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Evaluations of the Fates of Alkali Metals, Actinides, Mercury, and Iodine During DWPF Recycle Diversion

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EXECUTIVE SUMMARY

The fates of alkali metals, actinides, mercury, and iodine in the Defense Waste Processing Facility Recycle Diversion process (as currently conceptualized) have been evaluated through paper studies based on available knowledge of the chemistry, physical properties, solubility, and volatility of the various species involved. The effect of pH in the range from 9 to 13 has been discussed. Recommendations for additional studies to close technology gaps have been provided, many of which are contingent upon the results of pending testing and sample characterization efforts. There is uncertainty in the amounts of soluble actinides passing through the process filter, though the bulk of the actinides should be captured on the filter with the Recycle Collection Tank solids and the total amounts of actinides should be relatively low. The Recycle Collection Tank pH could impact the fraction of actinides reaching the evaporator, but the primary factors determining the actinide fate are expected to be the amount of CO_2 sorption from air sparging or, for certain actinides (such as plutonium), oxidation and/or sorption to MnO_2 solids from permanganate additions to destroy the glycolate anion. Process optimization could minimize the amounts of actinides passing the filter. Depending upon the levels of mercury observed in recycle stream samples and because of the volatility of mercury, the evaporator should be designed with the capability to remove dense mercury phases from the condensate to avoid exceeding ETP WAC limits. The facility design must be adequate to transfer dense mercury phases and testing to confirm mercury transfer is needed. Simulant containing mercury is recommended for both filtration and evaporation testing. OLI Modeling of the various recycle streams is recommended to provide insight on the fate of iodine. Iodine-spiked simulants are recommended for upcoming evaporation tests. The project should consider the likelihood and impact of NAS scale formation in the evaporators. Process optimization may be needed to minimize the accumulation of NAS scale and possibly the sorption of actinides in the evaporator. Actual waste testing of the Recycle Diversion filtration and evaporation should include the analysis of actinides, mercury, and iodine to determine their partitioning.

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LIST OF ABBREVIATIONS

ABD	Accelerated Basin De-inventory
ARP	Actinide Removal Process
CCP	Corrosion Control Program
CPC	Chemical Processing Cell
CSTF	Concentration Storage and Transfer Facilities
DWPF	Defense Waste Processing Facility
DL	Detection Limit
DWTT	Decontamination Waste Treatment Tank
ELN	Electronic Laboratory Notebook
ETP	Effluent Treatment Project
HLW	High Level Waste
MST	Monosodium titanate
NAS	Sodium Aluminosilicate
OGCT	Off Gas Condensate Tank
RCT	Recycle Collection Tank
REDOX	Reduction Oxidation
SBS	Submerged Bed Scrubber
SEE	Systems Engineering Evaluation
SME	Slurry Mix Evaporator
SMECT	Slurry Mix Evaporator Tank
SRNL	Savannah River National Laboratory
SWPF	Salt Waste Processing Facility
SRAT	Sludge Receipt and Adjustment Tank
SRR	Savannah River Remediation
SRR-E	Savannah River Remediation-Engineering
SRS	Savannah River Site
TTQAP	Task Technical and Quality Assurance Plan
TTR	Technical Task Request
VSL	Vitreous State Laboratory
WAC	Waste Acceptance Criteria
WAPS	Waste Acceptance Product Specification
WESP	Wet Electrostatic Precipitator
WFE	Wiped-film Evaporator
WTP	Waste Treatment and Immobilization Plant

1.0 Introduction

The Savannah River Site (SRS) Defense Waste Processing Facility (DWPF) processes radioactive High-Level Waste (HLW) sludge solids from the Concentration, Storage, and Transfer Facilities (CSTF; which includes the SRS Tank Farm and Evaporator facilities) and a concentrated Cs-137 laden stream and a Monosodium Titanate (MST) and sludge solids stream from the SRS Salt Waste Processing Facility (SWPF). The waste is chemically adjusted (currently with 50 wt.% nitric acid and ~90 wt.% formic acid, but eventually formic acid will be substituted with ~70 wt.% glycolic acid[1]) with acids and reductant. Then frit is added so that a durable, borosilicate glass waste form can be produced when the material is vitrified in the melter. As a result of the evaporation of water during both the melter feed preparation and the melter feed vitrification steps in DWPF, a recycle waste stream is generated, adjusted for pH, and sent back to the CSTF. The recycle waste is a dilute aqueous stream originating from the collection of condensate liquids containing some minor sludge, MST, and frit solids and other waste components resulting from melter feed entrainment during foam over events and transfer of volatile species into the condensate. The recycle stream volume is significant and is expected to approach 3 million gallons per year once SWPF reaches full operation. The recycle waste is currently collected in the SRS Tank Farm and periodically evaporated in the 242-16H (2H) Evaporator to conserve storage space.

Diverting the bulk of the recycle waste stream from the Tank Farm is essential for the eventual closure of the waste tanks, and hence the completion of the SRS liquid waste mission. Savannah River Remediation (SRR) recently performed a Systems Engineering Evaluation (SEE) for diverting the DWPF recycle stream.[2] Crossflow filtration and wiped-film evaporation (WFE) were selected as the preferred methods for processing the diverted recycle. The final streams produced from these unit operations, including filter solids, evaporator bottoms, and evaporator overheads, will be transferred to the sludge batch preparation tank feeding DWPF, the salt batch preparation tank feeding SWPF, and the SRS Effluent Treatment Project (ETP), respectively, with the ETP receiving the bulk of the recycle volume.[3] Transfer of much of the water from the DWPF recycle to ETP accomplishes the primary goal of diverting the bulk of the material from the CSTF.

The Recycle Collection Tank (RCT) in the DWPF Chemical Processing Cell (CPC) is the starting point for evaluating the process chemistry for the Recycle Diversion process. OLI calculations recently conducted by SRR evaluated the composition of the DWPF recycle stream under various processing scenarios and conditions.[4] The RCT mainly receives transfers from the Slurry Mix Evaporator Condensate Tank (SMECT), the Off Gas Condensate Tank (OGCT), the Decontamination Waste Treatment Tank (DWTT), and from laboratory drains. The SMECT and OGCT sources represent the largest volume contributors to the RCT and are acidic, primarily due to DWPF nitric acid additions and the condensation of nitric acid vapors during processing. The other streams that are transferred to the RCT can be acidic or caustic. Currently, the recycle condensate is adjusted using sodium hydroxide and sodium nitrite additions to give a pH ≥13 and a nitrite concentration sufficiently high to meet Corrosion Control Program (CCP) criteria for the CSTF carbon steel tanks. The DWPF Recycle Diversion process needs to meet the CSTF CCP criteria for streams transferred to the CSTF, but the same levels of sodium hydroxide and sodium nitrite additions may not be required for diverted recycle. However, previous investigations of evaporation of the recycle under acidic conditions were shown to be problematic due to foaming, iodine volatility, and other issues.[5,6] Thus, to ensure that the recycle condensate is not acidic when evaporated and assuming that the CCP requirements could be relaxed, the RCT may be adjusted by the addition of sodium hydroxide to a pH target as low as 9 (depending on corrosion control requirements selected for the diverted recycle), versus the current requirement of ≥13. Under the Nitric-Glycolic Acid Flowsheet planned for future implementation in DWPF, sodium permanganate will also be added to the RCT to reduce the concentration of glycolate in the recycle stream to low levels (near 1 mg/L) in the CSTF.[7,8,9]

Savannah River Remediation-Engineering (SRR-E) requested that SRNL evaluate the fates of alkali metals, actinides, mercury, and halides (specifically iodine) during the processing of the Diverted Recycle Stream with and without the addition of sodium permanganate to the RCT and across the pH range (9 to 13) of interest.[10] Recycle diversion is being implemented in the DWPF process following the change to the new DWPF antifoam, Momentive™ Y-17112, and is expected to be implemented after the transition from formic to glycolic acid reductant. SRR is in the process of selecting an evaporator for processing the diverted recycle stream and is considering both vacuum and atmospheric evaporator alternatives. Although permanganate addition to the RCT is expected, SRR requested that processing scenarios with and without permanganate addition be considered. Results of these evaluations are provided below.

2.0 Method

2.1 Assumptions

The following chemical and process assumptions applied for the initial evaluations of the DWPF Recycle Diversion Process, though other conditions were also evaluated in specific cases as indicated in the body of the document.

- Nitric-Glycolic Acid Flowsheet implemented
- New DWPF Antifoam, Momentive™ Y-17112, implemented with no new degradation species observed in the SMECT and OGCT condensate streams (due to the high stability of the new antifoam and the expectation that lower antifoam addition rates are expected relative to the current antifoam)
- Only SMECT and OGCT contributions to the RCT considered
- RCT volume: 9,000 gallons (including NaOH and $NaNO_2$ additions to heel)
- RCT Hydroxide: 0.16 M (calculated amount disregarding reaction with acid and assuming 75 gallons of 19.11 M NaOH added to heel; current addition amount targeting pH ≥13 and amount recently assumed by SRR-E[4])
- RCT Nitrite: 0.16 M (due to addition of 215 gallons of 6.6 M $NaNO_2$ to heel; amount recently assumed by SRR-E[4])
- RCT Permanganate: 0.018 M (initial concentration prior to reaction with glycolate, due to addition of 135[a] gallons of 1.64 M $NaMnO_4$ (20 wt. %) to 9,000 gallons of RCT; amount recently assumed by SRR-E[4])
- RCT volume with added permanganate: 9,135 gallons
- Total Na^+: 0.35 M (assuming chemical reagent addition amounts above)
- Assumed liquid density: 1.0 g/mL
- RCT Frit: 0.12 wt. % Frit 803 (due to assumed presence of 41 kg frit per 9,135 gallon RCT batch; partial dissolution expected)
- Frit 803 Composition: SiO_2 – 78.0 wt. %, Na_2O – 8.0 wt. %, B_2O_3 – 8.0 wt. %, Li_2O – 6.0 wt. %
- RCT pH: 9 to ≥13 (due to addition of 50 wt. % NaOH to tank heel; amount above targets pH 13)
- RCT Permanganate Reaction Time before filtration: 4-48 hours

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[a] 135 gallons is the working volume of the permanganate tank and is considered the maximum amount for a single addition unless there is a special evolution to address a carryover event. The expected nominal amount is closer to 60 gallons.

- Initial RCT Glycolate: 125 mg/L[11,b]
- Final RCT Glycolate (following permanganate strike): 1 mg/L
- RCT Temperature: 30 °C
- Filtration Temperature: <50 °C
- Evaporator Temperature: 60-120 °C (based on vacuum or atmospheric operations, respectively; upper temperature conservatively based on calculated atmospheric boiling point for 7.0 M Na^+ solution of 107 °C)[12]
- Evaporator Concentrate Na^+: 5.6 to 7.0 M
- Evaporator Cleaning Acid: nitric or oxalic
- Total RCT Insoluble Solids: 0.2 (without a permanganate strike) to 0.4 wt. % (including MnO_2 from sodium permanganate addition)

The SMECT and OGCT Stream Compositions provided in Table 2-1 were recently reported by SRNL[7] and were used as a compositional basis by SRR-E in the RCT OLI Modeling report[4]. Since the OGCT is the stream from the melter off-gas, it is generally a more concentrated stream than the SMECT. Based on the assumed chemical (NaOH, $NaNO_2$ and $NaMnO_4$ reagent solutions) additions above and the concentration factor in the evaporator, the estimated concentrations of the major species in the chemically adjusted RCT stream are provided in Table 2-2. The RCT sodium concentration after chemical additions is expected to be near 0.35 M (at pH 13), and the RCT stream could be concentrated to as high as 7.0 M Na^+ in the evaporator. This corresponds to a concentration factor of 20. Based on this factor and the chemical addition amounts, the expected concentrations of the other major species in the evaporator pot are provided in Table 2-2. Nitrite, hydroxide, and nitrate are the dominant anionic species, and manganese (primarily from permanganate) is another significant chemical additive and stream component. Sodium is the dominant cation.

