014	1.90	0*		7 (as PO_4^{3-})
S	806	2.1	809	0.71	812	3.5		780 (as SO_4^{2-})
Si	52.3	1.5	52.6	0.071	52.0	0.57		GFC$^{\#}$
Ti	<0.100	n/a	<0.100	n/a	<0.100	n/a		GFC$^{\#}$
Zn	20.1	0.64	17.1	0*	20.5	0.14		GFC$^{\#}$
Zr	<0.500	n/a	<0.500	n/a	<0.500	n/a		GFC$^{\#}$
F^-	1295	7.1	1290	14.1	1300	0*		1.45E3
Cl^-	965	35.4	953	0.71	952	0*		950
NO_2^-	<100	n/a	<100	n/a	<100	n/a		10.7
NO_3^-	2420	14.1	2410	28.3	2520	0*		5.53E3
SO_4^{2-}	2185	7.1	2180	14.1	2340	0*		2.34E3
PO_4^{3-}	<100	n/a	<100	n/a	<100	n/a		21.5
NH_4^+	1400**	n/a	1380**	n/a	1400**	n/a		1.51E3

*Standard Deviation of zero indicates the two analysis results were identical
**analysis of a single sample
$^{\#}$Glass Forming chemical; minimal HTWOS projected concentration

3.2 Radionuclide Solubilities

3.2.1 SBS/WESP 2014 Simulant

Two separate aliquots of the 2014 batch of SBS/WESP simulant were spiked with radionuclides at separate times. Aliquot "A" was used for the Phase 3 precipitation experiments, while aliquot "B" was used for the Phase 4 precipitation experiments as well as the first set of stability experiments. The characterization of the spiked samples has been previously reported,[4,15] but the results are shown below in Table 3-3 for completeness.

Table 3-3. SBS/WESP 2014 Simulant Radionuclide Compositions

	Aliquot A			**Aliquot B**		
Isotope	**Activity (dpm/mL)**	**Reported Method Uncertainty**	**% of Target Activity**	**Activity (dpm/mL)**	**Reported Method Uncertainty**	**% of Target Activity**
^{85}Sr	5.94E4	5.0%	103	4.85E4	5.0%	84
^{99}Tc	7.59E4 (2.01 mg/L)	20%	82	6.19E4 (1.64 mg/L)	20%	67
^{137}Cs	2. 61E4	5.0%	225	1.20E4	5.0%	103
^{238}U	5.65E-1 (0.758 mg/L)	20%	91	4.43E-1 (0.594 mg/L)	20%	72
$^{239/240}$Pu	8.36E0	32.7%	9.9	5.83E0	33.5%	6.9
^{241}Am	<5.66E1	mda	<11	NM	n/a	n/a

mda = minimum detectable activity
NM = not measured

3.2.2 SBS/WESP 2015 Simulants

In an attempt to increase the solubility of the actinides, specifically Pu and Am, the 2015 simulants were heated to 50 °C for 48 hours after spiking. Samples were then removed, filtered and analyzed 24 hours, 4 days, and 1 week after heating had ceased. Tables 3-4 through 3-6 show the radionuclide activities in the three simulants. 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. The ICP-MS analyses (Tc and U) are from the 24 hour samples, while the remaining results are from the 1 week samples. There was no measureable change in activities between the 24 hour, 4 day, and 1 week samples. Despite the heating, the ^{241}Am and $^{239/240}$Pu remain insoluble in these simulants.

The other radionuclide activities were reasonably close to the target values in all three simulants with the following exceptions. The ^{137}Cs activity was consistently ~30% low across all three simulants, indicating the activity of the stock was likely lower than expected. The simulant containing the glass formers had ^{85}Sr and U levels below the target, likely due to their removal by sorption onto the glass formers that were removed by filtration prior to analysis.

The ^{85}Sr activity in the SBS/WESP w/GFC simulant was only ~50% of the target value at the time of analysis. It was speculated that this was due to ^{85}Sr being removed by the glass formers. To confirm this speculation, control samples during the effect of glass former experiments were submitted both filtered and unfiltered for gamma analysis to determine the total ^{85}Sr versus the soluble ^{85}Sr activity. Gamma analysis of the unfiltered simulant indicated a ^{85}Sr activity of 5.76×10^4 dpm/mL, 99.4% of the target value, which confirms that the glass formers removed it. The ^{241}Am, which was insoluble in the simulant, was also detected in the unfiltered sample with an activity of 1.07×10^3 dpm/mL, 207% of the target, confirming that it was spiked correctly, but not soluble. The ^{137}Cs activity was the same between the filtered and unfiltered samples, indicating no ^{137}Cs is removed by the glass formers, as expected.

Table 3-4. SBS/WESP 2015 Simulant Radionuclide Composition

Isotope	Activity (dpm/mL)	Reported Method Uncertainty	% of Target Activity
^{85}Sr	5.17 x 10^4	5.0%	89
^{99}Tc	7.65 x 10^4 (2.03 mg/L)	20%	83
^{137}Cs	7.68 x 10^3	5.0%	66
^{238}U	0.629 (0.843 mg/L)	20%	102
$^{239/240}$Pu	< 5.68	mda	< 6.8
^{241}Am	< 30.9	mda	< 6.0

mda = minimum detectable activity

Table 3-5. SBS/WESP – No Cr Simulant Radionuclide Composition

Isotope	Activity (dpm/mL)	Reported Method Uncertainty	% of Target Activity
^{85}Sr	5.94 x 10^4	5.0%	103
^{99}Tc	7.32 x 10^4 (1.94 mg/L)	20%	79
^{137}Cs	7.88 x 10^3	5.0%	68
^{238}U	0.615 (0.825 mg/L)	20%	100
$^{239/240}$Pu	< 10.2	mda	< 12
^{241}Am	< 31.6	mda	< 6.1

mda = minimum detectable activity

Table 3-6. SBS/WESP w/GFC Simulant Radionuclide Composition

Filtered Sample			
Isotope	**Activity (dpm/mL)**	**Reported Method Uncertainty**	**% of Target Activity**
^{85}Sr	2.63 x 10^4	5.0%	45
^{99}Tc	9.04 x 10^4 (2.40 mg/L)	20%	98
^{137}Cs	7.98 x 10^3	5.0%	69
^{238}U	0.393 (0.527 mg/L)	20%	64
$^{239/240}$Pu	< 0.364	mda	< 0.43
^{241}Am	< 68.1	mda	< 13
Unfiltered Sample			
Isotope	**Activity (dpm/mL)**	**Reported Method Uncertainty**	**% of Target Activity**
^{85}Sr	5.76 x 10^4	5.0%	99
^{137}Cs	8.09 x 10^3	5.0%	70
^{241}Am	1.07 x 10^3	5.0%	207

mda = minimum detectable activity

3.3 Phase 3 and 4 Precipitation Experiments

Results of the precipitation tests are shown in Tables 3-7 and 3-8. Details of the test results can be found in Appendix A. Analysis of the Tc and U were done by ICP-MS. If the target minimum Tc DF (100) was achieved, samples were also submitted for analysis of the other radionuclides.

