

Investigation of Variable Compositions on the Removal of Technetium from Hanford Waste Treatment Plant Low Activity Waste Melter Off-Gas Condensate Simulant

Kathryn M. L. Taylor-Pashow

Daniel J. McCabe

John M. Pareizs

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REVIEWS AND APPROVALS

AUTHORS:

Kathryn M. L. Taylor-Pashow, Advanced Characterization and Processing	Date
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Daniel J. McCabe, Waste Form Processing Technologies	Date
--	------

John M. Pareizs, Process Technology Programs	Date
--	------

TECHNICAL REVIEW:

Thomas B. Peters, Advanced Characterization and Processing, Reviewed per E7 2.60	Date
--	------

APPROVAL:

Elizabeth N. Hoffman, Manager Environmental Management Technology Integration	Date
--	------

Andrew P. Fellingner, Manager Environmental Management Technology Integration	Date
--	------

EXECUTIVE SUMMARY

The Low Activity Waste (LAW) vitrification facility at the Hanford Waste Treatment and Immobilization Plant (WTP) will generate an aqueous condensate recycle stream (LAW Off-Gas Condensate) from the off-gas system. The plan for disposition of this stream during baseline operations 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. The primary reason to recycle this stream is so that the semi-volatile ^{99}Tc isotope eventually becomes incorporated into the glass. This stream also contains non-radioactive salt components that are problematic in the melter, so diversion of this stream to another process would eliminate recycling of these salts and would enable simplified operation of the LAW melter and the Pretreatment Facilities. This diversion from recycling this stream within WTP would have the effect of decreasing the LAW vitrification mission duration and quantity of glass waste. The concept being tested here involves removing the ^{99}Tc so that the decontaminated aqueous stream, with the problematic salts, can be disposed elsewhere.

Technetium will not be removed from the aqueous tank waste during pretreatment in the Hanford WTP and will be sent to the LAW melter. It is intended that ^{99}Tc will be immobilized in the LAW glass. Because it is semi-volatile at melter temperatures and roughly 70% vaporizes, the only way to get it to stay in the glass is by repeated recycle into the LAW melter. Although other radionuclides are expected to be present in low concentration in the LAW Off-Gas Condensate, such as ^{129}I , ^{90}Sr , ^{137}Cs , ^{241}Pu , and ^{241}Am , it is the long-lived and environmentally mobile ^{99}Tc that is the primary component of concern.

This LAW Off-Gas Condensate stream originates from the Submerged Bed Scrubber (SBS) and the Wet Electrostatic Precipitator (WESP) from the LAW melter off-gas system. Pilot simulant tests indicate that this 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 salt components are expected to be mostly sodium and ammonium salts of nitrate, chloride, and fluoride. Although this stream has not yet been generated and will not be available until the WTP begins operation, a simulant has been produced based on models, calculations, and comparison with pilot-scale tests.

The recycled components in the LAW Off-Gas Condensate that are problematic for the glass waste form are halides and sulfate, which are volatile at melter temperatures. Recycling in order to incorporate the ^{99}Tc in the glass causes these components to 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 melter 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 because the evaporator in the Pretreatment facility will not be operational. This task examines the potential treatment of this stream to precipitate radioactive ^{99}Tc and subsequently disposition the decontaminated aqueous stream elsewhere, perhaps at the Effluent Treatment Facility (ETF). The treatment process envisioned focuses on using mature radionuclide removal technologies that are also compatible with long-term tank storage and immobilization methods. For this new process, testing is needed to demonstrate acceptable precipitation agents and measure decontamination factors for Tc removal from this unique waste stream.

Previous work has shown SnCl_2 to be an effective agent for the ^{99}Tc removal from this stream through reductive precipitation. This is believed to work by reducing the Tc(VII) ion in the soluble pertechnetate (TcO_4^-) to Tc(IV) , precipitating as technetium dioxide (TcO_2). The present work focused on quantifying the competing reactions that impact the removal of ^{99}Tc , consume Sn(II) ion, or that have potential to cause operational issues. Prior work demonstrated that the Cr(VI) in this stream will consume most of the SnCl_2 ; but the impact of Hg(II) and nitrite ion had not been examined. As expected, it was observed in this testing

that Hg(II) is reduced and removed from the aqueous phase upon addition of Sn(II). Conversely, no reaction was observed with nitrite ion. It was also observed that only trace amounts of hydrogen were generated in the reaction, even with a large excess of SnCl₂, which will avoid flammable gas operational issues. Additionally, tests showed that perrhenate ion (ReO₄⁻) is not a suitable surrogate for pertechnetate, as it is not reduced by Sn(II) in this simulant.

Another component of this program is to begin to mature the technology readiness of this process. A key component of that readiness is the scale-up of the reaction and the solid-liquid separation method. These two are related because the mixing of the chemicals during the reaction affects the particle size of the solids, thereby impacting the solid-liquid separation method. To begin addressing this, kinetics testing was performed to determine the speed of the Tc removal reaction so that appropriate equipment for mixing scale-up tests can be selected. It was found that at small scale, the Tc is removed to below the detection limit within 5 minutes of the addition of stannous chloride. The chromium is similarly removed very quickly, although there may be some small delay in reaching equilibrium.

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.

TABLE OF CONTENTS

LIST OF TABLES	viii
LIST OF FIGURES	ix
LIST OF ABBREVIATIONS	x
1.0 Introduction	1
1.1 Simulant Formulation Basis	3
1.2 Decontamination Process	3
2.0 Experimental Procedure	4
2.1 Simulant Preparation	4
2.2 Simulant Spiking with Radionuclides	6
2.3 Precipitation Tests – Effect of Nitrite Anion.....	7
2.4 Precipitation Tests – Fate of Mercury	7
2.5 Gas Generation Testing	7
2.6 Kinetic Testing	8
2.7 Quality Assurance	8
3.0 Results and Discussion	9
3.1 Simulant Compositions	9
3.1.1 SBS/WESP 2015 Radioactive Simulant.....	9
3.1.2 SBS/WESP 2016 Non-Radioactive Simulant.....	11
3.2 Precipitation Tests – Effect of Nitrite Anion.....	11
3.3 Precipitation Tests – Fate of Mercury	12
3.4 Gas Generation Testing	12
3.5 Kinetics Testing.....	13
4.0 Conclusions.....	13
5.0 Future Work	14
6.0 References	14
Appendix A . Detailed Results.....	A-1