2.2 Process Summary and Basis for Evaluations

Evaluations of the fates of the various species of interest were based on relevant information provided in the referenced reports and general chemical knowledge of the species involved. Reagent additions result in the precipitation of some species so that they can be removed by filtration. Permanganate addition results in glycolate destruction and eventual MnO_2 precipitation. In some instances, OLI Thermodynamic Modeling was utilized to provide additional insight regarding the fates of these species based on the conditions experienced during recycle diversion. Species known to be volatile can partition into the condensate streams, and entrainment of species into the condensate can occur during foam over events. During evaporation, scale solids can form on the evaporator internals which may not be recovered without chemical cleaning with acid.

2.3 Quality Assurance

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. This work was performed following the applicable TTQAP.[13] The Task Technical Request (TTR) associated with this work[10] requested a functional classification of Safety Class. This report and calculations within received a technical review by design verification (Manual E7 2.60, Section 5.3). Data and calculations are recorded in the electronic laboratory notebook (ELN) system as notebook/experiment number A2341-00117-17.

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[b] 125 mg/L glycolate is believed to be a conservatively high value is based on X-ESR-S-00414. The expected glycolate concentration in the absence of glycolate destruction is approximately half of this value.

The OLI Studio™ program used in this work is an acquired software that meets the commercial grade definition criteria in accordance with Manual E7 Procedure 3.46 and is accepted from the vendor by verifying that the parts identifiers are correct. Dedication of the commercial grade software in accordance with Manual E7, Procedure 5.07 is not required for the OLI software, which was classified as Level D.[14] All the activities related to the verification and validation of the OLI software database and the resulting models were documented in accordance with Manual E7 Procedure 5.40, Software Testing, Acceptance and Turnover. The OLI software is classified as Level D. Therefore, it cannot be used for safety-related calculations and results are only to be used directly for General Services activities. Confirmatory experiments were not performed for these modeling calculations.

Table 2-1 SMECT and OGCT Compositions (RCT Feed) Reported by SRNL[7] and Used by SRR-E for RCT OLI Calculations[4] (not charge balanced).

Component	SMECT	OGCT
	M	
Al	1.6E-04	3.1E-03
Ca	6.1E-05	3.7E-04
Cr	<6.2E-06	1.5E-04
Fe	1.2E-04	2.3E-03
Hg	5.0E-04	1.1E-03
Mg	1.4E-05	1.2E-04
Mn	7.0E-05	1.1E-03
Na	1.6E-03	1.5E-02
Ni	<2.1E-05	1.8E-04
Si	2.1E-03	4.9E-03
Sr	3.2E-05	2.7E-06
Th	<7.8E-06	3.3E-05
U	<4.1E-05	1.3E-04
Zn	<2.8E-05	3.9E-05
formate	1.3E-03	<2.6E-03
oxalate	<1.1E-04	<1.3E-03
nitrate	5.8E-02	4.5E-02
nitrite	<2.2E-04	<2.5E-03
pH	1.6	0 to 1

Table 2-2 Estimated RCT and Recycle Diversion Evaporator Pot Major Species Concentrations Assuming Current RCT Reagent Additions, Permanganate Addition, 20x Evaporator Concentration, and No Precipitation

Component	RCT[a,b]	Recycle Diversion Evaporator Concentrate[c]
	M	
Na	0.35	7.0
nitrite	0.16	3.1
free hydroxide	0.10[d]	2.0
nitrate	0.044	0.9
Mn[e]	0.024[e]	0.5[e]
pH	13[d]	>14[d]

[a] based on addition of: 75 gallons of 19.11 M NaOH, 215 gallons of 6.6 M $NaNO_3$, and 135 gallons of 1.63 M $NaMnO_4$ giving a final RCT volume of 9,135 gallons; lower levels of all reagents being considered

[b] all other species expected to be <0.01 M

[c] all other species expected to be <0.2 M

[d] assuming some base neutralization with acid

[e] Calculated value assuming no MnO_2 precipitation. It is expected that some of the manganese will form insoluble solids which will be removed by filtration. The amount of manganese removed will be dependent upon the reaction time in the RCT prior to filtration.

3.0 Results and Discussion

3.1 Fate of Alkali Metals During DWPF Recycle Diversion

Sodium is the primary and dominant cation in the RCT. Sodium contributions from the SMECT and OGCT streams are very small with NaOH, $NaNO_2$, and $NaMnO_4$ reagent additions representing the majority of sodium present in the RCT. The total sodium in the RCT is estimated to range from 0.1 to 0.5 M depending on the amounts of chemical reagents added. Addition of the current DWPF sodium hydroxide and nitrite reagent levels and 135 gallons of sodium permanganate reagent to a full RCT to produce 9,135 gallons of liquid and, assuming that no precipitation occurs, would produce a total sodium concentration of 0.35 M. Based on the assumed reagent addition amounts, the concentrations of the other major species in the chemically-adjusted RCT stream are also provided in Table 2-2. It is expected that the precipitation of sodium salts in the RCT will be minimal since most sodium species are soluble under these conditions. Therefore, filtration of the RCT contents should not result in the removal of significant sodium.

Diverted recycle stream compositions in the RCT have been calculated by SRR-E using the OLI Thermodynamic model under various processing scenarios.[4] With added sodium nitrite (215 gallons of 6.6 M $NaNO_2$ to give a total RCT volume of 9,000 gallons), no added sodium permanganate, with sodium hydroxide added to give a final pH near 10 (OLI run: M-NO2), and using a 15.6:84.4 SMECT:OGCT blend (based on the assumption of a heel of SMECT material with the balance being OGCT material), the soluble sodium concentration was calculated to be 0.21 M (at 30 °C). Two sodium-containing salts were predicted to precipitate under this condition, the sodium aluminosilicate (NAS) $NaAlSi_{2.3}O_{6.6}\cdot 4H_2O$ and the uranium compound $NaUO_2OOH\cdot H_2O$ (clarkeite). The amount of sodium in the insoluble solids corresponded to <1 mole or weight % of the total sodium. Without the addition of sodium nitrite and at a pH of 10, the predicted types and amounts of sodium-containing solids formed were virtually unchanged (OLI run: Baseline). The soluble sodium in this case was calculated to be 0.06 M, and the insoluble sodium increased to ~4 mole % of the total (increase due to reduction in total sodium). The addition of sodium permanganate (but still with no added sodium nitrite) to the baseline solution resulted in a pH near 12 (due to hydroxide production from the reaction of permanganate) and a predicted soluble sodium concentration of 0.07 M (OLI Run: M-MnO4). Minor changes in the amounts of sodium-containing solids were predicted with added permanganate, and ~4 mole % of the total sodium was insoluble. A higher pH of ~13 (with no added sodium permanganate or sodium nitrite) was predicted to result in a soluble sodium concentration of 0.17 M (OLI Run M-pH-13). A different sodium aluminosilicate solid, $Na_6Al_6Si_6O_{24}\cdot 12H_2O$, was formed under this condition, and the percentage of insoluble sodium was ~1 mole %.

Based on the OLI calculations, the amounts of sodium-containing solids (<5% in all of the cases described above), both aluminosilicates and uranium-bearing solids, are somewhat insensitive to changes in the total sodium concentration and are primarily dependent upon the concentrations of silicon, aluminum, and uranium. NAS formation is limited by the amount of aluminum in the RCT feed. All of the OLI calculations are expected to overpredict the amounts of sodium-containing aluminosilicate solids since the model represents equilibrium conditions and does not take into account the timescale of silicon dioxide (from glass frit) dissolution. Given that the timescale of RCT turnover is on the order of several hours,[15] the dissolution of SiO_2 and the resulting formation of sodium aluminosilicate solids in the RCT is expected to be lower than the OLI predictions.

Estimated concentrations of major species in the Recycle Diversion Evaporator Pot assuming current and planned reagent additions and RCT stream concentration to 7.0 M Na^+ (current evaporator maximum target concentration) are provided in Table 2-2. Additional OLI calculations were conducted by SRNL using the output from SRR-E OLI run M-NO2 as input. This model run involved the typical sodium nitrite addition and a pH of 10 to give a total initial sodium concentration of 0.21 M. Concentration of this stream was accomplished by simply removing moles of water from the OLI input until the final sodium concentration was 7 M. These calculations represent a simple approximation of the evaporation process and ignore the dynamics of volatilization of certain species as water is removed. However, the calculation should be useful in predicting the fates of the major species including sodium. The results indicated that the major species (sodium hydroxide, nitrite, and nitrate salts) in the diverted recycle stream will remain soluble at a sodium concentration of 7.0 M, even after cooling of the solution to 30 ºC. In fact, concentrating this stream further to 9.0 M Na^+ also does not result in the precipitation of the major salts. Therefore, it is expected that the majority (>90%) of the sodium in the diverted recycle stream will pass through the filter, will remain soluble in the evaporator pot concentrate, and will presumably be transferred to SWPF. Note discussion in Section 3.5 about NAS scale formation.

Cesium is expected to be present in the RCT at concentrations significantly lower than sodium. Recent analysis of SMECT and OGCT samples indicated that the OGCT contained a significantly higher total Cs^+ concentration (relative to the SMECT) of 4.1E-05 M with 1.3E-05 M Cs-137 (3.3E+08 dpm/mL).[7] The SRNL OLI calculations discussed above based on the SRR-E OLI output for the RCT including sodium nitrite addition at a pH near 10 (OLI run: M-NO2) included cesium nitrate in the input at the recently measured RCT concentration mentioned above. No cesium-containing solids were predicted in the evaporator even after concentrating the pot solution to 9 M Na^+ and allowing the solution to cool to 30 °C. Concentration of a recycle stream containing the cesium concentration above by a factor of 20x in the evaporator would lead to total cesium concentrations of 8E-04 M and a Cs-137 activity of 7E+09 dpm/mL. Lithium, another alkali metal, could be present in the RCT at levels near 2.5E-05 M based on the expected silicon levels and the assumed frit composition due to the entrainment of some frit into the condensate. Lithium oxide (Li_2O) comprises 6 wt. % of Frit 803 (recently used DWPF frit blend). This metal oxide compound is known to react with water to form soluble lithium as dissociated lithium hydroxide ($2Li^+_{(aq)}$ + $OH^-_{(aq)}$), and the oxide may dissolve, along with the boron oxide (B_2O_3) also present in Frit 803, to some degree on the RCT processing timescale. It should be noted that no soluble Li nor B from potential Frit 803 dissolution was included in the SRR-E OLI modeling.[4] Potassium will also be present at low levels and is expected to remain soluble.

Gap
No major gaps in information have been identified associated with the fate of the alkali metals. It is believed that the behavior of both sodium and cesium are well understood and their fates in the Diverted Recycle Process are known. A small fraction of the sodium may precipitate in the RCT following caustic adjustment and be captured on the filter. The bulk of the major sodium and cesium salts are expected to be transferred to the recycle evaporator and ultimately to SWPF. If NAS solids do not form until the waste reaches the evaporator at elevated temperature, NAS scale could accumulate in the evaporator over time. The degree of scale formation may be impacted by temperature, which could impact the preferred evaporator (traditional versus low temperature WFE) for the process.

