

## **Initial Testing of Off-Gas Recycle Condensate Liquid from the WTP Low Activity Waste Vitrification Process - 16432**

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### **ABSTRACT**

The Waste Treatment and Immobilization Plant (WTP) under construction at the Hanford site is designed to treat and immobilize the inventory of High-Level Waste stored in the 177 underground storage tanks. The WTP process flow was designed to pre-treat this waste, separating it into High Level Waste (HLW) and Low Activity Waste (LAW) fractions for vitrification.

Vitrification of the waste generates a condensate stream from the off-gas processes originating from two off-gas treatment unit operations, the Submerged Bed Scrubber (SBS) and the Wet Electrostatic Precipitator (WESP). The baseline plan for disposition of the stream from the LAW melter is to recycle it to the Pretreatment facility where it gets evaporated and processed through the LAW melter again. If the Pretreatment facility is unavailable, this baseline disposition pathway is not viable. Additionally, chloride, fluoride, and sulfate are partially volatile in the melter, accumulating to high concentrations while recycling and impacting the glass waste loading and facility throughput. The primary radionuclide that volatilizes and accumulates is  $^{99}\text{Tc}$ . The long half-life and environmental mobility of  $^{99}\text{Tc}$  complicates disposal options for this secondary aqueous waste stream. This task is investigating  $^{99}\text{Tc}$  removal to examine the potential for diverting this stream to an alternate disposition path and avoiding impacting the glass waste loading. Separation methods for  $^{99}\text{Tc}$  have focused on using inorganic precipitation agents that can remove it by reducing it from soluble pertechnetate ion, with a +7 oxidation state, to insoluble technetium dioxide in the +4 oxidation state. Stannous chloride ( $\text{SnCl}_2$ ) has been found highly effective at causing the reduction and precipitating  $^{99}\text{Tc}$  for removal, but it also precipitates other components. The primary competitor that precipitates is chromium, which consumes the redox activity of the  $\text{Sn(II)}$ , causing addition of more of the  $\text{SnCl}_2$ . Research has examined the optimum quantity of  $\text{SnCl}_2$ , mixing time, and the impact of other redox-active species. It is also important to know the stability of the precipitated  $^{99}\text{Tc}$  in process conditions, since it is expected it will eventually be re-oxidized by oxygen and dissolve. This work is expected to determine if a  $^{99}\text{Tc}$  removal step could be used to decontaminate the bulk of this stream, and make it suitable for other disposal paths so that the chloride, fluoride, and sulfate can be diverted away from the glass melter.

### **INTRODUCTION**

The Hanford WTP will treat and immobilize the ~2E8 L of tank waste currently in storage. The LAW portion will be melted as a borosilicate glass in air-bubbled

Joule-heated ceramic melters that will generate a condensate stream by cooling and scrubbing of the LAW melter off-gas system by a SBS and WESP, as shown in Figure 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 the LAW stream and evaporated. The halide and sulfate components are only marginally soluble in glass, and often dictate the waste loading. Additionally, long-lived  $^{99}\text{Tc}$  and  $^{129}\text{I}$  are volatile radionuclides at melter temperatures that accumulate in the LAW system, and are challenging to incorporate in glass under the Hanford LAW melter operating conditions. Although the melter operates at  $\sim 1150\text{ }^\circ\text{C}$ , the volatile radionuclides are partially retained in the glass by the cold cap in the melter. Because  $^{99}\text{Tc}$  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 it is largely un-leachable from the glass. 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 further mature a process for decontamination of  $^{99}\text{Tc}$  from this stream using precipitation agents (Figure 2). The concept for this decontamination process adapts the use of precipitation agents to enable alternative disposition. Implementation would make available both a short-term disposition path if the LAW facility commences operation prior to operation of the Pretreatment facility and a long term path to divert the stream from recycling [2].

