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

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DISCLAIMER

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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 de-coupled operation of the LAW melter and the Pretreatment Facilities. Eliminating this stream from recycling within WTP would also decrease the LAW vitrification mission duration and quantity of glass waste.

This LAW Off-Gas Condensate stream contains components that are volatile at melter temperatures and are problematic for the glass waste form. Because this stream recycles within WTP, these components accumulate in the Condensate stream, exacerbating their impact on the number of LAW glass containers that must be produced. Approximately 32% of the sodium in Supplemental LAW comes from glass formers used to make the extra glass to dilute the halides to acceptable concentrations in the LAW glass, and diverting the stream reduces the halides 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 is very similar to that used for the Actinide Removal Process (ARP) that has been operating for years at the Savannah River Site (SRS), and focuses on using mature radionuclide removal technologies that are also compatible with long-term tank storage and immobilization methods. For this new application, testing is needed to demonstrate acceptable treatment sorbents and precipitating agents and measure decontamination factors for additional radionuclides in this unique waste stream.

The origin of this LAW Off-Gas Condensate stream will be the liquids from the Submerged Bed Scrubber (SBS) and the Wet Electrostatic Precipitator (WESP) from the LAW melter off-gas system. The stream is expected to be a dilute salt solution with near neutral pH, and will likely contain some insoluble solids from melter carryover. The soluble components are expected to be mostly sodium and ammonium salts of nitrate, chloride, and fluoride. This stream has not been generated yet 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.

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 low but are also expected to be in 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. This report discusses results of optimized ^{99}Tc

decontamination testing of the simulant. Testing examined use of inorganic reducing agents for ^{99}Tc.

Testing focused on minimizing the quantity of sorbents/reactants added, and minimizing mixing time to reach the decontamination targets in this simulant formulation. Stannous chloride and ferrous sulfate were tested as reducing agents to determine the minimum needed to convert soluble pertechnetate to the insoluble technetium dioxide. The reducing agents were tried with and without sorbents. The sorbents, hydroxyapatite and sodium oxalate, were expected to sorb the precipitated technetium dioxide and facilitate removal. The Phase 1 tests examined a broad range of conditions and used the initial baseline simulant (Table ES-1). The Phase 2 tests narrowed the conditions based on Phase 1 results, and used a slightly modified simulant (Table ES-2). Test results indicate that excellent removal of ^{99}Tc was achieved using $SnCl_2$ as a reductant, and was effective with or without sorption onto hydroxyapatite. This reaction worked even in the presence of air (which could oxidize the stannous ion) and at room temperature. This process was very effective at neutral pH, with a Decontamination Factor (DF) >199 in one hour with only 1 g/L of $SnCl_2$. Prior work had shown that it was much less effective at alkaline pH. The only deleterious effect observed was that the chromium co-precipitates with the ^{99}Tc during the $SnCl_2$ reduction. This effect was anticipated, and would have to be considered when managing disposition paths of this stream. Reduction using $FeSO_4$ was not effective at removing ^{99}Tc, but did remove the Cr. Chromium is present due to partial volatility and entrainment in the off-gas, and is highly oxidizing, so would be expected to react with reducing agents more quickly than pertechnetate. Testing showed that sufficient reducing agent must be added to completely reduce the chromium before the technetium is reduced and removed.

Other radionuclides are also present in this off-gas condensate stream. To enable sending this stream to the Hanford ETF, and thereby divert it from the recycle where it impacts the LAW glass volume, several of these also need to be removed. Samples from optimized conditions were also measured for actinide removal in order to examine the effect of the Tc-removal process on the actinides. Plutonium was also removed by the $SnCl_2$ precipitation process.

Results of this separation testing indicate that sorption/precipitation is a viable concept and has the potential to decontaminate the ^{99}Tc from the stream, allowing it to be diverted away from WTP and thus eliminating the impact of the recycled halides and sulfate on the LAW glass volume. Based on the results, a possible treatment scenario could involve the use of a reductive precipitation agent ($SnCl_2$) with or without sorbent at neutral pH to remove the Tc. Although hydroxyapatite was not necessary to effect the ^{99}Tc removal, it may be beneficial in solid-liquid separations. Other testing will examine removal of the other radionuclides.

This testing was the second phase of testing, which aimed at optimizing the process by examining the minimum amount of reductant needed and the minimum reaction time. Although results indicated that $SnCl_2$ was effective, further work on a pH-adjusted $Fe(SO_4)$ mixture are needed. Additional tasks are needed to examine removal of the other radionuclides, solid-liquid separation technologies, slurry rheology measurements, composition variability impacts, corrosion and erosion, and slurry storage and immobilization.

Table ES-1. Summary of Results of Sorbent/Reagent Tests – Phase 1

SnCl$_2$ g/L	Hydroxy-apatite g/L	2 hour Tc DF	18 hour Tc DF	2 hr Pu DF	2 hr Cr DF
0	3	0.99 (0.01)	1.00 (0.0)	NM	NM
0.53	2	2.66 (1.8)	2.44 (1.5)	NM	NM
1	3	95.3 (131)	94.4 (130)	NM	NM
2	3	>192 (5.4)	>192 (8.7)	7.62 *(2.5)*	29.3 (1.0)
3	3	>192 (5.4)	>192 (8.7)	NM	NM
2	1	>192 (5.4)	>192 (8.7)	NM	NM
2	0	>192 (5.4)	>192 (8.7)	5.25 (0.69)	24.5 (4.1)
SnCl$_2$ g/L	**Na-oxalate g/L**				
3	6	47.3 (29)	39.0 (29)	NM	NM
Fe(SO$_4$) ·7H$_2$O g/L	**Hydroxy-apatite g/L**				
8.96	0	NM	1.1 (0.01)	NM	NM
8.96	3	NM	1.09 (0.11)	NM	NM
SnCl$_2$ g/L	**Hydroxy-apatite g/L**	**1 hour Tc DF**	**2 hour Tc DF**	**2 hr Pu DF**	**2 hr Cr DF**
1	3	>192 (0.0)	>192 (0.0)	NM	NM

Notes: Values in parenthesis represent either the standard deviation from duplicate measurements or the method uncertainty for single measurements (italicized values). NM = not measured.

Table ES-2. Summary of Results of Sorbent/Reagent Tests – Phase 2

SnCl$_2$ g/L	Hydroxy-apatite g/L	1 hour Tc DF	2 hour Tc DF
1	3	>199 (0.0)	>201 (0.0)
1	0	>199 (0.0)	>201 (0.0)
2	0	>199 (0.0)	>201 (0.0)

Notes: Values in parenthesis represent either the standard deviation from duplicate measurements or the method uncertainty for single measurements (italicized values).

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LIST OF ACRONYMNS and ABBREVIATIONS

ARP	Actinide Removal Process
Avg	Average
DF	Decontamination Factor
dpm	Disintegrations per minute
ETF	Effluent Treatment Facility
g	grams
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
SBS	Submerged Bed Scrubber
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
µg	micrograms
WESP	Wet Electrostatic Precipitator
WG	Weapons Grade
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. 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) [Mann, 2003], 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. "*Much of the load for the Supplemental LAW Facility is caused by internal recycles – namely the halides (chlorine and fluorine) and to a lesser extent sulfur (mostly as sulfates). The halide concentrations can be so high that extra LAW glass needs to be made to accommodate the halides in the glass. Approximately 32 % of the sodium in the supplemental LAW product comes from glass formers used to make the extra glass to dilute halides down to tolerable concentrations.*" [Arakali, 2012].