In the Phase 3 tests, the Sn(II) reducing agent was demonstrated at only 1.5 eq relative to the Cr(VI) concentration. In these experiments ^{99}Tc was removed to below detection limit values, with a DF of > 204 within 1 hour. For the Fe(II) reducing agent, without the addition of NaOH to control the pH, the addition of $FeSO_4$ causes a drop in pH from ~7.8 to ~5.5. In these tests, no Tc was removed. The addition of NaOH to increase the pH does result in some removal of the Tc, although not to the extent that Sn(II) does. The maximum Tc DF obtained in these experiments was 17.8 after 6 hours with 2:1 Fe(II) + 1 X caustic. In all cases, however, the Tc decreased at the 24 hour sample time, indicating release of Tc back into solution. These observations guided testing in Phase 4, which tested increased amounts of

NaOH, along with a double strike of Fe(II), where a second aliquot of Fe(II) was added 1 hour after the first.

Results from the Phase 4 tests (Table 3-8) showed improvement in the Tc DF with the double strike of Fe(II), reaching an average DF of 26.7 after 6 hours, but dropping to ~7.7 at 24 hours. Although improvements were seen over previous tests with Fe(II), the level of ^{99}Tc removal does not approach that obtained using stannous chloride as the reductant.

Table 3-7. Average Decontamination Factors for Phase 3 Experiments

	Sn(II) 1.5:1	**Fe(II) 2:1**	**Fe(II) 2:1 + 1 X caustic (Fe 1st)**	**Fe(II) 2:1 + 1 X caustic (NaOH 1st)**	**Fe(II) 2:1 + 1.5 X caustic (Fe 1st)**
1 or 6 h Tc DF*	> 204 (0)	1.00 (0.03)	13.2 (6.53)	11.2 (0.31)	10.3 (1.31)
1 or 6 h U DF*	1.30 (0.05)	1.02 (0.01)	3.39 (0.14)	3.33 (0.04)	3.15 (0.04)
1 h Cr DF	65.9 (3.34)	NM	NM	NM	NM
1 h Sr DF	6.29 (2.16)	NM	NM	NM	NM
1 h Cs DF	1.00 (0.00)	NM	NM	NM	NM
1 h Pu DF	25.5 (12.6)$^\#$	NM	NM	NM	NM
24 h Tc DF	NM	1.00 (0.01)	5.70 (0.78)	5.67 (0.17)	4.73 (0.16)
24 h U DF	NM	0.99 (0.00)	4.28 (0.21)	3.82 (0.03)	3.82 (0.04)
Final pH	*6.67 (0.05)*	*5.56 (0.04)*	*8.00 (0.07)*	*8.07 (0.01)*	*8.60 (0.04)*

NM = not measured

Value in parentheses indicated standard deviation of replicate trials.

*First data point at 1 h for Sn(II) experiment and 6 h for Fe(II) experiments.

$^\#$Replicate trials gave significantly different results with one being below detection limit, DF values were 16.6 and >34.4.

Table 3-8. Average Decontamination Factors Obtained in Phase 4 Experiments

	Double Strike (2:1 + 1:1) Fe(II) + 2 X caustic	**Fe(II) 2:1 + 2 X caustic**	**Fe(II) 3:1 + 2 X caustic**	**Fe(II) 2:1 + 3 X caustic**
6 h Tc DF	26.7 (1.22)	10.7 (3.75)	15.0 (14.1)$^\#$	5.07 (1.75)
6 h U DF	5.24 (0.30)	2.64 (0.44)	3.49 (0.25)	2.66 (0.34)
24 h Tc DF	7.75 (0.82)	4.76 (0.76)	4.04 (0.66)	3.39 (0.54)
24 h U DF	6.68 (0.25)	3.32 (0.57)	4.24 (0.22)	3.14 (0.43)
Final pH	*9.06 (0.03)*	*8.83 (0.02)*	*9.07 (0.01)*	*9.24 (0.00)*

Value in parentheses indicates standard deviation of replicate trials.

$^\#$Replicate trials gave significantly different results; DF values were 25.0 and 5.03.

3.4 Impact of Cr Concentration

Two 100-mL aliquots of the SBS/WESP – no Cr were spiked to target levels of 30 ppm and 140 ppm Cr by the addition of sodium chromate. ICP-ES analyses of the simulants after Cr addition show Cr concentrations of 28.2 ppm and 122 ppm, which represent 94% and 87% of the target values, respectively. These two simulants, along with the 0 ppm Cr simulant were used for the precipitation experiments. For the precipitation experiments, 1.5 eq of $SnCl_2$ were added relative to the equivalents of electrons needed to reduce the Cr and Tc (2.25 moles/mole). This corresponded to $SnCl_2$ concentrations of 0.0105 g/L, 0.24 g/L, and 1.01 g/L for the 0, 28, and 122 ppm Cr solutions. Table 3-9 provides the results of these experiments.

Table 3-9. Average Decontamination Factors Obtained in Variable [Cr] Experiments

1-h DF	0 ppm Cr Simulant			Low Cr Simulant (28 ppm)	High Cr Simulant (122 ppm)
	Expt. 1	Expt. 2	Expt. 3		
Tc DF	39.7 (53.6)[#]	1.44 (0.07)	> 186 (0.00)	179 (14.7)[$]	> 189 (0.00)
U DF	1.02 (0.00)	1.02 (0.00)	1.04 (0.00)	1.20 (0.01)	1.28 (0.07)
Cr DF	n/a	n/a	n/a	> 62.2 (0.00)	73.1 (6.97)
Zn DF	2.10 (0.85)	NM	2.31 (0.10)	23.8 (3.23)	13.6 (6.23)

NM = not measured

Value in parentheses indicates standard deviation of replicate trials.

