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Development of a Macro-Batch Qualification Strategy for the Hanford Tank Waste Treatment and Immobilization Plant

Connie C. Herman

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C. C. Herman

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REVIEWS AND APPROVALS

AUTHORS:

C. C. Herman, E&CPT Research Programs Date

TECHNICAL REVIEW:

M.E. Stone, Process Technology Programs Date

S.H. Reboul, Advanced Characterization & Processing Date

APPROVAL:

S. L. Marra, Manager Date
Environmental & Chemical Process Technology Research Programs

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EXECUTIVE SUMMARY

The Savannah River National Laboratory (SRNL) has evaluated the existing waste feed qualification strategy for the Hanford Tank Waste Treatment and Immobilization Plant (WTP) based on experience from the Savannah River Site (SRS) Defense Waste Processing Facility (DWPF) waste qualification program. The current waste qualification programs for each of the sites are discussed in the report to provide a baseline for comparison. Recommendations on strategies are then provided that could be implemented at Hanford based on the successful Macrobatch qualification strategy utilized at SRS to reduce the risk of processing upsets or the production of a staged waste campaign that does not meet the processing requirements of the WTP. Considerations included the baseline WTP process, as well as options involving Direct High Level Waste (HLW) and Low Activity Waste (LAW) processing, and the potential use of a Tank Waste Characterization and Staging Facility (TWCSF).

The main objectives of the Hanford waste feed qualification program are to demonstrate compliance with the Waste Acceptance Criteria (WAC), determine waste processability, and demonstrate unit operations at a laboratory scale. Risks to acceptability and successful implementation of this program, as compared to the DWPF Macro-Batch qualification strategy, include:

- Limitations of mixing/blending capability of the Hanford Tank Farm;
- The complexity of unit operations (i.e., multiple chemical and mechanical separations processes) involved in the WTP pretreatment qualification process;
- The need to account for effects of blending of LAW and HLW streams, as well as a recycle stream, within the PT unit operations; and
- The reliance on only a single set of unit operations demonstrations with the radioactive qualification sample.

This later limitation is further complicated because of the 180-day completion requirement for all of the necessary waste feed qualification steps.

The primary recommendations/changes include the following:

- Collection and characterization of samples for relevant process analytes from the tanks to be blended during the staging process;
- Initiation of qualification activities earlier in the staging process to optimize the campaign composition through evaluation from both a processing and glass composition perspective;
- Definition of the parameters that are important for processing in the WTP facilities (unit operations) across the anticipated range of wastes and as they relate to qualification-scale equipment;
- Performance of limited testing with simulants ahead of the waste feed qualification sample demonstration as needed to determine the available processing window for that campaign; and
- Demonstration of sufficient mixing in the staging tank to show that the waste qualification sample chemical and physical properties are representative of the transfers to be made to WTP.

Potential flowcharts for derivatives of the Hanford waste feed qualification process are also provided in this report.

While these recommendations are an extension of the existing WTP waste qualification program, they are more in line with the processes currently performed for SRS. The implementation of these processes at SRS has been shown to offer flexibility for processing, having identified potential processing issues ahead of the qualification or facility processing, and having provided opportunity to optimize waste loading and throughput in the DWPF.

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LIST OF ABBREVIATIONS

ARP	Actinide Removal Process
BBI	Best Basis Inventory
CPC	Chemical Process Cell
CUF	Cell Unit Filter
DOE-ORP	Department of Energy – Office of River Protection
DQO	Data Quality Objectives
DST	Double Shell Tank
DWPF	Defense Waste Processing Facility
EA	Environmental Assessment
EM	Environmental Management
ESP	Extended Sludge Processing
ESS	Extraction, Scrub, and Strip
FEP	waste feed evaporation process system
HLW	High-Level Waste
HTWOS	Hanford Tank Waste Operations Simulator
ICD	Interface Control Document
IEWO	Inter-Entity Work Order
IHLW	Immobilized High-Level Waste
ILAW	Immobilized Low-Activity Waste
IWFDP	Integrated Waste Feed Delivery Plan
LAW	Low-Activity Waste
MCU	Modular Caustic Side Solvent Extraction
MFT	Melter Feed Tank
MST	monosodium titanate
PCCS	Product Composition Control System
PCT	Product Consistency Test
PNNL	Pacific Northwest National Laboratory
PRFT	Precipitate Reactor Feed Tank
PT	Pretreatment Facility
RCRA	Resource Conservation and Recovery Act
RPP	River Protection Project
SEFT	Strip Effluent Feed Tank
SME	Slurry Mix Evaporator
SRAT	Sludge Receipt and Adjustment Tank

SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SRS	Savannah River Site
SST	Single Shell Tank
SWPF	Salt Waste Processing Facility
TLP	treated LAW evaporation process system
TOC	Tank Operations Contractor
TT&QAP	Task Technical & Quality Assurance Plan
TWCSF	Tank Waste Characterization and Staging Facility
UFP	-ultrafiltration process system
USDOE	U.S. Department of Energy
WAC	Waste Acceptance Criteria
WAPS	Waste Form Acceptance Product Specifications
WASRD	Waste Acceptance System Requirements Document
WCP	Waste Form Compliance Plan
WCS	Waste Characterization System
WTP	Hanford Tank Waste Treatment and Immobilization Plant

1.0 Introduction

The Savannah River National Laboratory (SRNL) and the Pacific Northwest National Laboratory (PNNL) were tasked by the U.S. Department of Energy (USDOE) Office of Environmental Management (EM) to jointly coordinate the engagement of the broader national laboratory community to bring the scientific and technological rigor needed to evaluate/prioritize alternatives, define/execute technology development opportunities, and inform decisions that will reduce technical and programmatic risks. For the Hanford Tank Waste treatment program, identification of the initiative areas occurred in meetings and discussions with the national laboratories, site field offices, and site contractors. The focus of this report is the Waste Feed Acceptance and Product Qualification initiative area, and, specifically, improvement to the Hanford waste feed qualification strategy to increase the chances of successful WTP operation. Working with the Department of Energy – Office of River Protection (DOE-ORP) and Hanford contractor personnel, the laboratories completed a preliminary assessment of the technology gaps and potential areas for improvement earlier in the fiscal year. Technical report, SRNL-STI-2012-00776/PNNL-22116¹, was issued to document this assessment and subsequent discussions with the DOE-ORP and Hanford contractors refined this initiative area further.