The objective of this development task is to evaluate decontamination of this stream using sorbents and precipitating agents so that it can be diverted elsewhere (Figure 2). The process would be comparable to the ARP[1] 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 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 [McCabe, et.al, 2013]. The preliminary testing of this process has

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[1] 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. 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.

Figure 1 Simplified LAW Off-gas System
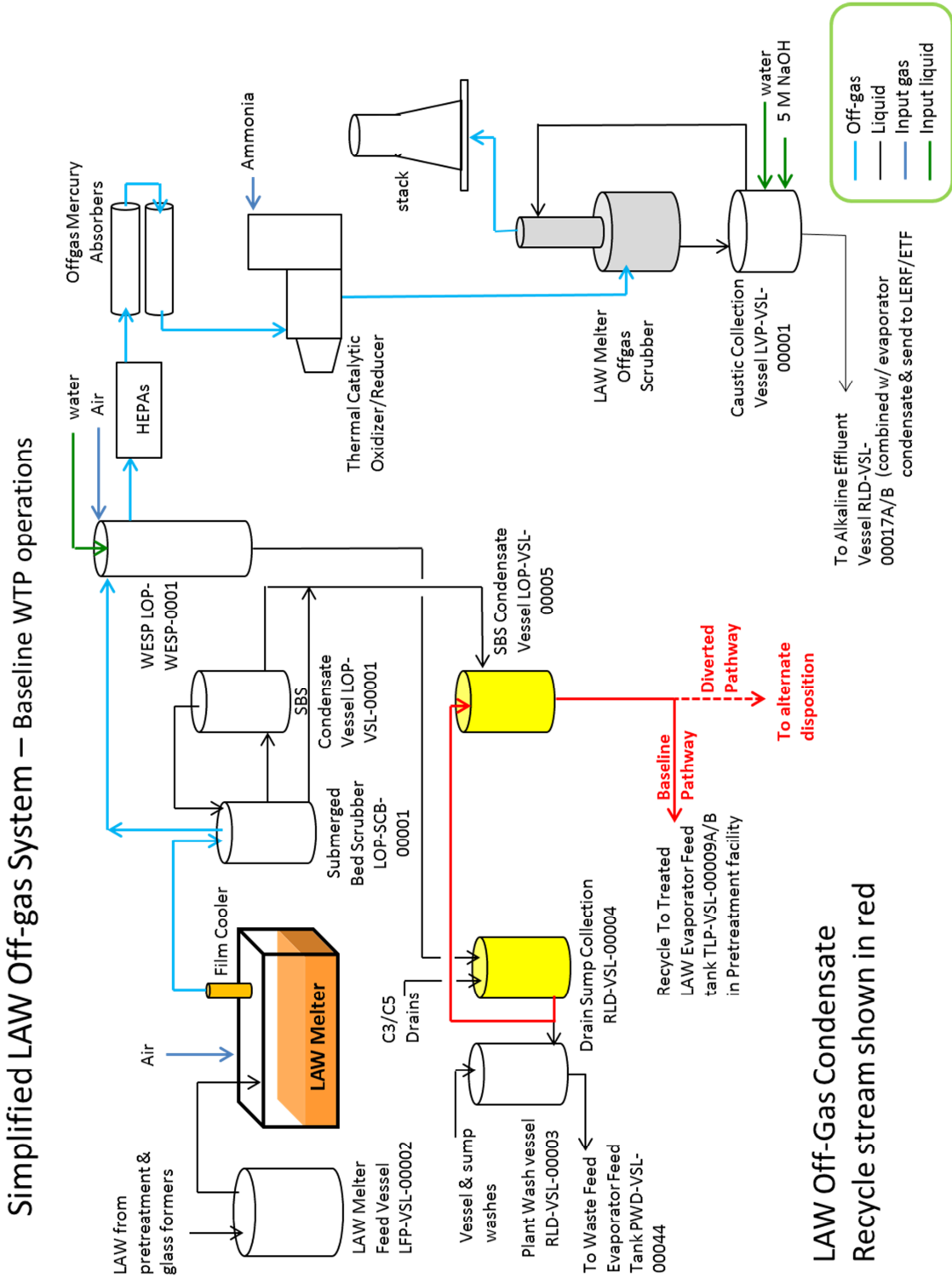
(adapted from 24590-WTP-RPT-PT-02-005, Rev. 6); (yellow indicates SBS/WESP LAW Off-Gas Condensate collection tanks, red lines indicate the collected off-gas condensate pathway)
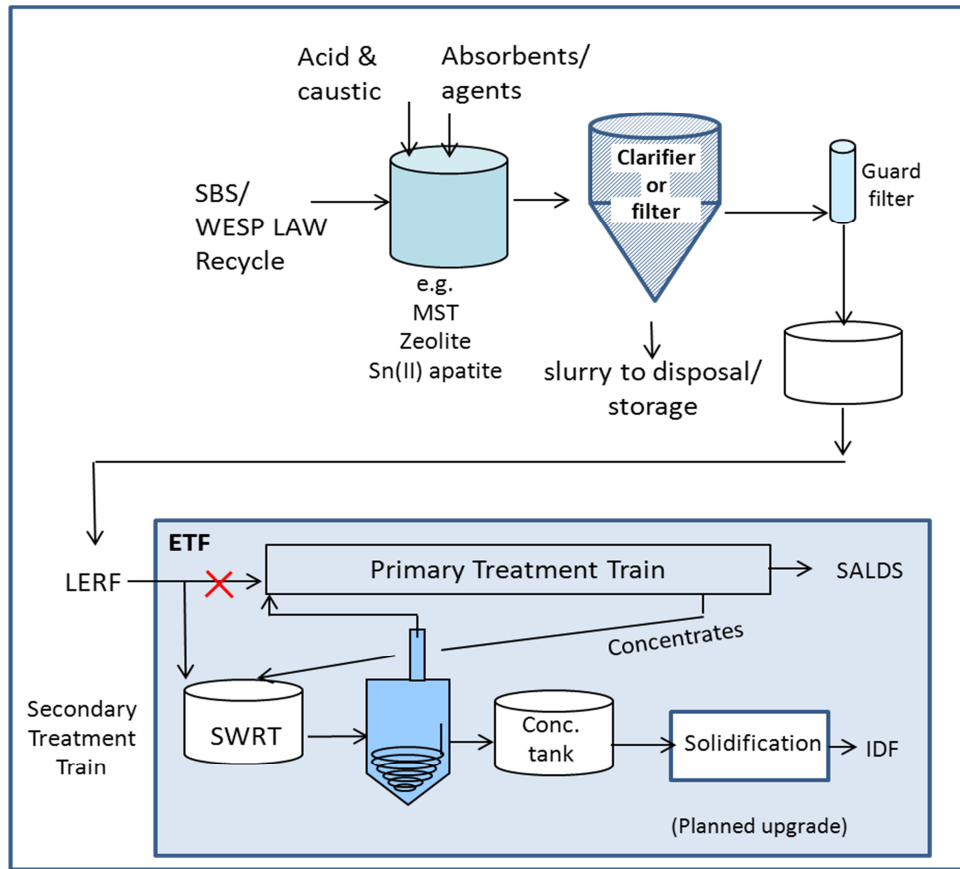
Figure 2 Schematic of a Proposed Decontamination Process and Disposition Path of LAW Off-Gas Condensate

also been documented [Taylor-Pashow et.al, 2014]. Other alternative disposal paths could be considered as well, including tank farm storage options.

