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Technical Evaluation of Accelerated Basin De-Inventory Material Addition to Sludge Batch 11

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Revision 0, January 2023	• Initial Issue
Revision 1, March 2023	• Substantial changes to the report are tracked by revision bars. Changes in the headers, footers, Table of Contents, List of Tables, and reference numbering are not tracked by revision bars. • Title Page: Replaced page i to reflect the current SRNL report template • Executive Summary: Added a conclusion regarding soluble enriched uranium. Added a conclusion that allowing for concurrent transfers of sodium hydroxide and Accelerated Basin De-inventory (ABD) material does not alter the conclusions of the document. Removed a recommendation regarding depleted uranium additions and the impact on soluble enriched uranium. Added a recommendation for Savannah River Mission Completion (SRMC) to evaluate the applicable risk. • Section 1.0: Added description of email request for technical evaluation of allowing concurrent transfers of sodium hydroxide and ABD material. Added a clarification of the depleted uranium addition plan. • Section 3.1: Added a clarification of the depleted uranium addition plan. • Section 3.1.3: Described the depleted uranium addition plan and gave a more detailed description of its impacts on the supernate uranium enrichment in Tank 51. Described the risks involved. • Section 3.1.4: Changed the wording to indicate a risk involving uranium enrichment of Tank 51 supernate • Section 3.2.2.2, changed free hydroxide concentration from “0.6 to 1.2 mol/L” to “>1.2 mol/L” • Section 3.3: New section containing a technical evaluation of allowing concurrent transfers of sodium hydroxide and ABD material. Specific areas addressed included aluminum removal, actinide enrichment in the decanted supernate, rheological behavior, and Gd solubility. • Section 4.0: Added a conclusion regarding soluble enriched uranium. Added a conclusion that allowing for concurrent transfers of sodium hydroxide and ABD material does not alter the conclusions of the document. Removed a recommendation regarding depleted uranium additions and the impact on soluble enriched uranium. Added a recommendation for SRMC to evaluate the applicable risk. • Section 5.0: Added Reference 9 and updated References 15, 16, and 31.

EXECUTIVE SUMMARY

The Accelerated Basin De-inventory (ABD) program involves discarding spent nuclear fuel that is currently stored in L-Basin to the Defense Waste Processing Facility (DWPF) for vitrification. The first ABD discards will occur during the preparation of Sludge Batch (SB) 11. Savannah River Mission Completion has requested that the Savannah River National Laboratory assess the technical gaps related to the increased gadolinium poisoning requirement and the impacts of performing the Low Temperature Aluminum Dissolution (LTAD) process in Tank 51 with H-Canyon discards present.

The following summarizes the evaluation of the impacts of increasing the quantity of gadolinium (and related topics) from what was previously evaluated in the SRNL studies of gadolinium-poisoned ABD material solubility, the overall ABD flowsheet review, and increasing the fissile mass loading in glass:

- Based on literature surveys, there is no indication that organic interactions with gadolinium will be significant at the high pH (typically >13) conditions of the Concentration, Storage, and Transfer Facilities. Any interactions of gadolinium with organics in DWPF are not expected to adversely impact DWPF or downstream facilities. Thus, there is little-to-no residual risk from organic interactions with gadolinium. [Gap closed]
- Adding depleted uranium to ABD material, targeting ^{235}U enrichment of 4.90% within each transfer window, will mitigate potential impacts from an increase in soluble ^{235}U enrichment during sludge washing and LTAD. The plan to take advantage of previous transfers and allow ^{235}U enrichment of >5% during the final transfer window carries a risk that Tank 51 supernate will have a ^{235}U enrichment of >5%, which should be evaluated for acceptance.
- Increasing the gadolinium mass ratio to 3.0:1 Gd:$^{235}U(eq_{SLU})$ should lead to the same or higher partitioning of gadolinium into the solid phase within the DWPF Chemical Process Cell, resulting in both liquid and solid phases with expected partitioning of Gd consistent with the prior solubility study. [Gap closed for SB11]
- There are no expected impacts on DWPF melt temperature and melter operations due to the minimal ~0.2 weight percent (wt%) increase in Gd concentration relative to previous sludge batches. [Gap closed for SB11]
- As observed previously, Gd is expected to enter the off-gas system via physical entrainment, but at a slightly higher concentration than what was observed for SB9 melter off-gas pluggage deposits (0.07 wt%). [Gap closed for SB11]
- There are no expected impacts on DWPF recycle or the Recycle Collection Tank glycolate destruction process. [Gap closed for SB11]
- Gd is projected to be a trace component in the SB11 glass (<0.5 wt%) and can be ignored for process control. Trace components do not significantly impact glass durability, thus the conclusions of the previous Product Consistency Test evaluation at a fissile mass loading of 2,500 g fissile/m^3 glass still applies to SB11. The ~0.1 wt% increase in Gd_2O_3 concentration relative to the previous study will not impact the predictability of SB11 glass with the DWPF Product Composition Control System (PCCS) models for durability or the acceptability of glass according to the Waste Acceptance Product Specifications (WAPS) criterion for product consistency. [Gap closed for SB11]
- No additional Toxicity Characteristic Leaching Procedure testing is necessary for SB11 and the hazardous waste specification of the SB11 DWPF waste form is unchanged after the addition of the ABD stream. [Gap closed for SB11]

The following summarizes the evaluation of the impacts of adding two-thirds of the ABD material to Tank 51 prior to LTAD:

- The addition of two-thirds of the ABD increases overall aluminum mass from 1.39×10^4 kg to 1.64×10^4 kg (15.5% ABD Al). The form of the insoluble portion of the Al resulting from ABD

addition should be the more readily dissolved $Al(OH)_3$ and amorphous forms. The portion of the ABD aluminum that is processed by LTAD is expected to be completely soluble, thus requiring that less of the boehmite in the sludge be dissolved to reach the same Al target in the SB. [Gap closed for SB11]

- The expected LTAD impact on other components, as related primarily to the components in ABD, are discussed. Gd is expected to remain insoluble during LTAD and not impact the solubility of other components. [Gap closed for SB11]
- The addition of two-thirds of the ABD increases overall projected SB11 uranium mass from 4,740 kg to 13,100 kg (63% ABD U) and the projected plutonium mass from 86.0 kg to 89.5 kg (3.9% ABD Pu). The addition of all of the ABD increases overall projected SB11 uranium mass from 4,740 kg to 16,100 kg (70% ABD U) and the projected plutonium mass from 86.0 kg to 90.4 kg (5.3% ABD Pu). The ^{235}U enrichment will be ≤5%. The fissile uranium will be adequately poisoned by Gd and the fissile Pu will be adequately poisoned by Fe from the sludge. [Gap closed for SB11]
- There is a low risk that ABD addition will impact the rheology or pumpability of the slurry. There is a low but higher risk of ABD addition prior to LTAD impacting the settling rate.
- Based on the evaluation of adding two-thirds of the ABD material and all of the ABD material prior to the LTAD process, there is no volume or mass limit that would need to be imposed on ABD additions prior to LTAD. [Gap closed for SB11]

Revision 1 of this report addresses a variation on the ABD additions and LTAD strategy where sodium hydroxide additions for LTAD may be performed intermittently or concurrently with an ABD addition window. The proposed change does not alter the conclusions of this evaluation.

Recommendations resulting from this work are as follows:

- Inductively Coupled Plasma – Emission Spectroscopy is recommended for the measurement of Gd in DWPF Slurry Mix Evaporator (SME) acceptability samples if it becomes a reportable element (> 0.5 wt%) in future sludge batches.
- If future sludge batch projections indicate that Gd becomes a reportable element (>0.5 wt% in glass), then an evaluation of PCCS constraints and models will need to be performed followed by a revision to the SME acceptability document.
- If Gd concentrations are projected to exceed the 0.5 wt% reportable limit in glass, then a time-temperature-transformation diagram will need to be developed to continue to satisfy the WAPS criteria for phase stability.
- Savannah River Mission Completion should evaluate whether the risk introduced by allowing the final ABD transfer window to have ^{235}U enrichment of >5% should be accepted.
- A sample of Tank 51 slurry is recommended for a more accurate determination of composition prior to LTAD.
- Samples of Tank 51 slurry or supernate that are taken during the assembly of SB11, especially samples after ABD addition and during LTAD and in-tank sludge washing, could provide useful additional information on gadolinium and supernate fissile uranium enrichment. This information could be used to aid in planning future ABD addition timing and potentially relax uranium enrichment requirements.
- Consider sampling Tank 51 earlier in the LTAD process in case the aluminum dissolution target is met sooner than expected.

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LIST OF ABBREVIATIONS

ABD	Accelerated Basin De-inventory
CPC	Chemical Process Cell
CSTF	Concentration, Storage, and Transfer Facilities
DOE	Department of Energy
DOTA	1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid
DTPA	diethylenetriaminopentaacetic acid
DWPF	Defense Waste Processing Facility
EPA	Environmental Protection Agency
HIFR	High Flux Isotope Reactor
ICP-ES	inductively coupled plasma-emission spectrometer
KMA	Koopman minimum acid
LW	Liquid Waste
LTAD	Low Temperature Aluminum Dissolution
LPPP-SPT	Low Point Pump Pit-Sludge Pump Tank
MRI	Magnetic Resonance Imaging
MST/SS	Monosodium Titanate/Sludge Solids
MTR	Materials Test Reactor
NCSE	Nuclear Criticality Safety Evaluation
NGA	Nitric-Glycolic Acid
PCCS	Product Composition Control System
RCRA	Resource Conservation and Recovery Act
RCT	Recycle Collection Tank
SB	Sludge Batch
SME	Slurry Mix Evaporator
SNF	Spent Nuclear Fuel
SRAT	Sludge Receipt and Adjustment Tank
SRE	Sodium Reactor Experiment
SRMC	Savannah River Mission Completion
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
TCLP	Toxicity Characteristic Leaching Procedure
TS	total dried solids
TTQAP	Task Technical and Quality Assurance Plan
TTR	Technical Task Request
TTT	time-temperature-transformation
WAC	Waste Acceptance Criteria
WAPS	Waste Acceptance Product Specifications
WCP	Waste Form Compliance Plan
WL	waste loading
wt%	weight percent

1.0 Introduction

Savannah River Nuclear Solutions has a need to discard spent nuclear fuel (SNF), currently stored in L-Basin, to the Defense Waste Processing Facility (DWPF) for vitrification. The Department of Energy (DOE) has approved the Accelerated Basin De-inventory (ABD) Program for discarding SNF via transfers from H-Canyon to the Savannah River Site (SRS) Liquid Waste (LW) system.[1-2] The first ABD discards will occur during the preparation of Sludge Batch (SB) 11.[3]

An initial impact evaluation of the LW flowsheet was performed by the Savannah River National Laboratory (SRNL) prior to the approval of the ABD Program.[4] This evaluation addressed the LW downstream facilities based on the current H-Canyon flowsheet sequence for the average ABD discard. The flowsheet evaluation only included aluminum-clad SNF, specifically Materials Test Reactor (MTR) fuel and High Flux Isotope Reactor (HFIR) fuel similar to the planned SB11 discard.

Following this evaluation, the flowsheet has been slightly altered to address (i) new nuclear criticality safety controls for DWPF that credit a higher amount of gadolinium as a neutron poison for all of the enriched uranium contained in a SB and (ii) potential additions of the H-Canyon neutralized fuel stream prior to the Low Temperature Aluminum Dissolution (LTAD) process in Tank 51. The early introduction of ABD material into the SB assembly process is being investigated to provide flexibility regarding transfer opportunities for H-Canyon to Tank 51 for SB11 and future sludge batches.

The assumptions and conclusions of three past SRNL studies could potentially be impacted by these flowsheet changes. The studies include the following:

i) the study of solubility of gadolinium-poisoned ABD material through DWPF,[5]
ii) the overall ABD flowsheet review through all impacted facilities,[4] and
iii) the study of impacts of increasing the fissile mass loading in glass.[6]

Based on the planned additions of ABD discards from H-Canyon to SB11, Savannah River Mission Completion (SRMC), the SRS LW contractor, issued a Technical Task Request (TTR) requesting that SRNL assess the technical gaps related to the following items:[7]

- increased gadolinium poisoning requirement
- impacts of performing the LTAD process in Tank 51 with H-Canyon discards present.

SRNL issued a Task Technical and Quality Assurance Plan (TTQAP) addressing the plan and requirements for this evaluation.[8]

After completion of the initial evaluation, SRMC asked SRNL to evaluate a variation on the timing of ABD addition in relation to the LTAD process that was not considered in the evaluation.[9] The initial plan was to add ABD material and then add sodium hydroxide to perform aluminum dissolution of the material in Tank 51. In order to allow for larger ABD transfer windows, SRMC is considering allowing transfer of ABD streams to Tank 51 intermittently as time allows either before or after sodium hydroxide additions. This addition to Revision 1 of this evaluation is added as Section 3.3.

Revision 1 also addresses a requested clarification of the H-Canyon plan for depleted uranium addition to the ABD material. The plan involves taking credit for previous depleted uranium additions in allowing the final transfer window to have a ^{235}U isotopic enrichment >5% on a mass basis.

2.0 Methodology

The approach for assessing the impacts of ABD to SB11, which is Task 1 of the TTR, was outlined in Section 4.1 in the TTQAP and is paraphrased in this section.[7-8]

Through performance of TTR Tasks 2 and 3, SRNL conducted a technical evaluation that addressed the "technical readiness" of SRMC to implement changes to the LW ABD flowsheet, involving increased amounts of gadolinium (TTR Task 2) and adding a portion of ABD to Tank 51 prior to the LTAD process (TTR Task 3). The evaluation was not a formal "technology readiness assessment", "readiness review", or "risk assessment", which have set procedures and guides. Rather, this evaluation reviewed the relevant data from studies performed within the DOE complex and in the open scientific literature and used that information to identify and document technical gaps. The evaluation used technical judgement and engineering calculations. This evaluation did not perform new testing or generate new data. This evaluation recommended aspects of the flowsheet to monitor during implementation when applicable.

