Tc Removal from the Waste Treatment and Immobilization Plant Low Activity Waste Vitrification Off-Gas Recycle

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Vitrification of Low Activity Waste in the Hanford Waste Treatment and Immobilization Plant generates a condensate stream from the off-gas processes. Components in this stream are partially volatile and accumulate to high concentrations through recycling, which impacts the waste glass loading and facility throughput. The primary radionuclide that vaporizes and accumulates in the stream is ^{99}Tc. This program is investigating Tc removal via reductive precipitation with stannous chloride to examine the potential for diverting this stream to an alternate disposition path. Research has shown stannous chloride to be effective, and this paper describes results of recent experiments performed to further mature the technology.

Keywords: decontamination, technetium, stannous chloride, WTP

Shortened Title: Tc Removal from the WTP LAW Off-Gas Recycle

Introduction

The Department of Energy (DOE) Hanford site located in Washington state currently houses 53 million gallons of high level radioactive waste in 177 underground storage tanks. This waste was generated from plutonium production for nuclear weapons starting in the 1940s through the end of the cold war. Currently under construction, the Waste Treatment and Immobilization Plant (WTP) will treat and immobilize the inventory of High-Level Waste stored in the underground storage tanks. The WTP consists of a pre-treatment facility, which will separate the tank waste into High Level Waste (HLW) and Low Activity Waste (LAW) fractions, as well as separate vitrification facilities for converting these two waste streams into glass. The LAW portion of the waste will be melted as a borosilicate glass in air-bubbled Joule-heated ceramic melters. This process will generate a condensate stream by cooling and scrubbing of the LAW melter off-gas system by a submerged bed scrubber (SBS) and wet electrostatic precipitator (WESP), as shown in Figure 1. This stream, which will contain substantial amounts of chloride, fluoride, ammonia, and sulfate ions, will get recycled within the WTP process by return to the Pretreatment Facility where it will be combined with the LAW stream and evaporated. The halide and sulfate components are only marginally soluble in glass, and often dictate the waste loading. Additionally, long-lived ^{99}Tc and ^{129}I are volatile radionuclides at melter temperatures that accumulate in the LAW system, and are challenging to incorporate in glass under the Hanford LAW melter operating conditions. Although the melter operates at ~1150 °C, the volatile radionuclides are partially retained in the glass by the cold cap in the melter. Because ^{99}Tc has a very long half-life and is highly mobile in the environment [1], it is the largest dose contributor to the Performance Assessment (PA) of the Integrated Disposal Facility (IDF) [2], although it is largely retained in the disposed glass waste form by the durability of the glass. Diverting this LAW Off-Gas Condensate stream to an alternate disposal path would have substantial beneficial impacts on the cost, life cycle, and operational complexity of WTP.

However, in order to divert this stream to another disposal path, it is necessary to remove the ^{99}Tc, which is the principal radionuclide. The ideal method would be one that is rapid at room temperature and in an aerated environment, is highly selective for ^{99}Tc, uses only a small amount of readily available inorganic chemicals, can be performed with equipment already used in the process or at least elsewhere in the nuclear industry, and generates a ^{99}Tc-containing stream that is compatible with existing radioactive immobilization methods at the facility. Although many methods have been investigated for removal of Tc from ground-water, such as sorption onto organoclays [3], mesoporous carbon [4], zerovalent iron nanoparticles [5], and hydroxyapatite [6,7], none of them are ideal, generally because of the presence of other constituents (e.g. carbon or phosphates) that increase the volume of the Tc-containing stream and must be accommodated in the final waste form. It is assumed for this project that the Tc-containing stream would be disposed by mixing into the High Level Waste glass, so the stream must be of minimal volume and contain only “glass friendly” constituents. To that end, inorganic reducing agents were investigated because of the expectation that they would most readily be adapted into the existing nuclear waste processing flow sheet. Initial testing focused on stannous and ferrous ion precipitation of ^{99}Tc. Prior work by Moore, et.al., had indicated that Sn-substituted apatites were effective at removing Tc from similar waste streams and sequestering it for long periods [6]. For this application, however, it was desirable to examine excluding the apatite because of its adverse impact on the subsequent disposal of the ^{99}Tc stream in a glass waste form. Further, long-term sequestration of the Tc was not necessary because it was envisioned that the stream could be treated and processed within a few hours. Since earlier work in the program indicated that Sn(II) was much more effective than Fe(II), ongoing work has focused on optimizing the process [8]. A precipitation process is also desirable because commercial filtration equipment is already used in the Hanford waste treatment plant flow sheet, and so could be readily implemented. Although tin has not been studied extensively in sludge waste glass, its similarity to lead indicates it should be highly soluble in glass waste forms.

The objective of this program is to further mature a process for decontamination of ^{99}Tc from this stream using precipitation agents (Figure 2). The concept for this decontamination process adapts the use of precipitation agents to enable alternative disposition. Implementation would make available both a short-term disposition path if the LAW facility commences operation prior to operation of the Pretreatment facility and a long term path to divert the stream from recycling [9].