1.1 <u>Simulant Formulation Basis</u>

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 [Belsher, 2012] performed by WRPS [SVF-2732]. 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. It did vary from the baseline model scenario however by diverting this stream away from recycling into the WTP, which is the scenario that would be encountered if this stream could be diverted and treated elsewhere. This had the beneficial effect of decreasing the LAW melter feed concentrations of ^{99}Tc, Cl$^-$, F$^-$, and SO$_4^-$ because they do not recycle and accumulate. Insoluble solids composition was primarily based on analysis of LAW Off-Gas Condensate obtained from pilot-scale simulant melter testing [Matlack, 2006]. Basing the solution chemistry and radionuclide content on the computer modeling rather than melter testing results extends the range of compositions and allowed evaluation of process conditions for treatment of all tank

wastes. This approach also accounts for internal WTP process streams, making it more comprehensive. However, since the computer model does not account for carryover of solids by physical entrainment, the insoluble solids were based on results from pilot-scale melter off-gas system testing. Those results showed that the insoluble solids were high in iron, indicating that they are largely glass-formers. Therefore, glass formers were added to the aqueous phase as the insoluble solid phase, where they react and either remain unreacted, dissolve, or precipitate other species. Adding the glass formers to the aqueous phase in this way is an attempt to mimic the expected conditions in the off-gas system, and is the best simulation of the stream currently available. The glass formers are then filtered out to prevent their further reaction or sorption of the radionuclides which would otherwise convolute the test results. After collecting and comparing this information, the major individual components were further assessed by comparison between the measured and computed values, and adjustments were made based on scientific judgment. The HTWOS model run scenario selected as the basis for the solution chemistry was full operation of all of the WTP facilities, including second LAW melters, albeit with diversion of the LAW Off-Gas Condensate streams from the LAW melter facilities. This diversion has the effect of lowering the concentration of volatile species (versus the condition where it is recycled and concentrations escalate), but is more realistic of the condition that would be encountered if the stream is diverted from WTP.

More detail on the basis for and synthesis of the simulant has been documented [Adamson, 2013]. An initial formulation was used for Phase 1, and a second optimized formulation of the simulant, which more closely matched the predicted composition, was also prepared and used in Phase 2 of this study. In particular, the ammonia and nitrate concentrations are adjusted. These are present in this stream due to the destruction of nitrate by reaction with sucrose in the melter, generating ammonia and NOx, which are scrubbed out in the WESP and condense into the aqueous phase. Sucrose is added to the LAW melter feed to destroy the nitrate/nitrite and expected to convert completely to carbon dioxide, which passes through the SBS/WESP scrubbers.

The radionuclide contents in the LAW Off-gas Condensate Recycle were based on the HTWOS model run by WRPS [SVF-2732]. For most radionuclides, a small fraction of each is volatile and captured in the off-gas scrubbers. Some fraction of them is also carried over by entrainment in the air sweep and bubbling in the LAW melter. Radionuclides selected for inclusion were based on a comparison to the Liquid Effluent Retention Facility (LERF)/ETF limits [McCabe, 2013]. Radionuclides that exceeded the limits were included, except for [129]I and [151]Sm. The [129]I was excluded because current aqueous separation technologies are expected to be overwhelmed by the high halide concentrations, and because the ETF is currently equipped to handle some [129]I. Furthermore, since one potential disposition path of the contaminated solids is vitrification, the [129]I would vaporize again in the melter, so a more comprehensive evaluation of its fate is needed. The [151]Sm was excluded because its calculated quantity is not credible and not expected to actually be present. It is also not appreciably soluble in LAW, based on comparison with SRS waste samples, and would be filtered in High Level Waste (HLW) and not be present in the LAW or LAW Off-Gas Condensate streams.

1.2 Decontamination Process

One option that has been previously evaluated is disposal of the LAW Off-Gas Condensate stream directly to the ETF. This option has a number of consequences to ETF including

increases in waste volume, halide levels, and radioactivity [Lueck, 2008; May, 2009]. The amount of halide sent to ETF will increase substantially, which is expected to impact corrosion [Lueck, 2008]. Likewise, the radionuclide content would substantially increase, and would challenge existing treatment capabilities [May, 2009]. If the radionuclides are removed from the Condensate stream in an alternate process and the decontaminated liquid is then sent to the ETF (Figure 2), the fluoride, sulfate, and chloride would be purged from the LAW system, yielding substantial benefits to WTP and mitigating the consequences of radioactive contamination at ETF, but still impacting the operation of ETF due to high halide levels.

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. and 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 volatile Tc specie(s) formed during vitrification has not been determined definitively, but could be Tc_2O_7, which boils at 311 °C [Rard, 2005], although $KTcO_4$ is also possible, since it sublimes at 1000 °C [Friedman, 1981].

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 [Abramowitz, 2012]. The LAW glass will be disposed in the IDF. Because ^{99}Tc has a very long half-life and is highly mobile [Icenhower, 2008, 2010], it is the major dose contributor to the Performance Assessment (PA) of the IDF [Mann, 2003], 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, or sorption onto pre-formed materials, 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) coupled with absorbents (e.g. hydroxyapatite). The Sn(II) with hydroxyapatite and oxalate has previously been found effective for precipitating Tc from water samples [Moore, 2003].

For this proposed alternative treatment process, disposal of the aqueous decontaminated Condensate stream at ETF is used as an example pathway. To accomplish this, the stream will be routed to the LERF, and transferred into the Secondary Waste Receiver Tanks in the ETF Secondary Treatment Train (similar to *case 2* in [May, 2009]). Ultimately, disposition of the solidified waste in IDF would likely require a PA calculation. In the absence of such a calculation, constituents that are in appreciable quantities will also be removed by the currently available technology to the extent practical.

The basis for the target DF for the radionuclides was described previously [Taylor-Pashow, et.al, 2014]. 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 adsorbent/precipitate slurry containing the radionuclides will be characterized in a future phase, and its potential disposition pathways will be evaluated. Immobilization testing will be in a subsequent phase of this program, once the slurry composition and quantities are defined.

2.0 Experimental Procedure

2.1 Simulant Preparation

Detail on the basis and synthesis of the simulant has been documented [Adamson, 2013]. The target concentrations of chemicals and radionuclides were derived from the output from the HTWOS calculation, documented in SVF-2732 and shown in Appendix A. The aqueous phase was prepared from dissolution of laboratory chemicals, as shown in Table 2-1. A single batch of 3.5 L of simulant (i.d.: SBS Sim. batch 3) was prepared and used for the sorbent/reagent tests for Phase 1, and a second, optimized formulation was used for Phase 2. That formulation reduces the sodium, ammonium, and nitrate concentrations. The change in these three species is not expected to impact the ^{99}Tc removal process. 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. The glass formers were then added, and mixed for five days at ambient temperature of ~ 23 ˚C. The filtrate pH was measured to be 8.2 after mixing and the 3.5 L batch was slightly adjusted to a pH of 7.3 ± 0.3 with ~ 50 drops (~2.5 mL) of concentrated nitric acid to be within the range measured in pilot-scale testing. The Phase 2 simulant (1.75 L batch) required approximately 12.5 mL of 0.4 M nitric acid and was pH 7.54 after adjustment.