[#] Replicate trials gave very different results, DF values of 77.6 and 1.80.

[$] One replicate was below detection limit, DF values of 169 and >190.

Results of these experiments showed successful removal of ^{99}Tc in both the low and high Cr concentration simulants. Small amounts of U were also removed in these experiments, as has been seen in prior work with $SnCl_2$ reductive precipitation.[4] As expected, Cr was also removed from the simulant through reduction of the Cr(VI) to Cr(III) and precipitation as the oxide (Cr_2O_3). The results from the 0 ppm experiments (Expt. 1) were not consistent between the replicate trials, and were therefore repeated (Expt. 2).

When the 0 ppm Cr experiments were repeated with 1.5 eq of $SnCl_2$ based upon the electrons needed for reduction of Tc, little Tc was removed (Expt. 2). As seen in Table 3-9, the addition of $SnCl_2$ appears to remove Zn in addition to the Cr and ^{99}Tc. The mechanism for Zn removal is unknown; however, it was speculated that perhaps Zn is consuming the $SnCl_2$ added in the 0 ppm Cr experiments. In simulants containing Cr, the Cr concentration is much higher than Zn, and therefore the 1.5 eq based on Tc and Cr likely provides sufficient Sn(II) for some to be consumed by the Zn. However, in the 0 ppm Cr simulant, the Zn concentration is approximately three times the amount of $SnCl_2$ added. To examine this, experiments were repeated with the 0 ppm Cr simulant increasing the amount of $SnCl_2$ from 0.0105 g/L (in Expts. 1 and 2) to 0.059 g/L (Expt. 3). The 0.059 g/L represents 1.5 eq of $SnCl_2$ relative to Tc and Zn, assuming a 2 electron reduction of the Zn. Results showed that 0.059 g/L $SnCl_2$ is sufficient to quantitatively remove the Tc from this simulant.

3.5 Effect of Glass Formers

Results from testing of $SnCl_2$ reductive precipitation in the presence of glass formers are shown in Table 3-10. In these experiments $SnCl_2$ was added at a concentration of 0.79 g/L, which is 1.5 eq relative to the Cr and Tc concentrations. In addition to ICP-MS and ICP-ES analyses to determine the Tc and Cr concentrations, respectively, samples were also submitted for gamma spectroscopy analysis to monitor the behavior of the Cs, Sr, and Am under these conditions. As discussed in Section 3.2, the glass formers removed some of the Sr and U. Samples of the control tests, without $SnCl_2$, were analyzed both filtered and unfiltered.

The results from these experiments showed that the presence of glass formers in the simulant did not affect the reductive precipitation of the ^{99}Tc with $SnCl_2$. The ^{99}Tc was removed to below the detection limit within 1 hour. The $SnCl_2$ also removed the Cr to below the detection limit, with a DF of >114.

The addition of $SnCl_2$ appeared to cause some of the U that had either precipitated or been removed by the glass formers to redissolve, as the concentrations were slightly higher in the test samples than in the controls, resulting in DF values of less than 1. The [U] measured after initial spiking was 527 μg/L (64% of the target). Spiking of the other simulants without glass formers had resulted in U concentrations close to the target values, so it was believed some of the U was removed from solution by the glass formers. The control samples in these tests measured an average of 414 μg/L U, indicating additional U had precipitated or been removed by the glass formers since the initial spiking. The [U] in the test samples with $SnCl_2$ measured an average of 580 μg/L.

A similar effect was seen with Zn, where the addition of $SnCl_2$ appeared to increase the soluble Zn concentration. The Zn present in the simulant is due to partial dissolution of the zinc oxide glass former when the aqueous phase is mixed with the glass formers initially during simulant preparation. Since the glass formers were not filtered out of this simulant, it appears the addition of $SnCl_2$ caused additional dissolution of the zinc oxide, likely due to both a small change in the solution pH and the Zn in the excess zinc oxide glass former dissolving to replace that removed by the reduction. This increase in concentration in the test bottles resulted in DF values of less than 1.

A small amount of ^{85}Sr appeared to have been removed in the $SnCl_2$ tests, reaching an average DF of 1.23. There was no measurable removal of ^{137}Cs.

Table 3-10. Average Decontamination Factors in SBS/WESP w/GFC Simulant

	1-h DF
Tc DF	> 238 (0.00)
U DF	0.71 (0.00)
Sr DF	1.23 (0.03)
Cs DF	1.06 (0.01)
Cr DF	> 114 (0.00)
Zn DF	0.10 (0.00)

Value in parentheses indicates standard deviation of replicate trials.

3.6 Characterization of Solids

To generate sufficient solids to allow for digestion and characterization, a larger scale (800 mL) precipitation was performed with 1.5 eq of $SnCl_2$ relative to Tc and Cr (0.77 g/L $SnCl_2$) using the SBS/WESP 2015 simulant. Assuming the reductive precipitation results in the formation of the following solids: Cr_2O_3, SnO_2, and TcO_2, this reaction should produce 0.60 g of total solids. After air-drying the product collected, the total mass of solids was 0.7870 g. This sample was then oven dried at 115 °C for approximately 1.5 hours, until reaching a constant weight of 0.7443 g. Two samples of the solids were then independently digested in aqua regia, and the resulting solutions were analyzed by ICP-MS, ICP-ES, gamma spectroscopy, and PuTTA analyses.

Table 3-11 provides the decontamination factors obtained after the precipitation reaction. These DF values are consistent with previous experiments, where Tc is removed to below detection limit values rapidly.

Table 3-11. Decontamination Factors Obtained After Precipitation

	2-h DF
Tc DF	> 203
U DF	1.29
Sr DF	6.02
Cs DF	0.98
Cr DF	95.7
Zn DF	30.4

Table 3-12 provides the analysis results from the digested solids. As expected, a large portion of the mass of the precipitated solids is Sn (45 wt%), followed by Cr (8.32 wt%). The precipitated ^{99}Tc accounts for 0.17 wt% of the solids. Other elements, such as B, K, and Na are likely present due to the drying of residual simulant on the solids. The solids were rinsed briefly with water after filtering; however, this evidently did not remove all of the residual simulant. This also partially explains the additional mass above the theoretical amount of solids expected to be produced. Table 3-13 provides a summary of the mass balance for the key elements. With the exception of Zn, the mass balance for all of the other key elements was greater than 80%. Some of the Sn would have remained soluble as has been previously observed,[3] but this has been accounted for in the calculation. However, some of the precipitated elements could have also dissolved and been lost to the filtrate during the brief washing of the solids. The starting amounts were based on the original analysis of the simulant several months prior to these experiments. It is possible that some of the Zn precipitated from solution after the original analysis, and the starting Zn concentration was actually lower at the start of this experiment. This would also explain the higher Zn DF compared to what is normally observed.

