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Evaluation of a Material Balance Only and Material Balance with Real-Time In-line Monitoring Approaches for DFLAW Processing

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1.0 EXECUTIVE SUMMARY

The Assistant Manager, WTP chartered an Integrated Technical Team (ITT), which includes personnel from the Savannah River National Laboratory (SRNL), Pacific Northwest National Laboratory (PNNL), Bechtel National, Inc., and DOE-ORP, to evaluate the capability and potential benefits of replacing sample collection/analyses requirements with real-time, in-line monitoring.[1,2] The initial focus of the ITT is the Direct Feed Low Activity Waste (DFLAW) Program. This work scope is being performed in multiple phases. The Phase 2 work scope contains tasks to evaluate a materials balance only approach as well as continuing scoping evaluations for instruments that could be used for Real-Time In-Line Monitoring (RTIM). The Phase 2 work scope for evaluation of a materials balance approach was completed by both SRNL and PNNL and is documented in this report.

The material balance evaluation included a review of the WTP Low Activity Waste (LAW) vitrification process as well as the WTP Effluent Management Facility (EMF) process. Sampling requirements and unit operations were reviewed to determine which sample requirements could be met with a material balance without significantly increasing processing or reporting uncertainties. The following conclusions and recommendations were made:

Conclusions

- A material balance approach for determination of the CRV composition was determined to be feasible during the DFLAW portion of the WTP mission. Eliminating the CRV sample for routine analyses (LAW-1) did not lead to a significant increase in the compositional uncertainty of the glass as determined by evaluation of the waste loading achievable.
- Elimination of the MFPV sample (LAW-6) was determined to be technically feasible with a material balance approach. If routine sample analysis is retained, it is recommended that the batched Glass Former Chemicals (GFCs) be sampled in the Glass Feed Reagent System (GFR) blend hopper versus sampling the MFPV.
  - Development of LIBS system would allow on-line validation of the GFC composition
- The composition of the offgas condensate and other streams downstream of the melter cannot be reliably predicted with a material balance approach.
- The current sampling protocols for EMF operation cannot be reduced through a material balance approach as the melter condensate composition is not reliably predicted and the high turn-down ratio in the evaporator creates unacceptable uncertainty if attempting to predict the evaporator concentrate composition from the feed composition.
- The control software for the LAW facility can be updated to include an automated material balance for the CRV and MPFV batches based on detailed analysis of LAW feed and EMF concentrate without impacting the current sampling practices provided resources are available.
- Continued development of RTIM instruments for anion and metals analysis is needed if elimination of sampling for processes downstream of the melter is desired.
  - Raman/ATR-FTIR for anions (except Cl^-)
  - LIBS for metals and Cl

Recommendations

- A material balance approach for the CRV, based on LAW feed and EMF concentrate samples should be pursued to allow elimination of the routine CRV sample. It is not expected that use of a real-time monitoring system is needed to allow the sample analysis to be reduced to infrequent samples.
- The required frequency of periodic CRV samples should be estimated from known data on the uncertainty in material balance inputs.

- The sample analysis used for glass composition reporting should be moved from the CRV (LAW-1b) to the waste feed qualification sample
- A material balance approach should be pursued for the MFPV sample (LAW-6) based on the independent cross-checks performed during GFC batching with infrequent confirmation samples.
- Testing of a LIBS instrument for measurement of the GFC batch in the GFR System should be pursued to allow implementation of an on-line instrument if the material balance approach for the MFPV is not accepted by stakeholders.
- Development of RTIM instruments and data for EMF streams should continue, leveraging the information gained for evaluations of the LAW feed including RAMAN and LIBS.
- Communication with regulators and other stakeholders early in the process is recommended to gain their buy-in to the process and approval of required changes to regulatory documents.

It should be noted that the capability to take routine samples is not impacted by implementing an automated material balance for the DFLAW facility. Thus, the facility could proceed through cold commissioning and startup using the current sample plan and the data collected used to determine the efficacy of reducing the frequency or eliminating selected samples. This approach was used at the Defense Waste Processing Facility to eliminate routine sampling of the Melter Feed Tank. This type of phased implementation would reduce the risk that any unexpected processing issues would lead to unacceptable performance during startup.

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LIST OF ACRONYMS

ARP	Actinide Removal Process
BARD	Bases and Requirements Document
BNI	Bechtel National, Inc.
BOF	Balance of Facilities
CRV	Concentrate Receipt Vessel
DFLAW	Direct-Feed Low Activity Waste
DOE	U.S. Department of Energy
DWPF	Defense Waste Processing Facility
EMF	Effluent Management Facility
ATR-FTIR	Attentuated Total Reflectance – Foirier Transform InfraRed Spectroscopy
GFC	Glass Former Chemical
GFR	Glass Former Reagent system
HLW	High-Level Waste
IC	Ion Chromatography
IDF	Integrated Disposal Facility
ILAW	Immobilized Low-Activity Waste
ITT	Integrated Technical Team
LAW	Low-Activity Waste
LAWPS	Low-Activity Waste Pretreatment System
LIBS	Laser Induced Breakdown Spectroscopy
MCU	Modular Caustic Side Solvent Extraction Unit
MFPV	Melter Feed Preparation Vessel
MFV	Melter Feed Vessel
ORP	Office of River Protection
PNNL	Pacific Northwest National Laboratory
RTIM	Real-Time In-Line Monitoring
SBS	Submerged Bed Scrubber
SME	Slurry Mix Evaporator
SRAT	Sludge Receipt and Adjustment Tank
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
SWPF	Salt Waste Processing Facility
TSCR	Tank-Side Cesium Removal
WAC	Waste Acceptance Criteria

WESP	Wet Electrostatic Precipitator
WTP	Hanford Tank Waste Treatment and Immobilization Plant

3.0 INTRODUCTION

Effective operation of the Hanford Tank Waste Treatment and Immobilization Plant (WTP) will require information collected from sampling and/or monitoring to maintain environmental compliance, product quality, and operating efficiency. The U.S. Department of Energy (DOE) – Office of River Protection (ORP) recognizes the potential long-term benefit of developing real-time, in-line monitoring (RTIM) at the WTP to improve the current strategy of collecting tens of thousands of samples and analyzing them. In-line monitoring can decrease processing time associated with waiting for sample analysis, reduce workers' exposure to radiation and chemical hazards, decrease secondary waste volumes, potentially improve product quality, and provide production support and enhance overall operational control.

The Assistant Manager, WTP chartered an Integrated Technical Team (ITT), which includes personnel from the Savannah River National Laboratory (SRNL), Bechtel National, Inc., and DOE-ORP, to evaluate the capability and potential benefits of replacing routine sample collection requirements with real-time, in-line monitoring[1,2]. The initial focus of the ITT is the Direct Feed Low Activity Waste (DFLAW) Program. This work scope is being performed in multiple phases. Phase 1 is Requirements and Opportunities Analysis, Phase 2 is Applications and Benefits Determination, and Phase 3 is Qualification and Demonstration.

Phase 1 included 6 tasks[3] and was completed by SRNL in 2017. The tasks in Phase 1 were: (1) determining the functional requirements for determining analytes and properties of streams, (2) determining the technical basis for process control, (3) determining the sampling points within the Low Activity Waste (LAW) facility and Effluent Management Facility (EMF), (4) data quality and management, (5) process control challenges, and (6) preparing a Preliminary Analysis Plan[4-7]. DOE-ORP was briefed on the findings from the Phase 1 tasks and requested that Phase 2 work focus on establishing a basis for a materials balance approach that minimized process sampling[8].

The Phase 2 work scope contains tasks to evaluate a materials balance only approach as well as continuing scoping evaluations for instruments that could be used for RTIM[3]. The Phase 2 work scope was completed by both SRNL and Pacific Northwest National Laboratory (PNNL). The tasks performed in Phase 2 were:

1. Overall program administration and technical oversight
2. Evaluation of a Material Balance Approach
    a. Evaluation of uncertainty of this approach compared to uncertainty of current methods
    b. Evaluation of automating the material balance within the framework of existing control software
    c. Development of the methodology to obtain and evaluate data during cold commissioning to support a material balance approach
    d. Development of a framework to utilize during presentation of the revised approach to stakeholders and regulators
3. Screening Evaluations of Instruments to Supplement the Material Balance Approach
    a. AP-105 melter condensate evaluations
    b. Screening testing with simulants
4. Evaluation of the current DFLAW feed qualification program to identify analytes that could be eliminated
    a. Inorganic analytes
    b. Radionuclides
    c. Organic analytes

This report describes the results of Task 2, Evaluation of a Material Balance Approach. As shown above, this task was divided into 5 subtasks:

1. Perform an assessment of the uncertainty for replacement of the CRV samples (LAW-1a and b) with the waste feed qualification analysis including evaluation of utilizing an overall campaign approach for glass composition reporting versus a container specific composition. This assessment will provide a recommendation for frequency of periodic sampling of the CRV. This estimate will be provided by updating a previous PNNL evaluation[9], thus PNNL was the lead for this task. PNNL prepared a technical report to document the first half of this assessment[10].
2. Evaluation of automating the material balance calculation using the current LAW control system software or a separate software package that automatically gathers the required data from the analytical laboratories, pretreatment control system, LAW control system, and EMF control system. This task will result in a determination, documented in the combined report for the material balance evaluation, of the feasibility of implementation of an automated material balance program and a framework for implementation.
3. Development of a roadmap to utilize during cold commissioning to evaluate replacement of the MFPV sample with a material balance only approach. This evaluation will assess the required frequency of MFPV sampling as well as to recommend any additional controls for GFC additions that could reduce the needed sample frequency.
4. Prepare a combined report documenting the results of the evaluation of material balance approaches as well as to describe a framework to be utilized to present results to stakeholders. The document will be reviewed by BNI, PNNL, and DOE-ORP prior to issue.
5. Present results to ORP.