Table 2-1. Aqueous Simulant Formulation Targets

Chemical	Formula	Phase 1 Mass (g)/L simulant	Phase 1 Molarity	Phase 2 Mass (g)/L simulant	Phase 2 Molarity
Aluminum nitrate nonahydrate	$Al(NO_3)_3 \cdot 9H_2O$	0.400	0.0011	0.400	0.0011
Sodium chromate	Na_2CrO_4	0.283	0.0017	0.283	0.0017
Potassium chloride	KCl	0.219	0.0029	0.219	0.0029
Sodium chloride	NaCl	1.395	0.0239	1.395	0.0239
Sodium fluoride	NaF	3.209	0.0764	3.209	0.0764
Ammonium nitrate	NH_4NO_3	4.760	0.0595	2.820	0.0352
Sodium nitrate	$NaNO_3$	1.221	0.0144	0	0*
Sodium nitrite	$NaNO_2$	0.016	0.0002	0.016	0.0002
Ammonium sulfate	$(NH_4)_2SO_4$	3.220	0.0244	3.220	0.0244
Dibasic sodium phosphate dihydrate	$Na_2HPO_4 \cdot 2H_2O$	0.040	0.0002	0.040	0.0002

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

The glass formers added to the simulant are shown in Table 2-2. These were derived from the overall mission average quantity [Arakali, 2012]. Sucrose was excluded because it is destroyed in the melter.

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	$Mg_2SiO_4\text{-}Fe_2SiO_4$	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

The solids were then removed from the neutralized solution by filtration with a 0.45-µm Nalgene®[2] filter. A portion of the filtrate was then spiked with the radioisotope tracers. Samples were analyzed for elemental composition by Inductively Coupled Plasma – Emission Spectroscopy (ICP-ES), anions and ammonium by Ion Chromatography.

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[2] Nalgene is a registered trademark of the Nalge Company Corporation, Rochester, New York.

2.2 Simulant Spiking with Radionuclides

A sample of the filtrate was spiked with the radiotracer solutions shown in Table 2-3.

Table 2-3. Radiotracer Solutions added to Simulants for Phases 1 and 2

Isotope	Matrix	Target concentration (dpm/mL)
^{137}Cs	^{137}Cs in 0.1 M HCl	1.16E4
^{238}U	$UO_2(NO_3)_2 \cdot 6H_2O$ solid	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

After stirring for at least 3 hours, the batch was filtered with a 0.45-µm Nalgene® filter. The filtrate was then analyzed for radionuclide contents. Analysis methods utilized 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 ($^{239/240}$Pu). Non-radioactive constituents were analyzed as described above. Results are summarized in Section 3 and detailed in Appendix A.

2.3 Sorption/Precipitation Tests

In general, tests were performed by adding a small amount of each solid sorbent/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 (the Tc reduction test samples were sampled at approximately two and 18 hours in Phase 1, and approximately one and two hours in Phase 2). 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 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 B.

Tables 2-5 and 2-6 show the test matrix for reagent/sorbent addition for phases 1 and 2, 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. This testing was designed to determine if the reductant reacts with Tc selectively by adding only enough Sn(II) to reduce the Cr(VI) to see if the Tc is removed instead. The calculated moles of electrons needed to reduce all of the Cr(VI) to Cr(III) is 0.0055 M, (i.e., ~3X the 0.0017 molar concentration of Cr(VI)). So, for Sn(II), 0.00275 M is 1:1, since Sn(II) is assumed to provide two electrons per atom. Reduction by Fe(II) yields only one electron per atom, so the 1:1 ratio in that case is 0.0055 M of Fe(II).

Table 2-4 Sorbent/Reagent Test Matrix for Phase 1

Molar Phase ratio (moles reductant electrons:moles oxidizer electrons)	Reductant* Mass (g/L)	Sorbent** Mass (g/L)	Target Duration (hours)
Sn(II) + hydroxyapatite			
0:1	0	3	2, 18
1:1	0.53	2	2, 18
2:1	1	3	1, 2, 18
4:1	2	3	2, 18
6:1	3	3	2, 18
4:1	2	1	2, 18
4:1	2	0	2, 18
Sn(II) + sodium oxalate			
6:1	3	6	2, 18
Fe(II) + hydroxyapatite			
6:1	8.96	0	2, 18
6:1	8.96	3	2, 18

*reductant mass is shown as $SnCl_2$ (anhydrous) or $FeSO_4 \cdot 7H_2O$
**sorbent mass is mass as hydroxyapatite or sodium oxalate

Table 2-5 Sorbent/Reagent Test Matrix for Phase 2

Molar Phase ratio (moles reductant electrons:moles oxidizer electrons)	Reductant* Mass (g/L)	Sorbent** Mass (g/L)	Target Duration (hours)
Sn(II) + hydroxyapatite			
2:1	1	3	1, 2
2:1	1	0	1, 2
4:1	2	0	1, 2

The sources of the sorbents and precipitation reagents were:
Tin(II) chloride dihydrate ($SnCl_2 \cdot 2H_2O$): Fisher chemical, Lot # 096665
Hydroxyapatite ($Ca_5(PO_4)_3OH$): Aldrich chemical, Lot # MKBK2210V
Sodium oxalate ($Na_2C_2O_4$): Aldrich chemical, Lot # 12628KO
Iron (II) sulfate heptahydrate: Fisher chemical, Lot# 984410

2.4 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 [Wilmarth, 2013]. Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60. Savannah River National Laboratory (SRNL) documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.

3.0 Results and Discussion

3.1 Simulant Composition

Results of the average and standard deviation of the duplicate chemical analysis of the neutralized, filtered simulants are shown in Table 3-1. These match the target compositions reasonably well, although for Phase 1, more ammonium was added than the target (~ 18% higher than the 'Average' case and ~ 9% higher than the 'Maximum' case). The Phase 2 had a better match for ammonium, but was low in nitrate. Both formulations are relatively good matches versus the accuracy and range of the projected composition, and these 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. Additionally, the analyzed soluble fluoride in the Phase 1 simulant was about 200 mg/L lower (1.25E3 mg/L) than the target (1.45E3 mg/L), but Phase 2 was very close. The sulfur analysis by ICP-ES for Phase 2 indicated higher than expected, but the sulfate analysis by IC indicated it is very 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 [Matlack, 2006]. 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.

3.2 Decontamination Test Results

For each test, a freshly filtered control sample was submitted for analysis alongside the decontaminated test sample to ensure consistency, and those results were used to calculate the DF. Averaged results of the radionuclide analyses on the control samples of the spiked filtered simulant are shown in Table 3-2 for Phase 1 simulant, and Table 3-3 for Phase 2. Results shown for Tc and U analysis 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 ^{241}Am appears to be insoluble in the as-prepared simulant. Spiking of the simulant with a recently analyzed stock solution of known activity was unsuccessful at achieving a measurable amount of ^{241}Am in the filtered simulant. The $^{239/240}$Pu also appears to have limited solubility, as the target activity could not be achieved. The $^{239/240}$Pu activity in the Phase 1 simulant was ~23% of the target. The amount added to the Phase 2 simulant was scaled up to account for not achieving the target in the Phase 1 simulant, but the $^{239/240}$Pu activity still only reached ~27% of the target. Immediately after spiking, there was more soluble Pu than shown below, and it was observed that there was less soluble Pu present as time progressed, suggesting it was not at equilibrium. The reported DF measurements account for this potential non-equilibrium condition by using the initial Pu concentration measured in that same sample batch that was filtered and analyzed at the same time. Future testing will examine if the Pu continues to precipitate. Note that the non-equilibrium condition may be due to either a slow approach to solubility or a slowly changing Pu oxidation state. The ^{137}Cs content was higher than the target, which appears to be due to a higher than expected concentration in the stock solution, which was also observed in other tests.