LIST OF TABLES

Table 2-1. Non-Radioactive Simulant Formulation Targets.....	5
Table 2-2. Radioactive Simulant Aqueous Formulation Targets.....	6
Table 2-3. Target Glass Former Quantities.....	6
Table 2-4. Radiotracer Solutions added to Simulants.....	6
Table 3-1. Neutralized Simulant Filtrate Compositions	10
Table 3-2. SBS/WESP 2015 Simulant Radionuclide Composition	10
Table 3-3. Neutralized SBS/WESP 2016 Simulant Filtrate Composition	11
Table 3-4. Average Decontamination Factors for Effect of Nitrite Experiments	12
Table 3-5. Average Decontamination Factors for Fate of Mercury Experiments.....	12
Table 3-6. Average Decontamination Factors for Kinetic Experiments.....	13

LIST OF FIGURES

Figure 1-1. Simplified LAW Off-gas System	2
Figure 1-2. Schematic of a Proposed Decontamination Process and Disposition Path of LAW Off-Gas Condensate.....	3
Figure 2-1. Photo of experimental set-up for gas generation testing.	8

LIST OF ABBREVIATIONS

ARP	Actinide Removal Process
Avg	Average
CVAA	Cold Vapor Atomic Absorption Spectroscopy
DF	Decontamination Factor
DOE	Department of Energy
dpm	Disintegrations per minute
eq	Equivalents
ETF	Effluent Treatment Facility
g	grams
GC	Gas Chromatography
GFC	Glass Forming Chemical
h	Hour
HLW	High-Level Waste
HTWOS	Hanford Tank Waste Operations Simulator
IC	Ion Chromatography
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
WRPS	Washington River Protection Solutions
WTP	Waste Treatment Plant

1.0 Introduction

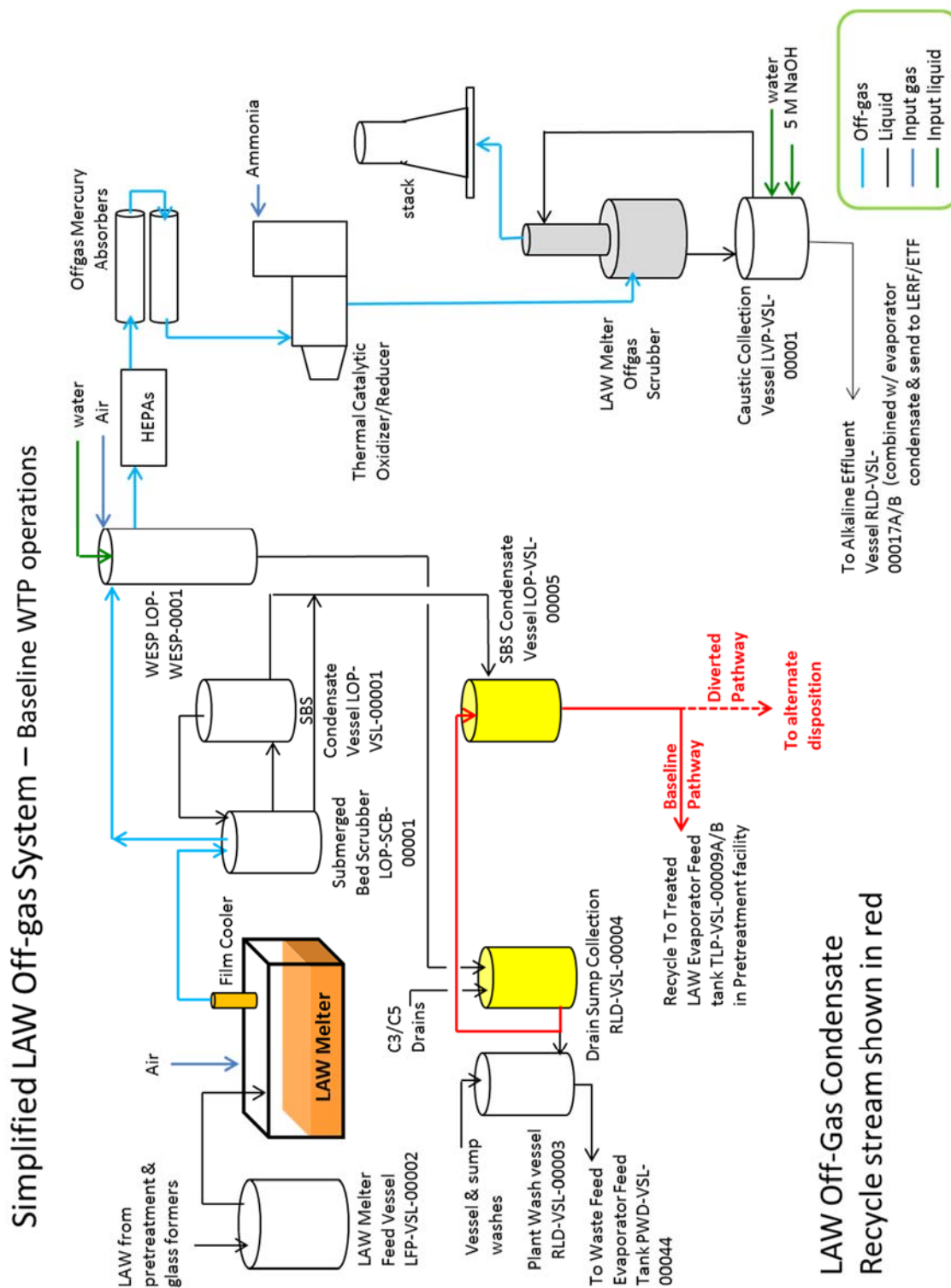
The Hanford LAW Off-Gas Condensate stream will be generated in the WTP by condensation and scrubbing of the LAW melter off-gas system by a SBS and WESP, as shown in Figure 1-1. This stream, which will contain substantial amounts of chloride, fluoride, ammonia, and sulfate ions, will get recycled within 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 because it would reduce the halides and sulfate in the melter feed.