Table 3-12. Composition of Digested Solids

Element	Average	Std. Dev.	wt%
^{99}Tc (µg/g)	1.75E+03	4.95E+01	0.17
Sn (µg/g)	4.50E+05	6.55E+03	45.0
^{238}U (µg/g)	1.69E+02	1.41E+00	0.02
B (µg/g)	2.64E+03	5.66E+01	0.26
Ca (µg/g)	1.28E+02	9.19E+00	0.01
Cr (µg/g)	8.32E+04	1.70E+03	8.32
K (µg/g)	4.75E+02	1.98E+01	0.05
Na (µg/g)	2.31E+03	1.13E+02	0.23
Si (µg/g)	4.41E+03	2.97E+02	0.44
Zn (µg/g)	8.16E+03	1.41E+02	0.82
^{85}Sr (dpm/g)*	2.20E+07	1.48E+05	n/a
^{137}Cs (dpm/g)	2.31E+04	3.32E+03	n/a
^{241}Am (dpm/g)	2.19E+04#	n/a	n/a
$^{239/240}$Pu (dpm/g)	6.74E+03	2.01E+03	n/a
$^{239/240}$Pu (µg/g)	4.30E+01	1.28E+01	0.004

*Decay corrected to date of original simulant preparation.
#Single replicate, the other sample was below detection limit (<7.28E+04 dpm/g).

Table 3-13. Mass Balance from Solids Precipitation and Characterization

Element	Starting Amount (µg)	Amount in Solution (µg)	Avg. Amount in Solids (µg)	Total (µg)	% of Starting Amount
^{99}Tc	1.62E+03	< 8.00E+00	1.30E+03	1.31E+03	80.6%
Sn	3.88E+05	4.57E+03	3.35E+05	3.39E+05	87.4%
U	6.74E+02	5.22E+02	1.26E+02	6.48E+02	96.1%
Cr	7.46E+04	7.80E+02	6.19E+04	6.27E+04	84.0%
Zn	1.60E+04	5.28E+02	6.07E+03	6.60E+03	41.2%

3.7 Stability of Precipitated Solids

In order to examine the stability of the precipitated ^{99}Tc to reoxidation and redissolution in the off-gas condensate, experiments were performed to monitor the soluble ^{99}Tc concentration over a period of 72 hours. These experiments were performed in bottles with excess head space to ensure there was sufficient oxygen to allow for the oxidation of the ^{99}Tc. In addition, the bottles were opened twice daily to replenish the air if it was consumed. Results, shown in Table 3-14, demonstrated the precipitated Tc is stable to reoxidation for at least 72 hours. The soluble ^{99}Tc concentration remained below the method detection limit for the duration of the experiment. The reduced and precipitated Cr also resisted reoxidation. The U that was removed during the precipitation remained precipitated, and in one experiment it appeared additional U continued to precipitate over the test period.

Table 3-14. Results of Stability Tests in SBS/WESP Simulant

Sample Time	Tc DF	U DF	Cr DF	
			Trial 1	Trial 2
1 h	> 164 (0)	1.40 (0.09)	142	377
6 h	> 162 (0)	1.43 (0.19)	175	452
24 h	> 162 (0)	1.54 (0.32)	201	> 777
48 h	> 163 (0)	1.75 (0.55)	269	> 769
72 h	> 161 (0)	1.89 (0.76)	248	> 723

One possible disposal path for the separated solids after reductive precipitation of the ^{99}Tc would be return to the tank farms. Therefore, tests were performed to examine the stability of the precipitated solids in a low activity waste (LAW) simulant. Solids were first precipitated from the SBS/WESP 2015 simulant by the addition of 1.5 eq of $SnCl_2$ (0.77 g/L). After allowing the solids to settle from solution for approximately 1 week, the supernatant was removed and a sample was analyzed to determine the extent of precipitation. The decanted supernatant was then replaced with an equal volume of LAW simulant. Approximately 5 mL of decontaminated SBS/WESP remained with the solids after settling, and therefore the final solution volume was approximately 45 mL after the addition of 40 mL of LAW simulant to each test. Table 3-15 shows the decontamination factors obtained at the end of the settling period. The ^{99}Tc DFs were lower than what is typically obtained, indicating that perhaps some of the initially precipitated ^{99}Tc reoxidized and redissolved during the settling period, or, more likely, poorer solid-liquid separation occurred during decanting versus filtering.

Table 3-15. Decontamination Factors Obtained after Initial $SnCl_2$ Precipitation and Solids Settling

	Trial 1	Trial 2
Tc DF	36.2	23.0
U DF	1.17	1.23
Sr DF	2.42	2.29
Cs DF	0.84	1.04
Cr DF	29.8	13.6
Zn DF	15.8	15.5

Results from the leaching are provided in Table 3-16. The first row of Table 3-16 indicates the calculated concentration that should be obtained if 100% of the precipitated solids redissolve (100% leached concentration). The remaining rows include the measured concentrations along with the fraction of the 100% leached concentration obtained. These results show that nearly all of the ^{99}Tc that precipitated redissolves almost immediately (at least within 1 hour) upon contact with the LAW simulant. The precipitated U and Sn also redissolve. Slightly lesser amounts of the precipitated Cr appear to redissolve, with some evidence of reprecipitation at longer times. The Cr concentration appears to reach a maximum in the 1 hour samples (See Figure 3-1). The Zn followed a similar trend to the Cr, although the initial redissolution was to a lesser extent.