Table 3-1 Neutralized Simulant Filtrate Chemical Composition

Component	Phase 1 Simulant Concentration (mg/L)	Std. Dev.	Phase 2 Simulant Concentration (mg/L)	Std. Dev.	HTWOS projection (avg. SVF-2732) (mg/L)
Al	<0.100		<1.0		28
B	253	8	242	8.8	GF[1]
Ca	<0.100		1.1	0.014	GF[1]
Cr	91.0	0.4	89.9	0.86	91
Fe	<0.100		<1.0		GF[1]
K	150	1	103	0.54	115
Li	80.3	0.4	80.9	0.80	GF[1]
Mg	<0.100		<1.0		GF[1]
Na	2.98E3	0*	2.28E3	14	2.29E3
P	<10.0		<1.0		7 (as PO_4^{-3})
S	832	5	1.26E3	15	780 (as SO_4^{-2})
Si	52.7	0	55.0	0.42	GF[1]
Ti	<0.100		<1.0		GF[1]
Zn	28.6	0.2	14.6	0.15	GF[1]
Zr	<0.100		<1.0		GF[1]
F^-	1.25E3	7	1.41E3	0*	1.45E3
Cl^-	934	5	945	1.4	950
NO_2^-	<10				10.7
NO_3^-	4.90E3	21	3.20E3	57	5.53E3
SO_4^{-2}	2.41E3	0*	2.23E3	14	2.34E3
PO_4^{-3}	<10				21.5
NH_4^+	1.77E3**		1.54E3**		1.51E3

*Standard Deviation of zero indicates the two analysis results were identical
**analysis of a single sample
[1]Glass Former component; minimal HTWOS projected concentration

Table 3-2 Average Phase 1 Simulant Control Sample Radionuclide Composition

Isotope	Concentration (dpm/mL)	Reported Method Uncertainty	% of Target Concentration
^{137}Cs	2.46E4	5.0%	212
^{238}U	5.62E-1 (0.754 mg/L)	20%	90
$^{239/240}Pu$	1.90E1	9.0%	23
^{85}Sr	6.26E4	5.0%	108
^{99}Tc	7.24E4 (1.92 mg/L)	20%	79
^{241}Am	<3.36E1	mda	<6.5

mda = minimum detectable activity

Table 3-3 Average Phase 2 Simulant Control Sample Radionuclide Composition

Isotope	Concentration (dpm/mL)	Reported Method Uncertainty	% of Target Concentration
^{137}Cs	2.58E4	5.0%	222
^{238}U	5.96E-1 (0.799 mg/L)	20%	96
$^{239/240}$Pu	2.28E1	11.9%	27
^{85}Sr	7.29E4	5.0%	126
^{99}Tc	7.51E4 (1.99 mg/L)	20%	82
^{241}Am	<9.87E1	mda	<19

mda = minimum detectable activity

Results of the Sorbent/Reagent tests are shown in Tables 3-4 and 3-5. Details of the test results can be found in Appendix B. Analysis of the Tc, Sr, and U were done by ICP-MS. The reported Sr is based on mass 88, i.e., non-radioactive strontium present as an impurity in the chemicals used for simulant preparation. Selected samples were also measured for Sr removal by gamma counting the Sr-85, and those results are substituted below, if available. The U is reported based on mass 238. No cesium was removed from the samples that were analyzed, so the results are not shown here but are provided in Appendix B.

In Phase 1 tests, the Sn(II) reducing agent with or without hydroxyapatite sorbent worked extremely well for Tc removal. The Sn(II) hydroxyapatite system removed essentially all of the Tc (to below a method detection limit of 10 μg/L) within 2 hours. Results of both Tc removal and pH for the duplicate tests with the first trial of 1 g/L SnCl$_2$ and 3 g/L hydroxyapatite did not agree, so the test was repeated (last row in Table 3-4). Results suggest that as little as 1 g/L of SnCl$_2$ may be sufficient to remove Tc, and that hydroxyapatite may not be needed. These observations guided testing in Phase 2, which focused on narrowing the minimum required conditions. Phase 1 results also indicated that using sodium oxalate as a sorbent was less effective. It is not known why the sodium oxalate test had a poorer DF than the other test with comparable levels of SnCl$_2$ but without any sorbent. Perhaps the oxalate ion precipitates or complexes the stannous ion, prohibiting its reaction with Tc.

The Fe(II) did not appear to be an effective Tc removal agent. The 2-hour samples were not analyzed because after being stored overnight, solids appeared in the filtered samples, indicating a post-filtration precipitation. The 18-hour samples remained solids-free after filtration, but analysis results indicated no removal of Tc. The pH decreased to ~3.3, which might impact the solubility or stability of the reduced Tc, perhaps explaining why ferrous was less effective than stannous.

Consistent with preliminary tests, the Sn(II) reductions caused precipitation of chromium, presumably due to reduction of Cr(VI) to Cr(III). Since Cr(VI) is in much higher concentration than Tc(VII), it appears that sufficient Sn(II) must be added to reduce both the Cr(VI) and Tc(VII) to achieve a good decontamination of ^{99}Tc.

Table 3-4 Summary of Results of Sorbent/Reagent Tests – Phase 1

SnCl₂ g/L	Hydroxy-apatite g/L	2 hour Tc DF	18 hour Tc DF	2 hour Sr DF	18 hr Sr DF	2 hr U DF	18 hr U DF	2 hr Pu DF	2 hr Cr DF	pH**
0	3	0.99 (0.01)	1.00 (0.0)	0.83 (1.0)	1.36 (0.39)	0.99 (0.04)	1.01 (0.0)	NM	NM	7.74 7.70
0.53	2	2.66 (1.8)	2.44 (1.5)	>2.18 (0.54)	>2.07 (0.59)	1.22 (0.02)	1.26 (0.01)	NM	NM	7.09 7.53
1	3	95.3 (131)	94.4 (130)	>2.18 (0.54)	>2.07 (0.59)	1.30 (0.0)	1.34 (0.03)	NM	NM	7.24 6.35
2	3	>192 (5.4)	>192 (8.7)	2.29* (0.12)	1.68 (0.47)	1.44 (0.03)	1.54 (0.22)	7.62 (2.5)	29.3 (1.0)	5.57 5.58
3	3	>192 (5.4)	>192 (8.7)	1.06 (0.07)	1.25 (0.48)	1.88 (0.31)	2.56 (1.1)	NM	NM	5.22 5.31
2	1	>192 (5.4)	>192 (8.7)	0.92 (0.57)	1.07 (0.30)	1.27 (0.01)	1.39 (0.12)	NM	NM	5.52 5.52
2	0	>192 (5.4)	>192 (8.7)	1.65* (0.03)	1.07 (0.30)	1.16 (0.01)	1.10 (0.0)	5.25 (0.69)	24.5 (4.1)	5.44 5.59
SnCl₂ g/L	**Na-oxalate g/L**									
3	6	47.3 (29)	39.0 (29)	0.52 (0.07)	0.44 (0.12)	1.07 (0.02)	1.03 (0.0)	NM	NM	5.31 5.48
Fe(SO₄)·7H₂O g/L	**Hydroxy-apatite g/L**									
8.96	0	NM	1.1 (0.01)	NM	1.84 (0.52)	NM	1.01 (0.03)	NM	NM	3.20 3.20
8.96	3	NM	1.09 (0.11)	NM	>2.07 (0.59)	NM	1.00 (0.01)	NM	NM	3.21 3.29
SnCl₂ g/L	**Hydroxy-apatite g/L**	**1 hour Tc DF**	**2 hour Tc DF**	**1 hour Sr DF**	**2 hr Sr DF**	**1 hr U DF**	**2 hr U DF**	**2 hr Pu DF**	**2 hr Cr DF**	
1	3	>192 (0.0)	>192 (0.0)	NM	NM	1.29 (0.06)	1.27 (0.02)	NM	NM	

Notes: Values in parenthesis represent either the standard deviation from duplicate measurements or the method uncertainty for single measurements (italicized values). NM = not measured. *Sr-85 spike DF is reported instead of ICP-MS. **Two pH values are shown, one for each duplicate.