The LAW that is fed to the melters is a highly alkaline, high ionic strength salt solution, adjusted to ~7.8 M [Na+] and contains an estimated 8.8E-5 Ci/L of ^{99}Tc [10]. If the radionuclides are removed from the Recycle stream and the decontaminated liquid is then sent to an alternate disposal path, the fluoride, sulfate, and chloride would be purged from the LAW system, yielding substantial benefits to WTP and mitigating the complications of recycling this stream.

Previous work has shown that treating the SBS-WESP Off-Gas Condensate Recycle simulant with $SnCl_2$ is successful for the removal of Tc within one hour. This stream also has the potential to include significant amounts of chromate; which will compete with the reductant added to precipitate the pertechnetate, so must also be accounted for in the reactions. Sn(II) has been shown to be much more successful at removal of Tc than Fe(II) [8], presumable because Sn(II) is a stronger reducing agent, as evidenced by the higher oxidation potential of -0.15 compared to -0.771 V for Fe(II). Only 1.5 eq of Sn(II) (relative to the equivalents of electrons needed to reduce the Cr and Tc), which corresponds to ~0.8 g/L $SnCl_2$ in the average simulant, is necessary for good Tc removal from the baseline simulant formulation. Addition of $SnCl_2$ causes reduction from soluble TcO_4^- to form TcO_2 solids, which can be removed by settling or filtration. Tc removal by reduction with Fe(II) can be improved by the addition of sodium hydroxide; however, the extent of Tc removal is still much less than can be obtained with Sn(II) [8].

The solids from the stannous chloride reduction reaction are predominately Sn, as expected, making up 45 wt% of the solids. The Cr concentration in the solids is also appreciable, as the stannous also reduces chromate present in the simulant. This is an interference, consuming the stannous and requiring a higher dose of $SnCl_2$ to achieve the Tc precipitation.

Stability testing of the precipitated solids in the neutral SBS/WESP simulant has demonstrated that the solids are stable to re-oxidation and dissolution for up to 72 hours, which should provide sufficient time for a solid-liquid separation. However, the precipitated solids would not be stable if returned to a waste tank for storage, as demonstrated by rapid re-dissolution of the ^{99}Tc when the precipitated solids were mixed with a LAW simulant. [8]

Additional experiments have recently been performed to further the maturation of this technology, and results are presented in this paper. Recent testing included examining the impact of chromate concentration on the reductive precipitation, examining the impact of glass forming chemicals (GFC) on the process, and examining the potential effectiveness of a sequential Fe(II)/Sn(II) strike to reduce the amount of Sn(II) required in the process.

Simulant Formulation Basis

Because this stream is not yet available for characterization, the simulant formulation was based on input from two sources. The projected solution chemistry and radionuclide content were based on version 7.4 of the Hanford Tank Waste Operations Simulator (HTWOS) modeling of the flow sheet [11]. Insoluble solids composition was primarily based on analysis of LAW Recycle obtained from pilot-scale simulant melter testing [12]. Basing the solution chemistry and radionuclide content on the computer modeling rather than melter testing results allowed evaluation of process conditions for treatment of all tank wastes, and accounts for internal WTP process streams. Since the computer model does not account for physical carryover of material, the insoluble solids added were based on results from large-scale melter tests. Results from those tests indicated that the solids were primarily GFCs because the solids were observed to contain iron and other components not typically in the aqueous LAW. Therefore, GFCs were added as the solids to the simulant formulation. The radionuclide activities were based on the HTWOS model calculations.

Decontamination Process

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 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. [13] 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. For this proposed treatment process, separation of the ^{99}Tc is accomplished by precipitation with chemical reagents, and settling and/or filtration. Emphasis was placed on using entirely inorganic materials to enable easier storage and disposal of the precipitate as immobilized waste. For Tc 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;[6] however, previous work has shown Sn(II) alone, without an absorbent, is sufficient for precipitation of the ^{99}Tc [14].

For this proposed alternative treatment process, disposal of the aqueous decontaminated Condensate stream at the Effluent Treatment Facility (ETF) is used as an example pathway. The required decontamination factor (DF) for ^{99}Tc sent to the ETF has not been definitively established, so a DF of 100 was arbitrarily selected to minimize the impact of the final disposed waste form from ETF, which is disposed in the IDF. The DF is defined as the initial concentration (C_0) divided by the concentration at time *t* (C_t).