3.1 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60. The SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.

3.2 Background

The current DFLAW process flowsheet is shown in Figure 1[5]. Feed is received from the pretreatment process and blended with recycle (concentrated melter offgas condensate) in the Concentrate Receipt Vessel (CRV). A sample is taken of each CRV batch with a hold point for components that impact the GFC additions. After the required analytical results are received, the blended feed is transferred to the Melter Feed Preparation Vessel (MFPV) where the GFCs are added. A sample is taken after the GFCs are blended with the waste, but this sample is not a hold point. The MFPV batch is transferred to the Melter Feed Vessels (MFV) which meter feed into the melter. The high temperature of the melter evaporates all water and other volatile species, some of the semi-volatile species, and leads to the partial destruction of many species (nitrate, nitrite, most organics, carbonates, etc.). A molten glass is produced by the melter and poured into containers. The containers are decontaminated and disposed into the Integrated Disposal Facility (IDF). The treatment process is established and designed so that the resultant product will meet the waste acceptance criteria (WAC) for the IDF.

The water, species volatilized from the melter, and any entrained solids are sent to an offgas treatment system. This system condenses the water, scrubs any entrained particulate, and absorbs many of the volatile species not condensed. The resulting condensate contains approximately two-thirds of the technetium fed to the melter. A recycle loop is utilized to return this technetium to the melter to allow higher incorporation of the technetium into glass. Water is evaporated from the recycle stream in the EMF with the concentrate collected in the Evaporator Concentrate Vessel. A sample of the concentrate is taken and analyzed prior to recycling the material to the CRV.

Reporting of the glass composition of each ILAW container currently relies on the CRV sample results and known compositions and measured masses of GFC's, as shown in Figure 2[11]. MFPV results are not utilized in the glass composition reporting unless a significant issue is noted in the actual sample results versus the expected composition. Thus, a material balance is currently performed to allow the containerized glass composition to be calculated from the CRV composition. This material balance includes adjustment for heels in the MFPV, MFV, and melter. The measured GFC masses transferred to each MFPV batch are used in the calculations. Finally, the glass composition must be adjusted to account for volatility and entrainment during the melting process. Each glass species is assigned an assumed melter retention factor based on averages from pilot scale testing to convert the melter feed composition to a glass composition. The retention factors are not adjusted for any variations in melter processing and do not account for increased volatile losses if the melter is idled. It is noteworthy that sampling of the glass containers during operation is not planned. Therefore, the assumptions for single pass retention of radionuclides in the glass will not be validated during operation, although the mass balance will be validated during commissioning.