The LAW that is fed to the melters is a highly alkaline, high ionic strength salt solution, adjusted to  $\sim 7.8\text{ M }[\text{Na}^+]$  and contains an estimated  $8.8\text{E-}5\text{ Ci/L}$  of  $^{99}\text{Tc}$  [3]. If the radionuclides are removed from the Recycle stream and the decontaminated liquid is then sent to an alternate disposal path, the fluoride, sulfate, and chloride would be purged from the LAW system, yielding substantial benefits to WTP and mitigating the complications of recycling this stream.

### **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 were based on version 7.4 of the Hanford Tank Waste Operations Simulator (HTWOS) modeling of the flow sheet [4]. Insoluble solids composition was primarily based on analysis of LAW Recycle obtained from pilot-scale simulant melter testing [5]. Basing the solution chemistry and radionuclide content on the computer modeling rather than melter testing results allowed evaluation of process conditions for treatment of all tank wastes, and accounts for internal WTP process streams. Since the computer model does not account for physical carryover of material, the insoluble solids used were based on test results. Results from pilot-scale melter off-gas system testing indicated that the solids were primarily glass formers because the solids were observed to contain iron and other components not typically in the aqueous LAW. Glass formers were added as the solids to the simulant formulation. The radionuclide contents were based on the HTWOS model calculations.