Experimental

Simulant Preparation

The basis of the simulant of chemicals and radionuclides were derived from the output from the HTWOS calculation, documented in SVF-2732 [15]. The aqueous phase of the simulant was prepared from dissolution of laboratory chemicals, as shown in Table 1. A 2-L batch of simulant (i.d.: SBS/WESP 2015) was prepared using the amounts shown in Table 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 prepared. Note that the information in Table 1 does not necessarily reflect the final composition of the aqueous phase because it is impacted by precipitation and reaction with the GFCs, and with the nitric acid added during pH adjustment. The chemicals were added to deionized water in the order shown in Table 1, and the resulting solution was diluted to a total volume of two liters. 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. This 500 mL was later subdivided to prepare simulants with 3 different Cr concentrations (0, 30, and 140 ppm). An additional 200-mL aliquot was also removed from the remaining 1.5 L batch after Cr addition to prepare simulant that would not have the GFCs filtered out (i.d.: SBS/WESP w/GFC). The GFCs (Table 2) were then added to all three aliquots, and mixed for five days at ambient temperature. The order of addition of the GFCs is not important, and it is not expected that these chemicals will completely dissolve in the simulant. The pH of all three solutions was measured to be 8.0 after the 5 days of mixing. The pH of each bottle was then adjusted to approximately 7.3 with the addition of concentrated nitric acid. The amount of acid required for each bottle of simulant varied slighlty in the range of 4.8 to 5.4 mM of acid. After pH adjustment, the glass formers were filtered from the 1.3-L and 500-mL aliquots, but were left in the 200-mL aliquot. Samples were analyzed for elemental composition by Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES), anions and ammonium by Ion Chromatography. The prepared simulants were then spiked with the radiotracer solutions shown in Table 2.

The simulant was stored under ambient conditions until use. All experiments were carried out at ambient laboratory conditions, with no attempts to provide a controlled anaerobic atmosphere. All reductant chemicals were stored under ambient laboratory conditions and used as received and added to the simulant as dry solids.

Precipitation Tests – Impact of Cr Concentration

Preparation of Simulant

The baseline SBS/WESP simulant formulation includes 91 ppm Cr, which represents the average value from the projected composition based on version 7.4 of the HTWOS modeling of the flowsheet [11] performed by Washington River Protection Solutions (WRPS); [15] however, this projection also includes a minimum of 34 ppm and a maximum of 139 ppm Cr. Since it is known that the Sn(II) reductant is also consumed by Cr, a series of experiments were performed with simulants targeting 0 ppm, 30 ppm, and 140 ppm Cr. Based on the differences in reduction potentials between chromate and pertechnatate, it is expected that all of the chromate must be reduced prior to the pertechnetate being reduced.

The SBS/WESP – No Cr simulant described above was used for these experiments. Two 100-mL aliquots of this simulant were spiked with 30 and 140 ppm of Cr by the addition of

0.0096 g and 0.044 g of sodium chromate, respectively. After addition of the sodium chromate the bottles were stirred at ambient temperature overnight. A sample of each solution was then filtered and analyzed by ICP-OES to determine the final Cr concentration.

Precipitation Tests

Precipitation tests were performed by adding the appropriate amount of $SnCl_2 \cdot 2H_2O$ to separate LDPE bottles, followed by the addition of 19 mL of the appropriate radioactive simulant solution to each. The bottles were then agitated in a shaker oven at ~25 ˚C for the specified time (samples were removed after 1 and 6 hours; however, only the 1 hour samples were analyzed because the reaction was shown to be complete). Each sample was then filtered through a 0.1-µm filter. The filtrate was then analyzed by ICP-MS for ^{99}Tc and ICP-OES for Cr.

Previous testing had shown 1.5 eq of Sn(II) added relative to the amount of Cr and ^{99}Tc to be sufficient to remove essentially all of the ^{99}Tc; [14] therefore that ratio was used for these tests. This ratio is based on the moles of reductant (i.e. Sn(II)) versus the moles of electrons needed to reduce the Cr(VI) to Cr(III) and the Tc(VII) to Tc(IV). Based on insufficient removal of ^{99}Tc in the 0 ppm Cr simulant, an additional experiment was performed using a higher concentration of Sn(II). This higher amount was calculated to provide 1.5 eq of Sn(II) based on the concentrations of ^{99}Tc and Zn. For this calculation it was assumed the Zn could undergo a 2 electron reduction from Zn(II) to Zn(0), although this reaction is not expected to actually occur due to the redox potentials.

In the high Cr simulant, although the ratio of Sn:Cr was constant, the amount of Sn(II) added was in much higher molar excess concentration than the amount needed just to convert the Tc. To examine the minimum amount of Sn needed, an additional experiment was also performed for the high Cr simulant, using 1 equivalent of Sn(II) relative to the amount of Cr(VI) with the addition of 0.25 or 0.5 equivalents of Sn(II) relative to the Cr(VI) concentration in the baseline simulant. This experiment was designed to test a "constant excess" of Sn(II), where the 1 eq. amount is based upon the amount of Cr(VI) in the simulant, but the excess amount (i.e. the 0.25 or 0.5 eq.) is held constant as the Cr(VI) concentration increases from the baseline amount to the maximum amount.

Precipitation Tests – Impact of Glass Forming Chemicals

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

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

Precipitation Tests – Fe(II)/Sn(II) Sequential Strike

Testing has shown Fe(II) to be less effective than Sn(II) for Tc removal in this stream, however much of the Sn(II) added is consumed reducing the Cr(VI) to Cr(III). This set of experiments was designed to test the effectiveness of Fe(II) for reduction of the Cr(VI), followed by the addition of Sn(II) to reduce the pertechnetate. This would reduce the amount of Sn(II) that must be used in the process.