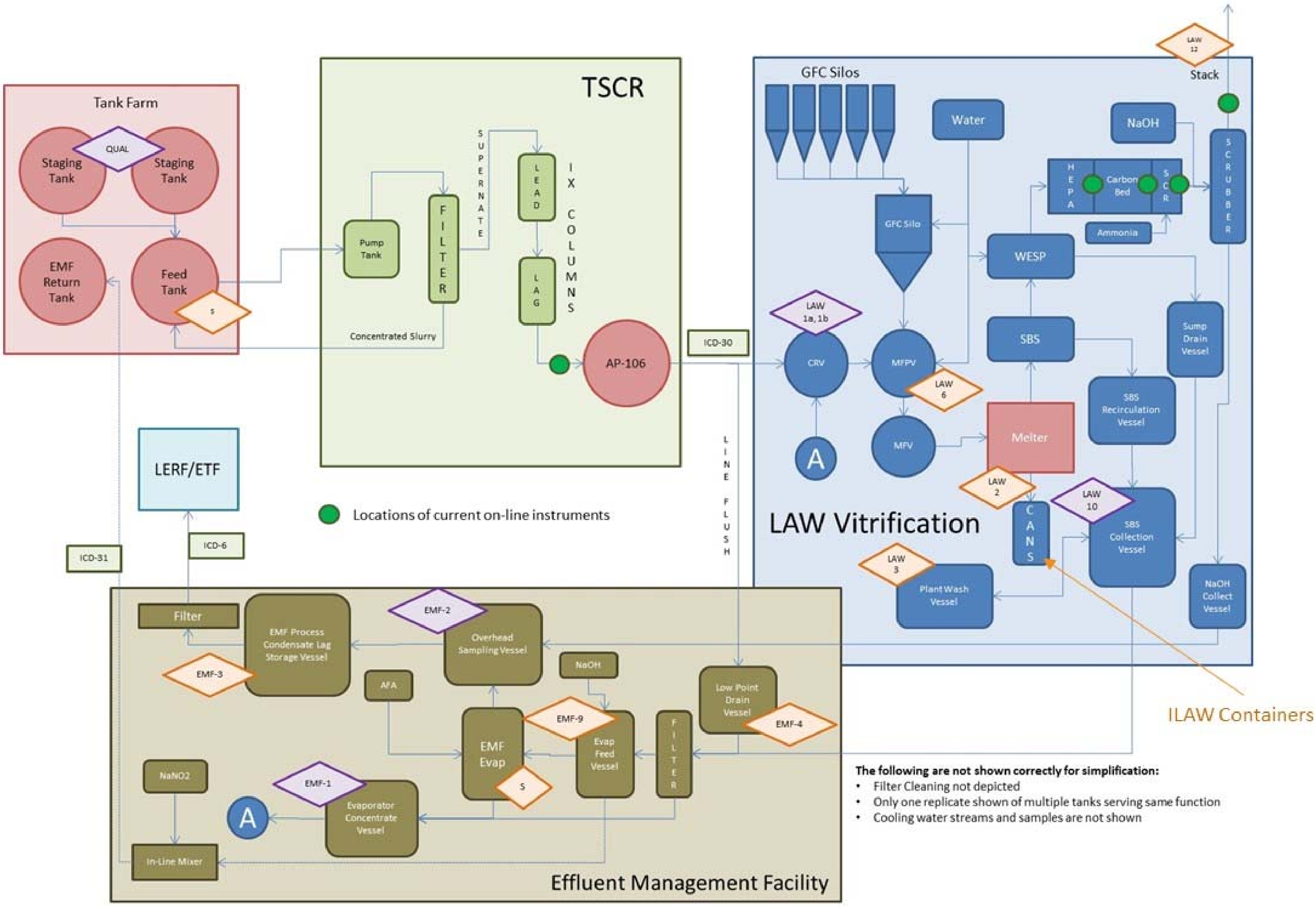

Figure 1. DFLAW Simplified Process Diagram

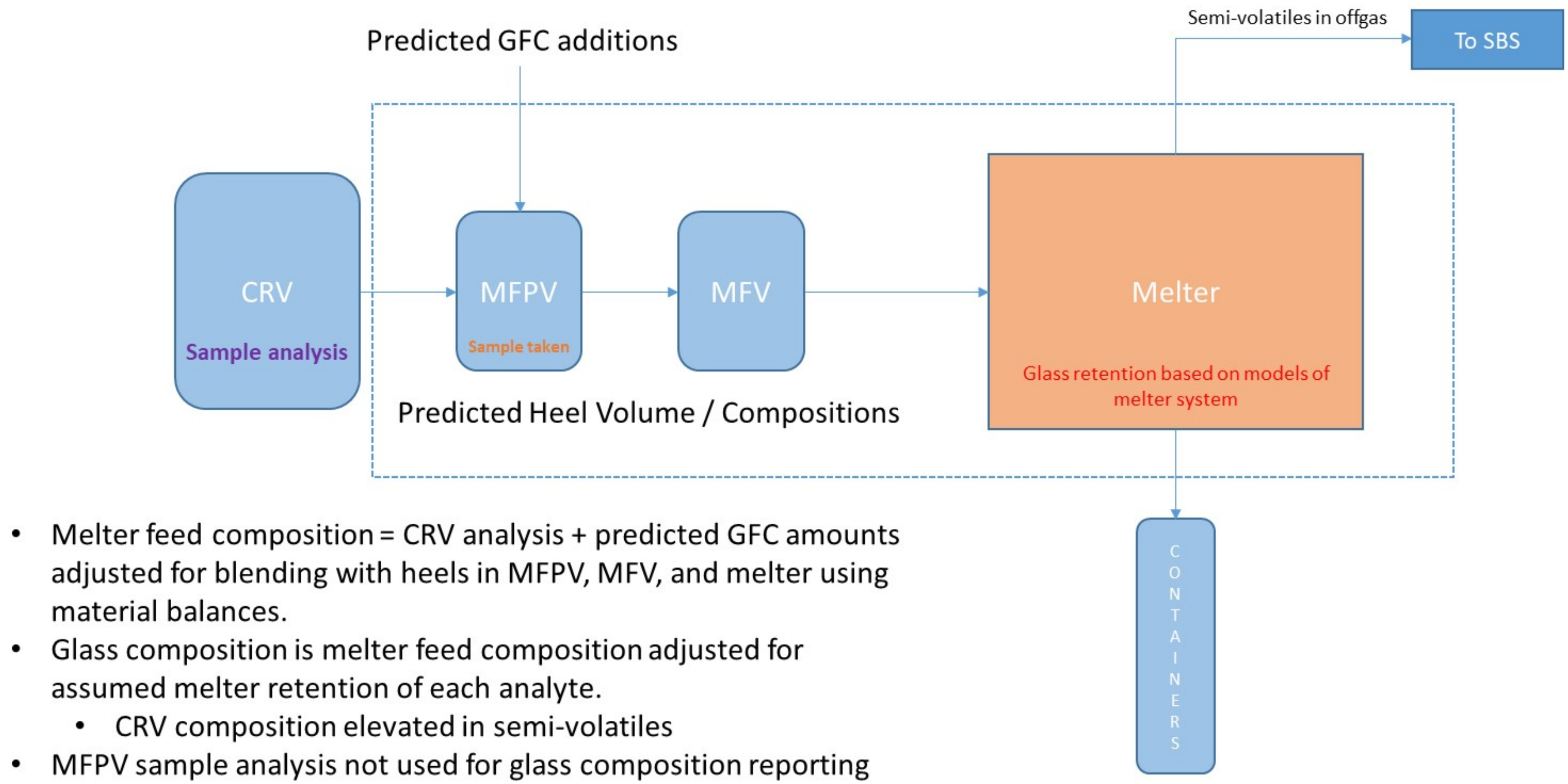

Figure 2. CRV Based Glass Composition Reporting

4.0 DISCUSSION

An evaluation was performed to determine the efficacy of using a material balance in place of sampling for the CRV and MFPV samples. The evaluation during Phase I of the current sample requirements for WTP LAW vitrification shows that elimination of the requirement to sample every batch of the CRV and MFPV would have the greatest impact on the number of samples taken during LAW vitrification facility operation. Of the 2600 samples estimated each year for LAW operation, over half are taken from these two vessels. These two vessels have the shortest cycle time, and the CRV sample is a hold point in the process. Utilization of a material balance only approach for these samples could allow minimization of these samples without needing additional process instrumentation.

It is noted that any material balance approach has limitations, described below, such that periodic re-baselining would be required. This re-baselining would most likely consist of taking samples and correcting the material balance for any differences noted. The frequency of the periodic rebaselining can be estimated from expected uncertainties; adjustments could be made as experience is gained during operations.

Material balances vulnerabilities include:

- Processing conditions that do not match expectations such as excessive holdup in process equipment from fouling or plugging
- Processing conditions outside of the assumed reactions/conditions in the material balance
- Processing upsets such as spills, foam overs, etc. that cause conditions that typically cannot be accurately accounted during material balance calculations

4.1 LAW Vitrification

4.1.1 *Reducing Frequency of CRV (LCP-VSL-00001/00002) Sampling (LAW 1a, 1b)*

During DFLAW, the CRV receives material from the LAWPS or TSCR process as well as concentrated recycle from the EMF[12]. The feed from the LAWPS/TSCR will match the composition of the feed qualification sample except for the solids removal and cesium absorption that occurs in the pretreatment step. It was assumed that evaluations of the pretreatment processes will allow accurate and conservative estimation of the feed to the CRV from LAWPS/TSCR. The EMF recycle is collected and sampled in the Evaporator Concentrate Vessel. It was assumed that this sample is not eliminated.

Each batch of the CRV is currently required to be sampled with a hold point in place for species required to perform the GFC additions during the Melter Feed Preparation Vessel cycle [4]. This sample was originally specified since the full WTP operation would result in significant blending of supernate from the LAW feed tank with washing and leaching effluents from HLW processing as well as HLW and LAW melter condensate. Thus, the chemical and radionuclide composition of the stream could be significantly different than the LAW feed during full WTP operation and a sample was deemed to be required. During DFLAW, the blending of the LAW feed with HLW effluents is eliminated, simplifying approaches to using a material balance to estimate the CRV composition.

An approach using the LAW qualification sample with validation of cesium removal, GFC weights, and the EMF concentrate sample could replace the CRV samples, provided an analysis of the uncertainty yielded acceptable results.

It should be noted that a similar approach is assumed for DFLAW operation in the Bases and Requirements Document for WTP[13]. Section 3.8.3.4 of that document states:

"It's assumed sampling at LCP-VSL-00001/00002 is eliminated. The elimination of sampling in LCP-VSL-00001/00002 will require a revision of 24590-WTP-PL-RT-03-001, Rev 5, *ILAW Product Compliance Plan*. Batch size and GFC amounts for making glass in the melters are to be estimated from (1) LAWPS treated LAW feed and DEP-VSL-00003A/B/C recycle samples, and (2) the volume of recycles expected to be delivered to the LCP-VSL-00001/00002 during the next LCP-VSL-00001/00002 batch cycle."

The statement in the BARD predates the recent changes to the LAWPS/TSCR process which eliminated the LAWPS lag storage tanks. Since the sampling that would have occurred in these deleted tanks is not planned in the revised strategy to utilize AP-106 for lag storage of treated feed as well as the feed tank for LAW vitrification, an updated uncertainty analysis was required for the RTIM program. This analysis is being performed by PNNL with initial results indicating that the uncertainty added by elimination of the CRV sample is acceptable[10].

4.1.2 *Flush Volumes*

Some flushing of process equipment and transfer lines is expected, but these volumes are expected to be minimal during DFLAW processing. However, when flush volumes are added to the waste feed to LAW, the resulting dilution in waste compositions will need to be accounted for. Periodic sampling of the CRV contents would allow the material balance to be reset from any errors in composition due to inaccuracies in the flush volume estimates.

4.1.3 *Radionuclides Removed during Pretreatment*

The qualification sample is taken upstream of the LAW pretreatment processes[14,15]. The pretreatment processes will remove solids and cesium from the LAW. Depending on the pretreatment process utilized, additional species could be removed (such as U, Np, Pu, Ca, and Sr). It is not expected that the GFC recipe will be changed by the differences in composition, but accurately reporting the radionuclide content of the immobilized LAW will require estimation of the removal of these species during pretreatment. Periodic sampling of the CRV contents would allow the material balance to be reset from any errors in composition due to inaccuracies in the assumptions for pretreatment partitioning.

4.1.4 *Glass Composition Reporting*

A revision to the glass composition methodology is recommended even if the CRV sample frequency is not changed. The revision would utilize the feed qualification sample for container composition reporting, as shown in Figure 3. This accounting method eliminates the need for assumptions of single pass melter retention; but requires assumptions for removal of species by the pretreatment processes. The periodic sampling from the CRV would be utilized to validate the assumptions of radionuclides removed by the LAW pretreatment process. Analytes to be measured during the periodic sampling would include Na, K, Cs-137, Sr-90, and all anions measured by IC.

The material balance would utilize the estimated GFC additions and would likely assume losses from other effluents (stacks, liquid secondary waste, solids secondary waste) are zero for most elements (notable exceptions include I-129 and Tc-99). It is noted that the amount of Tc-99 lost is expected to be very small (<100 Ci out of ~27,000) therefore an assumption of zero loss to the offgas for Tc-99 would not appreciably impact the container reporting. I-129 losses to the stack could be much higher on a percentage basis, but the offgas partitioning of I-129 is currently under review. It should be noted that the current method of partitioning Tc-99 and I-129 rely on single parameter estimates of melt retention that could be less accurate than assuming no loss on the entire system accounting for recycle. This revised approach is expected to provide better estimates for the overall contents of the LAW containers but it is acknowledged that using this approach for I-129 should be reviewed once the work in progress on I-129 partitioning is finalized.