Funding was provided by the DOE-ORP under Inter-Entity Work Order (IEWO) M0SRV00091 Revision 1² for SRNL to work with DOE-ORP and the Hanford contractor team to help close the gaps or provide alternative strategies for improvement in areas related to waste feed qualification and acceptance for the Hanford Tank Waste Treatment and Immobilization Plant (WTP). The specific scope of this report is the development of a sampling and characterization strategy to provide better assurance of macro-batches or campaigns meeting WTP Waste Acceptance Criteria (WAC). WAC processability and regulatory information parameters are defined as information needed to comply with WTP contract specifications, regulatory requirements, and for optimizing the processing of the waste. Risks have been identified in the ability of the Tank Operations Contractor (TOC) to homogeneously mix and representatively sample the campaign feed to meet the requirements of the WAC.³ If the waste is not homogeneously mixed and samples are not representative, then the uncertainty associated with the analyses will be greater and the processing parameters will be harder to define. Outside of the WAC, changes in the strategy that would increase the chances of successfully meeting the 180-day turn-around for the waste feed qualification sample and/or providing flexibility in processing would also be desirable.

A campaign is a volume of staged waste feed that is to be treated using a similar processing strategy and may consist of multiple batches that have similar physical and chemical properties. For Hanford, a Low-Activity Waste (LAW) campaign consists of one LAW feed batch of approximately 1 Mgal of certified feed to be delivered to the WTP from a single source tank. A High-Level Waste (HLW) feed campaign consists of six or seven feed delivery batches of approximately 120 kgal each of certified feed to be delivered to the WTP from a single source tank⁴. Given the large volume of Hanford waste, a significant number of macro-batches or campaigns are anticipated for the WTP mission (i.e., 43 LAW campaigns in single batches and 92 HLW campaigns in 600 feed batch transfers⁵). Therefore, increasing the chances of successfully staging compliant campaigns, while qualifying as large a campaign as possible, will benefit the overall mission. SRNL was requested to perform this scope based on the Macro-Batch strategy used at the Savannah River Site (SRS) Defense Waste Processing Facility (DWPF) for HLW qualification. The Hanford/WTP campaign is equivalent to a Macro-Batch at SRS. The DWPF has consistently produced acceptable HLW glass product for 17 years using a Macro-Batch concept where feed is staged, mixed, prepped and sampled in a one million gallon tank and processed under relatively constant conditions over the entire batch. Therefore, applying aspects of the DWPF program, including the steps to demonstrate acceptable processing and to optimize the flowsheet, may have benefit to the Hanford/WTP waste treatment program.

As with DWPF, the Hanford/WTP strategy will need to consider the reporting requirements and parameters of importance for processing in combination with the necessary data quality objectives. One difference from the DWPF will be consideration for the amount of time taken to complete qualification since the baseline plan for WTP is 180 days and multiple campaigns could be qualified at the same time. Another difference is that different treatment strategies are used for LAW and HLW at the SRS, whereas the strategies are currently the same at Hanford with vitrification processing of both HLW and LAW.

The WTP project has developed a Waste Feed Qualification Program Plan⁶ to protect the WTP design, safety basis, and technical basis by assuring waste acceptance requirements are met before the transfer of waste from the TOC to the feed receipt vessels inside the Pretreatment Facility (PT). As discussed above, near-term needs of the WTP waste feed qualification program were identified during laboratory, DOE-ORP, and contractor discussions as being integral to effective start-up and operation. A Task Technical & Quality Assurance Plan (TT&QAP), SRNL-RP-2013-00364⁷, was written to cover the strategy development scope, as well as to cover three other initiative areas from the April 2013 planning meeting. The strategy development scope was worked in conjunction with the other waste feed acceptance activities being performed at SRNL as outlined in TT&QAP SRNL-RP-2013-00310⁸. SRNL also worked with the One System Integrated Project Team to develop the strategy.

Generally speaking, two strategies were considered in this evaluation. The first considered the baseline assumptions for the Hanford processing facilities using the current Tank Farm limitations. The second strategy considered improvements or changes to these assumptions, as well as potential changes to the baseline flowsheet, to improve the chances of success. This strategy set considered the design and construction of a Tank Waste Characterization and Staging Facility (TWCSF). The objective of the facility is to provide the Tank Farms with the capability to stage, mix, and blend tank waste to allow the delivery of a consistent, certifiable, and compatible waste feed to the WTP. This facility would be similar in concept to Tank 51/Tank 40 at the SRS, where HLW is staged for the DWPF. These strategies are discussed in Section 4.0 after a brief discussion of the existing strategy for the baseline Hanford process (Section 2.0) and the DWPF qualification process (Section 3.0). Finally, Section 5.0 provides a high level summary of the recommended changes to implement the strategy.