Gaps are considered closed if enough technical information from the review of the existing information is available to either determine that there is no likelihood of a gap occurring or that there is no impact if the gap occurs. Some gaps persist to a degree due to previous testing and information not being obtained at the precise conditions covering the possible implementations of the ABD flowsheet, including the currently proposed implementation. In cases where gaps cannot be fully closed with existing information and continue to persist to some degree, the evaluation provides information that can be used to judge the likelihood that the gap will affect processing, and the relative severity of the potential impact. Thus, the evaluation aims to provide the context necessary to determine whether the risks introduced by not testing the gaps should be acceptable. Additional recommendations follow from the results of the evaluation, which are documented in this report. SRMC may either accept or reject recommendations.

The focus of the gaps analyzed are specific to the aluminum clad SNF consistent to that which will be added to SB11. Some extensions might be applicable to future sludge batches, but additional gaps will be present for portions of the non-aluminum SNF portions of ABD.[10-12]

2.1 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in Manual E7 Procedure 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. To match the requested Safety Class functional classification, this report has received a Design Verification by document review per Manual E7, Procedure 2.60, Section 5.3.[13] Sludge batch projections, analytical data for H-Canyon samples, and Design Checklists for this report are stored in electronic laboratory notebook experiment C7592-00311-45.

3.0 Results and Discussion

3.1 Increased Gadolinium Addition

TTR Task 2 primarily relates to the evaluation of changes in the inputs and assumptions in past SRNL studies due to expected requirements from various SRMC nuclear criticality safety evaluations (NCSEs). TTR Task 2a is specific to gadolinium interactions with organics in the waste. TTR Task 2b requests an evaluation of the conclusions of the three previous SRNL reports[4-6] with regards to the new minimum mass ratio of gadolinium to equivalent uranium-235 in sludge. Since the three past SRNL reports on ABD, the minimum mass ratio of gadolinium to equivalent uranium-235 ($^{235}U(eq_{SLU})$) has been increased to 2.5:1. Specifically for SB11, additional gadolinium will be added in ABD to ensure that the 2.5:1 ratio is also met in Tank 40 and through DWPF. For the purposes of this evaluation, the minimum mass ratio Gd:$^{235}U(eq_{SLU})$ will be assumed as approximately 3:1. This is due to H-Canyon's desire to exceed the "target" Gd addition of Gd:$^{235}U(eq_{SLU})$ mass ratio of 2.76:1. SRMC Planning Group provided an SB11 projection based on Gd:$^{235}U(eq_{SLU})$ mass ratio of 2.73:1 that indicated Gd concentration in the washed Tank 51 sludge and blended Tank 40 Sludge Receipt and Adjustment Tank (SRAT) receipt as 0.42 and 0.35 weight percent (wt%) of total dried solids (TS), respectively.[14]

Equivalent uranium-235 mass for use in sludge and within DWPF is defined as $^{235}U(eq_{SLU}) = {}^{235}U + 1.4({}^{233}U)$, where all species are on a mass basis.[15] Equivalent uranium-235 mass for use elsewhere is defined as $^{235}U(eq) = {}^{235}U + 1.4({}^{233}U) + 2.25({}^{239}Pu + {}^{241}Pu)$ where all species are on a mass basis.

The baseline plan is that H-Canyon will add enough depleted U to target a 0.0490 (4.90%) ^{235}U/total U mass ratio for the ABD stream to ensure less than or equal to 0.05 (5%).[16] Ideally, the depleted U would be added to each batch that is transferred from H-Canyon. However, the tentative (verbally communicated) plan ensures that the targeted amount of depleted uranium is added during each transfer window to ensure that ^{235}U/total U ≤ 0.05 (5%) at the end of each transfer window. H-Canyon may target a higher ^{235}U/total U in the final transfer window to take credit for excess depleted uranium added during the earlier transfer windows. This topic is discussed further in Section 3.1.3.

Although the focus of the TTR request is for increased gadolinium addition over the original planned amount, this section also considers the impacts of other components in the ABD stream (such as the enriched uranium and Resource Conservation and Recovery Act (RCRA) metals).

3.1.1 *Gadolinium and Organics*

TTR Task 2a involves a question about whether the potential exists for organic gadolinium complexes to form in Tank 22 or other Concentration, Storage, and Transfer Facilities (CSTF) locations. The TTR provided references for the organics identified in the CSTF.[17-22] While this item does not appear to be related to the increase in required gadolinium over what was used in the previous SRNL studies, the potential and impacts (i.e., fate) of gadolinium interactions with CSTF organics were requested to be addressed through an evaluation of the related literature and historical processing observations.

From the analysis in this section, the possibility of forming persistent organic gadolinium complexes in the CSTF is very low and, if formed, the organic complexes will not have impacts. The following is a summary:

- With the exception of carboxylate ions, the types and concentrations of organics in the CSTF are not optimal for forming gadolinium complexes.
- The high pH condition of CSTF supernate does not favor the formation and stability of organic gadolinium complexes.
- In the rare instances where there is SRS tank data showing measurable gadolinium in sludge in the presence of organics, there was no detectable gadolinium in the supernate.
- If a minor amount of Gd complexing were to occur in the CSTF, there will be no impacts to the poisoning of the sludge in Tank 22 or other CSTF locations.

SRS CSTF high-level waste supernates are aqueous solutions with low levels of soluble organic carbon (typically <1000 mg/L, but up to 3000 mg/L in some cases due to high oxalate concentration).[23] The major organic carbon contributors to the CSTF are from a diverse set of processes and are summarized most recently by Woodham and Martino.[24] Some of the general classes of compounds and specific organic species are as follows:

- Tri-n-butylphosphate from SRS Canyons separations, including degradation products dibutylphosphate, butylphosphate, and butanol.
- Resins from SRS Canyons and CSTF use, both digested with potassium permanganate and transferred without digestion, and degradation products.
- Kerosene-like solvents from SRS Canyons and salt processing.
- Antifoams and Antifoam 747 degradation products (trimethylsilanol, hexamethyldisiloxane, propanal, and poly-ethyleneoxide) transferred from DWPF.
- CSTF evaporator antifoam (Dow H-10/Xiameter AFE-1010) and breakdown products (various poly-dimethylsiloxanes).
- Formate from formic acid use in DWPF.

- Glycolate from glycolic acid use in DWPF.
- Oxalate from oxalic acid use in tank cleaning and transferred from other facilities.
- Methylmercury and other organic mercury, either created within CSTF or transferred from other facilities.

Information on organic complexes of gadolinium is widely published in the scientific literature. The large amounts of published data on gadolinium chelation could give an indication that gadolinium is particularly or uniquely susceptible to interactions with organics that increase its solubility. However, the reason behind so much investigation is that chelated gadolinium complexes are very important for use as magnetic resonance imaging (MRI) contrast agents. The use of gadolinium in this way is due to the paramagnetic properties of gadolinium. The need for ligand addition for the complexation of gadolinium in MRI contrast agents is to reduce its toxicity for that application.

The predominant oxidation state of gadolinium is the +3 state or Gd^{3+}. Gd^{3+} is highly soluble in acidic solutions and is present as the hydrated complex, $Gd(H_2O)_7^{3+}$. Under alkaline conditions, the gadolinium precipitates as $Gd(OH)_3$. Organic complexes of gadolinium are typically formed by the addition of an organic compound to an aqueous solution of $Gd(H_2O)_7^{3+}$. Some of the most common MRI contrast agents are gadolinium(III) complexes that are macrocycles such as DOTA (1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid) in the complex $Gd(DOTA)^-$ and DTPA (diethylenetriaminopentaacetic acid) in the complex $Gd(DTPA)^{2-}$.[25-26] The gadolinium ion can coordinate with the ring amine nitrogen atoms and the deprotonated carboxylic acid oxygen atoms. Gadolinium can form complexes with glycolic acid or oxalic acid.[27] A review of metal-glycolate complex formation showed that carboxylic acid or carboxylate ion complexes with Gd are only prominent at acidic to neutral conditions.[27-30] Thus, Gd would not be expected to form complexes at CSTF high pH conditions ($pH > 12$) with carboxylate ions such as oxalate, formate, and glycolate. Also, glycolate concentrations in the CSTF are currently limited to insignificant levels: ≤3 mg/L in transfers of DWPF recycle, ≤19 mg/L in 3H Evaporator system tanks, and ≤50 mg/L in other tanks.[31] The CSTF waste also has insignificant amounts of amines and thus should not have structured cyclic amine compounds like those that are most effective in chelating gadolinium for use as MRI contrast agents. Within DWPF after nitric and glycolic acid addition, some complexation of gadolinium with carboxylic acids (primarily glycolic acid, but possibly oxalic and formic acids) at neutral to acidic pH should be expected. From the DWPF Nitric-Glycolic Acid (NGA) flowsheet testing, the solubilities of many metals are seen to increase at acidic DWPF conditions to a greater extent than seen in the previous Nitric-Formic Acid flowsheet. This is at least partially due to the complexing of those metals with glycolic acid[28] in the NGA flowsheet and is not thought to negatively impact DWPF processing.

There is no indication that organic interactions with gadolinium will be significant at the high pH (typically >13) conditions of the CSTF. It is expected that metal complexes with glycolic acid formed in the SRAT would be largely dissociated and form solid $Gd(OH)_3$ during pH adjustment in the Recycle Collection Tank (RCT), and thus would not persist at the high pH CSTF conditions. Additionally, the chelates of gadolinium used in MRI contrast agents also tend to exchange with soluble iron, copper, and zinc. As there is typically more soluble iron in the high pH system than soluble gadolinium, the presence of iron would hinder the ability to have stable gadolinium complexes.

Historical processing observations also support the expectation that CSTF organics will not increase the solubility of gadolinium to above a detectable level in caustic CSTF supernate. Tank 22 slurry and supernate was used in hydrogen generation rate testing.[32] The sample material itself contained oxalate and had the potential to contain antifoam breakdown products and methylmercury from DWPF, and a portion of the testing was performed with added sodium glycolate. The gadolinium in the Tank 22 slurry was measured as approximately 4 mg/kg. After the heated testing of the slurry, the soluble concentration of gadolinium remained below the detection limit of approximately 0.2 mg/L. Thus, the small quantities of DWPF antifoam breakdown products, methylmercury, and glycolate ion did not appear to influence the gadolinium solubility.

Tank 44 dissolved saltcake was also used in hydrogen generation rate testing.[33] The sample may have had various legacy CSTF organic compounds and was shown to contain oxalate and potential breakdown products from the prior CSTF evaporator antifoam agent. When preparing the dissolved saltcake for testing, the soluble and insoluble portions were characterized. Gadolinium was noted in both the upper and lower Tank 44 saltcake composite residual solids (approximately 0.4 and 1.2 mg/kg, respectively) and was below the detectable level (approximately 0.05 mg/kg) in the aqueous solution. This is an additional indication that the soluble gadolinium concentration is expected to stay extremely low in the presence of organics and gadolinium-containing solids in the CSTF.

There are also possible interactions of gadolinium with organics within DWPF. During and after acid addition in the DWPF Chemical Process Cell (CPC), acidic conditions could lead to Gd^{3+} interactions with one or more the carboxylic acids (glycolic, formic, and oxalic acid). It is unknown whether other interactions may occur with antifoam components, but any such interactions with Gd or other metals in the system had not been observed to impact the effectiveness of antifoam during SB10 qualification testing.[34] Due to the lack of a study specifically designed to elucidate gadolinium interactions, it has not been determined whether there is a glycolic acid and gadolinium interaction beyond what is expected from the lowering of the pH. Studies have shown that the gadolinium goes from partitioning completely in the solid phase in the basic SRAT Receipt to partitioning almost fully (≥80%) into the liquid phase in the acidic DWPF CPC products that have received excess acid addition.[5, 35-36] Regardless if an organic interaction is contributing to this observation, an increase in gadolinium solubility within DWPF is expected. Increases in metal solubilities after moderate to high acid addition (approximately ≥100% Koopman minimum acid (KMA)) in the NGA flowsheet can lead to higher supernate densities and soluble solids in the SRAT and SME Products.[34, 37-38] This dissolution of metals is part of the NGA flowsheet and does not have significant adverse chemical or physical impacts on the remainder of the DWPF process.[39] If there is a foamover that introduces SRAT or Slurry Mix Evaporator (SME) material containing glycolate into the SME condensate tank, the glycolate (and glycolate complexes) will be destroyed in the RCT by sodium permanganate added to the RCT prior to transfer to Tank 22.[40-43] Thus, no impacts from glycolate-gadolinium complexes on the RCT or downstream facilities are expected.

3.1.2 *Gadolinium Solubility Basis – SRNL-STI-2021-00006*

SRNL performed testing to evaluate gadolinium as an alternative poison for use in the CSTF and DWPF to maintain criticality safety and processability of the material.[5] An aliquot of Tank 51 (SB10) material was combined with Gd-poisoned (via gadolinium nitrate solution) H-Canyon blended dissolver (Tank 10.2) material to produce a feed representing proposed future additions to DWPF. The targeted SB10 to Tank 10.2 ratio was such that vitrified glass from the feed would contain approximately 2,500 grams of fissile material per cubic meter of glass (g fissile/m^3 glass). This mixture represented the relatively low solubility conditions in the CSTF. Six aliquots of sludge and ABD material received DWPF NGA flowsheet SRAT-like acid additions of nitric and glycolic acids (approximately 70, 100, and 130% KMA addition) followed by being heated for 10 hours at 95 °C. Three of those aliquots received additional pH adjustment after cooling to represent the extreme low-end of pH conditions throughout DWPF (targeting pH 3, 2, and 1 that might be found in process vessels, sumps, etc.).