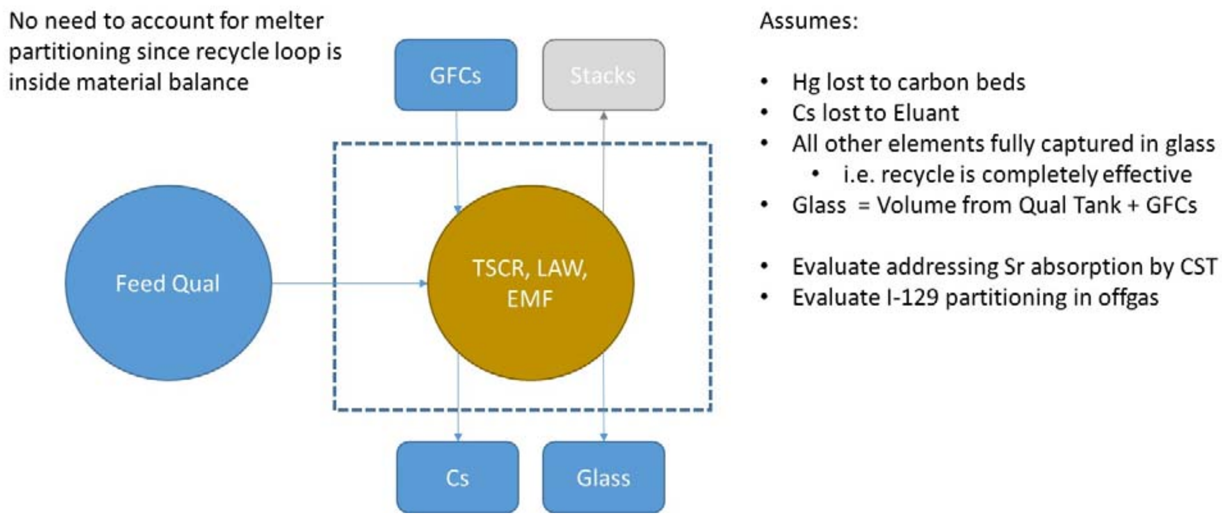

Figure 3. Feed Qualification based Glass Composition Material Balance

4.1.5 *Reduce frequency of MFPV (LFP-VSL-00001/00003) Sampling (LAW 6)*

The MFPV receives feed from the CRV and GFCs from the GFR[12]. The MFPV sample is taken as validation of the process to batch the GFCs and waste for each batch [4]. The GFCs are batched in a facility outside the LAW facility. The batching process involves using silos with mass recording systems to transfer the specified amount of each GFCs into a blend hopper. The GFCs are blended, then transferred to a feed hopper in the LAW facility where weight is confirmed. The feed hopper then transfers the GFCs to the correct MFPV. The mass transfer silos allow independent verification that the correct weight of each GFC was blended. It is expected that operations of the LAW facility will be as close as possible to the operational limits to allow waste loadings to be as high as possible once the commissioning process is complete. Thus, it is important that the GFC batching process is performed accurately.

Material Balance Only Approach

One approach that could be taken to eliminate the sampling of every MFPV batch would be to evaluate the GFC blending operations to determine if the accuracy of the blending process is sufficient to meet the process needs without the MFPV samples. As described in

Appendix B. Glass Former Reagent System, the GFCs weights are verified on several occasions during the GFC batching process. If reasonable assurances can be made that the batching errors would be sufficiently small or rare as a result of the cross-checking, then elimination of the regular MFPV sample would be feasible. One approach to provide this assurance would be to evaluate the GFC batching performance during cold-commissioning to assess the need for the MFPV sample.

It is noted that chemical operations in other industries have encountered issues with chemicals being delivered into the wrong silos/vessels which would lead to a misbatch even if no mistakes were made in batching. In addition, transcription errors during data entry could lead to an incorrect amount for the GFC blend to be entered into the automated systems for preparing the GFC blend. Thus, batching errors during GFC blend preparation may not be automatically captured by the cross-checking of weights.

Methods to reduce human errors during operations are widely used for critical steps during chemical plant operations. For example, independent verification can be used to reduce errors in batching. However, it is noted that implementation of these additional controls could lead to extension of the time required for GFC batching as well as increase the cost for GFC batching. It is not desirable to simply replace the time and cost to sample the MFPV with time and costs for increased controls during GFC batching.

As with the CRV, the MFPV would be sampled on a periodic basis to perform checks on the batching systems. Initial estimates are that every tenth batch would be sampled, but an evaluation of the uncertainties in the melter feed processing would be performed to determine the initial frequency. As experience is gained with the material balance approach, the frequency of the periodic samples could be adjusted.

Material Balance with Routine Sampling

If sampling of the blended GFCs is required to ensure an accurate blend, measurement of the GFC blend in the BOF GFC blend silo is recommended as an alternative to the MFPV sample. It should be noted that not all components in the glass would be measured during the current MFPV sample analysis as the analysis is not currently used in container composition reporting. The analysis is limited to the analytes needed to verify the GFC addition.

The current practice of sampling the MFPV is not an ideal approach for verification of the GFC addition for two reasons. First, the sample and send approach for the sample assumes that the error in any one MFPV batch cannot be large enough to cause a container of glass to be out-of-specification due to the heels in the MFV and melter. Validation of this principle is similar to validation that the controls in place during GFC blending eliminate the need for sampling. Second, this approach does not allow correction or rework of a gross error unless the MFPV has not been sent forward. Given the cycle time of the MFPV, it should be assumed that the MFPV will be transferred prior to obtaining sample data. (Current time in process models estimate 2 hours between receipt of LAW-6 analysis and transfer of batch to MFV assuming nominal TAT).

Two approaches are possible for verification of the GFC batch composition in the GFR system: 1) Take a sample and measure the sample with a dedicated laboratory instrument at the BOF silos or 2) Install an in-situ probe to measure the GFC composition in the blend silo. Either of these approaches would capture any errors prior to transfer of the GFCs into the LAW facility and would allow rework in a timely manner. In addition, the required sample is from a non-radioactive process and would be simpler to take than a radioactive sample. Finally, disposition of the out-of-specification material would occur in a non-rad facility. An assumption of this approach is that errors in transfer volumes from the CRV to the MFPV would be noted by the installed instrumentation. It is likely that LIBS can be adopted to performing GFC measurements with required precision.

4.1.6 *Elimination of Glass Sampling (LAW 2)*

Sampling of the glass from the poured into a product container is provided in the design of the LAW facility, but this sample is not expected to be taken during routine operations[4]. Thus, no changes to the current program are required.

As described above, it is recommended that the material balance currently performed using the CRV sample results to estimate the glass composition be revised to utilize the feed qualification sample. The revision would eliminate reliance on modeling the highly variable single-pass retention of semi-volatile species during the melting process and is expected to improve the accuracy of the glass composition estimate.

4.1.7 *Plant Wash Vessel (LAW 3)*

This vessel collects miscellaneous effluents from the LAW facility[16]. A material balance cannot be used to reliably estimate the composition of this vessel; therefore, no changes to the sampling protocol for this vessel are recommended. This sample is a non-routine sample and the expected frequency is not expected to allow an RTIM system for this vessel to be cost-effective.

4.1.8 *SBS Condensate Collection Vessel (RDL-VSL-00005) (LAW 10)*

This vessel collects liquid effluents from the Submerged Bed Scrubber (SBS) and (Wet Electrostatic Precipitator) WESP operations[16]. The composition of these streams will vary depending on the feed composition and operating history (e.g., single pass retention of species in the melter). As noted above, the single pass retention can be highly variable and can be significantly impacted by operating conditions during melter operations as well as any melter idling. A reliable method to predict the composition of this stream using a material balance approach was not identified. No changes to the sampling protocol for LAW 10 are recommended. It is noted that the operation of the EMF will likely rely on the results from these samples. Inaccuracies in the composition of the collected condensate would be expected to cause processing difficulties in the EMF, as described below.

However, it should be noted that the current glass reporting methodology requires use of estimates of the single pass retention during the melting process for each component in the feed. These sample "split factors" could be used to estimate the SBS and WESP effluent compositions with similar accuracy to the glass composition. A sensitivity study could be performed to assess if the accuracy of this approach is sufficient for transfer of melter offgas effluents to the EMF; however, it is not expected that this evaluation would indicate acceptable levels of uncertainty. In addition, the inclusion of significant amounts of Plant Wash effluents would eliminate the ability to utilize a material balance to estimate the SBS composition even if the use of melter split factors led to acceptable estimates of SBS condensate compositions.

4.1.9 *Stack Emissions (LAW 12)*

The composition of the stack exhaust is periodically measured to assess the performance of the offgas system [4]. No changes to the sampling protocol for this sample is recommended.

4.2 Effluent Management Facility

The current evaluation of uncertainties for using a material balance only approach does not include evaluations of a material balance to replace any samples in the EMF facility[5]. The EMF will receive material from the LAW facility as well as flush solution from the transfer line to the LAW facility. Accurate data for the composition of these streams is needed to allow the evaporation process to remove as much water as possible. The use of material balances only to provide the composition information to the EMF would likely reduce the evaporator turn down to prevent process issues. Given the uncertainties in determining the melter offgas condensate compositions, no changes in the protocols for obtaining sample information for evaporator operation are recommended.

An evaluation could be performed of using a material balance to estimate the evaporator concentrate composition from the sample data available from the evaporator feed. This evaluation was not performed during this study and is not recommended as a path forward for minimizing the sample requirements for combined LAW/EMF operations. The desired high turn-down ratio of the EMF evaporator would be expected to lead to high uncertainty in the composition of the EMF concentrate as small changes from the assumed turn-down ratio would have significant impacts on the calculated concentrate composition. Thus, the use of material balances is not recommended for the EMF facility for control of the evaporator or estimation of the EMF evaporator concentrate composition. No changes to the EMF sampling protocols are recommended unless an installed instrument is utilized to replace the current sample measurements. However, RTIM devices may be adopted to supply the needed data for efficient EMF operation without the need for routine sampling and analyses. Examples could include RAMAN for anion analysis and/or LIBS for elemental and Cl measurements as well as on-line pH measurement.

4.3 Roadmap for MB Implementation

The use of a material balance is recommended for minimizing the amount of sampling performed for the CRV and MFPV processes. Implementation of this approach will require acceptance of the uncertainties added by eliminating the routine sampling of each batch. The approach required for the CRV and MFPV are necessarily different, as the rationale for taking the samples is different. As described above, the CRV sample was proscribed to ensure that the composition for GFC additions and glass composition was accurate while the MFPV sample is taken to ensure the GFC addition is accurately performed.