2.0 Baseline Hanford WTP Waste Feed Qualification Strategy

As mentioned above, the Hanford Waste Feed Qualification Program⁶ is being developed to protect the WTP design, safety basis, and technical basis by assuring waste acceptance requirements are met for each staged waste campaign or macro-batch prior to transfer from the TOC to the feed receipt vessels inside PT. The objectives of the program are to characterize the waste to meet acceptance criteria and reporting requirements and to determine an acceptable range of operator-controllable parameters needed to treat the staged waste. A schematic of the WTP Waste Feed Qualification and Batch Processing Methodology Interaction strategy was developed by WTP and is provided in Figure 2-1.⁶ The attributes of this program will be discussed at a high level in this section.

As with the SRS, the TOC uses a series of models and a System Plan to provide a modeling estimate of the River Protection Project (RPP) mission operations based on a set of processing and operating assumptions. For Hanford, the One System Integrated Project Team uses the Integrated Waste Feed Delivery Plan (IWFDP) to outline plans/strategies for any Tank Farm pretreatment, blending/mixing, retrieval and delivery of feed for treatment. The IWFDP consists of 3 volumes each with a different focus:

- Volume 1 (Process Strategy) provides the basis for how the Double Shell Tanks (DST) will be used to receive, stage, and deliver feed to the WTP⁴,
- Volume 2 (Campaign Plan) describes the plan for the first eight feed campaigns for delivery to the WTP and evaluates the projected feed for the entire system for systematic issues⁵, and
- Volume 3 (Project Plan) provides the basis for upgrading the equipment and infrastructure for the DSTs to deliver waste feed to the treatment facilities⁹.

Ultimately this plan sets the tank waste retrieval, blending, processing, and disposition strategy and is integrated with the River Protection Project System Plan (Rev. 6)¹⁰. The Tank Waste Retrieval Work Plans are used with the Volume 2 Campaign Plans as the means for WTP to assess the proposed campaigns. This feedback loop supports the evolution and maturation of the IWFDP through an ongoing iterative process of successive refinements to improve processability. This process is depicted in Figure 2-2.⁴ The inputs from these efforts are incorporated into the Hanford Tank Waste Operations Simulator (HTWOS), which is a dynamic event-simulation model that tracks waste as it moves through storage, retrieval, feed staging, and multiple treatment processes from the present day until the end of the RPP mission⁴. The HTWOS allows the prediction of staged waste feed properties to provide an early indication of acceptability against both Tank Farm and WTP waste acceptance criteria, safety-related constraints, and/or other interface requirements. WTP uses the information to identify the key unit operations that will be necessary for the campaign and to provide input to the waste feed qualification testing parameters and requirements. The information is documented in a Preliminary Campaign Sheet once the operational plan for the campaign is finalized.

To prepare the campaign, the TOC would stage the feed in a Double Shell Tank (DST) and the waste feed qualification sample(s) would be collected after staging and any necessary Tank Farm Special Case Flowsheets are completed (see Figure 2-2). Once the waste feed qualification sample(s) are collected, the staging tank is in a hold status until the qualification is completed. During the staging and retrieval of the waste, the TOC may sample the waste for waste compatibility and process control requirements.⁴ Characterization of these samples does not currently include a full characterization that might be needed to determine WTP processability. The TOC provides samples of the staged waste at the volume to be defined by WTP no less than 180 calendar days before the scheduled waste transfer. This is sample point TF1 in the *Integrated Sampling and Analysis Plan* (ISAP¹¹). The waste feed qualification process would then be initiated. The three main components of waste feed qualification are as follows:

- Demonstrate compliance with the WAC,
- Determine waste processability, and
- Demonstrate unit operations at laboratory scale.⁶

A flowsheet of the program and the relevant interfaces is outlined in Figure 2-3.

The goal of the waste feed qualification program is to perform laboratory testing using standard and custom-developed laboratory instruments and techniques to quantify the acceptance parameters established in the *Interface Control Document for Waste Feed* (ICD-19)³ and further defined in the *Initial Data Quality Objectives for WTP Feed Acceptance Criteria* (WAC-DQO)¹². The Qualification Laboratory or Testing Laboratory will perform the analyses and qualification using guidance from the WTP Preliminary Campaign Sheet. Assuming acceptable results from waste feed qualification testing, the results will be used by WTP to determine a batch processing methodology (as depicted in Figure 2-1). The goal is to also provide an acceptable range of operator-controllable parameters to treat the staged waste with consideration for current process conditions such as vessel and heel volumes.⁶ The parameters would be identified on the Final Campaign Sheet, and those parameters (including process decisions) will be further defined during the development of unit operation specific Batch Sheets. If the campaign or macro-batch is not in compliance with the WAC, the waste feed may either be rejected or an assessment may be prepared by WTP with the TOC to recommend an alternative method to alter the feed and submit that proposal to DOE for approval.⁶

Upon demonstration by the Qualification Laboratory that the WAC have been met through analytical characterization (18 parameters for waste transfer and 240 parameters for processability), waste processability is then determined by evaluating the analytical results and performing testing using *Specification 12 - Procedure to Determine the Waste Feed Treatment Approach* (24590-WTP-RPT-PET-11-002¹³) to determine the process parameters to leach the waste including caustic leaching temperature, caustic to aluminum in solids ratio, caustic leach time, and permanganate to chromium in solids ratio. A key objective of the Specification 12 testing is the prediction of the quantity of Immobilized High-Level Waste (IHLW) and Immobilized Low-Activity Waste (ILAW) product to be produced in WTP.¹³ The quantity is a strong function of the solids washing, caustic washing and leaching, and oxidative leaching and washing. Caustic and oxidative leaching are performed to remove the Al and Cr from the HLW solids when benefit is shown to the total glass volume production.