As expected, removal of Sr was minimal. Although the result indicates a DF of >2 for some mixtures, the results are very close to the detection limit of the ICP-MS for mass 88 and are therefore suspect. Curiously, adding oxalate as the sorbent indicated a DF <1, suggesting either an analysis detection limit issue, or, perhaps, the presence of a small amount of strontium in the sodium oxalate.

The Sn(II) also removed some of the Pu, with a DF of 7.62 with hydroxyapatite and 5.25 without it. The mechanism of this removal is not known. Since the Pu was added as a nitric acid

solution, it should have been as (IV) oxidation state. Although the stannous may have reduced it, it also may simply be a co-precipitation phenomenon with the precipitated tin oxide/hydroxide, since it had also been observed that the Pu solubility was not at equilibrium.

Based on Phase 1 results, additional testing was performed using the Phase 2 simulant formulation. Testing focused on small amounts of Sn(II), short mixing durations, and the absence of hydroxyapatite. Results, shown in Table 3-5, indicate excellent removal of Tc in all conditions. As little as 1 g/L of $SnCl_2$ and one hour of mixing removed the Tc to less than the detection limit.

Table 3-5. Summary of Results of Sorbent/Reagent Tests – Phase 2

$SnCl_2$ g/L	Hydroxy-apatite g/L	1 hour Tc DF	2 hour Tc DF	1 hr U DF	2 hr U DF
1	3	>199 (0.0)	>201 (0.0)	1.38 (0.03)	1.37 (0.04)
1	0	>199 (0.0)	>201 (0.0)	1.22 (0.03)	1.21 (0.02)
2	0	>199 (0.0)	>201 (0.0)	1.23 (0.02)	1.20 (0.01)

Note: Values in parenthesis represent the standard deviation from duplicate measurements.

Stannous chloride addition results in some of the tin remaining soluble after the chromium and technetium are removed. Results of measurements using ICP-MS after two hours are shown below, and similar results were observed on samples after 18 hours. Addition of 2 g/L or more of stannous chloride resulted in nearly half of the tin remaining in solution. The form or valence state of the soluble tin was not investigated. The sample that contained sodium oxalate had the highest concentration of soluble tin, suggesting that the oxalate ion solubilizes it. These results suggest that only 1 g/L of stannous chloride removes the Tc and leaves a small amount that is soluble in solution. The resulting solid is expected to contain Sn, Cr, and Tc. If the soluble tin is still present as Sn(II), it may delay re-oxidation and thereby re-solubilizing Tc, giving time for solid-liquid separation or further processing to occur. Since the results in Phase 1 indicate that the DF was not diminished in 18 hours of mixing, this suggests that the solution is stable, although contact with air was not controlled in that experiment.

Table 3-6. Filtrate Tin Measurements for Phases 1 and 2

$SnCl_2$ g/L	Hydroxy-apatite g/L	Soluble Sn (2 hr) (mg/L)	Actual amount Sn added (mg/L)	% soluble Sn
0.53	2	2.50	355	0.70
1	3	1.48	629	0.24
2	3	581	1.27E3	46
3	3	1.02E3	1.88E3	54
2	1	631	1.25E3	50
2	0	616	1.26E3	49
1	3	19.5	634	3.1
1*	3	42.1	624	6.7
1*	0	72.8	622	12
2*	0	503	1.25E3	40
$SnCl_2$ g/L	Na-oxalate g/L			
3	6	1.31E3	1.88E3	70

*phase 2 results

4.0 Conclusions

Treating the SBS-WESP Off-gas Condensate Recycle simulant using $SnCl_2$ proved successful for the removal of Tc. The Sn(II) was much more successful at removal of Tc than Fe(II). Only 1 g/L of $SnCl_2$ was necessary for good Tc removal from this simulant formulation. Although not measured directly, it is expected that the Tc would be in the form of pertechnetate in the 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.

The Sn(II) reducing agent, with or without hydroxyapatite sorbent, worked extremely well for Tc removal. Although the hydroxyapatite does not appear to be vital to the initial removal of Tc, perhaps it will be important to the re-oxidation and dissolution rate. Prior work [Moore, 2003], demonstrated that addition of hydroxyapatite to the $SnCl_2$ solution delayed re-oxidation and dissolution of precipitated Tc. Future testing will examine the dissolution rate.

Technetium removal by reduction with Fe(II) was not effective, although the concomitant reduction in pH may have had the effect of dissolving the Tc even if it had been reduced. Further testing would be needed to determine if a lower Fe(II) dose could be effective for Tc removal, or if addition of a small amount of caustic would permit removal.

A key parameter for development of the flow sheet for this process is understanding which species consume Sn(II) before it can work to remove Tc. These other reactions will cause addition of more Sn(II) and generate more precipitated slurry waste. The molar ratio of Sn(II) to Cr(VI) is roughly 1.5:1 at the 0.53 g/L dose of $SnCl_2$, and is roughly 3:1 at 1 g/L of $SnCl_2$. Since Sn(II) can yield two electrons on oxidation to Sn(IV), and Cr(VI) would consume three electrons

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to convert to Cr(III), the 1.5:1 ratio would be the minimum necessary to react with all of the Cr in solution. Since the 0.53 g/L concentration of Sn(II) was not sufficient to remove Tc, this indicates that the Sn(II) does not selectively reduce the Tc versus Cr. Thus, the amount of Sn(II) needed to remove Tc must exceed the amount needed to remove all of the Cr(VI). Other oxidizers in solution appear to have only a minor effect on Tc removal, with only a small amount (~0.5 g/L) of excess $SnCl_2$ needed to remove the Tc. These results indicate that this is a viable process and needs only about 0.1 wt% $SnCl_2$ to remove the Tc, which would be a relatively small volume waste stream to disposition. The amount of Sn(II) needed appears directly correlated with the amount of Cr(VI) present, so it will dictate the dosing needed and thus the precipitated waste volume. This testing indicates that the ^{99}Tc is easily removed from this stream.

The Am and Pu were not very soluble in this stream composition, indicating that if they are present at the projected concentrations, solid-liquid separation, without a sorbent, may be sufficient.

5.0 Future Work

Additional work is needed to examine stability of the stream toward oxidation to determine if sufficient time is available to filter or settle the solids prior to re-dissolution of Tc. Additionally, depending on the final fate of the aqueous stream, removal of additional radionuclides may be needed, so testing is needed to examine coupling this Tc removal process with additional process steps. Solid-liquid separation, such as settling or filtration, also needs to be investigated.

6.0 References

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Appendix A. Sorbent/Reagent Decontamination Test Detail

Below are the details of the results from the Sorbent/Reagent decontamination tests.