3.2 Fate of Actinide Elements During DWPF Recycle Diversion

A recently analyzed OGCT sample was reported to have a total uranium concentration of 1.3E-04 M.[7] This uranium concentration is judged to be relatively high for DWPF Recycle material. For example, a Tank

15H sludge slurry sample was reported to have a comparable total uranium concentration of 1.9E-04 M.[16] SMECT contributions to the RCT are expected to dilute the total uranium. A concurrent RCT sample analysis indicated a significantly lower total uranium concentration.[17] DWPF feed slurry typically has much higher total uranium concentrations than have been observed for the DWPF condensate stream. Uranium levels vary significantly in SRS tank waste, but the uranium result reported by Nash[7] reveals that uranium concentrations in the RCT may not be as low as might be expected for a condensate stream. In addition, future planned Accelerated Basin De-inventory (ABD) operations at SRS may slightly increase the total uranium being processed through DWPF.[18] Current plutonium concentrations in tank waste on a molar or weight percent basis are typically lower than uranium by at least an order of magnitude, but based on activities (rather than molar concentrations or weight percent) the total activity from plutonium isotopes is typically at least two orders of magnitude higher than the activities from uranium isotopes.[19] Other actinides, such as thorium, neptunium, americium, and curium will be present in the recycle stream at levels dependent upon their concentrations in the DWPF sludge batch feed stream and the degree of entrainment into the recycle condensate stream. The activities of americium and curium isotopes can approach the plutonium isotope activity in some tanks.[19] Most of the discussion on the fates of the actinides focuses on uranium and plutonium.

3.2.1 RCT with NaOH and $NaNO_2$ Additions, but Without Added $NaMnO_4$

Initial evaluations of the anticipated actinide chemistry in the DWPF RCT were conducted assuming that permanganate had not been added to the RCT in order to consider the tank chemistry in the absence of a strong oxidant. Soluble uranium and plutonium from the acidic SMECT and OGCT streams which are exposed to caustic (current target pH: 13) in the RCT are expected to form hexavalent uranyl ion, UO_2^{2+}, and plutonium species with oxidation states ranging from 4 to 6.[20] If uranyl solubility limits are exceeded under these conditions (and a supersaturated state does not exist), uranium will likely precipitate as clarkeite, $NaUO_2(O)OH \cdot H_2O$. Clarkeite was observed to precipitate from a DWPF recycle stream sample containing 0.17 M free OH^- (pH 13.2) and 0.5 M Na^+ following addition of excess U(VI).[20] Plutonium solids formed in this sample by the addition of excess plutonium were amorphous and were expected to be tetravalent $Pu(OH)_4$ or $PuO_2 \cdot H_2O$. The formation of plutonium solids can be slow, as colloidal plutonium species are believed to form in solution and slowly agglomerate and precipitate. Uranium and plutonium solubilities in the DWPF Recycle sample were observed to range from 5 to 10 mg U/L and 4 to 7 µg Pu/L over a 250-day time period. Uranium is frequently several orders of magnitude more soluble than plutonium in caustic SRS waste solutions. Due to the higher total amounts and the higher solubility, it is expected that some soluble uranium will be observed in the evaporator (post-filtration) during Diverted Recycle processing. Plutonium may be present in the evaporator at much lower concentrations relative to uranium given both the lower RCT molar concentration and the lower solubility of this actinide in caustic solution (though as discussed above the activity of plutonium is higher than uranium).

In the absence of significant nitrate ion, nitrite is expected to act as a mild reductant, increasing the proportion of tetravalent plutonium and decreasing the total plutonium solubility.[20] The addition of sodium nitrite to the RCT to minimize corrosion will produce a more reducing environment which should promote greater precipitation of tetravalent plutonium. Uranium is not expected to be reduced under these conditions. SRR-E OLI modeling (run M-NO2), which involved the typical sodium nitrite addition and a pH of 10 (producing a total Na^+: 0.21 M) indicated that only 0.08 mol or weight % of the total uranium should be soluble under these conditions.[4] The soluble uranium concentration was predicted to be 9E-08 M (0.02 mg U/L). OLI is not believed to accurately predict plutonium solubility in these solutions, therefore, plutonium species were not included in the SRR-E calculations. Thorium was included in the SRR-E OLI modeling runs (OLI Runs: Baseline, M-NO2, M-MnO4, M-pH-13) and essentially 100% of the thorium was predicted to exist as solid ThO_2 with liquid phase thorium concentrations predicted to be near 5E-08 M.

Actinide solubility tests conducted with other more concentrated waste samples indicated high hydroxide concentrations result in increased actinide solubility.[20] However, literature reviews indicate that the relative amounts of carbonate and hydroxide anions may be the most important waste characteristic determining actinide solubility.[21] Increasing carbonate levels relative to hydroxide can result in significantly higher actinide solubility due to the formation of highly soluble carbonate complexes. In the absence of carbonate ion, as the pH is decreased from 13 to near 9 (range of pH values expected in the RCT), the actinide solubilities may decrease slightly due to the lower hydroxide concentration and decreased formation of soluble actinide hydroxy complexes. However, in the presence of carbonate anion, lower hydroxide is expected to lead to formation of soluble carbonate complexes. Additional solubility tests were conducted with a chemically modified sample of the DWPF recycle solution discussed above at a pH near 13.[20] The total sodium concentration of a sub-sample of recycle solution was increased to near 2 M from the original value of 0.5 M Na^+ by the addition of sodium carbonate. The final carbonate concentration in the chemically modified sample was 0.75 M, versus the free hydroxide concentration of 0.17 M (CO_3^{2-}:OH^- mole ratio of 4.4 versus the original ratio of 0.24 corresponding to 0.044 M CO_3^{2-}). Chemical modification allowed for evaluation of the impacts on uranium and plutonium solubility from increasing the carbonate concentration relative to hydroxide. Analysis of the sample after approximately 150 days of agitation revealed that the uranium and plutonium concentrations for the carbonate-spiked sample were 17 mg U/L and 351 µg Pu/L (0.351 mg/L), respectively. Increased carbonate anion resulted in a 3-fold increase in uranium solubility and an increase in the plutonium concentration of 70 times the initial value. Additional tests with the DWPF sample involving the addition of sodium nitrate revealed that higher solution ionic strength results in slightly lower uranium and plutonium solubilities.[20]

Concurrent analysis of a recent filtered RCT sub-sample revealed the presence of carbonate.[17] It is not expected that the acidic condensate streams entering the RCT would contain carbonate. Analysis of recently collected SMECT and OGCT samples confirmed no measurable carbonate (<20 mg/L Total Inorganic Carbon - TIC).[7] RCT caustic adjustment and sparging using air containing CO_2 is the assumed source of carbonate. Alternatively, the RCT sub-sample analyzed at SRNL could have absorbed CO_2 after collection and prior to analysis. The reaction of dissolved carbon dioxide with hydroxide in a basic solution results in the consumption of 2 moles of OH^- per mole of CO_2 as shown in the equation below.

$$2OH^-_{(aq)} + CO_{2(g)} \rightarrow CO_3^{2-}{}_{(aq)} + H_2O$$

Based on this equation, a 0.1 M NaOH aqueous solution (pH 13) could absorb CO_2 from the air to produce a 0.025 M carbonate solution with a free hydroxide concentration of 0.05 M (pH 12.7). More CO_2 sorption from a 0.1 M OH^- solution to form 0.045 M CO_3^{2-} would result in a free OH^- concentration of 0.01 M (pH 12) and a CO_3^{2-}:OH^- ratio of 4.5 (similar to the condition tested using the DWPF recycle sample with added sodium carbonate[20]). Addition of actinides to this solution would be expected to promote the formation of soluble actinide carbonate complexes. Chemical adjustment of the RCT sample to a lower hydroxide level near pH 9 would result in less CO_2 sorption and carbonate formation. But the ratio of carbonate to hydroxide across the pH range of 9 to 13 following sparging and air contact is likely the most important factor impacting the actinide solubility. Separate leaching studies performed at SRNL indicated that extended exposure of residual waste to the tank air atmosphere can result in the formation of highly soluble uranium carbonate solid phases in SRS High Level Waste.[22] The SRR-E OLI modeling did not include carbonate in the input.[4] Addition of carbonate at a concentration of 0.02 M to the SRNL OLI model discussed in Section 3.1 utilizing the output from SRR-E model run M-NO2 resulted in the predicted formation of soluble uranium carbonate complexes and a 5-fold increase in soluble uranium (total soluble U: 4.4E-07 M). However, the percentage of soluble uranium was only 0.4 mol % of the total U.

Carbonate complexation can greatly enhance actinide solubility, especially for plutonium, although the timescale of actinide dissolution is not known. In order to maintain the actinides in the solid phase and minimize transfer of actinides through the filter, to the evaporator, and ultimately to SWPF, the introduction of carbon dioxide or carbonate into the recycle stream should be avoided and higher pH may be preferred. Given that an air sparge is used in the RCT, these characteristics of actinide chemistry could impact the fates of the actinides in the process. Although the carbonate concentration is not expected to be high relative to the other major anions, CO_2 absorption could result in the formation of soluble actinide carbonate complexes in the RCT. It is possible that the short timescale (hours) of RCT turnover will minimize the formation of soluble carbonate complexes. Alternatively, given the relatively low actinide concentrations present in the RCT, the fraction of the actinides passing through the filter may not be significant to the project. However, if a project goal is to minimize the transfer of actinides through the filter, it is recommended that the impacts of CO_2 sorption from air sparging be evaluated by SRR. Utilization of a sparge system that does not contain CO_2 would remove the impacts of carbonate complex formation on the fate of the actinides, and longer reaction times could be implemented without this concern.

A potential issue regarding plutonium solubility in the DWPF recycle is the kinetics of precipitation from the acidic SMECT and OGCT streams following caustic adjustment. The agglomeration and precipitation of colloidal plutonium hydroxides/oxides following caustic adjustment may be slow, resulting in the persistence of elevated concentrations and apparent plutonium supersaturation in the RCT. Solids have been observed in RCT samples that could serve as nucleation sites to promote plutonium precipitation.[17] Depending on the storage time scale in the RCT, plutonium supersaturation could result in the transfer of plutonium through the crossflow filter to the evaporator and possibly in post-filtration plutonium precipitation downstream. Given the low concentrations of plutonium typically observed in the waste, transfer of significant amounts of plutonium reaching the evaporator into the overheads seems unlikely, unless carbonate complexation results in much higher plutonium concentrations than expected. Longer storage times in the RCT may allow sufficient time for precipitation of colloidal plutonium species such that more complete removal of plutonium in the filter can be accomplished. However, if increased storage time results in the sorption of carbon dioxide and significant increases in the waste carbonate concentration, this could result in higher actinide solubility and transfer of actinides to the evaporator. These chemistry impacts on the actinide speciation in the RCT should be considered by SRR when developing waste processing strategies unless the relatively low actinide levels do not significantly impact processing. Adjustments to the processing strategy may be required if actinides are observed in non-preferred locations.

Utilization of glycolic acid rather than formic acid reductant during DWPF processing is expected to result in some transfer of glycolic acid into the RCT. In caustic high-level waste solutions, glycolic acid can decompose at elevated temperatures producing hydrogen gas as well as formate and oxalate. The decomposition reaction sequence is complex and may require the presence of nitrite and possibly aluminum.[23] These reactions are not expected to occur to a large degree in DWPF including the RCT due to the fact that the sludge is washed to remove residual supernate and aluminum is removed from the sludge by caustic dissolution. Glycolic acid decomposition occurs in the DWPF melter under acidic conditions producing CO_2. Formic acid is currently utilized as a reductant in the process, so formate is currently present in the system, though glycolic acid will soon replace formic acid as the process reductant. Oxalate is in the Sludge Receipt and Adjustment Tank (SRAT) feed from the Tank Farm as well. As a result, glycolate, formate, and oxalate can be present in the RCT due to carryover, decomposition, and volatilization (specifically true for formate due to formic acid volatility) of these materials into the condensate streams.