Table 3-16. Leaching of Precipitated Solids in LAW Simulant

	Tc (µg/L)		U (µg/L)		Sn (µg/L)		Sr (dpm/mL)		Cr (mg/L)		Zn (mg/L)	
	Trial 1	Trial 2	Trial 1	Trial 2	Trial 1	Trial 2	Trial 1	Trial 2	Trial 1	Trial 2	Trial 1	Trial 2
100% Leached Conc.	*1.76E3*	*1.73E3*	*190*	*216*	*4.15E5*	*4.15E5*	*2.94E4*	*2.84E4*	*80.5*	*77.6*	*16.8*	*16.8*
0 h Conc. (% Leached)	6.21 (0)	9.79 (0)	79.9 (0)	76.1 (0)	2.82E3 (0)	3.08E3 (0)	2.37E3 (0)	2.51E3 (0)	0.348 (0)	0.760 (0)	0.141 (0)	0.143 (0)
1 h Conc. (% Leached)	1.74E3 (98.8)	1.62E3 (93.7)	187 (98.5)	212 (97.9)	4.50E5 (109)	4.02E5 (96.8)	2.18E4 (74.3)	2.44E4 (86.1)	73.4 (91.2)	69.8 (89.9)	9.78 (58.1)	9.76 (58.0)
6 h Conc. (% Leached)	1.72E3 (97.5)	1.71E3 (98.6)	188 (99.3)	203 (93.8)	4.52E5 (109)	4.14E5 (99.8)	2.26E4 (77.1)	2.56E4 (90.2)	72.2 (89.7)	69.4 (89.4)	9.82 (58.3)	9.66 (57.4)
24 h Conc. (% Leached)	1.75E3 (99.7)	1.68E3 (96.7)	186 (98.1)	203 (93.7)	4.55E5 (110)	4.12E5 (99.3)	2.22E4 (75.7)	2.46E4 (86.7)	67.2 (83.5)	65.8 (84.8)	8.50 (50.5)	8.70 (51.7)
48 h Conc. (% Leached)	1.72E3 (97.9)	1.63E3 (93.8)	186 (97.9)	206 (95.1)	4.53E5 (109)	4.07E5 (98.0)	2.21E4 (75.3)	2.52E4 (88.7)	63.4 (78.8)	61.4 (79.1)	7.52 (44.7)	7.36 (43.8)
72 h Conc. (% Leached)	1.73E3 (98.3)	1.64E3 (94.6)	188 (98.9)	206 (95.4)	4.49E5 (108)	4.13E5 (99.4)	2.16E4 (73.7)	2.44E4 (85.8)	60.2 (74.8)	58.8 (75.8)	6.68 (39.7)	6.78 (40.3)

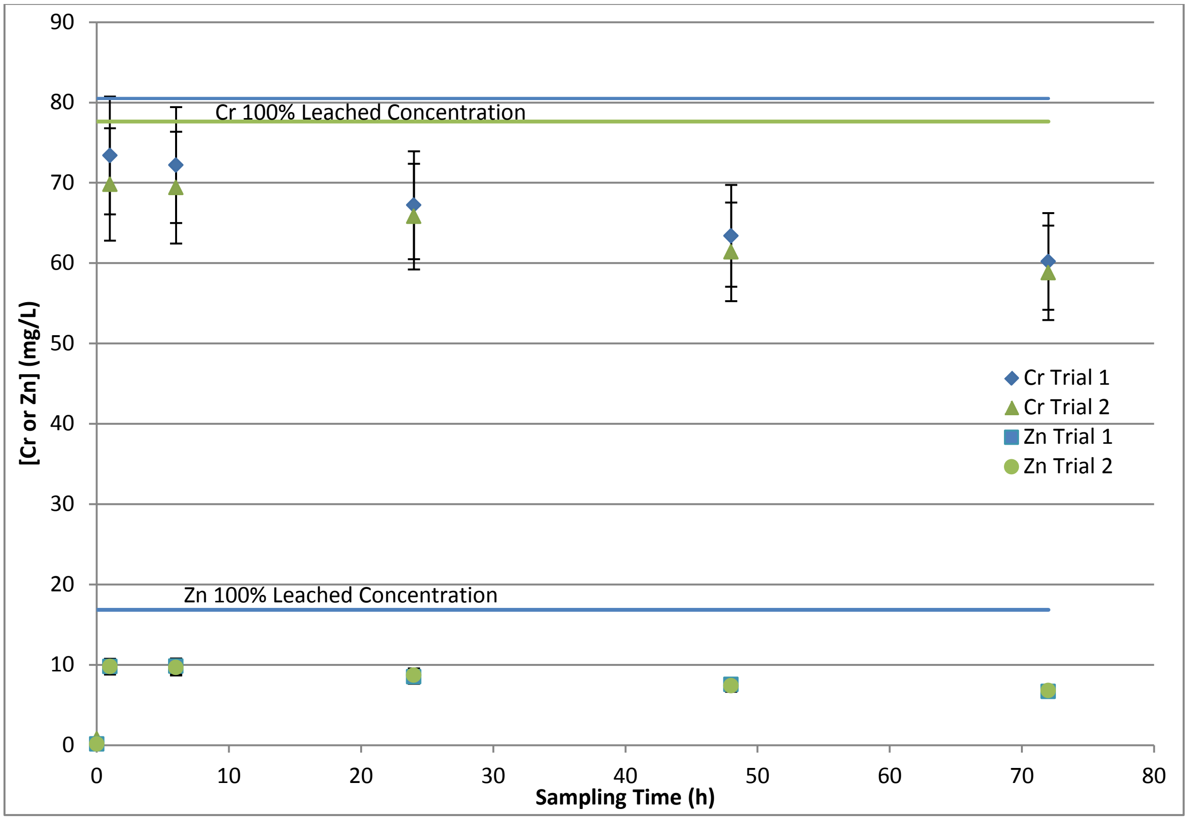


Figure 3-1. Leaching of Cr and Zn from precipitated solids in LAW simulant.

4.0 Conclusions

Treating the SBS-WESP Off-gas Condensate Recycle simulant using $SnCl_2$ proved successful for the removal of Tc and reaffirmed that this is a viable process. The Sn(II) was much more successful at removal of Tc than Fe(II). Only 1.5 eq of Sn(II), which corresponds to ~0.8 g/L $SnCl_2$ in the average simulant, was necessary for good Tc removal from this simulant formulation. Although not measured directly, it is expected that the Tc will be in the form of pertechnetate in the WTP melter off-gas condensate recycle stream due to the highly oxidizing conditions. Addition of $SnCl_2$ causes reduction from soluble TcO_4^- to form TcO_2 solids, which can be removed by settling or filtration.

Technetium removal by reduction with Fe(II) was improved versus prior testing by the addition of sodium hydroxide to mitigate the pH drop caused by the addition of $FeSO_4$; however, the extent of Tc removal is still much less than can be obtained with Sn(II).