The only chemical form of ^{99}Tc expected in the stream is pertechnetate anion (TcO_4^-) with a +7 Tc oxidation state because the high melter temperature should decompose any other form, although this has not been definitively proven. The volatility of Tc under oxidizing melter conditions is well known, where the most likely volatile species is the heptoxide (Tc_2O_7) because of its boiling point of 311 °C, although it could also sublime as an alkali metal pertechnetate, ammonium pertechnetate, or perhaps TcO_2 .² There is no direct evidence that Tc_2O_7 is the actual volatile species because the characterization is based on examining the condensed product and not directly on the vapor. Once the Tc_2O_7 contacts water, it would disproportionate to the pertechnetate.³

The objective of this development task is to evaluate decontamination of this stream using sorbents and/or precipitation agents so that it can be diverted elsewhere (Figure 1-2). The equipment needed for this process would be comparable to the ARPa at SRS that has been operating successfully for years. Although that process treats tank waste (comparable to “LAW” at Hanford), it demonstrates successful deployment of filtration processes for radionuclide removal using a porous stainless steel filter. The concept for this new process utilizes common industrial chemicals and equipment. This task specifically examined removal of ^{99}Tc using reducing agents, but other sorbents may be needed if removal of other radionuclides is required. Use of these inorganic materials is expected to simplify down-stream issues, such as storage and immobilization. Implementation of this process at WTP 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 viable options. The ETF is used here as an example of a potential path and is used for an estimation of decontamination requirements.

The overall plan for technology development of this process, along with options for disposal has been documented.⁴ The preliminary testing of this process has also been documented.^{5,6} Other alternative disposal paths for the Tc-containing slurry could be considered as well, including tank farm storage options.

^a 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

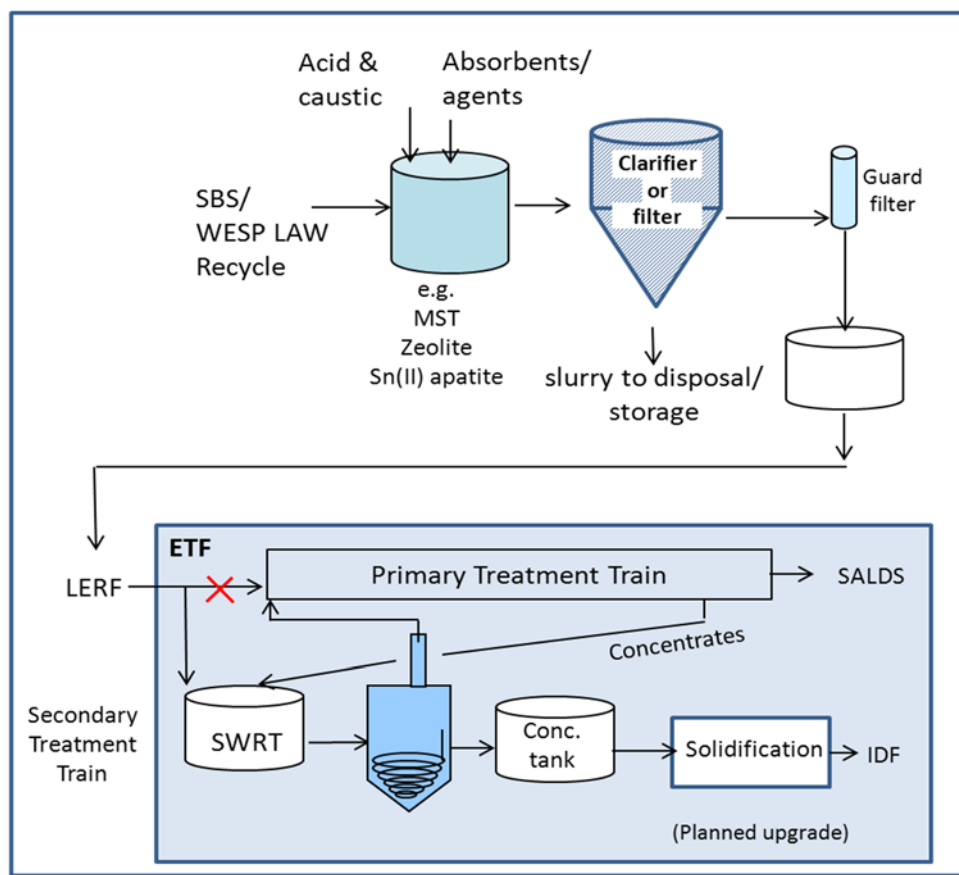


Figure 1-2. Schematic of a Proposed Decontamination Process and Disposition Path of LAW Off-Gas Condensate

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 sheet⁷ performed by WRPS.⁸ 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.^{5,6,9}

1.2 Decontamination Process

One option that has been previously evaluated is disposal of the LAW Off-Gas Condensate stream directly to the ETF, however, this option has a number of consequences to ETF including increases in waste volume, halide levels, and radioactivity.^{10,11} These have not been evaluated any further in this study, but it is recognized that this would have significant impacts that must be addressed by the facility.

The LAW Off-Gas Condensate stream is expected to contain ⁹⁹Tc due to its volatility at melter temperatures. The only chemical form of ⁹⁹Tc expected in the stream is pertechnetate anion (TcO₄⁻) with a +7 technetium oxidation state. Although some fraction of the ⁹⁹Tc is present in the initial LAW stream as a soluble “non-pertechnetate” species, the LAW melter is expected to convert it to the same volatile species formed by vitrifying the pertechnetate form. The volatile species then becomes pertechnetate ion again when it contacts the water in the SBS and WESP. (Note that this has not been demonstrated.)

The current WTP baseline assumption is that technetium will not be removed from the aqueous waste in the WTP, and will primarily end up immobilized in the LAW glass waste form after several recycle passes to improve retention.¹² The LAW glass will be disposed in the IDF. Because ⁹⁹Tc has a very long half-life and is highly mobile,^{13,14} it is the major dose contributor to the Performance Assessment (PA) of the IDF,¹ even though it is largely retained by the glass. Due to the high water solubility, high volatility during vitrification, and potential for impact to the PA, effective management of ⁹⁹Tc 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 ⁹⁹Tc disposed in LAW glass at the IDF would decrease substantially.

For this proposed alternative treatment process, separation of the ⁹⁹Tc is accomplished by precipitation with chemical reagents, and settling and/or filtration. 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;¹⁵ however, previous work by SRNL has shown Sn(II) alone without an absorbent is sufficient for precipitation of the ⁹⁹Tc and remains insoluble for at least 72 hours in air.^{6,16,17}

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.⁵ The target DF for ⁹⁹Tc 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 (C₀) divided by the concentration at time *t* (C_{*t*}) (Equation 1).