Other organics and polymeric species in the DWPF process stream which may be present in the RCT are associated with the use of antifoam reagents. The current antifoam (IIT747 or Antifoam 747) utilized in DWPF is a silane polyalkyleneoxide copolymer containing trimethylsiloxane, ether, and alkyl functionalities.[24] Antifoam 747 is known to degrade under the processing conditions to form three decomposition products: trimethylsilanol, hexamethyldisiloxane, and propanal. A new antifoam, Momentive Y-17112, is planned for implementation in DWPF in the near future which does not degrade significantly under the processing conditions upstream of the melter.[25] In the melter, the new antifoam is expected to decompose completely, but some entrainment of antifoam at low levels into the RCT is expected. Momentive Y-17112 has similar structure and functional groups to Antifoam 747. These antifoams and their nongaseous decomposition products will be observed in the RCT. Small amounts of Momentive Y-17112 antifoam are needed to support DWPF processing relative to Antifoam 747, so levels of this material in the recycle stream may be low.

Glycolate, oxalate, formate, and Antifoam 747 and its degradation products are expected to be present at low levels due to entrainment and foam over events and due to volatility of some species in the melter. A recently analyzed SMECT sample contained 60 mg formate/L, while no measurable formate was observed in an OGCT sample. Both the SMECT and OGCT samples contained below detectable levels of oxalate.[7] Glycolate could presumably be entrained into the SMECT at comparable levels to formate during Nitric-Glycolic Acid Flowsheet processing. Uranium glycolate complexes are known.[26,27] Of the various actinide oxidation states, tetravalent actinides such as Pu (IV) generally form the strongest complexes.[28] Glycolate is one of the complexing agents present in Hanford HLW.[29] Some actinide oxalate complexes tend to be insoluble even under acidic conditions.[30] These species could react with dissolved actinides to form metal complexes, impacting the fates of the actinides in the process. In addition, complexes of these anions expected to be present in the DWPF recycle stream with other actinides (thorium, neptunium, americium, and curium) are known.

Gap
Excluding the process impacts of sodium permanganate addition, in order to determine the amounts of the actinides that will pass through the filter under this condition (though expected to be small fractions of the total amounts), optimization of the RCT turnover time and evaluation of the impacts of the air sparge on actinide speciation (specifically the impact on carbonate complex formation) may be necessary. The RCT pH and the kinetics of carbonate complex formation could impact the amounts of soluble actinides passing through the filter.

3.2.2 RCT with NaOH, $NaNO_2$, and $NaMnO_4$ Additions

Current plans for implementation of the Nitric-Glycolic Acid Flowsheet involve the addition of sodium permanganate to the RCT to destroy glycolate. Recent permanganate oxidation testing was conducted on actual SMECT and OGCT samples collected during Nitric-Formic Acid flowsheet processing.[7] Subsamples of these solutions were mixed with simulated RCT heel and actual Slurry Mix Evaporator (SME) product sludge containing glycolate. Oxidant was added at a permanganate to glycolate molar ratio of 5.7, which is greater than the amount stoichiometrically required (ratio of 4) to fully convert the glycolate to oxalate ($C_2O_4^{2-}$) in caustic solution, assuming that permanganate is reduced to form MnO_4^{2-}. In caustic solution, the permanganate will also react with any residual formate. This testing indicates that in the RCT most of the formate should be converted to CO_2, and most of the glycolate should be converted to oxalate. In basic solution, the CO_2 will react to form carbonate anion which could lead to the formation of soluble actinide carbonate complexes.

Addition of permanganate to the RCT to destroy glycolate and glycolate decomposition products, like formate ion, will impact the oxidation states of some actinides. Uranium is expected to be in the hexavalent state and will not react with permanganate. Tetravalent plutonium will be oxidized to more soluble oxidation states such as Pu(V) and Pu(VI). 0.2 M permanganate was reported to increase the solubility of plutonium in highly caustic (10 M NaOH) solution to as high as 1E-02 M Pu over a 33-day time period relative to 10 M NaOH with no added permanganate (Pu solubility <1E-05 M).[31] Plutonium solubility was also observed to increase with a 1.0 M carbonate/bicarbonate solution at pH 9.5 relative to a concentrated caustic solution to concentrations near 4E-03 M Pu. Similar solubility results were observed with these permanganate solutions and neptunium and americium solids co-precipitated with the plutonium, leading to actinide concentrations near 5E-04 M Np and 1E-05 M Am. In the case of americium, slightly higher solubility was observed for the carbonate solution at pH 9.5 relative to the permanganate solution. The permanganate solution was believed to be less effective at dissolving americium due to the oxidation of the americium to the pentavalent oxidation state followed by coprecipitation or sorption to the MnO_2 solids. Higher actinide solubilities might be expected in these studies relative to sludge solids since these tests were performed using a co-precipitate of plutonium, neptunium, and americium solids that did not include the major sludge iron and aluminum phases. Permanganate is also expected to decompose actinide complexes with glycolate or formate.[32] The formation of freshly precipitated manganese dioxide solids from the addition of permanganate will result in the sorption of some actinides to the MnO_2 surface. Permanganate has been utilized in Hanford waste to destroy free complexants and metal organic complexes including glycolate complexes, resulting in MnO_2 precipitation and actinide sorption to the solids.[33,34]

Sorption of the actinides to the manganese solids should result in the capture of the actinides on the filter. However, under the conditions expected in the RCT, the permanganate is expected to be initially reduced to soluble manganate ion, MnO_4^{2-}, with MnO_2 solids being formed on a slower time scale. Most manganese was observed to precipitate from a SMECT sample within three hours following permanganate addition, but most of the manganese remained in solution with an OGCT sample after three hours.[7] After one month, little soluble manganese remained in either sample. The RCT reaction timescale between permanganate addition and filtration is on the order of 4-8 hours. It is expected that some soluble permanganate or manganate will be present in the RCT on this timescale which will be transferred to the evaporator.

In summary, the fates of the actinides in the Diverted Recycle Stream are dependent upon several factors impacting solubility. In general, the addition of hydroxide producing a solution pH ranging from 9 to 13 should primarily result in actinide precipitation, although slow agglomeration of colloidal plutonium particles could result in apparent Pu concentrations exceeding solubility limits. Higher solution ionic strength and high nitrite tend to shift the actinides more toward the solid phase. Significantly overshooting pH 13 in the RCT could lead to the formation of more soluble anionic actinide hydroxy species, though the bulk of the actinides would be in the solid phase. The presence of carbonate (from CO_2 absorption from the air sparge or from formate oxidation) and a high carbonate:hydroxide mole ratio could increase actinide solubility. Permanganate addition could lead to plutonium oxidation and increased solubility, although actinide sorption to freshly precipitated MnO_2 solids may offset this effect, shifting the actinides to the solid phase where they can be removed by filtration. The timescale of reaction and precipitation prior to filtration can impact carbonate formation, plutonium colloid agglomeration, and MnO_2 formation and actinide sorption. Optimization of the process may be necessary, specifically the timescale of reaction in the RCT prior to filtration, although the low levels of actinide concentrations in the RCT may minimize the value of optimization efforts. The bulk of the actinides are expected to be captured by the process filter upstream of the evaporator, presumably resulting in the transfer of these materials to DWPF. Soluble actinides reaching the evaporator are expected to be present at low levels. Based on SRR-E OLI modeling, NAS solids are expected to form at low levels from the Recycle Diversion Waste Stream with the mass formed being dependent upon the amount of aluminum. If these solids form in the RCT they will be removed by filtration. If they do not form until the waste reaches the evaporator at elevated temperature, these solids could result in the sorption and accumulation of actinides in the evaporator scale, as has been observed in other SRR evaporators.[35] No volatile actinide species are expected under the processing conditions, so transfers to the evaporator overhead condensate should only occur by entrainment/boil over events.

Gap
The impact of sodium permanganate addition to the RCT could lead to increased solubilization of plutonium and other actinides due to oxidation. Production of CO_2 from formate/permanganate reaction could also lead to increased formation of actinide carbonate complexes, though RCT air sparging may be the dominant source of CO_2. Destruction of glycolate and formate by permanganate should eliminate soluble metal complexes of these ligands. MnO_2 formation should drive the actinides toward the solid phase. The timescale of reaction and precipitation prior to filtration could impact carbonate formation, plutonium colloid agglomeration, and MnO_2 formation and actinide sorption. Optimization of the process and the RCT turnover time may be necessary given these various impacts.

3.3 Fate of Mercury During DWPF Recycle Diversion

3.3.1 Current state of Hg in DWPF Recycle

DWPF is designed to remove mercury from the sludge. Addition of a chemical reductant (formic acid) to the sludge in the CPC, followed by heating and evaporation, leads to reduction of the mercury species to metallic mercury and its partitioning to the offgas condensate. Some of the mercury does not get stripped and remains in the sludge during this processing, but it is vaporized in the melter and captured in the offgas condensate stream. The system is designed to segregate the metallic mercury in the offgas condensate stream by settling and then send it to the mercury purification cell where it is purified and removed. However, the functionality of the mercury processing cell has always been challenging and it has not been operable for several years and is offline. Currently, the mercury returns to the Tank Farm (Tank 22) along with the offgas condensate stream. It is anticipated that the mercury purification system will return to service prior to diversion of the recycle stream, thereby diverting most (design is 75%) of the mercury away from the filter-evaporator system. Since it is not known exactly how much mercury will be in this stream, it is useful to examine the current chemistry and partitioning.

Most of what is known about the speciation and behavior of mercury in the DWPF Recycle Stream is based on analysis of samples from Tank 22H (which is the current receipt tank in the CSTF from the RCT), including two liquid samples collected in 2015, a liquid sample and sludge core sample collected in 2018, and liquid samples collected from within DWPF. Table 3-1 below shows the range of concentrations of mercury species from the Tank 22H liquid samples (rather than solid core samples) that have been collected and analyzed.[36,37,38]

Table 3-1 Concentrations of Various Mercury Species Observed in SRS Tank 22H Liquid Samples from 2015.

Total Hg (mg/L)[a]	Dissolved Hg (mg/L)[a]	Particulate Hg (mg/L)[a]	Elemental Hg (mg/L)[a]	Inorganic Hg (mg/L)[a]	MeHg (mg/L)[a,b]	DMHg (mg/L)[a,c]	EtHg (mg/L)[a,d]
105-119	97.9-111	0-3.8	3.13-116	56.5-90.4	15.0-31.2	0.00468-0.00679	<DL[e]

[a] all values are in [Hg] concentration
[b] MeHg = methyl mercury
[c] DMHg = dimethyl mercury
[d] EtHg = ethyl mercury
[e] DL = Detection Limit

In Tank 22H, insoluble solids present in the stream will agglomerate and settle, and some species will likely undergo transformation through reactions. The above information may not be representative of the freshly produced Recycle stream. The recycle in Tank 22H has also been mixed with a significant amount of sodium nitrite and sodium hydroxide to remain compliant with corrosion control limits, which changed the stream from the original composition.

A sludge core and accompanying supernate sample from Tank 22H were collected in 2018 and analyzed.[39] The supernate sample contained 114 mg/L of total Hg including 21 mg/L of methyl mercury (MeHg, expressed as Hg in this report). Note that these concentrations are within the range of those measured in the 2015 samples shown above. Elemental analysis of the core sample from Tank 22H indicated 42.5 wt% total solids, including 5.12 wt% Hg. The X-ray diffraction analysis indicated the presence of mercury mineral phases montroydite (HgO) and mosesite ($Hg_2NCl{\cdot}H_2O$). (Note that metallic mercury, if present, would not be observable in X-ray analysis because it is not crystalline.)

Samples collected within DWPF have included the SMECT, OGCT, and RCT tanks.[40] The SMECT contains predominantly elemental and ionic mercury, with lower amounts of methylmercury. Ionic mercury is defined as Hg(I) or Hg(II), which could be present in the waste as a mixture of neutral and ionic species, such as HgO, $Hg(OH)_2$, and $Hg(OH)_3^-$ or other ion pair species. OGCT samples contained some elemental mercury, but two of the three samples were overwhelmingly ionic mercury. Samples from the RCT were widely varying, with mostly elemental and ionic mercury, but larger amounts of methyl mercury have been observed in some samples.

Previous analyses indicate that there is minimal dimethylmercury (DMM) present in the recycle stream.