Once Specification 12 testing is completed, unit operations are demonstrated using laboratory-scale unit operations test apparatus as necessary including the following:

- Waste concentration by evaporation;
- Sludge washing, leaching, and separation by cross-flow ultrafiltration;
- Ion exchange for ¹³⁷Cs removal; and
- Glass formulation.

For the processes that will be affected by recycle, an approximate steady state recycle simulant will be used during unit operations testing. During the demonstrations, measurements will be made of unit-specific parameters, hydrogen generation rate, and rheology. Visual observations will be recorded with particular interest for the presence of foaming. More detailed descriptions of the individual unit operations are provided in the following paragraphs.

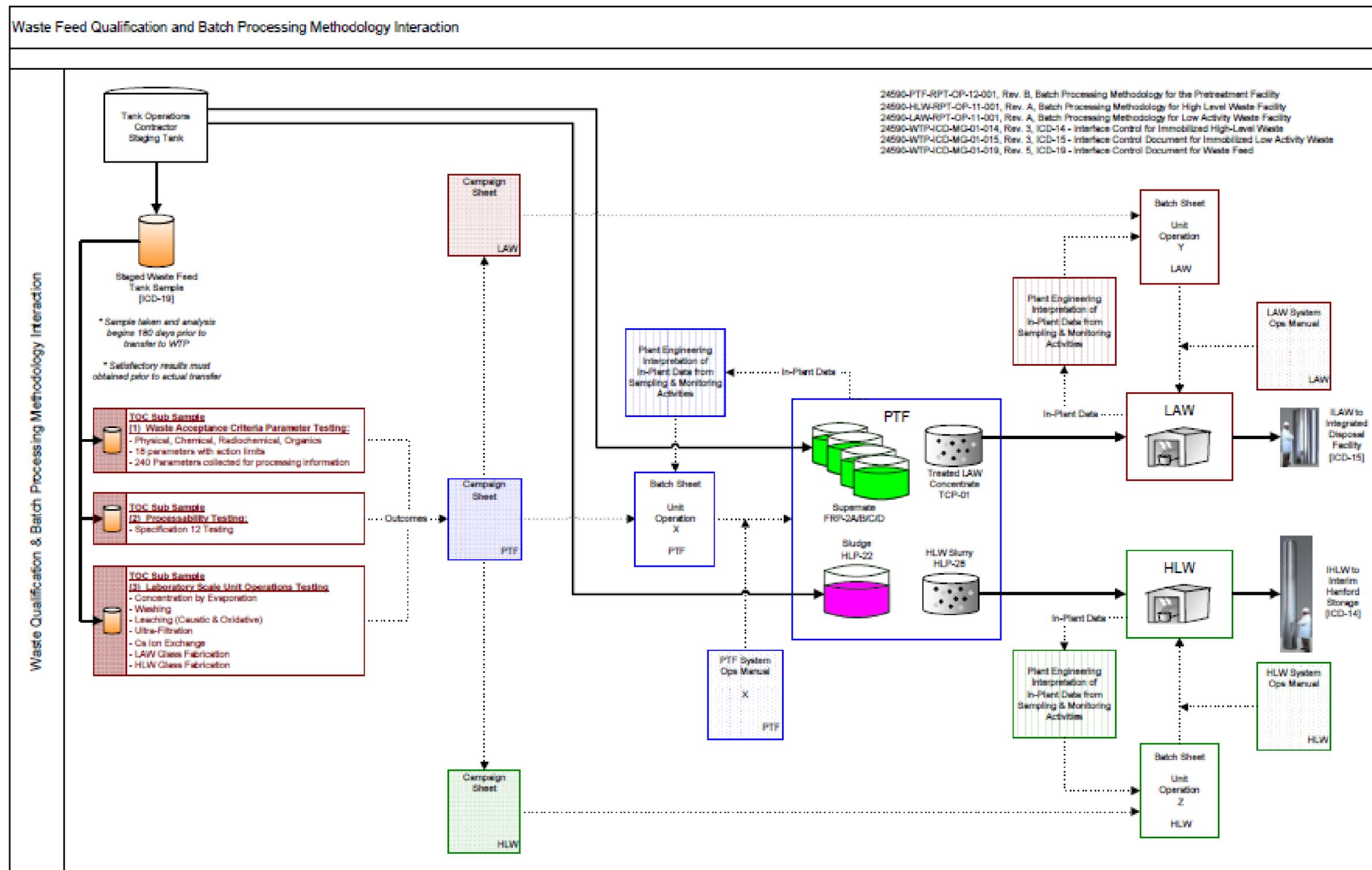


Figure 2-1. WTP Waste Feed Qualification and Batch Processing Methodology Interaction from Reference 6.