From this solubility testing, the uranium percent soluble values exceeded the percent soluble values for gadolinium over the entire range tested for CSTF and DWPF, indicating that gadolinium poisoning in the solid phase will always be maintained. When the acid addition was at the calculated stoichiometric ratio and above, the percent solubilities of both uranium and gadolinium tended to be high (≥80%) as a result of acid addition in the DWPF NGA flowsheet. At lower stoichiometric ratios, gadolinium closely mimicked the behavior of manganese, which has been used as the uranium poison in DWPF through SB10. Absolute and percent solubility values of plutonium were much lower than those observed for uranium at DWPF conditions. Because gadolinium tended to be dissolved from the sludge more than plutonium at neutral to acidic conditions in the NGA flowsheet (as evident by the higher fraction of dissolved gadolinium relative to plutonium), gadolinium alone did not appear to be an adequate poison for plutonium within DWPF.

The increase in $^{235}U(eq_{SLU})$ due to ABD was covered in the solubility task, which increased the slurry fissile concentration up to approximately 2,500 g fissile/m^3 glass. The Gd:$^{235}U(eq_{SLU})$ of up to 3:1 is an increase from the gadolinium levels included in the solubility testing. The amount of gadolinium used in the solubility study feed was approximately 0.12 wt% of TS,[5] versus gadolinium of approximately 0.4 wt% of TS projected in SB11 feed with ABD.[14] From the seven determinations during solubility testing, the overall "feed" Gd:$^{235}U(eq_{SLU})$ mass ratio averaged 0.68:1. Increasing the ratio from what was used in the solubility testing, approximately 4 times the concentration of gadolinium will be added to SB11. This additional gadolinium will still be insoluble at CSTF conditions. At DWPF conditions, the fraction of gadolinium dissolved is expected to be equal to or less than the fraction of gadolinium dissolved during the solubility testing. A fraction of soluble Gd equal to that of the testing would not impact the conclusions of the testing. A fraction of soluble Gd that is less than that of the testing may indicate that gadolinium behavior has diverged from the manganese behavior, but would result in a greater fraction of the gadolinium remaining in the solids, which is beneficial from the perspective of poisoning the solids and thus is not an adverse impact.

3.1.3 *Uranium Enrichment Observations*

The TTR focuses on the impact of increasing the Gd from what was included in the previous SRNL reports and receiving a portion of ABD prior to LTAD. However, as part of the TTR scope of Tasks 2b and 3h, this evaluation is to address other questions or open items that require investigation. One such item is the impact of testing and field observations related to differences between supernate and slurry uranium enrichment after addition of freshly precipitated enriched uranium materials to CSTF sludge materials.

Several recent experiments involved the addition of pH-adjusted H-Canyon streams to a sludge batch preparation tank. The H-Canyon slurries had relatively high ^{235}U isotopic enrichment while the Tank Farm sludges initially had a much lower ^{235}U isotopic enrichment.[a] When compared with the ^{235}U enrichment of the bulk slurry resultant from mixing these two slurries, the soluble phase (filtrate or supernate) appeared to have a higher ^{235}U isotopic enrichment than would have been expected. The uranium concentration in the soluble phase remained relatively low compared with that of the bulk slurry. The increase in soluble phase ^{235}U enrichment would have the potential to impact processes that receive supernate from the sludge batch preparation tank, such as sludge-washing decants and aluminum-dissolution decants.

The first recent test for which an increased ^{235}U isotopic enrichment was noted for the soluble phase was the small-scale test that investigated the Gd and U solubility through the DWPF process in support of ABD tests, as discussed in Section 3.1.2. The Tank 51 sludge sample had a ^{235}U isotopic enrichment of 0.58% and the H-Canyon Tank 10.2 ABD stream had a ^{235}U isotopic enrichment of 60.9%. The ABD mixture was composed of the acidic Tank 10.2 sample, gadolinium nitrate solution, and a quantity of sodium hydroxide to bring the free hydroxide to 1.2M excess hydroxide. No depleted uranium was added to the ABD mixture. This resulted in a mixture of Tank 51 with ABD that had ^{235}U isotopic enrichment in the slurry of 6.7%. The supernate had a ^{235}U isotopic enrichment of 47.5% and a soluble uranium concentration of 7.2 mg/L.

In similar small-scale testing for Mn poisoning of added H-Canyon Sodium Reactor Experiment (SRE) material to SB10 Tank 51 sample material, the soluble portion of the feed sludge was not analyzed for uranium isotopic distribution. Thus, that solubility test did not provide any additional information related

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[a] ^{235}U isotopic enrichment is defined as the mass of ^{235}U divided by the total U mass and multiplied by 100%

to an increase in soluble phase ^{235}U enrichment. However, two other pieces of information from SB10 with the addition of SRE material provide similar insight to the small scale ABD test. The uranium enrichment was measured in the supernate of the lab-prepared SB10 washed slurry and the filtrate of the field-prepared SB10 washed slurry.

The SRE material was a combination of material from H-Canyon Tank 16.3 and 16.4, which had ^{235}U isotopic enrichment of 52% and 37%, respectively. Based on the SRNL addition of neutralized SRE material to Tank 51 sample material and subsequent washing, the Tank 51 sample ^{235}U isotopic enrichment was 0.58% and the SRE material ^{235}U isotopic enrichment was 45.5%. This resulted in a mixture of Tank 51 with SRE that had ^{235}U isotopic enrichment in the slurry of approximately 1.3%. From the analysis of the SRAT Receipt during the SB10 Qualification test, the SRNL prepared and washed slurry, the supernate had a ^{235}U isotopic enrichment of 9.0% and a soluble uranium concentration of 4.5 mg/L. From analysis of a washing progress sample taken during Decant S of the SB10 field prepared and washed slurry, the supernate had a ^{235}U isotopic enrichment of 2.9% and a soluble uranium concentration of 0.65 mg/L. From the confirmation sample taken during Decant Y of the SB10 slurry near the end of field washing, the supernate had a ^{235}U isotopic enrichment of 2.2% and a soluble uranium concentration of 3.9 mg/L.[44] Uranium enrichment of the lab-washed and the two field-washed slurry supernates (9.0%, 2.9%, and 2.2%, respectively) were greater than bulk slurry ^{235}U isotopic enrichment of approximately 1.3%. However, lab-washed and field-washed slurry supernates differed significantly from each other in ^{235}U isotopic enrichment and uranium concentration, indicating that some timing or processing differences are significant in the ability to replicate the field washing in the laboratory testing. Additionally, based on the two slurry samples taken during SB10 field washing, it appears that the difference between the soluble and bulk slurry ^{235}U isotopic enrichment may be reduced at later stages of washing or longer equilibration times.

The baseline plan is that H-Canyon will add enough depleted U to target a 0.0490 (4.90%) ^{235}U/total U mass ratio for the ABD stream.[16] This is done for two reasons. First, DWPF has a feed ^{235}U(eq$_{SLU}$) limit of 5% on a mass basis.[15] Second, there is a desire for DWPF recycle back to the CSTF to meet the ^{235}U(eq) limit of 5.5% on a mass basis for processing in the 2H Evaporator system.[31, 45] Ideally, the depleted U would be added to each batch that is transferred from H-Canyon. However, the original tentative plan was to ensure that the targeted amount of depleted uranium will be added during each transfer window to ensure that ^{235}U/total U ≤ 0.05 (5%) at the end of each transfer window. For the initial transfer windows, the additions of depleted U by H Canyon will assure that the material transferred during a transfer window will meet these limits, even if the depleted uranium and ABD are precipitated separately. H-Canyon may modify the original plan and target a higher ^{235}U isotopic in the final transfer window to take credit for excess depleted uranium added during the earlier transfer windows.

The plan of precipitating the ABD and depleted uranium separately has several postulated impacts of varying degrees of credibility. The first risk is introduced by having the depleted and enriched uranium as separate particles. The expectation is that the neutralization process that precipitates the depleted and enriched uranium particles will be similar enough that the particles will have overlapping particle size distributions and density ranges. Thus, there is also little physical or chemical driving force to separate these separate particles once they are mixed together in Tank 51. Also, assuming that the majority of the Gd poison will be added to the enriched uranium stream, there will be no transient under-poisoned periods during the ABD transfers to Tank 51. The second risk involves the possibility to bias the Tank 51 supernate enrichment toward that of the recently precipitated and transferred ABD material (the main topic of this section). Depending on how the enriched and depleted batches are staged during a transfer window, starting with enriched uranium transfers may lead to periods in the transfer window where the supernate exceeds the ^{235}U(eq) limit of 5.5% on a mass basis for processing in the 2H Evaporator system. For that reason, the supernate ^{235}U isotopic enrichment should be considered if transfers of supernate out of Tank 51 are going to be planned during an ABD transfer window.

The plan to take advantage of previous transfers and allow the final transfer window to have a ^{235}U isotopic enrichment of >5% carries additional risk. A potentially large portion of supernate from Tank 51 will have been decanted prior to the final ABD transfer window. That transferred supernate would have had material from previous ABD batches with ^{235}U enrichment <5%. In transferring ABD material with ^{235}U enrichment >5% during the final transfer window, the Tank 51 supernate blend may have ^{235}U enrichment >5%. The slurry ^{235}U enrichment will remain below 5%. In sludge tanks that are frequently mixed, such as Tanks 51 and 40, the supernate and slurry ^{235}U enrichment are expected to eventually equilibrate, in this case bringing both below 5%. However, the time scale of this equilibration is not known.

There are two potential impacts if the Tank 51 supernate ^{235}U enrichment were to exceed 5% after the final ABD transfer window. First, if subsequently transferring Tank 51 supernate into a salt batch, supernate with ^{235}U enrichment >5% needs to be anticipated so that it can be blended with supernates of lower enrichment. Second, if the sludge batch transfer to Tank 40 results in Tank 40 supernate ^{235}U enrichment of >5%, there is a risk that the DWPF recycle stream returned to CSTF would have a higher enrichment than the bulk SRAT Receipt slurry. This risk originates because a CPC foamover while at caustic conditions may result in a DWPF recycle stream with supernate ^{235}U enrichment of >5%. To allow for subsequent processing in the 2H Evaporator system, the DWPF recycle stream sent to Tank 22 (and subsequently to the 2H evaporator system) must be ≤5.5% enrichment (on ^{235}U(eq) mass basis).[31] SRMC should evaluate whether the risks introduced by allowing the final ABD transfer window to have ^{235}U enrichment of >5% are acceptable.

Samples of Tank 51 during the in-tank sludge washing and LTAD processes that occur after a portion or all of ABD material additions could provide useful information on ^{235}U supernate enrichment. This information could be used to plan future ABD addition timing and potentially relax uranium enrichment requirements.

3.1.4 *ABD Flowsheet Review – SRNL-STI-2021-00156*

This section addresses the questions posed in TTR Tasks 2b items i, ii, and iii:

- Evaluate the impacts to processing in the CPC and off-gas in the CPC.
- Evaluate the impacts to processing in the melter and melter off-gas system processing.
- Evaluate the impacts to processing in the recycle stream and processing for the destruction of glycolate in the recycle stream.

Gadolinium solubility related aspects of the impacts to the CPC are addressed in Section 3.1.2. Even at increased levels of addition, gadolinium has a very low concentration compared to iron and aluminum and will not impact the physical properties such as rheology. The only chemical impact is that gadolinium will consume a small fraction of the acid added to the SRAT. This acid demand will be accounted for by the current analytical methods used to obtain the input information for the current acid calculation. The gadolinium is still at levels low enough that it will not impact any other chemical or physical properties within the CPC. The only other significant change since the flowsheet evaluation[4] was issued in 2021 is that two-thirds of the ABD will now be added to Tank 51 prior to LTAD to de-inventory the H-Canyon tanks sooner.

With regard to flammable gas generation in the CPC, additional gadolinium or uranium is not expected to have an impact on hydrogen generation regardless of concentration. No literature has been identified that indicates that gadolinium or a similar lanthanide group element would contribute to catalytic hydrogen generation with a mechanism similar to the noble metal catalysis of formic acid. Additionally, DWPF has implemented an NGA flowsheet that renders the catalytic production of hydrogen from formic acid much less of a concern. Radioactive qualification testing for several SBs, including SB9[46] and SB10[34] with the NGA flowsheet, included gadolinium in the sludge feed at very minor but measurable levels (Gd of approximately 0.08 and 0.05 wt% of TS in SB9 and SB10 testing SRAT Receipt, respectively). Although gadolinium will increase to approximately 0.4 wt% of TS in the SRAT Receipt sample due to ABD additions, the amount of gadolinium will still remain a minor component of the slurry. Thus, due to the lack of a known mechanism and the inclusion of Gd in previous testing, any major impact of gadolinium on CPC off-gas would have been captured in previous qualification testing and the risk of increasing gadolinium impacting CPC off-gas is very low.

The pour stream sample collected from Sludge Batch 7a had the highest measured Gd concentration of pour stream samples collected and analyzed thus far (0.04 wt.%).[47] As described in more detail in Section 3.1.6, the projected concentration of Gd in glass for SB11 is ~0.2 wt%, which is considered a trace component (<0.5 wt%) per the Glass Product Control Program.[48-49] Such a minimal increase in the anticipated Gd concentration relative to previous sludge batches is not expected to impact DWPF melt temperature or melter operations. Lanthanide series +3 elements (e.g. La, Nd, Gd) readily incorporate into borosilicate glass melts and solubility issues are not anticipated. Borosilicate glasses have been previously fabricated at SRNL for Pu disposition with up to 13.5 wt% Gd_2O_3 and crystalline Gd-species were not detected by X-ray diffraction.[50] While processing SB9, a low concentration of Gd (0.07 wt%) was detected in melter off-gas pluggage deposits along with other sludge components at higher concentrations (e.g. Al, Fe, Mn).[51] These components enter the off-gas system via physical entrainment. Due to the increase of the SB11 Gd concentration as compared to SB9, it is expected that a slightly higher concentration of Gd will enter the off-gas system.