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

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, and is repeated here for completeness.⁹ The target concentrations of chemicals were derived from the output from the HTWOS calculation, documented in SVF-2732.⁸ Two different batches of simulant were used in the testing described in this report. The majority of the experiments utilized a single 1.0-L batch of non-radioactive simulant prepared in August 2016; however, the kinetics experiments described below utilized a radioactive simulant previously prepared and characterized.¹⁷ For the non-radioactive simulant sodium perrhenate was added as a surrogate for the pertechnetate. The 1.0-L batch of non-radioactive simulant was prepared from dissolution of laboratory chemicals in deionized water, in the order 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. Previous simulant preparations have included the addition of glass forming chemicals (GFCs), which were allowed to come to equilibrium with the aqueous phase before the insoluble portion was removed by filtration. Based upon previous simulant analyses, the completely insoluble GFCs were excluded from this preparation, and only the soluble GFCs were added. That included borax, boric acid, lithium carbonate, and sodium carbonate; which were

completely soluble at the amounts added. The amount of silica and zinc oxide added is the portion shown to be soluble in previous simulant preparations. After preparing the simulant, the solution was mixed for five days at ambient temperature. The pH of the resulting solution was measured to be 8.1. The pH was then adjusted to 7.5 with the addition of 2.67 g of 2 M nitric acid. After pH adjustment, the simulant was filtered through a 0.45-micron Nylon filter to remove any insoluble material. Duplicate samples were analyzed for elemental composition by Inductively Coupled Plasma – Emission Spectroscopy (ICP-ES), anions and ammonium by Ion Chromatography (IC).

Table 2-1. Non-Radioactive Simulant Formulation Targets

Chemical	Formula	Target Mass (g)/L simulant	Target Molarity
Sodium fluoride	NaF	3.209	0.0764
Potassium chloride	KCl	0.219	0.0029
Sodium chloride	NaCl	1.395	0.0239
Sodium chromate	Na ₂ CrO ₄	0.283	0.0017
Sodium nitrite	NaNO ₂	0.016	0.0002
Ammonium sulfate	(NH ₄) ₂ SO ₄	3.220	0.0244
Ammonium nitrate	NH ₄ NO ₃	2.820	0.0352
Borax	Na ₂ B ₄ O ₇ ·10H ₂ O	0.0123	0.00003
Boric acid	H ₃ BO ₃	1.430	0.0231
lithium carbonate	Li ₂ CO ₃	0.392	0.0053
sodium carbonate monohydrate	Na ₂ CO ₃ ·H ₂ O	0.0035	0.00003
silica	SiO ₂	0.12	0.0020
zinc oxide	ZnO	0.018	0.0002
Sodium perrhenate	NaReO ₄	0.0067	0.00002
Sodium nitrate	NaNO ₃	0	0*

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

The 2015 batch of radioactive SBS/WESP simulant was prepared from dissolution of laboratory chemicals, as shown in Table 2-2. Note that the information in Table 2-2 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 2-L batch was initially prepared; however a 500 mL aliquot (i.d.: SBS/WESP – No Cr) was removed from the 2-L batch prior to adding the sodium chromate to the remaining 1.5 L. 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). Neither of these 2 aliquots were used in testing described in this report. The glass forming chemicals (Table 2-3) were then added to the remaining 1.3 L of simulant, and mixed for five days at ambient temperature. These were derived from the overall mission average quantity.¹⁸ Sucrose was excluded because it is destroyed in the melter. The pH of the solution was measured to be 8.0 after the 5 days of mixing. The pH was then adjusted to 7.2 with the addition of 0.63 g of concentrated nitric acid. After pH adjustment, the glass formers were filtered from the simulant with a 0.45-micron Nylon filter. Samples were analyzed for elemental composition by ICP-ES, and anions and ammonium by IC.

Table 2-2. Radioactive Simulant Aqueous 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	NH_4NO_3	2.820	0.0352
Sodium nitrate	NaNO_3	0	0*
Sodium nitrite	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	Na_2CrO_4	0.283	0.0017

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

Table 2-3. Target Glass Former Quantities

Mineral	Formula	Mass (g)/L simulant
kyanite	Al_2SiO_5	0.745
borax	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	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	$\text{Mg}_2\text{SiO}_4\text{-Fe}_2\text{SiO}_4$	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	$\text{C}_{12}\text{H}_{22}\text{O}_{11}$	0
	Total	7.67

2.2 Simulant Spiking with Radionuclides

The 2015 batch of SBS/WESP simulant was spiked with the radiotracer solutions shown in Table 2-4. Results of the analysis of this simulant have been previously documented.¹⁷

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	$\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ aqueous solution (5 mg/mL U)	6.24E-1
$^{239/240}\text{Pu}$	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 – Effect of Nitrite Anion

In order to determine if nitrite reacts with the stannous chloride, a series of experiments were performed with a high nitrite concentration simulant. This simulant was prepared by adding 0.0285 g of sodium nitrite to 100 mL of the prepared non-radioactive simulant described above to increase the nitrite concentration from 10 ppm to 200 ppm. After adding the sodium nitrite, the simulant was stirred overnight to ensure complete dissolution. The tests were then performed by adding the indicated amount of stannous chloride (as a solid) to separate low density polyethylene (LDPE) bottles, followed by the addition of 20 mL of the 200 ppm nitrite 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 IC anion for nitrite concentration and Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) for Cr, Re, and Sn. Results are summarized in Section 3, with details in Appendix A. The test matrix included stannous ratios of 1.5:1 and 3:1, with respect to the electrons needed to reduce the Cr and Re present in the simulant. A ratio of 1.5:1 has been previously shown to be the minimum amount needed to quantitatively reduce the Cr and Tc from the radioactive simulant. Samples were removed and analyzed after 1 and 24 hours.