## Simplified Low Activity Waste Off-gas System

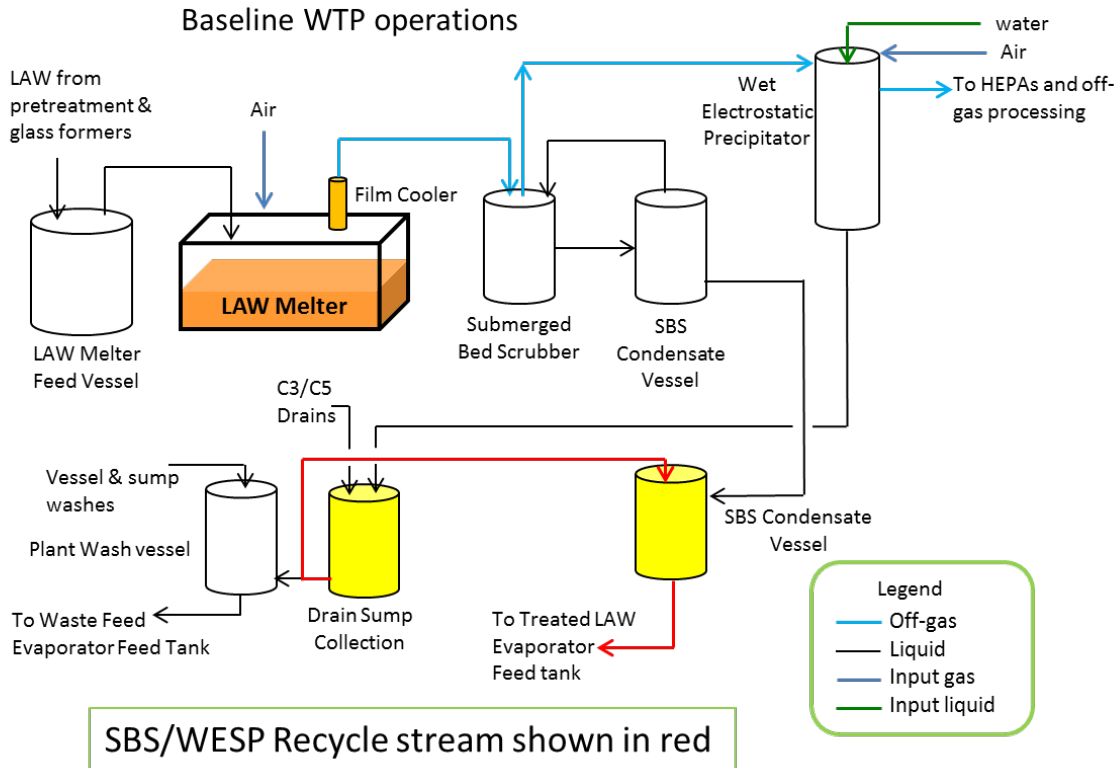


Figure 1. Simplified Low Activity Waste Off-gas System Schematic

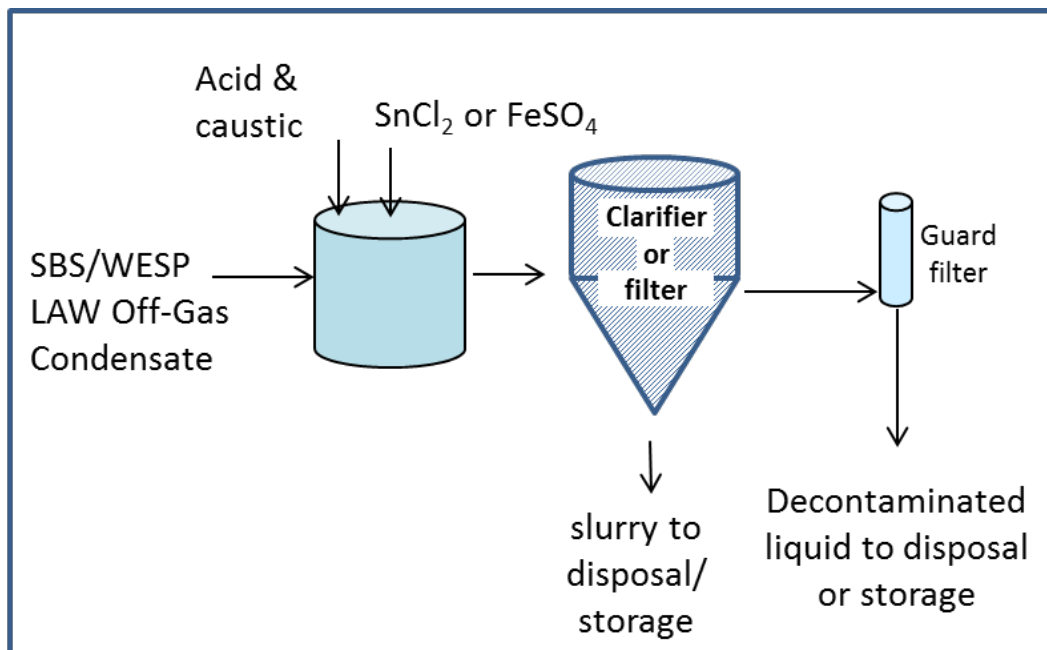


Figure 2. Off-Gas Condensate Decontamination Process Concept

### Radionuclide Removal Process

For this proposed alternative treatment process, separation of the  $^{99}\text{Tc}$  is done by precipitation and settling and/or filtration using entirely inorganic materials. For technetium removal, these materials included reducing agents (e.g. Sn(II) or Fe(II) compounds) possibly coupled with absorbents (e.g. hydroxyapatite). The Sn(II) with hydroxyapatite and oxalate has previously been found effective for precipitating Tc from water samples [6]. Prior testing showed that for this application, hydroxyapatite was not necessary [7, 8, 9]. The selected target decontamination factor for Tc is 100. The total volume of this waste stream will be well over the 2E8 L of waste volume because of tank waste dissolution and process water additions during treatment.

## **EXPERIMENTAL**

### Simulant Preparation

The basis of the simulant of chemicals and radionuclides were derived from the output from the HTWOS calculation, documented in SVF-2732[10]. 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 1. The first batch was previously prepared and characterized (i.d.: SBS/WESP 2014) [7]. 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 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 a 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) were then added to all three aliquots, and mixed for five days at ambient temperature. 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. 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.

### Simulant Spiking with Radionuclides

The prepared simulants were then spiked with the radiotracer solutions shown in Table 2.