Despite attempts to solubilize the ^{241}Am and $^{239/240}$Pu with heating to 50 °C, these actinides remain insoluble in the SBS/WESP off-gas condensate simulants. Other radionuclides were successfully spiked to the target concentrations in the three simulants prepared, with the exception of the simulant containing glass formers. The glass former containing simulant showed removal of both ^{85}Sr and U by the glass formers.

The 1.5 eq of Sn(II) relative to moles of electrons required to reduce the Cr(VI) and Tc(VII) was shown to be successful at removing Tc to below detection limit values at two different Cr concentrations (high and low, relative to the average composition). In the case of the simulant containing no Cr, 1.5 eq based only on Tc was insufficient; however, when the amount of Sn(II) was increased, successful removal of Tc was observed. The increased amount was based upon 1.5 eq of Sn(II) relative to Tc and Zn, which had also been shown to be removed by the Sn(II) precipitation.

The presence of glass formers in the simulant was shown to have no effect on the precipitation of the ^{99}Tc. The glass formers did remove some ^{85}Sr and U as discussed above, and the addition of $SnCl_2$ appeared to resolubilize some of the U that had been removed by the glass formers. The addition of $SnCl_2$ also appeared to increase the solubility of the zinc oxide.

The digested and analyzed solids were found to be predominately Sn, as expected, making up 45 wt% of the solids. Cr was also present at appreciable concentrations, representing 8.32 wt% of the solids. The precipitated ^{99}Tc accounted for 0.17 wt% of the solids. The balance of the mass was presumably the oxygen from the oxides and hydroxides of these metals, plus residual water of hydration and trace simulant constituents that were not washed away from the solids.

Stability testing in the neutral SBS/WESP simulant demonstrated that the precipitated solids are stable to reoxidation and dissolution for up to 72 hours, which should provide sufficient time for a solid-liquid separation. However, the precipitated solids would not be stable if returned to a waste tank for storage, as demonstrated by rapid redissolution of the ^{99}Tc when the precipitated solids were mixed with a LAW simulant. Approximately 94 – 99% of the precipitated Tc had redissolved within one hour after the addition of the LAW simulant to the precipitated solids. The precipitated Sn and U also followed a similar trend. The Cr that had precipitated also quickly redissolved (~90% at 1 hour); however, it then appeared to reprecipitate with time with only ~75% in solution after 72 hours.

5.0 Future Work

Additional tasks needed to further develop this technology include examination of scale-up behavior, solid-liquid separation technologies, slurry rheology measurements, corrosion and erosion studies, and slurry storage and immobilization.

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Appendix A. Detailed Results

Table A-1. Measured Radionuclide Compositions

Isotope	SBS/WESP 2015			SBS/WESP – No Cr			SBS/WESP w/GFC		
	24 h	**4 day**	**1 week**	**24 h**	**4 day**	**1 week**	**24 h**	**4 day**	**1 week**
^{85}Sr (dpm/mL)	5.17E4 (5.0%)	NM	NM	5.94E4 (5.0%)	NM	NM	3.03E4 (5.0%)	2.90E4 (5.0%)	2.63E4 (5.0%)
^{99}Tc (µg/L)	2.03E3 (20%)	NM	NM	1.94E3 (20%)	NM	NM	2.40E3 (20%)	NM	NM
^{137}Cs (dpm/mL)	7.33E3 (5.0%)	7.70E3 (5.0%)	7.68E3 (5.0%)	8.18E3 (5.0%)	7.82E3 (5.0%)	7.88E3 (5.0%)	8.38E3 (5.0%)	8.28E3 (5.0%)	7.98E3 (5.0%)
^{238}U (µg/L)	8.43E2 (20%)	NM	NM	8.25E2 (20%)	NM	NM	5.27E2 (20%)	NM	NM
$^{239/240}$Pu (dpm/mL)	< 9.35	< 4.16	< 5.68	< 7.02	< 16.3	< 10.2	< 3.70	< 6.53	< 0.364
^{241}Am (dpm/mL)	< 77.7	< 31.4	< 30.9	< 15.7	< 31.7	< 31.6	< 72.1	< 70.8	< 68.1

Value in parenthesis represents the reported method uncertainty.
NM = not measured

Table A-2. Summary of Concentration Data from Phase 3 Experiments (HLAW-83-94)

Test ID	**HLAW-83**	**HLAW-84**	**HLAW-85**	**HLAW-86**	**HLAW-87**	**HLAW-88**
Precip. Agent	None (Control)	None (Control)	Sn(II) (1.5:1)	Sn(II) (1.5:1)	Fe(II) (2:1)	Fe(II) (2:1)
Precip. Agent Conc. (g/L)	n/a	n/a	0.797	0.799	0.610	0.609
Contact Time (h)	1.00	6.12	1.00	1.00	6.10	6.12
Sr-85 (dpm/mL)	4.60E+04	4.80E+04	6.02E+03	9.87E+03	NM	NM
Cs-137 (dpm/mL)	2.52E+04	2.63E+04	2.59E+04	2.62E+04	NM	NM
$^{239/240}$Pu (dpm/mL)	1.98E+01	3.10E+01	1.51E+00	<7.28E-01	NM	NM
^{99}Tc (µg/L)	2.06E+03	2.02E+03	<1.00E+01	<1.00E+01	2.00E+03	2.08E+03
^{238}U (µg/L)	8.13E+02	8.12E+02	6.46E+02	6.10E+02	8.03E+02	7.98E+02
Sn (µg/L)	<2.00E+01	<2.00E+01	1.49E+04	1.62E+04	<2.00E+01	<2.00E+01
Cr (mg/L)	8.26E+01	8.27E+01	1.30E+00	1.21E+00	NM	NM
Zn (mg/L)	1.01E+01	1.04E+01	1.28E+00	1.51E+00	NM	NM
Contact Time (h)	21.72	24.27	n/a	n/a	24.30	24.33
^{99}Tc (µg/L)	2.05E+03	2.00E+03	n/a	n/a	2.01E+03	2.05E+03
^{238}U (µg/L)	7.97E+02	8.00E+02	n/a	n/a	8.02E+02	8.10E+02
Test ID	**HLAW-89**	**HLAW-90**	**HLAW-91**	**HLAW-92**	**HLAW-93**	**HLAW-94**
Precip. Agent	Fe(II) (2:1) + 1 X Caustic (Fe 1st)	Fe(II) (2:1) + 1 X Caustic (Fe 1st)	Fe(II) (2:1) + 1 X Caustic (NaOH 1st)	Fe(II) (2:1) + 1 X Caustic (NaOH 1st)	Fe(II) (2:1) + 1.5 X Caustic	Fe(II) (2:1) + 1.5 X Caustic
Precip. Agent Conc. (g/L)	0.611	0.609	0.611	0.609	0.610	0.610
NaOH Conc. (M)	0.021	0.021	0.021	0.021	0.032	0.032
Contact Time (h)	6.00	5.98	6.00	6.00	5.98	6.00
^{99}Tc (µg/L)	1.14E+02	2.37E+02	1.78E+02	1.85E+02	1.82E+02	2.18E+02
^{238}U (µg/L)	2.47E+02	2.33E+02	2.46E+02	2.42E+02	2.56E+02	2.61E+02
Contact Time (h)	24.22	24.20	24.22	24.22	24.22	24.23
^{99}Tc (µg/L)	3.23E+02	3.92E+02	3.49E+02	3.64E+02	4.17E+02	4.38E+02
^{238}U (µg/L)	1.93E+02	1.80E+02	2.08E+02	2.10E+02	2.10E+02	2.07E+02