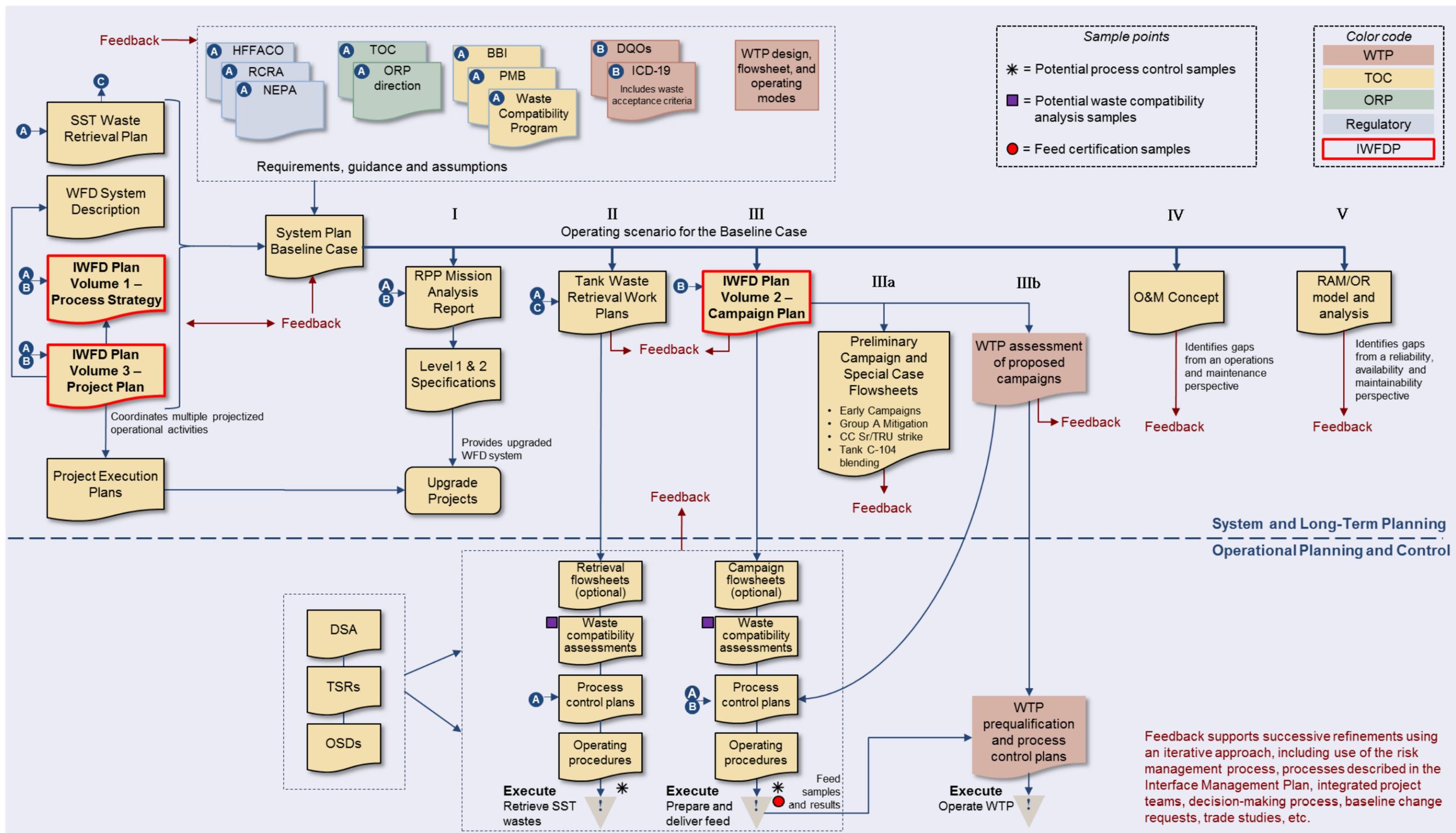


Figure 2-2. Integrated Waste Feed Delivery Planning Process from Reference 4

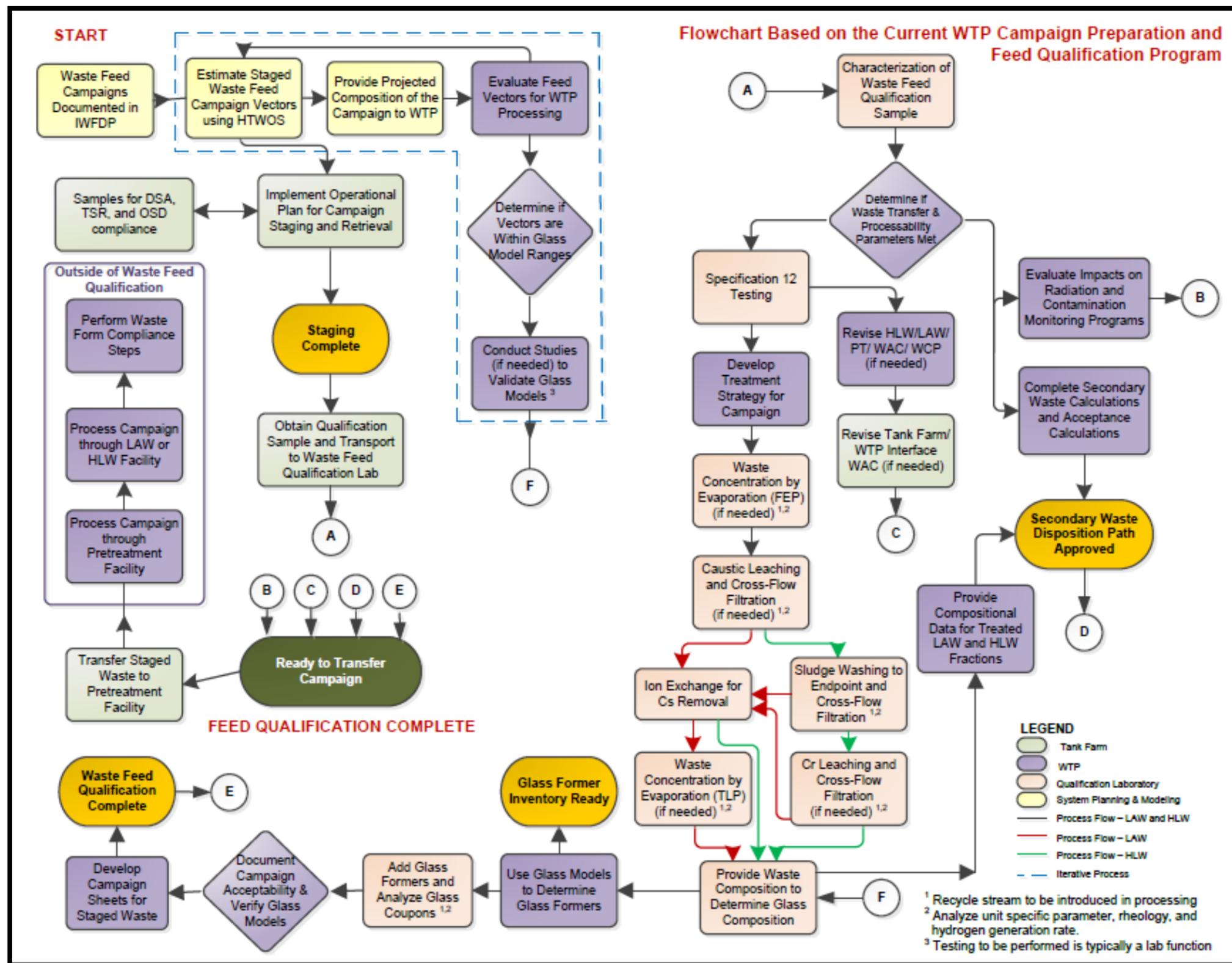


Figure 2-3. Flowchart for WTP Baseline Waste Feed Qualification Plan.

Waste feed concentration (or boil-down) is performed within two separate unit operations inside PT, and the objective is to adjust the sodium molarity and the solids concentration of some waste streams. The first occurrence is within the waste feed evaporation process system (FEP) and may be performed on LAW feed and approximate steady state recycle when necessary. The second occurrence is the treated LAW evaporation process system (TLP), which concentrates the treated LAW from the ion exchange system, as well as the LAW vitrification facility offgas recycles. When evaporation is required, evaluations are performed to analyze changes in physical properties and to observe for the occurrence of foaming. The evaluations are required to ensure waste concentrations are within both the FEP and TLP system operational limits.⁶

To demonstrate sludge leaching, washing, and separation of permeate and slurry by cross-flow ultrafiltration, a scaled cell unit filter (CUF) system is expected to be used following parameters selected during Specification 12 testing. The feed for the CUF runs will include blended staged LAW and HLW feeds along with an approximate steady state recycle simulant. The blend will target a nominal weight percent solids and sodium molarity consistent with the process identified in the ultrafiltration process system (UFP) description. Rheology will be evaluated as part of the demonstration at selected intervals and with consideration for different solids loadings. The products from the demonstration will include permeate necessary for Cs ion exchange testing and the slurry phase for HLW glass production.

Ultrafiltration permeate produced during the CUF system runs will undergo ion exchange processing in order to prepare treated LAW and HLW feed for vitrification. With the current WTP PT baseline, the ion exchange apparatus would be warmed to a minimum temperature prior to introduction of material in order to prevent undesired precipitation of the CUF run permeate samples. The ion exchange effluent will be used for treated LAW glass production after concentration through the TLP unit operation. The ion exchange regeneration eluate containing radioactive Cs will be used in HLW glass production after combining with the final CUF system slurry sample. Lastly, the spent resin will be evaluated to obtain information on the spent resin disposal path. This may include analysis for radiological content and Resource Conservation and Recovery Act (RCRA) metals.⁶