**Table 1. Aqueous Simulant Formulation Targets**

Chemical	Formula	Target Mass (g)/L simulant	Target Molarity
Aluminum nitrate nonahydrate	$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	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	$\text{NH}_4\text{NO}_3$	2.820	0.0352
Sodium nitrate	$\text{NaNO}_3$	0	0*
Sodium nitrite	$\text{NaNO}_2$	0.016	0.0002
Ammonium sulfate	$(\text{NH}_4)_2\text{SO}_4$	3.220	0.0244
Dibasic sodium phosphate dihydrate	$\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$	0.040	0.0002
Sodium chromate	$\text{Na}_2\text{CrO}_4$	0.283 <sup>#</sup>	0.0017 <sup>#</sup>

\*note that nitrate ion is added later as nitric acid during pH adjustment

<sup>#</sup>Sodium chromate added after removal of a 500 mL aliquot

**Table 2. Target Glass Former and Radiotracer Quantities**

Mineral	Formula	Mass (g)/L simulant	Isotope	Target concentration (dpm/mL)
kyanite	$\text{Al}_2\text{SiO}_5$	0.745	$^{137}\text{Cs}$	1.16E4
borax	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	0.0123	$^{238}\text{U}$	6.24E-1
boric acid	$\text{H}_3\text{BO}_3$	1.430	$^{239/240}\text{Pu}$	8.42E1
wollastonite	$\text{CaSiO}_3$	0.772	$^{85}\text{Sr}$	5.79E4
iron oxide (hematite)	$\text{Fe}_2\text{O}_3$	0.430	$^{99}\text{Tc}$	9.21E4
lithium carbonate	$\text{Li}_2\text{CO}_3$	0.392	$^{241}\text{Am}$	5.15E2
forsterite olivine	$\text{Mg}_2\text{SiO}_4\text{-Fe}_2\text{SiO}_4$	0.257		
sodium carbonate	$\text{Na}_2\text{CO}_3$	0.003		
silica	$\text{SiO}_2$	2.857		
rutile	$\text{TiO}_2$	0.114		
zinc oxide	ZnO	0.286		
zircon	$\text{ZrSiO}_4$	0.372		
sucrose	$\text{C}_{12}\text{H}_{22}\text{O}_{11}$	0		
	Total	7.67		

#### Precipitation Tests – Phases 3 and 4

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  $\sim 25^\circ\text{C}$  for the specified time and then filtered through a 0.1- $\mu\text{m}$  filter. The filtrate was analyzed by ICP-MS

for <sup>99</sup>Tc. Selected samples were also analyzed for Cr, Cs, Sr, and actinides to determine if the process impacts their solubility.

Tables 4 and 5 show the test matrix for reagent addition for Phases 3 and 4. The "phase ratio" indicates the moles of reductant electrons to the moles of electrons needed to reduce the Cr(VI) to Cr(III) (i.e., On a molar concentration basis, this is equivalent to a ratio of 2.25: 1 for Sn: [Cr+Tc] and 3: 1 for Fe: [Cr+Tc]). Phase 3 tests were designed to test the lower threshold of Sn(II) and to examine the effectiveness of ferrous ion to reduce the <sup>99</sup>Tc with the addition of sodium hydroxide to mitigate the drop in pH from the addition of ferrous sulfate, including 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 4. Reagent Test Matrix for Phase 3**

<b>Molar Phase Ratio (moles reductant electrons:moles oxidizer electrons)</b>	<b>Reagent Quantity</b>	<b>Target Duration (hours)</b>
<b>Sn(II)</b>		
1.5: 1	0.8 g/L SnCl <sub>2</sub>	1
<b>Fe(II)</b>		
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 5. Reagent Test Matrix for Phase 4**

<b>Molar Phase Ratio (moles reductant electrons:moles oxidizer electrons)</b>	<b>Reagent Quantity</b>	<b>Target Duration (hours)</b>
<b>Fe(II)</b>		
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

### Characterization of Solids

The addition of SnCl<sub>2</sub> results in the reductive precipitation of both <sup>99</sup>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<sub>2</sub> was added to 800 mL of the SBS/WESP 2015 simulant. After adding, the mixture was stirred at ambient temperature for 2 hours and then filtered through a 0.45-μm Nylon filter to collect the solids. 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 analyses.