2.4 Precipitation Tests – Fate of Mercury

Since the SBS/WESP stream is expected to contain mercury, the following experiments were performed to examine the fate of the mercury under the planned conditions for reductive precipitation of pertechnetate with stannous chloride. It was expected that the stannous would also reduce the Hg(II) present to elemental Hg; thereby consuming a portion of the stannous reagent. This testing was also performed using the baseline non-radioactive simulant described above. The simulant was then spiked with Hg(II) by adding 0.18 mL of a 1000 mg/L Hg standard to 90 mL of the prepared simulant, to reach a target Hg concentration of 2 mg/L. After adding the Hg standard to the simulant, the solution was stirred at ambient laboratory conditions overnight prior to testing. The tests were then performed by adding the indicated amount of stannous chloride (as a solid) to separate LDPE bottles, followed by the addition of 20 mL of the 2 ppm Hg spiked 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 cold vapor atomic absorption spectroscopy (CVAA) for Hg, and ICP-MS for Cr, Re, and Sn. Results are summarized in Section 3, with details in Appendix A. The tests were performed using a stannous ratio of 1.5:1, with respect to the electrons needed to reduce the Cr and Re present in the simulant. Samples were removed after 1 and 24 hours; however, only the 1 hour samples were analyzed because the mercury had been removed to below detection.

2.5 Gas Generation Testing

Previous work has shown that no hydrogen was generated up to the detection limit of 0.1 vol% H₂ during the reductive precipitation with stannous chloride using the SBS/WESP simulant. In order to confirm no H₂ was generated from secondary reactions or by products, this experiment was repeated, analyzing the reaction head space for H₂ using gas chromatography (GC) to obtain a lower detection limit than the previous work. Glassware for these experiments was fabricated by the SRNL glass shop, and consisted of a 25-mL two-neck round bottom flask and a gas sample bulb that could be connected to one neck of the flask, and also had a stopcock to close off the gas bulb to allow it to be separated from the reaction vessel. See Figure 2-1 for a photograph of the experimental set-up. The gas sample bulb also contained a sampling port on the side consisting of a rubber septum that could be pierced to sample the gas during the GC analysis. For each experiment, the indicated amount of stannous chloride was added to the reaction flask as a solid. The gas bulb was then connected to one neck of the flask, while the other neck was used to introduce the 20 mL of SBS/WESP simulant. The flask was immediately capped after the simulant had been added, and the reaction mixture was stirred with a magnetic stir bar. The stannous chloride was added in excess, at a 3:1 ratio to increase the conservatism in the results. The reactions were stirred overnight to allow sufficient time for equilibration of the head space between the flask and the bulb. The following morning the gas

bulbs were closed off and disconnected from the flasks. They were then analyzed later the same day by GC. In addition, a sample of the reaction mixture was removed, filtered, and submitted for ICP-ES to confirm Cr removal by reductive precipitation. Results are summarized in Section 3, with details in Appendix A.



Figure 2-1. Photo of experimental set-up for gas generation testing.

2.6 Kinetic Testing

Previous testing has shown the Tc reductive precipitation to be complete within 1 hour; however the true time for the reaction to complete was not known. In order to determine how quickly the pertechnetate and chromate are reduced by the stannous, a series of experiments were performed with samples taken at much shorter time intervals. These experiments utilized the 2015 batch of radioactive SBS/WESP simulant so that both the pertechnetate and chromate reaction could be monitored. These tests were performed by adding the indicated amount of stannous chloride (as a solid) to separate LDPE bottles, followed by the addition of 20 mL of the 2015 SBS/WESP simulant solution to each. The bottles were then agitated in a shaker oven at ~25 °C for the specified time. A stopwatch was used to track the sample times. Samples were removed at times of 5, 10, 15, and 30 minutes after the simulant was added to the stannous chloride in the bottle. Each sample was then filtered through a 0.1- μ m filter. The filtrate samples were then analyzed by ICP-MS for Cr, Tc, and Sn. Results are summarized in Section 3, with details in Appendix A. The baseline stannous ratio of 1.5 eq. with respect to the electrons needed to reduce the Cr and Tc present in the simulant was used for these experiments.

2.7 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.¹⁹ 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 #E7518-00211.

3.0 Results and Discussion

3.1 Simulant Compositions

3.1.1 *SBS/WESP 2015 Radioactive Simulant*

(Note: results were previously reported,¹⁷ but are included here for completeness)

Results of the average and standard deviation of the duplicate chemical analysis of the neutralized, filtered simulant prepared in 2015 are shown in Table 3-1 and the radionuclide activities are shown in Table 3-2. The results show a relatively good match 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 simulant was ~20% below the target, and the F^- was approximately 10% low. The nitrate concentration is only about half of the HTWOS projected concentration, but that target was adjusted because it is unrealistic due to the way the model works and does not account for the charge imbalance. Sodium nitrate was not added to this optimized formulation, and instead comes mainly from the nitric acid added during pH adjustment. Similar to previous batches of this simulant, the Al failed to reach the target concentration. None of these differences are expected to impact the test outcomes, since, if these species were reactive and consumed reductant, their concentrations are already high enough that their reaction would be evident.

Table 3-1. Neutralized Simulant Filtrate Compositions

Component	SBS/WESP 2015 Avg. mg/L (M)	SD	HTWOS projection (avg. SVF-2732) (mg/L)
Al	<0.500 ($<1.9\text{E-}5$)	n/a	28
B	158 (0.0146)	2.1	GFC [#]
Ca	0.970 ($2.4\text{E-}5$)	0.009	GFC [#]
Cr	93.3 (0.0018)	2.7	91
Fe	<0.100 ($<1.8\text{E-}6$)	n/a	GFC [#]
K	121 (0.0031)	0.71	115
Li	75.6 (0.011)	0.64	GFC [#]
Mg	<0.100 ($<4.1\text{E-}6$)	n/a	GFC [#]
Na	1780 (0.077)	0 [*]	2.29E3
P	2.00 ($6.5\text{E-}5$)	0 [*]	7 (as PO_4^{3-})
S	806 (0.025)	2.1	780 (as SO_4^{2-})
Si	52.3 (0.0019)	1.5	GFC [#]
Ti	<0.100 ($<2.1\text{E-}6$)	n/a	GFC [#]
Zn	20.1 ($3.1\text{E-}4$)	0.64	GFC [#]
Zr	<0.500 ($<5.5\text{E-}6$)	n/a	GFC [#]
F ⁻	1295 (0.068)	7.1	1.45E3
Cl ⁻	965 (0.027)	35.4	950
NO ₂ ⁻	<100 (<0.0022)	n/a	10.7
NO ₃ ⁻	2420 (0.039)	14.1	5.53E3
SO ₄ ²⁻	2185 (0.023)	7.1	2.34E3
PO ₄ ³⁻	<100 (<0.0011)	n/a	21.5
NH ₄ ⁺	1400 ^{**} (0.078)	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