The addition of $FeSO_4$ to the simulant results in a drop in pH, which makes the $FeSO_4$ less effective; therefore, 1 equivalent of sodium hydroxide was added along with the $FeSO_4$ to maintain the pH near neutral. $FeSO_4$ was selected since it is readily available. Other soluble Fe(II) salts could presumably be used instead. Two Fe(II) ratios were tested, 2:1 and 1.5:1, with the ratios based upon the number of electrons needed to reduce the Cr(VI) to Cr(III). Sn(II) was then added to each experiment at a ratio of 0.5:1, also relative to the electrons needed to reduce the Cr.

Precipitation tests were performed by adding the appropriate amount of $FeSO_4 \cdot 7H_2O$ to separate LDPE bottles, followed by the addition of 19 mL of the SBS/WESP 2015 simulant to each. The 1 equivalent of NaOH, relative to $FeSO_4$, was then added to each bottle, and the bottles were agitated in a shaker oven at ~25 ˚C for 6 hours. After 6 hours, each bottle was sampled by filtering ~4 mL through a 0.1-µm filter. After removal of the sample, the appropriate amount of $SnCl_2 \cdot 2H_2O$ was added to each original bottle, and the bottles were returned to the shaker oven for an additional 1 hour. A final sample was then removed from each bottle and filtered through a 0.1-µm filter. Both sets of samples were then analyzed using ICP-MS and ICP-OES.

Results and Discussion

Simulant Compositions

Results of the average and standard deviation of the duplicate chemical analysis of the neutralized, filtered simulants prepared in 2015 are shown in Table 3. All three simulants are relatively good matches versus the accuracy and range of the projected composition, and the small variations are not expected to impact results obtained here.

The radionuclide activities (as percentage of target activity) are provided in Table 4. The Pu and Am were found to be only marginally soluble in these simulants. The ^{137}Cs activity was consistently ~30% low across all three simulants, indicating the activity of the stock was likely lower than expected. The ^{85}Sr activity in the SBS/WESP w/GFC simulant was only ~50% of the target value at the time of analysis. It was speculated that this was due to ^{85}Sr being removed by the GFCs based on comparison to literature reports of Sr removal by minerals [16-19]. To confirm this speculation, samples were submitted both filtered and unfiltered for gamma analysis to determine the total ^{85}Sr versus the soluble ^{85}Sr activity. Gamma analysis of the unfiltered simulant indicated a ^{85}Sr activity of 5.76×10^4 dpm/mL, 99.4% of the target value, which confirms that it was removed by the GFCs. The ^{241}Am, which was insoluble in the simulant, was also detected in the unfiltered sample with an activity of 1.07×10^3 dpm/mL, 207% of the target, confirming that it was spiked correctly, but not soluble. The ^{137}Cs activity was the same between the filtered and unfiltered samples, indicating no ^{137}Cs is removed by the GFCs, as expected.

Impact of Cr Concentration

Two 100-mL aliquots of the SBS/WESP – no Cr were spiked to target levels of 30 ppm and 140 ppm Cr by the addition of sodium chromate. ICP-OES analyses of the simulants after Cr addition show Cr concentrations of 28.2 ppm and 122 ppm, which represent 94% and 87% of the target values, respectively. These two simulants, along with the 0 ppm Cr simulant, were used for the precipitation experiments. For the precipitation experiments, 1.5 eq of $SnCl_2$ were added relative to the equivalents of electrons needed to reduce the Cr and Tc (2.25 moles/mole). This corresponded to $SnCl_2$ concentrations of 0.0105 g/L (5.5E-5 M), 0.24 g/L (0.0013 M), and 1.01 g/L (0.0053 M) for the 0, 28 mg/L (5.39E-4 M), and 122 mg/L (2.35E-3 M) Cr solutions. Table 5 provides the results of these experiments.

Results of these experiments showed successful removal of ^{99}Tc in both the low and high Cr concentration simulants. Small amounts of U were also removed in these experiments, as has been seen in prior work with $SnCl_2$ reductive precipitation [14]. The U removal results in these experiments provide evidence that the U removal is due to a co-precipitation process, as little U is removed in the 0 ppm Cr experiments. Minimal solids are formed when no Cr is present, only the small amount of TcO_2 and SnO_2. Larger amounts of solids produced when the Cr_2O_3 is formed likely cause the co-precipitation of the U. As expected, Cr was also removed from the simulant, presumably through reduction of the Cr(VI) to Cr(III) and precipitation as the oxide (Cr_2O_3). The results from the 0 ppm experiments (Expt. 1) were not consistent between the replicate trials, and were therefore repeated (Expt. 2).

When the 0 ppm Cr experiments were repeated with 1.5 eq of $SnCl_2$ based upon the electrons needed for reduction of Tc, little Tc was removed (Expt. 2). As seen in Table 5, the addition of $SnCl_2$ appears to remove Zn in addition to the Cr and ^{99}Tc. The mechanism for Zn removal is believed to be removal by flocculation due to the precipitation of tin oxide. In simulants containing Cr the 1.5 eq based on Tc and Cr likely provides sufficient excess Sn(II) to allow for some to initially precipitate as tin oxide, as predicted by modeling of this simulant composition. To examine this, experiments were repeated with the 0 ppm Cr simulant increasing the amount of $SnCl_2$ from 0.0105 g/L (in Expts. 1 and 2) to 0.059 g/L (Expt. 3). Results, Expt. 3 in Table 5, showed that 0.059 g/L $SnCl_2$ is sufficient to quantitatively remove the Tc from this simulant, and the zinc removal was the same as in Expt. 1. This supports the hypothesis that the removal of Zn is due to co-precipitation, since it is a saturated solution.