The implementation of the material balance in place of sampling every batch for the CRV and MFPV will require approval from DOE, contractors, regulators, and other stakeholders. Approval of minimization of the CRV and MFPV sample frequency will require an adequate technical justification and an understanding of any process impacts. In addition, the risks caused by the material balance approach need to be understood as well as how these risks are managed.

4.3.1 *Technical Justification*

The evaluations of the material balance approach have focused on the amount of uncertainty added by elimination of the sampling. The increased uncertainty has two impacts. First, the waste loading of the glass is limited by various constraints on glass properties such as durability, viscosity, electrical conductivity, and solubility. In order to maximize the waste loading, processing will occur near one of the limits and the uncertainty in glass composition will determine how close to the limits the process can be while assuring that the limit is not exceeded. Thus, increases in the uncertainty would lead to lower waste loadings and higher costs.

Second, increases in uncertainty would decrease confidence in the reported composition of the vitrified waste form. If it can be shown that the uncertainty in glass composition from a material balance approach does not lead to decreased waste loading, it can be assumed that the uncertainty in glass composition for reporting purposes will be acceptable.

Therefore, for the material balance approach to be considered feasible, an evaluation of the uncertainty added to the DFLAW process needs to be evaluated as well as the practicality of maintaining the material balance using the existing control software.

Control Software Updates

It is assumed that the system in place to perform the material balances required for the current material balances for container composition reporting would be expanded to include the material balances required for elimination of the CRV sample. The material balance would be automated such that the control system automatically retrieves the required information from process instrumentation and performs the calculations for the balance without assistance from the operator.

The control software utilized was reviewed and found to have sufficient utility to allow an automated material balance to be added and maintained.

CRV Implementation

A calculational approach for evaluation of the added uncertainties for the CRV processes is deterministic. The transfer paths are not easily configured to allow the wrong material to be mistakenly added and the accuracy of the sampling analysis and level instruments is already available. Any errors in transfer amounts would be collected by the automated processes measuring liquid levels. PNNL has performed this evaluation and shown that the uncertainty added to the process from a material balance approach would not lead to a significant decrease in waste loading on a single CRV batch basis. Thus, container composition reporting would have similar accuracy as the baseline process [10].

Additional analysis is in progress to determine the sampling frequency needed to maintain the material balance within acceptable levels of uncertainty.

It is acknowledged that demonstration of the material balance approach may be required prior to elimination of the routine CRV sample. The LAW process will undergo a cold commissioning period; but two issues prevent reliance on the cold commissioning for demonstration of the material balance approach for the CRV analysis.

First, the cold commissioning will not be a combined LAWPS/LAW/EMF commissioning process since recycle from EMF will not be returned to the CRV during cold commissioning. Thus, the ability to demonstrate accuracy of the calculated blend for LAW feed/EMF recycle composition will not be possible. Incorporation of recycle during cold commissioning would lead to the ability to demonstrate the material balance; but the impact on overall schedule would need to be assessed.

Second, the material balance would need to account for removal of radionuclides during the LAWPS/TSCR process. Non-radioactive isotopes of selected species are expected to be utilized during cold commissioning, but not all radionuclides can be tested in this manner.

Thus, while some aspects of the material balance approach for the CRV can be demonstrated during cold commissioning, final demonstration will not be possible until hot-commissioning or the start of operations. It should be noted that establishing the material balance approach in the control software, etc. does not preclude the ability to sample each CRV batch.

Demonstration of the approach during initial operations of the LAW facility would require the facility to sample each CRV batch per the current protocols for a period of time. The material balance would run concurrently with the sampling. A comparison of the CRV compositions from the sampling data with the material balance would be performed to demonstrate that the material balance is acceptable as a replacement for routine sampling.

MFPV Implementation

The GFR System contains a number of independent verifications of the GFC addition amounts during the batching process[17]. If the batch weight inputs to the control system are independently verified prior to batching, then sufficient controls are likely in place to ensure that the GFC batch is correctly prepared and the MFPV sample is not needed to ensure that acceptable glass is prepared.

It is recommended that the verification of the GFC blend be moved from the MFPV to the blend silo in the GFR System if the sampling of the MFPV cannot be eliminated by reliance on the cross-checks during the GFR batching process. The direct measurement approach using a LIBS system installed on the blend silo would provide information in real-time and would eliminate all sampling handling.

Demonstration that measurement of the GFCs as blended in the GFR can replace the MFPV sample can be performed during cold commissioning since the batching requirements during cold commissioning will be nearly identical to the requirements during actual operations. The demonstration could be performed utilizing samples taken both from the blend silos to validate the measurements from an installed instrument as well as samples taken in the MFPV during cold commissioning. An evaluation would be performed to determine how well the installed instrument is performing and recommend whether elimination of the MFPV can proceed. The evaluation would also determine the frequency of periodic samples to rebaseline the MFPV material balance.

4.3.2 *Risks*

As stated above, material balances vulnerabilities include:

- Processing conditions that do not match expectations such as excessive holdup in process equipment from fouling or plugging
- Processing conditions outside of the assumed reactions/conditions in the material balance
- Processing upsets such as spills, foam overs, etc. that cause conditions that typically cannot be accurately accounted during material balance calculations

These vulnerabilities, or risks, are managed by taking periodic sampling to prevent excessive error or uncertainty in the material balance from the vulnerabilities above as well as drift due to uncertainty or biases in the sample and level instrumentation data used to perform the balance. As experience is gained with the process, the frequency of the periodic sampling can be adjusted to maintain control of the process while minimizing the number of samples taken.

The analysis of uncertainty by PNNL is currently being updated to include an initial assessment of the required frequency of the periodic rebaselining to maintain the material balance within acceptable levels of uncertainty[3].

It should be noted that the capability to take routine samples is not impacted by implementing an automated material balance for the DFLAW facility. Thus, the facility could proceed through cold commissioning and startup using the current sample plan and the data collected used to determine the efficacy of elimination of selected samples. This approach was used at the Defense Waste Processing Facility to eliminate routine sampling of the Melter Feed Tank. This type of phased implementation would reduce the risk that any unexpected processing issues would lead to unacceptable performance during startup.

Material Balance Implementation

Implementation of the material balance only approach for the CRV and MFPV requires changes to the current approach for regulatory compliance and process control approved by BNI, WRPS, and DOE with buy-in from regulatory agencies and other stakeholders. Changes to the sampling process will require revisions to the documentation that defines the current sampling protocols and will require approval of the Washington State Department of Ecology if the changes impact any of the approved Dangerous Waste Permit conditions. Thus, the implementation plan for a material balance approach not only needs to consider the technical justification for the changes, but how the changes will be communicated to the appropriate stakeholders to minimize concerns and expedite the approval process.

It is assumed that implementation of the material balance approach will be a contractor led program. An implementation outline has been developed, as described below to, as a guide for implementation of the changes required to adopt a material balance approach. Some aspects of the implementation plan are already in progress, such as defining the changes planned as well as performing evaluations to provide the technical justification for the changes. Other aspects, such as definition of all required changes to currently approved documents, have not been started.

Implementation Plan Outline

1. Define the samples that will be eliminated or minimized by the material balance approach.
    a. Decision point on elimination of routine CRV and MFPV samples
2. Continue to develop the technical justification for CRV material balance approaches
    a. Refine uncertainty of material balance approach
    b. Determine frequency of periodic sampling to manage risks and vulnerabilities of material balance approach
3. Define material balance approach
    a. Update control software to automatically perform material balance
    b. Define test protocols for evaluation of the automated material balance during commissioning, startup, and initial operations
        i. Define criteria for success
        ii. Define measurement period
    c. Define the number of batches needed for an initial period of material balance validation
    d. Determine how sampling will be eliminated
        i. Phased implementation with decreasing sampling frequency over time
    e. Determine if material balance validation should be done at the start of each new campaign
    f. Determine if any RTIM instruments will supplement the material balance
4. Develop schedule and cost estimates for implementation
5. Identify all documents that must be revised to implement change
    a. Draft suggested changes
6. Communicate approach to regulators
    b. Receive and disposition comments and/or issues identified
7. Finalize required changes to project documentation and obtain approval
8. Implementation

4.3.3 *Implementation Plan Details*

Define Samples to be Eliminated

As described above, the routine CRV and MFPV samples have been evaluated for elimination. A decision is needed whether elimination of these samples will be pursued.

Technical Justification

The technical justification for elimination of these samples is described above, but the evaluation is not complete. Additional evaluation is needed for the CRV samples to determine the impact on waste loading and the required frequency for periodic sampling to rebaseline the material balance. Elimination of the MFPV sample does not impact waste loading or glass composition reporting, but it does require justification since the sample was added in response to findings by an expert review team. The evaluations needed to provide the technical justification for elimination of these routine samples is in progress.

In addition, evaluations are in progress to evaluate RTIM as an additional approach for elimination of the routine MFPV samples.