The final step of unit operations testing is the formulation and production of glass. The types and quantities of glass forming materials to be mixed with the LAW and HLW feeds are determined using the appropriate glass formulation algorithm and the results of analysis of the treated LAW (ion exchange effluent) and concentrated HLW (CUF slurry). Once the glass formers are added, rheological measurements are made and the mixtures are then vitrified at the crucible scale using the nominal melt temperatures.⁶ The vitrified samples are used to facilitate analyses and to verify that the models accurately predict the glass compositions of the resulting product. No glass property testing is performed on the glass samples, but an initial read on the necessary glass processing region is gained from this process.

WTP has initiated development and construction of the necessary laboratory-scale equipment for waste feed qualification testing under a Scope of Work with SRNL and will include design of the hydrogen generation rate apparatus, the equipment needed for Specification 12 testing, and the individual unit operations equipment.¹⁴ This work is Phase 2 of the development of the Hanford Waste Feed Qualification Program and will also determine the sample volume required to perform these analyses. As currently defined, analytical measurements for the unit operations apparatus need to achieve an accuracy of $100\pm 20\%$ with a relative standard deviation between replicate measurements of $\pm 20\%$. These criteria apply to quantitation of elements, compounds, and radionuclides with concentrations greater than the minimum reportable quantity as defined by the WAC-DQO.⁶ Measurement error or variability will be determined for the WAC parameters, processability parameters, and unit operations analysis. The sources of error are likely to include

- Physical sample collection, which includes sample volume/mass, sample delineation, and sample extraction;
- Sample handling, which includes preservation, packaging, labeling, transportation, and storage; and
- Analysis, which includes sample preparation, sub-sampling, extraction, analytical determination, and data reduction.

Quality controls for other aspects of unit operations testing will be defined as part of the Phase 2 development.

Phase 3 will be the implementation of the waste feed qualification program to support WTP Cold Commissioning and implementation of interfaces between the waste feed qualification laboratory and Plant Engineering to support Campaign and Unit Operations Batch sheet development.