Results from testing Tc removal in the high Cr simulant with 1 equivalent of Sn(II) added relative to the amount of Cr(VI) and an additional 0.25 or 0.5 equivalents of "constant excess" (i.e. relative to the [Cr] in the baseline simulant) showed less than quantitative removal of the Tc within 1 hour. The 0.5 equivalents experiments removed >99% of the Cr and Tc, while the removal percentages with 0.25 eq. were much lower. Results from this experiment are summarized in Table 6. The amount of Sn remaining in solution at the end of the experiment was less than 1% of what was added, indicating that it was essentially all consumed and precipitated, presumably as the oxidized SnO_2. As had been seen in previous experiments, Zn was also removed, with an average DF of ~17 in these experiments.

Effect of Glass Forming Chemicals

Results from testing of $SnCl_2$ reductive precipitation in the presence of GFCs are shown in Table 7. In these experiments $SnCl_2$ was added at a concentration of 0.79 g/L, which is 1.5 eq relative to the Cr and Tc concentrations. In addition to ICP-MS and ICP-OES analyses to determine the Tc and Cr concentrations, respectively, samples were also submitted for gamma spectroscopy analysis to monitor the behavior of the Cs, Sr, and Am under these conditions. As discussed above, the GFCs removed some of the Sr and U, assumed to be due to chemisorption onto the minerals based on comparison to literature reports [16-19]. Samples of the control tests, without $SnCl_2$, were analyzed both filtered and unfiltered.

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

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

A similar effect was seen with Zn, where the addition of $SnCl_2$ appeared to increase the soluble Zn concentration. The Zn present in the simulant is due to partial dissolution of the zinc oxide GFC when the aqueous phase is mixed with the GFCs initially during simulant preparation. Since the GFCs were not filtered out of this simulant, it appears the addition of $SnCl_2$ caused additional dissolution of the zinc oxide, likely due to both a small change in the solution pH and the Zn in the excess zinc oxide dissolving to replace that removed by the precipitation. This increase in concentration in the test bottles resulted in DF values of less than 1. A small amount of ^{85}Sr appeared to have been removed in the $SnCl_2$ tests, reaching an average DF of 1.23. There was no measurable removal of ^{137}Cs, as would be expected.

Fe/Sn Sequential Strike

Results from the Fe(II)/Sn(II) sequential strike experiments are shown in Table 8. There was some discrepancy between the replicate trials for the 1.5:1 Fe(II) ratio, so the results from individual experiments are provided in the table. With the exception of the second trial with 1.5 eq. of Fe(II), the Cr was removed to below the method detection limit (DF > 844) after the Fe(II) strike. Some Tc removal was also seen with Fe(II) alone, which is consistent with previous work. The subsequent addition of 0.5 eq. of Sn(II) resulted in the quantitative removal of Tc to below the method detection limit (DF > 216) in all experiments. In addition to the Cr and Tc removal, U was also removed with the Fe(II) as seen previously when NaOH was added to mitigate the pH drop from adding $FeSO_4$. It appears the addition of $SnCl_2$ causes some of the U to redissolve, perhaps due to the change in pH.

Conclusions

Treating the SBS-WESP Off-Gas Condensate Recycle simulant using $SnCl_2$ has been shown to be successful for the removal of Tc. Previous work has shown that Sn(II) is much more successful at removal of Tc than is Fe(II) [8]. Only 1.5 eq of Sn(II), which corresponds to ~0.8 g/L $SnCl_2$ in the average simulant, is necessary for good Tc removal from this simulant formulation, and this is a function of Cr concentration. Although not measured directly, it is expected that the Tc will be in the form of pertechnetate in the WTP melter Off-Gas Condensate Recycle stream due to the highly oxidizing conditions. Addition of $SnCl_2$ causes reduction from soluble TcO_4^- to form (presumably) TcO_2 solids, which can be removed by settling or filtration. It was found that 1.5 equivalents of Sn(II) is needed to achieve the desired decontamination factor. The need for the excess equivalent (i.e., 0.5 eq.) is not truly known, but is likely due to hydrolysis and precipitation of some of the Sn(II) as Sn(OH)Cl which co-precipitates with the Sn(IV) and Cr(III) solids.