Define Approach for Material Balances

The technical evaluations will determine any expected impacts to waste loading and reporting uncertainty from the material balance approach. In order to determine if the approach is successful, targets need to be set for acceptable levels of process impacts (waste loading) and reporting uncertainty. If the material balance approach has a significant impact on waste loading, then the costs of the increase in process time and container count must be included in the evaluation whether elimination of the CRV sample should proceed. The following criteria will need realistic limits set to allow project decisions to be made:

- Acceptable differences in waste loading
- Acceptable differences (if any) in container reporting accuracy
- Sample reduction target
- Cycle time reduction target
- RTIM implementation costs
- RTIM implementation schedule

Replacement of the CRV samples with a material balance and MFPF samples with RTIM can utilize a number of approaches to minimize the impacts on the process and regulatory reporting uncertainty. As noted earlier, automating the calculations to perform the material balance and performing the material balance as part of the process control does not preclude taking the CRV and MFPV samples. Further, periodic sampling is expected as part of the mitigation of risks in the material balance approach. Thus, the material balance calculation can be performed and evaluated during operation with the current approach of sampling each batch from the CRV and MFPV. The data collected during operations with the current sampling protocols can be used to evaluate the material balance approach.

Implementation of the material balance can be phased in, gradually reducing the sampling frequency over time. This phased implementation would allow confidence to be gained in the material balance over time and represents a reasonable strategy for implementation. This strategy allows assumptions made during the technical evaluations performed prior to implementation to be verified with actual operational data during implementation. In particular, a phased approach allows the assumptions for partitioning during the solids and cesium removal processes to be verified. Using a phased approach requires determination for the duration of each phase of operation.

Additional considerations are needed for the approach to be taken during transition between feed campaigns. Depending on the sample frequency for periodically rebaselining the material balance, a change in sampling protocol may not be needed. However, initial operations with a new feed campaign could revert to sampling each batch until confidence is gained that the material balance approach is functioning correctly (i.e. no unexpected changes in partitioning during cesium removal).

Finally, the use of any RTIM instruments to supplement the material balance approach needs to be defined.

Develop costs and schedule estimates

Determination of the costs and schedule for implementation of an automated material balance can be developed, including the cost of any RTIM instruments and their installation as well as the costs for revisions to project documentation required.

Identify Documentation Changes

The current sample plan for process control and regulatory reporting is documented in a number of approved project documents. Once a decision is made on elimination of either the routine CRV or MFPV samples, changes will be needed to the project documentation to describe the revised protocols. The required changes would allow the material balance to be used in place of samples, but the ability to use sample data should not be eliminated.

While a partial list is included below; any listing made would have to be updated once implementation begins as significant changes could occur to project documentation before the RTIM program is implemented.

- Hanford Facility Dangerous Waste Permits[18]
- WTP Integrated Sampling and Analysis Requirements Document (ISARD)[19]
- Integrated DFLAW Feed Qualification Data Qualifty Objectives[20]
- ILAW Product Compliance Plan[21]
- Preliminary ILAW Formulation Algorithm Description[11]
- All associated operating procedures

Communicate Proposed Plan to Regulators

Communication of changes to accepted plans requires clear and concise communications with regulators. Several salient features of the changes required to implement a material balance approach for the CRV and MFPV samples will need to be conveyed clearly:

- Regulatory reporting that used CRV sample results will still rely on sampling data
    - Sample point for compliance shifted, not eliminated
    - Waste Feed Qualification will replace CRV sample for glass composition reporting
    - Material balance already used to estimate glass composition based on CRV sample and GFC mass data
        - Assumptions for melter partitioning included in this balance
- The ability to take samples from the CRV and MFPV is not eliminated
    - Periodic samples are planned

- Impacts to waste loading and composition uncertainty will be evaluated prior to implementation
    - Continued evaluation after implementation
- Comments from regulators will be dispositioned prior to implementation
- Changes to regulatory documents will be made in conjunction with the regulators, as is currently the process.

Technical experts should be available during initial and follow-up discussions with regulators to allow detailed questions to be answered during the meetings.

Finalize Implementation Plan

The final approach for implementation of the material balance approach will be set after any comments from stakeholders is received. This approach will be incorporated into the required regulatory documents and project documentation.

Perform implementation

Once approvals are received, the implementation will proceed. Technical experts should be available as needed to address any issues that arise. Regulators will be kept informed on a regular basis of implementation progress.

5.0 CONCLUSIONS

- A material balance approach for determination of the CRV composition was determined to be feasible during the DFLAW portion of the WTP mission. Eliminating the routine CRV sample did not lead to a significant increase in the compositional uncertainty of the glass as determined by evaluation of the waste loading achievable.
- Elimination of the MFPV was determined to be technically feasible with a material balance approach. If routine sample analysis is retained, it is recommended that the batched GFCs be sampled in the GFR System blend hopper versus the sampling the MFPV.
  - Development of Laser Induced Breakdown Spectroscopy (LIBS) system would allow on-line validation of the GFC composition
- The composition of the offgas condensate and other streams downstream of the melter cannot be reliably predicted with a material balance approach.
- The current sampling protocols for EMF operation cannot be reduced through a material balance approach as the melter condensate composition is not reliably predicted and the high turn-down ratio in the evaporator creates unacceptable uncertainty if attempting to predict the evaporator concentrate composition from the feed composition. However, RTIM can likely be applied to reduce the number of samples required during normal EMF operation.
- The control software for the LAW facility can be updated to include an automated material balance for the CRV and MPFV without impacting the current sampling practices provided resources are available.
- Continued development of RTIM instruments for anion and metals analysis is needed if elimination of sampling for processes downstream of the melter is desired.
  - Raman/ATR-FTIR for anions except Cl^-
  - LIBS for metals and Cl
  - pH measurement

6.0 RECOMMENDATIONS

- A material balance approach for the CRV should be pursued to allow elimination of the routine CRV sample. It is not expected that use of a real-time monitoring system is needed to allow the sample analysis to be eliminated.
- The required frequency of periodic CRV samples should be estimated from known data on the uncertainty in material balance inputs.
- The sample analysis used for glass composition reporting should be moved from the CRV to the waste feed qualification sample
- A material balance approach should be pursued for the MFPV based on the independent cross-checks performed during GFC batching.
- Testing of a LIBS instrument for measurement of the GFC batch in the GFR System should be pursued to allow implementation of an on-line instrument if the material balance approach for the MFPV is not accepted by stakeholders.
- Development of RTIM instruments for EMF streams should continue, leveraging the information gained for evaluations of the LAW feed.
- Development of the RAMAN and LIBS instruments for the composition measurement of low concentration offgas condensate and other streams downstream of the melter. The development should also reduce measurement uncertainties in reported compositions.
- Communication with regulators early in the process is recommended to gain their buy-in to the process and approval of required changes to regulatory documents.

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Appendix A. Savannah River Site Material Balance Approaches

The Savannah River Site (SRS) is currently treating and immobilizing High Level Waste (HLW) and Low Activity Waste (LAW). A simplified diagram of the overall SRS Waste Stabilization process is shown in Figure A- 1. SWPF is not shown; it will replace or supplement the combined Actinide Removal Process (ARP)/Modular Caustic Side Solvent Extraction Unit (MCU) processes shown when it comes online.

Material balances are used for at least a portion of the waste reporting requirements in both the HLW[22] and LAW processes. Material balances based on the qualification samples results are used for reporting of the radionuclides for HLW processing and after an initial period of analysis, process knowledge is used for metal species during acid addition calculations for HLW sludge pretreatment. A material balance approach with quarterly rebaselining is used for LAW feed compositions. These material balance approaches allow the waste treatment processes to operate efficiently while ensuring that the reporting requirements for the waste are addressed.