Table 3-2. SBS/WESP 2015 Simulant Radionuclide Composition

Isotope	Activity (dpm/mL)	Reported Method Uncertainty	% of Target Activity
⁸⁵ Sr	5.17×10^4	5.0%	89
⁹⁹ Tc	7.65×10^4 (2.03 mg/L)	20%	83
¹³⁷ Cs	7.68×10^3	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

3.1.2 SBS/WESP 2016 Non-Radioactive Simulant

Results of the average and standard deviation of the duplicate chemical analysis of the neutralized, filtered SBS/WESP 2016 non-radioactive simulant are shown in Table 3-3. 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. Note that the HTWOS model output is not charge balanced, so it is not possible to create an identical solution. Previous preparations of this simulant have shown the aluminum nitrate and disodium phosphate are insoluble in this simulant, and therefore, they were omitted from this preparation.

Table 3-3. Neutralized SBS/WESP 2016 Simulant Filtrate Composition

Component	Avg. Concentration (mg/L)	Std. Dev.	HTWOS projection (avg. SVF-2732) (mg/L)	Avg. Concentration (M)
B	242	1.41	GFC [#]	0.022
Cr	84.2	0.49	91	0.0016
K	111	0.71	115	0.0028
Li	71.3	1.56	GFC [#]	0.010
Na	2.19E3	57	2.29E3	0.095
Re	5.16	0.03	4.59 [^]	2.8E-5
S	794	4.9	780 (as SO ₄ ²⁻)	0.025
Si	12.1*	0.85	GFC [#]	4.5E-4
Zn	7.96*	0.028	GFC [#]	1.2E-4
F ⁻	1.50E3	28	1.45E3	0.079
Cl ⁻	941	12.7	950	0.027
NO ₂ ⁻	10.4	0.21	10.7	0.0002
NO ₃ ⁻	2.37E3	21	5.53E3	0.038
SO ₄ ²⁻	2.33E3	14	2.34E3	0.024
NH ₄ ⁺	1.43E3	14	1.51E3	0.079

[^]Based on molar equivalent to ⁹⁹Tc in HTOWS projection.

*Added in reduced amounts compared to previous preparations. Only the expected soluble amount was added.

[#]Glass Forming chemical; minimal HTWOS projected concentration

3.2 Precipitation Tests – Effect of Nitrite Anion

A 100-mL aliquot of the SBS/WESP 2016 simulant was spiked to a target level of 200 ppm nitrite by the addition of sodium nitrite to the prepared simulant. IC anion analysis of the simulant after the sodium nitrite addition showed a nitrite concentration of 204.5 ppm (0.0044 M), which represents 102% of the target value. This simulant was then used for the precipitation experiments with stannous chloride. Two different ratios of stannous chloride were tested. 1.5 eq. and 3 eq. of SnCl₂ were added relative to the equivalents of electrons needed to reduce the Cr and Re (2.25 and 4.5 moles/mole, respectively). This corresponded to SnCl₂ concentrations of 0.7 g/L (0.0037 M) and 1.4 g/L (0.0074 M). Table 3-4 provides the results of these experiments. Detailed concentration data from these experiments can be found in Appendix A. Samples were analyzed for nitrite by IC anion analysis and for Cr and Re by ICP-MS.

Since the nitrite concentration was in the same range as the stannous, it would be expected that if there was an appreciable reaction, it would have been readily identified by a decrease in the nitrite concentration. As can be seen from the results presented in Table 3-4, there was no reduction of nitrite observed upon the addition of the stannous chloride, even with an excess of stannous added in the 3:1 ratio set of experiments. The maximum nitrite DF value observed was 1.10 for the 24 hour sample from one of the 3:1 ratio experiments, which is within the experimental uncertainty. This experiment also indicated that Re is not a

suitable surrogate for Tc, as no Re was removed upon the addition of stannous chloride. Greater than 99% of the Cr was also removed within 1 hour, which is consistent with previous testing. The Cr DF in the higher Sn experiment (3:1 ratio) was lower than in the 1.5:1 ratio experiment, although it still represents 99.4% of the Cr being removed versus 99.8% in the 1.5:1 experiment. The slightly lower removal in the higher Sn(II) experiment may be due to a more significant drop in pH from the addition of stannous chloride. The detailed data can be found in Appendix A.

Table 3-4. Average Decontamination Factors for Effect of Nitrite Experiments

	Sn(II) 1.5:1	Sn(II) 3:1
1 h nitrite DF	1.07 (0.04)	0.98 (0.11)
1 h Cr DF	658 (182)	174 (7.33)
1 h Re DF	0.98 (0.03)	1.02 (0.01)
24 h nitrite DF	1.03 (0.03)	1.10 (0.01)
24 h Cr DF	1107 (492)	76.2 (24.9)
24 h Re DF	1.00 (0.001)	1.02 (0.01)

Value in parentheses indicated standard deviation of replicate trials.

3.3 Precipitation Tests – Fate of Mercury

A 90-mL aliquot of the SBS/WESP 2016 simulant was spiked to a target level of 2 ppm Hg by the addition of a 1000 mg/L Hg analytical standard. CVAA analysis of the simulant after Hg addition show the Hg concentration in the simulant was 1.46 ppm, which represents 73% of the target value. This simulant was then used for the precipitation experiments with stannous chloride. A single ratio of 1.5 eq. of stannous chloride relative to the equivalents of electrons needed to reduce the Cr and Re (2.25 moles/mole) was tested. This corresponded to a SnCl₂ concentration of 0.7 g/L (0.0037 M). Table 3-5 provides the results of these experiments. Detailed concentration data from these experiments can be found in Appendix A. Samples were analyzed for Hg by CVAA analysis and for Cr and Re by ICP-MS. Samples were removed after 1 and 24 hours, however, only the 1 hour samples were submitted for analysis since it was evident that the reaction was complete.

Table 3-5. Average Decontamination Factors for Fate of Mercury Experiments

	Sn(II) 1.5:1
1 h Hg DF	> 73.0
1 h Cr DF	648 (181)
1 h Re DF	1.05 (0.00)

Value in parentheses indicated standard deviation of replicate trials.