### Stability of Precipitated Solids to Re-oxidation

The successful removal of <sup>99</sup>Tc through the reductive precipitation with Sn(II) has been demonstrated. Testing was then performed to examine the stability of the reduced <sup>99</sup>Tc to re-oxidation and re-dissolution. The first set of tests was designed to determine the stability of the solids to re-oxidation to determine if sufficient time is available to filter or settle the solids prior to re-dissolution of the Tc. The second set of tests was to determine 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. For both sets of experiments, the solids were prepared by the addition of 1.5 eq of SnCl<sub>2</sub> to 40 mL aliquots (duplicate experiments) of the SBS/WESP simulant. The first set of tests used the SBS/WESP 2014 batch, 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 and approximately 4 mL of sample was then filtered through a 0.1-μm syringe filter and analyzed.

For the second set of tests, after mixing for 1 hour at ~25 °C, the mixtures were allowed to settle for 1 week. After settling, the supernatant was carefully removed and was replaced with 40 mL of LAW simulant (Table 6). 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 and a 4-mL sample was filtered through a 0.1-μm syringe filter, acidified, and analyzed.

**Table 6. Composition of LAW Simulant**

<b>Constituent</b>	<b>Molarity</b>		<b>Constituent</b>	<b>Molarity</b>
Na <sup>+</sup>	7.8		PO <sub>4</sub> <sup>2-</sup>	0.076
K <sup>+</sup>	0.051		NO <sub>2</sub> <sup>-</sup>	0.88
Al <sup>3+</sup>	0.48		NO <sub>3</sub> <sup>-</sup>	2.53
Cl <sup>-</sup>	0.066		CO <sub>3</sub> <sup>2-</sup>	0.43
F <sup>-</sup>	0.049		OH <sup>-</sup>	2.43
SO <sub>4</sub> <sup>2-</sup>	0.13		TOC Total (acetate)	0.12 (0.060)

## RESULTS AND DISCUSSION

### Simulant Compositions

Results of the average and standard deviation of the duplicate chemical analysis of the neutralized, filtered SBS/WESP simulants are shown in Table 7. 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. The soluble aluminum was lower than the computer modeling and comparison to the pilot scale melter off-gas condensate sample analyses [4]. All of the simulants are relatively good matches versus the accuracy and range of the projected composition, with the small variations. 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 sufficient to identify the interference.

**Table 7. Neutralized Simulant Filtrate Compositions**

	<b>SBS/ WESP 2014 Avg. (mg/L)</b>	<b>SD</b>	<b>SBS/ WESP 2015 Avg. (mg/L)</b>	<b>SD</b>	<b>HTWOS projection (avg. SVF- 2732) (mg/L)</b>
Al	<1.0		< 0.50	n/a	28.0
B	242	8.8	158	2.1	GFC <sup>#</sup>
Ca	1.10	0.01	0.970	0.009	GFC <sup>#</sup>
Cr	89.9	0.86	93.3	2.7	91
Fe	<1.0		<0.10	n/a	GFC <sup>#</sup>
K	103	0.54	121	0.71	115
Li	80.9	0.80	75.6	0.64	GFC <sup>#</sup>
Mg	<1.0		<0.100	n/a	GFC <sup>#</sup>
Na	2.28E3	14	1780	0 <sup>*</sup>	2290
P	<1.0		2.00	0 <sup>*</sup>	7.00
S	1260	15	806	2.1	780
Si	55.0	0.42	52.3	1.5	GFC <sup>#</sup>
Ti	<1.0		<0.100	n/a	GFC <sup>#</sup>
Zn	14.6	0.15	20.1	0.64	GFC <sup>#</sup>
Zr	<1.0		<0.500	n/a	GFC <sup>#</sup>
F <sup>-</sup>	1410	0 <sup>*</sup>	1295	7.1	1450
Cl <sup>-</sup>	945	1.4	965	35	950
NO <sub>2</sub> <sup>-</sup>	<500		<100	n/a	10.7
NO <sub>3</sub> <sup>-</sup>	3200	57	2420	14	5530
SO <sub>4</sub> <sup>2-</sup>	2230	14	2185	7.1	2340
PO <sub>4</sub> <sup>3-</sup>	<31		<100	n/a	21.5
NH <sub>4</sub> <sup>+</sup>	1540 <sup>**</sup>		1400 <sup>**</sup>	n/a	1510