The hypothesized risks for RCT processing involve the return of material to CSTF that does not meet the CSTF Waste Acceptance Criteria (WAC), and the potential that additional gadolinium will impact the glycolate destruction process in the RCT. The addition of gadolinium to the RCT will likely be the result of sump transfer, a CPC foamover, entrainment of melter feed in the melter offgas, or cleaning of a CPC coil or agitator in the Decontamination Waste Treatment Tank. The result of this would be a very low gadolinium concentration in the RCT. Additionally, any gadolinium transferred to CSTF will be expected to be very insoluble and will not be fed in large quantities to CSTF evaporators. Ultimately, the resulting gadolinium solids will be fed back to DWPF in future sludge batches. Thus, there are no expected impacts of additional gadolinium in the DWPF recycle stream.

As discussed in Section 3.1.3, testing with actual waste after the addition of H-Canyon enriched uranium streams revealed that SRAT Receipt supernate may have a higher ^{235}U/total U enrichment than that of the SRAT Receipt slurry. The DWPF recycle stream returned to CSTF must be below 5.5% enrichment (on ^{235}U(eq) mass basis) to allow for subsequent processing in the 2H Evaporator system.[31] There was a concern that a CPC foamover while at caustic conditions could contribute to a DWPF recycle stream that has a higher enrichment than the bulk SRAT Receipt slurry due to the potential supernate enrichment differences in the SRAT Receipt. H-Canyon plans to add depleted uranium such that the composite transferred to the sludge batch would bring the $^{235}U(eq_{SLU})$/total U to ≤5% enrichment.[16] As discussed in Section 3.1.3, there is a risk that ^{235}U enrichment in the Tank 51 supernate will be >5% after the final ABD transfer window if ^{235}U enrichment of the material sent during the final window is >5%.

There is a low risk that ABD addition will impact the rheology or pumpability of the slurry. There is a low but higher risk of ABD addition prior to LTAD impacting the settling rate.

Previous simulant testing on the glycolate destruction process in the RCT did not contain gadolinium.[41-42] Radioactive waste sample testing with DWPF off-gas condensate streams would have contained trivial quantities of gadolinium.[40] Gadolinium is not thought to take part in the reaction of sodium permanganate solution with glycolate anion. At the high pH of the RCT, the gadolinium will have a very low solubility and will be present as $Gd(OH)_3$ solids, as described above. Gadolinium(III) is already at its highest oxidation state and cannot be further oxidized in aqueous solutions and, thus, would not be expected to consume sodium permanganate. As discussed in Section 3.1.1, there is no expected interaction between glycolate and gadolinium at the high pH of the RCT. It is expected that metal complexes with glycolic acid formed in the SRAT would be largely dissociated during pH adjustment, forming solid $Gd(OH)_3$ in the RCT, and would not persist at the high pH CSTF conditions. For these reasons, any change in the H-Canyon addition amount of gadolinium to ABD material would not be expected to impact the glycolate destruction process in the RCT.

3.1.5 *Analytical Measurement of Gadolinium*

This section addresses the question posed in TTR Task 2b Item iv: If the new Gd:fissile U mass ratio exceeds the reportable limit in the glass, what instrument is recommended to report the concentration?

Per the DWPF Waste Form Compliance Plan (WCP), elements present in sludge at >1 wt% and melter feed/glass at >0.5 wt% are classified as reportable.[52] To date, Gd has not been a reportable element in either sludge or DWPF melter feed. Detectable concentrations of 0.01-0.04 wt% have been routinely measured in sludge batch qualification and pour stream glass samples at SRNL with an inductively coupled plasma-emission spectrometer (ICP-ES).[47, 53-61] If Gd is projected to become a reportable element in a future sludge batch, then ICP-ES is the recommended instrumentation for the measurement in the DWPF Laboratory. Method development activities include (1) procuring a Gd solution standard traceable to the National Institute of Standards and Technology, (2) developing the calibration curve, and (3) identifying the wavelength(s) associated with Gd and any potential interferences.

3.1.6 *Reportable Gd and Implications to Product Composition Control System (PCCS) – SRNL-STI-2021-00208*

This section addresses the question posed in TTR Task 2b, Item v: If Gd is reportable in the glass, what changes to PCCS are needed?

Previous glass testing in 2021 to support the increase in fissile mass loading from 897 to 2,500 g fissile/m^3 glass was performed to demonstrate that a glass with a fissile mass loading of 2,500 g fissile/m^3 glass met the Waste Acceptance Product Specifications (WAPS) acceptance criterion for product consistency.[6, 62] This study assumed a Gd to equivalent ^{235}U in the sludge mass ratio (Gd:$^{235}U(eq_{SLU})$) of 0.55:1 since the actual ratio had not been determined by an NCSE. The 0.55:1 ratio resulted in a Gd_2O_3 concentration in glass of 0.10 wt%.[6] More recently, nuclear criticality safety analysts have completed initial model evaluations and have determined a minimum Gd:$^{235}U(eq)$ ratio of ~2.5:1.[63]

To determine the projected Gd_2O_3 concentration in SB11 glass, the SRMC System Planning group provided a SB11 Tank 40 blend projection, which represents a Gd:$^{235}U(eq_{SLU})$ mass ratio of 2.73:1 in Tank 51 and includes conservatism relative to the ratio of ~2.5:1 proposed by nuclear criticality safety analysts.[b,14, 64-65] This 2.73:1 Gd:$^{235}U(eq_{SLU})$ ratio is consistent with the 2.76:1 Gd:$^{235}U(eq)$ ratio that H-Canyon will target for solutions transferred to SB11.[66] The SB11 Tank 40 blend elemental Gd concentration shown in Appendix A Table A-1 was first converted to an oxide basis (Gd_2O_3). Projected sludge-only Gd_2O_3 concentrations in glass were then calculated at 32-40% waste loading (WL), assuming a target WL of 36%. The resulting Gd and Gd_2O_3 concentrations are shown in Table 3-1. Sludge-only projections were evaluated rather than coupled operation projections since the Gd concentration in glass would be diluted by the addition of the monosodium titanate and sludge solids (MST/SS) stream from the Salt Waste Processing Facility. Thus, the values in Table 3-1 provide conservative estimates of the expected Gd and Gd_2O_3 concentrations in glass at 32, 36, and 40% WL.

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[b] Note that after this evaluation was completed, NCSE N-NCS-G-00182 Revision 1 was issued in October 2022 and is currently on hold for implementation (Reference 65). It states that the CSTF WAC shall limit the minimum Gd:$^{235}U(eq)$ ratio received in the Tank Farms to greater than or equal to 2.41:1.

Table 3-1. Projected SB11 Sludge-Only Gd and Gd_2O_3 Concentrations in Glass (wt%)

	32% WL	36% WL	40% WL
Gd	0.17	0.19	0.21
Gd_2O_3	0.19	0.22	0.24

Per the Glass Product Control Program, trace components do not significantly impact glass durability and are ignored for process control.[48] Trace components are defined as those elements whose concentration are less than the reportable limit of 0.5 wt%. Gd has projected concentrations of 0.17-0.21 wt% and is classified as a trace component for SB11. The projected Gd_2O_3 concentrations are 0.19-0.24 wt%, which are slightly increased as compared to the previous glass study at 2,500 g fissile/m^3 glass with a Gd_2O_3 concentration of 0.10 wt%[6]; however, these updated values are still classified as trace concentrations and do not impact the conclusions of SRNL-STI-2021-00208. The ~0.1 wt% increase in Gd_2O_3 concentration relative to the previous study will not impact the predictability of SB11 glass with the DWPF PCCS models for durability or the acceptability of the glass according to the WAPS criterion for product consistency. No changes to PCCS constraints and models are required for SB11 as long as Gd remains a trace component in glass. Gd concentrations will continue to be evaluated when projections for SB11 are updated as new analytical data becomes available.

If future sludge batch projections indicate that Gd becomes a reportable element (>0.5 wt% in glass), then an evaluation of PCCS constraints and models will need to be performed followed by a revision to the SME acceptability document.[67] Specific items include, but are not limited to:

- Updating the sum of oxides constraint to include Gd_2O_3
- Determining the partial molar free energy of hydration for Gd_2O_3 (ΔG_i, where i = Gd_2O_3)[68] and updating the PCCS durability models
- Fabricating and testing glasses with increased concentrations of Gd to determine whether the measured glass properties (viscosity, durability, and liquidus temperature) are adequately predicted by the existing DWPF PCCS models
- Revising PCCS glass models if measured property values are not predictable

In addition to this PCCS evaluation, an evaluation of previous time-temperature-transformation (TTT) diagrams was peformed.[69-71] The TTT study identifies the time-temperature conditions that cause significant changes in either phase structure or phase composition per the WAPS criteria for phase stability.[62, 72] The impact of any crystalline phases on durability is also determined. Gd was not included in any of the previously tested compositions; however, Nd (another lanthanide series +3 element) was present at Nd_2O_3 concentrations of 0.06-0.55 wt% in seven of the glasses.[71] The behavior of Gd and Nd in glass is expected to be similar at these concentrations. Nd-containing phases were not identified in any of the seven TTT glasses. At these concentrations, Gd-containing phases would also not be expected. If Gd concentrations are projected to exceed the 0.5 wt% reportable limit in glass, then another TTT diagram will need to be developed to continue to satisfy the WAPS criteria for phase stability.

3.1.7 *Toxicity Characteristic Leaching Procedure (TCLP) Evaluation*

This section addresses the questions posed in TTR Task 2b, Item vi: As more detailed information becomes available, are the planned additions of ABD material within the glass TCLP limits tested for barium, cadmium, chromium, lead, selenium, and silver; and will arsenic be present in the waste stream?

To support the initial DWPF WCP for start-up in 1996, several simulated DWPF glasses were evaluated by TCLP to address the hazardous waste specification of the WAPS (Section 1.5).[62, 73-74] RCRA metals including barium (Ba), cadmium (Cd), chromium (Cr), lead (Pb), selenium (Se), and silver (Ag) were doped in these glasses at both nominal concentrations and three times (3X) the nominal concentrations. Arsenic

(As) and mercury (Hg) were omitted since As was not found in SRS waste streams and Hg is removed during chemical processing and any residual Hg will volatilize from the glass melt during vitrification. Table 3-2 summarizes the RCRA oxide concentrations in glasses evaluated in this study.

Table 3-2. Target and Measured RCRA Oxide Concentrations for Original DWPF Waste Form TCLP Testing (wt%)

Oxide	**Nominal Flowsheet Concentration**		**3X Nominal Flowsheet Concentration**	
	Target	Measured	Target	Measured
AgO	0.0027	<0.0024-0.0202	0.0080	<0.0023-0.176
BaO	0.1460	0.1920-0.4629	0.4380	0.5668-0.8721
CdO	0.0004	<0.0012-0.0060	0.0012	<0.0012-0.0043
Cr_2O_3	0.1004	0.2956-0.4285	0.3012	0.3159-0.5709
PbO	0.1122	0.0294-0.1955	0.3366	0.2867-0.4271
SeO_2	0.0008	not detected-0.0511	0.0023	not detected-0.171

All of the glasses met the Environmental Protection Agency (EPA) limits as shown in Table 3-3, which demonstrated that the DWPF waste form is not characteristic hazardous waste.[74-75]

Table 3-3. EPA Regulatory RCRA Concentration Limits for the TCLP

RCRA Metal	**Regulatory Limit (mg/L)**
Ag	5
As	5
Ba	100
Cd	1
Cr	5
Hg	0.2
Pb	5
Se	1

To determine the impact of RCRA metals in the ABD stream on SB11, the analytical results of seven H-Canyon samples from various tanks were reviewed as shown in Appendix A Table A-2.[76] These samples were collected in February 2022 and are assumed to be representative of the future ABD discards to SB11. The measured values for all seven samples are below detection limits for a majority of the RCRA metals (Ag, As, Cd, Pb, and Se). SRMC System Planning included these metals at the detection limit values during the development of the Tank 40 blend projection to conservatively reflect the presence of these metals for this evaluation.

Projected RCRA metal oxide concentrations in SB11 glass were calculated at 32-40% WL using the sludge-only Tank 40 blend projection shown in Appendix A Table A-1. The resulting values are shown in Table 3-4. All of the projected concentrations fall within or below the previously evaluated TCLP glass oxide ranges shown in Table 3-2 except for As_2O_3, which was not included in the original testing. Arsenic is below detection limits in the H-Canyon samples and, thus, is not expected in the ABD discards that will be added to SB11; however, the potential extraction level during TCLP can be calculated by assuming that all As conservatively present in the glass at 40% WL is released (0.0002 wt%). Converting this concentration to parts per million (ppm) and accounting for the 20X dilution of the TCLP yields an extraction level of 0.1 ppm, which is well below the regulatory limit of 5 mg/L (ppm).[73, 75,c]

Table 3-4. Projected SB11 Sludge-Only RCRA-Metal Oxide Concentrations in Glass (wt%)

	32% WL	36% WL	40% WL
AgO	0.02	0.02	0.02
As_2O_3	0.0002	0.0002	0.0003
BaO	0.04	0.05	0.06
CdO	0.0007	0.0008	0.0009
Cr_2O_3	0.10	0.12	0.13
PbO	0.13	0.15	0.16
SeO_2	0.0004	0.0005	0.0005

The data presented in this section demonstrates that no additional TCLP testing is necessary for SB11 and the hazardous waste specification of SB11 DWPF waste form is unchanged after the addition of the ABD stream. As different fuel types are dissolved as part of the ABD mission, projected RCRA metals concentrations in glass for future sludge batches will continually need to be evaluated to ensure that expected concentrations are not outside of the previously tested ranges.

3.2 ABD Addition Prior to LTAD

3.2.1 *Impacts to Aluminum Dissolution*

This section addressed the questions from TTR Tasks 3a and 3b:

- Does the ABD material slow the leach rate of aluminum from the sludge? If so, what steps should be taken to minimize this?
- Does the ABD material need to be accounted for when determining the sodium hydroxide requirement for removal of aluminum? If so, how should SRMC compensate for this such that the correct targeted aluminum removal can be achieved?