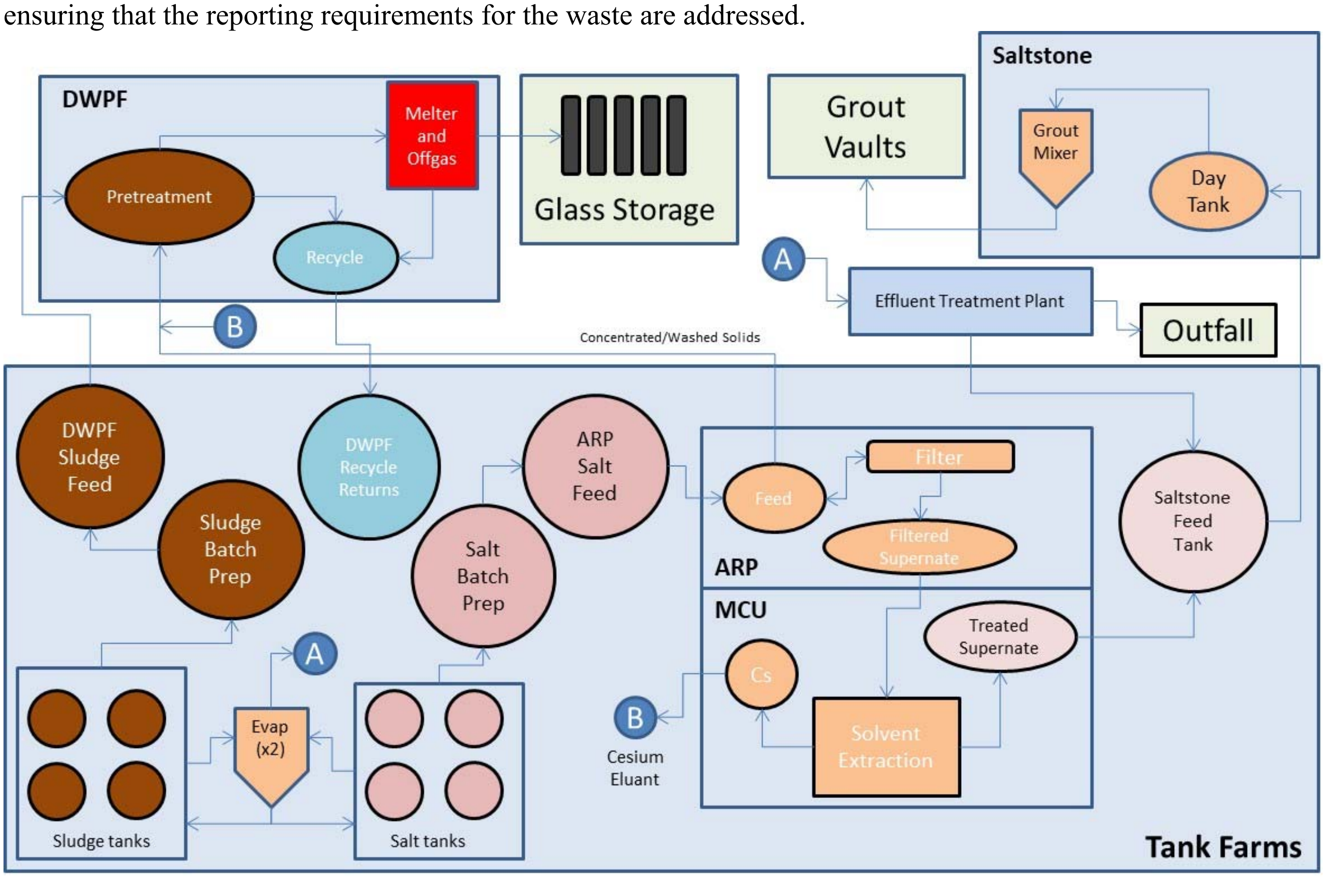

Figure A- 1. Simplified Diagram of SRS Tank Waste Treatment and Immobilization

HLW Radionuclide Reporting

The Defense Waste Processing Facility (DWPF) is currently vitrifying the HLW portion of the waste generated at SRS during nuclear material production. HLW sludge is prepared for processing at DWPF in large batches, called sludge batches, prepared and qualified in the tank farm[23]. The sludge batch can consist of sludge from several different tanks and is collected in the Sludge Batch Prep tank shown in *Figure A- 1*. The sludge batch is sampled once all the sludge to be processed is collected in the prep tank. The sample is used to qualify the batch for processing. Both the sample and the sludge batch go through a sludge washing process to remove soluble salts from the HLW sludge solids. Once qualified, the sludge batch is transferred onto the heel of the previous batch in the DWPF Sludge Feed tank and Waste Acceptance Product Specification (WAPS) sample is taken. This sample, from the tank farm feed tank to DWPF, is used for reporting of radionuclides for the sludge portion of the HLW glass product[24].

The DWPF reporting of radionuclides relies on a material balance performed using the WAPS sample results and similar data from the ARP/MCU streams added during DWPF processing to determine the radionuclide composition of the glass product. The approach for the sludge waste is to determine the ratio of each radionuclide in the sludge to the iron content of the sludge. The iron content is measured for each batch of melter feed prepared by DWPF by taking a sample of the melter feed. The iron ratio is then used to determine the amount of each radionuclide in the final glass product.

HLW Acid Additions

The sludge received at DWPF is acidified to allow mercury reduction as well as to reduce the yield stress of the melter feed, as shown in Figure A- 2. Calculation of the amount of acid required utilizes a titration to determine hydroxide composition, a total inorganic carbon measurement, ion chromatography for nitrite, nitrate, and formate, ion-coupled plasma-emission spectroscopy for manganese, and a cold vapor atomic absorption measurement for mercury content. These measurements take longer than desired and can delay the process. Thus, DWPF only waits for the results from these measurements for the first ten transfers of sludge to DWPF for each large sludge batch. After this initial period of waiting on the results, DWPF transitions to utilizing the IC analysis to determine how much flush water diluted the batch during transfer. This dilution is then applied to the averaged results from the first ten batches for the other species required for the acid calculation. Thus, the process knowledge gained from the initial batches is used to process subsequent batches instead of waiting on sample results.

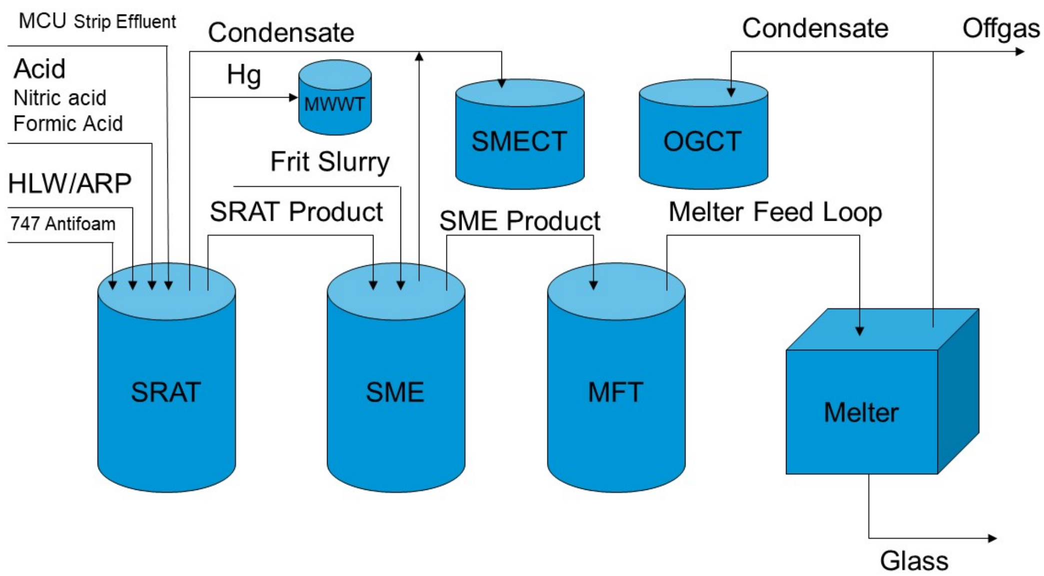

Figure A- 2. Simplified DWPF Flow Diagram

<u>Saltstone Feed and Grouted Waste Composition</u>

The Saltstone facility at SRS immobilizes low level waste from three sources, as shown in Figure A- 3: Bottoms from the Effluent Treatment Plant, low-level wastes from H-canyon operations, and treated LAW from the MCU. Future operations will include transfers of treated LAW from the Salt Waste Processing Facility (SWPF). The treated LAW from MCU closely resembles the treated LAW stream that will be fed to the Hanford LAW facility. Samples are taken of the Saltstone Feed tank four times a year to rebaseline the material balance that is maintained of the feed tank[25]. The composition from the material balance is used to ensure that the feed meets the Saltstone waste acceptance criteria and for reporting the composition of the grouted wasteform. Each of the facilities sending waste to the Saltstone Feed tank is responsible for ensuring the wastes sent to the feed tank are compliant and for providing the compositional information required to maintain the material balance for the Saltstone feed.

Similar to the Hanford LAW GFC preparation, the “grout premix” is prepared using individual mass transfer silos to add the specified amounts of each chemical used in the grouting process to a blend silo. The blended grout premix is then blended with the decontaminated salt supernate waste in a continuous mixer and transferred to the grout vaults. No routine samples are taken during Saltstone operation; therefore, the composition of the grouted waste is dependent on material balances that provide the composition of the feed tank as well as material balances that utilize the amount of each material added during the grouting process.