Gap
The speciation of mercury, particularly as suspended particulates of metallic mercury or as freshly precipitated mercuric oxide, can impact the downstream filter performance. Similarly, the dissolved metallic mercury would be expected to pass through the filter, and thus is important to the predicted partitioning of metallic mercury to the evaporator condensate. The current composition of the mercury species in the DWPF Recycle stream has been analyzed, but none without the nitrite and caustic additions that are performed in the RCT. The current program includes sampling and mercury speciation analysis of samples from the SMECT, OGCT, and RCT. The results from these analyses should provide more information on the makeup of mercury species in the tanks. Analysis of additional samples will likely be needed, particularly to examine the variability in this stream. It is not known if changes occur to the samples during storage, so it is imperative that the time between sample collection and transport to SRNL

is minimized. Once the results from the first set of samples are available, further refinement of the data needs can be developed.

3.3.2 Speciation changes due to glycolic acid/new antifoam

The upcoming change in the DWPF flowsheet to incorporate the glycolic acid as reductant and a new antifoam may alter the distribution of mercury species in the recycle stream to some degree. However, SRNL testing indicates that mercury is reduced with the Nitric-Glycolic Acid flowsheet, allowing it to be stripped during SRAT and SME processing into the condensate at about the same efficiency as for the Nitric-Formic flowsheet.[41,42] Laboratory testing is underway at this time that may provide additional information on the mercury speciation in the Nitric-Glycolic Acid flowsheet. However, a comparable experiment with the formic acid process using the baseline antifoam has not been performed, so a basis for comparison is not available. Further, the specific reaction chemistry that produces the various mercury species has not been determined.

Gap
The specific conditions that produce the range of mercury species in DWPF are not known in detail. Although laboratory testing can provide some insight into the possible products, differences in DWPF processing, waste batch composition, boil-up time, etc. are variable. Laboratory testing with simulants is underway at this time that examines mercury speciation for a series of test conditions in preparation for DWPF Sludge Batch 10 processing. An upcoming test is also planned with actual Sludge Batch 10 waste, and mercury speciation analyses will be performed on the products. Once those results are available, it is advisable to determine if additional testing is needed to examine other conditions to determine the distribution of mercury species in the products. Testing should determine where metallic mercury, MeHg, and ionic mercury are produced and at what point they are produced in the process cycle, along with determining the contributing factors that influence production. This knowledge would permit optimization of metallic mercury production and removal in DWPF. Testing to date indicates that the change to the Nitric-Glycolic Acid flowsheet is not too impactful to the bulk mercury speciation.

3.3.3 Glycolate Destruction

A separate process has been developed to destroy excess glycolate ion in the RCT, so that this chemical does not get introduced to the Tank Farms. The selected process uses sodium permanganate under alkaline conditions.

Testing was performed when the glycolate destruction process was first developed. The conditions included pH 13, 1440 mg/L of MeHg, and a 150% excess of permanganate (vs. the glycolate concentration). It was shown that permanganate did not react with methyl mercury.[43]

Another test was performed on the effectiveness of permanganate oxidation to destroy glycolate in a sample from the SMECT.[7] Analysis of the initial sample from the SMECT revealed that the methylmercury concentration was below the detection limit, so no information from that test is available on whether there is a reaction between methylmercury and permanganate. The test result did indicate that the soluble concentration of mercury did not change appreciably within a few hours but had decreased after one month. Whether the permanganate caused this decrease or whether it would have happened without permanganate was not tested. There are a few possible explanations for the decreased solubility that do not involve reaction between mercury species and permanganate. One possibility is that as permanganate is reduced by other species and forms insoluble manganese species that it would co-precipitate any marginally soluble mercury species, similar to how flocculants aid in heavy metal removal in water treatment plants.

Although the experiments indicate no reaction under the conditions tested, it is speculated that if permanganate ion were to react with mercury species, it is likely to cause oxidation. This could happen in the evaporator, for example, where the solution temperature is higher. Presumably, if reaction with permanganate occurred, methyl mercury would be expected to produce Hg(II) ion in solution, which would either remain soluble or react with sodium hydroxide to form HgO. If metallic mercury reacts, it would be expected to convert to Hg(I) or Hg(II), and likewise remain soluble or form HgO. Any Hg(I) would convert to Hg(II), and Hg(II) would be unchanged.

Gap
There are no reactions with permanganate expected that could impact the distribution of mercury species in this stream and adversely impact the amount of mercury in the evaporator off gas such that it would cause it to exceed the ETP Waste Acceptance Criteria (WAC).[44] Any reactions would be expected to decrease mercury volatility rather than increase it.

3.3.4 Transfers

It is evident that metallic mercury remains in the recycle stream. It is likely that some of this metallic mercury would coagulate and settle in stagnant areas of the equipment. The density of metallic Hg is 13.53 g/cm^3 compared to iron(III) oxide at 5.24 g/cm^3, so mercury will settle much faster and will be more difficult to suspend than sludge. Similarly, over time the dissolved ionic mercury probably converts to HgO, which has a density of 11.14 g/cm^3, so this phase will also tend to settle faster than sludge. The design of the new Diverted Recycle system should accommodate retrieval of settled metallic mercury and mercury oxide to avoid its long-term accumulation in the facility. Alternatively, design of the process could take advantage of this fast settling behavior to remove it from the bulk of the aqueous stream.

Gap
Design of the transfer system, tanks, and pumps will need to include the ability to homogenize and transfer the dense mercury species. At this time, there is insufficient information known about the equipment to determine if additional testing is needed.

3.3.5 Effect of pH

As the pH is adjusted in the RCT, the partitioning of some mercury species will change. The dissolved mercury that is present in the Recycle stream as Hg(II) ion in solution would be expected to quickly react with sodium hydroxide to form mercuric oxide, HgO, according to the reaction below (where “X” is any monovalent anion):

$$HgX_2 + 2NaOH \rightarrow HgO + 2NaX + H_2O$$

Some of this mercuric oxide would precipitate, as was observed in the Tank 22H core sample analysis.[40] If some of the dissolved mercury in the Recycle stream is present as Hg(I) ion, such as the chloride or iodide salt, it likely reacts with sodium hydroxide to disproportionate into Hg(0) and Hg(II) according to the reaction below (X is the halide anion):

$$Hg_2X_2 + 2NaOH \rightarrow Hg(0) + HgO + 2NaX + H_2O$$

Metallic mercury will likely tend to agglomerate and settle. If the new Diverted Recycle system targets a lower pH than the current value of ~13, this may have an impact on partitioning of elemental mercury. However, if the pH target is 9 or above, it is not expected to be dramatically different from current behavior. In alkaline conditions and with sufficient nitrate present, the elemental mercury can be slowly oxidized and converted to the oxide,[40] according to the reaction below:

$Hg(0) + NaNO_3 \rightarrow HgO + NaNO_2$

The kinetics of this reaction in tank waste conditions are not known. The mercury oxide can either remain dissolved, react with hydroxide to convert to soluble $Hg(OH)_3^-$, or precipitate, depending on the pH, temperature, and ionic strength.

A change in pH would not change the Hg^0 vapor pressure, but if the elemental mercury transforms to another species in the evaporator, the magnitude of that transformation could change with a change in pH. Further, since pH effects the reduction-oxidation potential of mercury species, a change to the pH could change their reactivity in the evaporator. A Pourbaix diagram[c] was generated using the OLI Studio v10 software package. A simple waste formulation was used in the OLI Systems Studio (v10) software to generate the diagram shown below. This formulation (shown in the Appendix) was based on the actual Tank 22H composition reported by Oji.[39] A small amount (1E-3 M) of mercury oxide was added to the formulation, and the Reduction-Oxidation (REDOX) function in OLI was turned on. The temperature parameter in the calculation was set to 25 ºC. Air was also included in the model, and the titrants were nitric acid and sodium hydroxide. Results indicate that above a pH of ~8 in a slightly oxidizing condition, the mercury is present predominantly as insoluble mercuric oxide. In general, at the same potential, a lower pH would decrease the tendency to form mercury oxide versus mercury metal. Formation of soluble ionic species does not occur until reaching acidic conditions.

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[c] Pourbaix diagrams plot electrochemical stability for different oxidation states of an element as a function of pH. These diagrams are essentially phase diagrams that map the conditions of potential and pH where different oxidation states and species are stable.

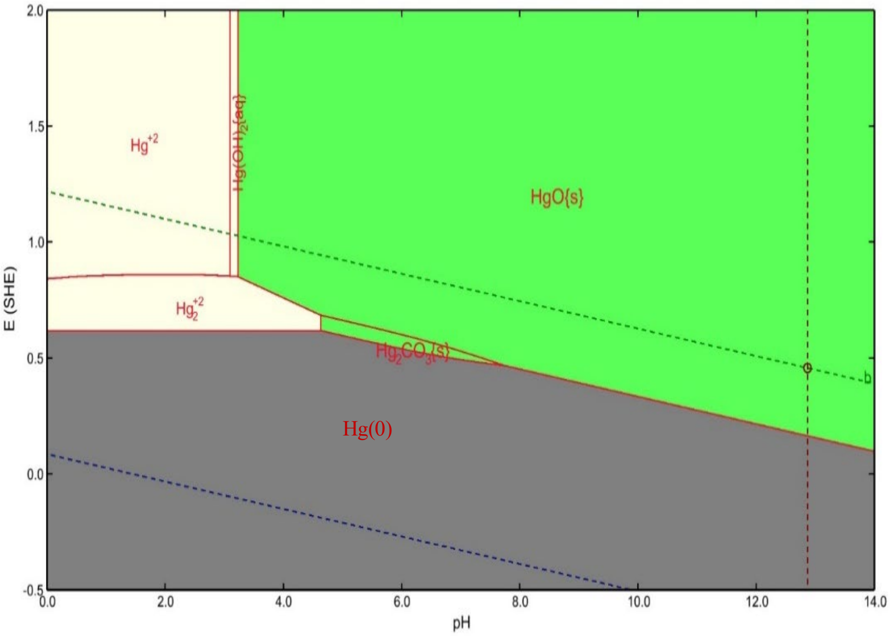

Figure 3-1 OLI-Generated Pourbaix Diagram for Mercury Species in SRS Tank 22H Simulant.

The dissolved mercury that is present as MeHg ion would not be expected to react appreciably as it is dissolved in the caustic waste. Analyses of tank samples, such as Tank 22H or Tank 50, indicate MeHg is relatively stable in caustic solution. Lowering the pH to 9 is not expected to impact the stability of MeHg. If there is any DMHg present, it is not expected to be impacted by a change in pH within the range of 9-13.

Gap
The effect of lowering the pH to 9 is not expected to have a significant impact on the speciation of mercury that could impact the evaporator condensate concentrations such that they would impact the ETP WAC,[44] but this expectation has not been verified. Upcoming testing of the evaporation of simulants and actual waste are expected to be performed near the baseline condition of pH 13, and the scope includes mercury speciation. The simulant testing should include a formulation that includes a distribution of mercury species that is comparable to that in the actual waste samples. If a lower pH target is selected for the Diverted Recycle stream, testing at a lower pH is recommended.