The addition of two-thirds of the ABD slurry prior to LTAD (and one-third of the ABD slurry after LTAD) will increase the rate of aluminum dissolution during SB11 LTAD. One step that should be considered is sampling Tank 51 earlier in case the aluminum dissolution target is met sooner than expected. The $Al(OH)_3$ from ABD will consume NaOH and will need to be a factor in calculating the sodium hydroxide requirement for LTAD. The gibbsite dissolution to aluminate will consume one mole of NaOH per mole of gibbsite but using the SRMC calculation methodology assuming all aluminum is boehmite might be more conservative in ensuring adequate kinetics and final percent aluminum dissolution.

Aluminum in the ABD stream will likely precipitate as $Al(OH)_3$ during the pH-adjustment operation in H-Canyon. Upon addition of excess NaOH to achieve a hydroxide concentration of 1.2 M, a portion of the aluminum redissolves to produce the soluble aluminate ion[77], $Al(OH)_4^-$. The dissolution of $Al(OH)_3$ in strongly alkaline solutions is indicative of the amphoteric behavior of aluminum. Given the equilibrium and kinetics involved, it is expected that approximately 17% of the aluminum would remain as solid $Al(OH)_3$ in the H-Canyon stream transferred to Tank 51 and remain as solid $Al(OH)_3$ in Tank 51. Due to the precipitation conditions, it is expected that the aluminum-containing solid contributed by ABD material

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[c] $\frac{0.0002\ wt.\%\ As \times 10{,}000}{20} = 0.1\ ppm\ As$

will be the aluminum hydroxide phases gibbsite (γ-$Al(OH)_3$) and bayerite (α-$Al(OH)_3$) rather than the aluminum oxyhydroxide phase boehmite (α-AlOOH). While the recent ABD neutralization flowsheet tests did not contain information on the crystalline form of precipitated aluminum, a previous similar neutralization study resulted in crystalline gibbsite and amorphous aluminum phases.[78-79] Aluminum in the sludge stream is typically a mixture of primarily boehmite solids[80] (AlOOH) with a smaller fraction of gibbsite solids ($Al(OH)_3$). During LTAD, the free hydroxide concentration and temperature of the sludge slurry are both raised, resulting in significantly increased aluminum solubility, which facilitates aluminum removal via decanting of the liquid phase.

During the LTAD operation in Tank 51[81-83], sodium hydroxide is added to increase the hydroxide to aluminum ratio to 6.4 (that results in a hydroxide concentration of approximately 4 mol/L) and the sludge slurry is mixed and heated to approximately 60 °C. The increased hydroxide concentration and higher temperature results in the dissolution of aluminum from the sludge solids. The process preferentially dissolves the aluminum hydroxide phases gibbsite and bayerite,[84] and is designed to ultimately dissolve a significant portion of the aluminum oxyhydroxide phase boehmite. The primary impact is that the solid aluminum hydroxide in the ABD slurry is expected to preferentially dissolve in relation to the aluminum hydroxide and aluminum oxyhydroxide in the legacy Tank Farm sludge that makes up a sludge batch.

The addition of the ABD stream increases the aluminum mass in the Tank 51 slurry. Thus, the overall aluminum in both ABD and Tank 51 should be considered when planning sodium hydroxide addition for LTAD. The assumed LTAD processing would target the same level of aluminum in the Tank 51 slurry batch for transfer to Tank 40 regardless of whether ABD is added to Tank 51 prior to or after the LTAD process. Adding ABD prior to LTAD appears to be a more efficient use of hydroxide because the gibbsite in the ABD is relatively easy to dissolve compared with the boehmite in the sludge. The amount of Al to be removed during LTAD also has to consider any ABD additions to Tank 51 after LTAD. Note that simulant testing indicates that 83% of aluminum in ABD is soluble at 1.2 M free hydroxide.[79]

3.2.2 *Impacts to Solubilities of Other Components*

This section addressed the questions posed in TTR Tasks 3c and 3e:

- Does the ABD material increase the solubility of U and Pu and/or other cations (i.e. gadolinium, mercury, cesium, etc.) beyond what is observed for the aluminum dissolution process currently performed on sludge, or impact the solubilities such that a cation that was not previously soluble becomes soluble? If so, what concentrations can be expected and what impact does the removal of these soluble cations have on the downstream facilities?
- Based on preliminary criticality modeling efforts, a minimum ratio has been determined regardless of its solubility that covers DWPF normal and credible abnormal operations. Due to the amount of gadolinium, it is not necessary to coprecipitate the gadolinium with the ABD stream. If the excess gadolinium (minus that which is needed for H-Canyon criticality controls) is not co-precipitated with the ABD stream, does the solubility increase under aluminum dissolution conditions? If so, by how much?

3.2.2.1 Prior LTAD Observations

Data collected during past LTAD campaigns are not typically useful for setting a baseline solubility without ABD for the other components mentioned in the TTR. For example, typical data only includes the aluminum, sodium, silicon, nitrite, nitrate, hydroxide, chloride, sulfate, carbonate, and cesium-137.[85] One study that was completed from 55-63 °C was the 2007-2008 LTAD demonstration in Tank 11 and the 2007 laboratory scale demo that preceded it.[82] It also reported the concentrations of uranium and plutonium, including isotopics. However, it did not include Gd. In addition, the ^{239}Pu concentration was greater than the ^{235}U concentration, which is very different than SB11, where ^{235}U will be much higher than ^{239}Pu. For these reasons, the in-tank dissolution analyses do not really help to address this question for the cation components that this gap focuses on.

3.2.2.2 ABD Expectations During Aluminum Dissolution

The TTR specified several specific elements of interest for impacts of ABD prior to aluminum dissolution. These included uranium, plutonium, gadolinium, cesium, and mercury. This list is not exclusive, and there is interest in impacts on the solubility of RCRA metals as well.

Cesium is already primarily in the supernate phase, and the addition of ABD material prior to the LTAD process will not change this fact.

Gadolinium will be used as a neutron poison for nuclear materials dissolved in H-Canyon as part of the ABD program. Prior to release to the CSTF, the highly acidic solutions are pH-adjusted with concentrated sodium hydroxide to final free hydroxide concentration of >1.2 mol/L.[16] The pH-adjustment precipitates the metallic elements including the actinides (U, Pu, Np, Am) and gadolinium. Previous studies indicated that the precipitated solids are small particles less than about 20 microns in size with the uranium, plutonium, and gadolinium intimately dispersed throughout the solids.[86-87] The bulk of the solids are amorphous hydroxides (e.g., $Gd(OH)_3$, $Pu(OH)_4$ and $UO_2(OH)_2$). In some cases, x-ray diffraction patterns identified crystalline uranium phases of Na_3UO_4 and $Na((UO_2O(OH)))$, $Gd(OH)_3$, and possibly a mixture of $Pu(OH)_4$ and $Gd(OH)_3$ or $NaGdPuO_x$.[86-87] From this evidence, U apparently does not co-precipitate with Gd and only a poorly defined mixed phase of Gd and Pu has been reported. Thus, if a portion of the $Gd(OH)_3$ in the overall slurry is introduced via precipitation in the absence of U and Pu, it is expected to behave similarly to the $Gd(OH)_3$ that was precipitated in the presence of U and Pu.

Upon addition of the alkaline ABD slurry to Tank 51, the $Gd(OH)_3$ will be mixed with the sludge slurry and encounters dissolved species in the supernatant liquid. Dissolved species include oxyanions (e.g., OH^-, NO_3^-, NO_2^-, AlO_4^-, CO_3^{2-}, SO_4^{2-}, and PO_4^{3-}) and halides (Cl^-, F^-). These anions could potentially react with $Gd(OH)_3$ to produce the corresponding salts such as gadolinium carbonate, $Gd_2(CO_3)_3$, and gadolinium sulfate, $Gd_2(SO_4)_3$, or mixed ligand salts such as $Gd_2(OH)_2(CO_3)_2$ and $Gd_2(OH)_2(SO_4)_2$. Of these possible salts, only $Gd_2(SO_4)_3$ is reported to have moderate solubility in water.[88-89] Gadolinium sulfate dissolves in water to produce the hydrated Gd^{3+} and sulfate ions. The hydrated Gd^{3+} ion begins to precipitate at a pH of 7 and above, and is completely precipitated at a pH of about 9.[89] Since the hydroxide concentrations in the ABD material and sludge batch in Tank 51 are both above 0.5 mol/L at the time of ABD addition, no soluble gadolinium species will be present upon addition of the ABD slurry to Tank 51. Gadolinium is expected to stay insoluble during sludge washing, where hydroxide concentration may be as low as 0.2 mol/L. Unlike aluminum, gadolinium is not amphoteric and does not form the soluble gadolinate, $Gd(OH)_4^-$, ion in alkaline solutions.

After completion of aluminum dissolution, the mixing pumps will be shut off and the sludge solids allowed to gravity settle. The clarified supernatant liquid will be decanted. The sludge solids will be washed (i.e., diluted with inhibited water) to reduce the sodium salt content of the supernatant liquid in multiple (>10) batch contacts. The diluted supernatant liquid will be much lower in hydroxide concentration but would still be well above pH 10 in the bulk solution. The pH of the diluted supernatant liquid can slowly react with carbon dioxide at the air/liquid interface to convert hydroxide to carbonate and bicarbonate anions which further lower the pH to between a pH of about 9 – 10. Thus, if the supernatant liquid were to reach a pH of 9 or less, a small fraction of the precipitated gadolinium could dissolve as $Gd(OH)_2^+$. Given the increased carbonate concentration, a portion of the dissolved gadolinium could be present as $Gd(CO_3)^+$.

The increase in aluminate concentration as well as the hydroxide concentration would be expected to increase the plutonium and uranium solubility. Plutonium and uranium are very weakly amphoteric resulting in very small Pu (~1 mg/L) and U (~10 mg/L) concentrations in strongly alkaline solutions.[90-91]

Previous studies on the solubilities of plutonium and uranium indicate that the concentrations of oxyanions (e.g., hydroxide, nitrate, nitrite, hydroxide, carbonate, sulfate, and aluminate) and temperature can affect the solubilities. For example, the general trend, is that the solubilities of plutonium and uranium increase with an increase in the free hydroxide concentration. Also, the predicted plutonium solubility increases slightly with an increase in the aluminate concentration.

Since $Gd(OH)_3$ does not dissolve in strongly alkaline solutions, gadolinate (oxyanions of gadolinium) will not be produced and the consumption of hydroxide by reaction with $Gd(OH)_3$ will not occur during LTAD. Thus, the $Gd(OH)_3$ will have no effect on the solubilities of plutonium and uranium during the LTAD process.

As discussed in Section 3.1.7, many of the RCRA metals have a very low concentration in SRS waste (arsenic, barium, cadmium, lead, selenium, and silver). Mercury and chromium typically have high concentrations in sludge, DWPF melter feed, and recycle. However, the concentrations of the RCRA metals will be the same whether ABD is added before or after LTAD, so the timing of the ABD addition relative to LTAD is not expected to impact any of the processing facilities.

3.2.3 *Impacts to In-tank Processing*

This section addresses the questions posed in TTR Task 3d:

- Does the aluminum dissolution process alter the physical properties/morphology of ABD material to hinder sludge settling during or after the aluminum dissolution process? If so, quantify the impact of the slower settling of sludge.
- Is the mixing sufficient in Tank 51 and Tank 40 to ensure a uniform dispersion of gadolinium in the sludge?
- Are the transfer pumps sufficient to transfer a uniform slurry from Tank 51 to Tank 40 and Tank 40 to the Low Point Pump Pit-Sludge Pump Tank (LPPP-SPT) and LPPP-SPT to the SRAT?

The preparation of every sludge batch comes with a risk of thick rheology or slow settling. This is one of the reasons that SRNL washes and concentrates a sample from each sludge batch, then processes the washed sludge through a SRAT and SME cycle as part of the qualification process. This process helps to ensure the sludge can be washed, transferred, and processed as planned. One of the advantages of the NGA flowsheet is that it can process thicker rheology sludges. If the sludge is too thick rheologically in Tank 51, the final decant will be smaller resulting in a slurry that can be pumped to DWPF. In our opinion, the likelihood that SB11 with or without ABD would have a thick rheology or a slow settling rate is greater than the likelihood than that an ABD addition will cause an otherwise well-behaved SB11 slurry to become too rheologically thick or too slow settling. The change from the addition of all the ABD after LTAD to adding two-thirds of the ABD before LTAD will be even less likely to cause a well-behaved slurry to become too rheologically thick or too slow settling.

From a rheology standpoint, the slurry will be very similar to what was studied in the H-Canyon related precipitation study.[79] This testing was performed at a lower Gd concentration (0.625:1 Gd:^{235}U(eq$_{SLU}$) mass ratio) than currently planned (raised to Gd:^{235}U(eq$_{SLU}$) mass ratio as high as approximately 3:1). The precipitated solids from the ABD material will be a mixture of hydroxides and hydrous oxides of uranium, aluminum, iron, and gadolinium, along with smaller amounts of plutonium, strontium, neptunium, calcium, chromium, mercury, and silicon. The testing revealed that the slurry should be mixable and pumpable as it moves from H-Canyon, to Tank 51, to Tank 40, to the SRAT. If there are problems, they will likely be slow settling of the slurry. But as the ABD addition is a small fraction of the sludge batch (~18.2% by mass) it is unlikely to cause significant rheology issues. Additionally, the precipitation and settling tests were performed at a relatively small scale, so it is difficult to definitively determine settling behavior based solely on this study. Also, during LTAD, significant quantities of aluminum will be dissolved along with minor amounts, if any, of the other precipitated components. The loss of aluminum and other minor components from ABD particles could result in more porous and less dense particles.

In summary, the risks related to rheology or settling impacts resulting from adding ABD to SB11, either after LTAD or with two-thirds added prior to LTAD, are consistent and within the typical level of these risks involved with assembling a sludge batch.