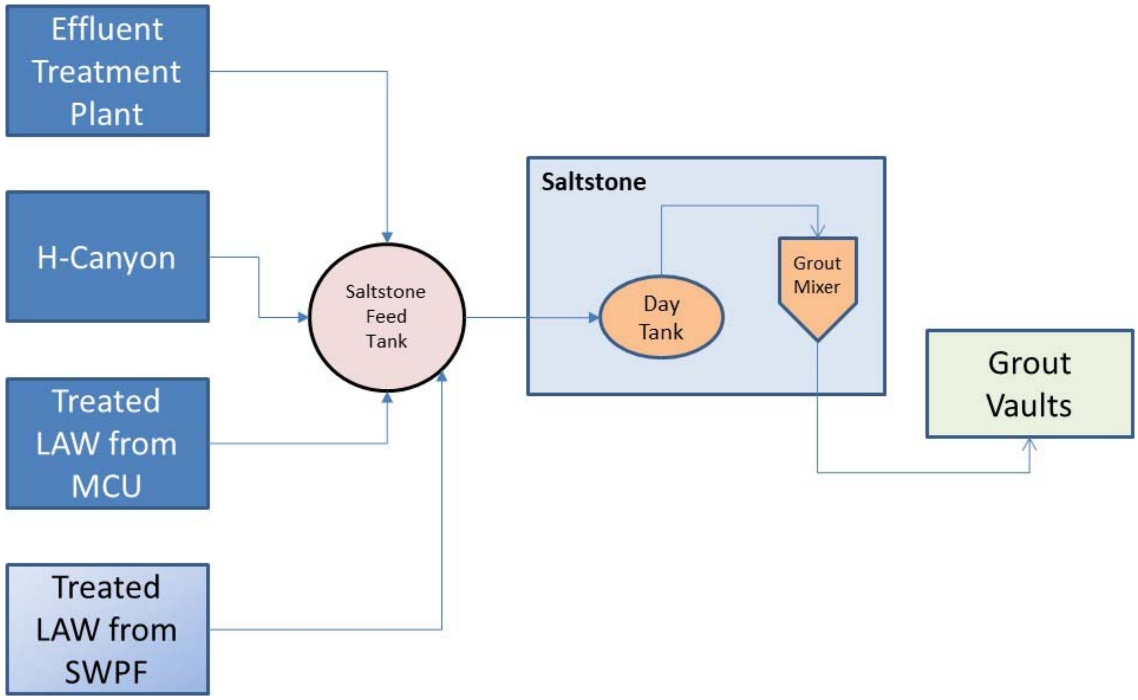

Figure A- 3. Simplified Diagram of SRS Saltstone Process

Appendix B. Glass Former Reagent System

The GFCs are received, batched, blended, and transferred to the LAW facility by the GFR System[17], as shown in

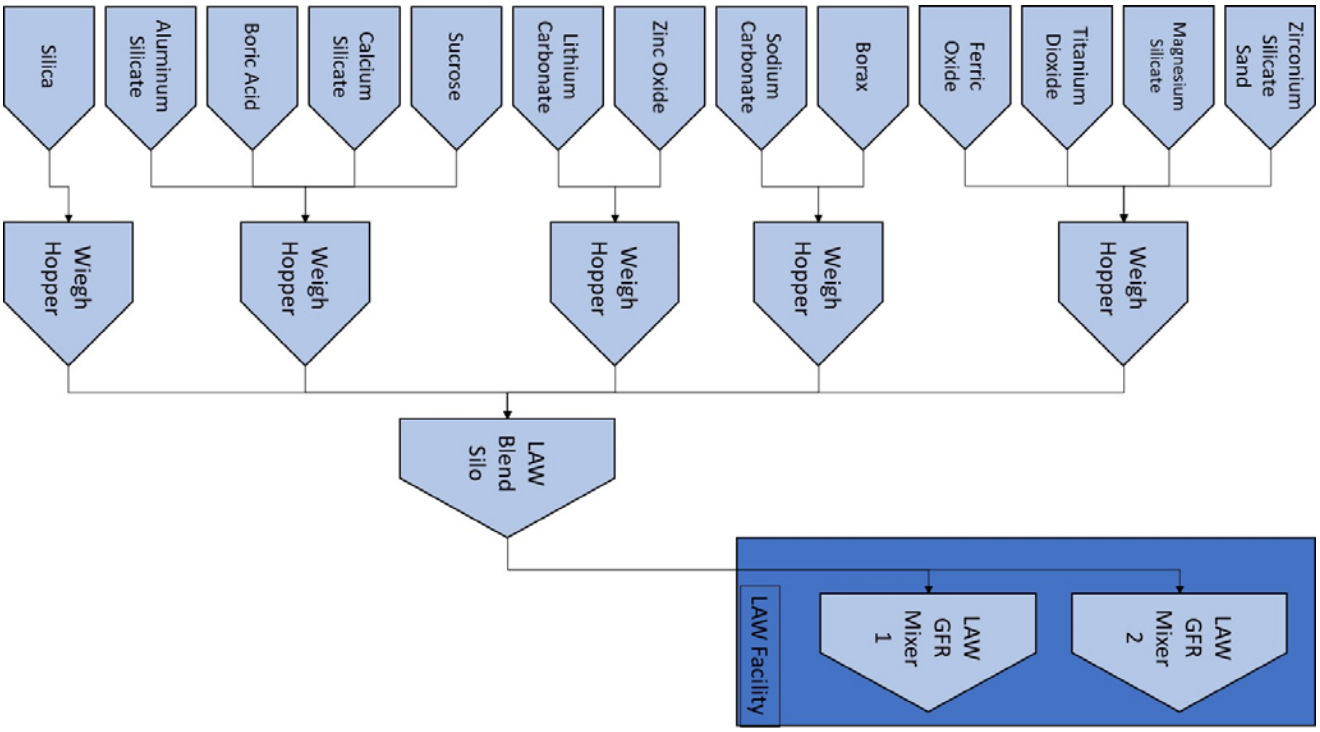

Figure B- 1. GFCs are received into silos designed to hold a ten day supply of each GFC; the silos range in size from 8500 cubic feet for the silica to 1000 cubic feet for the ferric oxide and other components that feed the System 500 weigh hopper. The GFCs are grouped into 5 different systems to allow the weigh hoppers to be sized correctly for the expected amounts for each component.

A unique GFC recipe will be determined for each MFPV batch. The recipe will be entered into the control system for the GFR System and verified prior to batching. Batching of the GFCs is performed by transferring the GFC from the storage silos into weigh hoppers. Once the weight of the GFC in the blend hopper is verified, the GFC is conveyed into the blend hopper. The blend hopper is mounted on a load cell and independently verifies the correct weight for each GFC as well as the total GFC weight once the additions are complete. If the total weight of the completed batch is not within 2% or any individual addition is not within 0.5% of the specified weight, the batch is rejected.

Pneumatic blending is used to mix the GFCs in the blend hopper prior to transferring the batch to the LAW facility. GFCs are received into the LAW GFR mixers and mixed with water (~4 wt.%) to control dusting. Load cells in the mixers ensure the correct amount of GFCs has been transferred. After blending with water, the GFCs and sent to the Melter Feed Preparation Vessels to be blended with the treated LAW.

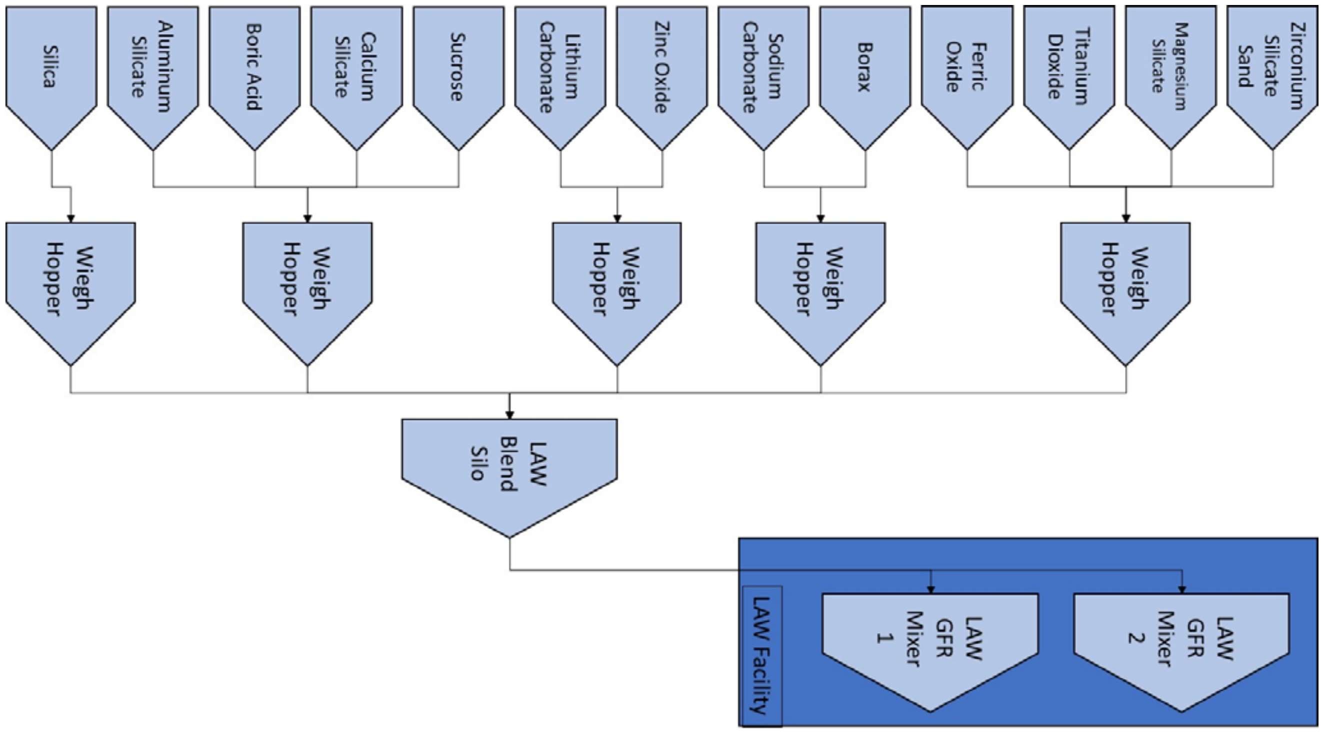

Figure B- 1. Glass Former Reagent System Simplified Diagram