3.3.6 Filtration

The crossflow filter is expected to remove any insoluble mercury species, primarily HgO and elemental Hg(0), to its solubility limit. The solubility limit of the metallic mercury species in tank waste has not been explicitly determined. Tanks 43H and 38H (2H Evaporator feed and drop tanks, respectively) were measured to contain 1-4 mg/L of metallic mercury,[37] and another report indicated 12.5 and 55.5 mg/L metallic mercury in Tank 38H.[36] A Tank 22H sample was measured to contain 116 mg/L metallic mercury.[37] Analysis of another Tank 22H sample indicated 3.1 and 9.6 mg/L metallic mercury.[36] The wide range of analysis results in tank waste grab samples may be caused by several factors, primarily that there may not be sufficient metallic mercury in the tanks to fully saturate the solution, and metallic mercury would settle rapidly, making the collection of representative samples challenging. The data is therefore not available to indicate the maximum amount that could be present in the filtrate. Regardless, the filter should remove any insoluble portion, sending the soluble portion to the evaporator. It is not known how the filter will perform if presented with metallic mercury particles. It is known that similar crossflow filters will reject suspended organic species,[45] and there was no impact of the separate organic phase on filter flow rate for a metal hydroxide slurry. It is expected that the filter will also reject particles of metallic mercury; but whether these particles will plug pores in the filter is unknown. Presumably, particles of metallic mercury should be swept along with the filter reject stream and would not penetrate the pores. Any metallic mercury that does enter the pores would be expected to be deformable such that it would plug the pores, but whether this happens or is appreciably different from fouling due to metal hydroxide precipitates is unknown. Likewise, the impact of the presence of particles of mercury mixed with the precipitated solids that form a filter cake is unknown.

The filter should remove insoluble Hg(0) and ionic mercury to their level of solubility, and the filtrate will contain the soluble neutral species and any ionic species. These species would be expected to exhibit filter behavior comparable to other metal oxides and hydroxides, where the solids are rejected by the filter. Mercury oxide/hydroxide species are not expected to exhibit unique filter performance behavior that is significantly different from other metal oxides/hydroxides.

Chemical cleaning of the filter should likewise be as effective with mercury oxide species as other metal oxide species. Theoretically, it is possible that the mercury(II) oxide or hydroxide could be reduced to mercurous ion (Hg(I)) during chemical cleaning of the filter if oxalic acid is used. It is not expected that oxalic acid will reduce the ionic mercury species to metallic mercury. This reaction was tested during the search for an alternate reductant for DWPF, and no metallic mercury was produced under those conditions.[46] Even if reduction to metallic mercury did happen, there are currently no known impacts to the overall process or fate from this change in mercury oxidation state. It should be noted, however, that mercury(II) oxalate is a shock sensitive compound; although whether it would form and produce a separable quantity of material during chemical cleaning is uncertain. If nitric acid is used as the filter cleaning agent, it is expected that the mercury oxide and hydroxides would partially dissolve and be removed from the filter. Metallic mercury would also slowly react with nitric acid and be removed from the filter; with the rate depending on surface area, temperature, and acid concentration.

If aqueous DMHg is present, it is expected to pass through the filter unhindered, up to its solubility limit.

Gap
Although it has not been explicitly tested, it is not expected that the presence of mercury oxide/hydroxide species will have an unusual impact on the filter performance. Actual waste testing has been performed with slurries that presumably would have contained mercury oxide/hydroxide species, as well as years of operation of the crossflow filter in the Actinide Removal Process (ARP) at SRS. There are no known specific issues with these mercury species. Alternatively, the presence of metallic mercury has not been tested, and no known data exists. Upcoming testing with simulants should include a formulation that includes the range of mercury species, although production of a simulant containing a representative form of insoluble metallic mercury droplets is challenging. Actual waste testing should address the challenge of representativeness of a simulant. Similarly, collection of the actual waste for testing needs to account for the presence of mercury to ensure that the sample is representative of the stream. Speciation analyses of both simulant and actual waste are needed to examine fate and transformation of the mercury species during filtration and chemical cleaning.

3.3.7 Evaporation

The conceptual behavior and transformation of mercury species during evaporation was discussed in a previous report.[37] The partitioning of the various species is expected to remain the same in the new Recycle evaporator, whether it is operated at atmospheric pressure or under vacuum. Since it is not understood exactly how much or which mercury species vaporize in the evaporator versus chemical transformation, it is not currently possible to quantify any expected changes. However, if the evaporator is operated under vacuum, it is expected that there would be less transformation of the mercury species because the temperature would be lower, which should slow the kinetics of any reactions. General trends from the previous work indicate that: 1) the elemental mercury is expected to partition predominantly to the condensate and collect in the Mercury Removal Tank; 2) dissolved ionic mercury species, Hg(I), Hg(II), and MeHg are expected to predominantly partition to the evaporator bottoms; 3) if any DMHg is present, it would be expected to partition to the vapor phase, where it may condense or more likely will pass to the off gas system; and 4) any mercury oxide-containing particulates will either be transferred out with the evaporator bottoms or accumulate within the evaporator. (Note: No particulates of any kind should be present because of the filtration prior to evaporation unless they unexpectedly form in the evaporator. The evaporator should be designed with the capability to remove dense mercury phases or other solids.). Data collected from analysis of actual waste samples match these general expectations, but each species does not partition exclusively to one stream or the other. Further, similar to the previous analysis,[47] little to no measurable DMHg is expected to be present in the Recycle stream to the new Recycle evaporator unless the new antifoam/glycolic flowsheet produces significantly more. There is currently no indication that DMHg is formed under these flowsheet conditions.[25]

As data in previous reports show,[37] evaporation of the Tank 22H waste will cause varying amounts of elemental mercury to partition to the condensate. The elemental mercury content in the Tank 22H waste, and Tank 43H waste (which contained material from Tank 22H) was ~1-3 mg/L. The condensate from the SRS 2H evaporator contained ~2% of the elemental mercury concentration (~0.06 mg/L), and the drop tank, Tank 38, contained 3-4 mg/L. This may be an accurate indication of the amount of mercury that vaporizes but may also be an underestimate of mercury vaporization to the condensate because the evaporator has a mercury collection system and the elemental mercury may have settled prior to sampling the condensate. It is expected that the new Recycle evaporator system will also partition elemental mercury to the condensate to a comparable degree, regardless if it operates at atmospheric or reduced pressure, and that a collection system will be needed as well to prevent exceeding the ETP WAC limit.[44] Most of the mercury is expected to partition to the evaporator bottoms. Analysis of samples from tank 43H, which is the 2H evaporator feed tank, contained 217-241 mg/L of total soluble mercury[48]. Samples from tank 38H, which is the drop tank for the 2H evaporator, were concentrated, containing 340-374 mg/L of total mercury.[48] The mercury was not speciated in these samples, but the total was concentrated by about the same ratio as the sodium ion was during the evaporation. Some fraction of this mercury is expected to partition to the condensate, but samples were not collected for analysis.

The SRS 3H evaporator system was observed to collect a large amount of insoluble metallic mercury in its mercury removal tank while waste that had originated in Tank 22H was being evaporated.[37] In 2015, slurry from Tank 22H was transferred into Tank 51, and the washing decant solutions were transferred to Tank 32, where they fed the 3H evaporator. As much as 6 L of metallic mercury was collected from the condensate in two days of this campaign. The monthly total of mercury collected from the 3H evaporator in 2015 varied from 0.15 to 7.4 L. This further illustrates that it is expected that the new DWPF Recycle evaporator will collect a significant amount of insoluble mercury in the condensate. Analysis results from the 3H evaporator system operations also indicate that there is very little soluble elemental mercury in condensate samples. Methyl mercury was also measured in the 3H condensate samples (~1-1.5 mg/L), although the amount of methyl mercury in the feed to the evaporator was lower than the 2H system.

It is also observed that ~3% of the MeHg in the Tank 43H feed to the 2H evaporator partitions to the condensate. Partitioning of MeHg to the condensate is not understood, but is evidently not entirely due to either entrainment or to its vapor pressure as a salt.[37] There may be a vapor-phase or condensate-phase reaction that occurs to produce MeHg under these conditions. It is also expected that this behavior would continue with the new Recycle evaporator, although if there is a reaction that occurs to produce MeHg, it is expected to occur at a lower rate if a vacuum evaporator is used because of the lower temperature. Secondly, if the pH is lowered beneath the current target of ~13, it is not known how this would impact partitioning of MeHg. A lower pH would also involve a lower ionic strength in the recycle stream (because of less caustic and possibly less sodium nitrite addition), which causes the boil-down ratio to change versus current conditions, and will lead to a larger quantity of MeHg partitioning to the condensate. Greater MeHg in the condensate in this case will be offset somewhat by the larger relative quantity of condensate produced.

Although the feed to the 3H evaporator is not directly from Tank 22H, it is useful to examine the partitioning of mercury species there as well.[37] After evaporation of feed containing ~1-4 mg/L of elemental mercury, only trace amounts of elemental mercury are present in the aqueous phase of the condensate, which, again, may be due to its settling in the mercury recovery system in the evaporator, causing its absence from the aqueous samples. Also, similar behavior, but at a higher ratio relative to elemental mercury, is the partitioning of MeHg, although the fraction of MeHg in the condensate is approximately 20% of the (much lower) feed concentration.

It was previously determined that the antifoam used in the SRS evaporators (Dow Corning H-10) was producing organomercury compounds.[37] Antifoam use in the evaporators ceased when this phenomenon was discovered, and it appears to have been effective in lowering the organomercury production. It is advisable that the new evaporator avoid addition of an antifoam that could contribute to organomercury formation.

Gap
Although it has not been explicitly tested, it is not expected that the presence of mercury oxide/hydroxide species will have an unusual impact on the evaporator performance. Actual waste testing has been performed with supernates that contained mercury oxide/hydroxide species, as well as years of operation of the Tank Farm evaporators at SRS. There are no known specific issues with these mercury species. Alternatively, data on behavior of metallic mercury in an alkaline tank waste evaporator exists, as cited above. Upcoming testing with simulants should include a formulation that includes the range of mercury species, although production of a simulant containing a representative form of dissolved metallic mercury is challenging. Actual waste testing should somewhat address the challenge of representativeness of a simulant. Speciation analyses during both simulant and actual waste tests are needed to examine the fate and transformation of the mercury species during evaporation.

3.4 Fate of Iodine During DWPF Recycle Diversion

3.4.1 Current state of iodine in DWPF Recycle

The WAC limit for ^{129}I at the SRS ETP is 1 dpm/mL (4.5E-10 Ci/L)[39]. The current tank farm evaporator condensates routinely meet this criterion when evaporating the alkaline tank waste. Limited information is known about the speciation and behavior of iodine in the DWPF Recycle Stream. Samples of DWPF sludge slurry feed batches are analyzed for ^{129}I as part of the Waste Acceptance Product Specification (WAPS) for glass disposal. Results for the last four sludge batches are shown in the Table 3-2.

Table 3-2. Previous Sludge Batch Analyses for ^{129}I.

Sludge Batch	^{129}I (Ci/gallon)	^{129}I (Ci/L)	Reference
7a	1.2E-06	3.2E-07	Table 4-1, Reboul et al., SRNL-STI-2011-00720[49]
7b	6.6E-07	1.7E-07	Table 3-1, Crawford et al., SRNL-STI-2012-00294[50]
8	1.5E-06	4.0E-07	Table 3-1, Bannochie et al., SRNL-STI-2014-00179[51]
9	2.5E-06	6.7E-07	Table 3-1, Trivelpiece et al., SRNL-STI-2018-00680[52]

The speciation of the insoluble iodine has not been determined, but it is known that the sludge samples contain some amount of silver.[53] The last few batches of sludge contained ~0.01 wt% silver, which would presumably be sufficient to form precipitates with iodine.

During testing of an evaporator under acidic conditions, analysis of a blend of slurry samples from OGCT and SMECT indicated 7.4 dpm/mL (3.3E-09 Ci/L) of ^{129}I.[54] The slurry being fed to the melter at that time was several years prior to those shown in the table above, and the concentration of ^{129}I in the feed slurry at that time was below detection.