3.2.4 *Flowsheet Evaluation*

This section addresses TTR Tasks 3f and 3g for SRNL to ensure that the conclusions of SRNL-STI-2021-00156 for the downstream facilities are still valid as recommended in Section 2.0 of the report based on this proposed flowsheet change,[4] and to address whether SRMC should consider or impose a volume or mass limit for H-Canyon ABD additions that will undergo aluminum dissolution.

The current plan for the SB11 ABD flowsheet is to add two-thirds of the ABD material prior to LTAD. The previous flowsheet evaluation report only considered adding the ABD after LTAD. This section considers additional potential impacts of adding all or a portion of the ABD material to the sludge prior to LTAD.

The slurry itself will be very similar to the slurry that was planned at the time of the previous flowsheet analysis.[4] The addition of two-thirds of the ABD increases overall aluminum mass from 1.39×10^4 kg to 1.64×10^4 kg (15.5% ABD Al). The freshly precipitated ABD Al will likely dissolve preferentially, but the plan is to stop at the same Al endpoint for LTAD, so the slurry should have the same basic composition as assumed in the previous analysis. The addition of two-thirds of the ABD increases overall projected SB11 uranium mass from 4,740 kg to 13,100 kg (63% ABD U) and the projected plutonium mass from 86.0 kg to 89.5 kg (3.9% ABD Pu). The addition of all of the ABD increases overall projected SB11 uranium mass from 4,740 kg to 16,100 kg (70% ABD U) and the projected plutonium mass from 86.0 kg to 90.4 kg (5.3% ABD Pu). Since the ABD material was recently precipitated, more fissile material will likely be in the supernate. The fissile material in the supernate will be very low in total mass and overall will have a $^{235}U(eq_{SLU})/U$ enrichment ≤5% on a mass basis.

As was discussed in the previous ABD flowsheet evaluation, after processing is complete in the DWPF CPC, the melter feed slurry composition (particularly nitrate and glycolate) in the cases where none or two-thirds of the ABD is added prior to LTAD is even more similar. Since there will likely be less nitrate in the Tank 40 slurry because more of the nitrate is decanted during LTAD, then more glycolate will be added and the melter feed is very similar in both cases to produce a melter feed with a balanced reduction/oxidation potential. Thus, from a melter and glass perspective, the addition of ABD prior to or after LTAD will result in slurries and melter feed that are very similar in composition.

Based on the discussion in this section and the rest of Section 3, there are no reasons to limit the fraction of the H-Canyon ABD additions that will undergo aluminum dissolution. Neither the plan to add two-thirds of the ABD material prior to LTAD nor adding all of the ABD material prior to LTAD should contribute to risks beyond what was present for adding the ABD material after the completion of LTAD.

3.2.5 *Other Issues*

The TTR Task 2h directed that SRNL add other questions or open items to the TTQAP identified by SRNL that require investigation. At the time of writing the TTQAP, an open item involving the observation of higher uranium enrichment in the soluble portion of the feed slurry used in the gadolinium solubility testing was identified. This item was addressed in Section 3.1.3 and elsewhere in this report. In the course of this flowsheet evaluation, there were no additional issues or open items identified that warranted further evaluation.

3.3 Addition of ABD During Pre-LTAD Sodium Hydroxide Additions

This section addresses the change in scope involving the transfer of ABD streams to Tank 51 intermittently along with LTAD-related sodium hydroxide additions, as communicated in an email request.[9] The initial plan was to only add sodium hydroxide needed for LTAD after the completion of the pre-LTAD ABD transfer windows. In order to allow for larger ABD transfer windows, the LTAD plan has evolved to also allow for sodium hydroxide additions prior to and concurrent with ABD transfer windows. SRMC requested that SRNL assess the gaps associated with this new proposed evolution for the neutralized ABD streams.

There were four specific areas of concern in the SRMC email:[9]

- Aluminum removal
- Actinide enrichment in the decanted supernate
- Rheological behavior
- Gd solubility

As communicated in Sections 3.1 and 3.1.3, and emphasized again in the email request,[9] there are two potential neutralized H-Canyon stream scenarios that have been discussed for the receipt of ABD. The first is that H-Canyon will co-precipitate the enriched and depleted uranium solutions together (targeting a ^{235}U enrichment of ~4.9 wt%). The second is that, if processing issues are encountered, H-Canyon may send separate transfers of precipitated enriched uranium streams and depleted uranium streams. New to this analysis, these streams would be sent intermittently as time allows, either before or after sodium hydroxide additions to Tank 51 have been initiated.

Section 3.2.1 described that during the pH-adjustment operation in H-Canyon, much of the aluminum in the ABD material is expected to precipitate as $Al(OH)_3$ (gibbsite and bayerite) solids and a portion of the aluminum will remain soluble as $Al(OH)_4^-$ (aluminate) ion. During LTAD, increasing the hydroxide concentration increases aluminum solubility, causing dissolution of a portion of the solid aluminum phases. As also discussed in Section 3.2.1, the $Al(OH)_3$ solids in the ABD material is relatively easy to dissolve, compared with the dissolution of the AlOOH solids prominent in the legacy SRS sludge. While heat contributes to both the equilibrium and kinetics of $Al(OH)_3$ dissolution, the added sodium hydroxide will likely start dissolving the easier-to-dissolve $Al(OH)_3$ prior to the heating period of the LTAD process. Thus, some additional aluminum dissolution from the ABD material may be expected when it comes in contact with the sodium hydroxide added for LTAD, even before intentionally heating as part of the LTAD process. However, the proposed changes to the hydroxide addition timing would not negatively impact aluminum removal. There are no changes to the conclusions regarding the aluminum dissolution expectations.

As described in Sections 3.1.3 and 3.1.4, recent applicable tests and Tank 51 measurements suggest that the uranium enrichment in the Tank 51 supernate after ABD transfers may be biased toward the enrichment in the ABD material versus the enrichment of the bulk ABD slurry. If the targeted amount of depleted uranium is added during each transfer window to ensure that the material transferred during the window had a combined $^{235}\text{U/total U} \leq 0.05$ (5%), any supernate subsequently transferred out of Tank 51 would be expected to also have $^{235}\text{U/total U} \leq 0.05$. As described in Section 3.2.2.2, an increase in the hydroxide and aluminate concentrations is expected to slightly increase the U and Pu concentrations in the supernate because U and Pu are weakly amphoteric. This factor may increase the propensity for bias of the U enrichment in the supernate to be towards that of the cumulative ABD material enrichment if sodium hydroxide is added before and during the ABD transfer window. For this reason, consideration should be given to front-weighting transfers of depleted uranium for transfer windows where sodium hydroxide and

ABD material additions will overlap. However, even without this consideration, there should be no impacts from the proposed changes to the hydroxide addition timing as long as there is no supernate transferred out of Tank 51 during a transfer window and the plan for depletion to ^{235}U/total U ≤ 0.05 in the transferred material is followed. Furthermore, there are no changes to the conclusions regarding the Tank 51 supernate uranium enrichment expectations resulting from the proposed changes to the hydroxide addition timing.

Section 3.2.3 could not completely close potential impacts related to settling behavior and rheological properties resulting from adding ABD to SB11. The risks for negative impacts to settling or rheology from the addition of ABD to SB11, either after LTAD or with two-thirds added prior to LTAD, were judged to be consistent and within the typical level of these risks involved with assembling a sludge batch. Based on the other arguments in this section, the proposed changes to the sodium hydroxide addition timing should not greatly impact the soluble and insoluble composition of the slurry mixture. Thus, risks for negative impacts to settling or rheology from the addition of ABD to SB11 with the proposed change in sodium hydroxide addition timing are still consistent and within the typical level of these risks involved with assembling a sludge batch; and therefore, there are no changes to the conclusions.

As discussed in Section 3.2.2.2, in the high pH ABD stream transferred to Tank 51, gadolinium is expected to be primarily insoluble $Gd(OH)_3$. Gadolinium is not amphoteric and will not dissolve to become the soluble $Gd(OH)_4^-$ ion, regardless of when it comes in contact with the additional sodium hydroxide added for LTAD. Changes to the hydroxide addition timing do not result in changes to the conclusions regarding the gadolinium solubility expectations.

4.0 Conclusions and Recommendations

The following summarizes the evaluation of the impacts of increasing the quantity of gadolinium (and related topics) from what was previously evaluated in the three SRNL studies:

- Based on literature surveys, there is no indication that organic interactions with gadolinium will be significant at the high pH (typically >13) conditions of the CSTF. Any interactions of gadolinium with organics in DWPF are not expected to adversely impact DWPF or downstream facilities. Thus, there is little-to-no residual risk from organic interactions with gadolinium. [Gap closed]
- Adding depleted uranium to ABD material, targeting ^{235}U enrichment of 4.90% within each transfer window, will mitigate potential impacts from an increase in soluble ^{235}U enrichment during sludge washing and LTAD. The plan to take advantage of previous transfers and allow ^{235}U enrichment of >5% during the final transfer window carries a risk that Tank 51 supernate will have a ^{235}U enrichment of >5%, which should be evaluated for acceptance.
- Increasing the gadolinium mass ratio to 3.0:1 Gd:^{235}U(eq$_{SLU}$) should lead to the same or higher partitioning of gadolinium into the solid phase within the DWPF CPC, resulting in both liquid and solid phases with expected partitioning of Gd consistent with the prior solubility study. [Gap closed for SB11]
- There are no expected impacts on DWPF melt temperature and melter operations due to the minimal ~0.2 wt% increase in Gd concentration relative to previous sludge batches. [Gap closed for SB11]
- As observed previously, Gd is expected to enter the off-gas system via physical entrainment, but at a slightly higher concentration than what was observed for SB9 melter off-gas pluggage deposits (0.07 wt%). [Gap closed for SB11]
- There are no expected impacts on DWPF recycle or the RCT glycolate destruction process. [Gap closed for SB11]
- Gd is projected to be a trace component in the SB11 glass (<0.5 wt%) and can be ignored for process control. Trace components do not significantly impact glass durability, thus the conclusions of the previous Product Consistency Test evaluation at a fissile mass loading of 2,500 g fissile/m^3 glass still applies to SB11. The ~0.1 wt% increase in Gd_2O_3 concentration relative to the previous study will not impact the predictability of SB11 glass with the DWPF PCCS models for durability or the acceptability of glass according to the WAPS criterion for product consistency. [Gap closed for SB11]
- No additional TCLP testing is necessary for SB11 and the hazardous waste specification of the SB11 DWPF waste form is unchanged after the addition of the ABD stream. [Gap closed for SB11]

The following summarizes the evaluation of the impacts of adding two-thirds of the ABD material to Tank 51 prior to LTAD:

- The addition of two-thirds of the ABD increases overall aluminum mass from 1.39×10^4 kg to 1.64×10^4 kg (15.5% ABD Al). The form of the insoluble portion of the Al resulting from ABD addition should be the more readily dissolved $Al(OH)_3$ and amorphous forms. The portion of the ABD aluminum that is processed by LTAD is expected to be completely soluble, thus requiring that less of the boehmite in the sludge be dissolved to reach the same Al target in the SB. [Gap closed for SB11]
- The expected LTAD impact on other components, as related primarily to the components in ABD, are discussed. Gd is expected to remain insoluble during LTAD and not impact the solubility of other components. [Gap closed for SB11]
- The addition of two-thirds of the ABD increases overall projected SB11 uranium mass from 4,740 kg to 13,100 kg (63% ABD U) and the projected plutonium mass from 86.0 kg to 89.5 kg (3.9% ABD Pu). The addition of all of the ABD increases overall projected SB11 uranium mass from 4,740 kg to 16,100 kg (70% ABD U) and the projected plutonium mass from 86.0 kg to 90.4 kg

(5.3% ABD Pu). The ^{235}U enrichment will be ≤5%. fissile uranium will be adequately poisoned by Gd and the fissile Pu will be adequately poisoned by Fe from the sludge. [Gap closed for SB11]

- There is a low risk that ABD addition will impact the rheology or pumpability of the slurry. There is a low but higher risk of ABD addition prior to LTAD impacting the settling rate.
- Based on the evaluation of adding two-thirds of the ABD material and all of the ABD material prior to the LTAD process, there is no volume or mass limit that would need to be imposed on ABD additions prior to LTAD. [Gap closed for SB11]

Revision 1 of this report addresses a variation on the ABD additions and LTAD strategy where sodium hydroxide additions for LTAD may be performed intermittently or concurrently with an ABD addition window. The proposed change does not alter the conclusions of this evaluation.

Recommendations resulting from this work are as follows:

- ICP-ES is recommended for the measurement of Gd in DWPF SME acceptability samples if it becomes a reportable element (> 0.5 wt%) in future sludge batches.
- If future sludge batch projections indicate that Gd becomes a reportable element (>0.5 wt% in glass), then an evaluation of PCCS constraints and models will need to be performed followed by a revision to the SME acceptability document.
- If Gd concentrations are projected to exceed the 0.5 wt% reportable limit in glass, then a TTT diagram will need to be developed to continue to satisfy the WAPS criteria for phase stability.
- SRMC should evaluate whether the risk introduced by allowing the final ABD transfer window to have ^{235}U enrichment of >5% should be accepted.
- A sample of Tank 51 slurry is recommended for a more accurate determination of composition prior to LTAD.
- Samples of Tank 51 slurry or supernate that are taken during the assembly of SB11, especially samples after ABD addition and during LTAD and in-tank sludge washing, could provide useful additional information on gadolinium and supernate fissile uranium enrichment. This information could be used to aid in planning future ABD addition timing and potentially relax uranium enrichment requirements.
- Consider sampling Tank 51 earlier in the LTAD process in case the aluminum dissolution target is met sooner than expected.

5.0 References

1. *Accelerated Basin Deinventory (ABD) Program Plan*; SRNS-RP-2019-00651, Rev. 1; Savannah River Nuclear Solutions: Aiken, SC, 2020.