Currently, the sample results from the staged waste qualification sample are necessary for process knowledge but are not required for product qualification and are not a part of a waste form compliance strategy. The waste form compliance strategies for both the IHLW¹⁵ and ILAW¹⁶ require sampling of the received waste in the vitrification facilities. The analyses of the waste are used to determine the necessary glass formers, and the resulting analyses of the melter feed are used to report the composition of the IHLW and ILAW. Thus, minimal ties are made from the waste feed qualification program to the waste form compliance plans for either the IHLW or ILAW. However, controlling the composition to the vitrification facilities will be integral to reliable plant operations and to meeting the waste form requirements, and preliminary information on the feed vectors may be obtained from the testing that is performed as part of the waste feed qualification program.

3.0 Overview of DWPF Macro-Batch Strategy

The DWPF Macro-Batch strategy was developed to demonstrate that DWPF would consistently produce a waste form that would meet the EM WAPS for vitrified high level waste forms¹⁷. The strategy includes the processes that are performed in the Tank Farm, the melter feed preparation performed in the Chemical Process Cell (CPC), and production of a predictable and durable glass waste form. The protocol for DWPF compliance is defined in the Waste Form Compliance Plan (WCP)¹⁸ and specific components of the Macro-Batch strategy as it relates to the sludge batch qualification program are further described in the Waste Qualification Report – Volume 6¹⁹. For DWPF, the components make up the Glass Product Control Program, which was put in place to ensure that an acceptable glass product would be made on a consistent basis with high accuracy.

An overview of the program and the lessons learned with implementation of the program (as well as from radioactive operation) was recently compiled by SRNL in a technical report for the DOE-ORP strategic efforts²⁰. Pertinent information on the SRS Macro-Batch and qualification strategy as it relates to the Hanford WTP campaign strategy will be discussed in this section. As currently envisioned, Hanford will stage their LAW and HLW in the same manner. The SRS does not vitrify their LAW so the strategy is slightly different than that used for sludge or HLW. Therefore, the DWPF discussion will focus mainly on the HLW portion but the LAW portion will be brought in as it relates to the sludge batch qualification strategy.

The section is subdivided into a discussion on the sludge processing aspects (Tank Farm preparation and melter feed preparation processing) and the waste form qualification aspects. The current waste feed qualification program for Hanford/WTP is analogous to the first element for DWPF (i.e., sludge processing) with the waste form qualification aspects being handled separately. Given some of the proposed changes to the baseline Hanford flowsheet, aspects of the DWPF's waste form qualification program may be applicable to Hanford as well.

3.1 DWPF Sludge Processing Qualification Strategy

For 17 years, the DWPF has consistently produced acceptable HLW glass product using a Macro-Batch concept where feed is staged, mixed, prepped and sampled in a one million gallon tank. The typical batch for the DWPF has ranged from 300,000 to 800,000 gallons of feed. A total of 10 Macro-Batches or Sludge Batches have been qualified to date for DWPF, and Sludge Batch 8 or Macro-Batch 10 is currently being processed. For DWPF, the Macro-Batch does not have to equate to one Sludge Batch if the combination of sludge, salt, and glass formers will produce a similar glass composition to the existing Macro-Batch. However, to date, each Sludge Batch has resulted in a Macro-Batch change for DWPF. The total production equates to the delivery of ~4M gallons of sludge feed and 5E+07 Ci of waste.

The SRS staging and preparation of the Sludge Batch or Macro-Batch is known as Extended Sludge Processing (ESP). ESP is performed in two dedicated million gallon tanks that contain four quad volute slurry pumps. These pumps have been shown to homogeneously mix slurry during ESP and for transfers to the DWPF. A discussion of the pump selection and data from samples taken during this large-scale mixing is given in reference 21. These tanks and the processes they perform are the first step in the Macro-Batch qualification strategy or the sludge batch qualification program. Originally, staging and preparation was performed in either tank, while the other was dedicated to feeding DWPF. Since Macro-Batch 3, all batches have been prepared in Tank 51, transferred to the Tank 40 heel, and fed to DWPF (received in the Sludge Receipt and Adjustment Tank) from Tank 40 through a low point pump pit by either 2 or 3 transfers of ~1500 gallons each. This process gives a constant feed composition to the DWPF for anywhere from 1 to 3 years.

Typically, sludge from more than one HLW tank is transferred to the ESP tank (Tank 51) to provide a blended sludge composition suitable for DWPF processing. See Figure 3-1 for a schematic of the process that is used to stage the waste and the associated sampling points. The tanks being blended are selected by Savannah River Remediation (SRR) based on necessary tank closure dates and expected sludge compositions that are tracked in the Waste Characterization System (WCS). Projections of the sludge composition are performed by SRR and include any washing or Al dissolution that might be performed in the Tank Farm. Over the years, the SRNL has also performed variations on the blending and washing scenarios to help determine the optimal blend. The tanks to be blended are typically sampled during the bulk sludge removal process to gain information on the sludge composition. These samples range in volume from 80 to 200 mL with the number of samples collected depending on the required analyses. Several samples are taken when rheology determinations or more complete characterization is required instead of just a few analytes of interest. The samples are typically grab samples taken after the mixing pumps have been shut-down. The sample information is used by the Tank Farm to ensure that they remain in compliance for their flammability and corrosion control programs as well as to provide better information for the blended sludge batch composition.