As can be seen from the results presented in Table 3-5, the Hg is removed from solution to below the method detection limit within in 1 hour after the addition of stannous chloride. This confirms the expected reduction of soluble Hg(II) to insoluble Hg(0) by Sn(II). Similarly to the effect of nitrite experiments, the Re was not removed upon the addition of stannous chloride and the Cr DFs were consistent with previous testing.

3.4 Gas Generation Testing

Duplicate experiments with 3 eq. of stannous chloride relative to the equivalents of electrons needed to reduce the Cr and Re (4.5 moles/mole) were performed using the apparatus shown in Figure 2-1, along with a control sample with no stannous chloride added. After equilibrating overnight, the gas sample bulbs were closed off and analyzed the same day. An Inficon 3000 series micro GC with a molsieve 5A module and argon carrier gas was used to analyze the gas samples. This configuration allows the detection and quantification of helium, hydrogen, oxygen and nitrogen. The detection limit of the GC was determined to be approximately 5 ppm using a calibration gas containing 5 ppm hydrogen gas. The calibration gas was

sampled by the GC and the instrument and software settings were adjusted to identify and quantify the hydrogen peak.

No quantifiable hydrogen was detected in any of the gas bulbs. There was a slight peak in the chromatogram from a single sample that was attributed to hydrogen; although it was below the quantifiable limit. Although the hydrogen concentration in the calibration gas is 5 ppm, the detection limit in the gas bulbs is estimated to be approximately 10 ppm. Prior to sampling the bulbs, room air was sampled. In the gas bulbs, oxygen and nitrogen areas (which are proportional to concentration) were approximately 85% of the areas for room air. This is likely due to the low volume of gas in the bulbs relative to the amount of gas that the GC could draw. In subsequent samples, oxygen and nitrogen areas declined further. This observation indicates the bulbs and the sampling system were leak tight.

In addition to analysis of the head space gas, samples of the reaction filtrate were analyzed by ICP-ES to confirm the reductive precipitation of Cr in these experiments. The average Cr DF for the duplicate samples was 29.1 with a standard deviation of 3.55. This is slightly lower than the DF obtained with 3 eq. of stannous chloride in the effect of nitrite experiments (see Table 3-4).

3.5 Kinetics Testing

These experiments used the 2015 batch of SBS/WESP radioactive simulant. Stannous chloride was added to the tests at the baseline ratio of 1.5 eq. SnCl_2 relative to the equivalents of electrons needed to reduce the Cr and Tc (2.25 moles/mole). This corresponded to SnCl_2 concentrations of 0.77 g/L (0.0041 M). Samples were removed after 5, 10, 15, and 30 minutes and were analyzed for Cr, ^{99}Tc , and Sn by ICP-MS analysis. Table 3-6 provides the results of these experiments and detailed concentration data can be found in Appendix A.

As can be seen from the results presented in Table 3-6, the pertechnetate reductive precipitation is complete, i.e., the ^{99}Tc concentration in the solution has dropped below the method detection limit, within 5 minutes. The Cr reductive precipitation is also essentially complete within 5 minutes, although there is evidence a small additional amount of Cr is removed up to 15 minutes of reaction time, but is within the experimental uncertainty of the test. These results will allow for the design of larger scale testing to examine the impact of mixing on the reaction kinetics. The larger scale experiments will be performed using non-radioactive simulant. Therefore, the Cr reduction will be monitored as a surrogate for the Tc. Since there is evidence the Cr reduction is not any faster than Tc, these results will be conservative.

Table 3-6. Average Decontamination Factors for Kinetic Experiments

	Tc DF	Cr DF
5 min.	> 195	123 (12.5)
10 min.	> 195	130 (8.70)
15 min.	> 195	153 (30.8)
30 min.	> 195	144 (15.0)

Value in parentheses indicates standard deviation of replicate trials.

4.0 Conclusions

Previous work has shown SnCl_2 to be an effective precipitation agent for the ^{99}Tc through reductive precipitation in the SBS/WESP simulant when added at a ratio of 1.5 equivalents relative to the electrons needed to reduce the ^{99}Tc and Cr. This is believed to work by reducing the Tc(VII) ion in the soluble pertechnetate (TcO_4^-) to Tc(IV), precipitating as technetium dioxide (TcO_2). A similar reaction is expected for the Cr, reducing from the Cr(VI) ion in the soluble chromate (CrO_4^{2-}) to Cr(III), precipitating as chromium oxide (Cr_2O_3). This testing further evaluated possible competing reactions that may impact the removal of ^{99}Tc , consume Sn(II), or have the potential to cause operational issues. Previous work had not

yet examined the impact of Hg(II) or nitrite ion. As expected, it was observed in this testing that Hg(II) is reduced and removed from the aqueous phase upon addition of Sn(II). This indicates that the Hg concentration will need to be considered when determining the quantity of SnCl₂ required. If Hg is present in significant quantities it will consume some of the available Sn(II) reagent. Conversely, no reaction was observed with nitrite ion. It was also observed that only trace amounts of hydrogen were generated in the reaction, even with a large excess of SnCl₂, which will avoid significant flammable gas operational issues. Additionally, tests showed that perrhenate ion (ReO₄⁻) is not a suitable surrogate for pertechnetate, as it is not removed by Sn(II) in this simulant under these conditions.

In support of future work to examine the scale-up of this reaction for technology maturation, the kinetics of the reductive precipitation were examined. Results from these experiments indicated that the Tc was removed to below the method detection limit within 5 minutes of the addition of the stannous chloride. These results will help guide the design of the mixing scale-up experiments planned during the next phase of this project. The chromium is similarly removed very quickly, although there may be some small delay in reaching equilibrium.