An analysis of a sample from Tank 22H (which is the current receipt tank for this stream) indicated <1.09E-09 Ci/L of ^{129}I.[55] (Note that the limit of detection for the Tank 22H sample was above the ETP WAC limit but 2 orders of magnitude below the concentrations in the DWPF feed.) This seems to indicate that the ^{129}I is either in the glass, in the settled sludge layer in Tank 22H, or is retained somewhere in the DWPF system. It is known that 90% of the ^{129}I in the sludge is not retained in the glass, presumably because of its high volatility at melter temperatures.[56] The majority of the ^{129}I is expected to be scrubbed from the melter off gas, along with water, and be collected in the OGCT. It is also evident that iodine is partially stripped from the slurry during evaporation under acidic conditions in the CPC before reaching the melter. In either case, the iodine is vaporized during processing or melting and collects in the condensate streams.[57] Previous data indicates 3.7E-09 to 1.2E-07 Ci/L is present in OGCT, RCT, and SMECT samples during processing of Sludge Batch 8, so it appears that it becomes insoluble and settles in Tank 22H.

The vapor phase iodine is expected to be present as iodine monochloride (ICl), hypoiodous acid (HIO), or diatomic iodine (I_2). These species were calculated to be present in the off gas from the Hanford Low Activity Waste melter.[58] As these species are scrubbed from the off-gas stream, they will dissolve in the condensates and collect in the RCT. The caustic conditions of the RCT will cause any of these species to convert to a mixture of iodide (I^-) and iodate (IO_3^-) ions.[59,60] Computer modeling was done to show that these are the only species present in a similar stream when the pH exceeds 6 in a fully aerated system[58], although a higher pH was needed if a lower oxygen content was present. Once the iodine is in the alkaline solution, it is speculated that the ^{129}I precipitates and settles in Tank 22H, which would explain why it is not present in the supernate. This speculation is akin to the observation that there is insoluble ^{129}I in the incoming slurry to DWPF. The mechanism for that precipitation, if it occurs, is not known.

From concurrent RCT sample characterization, ^{129}I is predominately insoluble in the current RCT recycle stream, which is in agreement with the above statements.[17]

Gap
The iodine behavior in DWPF off-gas condensates is not well understood. The upcoming measurements of ^{129}I distribution during characterization of SMECT and OGCT samples are expected to provide information on the concentration and solubility of these species.

3.4.2 Speciation changes due to glycolic acid/new antifoam

Although considered unlikely, the upcoming changes in the DWPF flowsheet to incorporate the glycolic acid as reductant and a new antifoam may alter the distribution of iodine species in the recycle stream. At this time, it is not possible to know specifics about how these changes will impact the distribution of iodine speciation. Currently, the iodine probably either strips to the SMECT during acidic boiling in the SME, or strips from the melter and partitions to the OGCT. Either way, the changes to glycolic acid and the new antifoam are not known to have an impact on iodine speciation or behavior.

Gap
The iodine speciation and specific conditions of partitioning in the off-gas condensates are not well understood. It would be useful to measure the ^{129}I distribution during testing of sludge processing during sludge batch qualification testing in the Shielded Cells using the Nitric-Glycolic Acid Flowsheet.

3.4.3 Glycolate Destruction

Largely due to flammability concerns, a separate process has been developed to destroy excess glycolate ion in the RCT so that this chemical does not get introduced to the Tank Farms. The selected process uses excess sodium permanganate under alkaline conditions. Depending on the initial speciation of iodine, it could be oxidized by permanganate to volatile I_2, but more likely would be completely oxidized to non-volatile IO_3^- in the alkaline conditions.[61]

Gap
The speciation of iodine in the RCT stream is not known, and it is not known if it reacts with permanganate. It is not expected to form a volatile species in alkaline solution. When testing of the glycolate destruction process is performed, the ^{129}I should be analyzed to determine if it remains soluble or if it vaporizes or precipitates.

3.4.4 Transfers

The ^{129}I is expected to remain soluble or precipitate along with other solids in the recycle stream. There is no known mechanism for it to partition to a separate phase or to vaporize during transfers.

Gap
No gaps are identified for ^{129}I behavior during transfers.

3.4.5 Effect of pH

At acidic pH, iodine would be expected to be present as I_2 or HIO. As the pH is adjusted to >9 in the RCT, the partitioning of some iodine species will change. The dissolved iodine that is present in the recycle stream would be expected to quickly react with dissolved oxygen to form a mixture of iodide (I^-) and iodate ion (IO_3^-). This expectation is based on earlier computer modeling using OLI Systems software that examined a comparable melter off-gas stream.[58] Modeling indicates that oxygen played a key role in the REDOX condition and thus the speciation of iodine, although other oxidizers such as nitrate ion may also play a role in this DWPF Recycle Stream as well.

A simple waste formulation was used in the OLI Systems Studio (v10) software to generate the diagram shown in Figure 3-2. This waste formulation (shown in the Appendix A, Table A-1) was based on the Tank 22H composition.[62] A small amount (1E-04 M) of potassium iodide and iodine (1E-04 M) was added to the formulation, and the REDOX function was turned on. The calculation was performed at 25° C. Air was also included in the model, and the titrants were nitric acid and sodium hydroxide. Results indicate that above pH ~3, the iodine is present entirely as the iodate ion (IO_3^-). Below pH 2, the iodine is present as hypoiodous acid. Inspection of the data shows that oxygen is key to generating iodate from iodide ion, as expected.

To show more detail, the Tank 22H composition was used to generate a Pourbaix diagram from OLI Systems Studio v.10 software. The titrants were sodium hydroxide and hydrochloric acid, and the titration was performed at 25 ºC. That diagram is shown below in Figure 3-3, and indicates that above pH ~6, no volatile I_2 would be present.

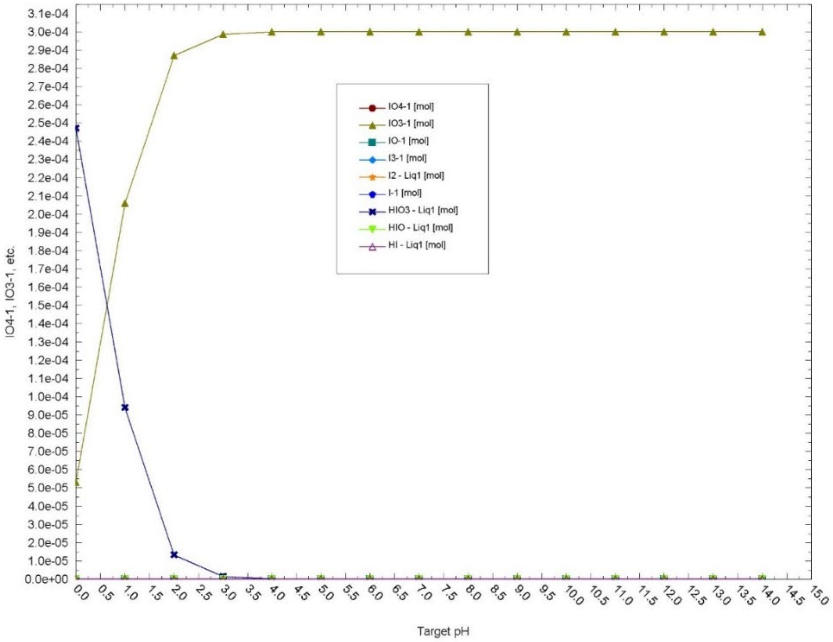

Figure 3-2. OLI Modeling Output of Tank 22H Simulant with Iodine Added as KI and I_2.

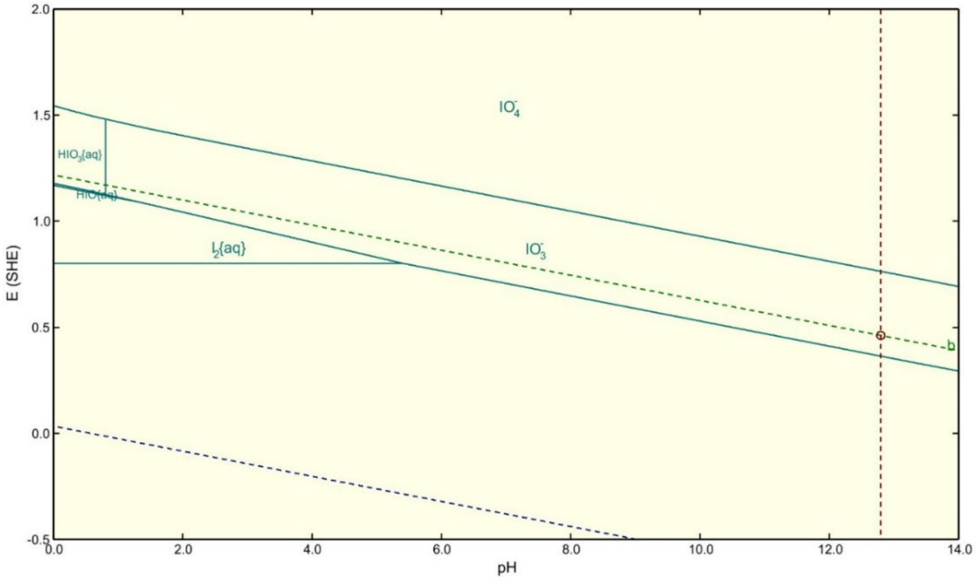

Figure 3-3 OLI-Generated Pourbaix Diagram for Tank 22H Simulant with Iodine Added as KI and I_2.

Gap
The effect of lowering the pH from the present value of ~13 to 9 is not expected to have a significant impact on the speciation of iodine, as long as the stream is fully aerated. According to the modeling of another stream, the oxygen will convert any volatile iodine (I_2) to non-volatile iodide and iodate ions. Preliminary modeling shown above indicates iodate is present at ambient temperature. Confirmatory modeling should be performed on the expected stream compositions and variable conditions to verify a similar outcome for the DWPF Recycle Stream. After pH adjustment of the OGCT and SMECT samples, the distribution of ^{129}I in the liquid and solids should be analyzed.

3.4.6 Filtration

If, as speculated above, the iodine in the DWPF Recycle Stream precipitates as a solid, the new crossflow filter is expected to remove any insoluble iodine species to its solubility limit. The solubility limit of any insoluble iodine species in waste has not been explicitly determined. Theoretically, the iodine could precipitate with heavy metals present in the waste stream, such as silver or mercury.

Gap
Testing of the filtration system should include analysis of the ^{129}I to determine its partitioning. The acid cleaning solution should also be analyzed to determine if ^{129}I is present.

3.4.7 Evaporation

Testing of evaporation of a melter off-gas condensate simulant for a Hanford process has been performed previously. Tests at Vitreous State Laboratory (VSL) indicated that condensates from a Submerged Bed Scrubber (SBS) and Wet Electrostatic Precipitator (WESP) were typically found to be slightly acidic pH (6-7).[63] Although the actual Waste Treatment and Immobilization Plant (WTP) plant will raise the pH of this stream prior to evaporation, the condensate from the simulant at VSL was evaporated without pH adjustment. At the conclusion of that test, it was observed that there was significant iodine in the evaporator condensate.

The VSL testing of the melter had added potassium iodide to the feed, but their results indicated that the iodine species in the liquid tank waste simulant are converted to molecular iodine (I_2) in the melter. This was based on an observation that iodine was found in an alkaline impinger off-gas sample but not on a preceding particle filter or in an acidic impinger. When the mildly acidic aqueous SBS/WESP condensate was evaporated, significant fractions of the iodine and organic species were found in the evaporator condensate – over 20% of the overall amount fed to the melter. Subsequent modeling by SRNL showed that at mildly acidic pH, some of the iodine is present as volatile molecular iodine (I_2). However, an aerated system at alkaline pH should convert to iodide and iodate. Testing by SRNL demonstrated that pH adjustment to 11.5-12, followed by evaporation, resulted in no measurable iodine in the evaporator condensate.[58]

Gap
Computer modeling indicates that adjustment of a comparable stream to slightly alkaline pH will result in minimal formation of volatile I_2. Similar modeling should be performed for the DWPF Recycle Stream and the various compositions expected. Testing of the evaporation should include simulants spiked with iodine, and effluent streams should be measured for iodine partitioning. Similarly, the radioactive testing should include analysis of ^{129}I in the feed, concentrate, and condensate to ensure the partitioning is determined. Detection levels of ^{129}I in the condensate should be lower than the ETP WAC of 1 dpm/mL for ^{129}I.[39]

3.5 Additional Comments on the Fate of Silicon During DWPF Recycle Diversion

Although SRR-E did not request an evaluation of the fate of silicon, some aspects of the impacts of silicon on the Recycle Diversion process and on the CSTF are discussed below.