2. *Spent Nuclear Fuel Management, Accelerated Basin De-Inventory Mission for H-Canyon, at the Savannah River Site*; 87 FR 23504 (Document Number 2022-08383); Department of Energy - Office of Environmental Management: Washington, DC, 2022.

3. Chew, D. P.; Hamm, B. A.; Wells, M. N. *Liquid Waste System Plan Revision 22*; SRR-LWP-2009-00001, Revision 22; Savannah River Remediation: Aiken, SC, 2021.

4. Lambert, D. P.; Hobbs, D. T. *Increased Fissile Loading Flowsheet Review*; SRNL-STI-2021-00156, Revision 0; Savannah River National Laboratory: Aiken, SC, 2021.

5. Williams, M. S.; Martino, C. J.; Coleman, C. J. *Gadolinium Poison Solubility Testing for the Downstream Impacts from Accelerated Basin De-Inventory*; SRNL-STI-2021-00006, Revision 0; Savannah River National Laboratory: Aiken, SC, 2021.

6. Crawford, C. L.; Hsieh, M. C.; Johnson, F. C.; Lambert, D. P.; Pareizs, J. M.; Williams, M. S. *Demonstration of Defense Waste Processing Facility (DWPF) Higher Fissile Content Glass*; SRNL-STI-2021-00208, Rev. 0; Savannah River National Laboratory: Aiken, SC, 2021.

7. Fellinger, T. L. *Receipt of H-Canyon ABD Streams into Liquid Waste - Proposed Flowsheet Sequence Change*; X-TTR-S-00091, Revision 0; Savannah River Mission Completion: Aiken, SC, 2022.

8. Johnson, F. C.; Martino, C. J.; Lambert, D. P. *Task Technical and Quality Assurance Plan for a Technical Evaluation of the Flowsheet for Accelerated Basin De-Inventory Discards to Sludge Batch 11*; SRNL-RP-2022-00384, Revision 0; 2022.

9. Fellinger, T. L. *Draft Scope - Email Request for X-TTR-S-00091*; received on January 30, 2023 at 11:02 AM and stored in Electronic Laboratory Notebook Experiment A6583-000142-34; 2023.

10. Reigel, M. M.; Truong, T. T. *Technology Maturation Roadmaps for Electrolytic Dissolution of Non-Aluminum Spent Nuclear Fuel (NASNF) at the Savannah River Site*; SRNL-L3100-2022-00042, Revision 0; Savannah River National Laboratory: Aiken, SC, 2022.

11. Reigel, M. M.; Moore, E. N.; Skidmore, T. E.; Boerstler, J. T. *Summary of FY2021 Lab Policy Office (LPO) Non-Aluminum Spent Nuclear Fuel (NASNF) Accomplishments and Proposed Scope for FY2022*; SRNL-TR-2021-00656, Revision 0; Savannah River National Laboratory: Aiken, SC, 2021.

12. Moore, E. N.; Pierce, R. A.; Reigel, M. M.; Truong, T. T. *NASNF Processing and Packaging Technical Study*; SRNL-TR-2020-00313, Revision 0; Savannah River National Laboratory: Aiken, SC, 2020.

13. *Technical Reviews*; Manual E7, Procedure 2.60, Rev. 20; Savannah River Site: Aiken, SC, 2021.

14. Le, T. A. *SB11 elemental compositions projection including RCRA metal*; to F.C. Johnson, received on August 2, 2022 at 7:47 AM and stored in Electronic Laboratory Notebook Experiment C7592-00311-45; 2022.

15. Horton, W. C. *Nuclear Criticality Safety Evaluation: Processing at DWPF*; N-NCS-S-00012, Rev. 2; Amentum: Aiken, SC, 2021.

16. Mellon, J. R. *Waste Characterization Report for H-Canyon Accelerated Basin De-Inventory Solution for Disposal to Sludge Batch 11*; SRNS-E1121-2022-00021, Revision 1; Savannah River Nuclear Solutions: Aiken, SC, 2022.

17. Walker, D. D. *Organic Compounds in Savannah River Site High-Level Waste*; WSRC-TR-2002-00391, Revision 0; 2002.

18. Hobbs, D. T. *Possible Explosive Compounds in The Savannah River Site Waste Tank Farm Facilities*; WSRC-TR-91-444; Savannah River Laboratory: Aiken, SC, 1991.

19. Britt, T. E. *Resolution of the Organic PISA*; WSRC-TR-2002-00094, Revision 3; Westinghouse Savannah River Company: Aiken, SC, 2003.

20. Swingle, R. F. *Organic PISA Table Top Review for Miscellaneous Organic Compounds in the Tank Farm*; SRT-LWP-99-00081, Revision 0; Savannah River Technology Center: Aiken, SC, 1999.

21. Crawford, C. L.; Fink, S. D.; Nash, C. A.; Pareizs, J. M. *Evaluation of the Current State of Knowledge for Thermolysis of Organics within SRS Waste Forming Volatile Organic Compounds (VOCs)*; SRNL-STI-2018-00163, Revision 1; 2019.

22. Britt, T. E. *Location of the Principal Volatile Organics, Ammonia Compounds, Organo-Metallics, and NOx Gasses Resident in the Tank Farm*; X-ESR-H-00020, Revision 0; Westinghouse Savannah River Company: Aiken, SC, 2004.

23. Ball, E. A. *Safety Analysis Input CST-I-PR-0054: Hydrogen Generation Rate for Bounding Supernate*; CST-I-PR-0054; Savannah River Remediation: Aiken, SC, 2020.

24. Woodham, W. H.; Martino, C. J. *Evaluation of Thermolytic Production of Hydrogen from Glycolate and Common Tank Farm Organics in Simulated Waste*; SRNL-STI-2019-00605, Revision 1; Savannah River National Laboratory: Aiken, SC, 2020.

25. Sherry, A. D.; Caravan, P.; Lenkinski, R. E., A Primer on Gadolinium Chemistry. *Journal of Magnetic Resonance Imaging*, *30* (6), pp 1240-1248, **2009**.

26. Clough, T. J.; Jiang, L.; Wong, K. L.; Long, N. J., Ligand design strategies to increase stability of gadolinium-based magnetic resonance imaging contrast agents. *Nat Commun*, *10* (1420), pp 1420-1433, **2019**.

27. Riri, M.; Hor, M.; Kamal, O.; Eljaddi, T.; Benjjar, A.; Hlaibi, M., New Gadolinium(III) Complexes with Simple Organic Acids (Oxalic, Glycolic, and Malic Acid). *Journal of Materials and Environmental Science*, *2* (3), pp 303-308, **2011**.

28. Adu-Wusu, K. *Literature Review on Impact of Glycolate on the 2H Evaporator and the Effluent Treatment Facility (ETF)*; SRNL-STI-2012-00132, Revision 0; 2012.

29. Sonesson, A., On the Complex Chemistry of the Tervalent Rare-Earth Ions III. The Glycolate Systems. *Acta Chem. Scand.*, *13*, pp 998-1010, **1959**.

30. Powell, J. E.; Suzuki, Y., Formation Constants of the Rare Earth Glyoxylate Complex Species. *Inorganic Chemistry*, *3* (5), pp 690-692, **1964**.

31. Arnold, J. P. *Waste Acceptance Criteria for Liquid Waste Transfers to the Tank Farms (U)*; X-SD-G-00009, Revision 11; Savannah River Mission Completion: Aiken, SC, 2023.

32. Martino, C. J.; Pareizs, J. M.; Newell, J. D. *Thermolytic Hydrogen Generation Testing of Tank 22 Material*; SRNL-STI-2018-00385, Revision 0; Savannah River National Laboratory: Aiken, SC, 2018.

33. Martino, C. J.; Pareizs, J. M.; Woodham, W. H. *Investigation of Thermolytic Hydrogen Generation Rate in Tank 44 Dissolved Saltcake Samples*; SRNL-STI-2019-00730, Revision 1; Savannah River National Laboratory: Aiken, SC, 2021.

34. Pareizs, J. M.; Siegfried, M. J.; Martino, C. J.; Williams, M. S.; Stanfield, A. N.; Johnson, F. C.; Crawford, C. L. *Radioactive Waste Sludge Washing and Demonstration of the Nitric-Glycolic Acid Flowsheet for Sludge Batch 10 Qualification*; SRNL-STI-2022-00255, Revision 0; Savannah River National Laboratory: Aiken, SC, 2022.

35. Martino, C. J.; Coleman, C. J. *Solubility Testing to Support the Addition of Sodium Reactor Experiment Material to Sludge Batch 10*; SRNL-STI-2020-00294, Revision 0; 2020.

36. Newell, J. D.; Pareizs, J. M.; Martino, C. J.; Reboul, S. H.; Coleman, C. J.; Edwards, T. B.; Johnson, F. C. *Actual Waste Demonstration of the Nitric-Glycolic Flowsheet for Sludge Batch 9 Qualification*; SRNL-STI-2016-00327, Revision 1; Savannah River National Laboratory: Aiken, SC, 2016.

37. Lambert, D. P.; Williams, M. S.; Brandenburg, C. H.; Luther, M. C.; Newell, J. D.; Woodham, W. H. *Sludge Batch 9 Simulant Runs Using the Nitric-Glycolic Acid Flowsheet*; SRNL-STI-2016-00319, Revision 0; 2016.

38. Woodham, W. H.; Howe, A. M.; Siegfried, M. J. *Sludge Batch 10 Flowsheet Testing with Non-radioactive Simulants*; SRNL-STI-2021-00349, Rev. 0; Savannah River National Laboratory: Aiken, SC, 2021.

39. Isom, S. T. *Technology Development Roadmap for Nitric-Glycolic Acid Flowsheet*; SRR-STI-2012-00676, Revision 1; Savannah River Remediation: Aiken, SC, 2020.

40. Nash, C. A.; Siegfried, M. J. *Permanganate Oxidation of Actual Defense Waste Processing Facility (DWPF) Slurry Mix Evaporator Condensate Tank (SMECT) and Offgas Condensate Tank (OGCT) Samples to Remediate Glycolate*; SRNL-STI-2020-00012, Revision 0; Savannah River National Laboratory: Aiken, SC, 2020.

41. Zamecnik, J. R.; Lambert, D. P.; Riley, W. T.; Ramsey, W. G. *Permanganate Oxidation of Defense Waste Processing Facility (DWPF) Recycle Collection Tank (RCT) Simulants – Protocol Runs for Nominal and Chemical Process Cell (CPC) Foamover Conditions*; SRNL-STI-2019-00292, Revision 0; Savannah River National Laboratory: Aiken, SC, 2019.

42. Siegfried, M. J.; Ramsey, W. G.; Williams, M. S. *Permanganate Oxidation of Defense Waste Processing Facility (DWPF) Recycle Collection Tank (RCT) Simulants Larger Scale Protocol Runs - Chemical Process Cell (CPC) Nominal and Foamover Conditions*; SRNL-STI-2019-00588, Revision 0; Savannah River National Laboratory: Aiken, SC, 2019.

43. Holtzscheiter, E. W. *Defense Waste Processing Facility (DWPF) Transition Plan from the Nitric-Formic Acid Flowsheet to the Nitric-Glycolic Acid Flowsheet*; X-ESR-S-00317, Revision 2; Savannah River Mission Completion: Aiken, SC, 2022.

44. Pareizs, J. M. *Characterization of the Sludge Batch 10 Confirmation Sample (HTF-51-22-87/88)*; SRNL-TR-2022-00592, Revision 0; Savannah River National Laboratory: Aiken, SC, 2022.

45. Ray, J. W. *Waste Acceptance Criteria for Raw Salt Solution, Sludge and SWPF Salt Streams Transfers to DWPF*; X-SD-S-00001, Revision 4; Savannah River Mission Completion: Aiken, SC, 2022.

46. Newell, J. D.; Pareizs, J.; Martino, C. J.; Reboul, S. H.; Coleman, C. J.; Edwards, T. B.; Johnson, F. C. *Actual Waste Demonstration of the Nitric-Glycolic Flowsheet for Sludge Batch 9 Qualification*; SRNL-STI-2016-00327, Revision 1; Savannah River National Laboratory: Aiken, SC, 2017.

47. Johnson, F. C. *Analysis of DWPF Sludge Batch 7a (Macrobatch 8) Pour Stream Samples*; SRNL-STI-2012-00017, Rev. 1; Savannah River National Laboratory: Aiken, SC, 2012.

48. Ray, J. W.; Culbertson, B. H.; Marra, S. L.; Jantzen, C. M.; Edwards, T. B.; Ramsey, A. A. *Technical Bases for the DWPF Glass Product Control Program*; WSRC-IM-91-116-5, Rev. 4; Savannah River Remediation: Aiken, SC, 2018.

49. Ray, J. W.; Culbertson, B. H.; Marra, S. L.; Plodinec, M. J. *DWPF Glass Product Control Program*; WSRC-IM-91-116-6, Rev. 9; Savannah River Remediation: Aiken, SC, 2018.

50. Marra, J. C.; Crawford, C. L.; Bibler, N. E. *Glass Fabrication and Product Consistency Testing of Lanthanide Borosilicate Frit X Composition for Plutonium Disposition* WSRC-STI-2006-00318 Rev. 0; Savannah River National Laboratory: Aiken, SC, 2006.

51. Crawford, C. L. *Characterization of DWPF Melter Primary Off-Gas Line Pluggage Deposits*; SRNL-STI-2022-00196, Rev. 0; Savannah River National Laboratory: Aiken, SC, 2022.

52. *DWPF Waste Form Compliance Plan*; WSRC-IM-91-116-0, Rev. 13; Savannah River Remediation: Aiken, SC, 2021.

53. Pareizs, J. M.; Bannochie, C. J.; Click, D. R.; Lambert, D. P.; Stone, M. E.; Pickenheim, B. R.; Billings, A. L.; Bibler, N. E. *Sludge Washing and Demonstration of the DWPF Flowsheet in the SRNL Shielded Cells for Sludge Batch 5 Qualification*; SRNS-STI-2008-00111, Rev. 0; Savannah River National Laboratory: Aiken, SC, 2008.