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. Summary of Concentration Data from Effect of Nitrite Experiments (HLAW-205-210)

Test ID	HLAW-205	HLAW-206	HLAW-207	HLAW-208	HLAW-209	HLAW-210
Precip. Agent	None (Control)	None (Control)	Sn(II) (1.5:1)	Sn(II) (1.5:1)	Sn(II) (3:1)	Sn(II) (3:1)
SnCl ₂ Conc. (g/L)	n/a	n/a	0.733	0.722	1.409	1.400
Contact Time (h)	1.00	n/a	1.02	1.05	1.07	1.10
Fluoride (mg/L)	1.44E+03	NM	1.40E+03	1.36E+03	1.48E+03	1.73E+03
Chloride (mg/L)	9.49E+02	NM	1.19E+03	1.17E+03	1.45E+03	1.73E+03
Nitrite (mg/L)	2.04E+02	NM	1.95E+02	1.86E+02	1.92E+02	2.26E+02
Nitrate (mg/L)	2.42E+03	NM	2.35E+03	2.25E+03	2.44E+03	2.89E+03
Sulfate (mg/L)	2.35E+03	NM	2.37E+03	2.23E+03	2.50E+03	2.85E+03
Cr (µg/L)	8.79E+04	NM	1.11E+02	1.65E+02	4.88E+02	5.18E+02
Re (µg/L)	4.98E+03	NM	4.92E+03	5.16E+03	4.81E+03	4.86E+03
Sn (µg/L)	<1.00E+01	NM	3.82E+02	9.63E+02	4.01E+04	3.76E+04
Contact Time (h)	n/a	24.05	24.05	24.07	24.07	24.08
Fluoride (mg/L)	NM	1.44E+03	1.36E+03	1.52E+03	1.41E+03	1.40E+03
Chloride (mg/L)	NM	9.53E+02	1.21E+03	1.32E+03	1.39E+03	1.39E+03
Nitrite (mg/L)	NM	2.05E+02	1.95E+02	2.04E+02	1.88E+02	1.85E+02
Nitrate (mg/L)	NM	2.39E+03	2.38E+03	2.46E+03	2.31E+03	2.29E+03
Sulfate (mg/L)	NM	2.39E+03	2.31E+03	2.47E+03	2.35E+03	2.33E+03
Cr (µg/L)	NM	8.67E+04	6.00E+01	1.15E+02	9.31E+02	1.49E+03
Re (µg/L)	NM	4.89E+03	4.91E+03	4.92E+03	4.88E+03	4.83E+03
Sn (µg/L)	NM	<1.00E+01	3.70E+02	8.04E+02	3.71E+04	4.14E+04

Table A-2. Summary of Concentration Data from Fate of Mercury Experiments (HLAW-211-214)

Test ID	HLAW-211	HLAW-212	HLAW-213	HLAW-214
Precip. Agent	None (Control)	None (Control)	Sn(II) (1.5:1)	Sn(II) (1.5:1)
SnCl ₂ Conc. (g/L)	n/a	n/a	0.708	0.705
Contact Time (h)	0.98	1.00	1.00	1.00
Hg (mg/L)	1.36E+00	1.56E+00	< 2.00E-02	< 2.00E-02
Cr (µg/L)	8.64E+04	8.74E+04	1.67E+02	1.12E+02
Re (µg/L)	4.87E+03	4.88E+03	4.64E+03	4.64E+03
Sn (µg/L)	<1.00E+01	<1.00E+01	8.81E+03	2.74E+02

Table A-3. Summary of Concentration Data from Gas Generation Experiments (HLAW-215-217)

Test ID	HLAW-215	HLAW-216	HLAW-217
Precip. Agent	None (Control)	Sn(II) (3:1)	Sn(II) (3:1)
SnCl ₂ Conc. (g/L)	n/a	1.408	1.413
Contact Time (h)	17.02	17.00	16.98
Cr (mg/L)	8.38E+01	3.15E+00	2.65E+00
Sn (mg/L)	<1.31E+01	1.49E+02	1.66E+02

Table A-4. Summary of Concentration Data from Kinetics Experiments (HLAW-218-220)

Test ID	HLAW-218	HLAW-219	HLAW-220
Precip. Agent	None (Control)	Sn(II) (1.5:1)	Sn(II) (1.5:1)
SnCl ₂ Conc. (g/L)	n/a	0.792	0.782
Contact Time (min)	5.10	5.17	5.17
Cr (µg/L)	8.78E+04	7.64E+02	6.63E+02
⁹⁹ Tc (µg/L)	1.94E+03	<1.00E+01	<1.00E+01
Sn (µg/L)	<1.00E+01	3.02E+04	1.19E+04
Contact Time (min)	10.22	10.10	10.32
Cr (µg/L)	8.78E+04	7.08E+02	6.44E+02
⁹⁹ Tc (µg/L)	1.94E+03	<1.00E+01	<1.00E+01
Sn (µg/L)	<1.00E+01	2.29E+04	8.98E+03
Contact Time (min)	15.17	15.10	15.15
Cr (µg/L)	8.71E+04	6.67E+02	5.01E+02
⁹⁹ Tc (µg/L)	1.94E+03	<1.00E+01	<1.00E+01
Sn (µg/L)	<1.00E+01	1.80E+04	6.42E+03
Contact Time (min)	30.15	30.03	30.17
Cr (µg/L)	8.80E+04	6.55E+02	5.65E+02
⁹⁹ Tc (µg/L)	1.97E+03	<1.00E+01	<1.00E+01
Sn (µg/L)	<1.00E+01	1.31E+04	4.16E+03

Distribution:

A. P. Fellingner, 773-42A
F. M. Pennebaker, 773-42A
D. E. Dooley, 773-A
M. J. Cercy, 773-42A
L. T. Reid, 773-43A
T. B. Brown, 773-A
B. J. Wiedenman, 773-42A
M. E. Stone, 999-W
A. A. Ramsey, 999-W
H. H. Burns, 773-41A
A. M. Howe, 999-W
K. M. Fox, 999-W
R. B. Wyrwas, 999-2W
M. R. Poirier, 773-42A
E. N. Hoffman, 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
J. R. Vitali, WRPS
Records Administration (EDWS)
E. N. Diaz, DOE-ORP
N. M. Jaschke, DOE-ORP
D.L. Noyes, DOE-ORP
G. D. Trenchard, DOE-ORP
A. A. Kruger, DOE-ORP
W. F Hamel, DOE-ORP
I. Wheeler, DOE-ORP
S. T. Arm, WRPS
W. G. Ramsey, 999-W
D. J. Swanberg, WRPS
R. B. Mabrouki, WRPS
N. P. Machara, DOE-EM
J. A. Poppiti, DOE-EM
D. J. Koutsandreas, DOE-EM
R. A. Gilbert, DOE-ORP
S. D. Reaksecker, WRPS
R. Gimpel, RPP-WTP
R. H. Davis, WRPS