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

\*\*analysis of a single sample

#Glass Forming chemical; minimal HTWOS projected concentration



**Table 8. SBS/WESP 2014 Simulant Radionuclide Compositions - % of Target Activity (See Table 2 for Targets)**

Isotope	2014		2015			
	Aliquot 1	Aliquot 2	SBS/WESP	SBS/WESP – No Cr	SBS/WESP w/GFC (filtered)	SBS/WESP w/GFC (unfiltered)
<sup>85</sup> Sr	103	84	89	103	45	99
<sup>99</sup> Tc	82	67	83	79	98	NM
<sup>137</sup> Cs	225	103	66	68	69	70
<sup>238</sup> U	91	72	102	100	64	NM
<sup>239/240</sup> Pu	9.9	6.9	< 6.8	< 12	< 0.43	NM
<sup>241</sup> Am	< 11	NM	< 6.0	< 6.1	< 13	207

NM = not measured

### SBS/WESP 2015 Simulants

The Pu and Am are only marginally soluble in these simulants. The <sup>137</sup>Cs activity was consistently ~30% low across all three 2015 simulants, indicating the activity of the stock was likely lower than expected. In other testing, it was shown that the <sup>85</sup>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 <sup>85</sup>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 <sup>85</sup>Sr versus the soluble <sup>85</sup>Sr activity. Gamma analysis of the unfiltered simulant indicated a <sup>85</sup>Sr activity of  $5.76 \times 10^4$  dpm/mL, 99.4% of the target value, which confirms that the glass formers removed it. The <sup>241</sup>Am, which was insoluble in the simulant, was also detected in the unfiltered sample with an activity of  $1.07 \times 10^3$  dpm/mL, 207% of the target, confirming that it was spiked correctly, but not soluble. The <sup>137</sup>Cs activity was the same between the filtered and unfiltered samples, indicating no <sup>137</sup>Cs is removed by the glass formers, as expected.

### Phase 3 and 4 Precipitation Experiments

Results of the precipitation tests are shown in Tables 9 and 10. 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 <sup>99</sup>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<sub>4</sub> 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 DF 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 10) 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 <sup>99</sup>Tc removal does not approach that obtained using stannous chloride as the reductant.

**Table 9. Average Decontamination Factors for Phase 3 Experiments**

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

<sup>1</sup>Replicate trials gave significantly different results with one being below detection limit, DF values were 16.6 and >34.4.

**Table 10. Average Decontamination Factors Obtained in Phase 4 Experiments**

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

Value in parentheses indicates standard deviation of replicate trials.

<sup>1</sup>Replicate trials gave significantly different results, DF values were 25.0 and 5.03.

### 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<sub>2</sub> relative to Tc and Cr (0.77 g/L SnCl<sub>2</sub>) using the SBS/WESP 2015 simulant. Assuming the reductive precipitation results in the formation of the following solids: Cr<sub>2</sub>O<sub>3</sub>, SnO<sub>2</sub>, and TcO<sub>2</sub>, 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 11 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 <sup>99</sup>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 12 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 [8, 9], 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 11. Composition of Digested Solids**

Element	Average	Std. Dev.	wt%
<sup>99</sup> Tc (µg/g)	1.75E+03	4.95E+01	0.17
Sn (µg/g)	4.50E+05	6.55E+03	45.0
<sup>238</sup> 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
<sup>85</sup> Sr (dpm/g)*	2.20E+07	1.48E+05	n/a
<sup>137</sup> Cs (dpm/g)	2.31E+04	3.32E+03	n/a
<sup>241</sup> Am (dpm/g)	2.19E+04 <sup>#</sup>	n/a	n/a
<sup>239/240</sup> Pu (dpm/g)	6.74E+03	2.01E+03	n/a
<sup>239/240</sup> Pu (µg/g)	4.30E+01	1.28E+01	0.004

\*Decay corrected to date of original simulant preparation.