Test ID	HLAW-33	HLAW-34	HLAW-35	HLAW-36	HLAW-37	HLAW-38	HLAW-39
Initial Soln Volume (L)	0.019	0.019	0.019	0.019	0.019	0.019	0.019
Simulant	SBS LAW	SBS LAW	SBS LAW	SBS LAW	SBS LAW	SBS LAW	SBS LAW
Sorbent	None (control)	Sn(II) & hydroxyapatite (0:1)	Sn(II) & hydroxyapatite (1:1)	Sn(II) & hydroxyapatite (2:1)	Sn(II) & hydroxyapatite (4:1)	Sn(II) & hydroxyapatite (6:1)	Sn(II) & hydroxyapatite (4:1)
Target Sorbent Concentration (g/L)	0	3 g/L hydroxyapatite	0.53 g/L SnCl2 + 2 g/L hydroxyapatite	1 g/L SnCl2 + 3 g/L hydroxyapatite	2 g/L SnCl2 + 3 g/L hydroxyapatite	3 g/L SnCl2 + 3 g/L hydroxyapatite	2 g/L SnCl2 + 1 g/L hydroxyapatite
Elapsed Time (h) - Sample 1	2.00	2.02	2.02	2.02	2.03	2.05	2.05
Elapsed Time (h) - Sample 2	18.03	18.07	18.07	18.08	18.08	18.08	18.08
final pH	7.76	7.74	7.09	7.24	5.57	5.22	5.52
Sample 1 Sr DF	1.00	1.53	> 2.56	> 2.56	1.17	1.11	1.32
Sr DF Uncertainty	2.83E-01	4.34E-01	7.25E-01	7.25E-01	3.90E-01	3.15E-01	3.74E-01
Sample 1 Tc DF	1.00	1.00	3.93	2.92	> 195	> 195	> 195
Tc DF Uncertainty	2.83E-01	2.84E-01	1.11E+00	8.26E-01	5.53E+01	5.53E+01	5.53E+01
Sample 1 U DF	1.00	1.02	1.24	1.29	1.41	1.65	1.26
U DF Uncertainty	2.83E-01	2.89E-01	3.50E-01	3.66E-01	4.00E-01	4.68E-01	3.56E-01
Sample 1 Sr DF (gamma)	1.00				2.37		
Sr DF Uncertainty	7.07E-02				1.68E-01		
Sample 1 Cs DF	1.00				1.00		
Cs DF Uncertainty	7.07E-02				7.10E-02		
Sample 1 Pu DF	1.00				> 3.95		
Pu DF Uncertainty	2.38E-01				#VALUE!		
Sample 1 Cr DF	1.00				30.1		
Cr DF Uncertainty	1.41E-01				5.25E+00		
Sample 2 Sr DF	1.00	1.36	> 2.07	> 2.07	1.68	1.25	1.07
Sr DF Uncertainty	2.83E-01	3.85E-01	5.86E-01	5.86E-01	4.74E-01	4.84E-01	3.02E-01
Sample 2 Tc DF	1.00	0.99	3.51	2.72	> 198	> 198	> 198
Tc DF Uncertainty	2.83E-01	2.81E-01	9.94E-01	7.70E-01	5.61E+01	5.61E+01	5.61E+01
Sample 2 U DF	1.00	1.01	1.27	1.32	1.38	1.78	1.30
U DF Uncertainty	2.83E-01	2.86E-01	3.60E-01	3.73E-01	3.89E-01	5.04E-01	3.69E-01

Appendix B continued. Sorbent/Reagent Decontamination Test Detail

Test ID	HLAW-40	HLAW-41	HLAW-42	HLAW-43	HLAW-44	HLAW-45	HLAW-46
Initial Soln Volume (L)	0.019	0.019	0.019	0.019	0.019	0.019	0.019
Simulant	SBS LAW	SBS LAW	SBS LAW	SBS LAW	SBS LAW	SBS LAW	SBS LAW
Sorbent	Sn(II) (4:1)	Sn(II) & Na oxalate (6:1)	Ferrous (6:1)	Ferrous & hydroxyapatite (6:1)	None (control)	Sn(II) & hydroxyapatite (0:1)	Sn(II) & hydroxyapatite (1:1)
Target Sorbent Concentration (g/L)	2 g/L SnCl2	3 g/L SnCl2 + 6 g/L Na oxalate	1.8 g/L Fe(II)	1.8 g/L Fe(II) + 3 g/L hyroxyapatite	0	3 g/L hydroxyapatite	0.53 g/L SnCl2 + 2 g/L hydroxyapatite
Elapsed Time (h) - Sample 1	2.20	2.08	2.08	2.05	2.00	2.03	2.05
Elapsed Time (h) - Sample 2	18.23	18.10	18.12	18.08	18.02	18.03	18.05
final pH	5.44	5.31	3.20	3.21	7.75	7.70	7.53
Sample 1 Sr DF	1.01	0.57			1.00	0.12	> 1.79
Sr DF Uncertainty	2.85E-01	1.60E-01			2.83E-01	3.33E-02	5.07E-01
Sample 1 Tc DF	> 195	26.7			1.00	0.98	1.38
Tc DF Uncertainty	5.53E+01	7.54E+00			2.83E-01	2.78E-01	3.91E-01
Sample 1 U DF	1.16	1.05			1.00	0.97	1.21
U DF Uncertainty	3.27E-01	2.97E-01			2.83E-01	2.74E-01	3.41E-01
Sample 1 Sr DF (gamma)	1.68				1.00		
Sr DF Uncertainty	1.19E-01				7.07E-02		
Sample 1 Cs DF	1.00				1.00		
Cs DF Uncertainty	7.07E-02				7.07E-02		
Sample 1 Pu DF	4.76				1.00		
Pu DF Uncertainty	1.40E+00				2.63E-01		
Sample 1 Cr DF	21.6				1.00		
Cr DF Uncertainty	4.12E+00				1.41E-01		
Sample 2 Sr DF	1.07	0.44	1.84	> 2.07	> 1.00	> 1.00	> 1.00
Sr DF Uncertainty	3.04E-01	1.25E-01	5.19E-01	5.86E-01	2.83E-01	2.83E-01	2.83E-01
Sample 2 Tc DF	> 198	18.7	1.10	1.17	1.0	1.00	1.36
Tc DF Uncertainty	5.61E+01	5.28E+00	3.12E-01	3.30E-01	2.83E-01	2.83E-01	3.84E-01
Sample 2 U DF	1.10	1.03	1.02	0.99	1.00	1.01	1.25
U DF Uncertainty	3.11E-01	2.92E-01	2.90E-01	2.81E-01	2.83E-01	2.84E-01	3.54E-01