Although Fe(II) alone is only marginally effective at removing Tc, it is effective for removal of the Cr. Since Cr "consumes" Sn when used alone, using Fe(II) and Sn(II) sequentially can reduce the amount of Sn(II) that must be added for ^{99}Tc removal. The removal of both Cr and Tc utilizing a sequential strike of Fe(II) followed by Sn(II) was demonstrated. As little as 1.5 eq. of Fe(II), followed by 0.5 eq. of Sn(II) (equivalents are relative to the equivalents of electrons needed to reduce the Cr and Tc) showed quantitative removal of ^{99}Tc. Sodium hydroxide was also added along with the Fe(II) to keep the pH near neutral. Although a disposition path for the Sn-Tc-containing slurry has not yet been tested, this result indicates that different options may be viable if Sn content is found to limit the waste loading or if other storage or compatibility issues arise.

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

Experiments in the high Cr simulant with reduced amounts of Sn(II) showed slightly less than quantitative removal of ^{99}Tc. The amount of Sn(II) added in these experiments corresponded to 1 eq. relative to the Cr concentration in the simulant, plus an additional 0.5 or 0.25 equivalents of “constant excess”, i.e. relative to the amount of Cr in the baseline simulant. The 0.5 equivalents of constant excess did remove >99% of the Tc (DF of 170), whereas the 0.25 eq. resulted in a Tc DF of only 3.75. The original target DF for Tc was 100, so the 0.5 equivalent excess did meet that target.

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

Additional tasks needed to further develop this technology include speciation of the precipitated solids, 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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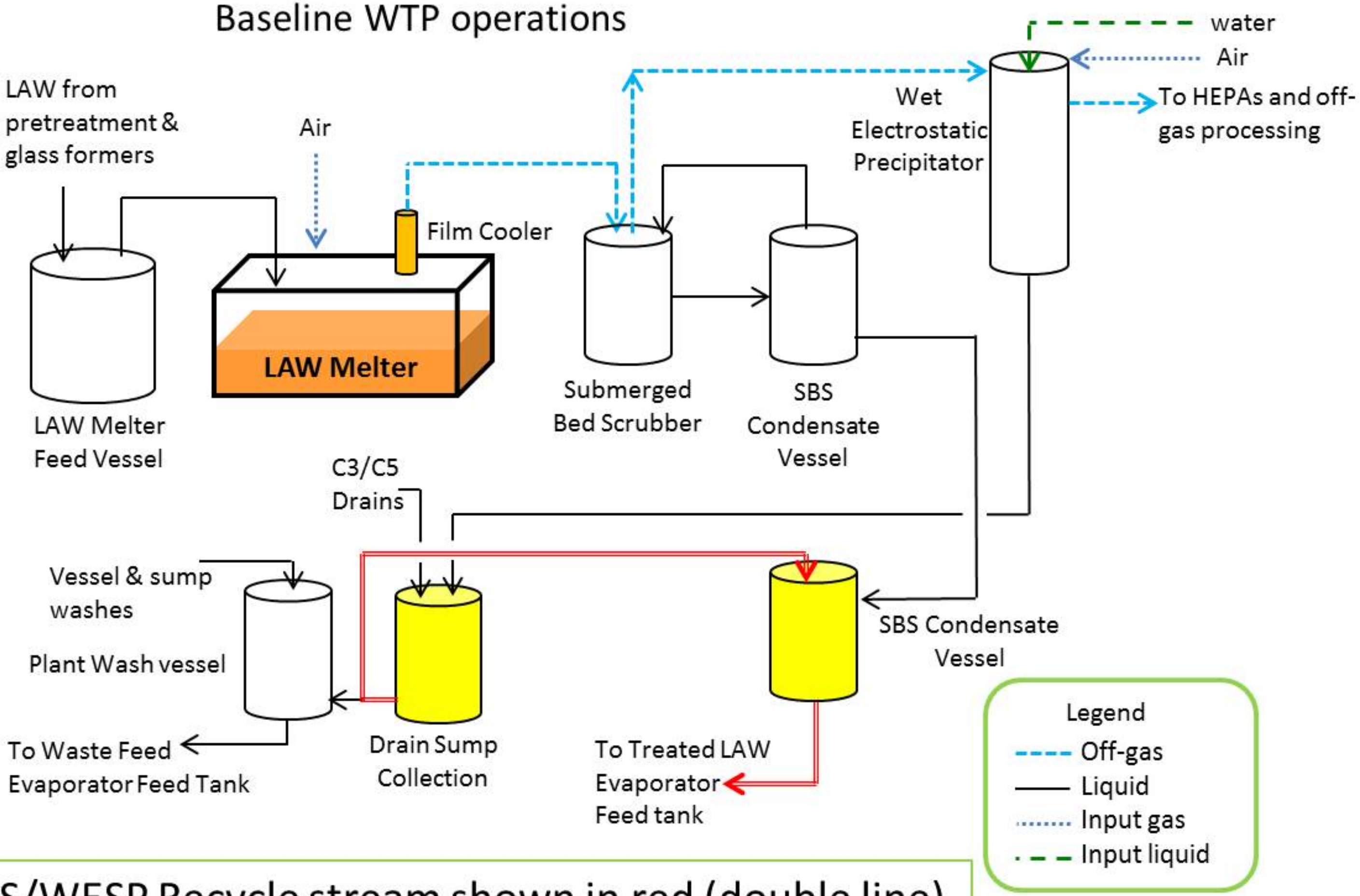
Simplified Low Activity Waste Off-gas System