Currently, due to criticality concerns associated with aluminosilicate scale formation, SRR controls the concentration of silicon in streams sent to evaporators associated with sludge batch preparation. The Recycle Diversion process proposes sending high silicon DWPF recycle to sludge batch preparation tanks via the crossflow filtration solids. The impacts of this silicon source on DWPF operations and controls should be considered by SRR-E. The soluble silicon concentration predicted by OLI for the baseline RCT case was 0.009 M, which corresponds to 53% of the total silicon in the RCT (remainder being insoluble). This soluble silicon would be a source for aluminosilicate solids formation, however based on the OLI prediction, 98% of the aluminum should be insoluble and therefore unavailable to form NAS solids. As mentioned previously in Section 3.1, it is expected that much less silicon will be dissolved on the RCT timescale than was predicted by OLI. Whether the SiO_2 dissolves or forms aluminosilicate solids, either of these solids would be removed by the filter. The solids speciation may matter during operations however, if significant soluble silicon and aluminum somehow reach the evaporator. This scenario may result in a tendency to form NAS scale formation in the evaporator.

Gap
If SiO_2 from the frit does not fully dissolve in the RCT (as expected due to the processing timescale), and the aluminum in the RCT does not precipitate as NAS due to reaction with the silicon prior to filtration, and the aluminum and silicon precipitate in the evaporator due to the elevated temperature, then NAS scale formation may be observed in the evaporator. This could impact evaporator operations and result in accumulation of actinides.

4.0 Recommendations and Conclusions

Identification and evaluation of the factors influencing the fates of alkali metals, actinides, mercury, and iodine have been conducted. Information gaps have been identified which are summarized and discussed in Table 4-1 below for each subsection in Section 3 above. Recommendations for addressing the gaps are also provided.

Table 4-1. Summary of Gaps and Recommendations.

Chemical	Gaps/Comments	Recommendations
alkali metals	none; behavior understood; primary fate: Evaporator Pot and SWPF; gradual accumulation of sodium containing solids (NAS) could impact evaporator operations (Section 3.1)	None.
actinides without permanganate addition	process optimization is needed for minimizing soluble actinide fraction passing filter; liquid concentration could vary considerably though soluble fraction is small percentage of total; primary fate: filter and DWPF; (Section 3.2.1) Note: Sorption of actinides to NAS scale in the evaporator is addressed below.	The project should determine the impact of soluble actinides considering the relatively low amounts, low soluble fractions, and low volatilities. If optimization is needed, testing could determine optimum RCT turnover/filtration time scale or preferred conditions (such as target pH, minimal air sparge or alternative sparge gas). RCT sample analysis after changes to the Nitric-Glycolic Acid flowsheet or alternative antifoam implementation should determine actual amounts of glycolate, antifoam, and degradation products due to the possible formation of actinide complexes and the potential impact on the fate of the actinides.

actinides with permanganate addition	process optimization is needed for minimizing soluble actinide fraction passing filter; permanganate oxidation could result in increases in soluble actinides though MnO_2 precipitation could promote sorption to solid phase; liquid phase concentrations could vary considerably though soluble fraction is small percentage of total; primary fate: filter and DWPF (Section 3.2.2)	The project should determine the impact of soluble actinides considering the relatively low amounts, soluble fractions, and volatilities and the impact of MnO_2 solids. If optimization is needed to minimize soluble actinides, actual waste testing could determine the optimum permanganate reagent amount and RCT turnover/filtration time scale and the preferred conditions.
mercury	1) Current state in DWPF Recycle - RCT analysis has not been conducted with final selected reagent addition amounts to determine mercury speciation which impacts fate during filtration and evaporation; dissolved mercury will be transferred to evaporator where volatility will result in some level of mercury in the condensate (Section 3.3.1)	The current program includes RCT/SMECT/OGCT sampling and mercury speciation analysis.

mercury	2) Speciation changes due to Nitric-Glycolic Acid Flowsheet and the new antifoam - specific conditions producing range of mercury species in DWPF are not known in detail (Section 3.3.2)	Laboratory testing with simulants is underway to examine mercury speciation for a series of conditions in preparation for DWPF Sludge Batch 10 processing. An upcoming qualification test is also planned with actual Sludge Batch 10 waste, and mercury speciation analyses will be performed on the products and condensates. Once those results are available, it is advisable to consider whether additional testing is needed to examine other conditions and determine the distribution of mercury species in the products. Testing should determine where metallic mercury, MeHg, and ionic mercury are produced, at what point in the process cycle they are produced, and identify contributing factors influencing production. This knowledge would permit optimization of metallic mercury production and removal in DWPF.
mercury	3) Glycolate Destruction - none; no reactions with permanganate are expected that could impact mercury species distribution and amount of mercury in the evaporator off gas; any reactions are expected to decrease rather than increase mercury volatility (Section 3.3.3)	Monitor the off-gas condensate for mercury once the Nitric-Glycolic Acid flowsheet is implemented.
mercury	4) Transfers - insufficient information is known about process equipment at this time to evaluate mercury transfer capabilities (Section 3.3.4)	Design of the transfer system, tanks, and pumps needs to include the ability to homogenize and transfer the dense mercury species. Testing should be conducted as needed to confirm the adequacy of the design.

mercury	5) Effect of pH - lowering the pH to 9 is not expected to have a significant impact on mercury speciation that could increase evaporator condensate concentrations, but this has not been verified (Section 3.3.5)	Upcoming testing of the evaporation of simulants and actual waste are expected to be performed near the baseline condition of pH 13, and the scope includes mercury speciation. The simulant testing should include a formulation that includes a distribution of mercury species that is comparable to that in the actual waste samples. If a lower pH target is selected for the Diverted Recycle Stream, testing at a lower pH may be necessary.
mercury	6) Filtration - filtration of solids including metallic mercury has not been tested, and no known data exists (Section 3.3.6)	Upcoming testing with simulants should involve a formulation that includes the range of expected mercury species (including metallic mercury). Actual waste filtration testing should address the challenge of representativeness of the simulant. Speciation analyses of both simulant and actual waste are needed to examine the fate and transformation of the mercury species during filtration and chemical cleaning. If a lower pH target is selected for the Diverted Recycle stream, testing at a lower pH may be necessary.
mercury	7) Evaporation - data on metallic mercury behavior in an alkaline tank waste evaporator exists, though no tests have been conducted for this specific stream (Section 3.3.7)	Upcoming testing with simulants should include a formulation that includes the range of mercury species. Actual waste testing should somewhat address the challenge of representativeness of a simulant. Speciation analyses of both simulant and actual waste are needed to examine the fate and transformation of the mercury species during evaporation.
iodine	1) Current state in DWPF Recycle - iodine volatility in off-gas condensates is not well understood (Section 3.4.1)	The upcoming measurements of ^{129}I distribution during characterization of SMECT and OGCT samples at SRNL are expected to provide information on the concentrations and solubilities of these species in the condensates.

iodine	2) Speciation changes due to Nitric-Glycolic Acid Flowsheet and the new antifoam - iodine speciation and specific conditions of partitioning in off-gas condensates are not well understood (Section 3.4.2)	It would be useful to measure the ^{129}I distribution during sludge batch qualification testing at SRNL using the Nitric-Glycolic Acid Flowsheet, but this only provides the filter partitioning. Planned SRNL simulant tests should include iodine in the simulant and in the analysis.
iodine	3) Glycolate Destruction - speciation of iodine in the RCT stream is not known, and it is not known if iodine reacts with permanganate (Section 3.4.3)	For upcoming filtration and evaporation testing, ^{129}I should be analyzed in tests with and without glycolate destruction to determine if iodine partitions to the solid or aqueous phase, and its subsequent volatility from the aqueous phase.
iodine	4) Transfers - no gaps identified for ^{129}I behavior during transfers (Section 3.4.4)	None.
iodine	5) Effect of pH - no data is available for this specific stream, but effect of lowering pH to 9 not expected to have a significant impact on speciation under fully aerated conditions (Section 3.4.5)	Confirmatory modeling of iodine should be performed on the expected stream compositions and variable conditions to verify a similar outcome for the DWPF Recycle Stream. After pH adjustment of the OGCT and SMECT samples, the distribution of ^{129}I in the liquid and solids should be analyzed.
iodine	6) Filtration - fate of iodine is unknown during filtration; speculated that iodine will precipitate with heavy metals such as silver or mercury (Section 3.4.6)	Actual waste testing of the filtration system should include analysis of the ^{129}I to determine its partitioning. The acid cleaning solution should also be analyzed to determine if ^{129}I is present.
iodine	7) Evaporation - computer modeling indicates adjustment of comparable stream to slightly alkaline pH results in minimal volatile I_2, but modeling of the fate of iodine in recycle stream has not been conducted; iodine analysis of this specific stream has not been conducted (Section 3.4.7)	OLI modeling of the Recycle Stream and the various compositions expected should be conducted including iodine. Testing of the evaporation should include simulants spiked with iodine and effluent streams should be measured for iodine partitioning. Similarly, the radioactive testing should include analysis of ^{129}I in the feed, concentrate, and condensate to ensure the partitioning is determined.

silicon, NAS, and actinide sorption	NAS scale accumulation may be observed in the evaporator which could impact evaporator operations and result in accumulation of actinides (Section 3.5)	The project should consider the likelihood and impact of NAS scale formation in the evaporators. Process optimization may be needed to attempt to minimize the transfer of aluminum through the filter and the formation of NAS in the evaporator. Vacuum evaporation at lower temperatures could be preferred if less scale is formed under these conditions. However, scale formation in the WFE could negatively impact the operation of this evaporator.

In conclusion, current planned testing and analyses should close many of the technology gaps for DWPF Recycle Diversion. There is uncertainty in the amounts of soluble actinides passing through the filter, though the bulk of the actinides should be captured on the filter with the RCT solids and the total amounts of actinides should be low. The RCT pH in the range from 9 to 13 could impact the fraction of actinides reaching the evaporator, but the primary factors determining the actinide fate could be the amount of CO_2 sorption from air sparging or, for certain actinides (such as plutonium), oxidation by permanganate and/or sorption to MnO_2 solids. Process optimization could minimize the amounts of actinides passing the filter. It is expected that the new Recycle evaporator system will partition elemental mercury to the condensate to a comparable degree as current evaporators and that a collection system will be needed to prevent exceeding the ETP WAC limit. The facility design must be adequate to transfer dense mercury phases and testing to confirm performance is needed. Simulant containing mercury is needed for both filtration and evaporation testing. OLI Modeling of the various recycle streams is recommended to provide insight on the fate of iodine. Iodine-spiked simulants are recommended for upcoming evaporation tests. Actual waste testing of the glycolate destruction, filtration, and evaporation system should include the analysis of actinides, mercury, and iodine to determine their partitioning.

5.0 Future Work

Planning is underway for simulant and actual waste testing to support Diverted Recycle process development. Characterization of actual waste samples from within DWPF is in progress. Depending upon the results of these efforts, other testing and needs may be identified. Recommendations to close other technology gaps are provided in Section 4.0. TTR's may need revision to complete any additional scope identified as needed.

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Appendix A

Table A-1. Simplified Tank 22H Waste Composition used for OLI Modeling.

Species	Concentration (M)
$NaNO_3$	0.1
$NaNO_2$	0.3
Na_2SO_4	0.003
Na_2CO_3	0.01
$NaAlO_2$	0.002
NaOH	0.1
HgO	1.0E-04
HNO_3	0.001
Vapor phase	
N_2	0.08 moles
O_2	0.02 moles

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