54. Pareizs, J. M.; Pickenheim, B. R.; Bannochie, C. J.; Billings, A. L.; Bibler, N. E.; Click, D. R. *Sludge Washing and Demonstration of the DWPF Flowsheet in the SRNL Shielded Cells for Sludge Batch 6 Qualification*; SRNL-STI-2010-00353, Rev. 0; Savannah River National Laboratory: Aiken, SC, 2010.

55. Pareizs, J. M.; Billings, A. L.; Click, D. R. *Sludge Washing and Demonstration of the DWPF Flowsheet in the SRNL Shielded Cells for Sludge Batch 7a Qualification*; SRNL-STI-2011-00226, Rev. 0; Savannah River National Laboratory: Aiken, SC, 2011.

56. Pareizs, J. M.; Billings, A. L.; Reboul, S. H.; Lambert, D. P.; Click, D. R. *Sludge Batch 7b Qualification Activities with SRS Tank Farm Sludge*; SRNL-STI-2011-00548, Rev. 0; Savannah River National Laboratory: Aiken, SC, 2011.

57. Pareizs, J. M.; Crawford, C. L. *The DWPF Flowsheet in the SRNL Shielded Cells for Sludge Batch 8 Qualification*; SRNL-STI-2013-00116, Rev. 0; Savannah River National Laboratory: Aiken, SC, 2013.

58. Reigel, M. M.; Bibler, N. E. *Analysis of Sludge Batch 4 (Macrobatch 5) for Canister S02902 and Sludge Batch 5 (Macrobatch 6) for Canister S03317 DWPF Pour Stream Glass Samples*; SRNL-STI-2010-00435, Rev. 0; Savannah River National Laboratory: Aiken, SC 2010.

59. Johnson, F. C. *Analysis of DWPF Sludge Batch 6 (Macrobatch 7) Pour Stream Glass Samples*; SRNL-STI-2011-00555, Rev. 0; Savannah River National Laboratory: Aiken, SC, 2012.

60. Johnson, F. C.; Crawford, C. L.; Pareizs, J. M. *Analysis of the Sludge Batch 7b (Macrobatch 9) DWPF Pour Stream Glass Sample*; SRNL-STI-2013-00462, Rev. 1; Savannah River National Laboratory: Aiken, SC, 2020.

61. McClane, D. L. *Analysis of the Sludge Batch 8 (Macrobatch 10) DWPF Pour Stream Glass Sample*; SRNL-STI-2018-00699, Rev. 0; Savannah River National Laboratory: Aiken, SC, 2019.

62. *Waste Acceptance Product Specifications (WAPS) for Vitrified High-Level Waste Forms*; DOE/EM-0093, Rev. 2; Department of Energy - Office of Environmental Management: 1996.

63. Tenpenny, D. W. *RE: ABD Gap Analysis Weekly Team Meeting*; to H.B. Shah, received on January 24, 2022 at 1:13 PM and stored in Electronic Laboratory Notebook Experiment C7592-00311-45; 2022.

64. Henley, D. B. *Preliminary System Impact Evaluation for Accelerated Basin De-inventory (ABD) Addition to Sludge Batch 11*; X-ESR-H-01129, Rev. 0; Savannah River Mission Completion: Aiken, SC, 2022.

65. Benhardt, H. C. *Nuclear Criticality Safety Evaluation: Transfer Facilities Operations*; N-NCS-G-00182, Rev. 1; Amentum: Aiken, SC, held for implementation.

66. Mellon, J. R. *Gadolinium: Equivalent Uranium-235 Ratio Criticality Safety Operating Limit for H-Canyon Sludge Batch 11 Solution*; N-CLC-H-01018, Rev. 0; Savannah River Nuclear Solutions: Aiken, SC, 2022.

67. Edwards, T. B. *SME Acceptability Determination for DWPF Process Control*; WSRC-TR-95-00364, Rev. 6; Savannah River National Laboratory: Aiken, SC, 2017.

68. Jantzen, C. M.; Pickett, J. B.; Brown, K. G.; Edwards, T. B.; Beam, D. C. *Process/Product Models for the Defense Waste Processing Facility (DWPF): Part I. Predicting Glass Durability from Composition Using a Thermodynamic Hydration Energy Reaction Model (THERMO)*; WSRC-TR-93-672, Rev. 1; Westinghouse Savannah River Company: Aiken, SC, 1995.

69. Billings, A. L.; Edwards, T. B. *Time-Temperature-Transformation (TTT) Diagrams for Future Waste Compositions*; SRNL-STI-2010-00373, Rev. 0; Savannah River National Laboratory: Aiken, SC, 2010.

70. Billings, A. L.; Edwards, T. B. *Time-Temperature-Transformation (TTT) Diagrams for the Sludge Batch 3 - Frit 418 Glass System*; SRNL-STI-2009-00025, Rev. 0; Savannah River National Laboratory: Aiken, SC, 2009.

71. Cicero, C. A.; Marra, S. L.; Andrews, M. K. *Phase Stability Determinations of DWPF Waste Glasses* WSRC-TR-93-00227, Rev. 0; Westinghouse Savannah River Company: Aiken, SC, 1993.

72. Ray, J. W.; Culbertson, B. H.; Marra, S. L.; Andrews, M. K.; Cicero, C. A.; Hardy, B. J.; Plodinec, M. J. *Phase Stability and Control of the Temperature of the DWPF Product*; WSRC-IM-91-116-7, Rev. 2; Savannah River Remediation: Aiken, SC, 2016.

73. *Toxicity Characteristic Leaching Procedure*; SW-846 Method 1311; Environmental Protection Agency: Washington, DC, 1992; pp 1-35.

74. Applewhite Ramsey, A.; Marra, S. L.; Plodinec, M. J. *Hazardous Waste Determination of the DWPF Product*; WSRC-IM-91-116-13, Rev. 0; Westinghouse Savannah River Company: Aiken, SC, 1995.

75. *Identification and Listing of Hazardous Waste*; 40 C.F.R. § 261; 2012.

76. *Analytical Laboratories Customer Sample Reports*; Sample IDs 40012567, 40012577, 40012578, 40012766, 40012767, 40012851, and 40012886; Savannah River National Laboratory: Aiken, SC, 2022.

77. Pereira, J. A. M.; Schwaab, M.; Dell'Oro, E.; Pinto, J. C.; Monteiro, J. L. F.; Henriques, C. A., The kinetics of gibbsite dissolution in NaOH. *Hydrometallurgy*, *96* (1), pp 6-13, **2009**.

78. Taylor-Pashow, K. M. L. *Neutralizations of High Aluminum Low Uranium Used Nuclear Fuel Solutions Containing Gadolinium as a Neutron Poison*; SRNL-STI-2011-00316, Rev. 0; 2011.

79. Taylor-Pashow, K. M. L.; Hansen, E. K.; Rudisill, T. S.; Trivelpiece, C. L. *Flowsheet for the Neutralization of Accelerated Basin De-inventory (ABD) Material*; SRNL-STI-2022-00114, Revision 0; Savannah River National Laboratory: Aiken, SC, 2022.

80. Gong, X.; Nie, Z.; Qian, M.; Liu, J.; Pederson, L. A.; Hobbs, D. T.; McDuffie, N. G., Gibbsite to Boehmite Transformation in Strongly Caustic and Nitrate Environments. *Industrial & Engineering Chemistry Research*, *42* (10), pp 2163-2170, **2003**.

81. Keefer, M. T.; Hamm, B. A.; Pike, J. A., Low Temperature Aluminum Dissolution of Sludge Waste. In *WM2008 Conference*, Phoenix, AZ, 2008; Vol. Abstract #8175.

82. Pike, J. A. *Evaluation of Low Temperature Aluminum Dissolution in Tank 51*; SRNS-STI-2008-00021, Revision 0; Savannah River National Laboratory: Aiken, SC, 2008.

83. Pike, J. A. *Risk Summary for Low Temperature Aluminum Dissolution (LTAD) in Tank 51*; LWO-LWE-2007-00223, Revision 0; Westinghouse Savannah River Company: Aiken, SC, 2007.

84. McCabe, D. J.; Peterson, R. A.; Pike, J. A.; Wilmarth, W. R. *Aluminum and Chromium Leaching Workshop Whitepaper*; WSRC-STI-2007-00168, Revision 0; Savannah River National Laboratory: Aiken, SC, 2007.

85. Clark, D. J. *Tank 12 Low Temperature Aluminum Dissolution Campaign: Engineering Log and Historical Events*; SRR-LWE-2013-00121; Savannah River Remediation: Aiken, SC, 2013.

86. Bronikowski, M. G.; Gray, J. H.; Hill, B. C.; Graham, F. R.; Karraker, D. G. *Caustic Precipitation of Plutonium using Gadolinium as the Neutron Poison for Disposition to High Level Waste*; WSRC-TR-2002-00198, Rev. 0; Westinghouse Savannah River Company: Aiken, SC, 2002.

87. Bronikowski, M. G.; Rudisill, T. C. *Neutralization of Plutonium and Enriched Uranium Solutions Containing Gadolinium as a Neutron Poison*; WSRC-TR-2004-00053, Rev. 0; Westinghouse Savannah River Company: Aiken, SC, 2004.

88. Gadolinium(III) Sulfate, CAS No. 13450-87-8. https://chemicalbook.com/ChemicalProductProperty_EN_CB5248081.htm (accessed September 25, 2022).

89. Pourbaix, M., *Atlas of Electrochemical Equilibria in Aqueous Solutions*. NACE: Houston, TX, 1974.

90. Hobbs, D. T.; Edwards, T. B.; Fleischman, S. D. *Solubility of Plutonium and Uranium in Alkaline Salt Solutions (U)*; WSRC-TR-93-056; Westinghouse Savannah River Company: Aiken, SC, 1993.

91. Rudisill, T. C.; Hobbs, D. T.; Edwards, T. B., Plutonium Solubility in Simulated Savannah River Site Waste Solutions. *Separation Science and Technology*, *45* (12-13), pp 1782-1792, **2010**.

92. Isom, S. T. *SB11 RCRA metals clarification*; to F.C. Johnson, received on November 9, 2022 at 12:53 PM and stored in Electronic Laboratory Notebook Experiment C7592-00311-45; 2022.

Appendix A. Data Used to Support Glass Evaluations in Sections 3.1.6 and 3.1.7

Table A-1. SB11 Tank 40 Blend Projection (Calcined Solids Basis)[14]

Element	Concentration (wt%)	Oxide	Concentration (wt%)
Ag	4.52E-02	AgO	5.19E-02
Al	1.16E+01	Al_2O_3	2.19E+01
As	4.86E-04	As_2O_3	6.42E-04
B	5.92E-02	B_2O_3	1.91E-01
Ba	1.24E-01	BaO	1.39E-01
Ca	1.39E+00	CaO	1.94E+00
Cd	2.04E-03	CdO	2.33E-03
Ce	1.78E-01	Ce_2O_3	2.08E-01
Cr	2.23E-01	Cr_2O_3	3.27E-01
Cu	6.30E-02	CuO	7.89E-02
Fe	1.47E+01	Fe_2O_3	2.10E+01
Gd	5.25E-01	Gd_2O_3	6.05E-01
K	1.81E-01	K_2O	2.18E-01
La	7.66E-02	La_2O_3	8.98E-02
Li	1.70E-01	Li_2O	3.66E-01
Mg	3.30E-01	MgO	5.48E-01
Mn	2.99E+00	MnO	3.87E+00
Mo	1.23E-02	MoO_3	1.84E-02
Na	2.12E+01	Na_2O	2.85E+01
Ni	5.45E-01	NiO	6.94E-01
P	6.28E-02	P_2O_5	1.44E-01
Pb	3.82E-01	PbO	4.11E-01
Pu	2.75E-02	PuO_2	3.11E-02
S	4.74E-01	SO_4^{2-}	1.42E+00
Se	8.97E-04	SeO_2	1.26E-03
Si	3.93E+00	SiO_2	8.40E+00
Sr	7.15E-02	SrO	8.46E-02
Th	1.66E+00	ThO_2	1.89E+00
Ti	1.60E-02	TiO_2	2.67E-02
U	5.68E+00	U_3O_8	6.70E+00
Zn	6.82E-02	ZnO	8.49E-02
Zr	2.84E-01	ZrO_2	3.84E-01

This SB11 Tank 40 blend projection includes the contribution of RCRA metals from both the source waste tanks and the expected ABD stream. Per SRMC System Planning, no data is available for As or Cd in any of the source tanks; however, a Cd value for the SB10 heel was included based on SRNL analysis.[92] Se was converted to a mass from Se-79 as no stable form of Se was tracked in the source tanks. H-Canyon samples representative of the expected ABD stream are shown in Table A-2.

Table A-2. Measured RCRA Metals Concentrations in ABD H-Canyon Samples (mg/L)[76]

Fuel Type	**Blend**	**HFIR**	**MTR**	**MTR**	**Blend**	**HFIR**	**Blend**
Tank(s)	10.2	8.3	7.4	11.1	16.3/16.4	11.2	10.4/12.1/12.3
Sample ID	40012567	40012577	40012578	40012766	40012767	40012851	40012886
Sample Date	2/2/2022	2/2/2022	2/2/2022	2/19/2022	2/19/2022	2/23/2022	2/19/2022
Ag	<0.345	<0.345	<0.335	<0.323	<59.1	<182	<74
As	<6.90	<6.91	<6.71	<6.46	<5.91	<6.64	<6.44
Ba	<104	<104	<101	74.6	53.8	42.5	52.8
Cd	<1.04	<1.04	<1.01	<0.969	<0.886	<0.995	<0.966
Cr	838	742	369	276	419	952	528
Pb	<20.7	<20.7	<20.1	<19.4	<17.7	<19.9	<19.3
Se	<6.90	<6.91	<6.71	<6.46	<5.91	<6.64	<6.44

ID = identification
HFIR = High Flux Isotope Reactor
MTR = Material Test Reactor

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