Table A-3. Summary of Concentration Data from Phase 4 Experiments (HLAW-117-126)

Test ID	**HLAW-117**	**HLAW-118**	**HLAW-119**	**HLAW-120**	**HLAW-121**	**HLAW-122**
Precip. Agent	None (Control)	None (Control)	Double Strike Fe(II) (2:1 + 1:1) + 2 X Caustic	Double Strike Fe(II) (2:1 + 1:1) + 2 X Caustic	Fe(II) (2:1) + 2 X Caustic	Fe(II) (2:1) + 2 X Caustic
Precip. Agent Conc. (g/L)	n/a	n/a	0.61 + 0.31	0.62 + 0.31	0.61	0.60
NaOH Conc. (M)	n/a	n/a	0.066	0.066	0.044	0.044
Contact Time (h)	6.00	6.02	6.00	6.02	6.02	6.02
^{99}Tc (µg/L)	1.59E+03	1.57E+03	6.13E+01	5.75E+01	1.97E+02	1.18E+02
^{238}U (µg/L)	6.11E+02	6.10E+02	1.12E+02	1.21E+02	2.07E+02	2.61E+02
Contact Time (h)	24.02	24.03	24.02	24.02	24.02	24.02
^{99}Tc (µg/L)	1.60E+03	1.62E+03	2.25E+02	1.93E+02	3.82E+02	3.04E+02
^{238}U (µg/L)	6.12E+02	6.26E+02	9.02E+01	9.52E+01	1.66E+02	2.13E+02

Test ID	**HLAW-123**	**HLAW-124**	**HLAW-125**	**HLAW-126**
Precip. Agent	Fe(II) (3:1) + 2 X Caustic	Fe(II) (3:1) + 2 X Caustic	Fe(II) (2:1) + 3 X Caustic	Fe(II) (2:1) + 3 X Caustic
Precip. Agent Conc. (g/L)	0.92	0.92	0.61	0.61
NaOH Conc. (M)	0.066	0.066	0.066	0.066
Contact Time (h)	6.00	6.00	6.00	6.00
^{99}Tc (µg/L)	6.32E+01	3.15E+02	4.12E+02	2.51E+02
^{238}U (µg/L)	1.84E+02	1.66E+02	2.10E+02	2.53E+02
Contact Time (h)	24.00	24.00	24.00	24.00
^{99}Tc (µg/L)	3.57E+02	4.51E+02	5.36E+02	4.27E+02
^{238}U (µg/L)	1.51E+02	1.41E+02	1.80E+02	2.18E+02

Table A-4. Summary of Concentration Data from Effect of Glass Former Experiments (HLAW-166-169).

Test ID	**HLAW-166**	**HLAW-167**	**HLAW-168**	**HLAW-169**
Precip. Agent	None (Control)	None (Control)	Sn(II) (1.5 eq)	Sn(II) (1.5 eq)
Precip. Agent Conc. (g/L)	n/a	n/a	0.787	0.794
Contact Time (h)	1.00	1.02	1.03	1.05
Sr-85 (dpm/mL)	1.68E+04	1.65E+04	1.37E+04	1.33E+04
Cs-137 (dpm/mL)	8.36E+03	8.31E+03	7.94E+03	7.86E+03
Am-241 (dpm/mL)	<5.51E+01	<5.46E+01	<5.01E+01	<4.95E+01
^{99}Tc (µg/L)	2.38E+03	2.38E+03	<1.00E+01	<1.00E+01
^{238}U (µg/L)	4.15E+02	4.13E+02	5.78E+02	5.82E+02
Sn (µg/L)	<1.00E+01	<1.00E+01	1.96E+03	1.74E+03
Cr (mg/L)	8.83E+01	8.80E+01	<7.75E-01	<7.75E-01
Zn (mg/L)	4.58E+00	4.68E+00	4.43E+01	4.46E+01

Table A-5. Summary of Concentration Data from Variable Cr Experiments (HLAW-170-181)

Test ID	**HLAW-171**	**HLAW-172**	**HLAW-173**	**HLAW-175**	**HLAW-176**	**HLAW-177**	**HLAW-179**	**HLAW-180**	**HLAW-181**
Simulant	SBS/WESP – No Cr			SBS/WESP – Low Cr			SBS/WESP – High Cr		
Precip. Agent	None (Control)	Sn(II) (1.5 eq)	Sn(II) (1.5 eq)	None (Control)	Sn(II) (1.5 eq)	Sn(II) (1.5 eq)	None (Control)	Sn(II) (1.5 eq)	Sn(II) (1.5 eq)
Precip. Agent Conc. (g/L)	n/a	0.011	0.011	n/a	0.270	0.282	n/a	1.052	1.050
Contact Time (h)	1.03	1.05	1.07	1.02	1.02	1.02	1.02	1.03	1.03
^{99}Tc (µg/L)	1.87E3	2.42E1	1.04E3	1.90E3	1.12E1	<1.00E1	1.89E3	<1.00E1	<1.00E1
^{238}U (µg/L)	8.88E2	8.74E2	8.76E2	8.82E2	7.35E2	7.30E2	8.88E2	7.19E2	6.68E2
Sn (µg/L)	<1.00E1	1.02E3	<1.00E1	<1.00E1	1.82E2	1.77E2	<1.00E1	2.14E4	8.97E3
Cr (mg/L)	<4.65E-1	<4.65E-1	<4.65E-1	2.89E1	<4.65E-1	<4.65E-1	1.24E2	1.82E0	1.59E0
Zn (mg/L)	1.11E1	4.11E0	7.42E0	1.11E1	4.25E-1	5.15E-1	1.19E1	1.29E0	6.60E-1