Appendix B continued. Sorbent/Reagent Decontamination Test

Test ID	HLAW-47	HLAW-48	HLAW-49	HLAW-50	HLAW-51	HLAW-52	HLAW-53	HLAW-54
Initial Soln Volume (L)	0.019	0.019	0.019	0.019	0.019	0.019	0.019	0.019
Simulant	SBS LAW	SBS LAW	SBS LAW	SBS LAW	SBS LAW	SBS LAW	SBS LAW	SBS LAW
Sorbent	Sn(II) & hydroxyapatite (2:1)	Sn(II) & hydroxyapatite (4:1)	Sn(II) & hydroxyapatite (6:1)	Sn(II) & hydroxyapatite (4:1)	Sn(II) (4:1)	Sn(II) & Na oxalate (6:1)	Ferrous (6:1)	Ferrous & hydroxyapatite (6:1)
Target Sorbent Concentration (g/L)	1 g/L SnCl2 + 3 g/L hydroxyapatite	2 g/L SnCl2 + 3 g/L hydroxyapatite	3 g/L SnCl2 + 3 g/L hydroxyapatite	2 g/L SnCl2 + 1 g/L hydroxyapatite	2 g/L SnCl2	3 g/L SnCl2 + 6 g/L Na oxalate	1.8 g/L Fe(II)	1.8 g/L Fe(II) + 3 g/L hyroxyapatite
Elapsed Time (h) - Sample 1	2.05	2.07	2.07	2.03	2.03	2.02	2.03	2.03
Elapsed Time (h) - Sample 2	18.05	18.08	18.08	18.05	18.05	18.03	18.03	18.03
final pH	6.35	5.58	5.31	5.52	5.59	5.48	3.20	3.29
Sample 1 Sr DF	> 1.79	1.01	1.01	0.51	0.96	0.47		
Sr DF Uncertainty	5.07E-01	2.87E-01	2.87E-01	1.45E-01	3.19E-01	1.34E-01		
Sample 1 Tc DF	> 188	> 188	> 188	> 188	> 188	67.9		
Tc DF Uncertainty	5.31E+01	5.31E+01	5.31E+01	5.31E+01	5.31E+01	1.92E+01		
Sample 1 U DF	1.30	1.46	2.10	1.28	1.17	1.08		
U DF Uncertainty	3.68E-01	4.13E-01	5.93E-01	3.62E-01	3.31E-01	3.06E-01		
Sample 1 Sr DF (gamma)		2.21			1.63			
Sr DF Uncertainty		1.56E-01			1.15E-01			
Sample 1 Cs DF		1.00			1.00			
Cs DF Uncertainty		7.10E-02			7.10E-02			
Sample 1 Pu DF		7.62			5.74			
Pu DF Uncertainty		2.46E+00			1.85E+00			
Sample 1 Cr DF		28.6			27.4			
Cr DF Uncertainty		4.88E+00			6.27E+00			
Sample 2 Sr DF	> 1.00	> 1.00	> 1.00	> 1.00	> 1.00	> 1.00	> 1.00	> 1.00
Sr DF Uncertainty	2.83E-01	2.83E-01	2.83E-01	2.83E-01	2.83E-01	2.83E-01	2.83E-01	2.83E-01
Sample 2 Tc DF	> 186	> 186	> 186	> 186	> 186	59.3	1.09	1.01
Tc DF Uncertainty	5.26E+01	5.26E+01	5.26E+01	5.26E+01	5.26E+01	1.68E+01	3.07E-01	2.86E-01
Sample 2 U DF	1.36	1.69	3.35	1.48	1.10	1.03	0.99	1.00
U DF Uncertainty	3.84E-01	4.79E-01	9.46E-01	4.17E-01	3.12E-01	2.92E-01	2.79E-01	2.83E-01

Appendix B continued. Sorbent/Reagent Decontamination Test

	HLAW-55	HLAW-56	HLAW-57	HLAW-58	HLAW-59	HLAW-60	HLAW-61	HLAW-62	HLAW-63	HLAW-64
Test ID	HLAW-55	HLAW-56	HLAW-57	HLAW-58	HLAW-59	HLAW-60	HLAW-61	HLAW-62	HLAW-63	HLAW-64
Initial Soln Volume (L)	0.019	0.019	0.019	0.019	0.019	0.019	0.019	0.019	0.019	0.019
Simulant	SBS LAW Simulant (2013 batch)		SBS LAW Phase 2 (2014 batch)	SBS LAW Phase 2 (2014 batch)	SBS LAW Phase 2 (2014 batch)	SBS LAW Phase 2 (2014 batch)	SBS LAW Phase 2 (2014 batch)	SBS LAW Phase 2 (2014 batch)	SBS LAW Phase 2 (2014 batch)	SBS LAW Phase 2 (2014 batch)
Sorbent	Sn(II) & hydroxyapatite (2:1) repeat	Sn(II) & hydroxyapatite (2:1) repeat	Control (None)	Control (None)	Sn(II) & hydroxyapatite (2:1)	Sn(II) & hydroxyapatite (2:1)	Sn(II) (2:1)	Sn(II) (2:1)	Sn(II) (4:1)	Sn(II) (4:1)
Target Sorbent Concentration (g/L)	1 g/L SnCl2 + 3 g/L hydroxyapatite	1 g/L SnCl2 + 3 g/L hydroxyapatite	0	0	1 g/L SnCl2 + 3 g/L hydroxyapatite	1 g/L SnCl2 + 3 g/L hydroxyapatite	1 g/L SnCl2	1 g/L SnCl2	2 g/L SnCl2	2 g/L SnCl2
Elapsed Time (h) - Sample 1	1.00	0.98	1.00	1.02	1.02	0.98	0.98	0.97	0.97	0.97
Elapsed Time (h) - Sample 2	1.98	1.97	1.98	2.00	2.00	1.97	1.98	1.98	1.98	2.00
Sample 1 Tc DF	>192	>192	1.00	1.00	>199	>199	>199	>199	>199	>199
Tc DF Uncertainty	3.88E+01	3.88E+01	2.84E-01	2.82E-01	5.62E+01	5.62E+01	5.62E+01	5.62E+01	5.62E+01	5.62E+01
Sample 1 U DF	1.34	1.25	1.01	0.99	1.36	1.40	1.23	1.20	1.21	1.25
U DF Uncertainty	2.85E-01	2.66E-01	2.85E-01	2.81E-01	3.84E-01	3.95E-01	3.49E-01	3.39E-01	3.43E-01	3.53E-01
Sample 2 Tc DF	>192	>192	1.00	1.00	>201	>201	>201	>201	>201	>201
Tc DF Uncertainty	3.88E+01	3.88E+01	2.82E-01	2.84E-01	5.69E+01	5.69E+01	5.69E+01	5.69E+01	5.69E+01	5.69E+01
Sample 2 U DF	1.33	1.21	1.00	1.00	1.34	1.40	1.22	1.20	1.19	1.20
U DF Uncertainty	2.84E-01	2.59E-01	2.84E-01	2.82E-01	3.79E-01	3.97E-01	3.46E-01	3.39E-01	3.37E-01	3.41E-01

Distribution:

S. L. Marra, 773-A
F. M. Pennebaker, 773-42A
T. B. Brown, 773-A
E. N. Hoffman, 999-W
D. H. McGuire, 999-W
S. D. Fink, 773-A
C. C. Herman, 773-A
K. M. L. Taylor-Pashow, 773-A
C. A. Nash, 773-42A
C. L. Crawford, 773-42A
D. J. McCabe, 773-42A
W. R. Wilmarth, 773-A
T. B. Peters, 773-42A
D. T. Herman, 735-11A
A. D. Cozzi, 999-W
D. K. Peeler, 999-W
K. A. Roberts, 773-43A
P. R. Jackson, 703-46A
K. H. Subramanian, WRPS
Records Administration (EDWS)
J. A. Diediker. DOE-ORP
T. W. Fletcher, DOE-ORP
B. J. Harp, DOE-ORP
C. C. Harrington, DOE-ORP
S. H. Pfaff, DOE-ORP
G. M. Duncan, WTP
S. T. Arm, WRPS
P. A. Cavanah, WRPS
T. W. Crawford, WRPS
W. G. Ramsey, WRPS
D. J. Swanberg, WRPS
N. P. Machara, DOE-EM
J. A. Poppiti, DOE-EM
D. J. Koutsandreas, DOE-EM
R. A. Gilbert, DOE-ORP
C. J. Winkler, WRPS
R. H. Spires, WRPS