Baseline WTP operations



SBS/WESP Recycle stream shown in red (double line)

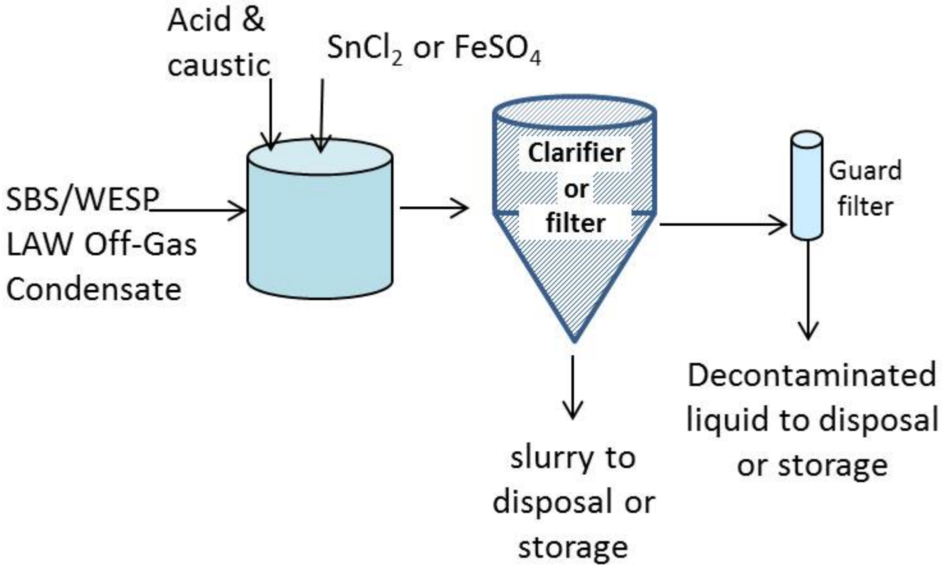

Acid &
caustic
$SnCl_2$ or $FeSO_4$
SBS/WESP
LAW Off-Gas
Condensate
Clarifier
or
filter
Guard
filter
slurry to
disposal or
storage
Decontaminated
liquid to disposal
or storage

Table 1. Aqueous Simulant Formulation Targets

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

[#] Sodium chromate added after removal of a 500 mL aliquot

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

Table 2. Target Glass Former and Radiotracer Quantities

Mineral	Formula	Mass (g)/L simulant		Isotope	Target concentration (dpm/mL)
kyanite	Al_2SiO_5	0.745		^{137}Cs	1.16E4
borax	$Na_2B_4O_7 \cdot 10H_2O$	0.0123		^{238}U	6.24E-1
boric acid	H_3BO_3	1.430		$^{239/240}Pu$	8.42E1
wollastonite	$CaSiO_3$	0.772		^{85}Sr	5.79E4
iron oxide (hematite)	Fe_2O_3	0.430		^{99}Tc	9.21E4
lithium carbonate	Li_2CO_3	0.392		^{241}Am	5.15E2
forsterite olivine	Mg_2SiO_4-Fe_2SiO_4	0.257			
sodium carbonate	Na_2CO_3	0.003			
silica	SiO_2	2.857			
rutile	TiO_2	0.114			
zinc oxide	ZnO	0.286			
zircon	$ZrSiO_4$	0.372			
sucrose	$C_{12}H_{22}O_{11}$	0			
	Total	7.67			