<sup>#</sup>Single replicate, the other sample was below detection limit (<7.28E+04 dpm/g).

**Table 12. 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
<sup>99</sup> 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%

#### Stability of Precipitated Solids

In order to examine the stability of the precipitated <sup>99</sup>Tc to re-oxidation and re-dissolution in the off-gas condensate, experiments were performed to monitor the soluble <sup>99</sup>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 <sup>99</sup>Tc. In addition, the bottles were opened twice daily to replenish the air if it was consumed. Results, shown in Table 13, demonstrated the precipitated Tc is stable to re-oxidation for at least 72 hours. The soluble <sup>99</sup>Tc concentration remained below the method detection limit for the duration of the experiment. The reduced and precipitated Cr also resisted re-oxidation. 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 13. 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  $^{99}\text{Tc}$  would be return to the tank farms. Therefore, tests were performed to examine the stability of the precipitated solids in a LAW simulant. Solids were first precipitated from the SBS/WESP 2015 simulant by the addition of 1.5 eq of  $\text{SnCl}_2$  (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 14 shows the decontamination factors obtained at the end of the settling period. The  $^{99}\text{Tc}$  DFs were lower than what is typically obtained, indicating that perhaps some of the initially precipitated  $^{99}\text{Tc}$  re-oxidized and re-dissolved during the settling period, or, more likely, poorer solid-liquid separation occurred during decanting versus filtering.

**Table 14. Decontamination Factors Obtained after Initial  $\text{SnCl}_2$  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 15. The first row of Table 15 indicates the calculated concentration that should be obtained if 100% of the precipitated solids re-dissolve (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  $^{99}\text{Tc}$  that precipitated re-dissolves almost immediately (at least within 1 hour) upon contact with the LAW simulant.

**Table 15. Leaching of Precipitated Solids in LAW Simulant**

	Tc ( $\mu\text{g/L}$ )		U ( $\mu\text{g/L}$ )		Sn ( $\mu\text{g/L}$ )		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
<b>100% Leached Conc.</b>	1.76E3	1.73E3	190	216	4.15E5	4.15E5	2.94E4	2.84E4	80.5	77.6	16.8	16.8
<b>0 h Conc. (% Leached)</b>	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)
<b>1 h Conc. (% Leached)</b>	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)
<b>6 h Conc. (% Leached)</b>	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)
<b>24 h Conc. (% Leached)</b>	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)
<b>48 h Conc. (% Leached)</b>	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)
<b>72 h Conc. (% Leached)</b>	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)

## CONCLUSIONS

Treating the SBS-WESP Off-gas Condensate Recycle simulant using  $\text{SnCl}_2$  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  $\sim 0.8$  g/L  $\text{SnCl}_2$  in the average simulant, was necessary for good Tc removal from this simulant formulation. Addition of  $\text{SnCl}_2$  causes reduction from soluble  $\text{TcO}_4^-$  to form  $\text{TcO}_2$  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; however, the extent of Tc removal is still much less than can be obtained with Sn(II).

The solids were found to be predominately Sn, as expected, making up 45 wt% of the solids. The Cr concentration was also appreciable.

Stability testing in the neutral SBS/WESP simulant demonstrated that the precipitated solids are stable to re-oxidation 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 re-dissolution of the  $^{99}\text{Tc}$  when the precipitated solids were mixed with a LAW simulant.

## FUTURE WORK

Additional tasks needed to further develop this technology include examination of scale-up behavior, solid-liquid separation technologies, slurry rheology, corrosion and erosion studies, and slurry storage and immobilization, including the effect of Sn on the waste form.

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