Table A-6. Summary of Concentration Data from Repeat 0 ppm Cr Experiments (HLAW-182-185)

Test ID	**HLAW-183**	**HLAW-184**	**HLAW-185**
Simulant	SBS/WESP – No Cr		
Precip. Agent	None (Control)	Sn(II) (1.5 eq)	Sn(II) (1.5 eq)
Precip. Agent Conc. (g/L)	n/a	0.0105	0.0105
Contact Time (h)	1.02	1.03	1.05
^{99}Tc (µg/L)	1.89E+03	1.36E+03	1.27E+03
^{238}U (µg/L)	8.55E+02	8.37E+02	8.33E+02
Sn (µg/L)	< 1.00E+01	< 1.00E+01	< 1.00E+01

Table A-7. Summary of Concentration Data from Repeat 0 ppm Cr Experiments (HLAW-189-192)

Test ID	**HLAW-190**	**HLAW-191**	**HLAW-192**
Simulant	SBS/WESP – No Cr		
Precip. Agent	None (Control)	Sn(II) (1.5 eq)	Sn(II) (1.5 eq)
Precip. Agent Conc. (g/L)	n/a	0.059	0.063
Contact Time (h)	1.03	1.05	1.05
^{99}Tc (µg/L)	1.86E+03	< 1.00E+01	< 1.00E+01
^{238}U (µg/L)	8.16E+02	7.86E+02	7.84E+02
Sn (µg/L)	< 1.00E+01	2.69E+03	2.28E+03
Cr (mg/L)	< 9.15E-01	< 9.15E-01	< 9.15E-01
Zn (mg/L)	7.36E+00	3.09E+00	3.29E+00

Table A-8. Concentration Data from Solids Precipitation Experiment (HLAW-186)

Test ID	**HLAW-186**
Simulant	SBS/WESP 2015
Precip. Agent	Sn(II) (1.5 eq)
Precip. Agent Conc. (g/L)	0.775
Contact Time (h)	2.25
^{99}Tc (µg/L)	< 1.00E+01
^{238}U (µg/L)	6.52E+02
Sn (µg/L)	5.71E+03
Cr (mg/L)	9.75E-01
Zn (mg/L)	6.60E-01
^{85}Sr (dpm/mL)	8.59E+03
^{137}Cs (dpm/mL)	7.85E+03

Table A-9. Composition of Digested Solids

Element	**Solids Sample 1**	**Solids Sample 2**
^{99}Tc (µg/g)	1.78E+03	1.71E+03
Sn (µg/g)	4.54E+05	4.45E+05
^{238}U (µg/g)	1.70E+02	1.68E+02
B (µg/g)	2.68E+03	2.60E+03
Ca (µg/g)	1.34E+02	1.21E+02
Cr (µg/g)	8.44E+04	8.20E+04
K (µg/g)	4.89E+02	4.61E+02
Na (µg/g)	2.39E+03	2.23E+03
Si (µg/g)	4.62E+03	4.20E+03
Zn (µg/g)	8.26E+03	8.06E+03
^{85}Sr (dpm/g)*	2.19E+07	2.21E+07
^{137}Cs (dpm/g)	2.07E+04	2.54E+04
^{241}Am (dpm/g)	< 7.28E+04	2.19E+04
$^{239/240}$Pu (dpm/g)	8.16E+03	5.32E+03
$^{239/240}$Pu (µg/g)	5.21E+01	3.39E+01

Table A-10. Concentration Data from Stability Testing in SBS/WESP Simulant (HLAW-113-116)

Test ID	**HLAW-114**	**HLAW-115**	**HLAW-116**	**HLAW-114**	**HLAW-115**	**HLAW-116**	**HLAW-114**	**HLAW-115**	**HLAW-116**
Precip. Agent	None (Control)	Sn(II) (1.5 eq)	Sn(II) (1.5 eq)	None (Control)	Sn(II) (1.5 eq)	Sn(II) (1.5 eq)	None (Control)	Sn(II) (1.5 eq)	Sn(II) (1.5 eq)
Precip. Agent Conc. (g/L)	n/a	0.798	0.801	n/a	0.798	0.801	n/a	0.798	0.801
	Tc (µg/L)			**U (µg/L)**			**Cr (mg/L)**		
1 h	1.64E+03	<10.0	<10.0	641	480	438	84.5	0.593	0.224
6 h	1.62E+03	<10.0	<10.0	628	484	401	85.4	0.489	0.189
24 h	1.62E+03	<10.0	<10.0	627	477	355	86.3	0.429	<0.111
48 h	1.63E+03	<10.0	<10.0	619	455	289	85.4	0.317	<0.111
72 h	1.61E+03	<10.0	<10.0	627	463	259	80.2	0.324	<0.111

Table A-11. Concentration Data from Initial Precipitation for Stability in LAW Tests (HLAW-187-188)

Test ID	**HLAW-187**	**HLAW-188**
Simulant	SBS/WESP 2015	SBS/WESP 2015
Precip. Agent	Sn(II) (1.5 eq)	Sn(II) (1.5 eq)
Precip. Agent Conc. (g/L)	0.781	0.784
Contact Time (days)	7	7
^{99}Tc (µg/L)	5.59E+01	8.81E+01
^{238}U (µg/L)	7.19E+02	6.85E+02
Sn (µg/L)	2.54E+04	2.78E+04
Cr (mg/L)	3.13E+00	6.84E+00
Zn (mg/L)	1.27E+00	1.29E+00
^{85}Sr (dpm/mL)	2.13E+04	2.26E+04
^{137}Cs (dpm/mL)	9.13E+03	7.35E+03

Distribution:

T. B. Brown, 773-A
M. E. Cercy, 773-42A
D. A. Crowley, 773-43A
D. E. Dooley, 999-W
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
R. B. Mabrouki, 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. Davis, WRPS
M. R. Thorson, WRPS