Table 3. Neutralized Simulant Filtrate Compositions

Component	SBS/WESP 2015 Avg. mg/L (M)	SD	SBS/WESP – No Cr Avg. mg/L (M)	SD	SBS/WESP w/GFC Avg. mg/L (M)	SD		HTWOS projection (avg. SVF-2732) (mg/L)
Al	<0.500 (<1.9E-5)	n/a	<0.500 (<1.9E-5)	n/a	<0.500 (<1.9E-5)	n/a		28
B	158 (0.0146)	2.1	164 (0.0152)	0.71	165 (0.0153)	3.5		GFC#
Ca	0.970 (2.4E-5)	0.009	0.932 (2.3E-5)	0.012	0.914 (2.3E-5)	0.012		GFC#
Cr	93.3 (0.0018)	2.7	<0.100 (<1.9E-6)	n/a	95.7 (0.0018)	0.71		91
Fe	<0.100 (<1.8E-6)	n/a	<0.100 (<1.8E-6)	n/a	<0.100 (<1.8E-6)	n/a		GFC#
K	121 (0.0031)	0.71	122 (0.0031)	6.4	118 (0.0030)	0*		115
Li	75.6 (0.011)	0.64	77.0 (0.011)	2.6	83.3 (0.012)	0.14		GFC#
Mg	<0.100 (<4.1E-6)	n/a	<0.100 (<4.1E-6)	n/a	<0.100 (<4.1E-6)	n/a		GFC#
Na	1780 (0.077)	0*	1775 (0.077)	35.4	1815 (0.079)	21.2		2.29E3
P	2.00 (6.5E-5)	0*	1.19 (3.8E-5)	0.014	1.90 (6.1E-5)	0*		7 (as PO_4^{3-})
S	806 (0.025)	2.1	809 (0.025)	0.71	812 (0.025)	3.5		780 (as SO_4^{2-})
Si	52.3 (0.0019)	1.5	52.6 (0.0019)	0.071	52.0 (0.0019)	0.57		GFC#
Ti	<0.100 (<2.1E-6)	n/a	<0.100 (<2.1E-6)	n/a	<0.100 (<2.1E-6)	n/a		GFC#
Zn	20.1 (3.1E-4)	0.64	17.1 (2.6E-4)	0*	20.5 (3.1E-4)	0.14		GFC#
Zr	<0.500 (<5.5E-6)	n/a	<0.500 (<5.5E-6)	n/a	<0.500 (<5.5E-6)	n/a		GFC#
F^-	1295 (0.068)	7.1	1290 (0.068)	14.1	1300 (0.068)	0*		1.45E3
Cl^-	965 (0.027)	35.4	953 (0.027)	0.71	952 (0.027)	0*		950
NO_2^-	<100 (<0.0022)	n/a	<100 (<0.0022)	n/a	<100 (<0.0022)	n/a		10.7
NO_3^-	2420 (0.039)	14.1	2410 (0.039)	28.3	2520 (0.041)	0*		5.53E3
SO_4^{2-}	2185 (0.023)	7.1	2180 (0.023)	14.1	2340 (0.024)	0*		2.34E3
PO_4^{3-}	<100 (<0.0011)	n/a	<100 (<0.0011)	n/a	<100 (<0.0011)	n/a		21.5
NH_4^+	1400** (0.078)	n/a	1380** (0.077)	n/a	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 4. SBS/WESP Simulant Radionuclide Compositions - % of Target Activity (See Table 2 for Targets)

Isotope	SBS/WESP	SBS/WESP – No Cr	SBS/WESP w/GFC (filtered)	SBS/WESP w/GFC (unfiltered)
^{85}Sr	89	103	45	99
^{99}Tc	83	79	98	NM
^{137}Cs	66	68	69	70
^{238}U	102	100	64	NM
$^{239/240}$Pu	< 6.8	< 12	< 0.43	NM
^{241}Am	< 6.0	< 6.1	< 13	207

Table 5. Average Decontamination Factors Obtained in Variable [Cr] Experiments

1-h DF	**0 mg/L Cr Simulant**			**Low Cr Simulant (28 mg/L, 5.39E-4 M)**	**High Cr Simulant (122 mg/L, 2.35E-3 M)**
	Expt. 1	**Expt. 2**	**Expt. 3**		
Tc DF	39.7 (53.6)[#]	1.44 (0.07)	> 186 (0.00)	179 (14.7)[$]	> 189 (0.00)
U DF	1.02 (0.00)	1.02 (0.00)	1.04 (0.00)	1.20 (0.01)	1.28 (0.07)
Cr DF	n/a	n/a	n/a	> 62.2 (0.00)	73.1 (6.97)
Zn DF	2.10 (0.85)	NM	2.31 (0.10)	23.8 (3.23)	13.6 (6.23)

NM = not measured

Value in parentheses indicates standard deviation of replicate trials.

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

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

Table 6. Results from "Constant Excess" Sn(II) Experiments

Average of Replicates	1:1 + 0.5 eq. Sn(II)	1:1 + 0.25 eq. Sn(II)
Tc DF	170 (17.6)	3.75 (0.114)
U DF	1.46 (0.008)	1.43 (0.032)
Cr DF	111 (0.00)	27.5 (1.44)
Zn DF	16.9 (0.737)	17.6 (1.15)
% Sn Soluble	0.70% (0.14%)	0.28% (0.16%)

Value in parentheses indicates standard deviation of replicate trials.

Table 7. Average Decontamination Factors in SBS/WESP w/GFC Simulant

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

Value in parentheses indicates standard deviation of replicate trials.

Table 8. Results from Fe/Sn Sequential Strike

	Fe(II) (2:1) + 1 eq. NaOH / Sn(II) (0.5:1)		Fe(II) (1.5:1) + 1 eq. NaOH / Sn(II) (0.5:1)	
	Trial 1	**Trial 2**	**Trial 1**	**Trial 2**
6 h Tc DF	12.4 (3.52)	18.2 (5.14)	2.80 (0.792)	1.10 (0.312)
6 h U DF	5.57 (1.58)	4.29 (1.21)	3.60 (1.02)	1.16 (0.327)
6 h Cr DF	> 844	> 844	> 844	141 (20.4)
6 h Zn DF	41.2 (7.57)	44.9 (7.84)	32.5 (4.82)	5.65 (0.799)
7 h Tc DF	> 216	> 216	> 216	> 216
7 h U DF	3.35 (1.85)	2.09 (1.02)	2.37 (0.860)	1.11 (0.330)
7 h Cr DF	> 838	> 838	> 838	49.7 (7.03)
7 h Zn DF	40.3 (6.77)	29.6 (4.67)	30.6 (4.69)	3.72 (0.526)
% Sn Soluble	0.02%	0.14%	0.08%	7.11%