Once all of the tanks to be blended have been transferred to the ESP tank (Tank 51), washing is initiated with the introduction of inhibited water (water with dilute concentrations of sodium hydroxide and sodium nitrite) or with dilute supernate from another tank. Decanting of supernate may also be the first step in the washing process to reduce the high sodium salt content of the sludge. During these early stages of the washing process, the qualification sample shown in Figure 3-1 is taken to initiate laboratory characterization and testing. The qualification sample is typically a 3-L sample that is also taken after the pumps have been shut-down. The sampler is typically staged so the sample can be taken within hours after the pumps are stopped. All four slurry pumps are run for a minimum of 8 hours to ensure the tank contents are homogeneous before the sample is pulled. No additional transfers are made to the sludge preparation tank that would affect the insoluble solids concentration after this sample is taken. Two exceptions exist for transfers. The first is the iterative washing process where inhibited water or dilute supernate is added. Since the washing process can be modeled fairly well and it is mostly the supernate composition that is affected, this Tank Farm processing can occur concurrently with the laboratory studies to qualify the batch. The iterative process of washing is repeated until the final sodium supernate concentration target and the insoluble/total solids target are obtained. This washing endpoint is determined from testing performed as part of the sludge batch qualification process and can include glass composition assessments based on modeling or with surrogates, flowsheet testing with simulants, and flowsheet testing with the qualification sample. The second transfer that has historically occurred has been canyon transfers of excess materials for disposition. These transfers can easily be replicated in the qualification process so the impact can be properly assessed.

Depending on when the qualification sample is taken, multiple wash and decant cycles may need to be performed by SRNL in the Shielded Cells to complete the sludge batch preparation process. The washing process has been shown to be repeatable on a small-scale in the Shielded Cells, while projections have been shown to be more conservative than actual field data. Thus the qualification demonstration has been shown to be beneficial in reducing the number of washes that are required in the Tank Farm. This is positive both from a schedule and water management perspective.

As the Tank Farm processes described above are being performed, laboratory qualification of the Macro-Batch is being performed in parallel on several fronts, see Figure 3-2 for the specific steps in the qualification process. With the initial projections on the sludge batch composition and as composition information becomes available from the tank samples collected from the individual tanks, SRNL begins assessments of the glass composition window and can initiate simulant development for flowsheet testing. Additionally, the washing demonstrations on the qualification sample provide feedback on the applicability of the washing endpoint and number of wash cycles while simultaneously providing insight

on rheology of the sludge batch. The information from the glass assessments, flowsheet testing, and washing of the qualification sample is used by SRNL to recommend the final washing endpoint (including sodium and anion concentrations and target insoluble solids). Based on SRS's experience to date, the washing and solids endpoints can change from batch to batch, which is possible because of the new information gained on the behavior of sludge components during DWPF processing with each batch. While the target endpoint has changed, the process for reaching the endpoint has consistently been shown to be repeatable on a laboratory scale. Critical components of the Shielded Cell's prepared sample are typically within 10% of the final composition of the Tank Farm prepared sample. The DWPF processes can accept this level of variation and stay within its nominal operating window for a prototypical batch. If the composition (typically supernate or total solids concentration) is not close to the target, adjustments can be made in the Tank Farm to ensure that the qualification compositions have been bounded. For this reason, a confirmation sample is taken near the end of washing in the Tank Farm. This sample is not shown on Figure 3-1 but is taken from Tank 51 or the ESP preparation tank. The sample can be anywhere from 80 to 200 mL or as large as a 1 or 3L sample depending the additional analyses or processing needs. As with the other samples, the grab sample is taken after thorough mixing and after the pumps are shut-down. If only confirmation of the endpoint is required, two to three 80 mL samples or one 200 mL sample is sufficient. The primary goal is to verify the composition and rheological properties. Typically, no flowsheet testing is performed on the sample.

After all of the qualification steps have been completed and the sludge has been staged and washed, a predetermined volume of sludge is transferred from Tank 51 to the residual heel of sludge in Tank 40. This heel can be as low as 40" or as high as 200" depending on the processing need. In some cases, Tank 51 is needed for sludge removal from another tank so the transfer to Tank 40 has to occur to accommodate this space need. In other cases, the blend ratio of the tanks is determined from laboratory studies to optimize the flowsheet or glass composition. Once the transfer has been made to Tank 40 and DWPF processing has been initiated, a sample will be taken from Tank 40 to represent the sludge reportable constituents for the Macro-Batch. This sample is taken after homogenous mixing is established and the pumps have been shut-down. The sampler is staged to take a 1 or 3L sample depending on the additional analyses or process demonstrations that may be required.

As with the Hanford WTP process, additional chemical processing of the sludge is performed to prepare it for feeding to the melter after the Macro-Batch is transferred from the Tank Farm to the DWPF. The adjustment occurs in the DWPF CPC. A wide range of sludge simulant compositions were tested before DWPF start-up spanning the expected range of sludge compositions, and perhaps more importantly, spanning the range of expected troublesome components (e.g. noble metals, Hg) to be processed in the DWPF. The testing helped define nominal operational parameters for the DWPF CPC and provided confidence to DWPF that the process chemistry could be fairly well predicted based on simulant studies. In the CPC process, a combination of nitric and formic acids is added at 93°C to initiate the necessary chemical reactions including the reduction of Hg. After all of the acid is added, the sludge is heated to boiling, where concentration and reflux occur, to complete the reactions and strip the Hg. These steps are performed in the Sludge Receipt and Adjustment Tank (SRAT) in DWPF, and then the slurry is transferred to the Slurry Mix Evaporator (SME) tank. In the SME, glass-forming frit is added at the targeted waste loading and the slurry is boiled further to the melter feed solids target, which is typically in the range of 42 – 50 weight percent total solids.

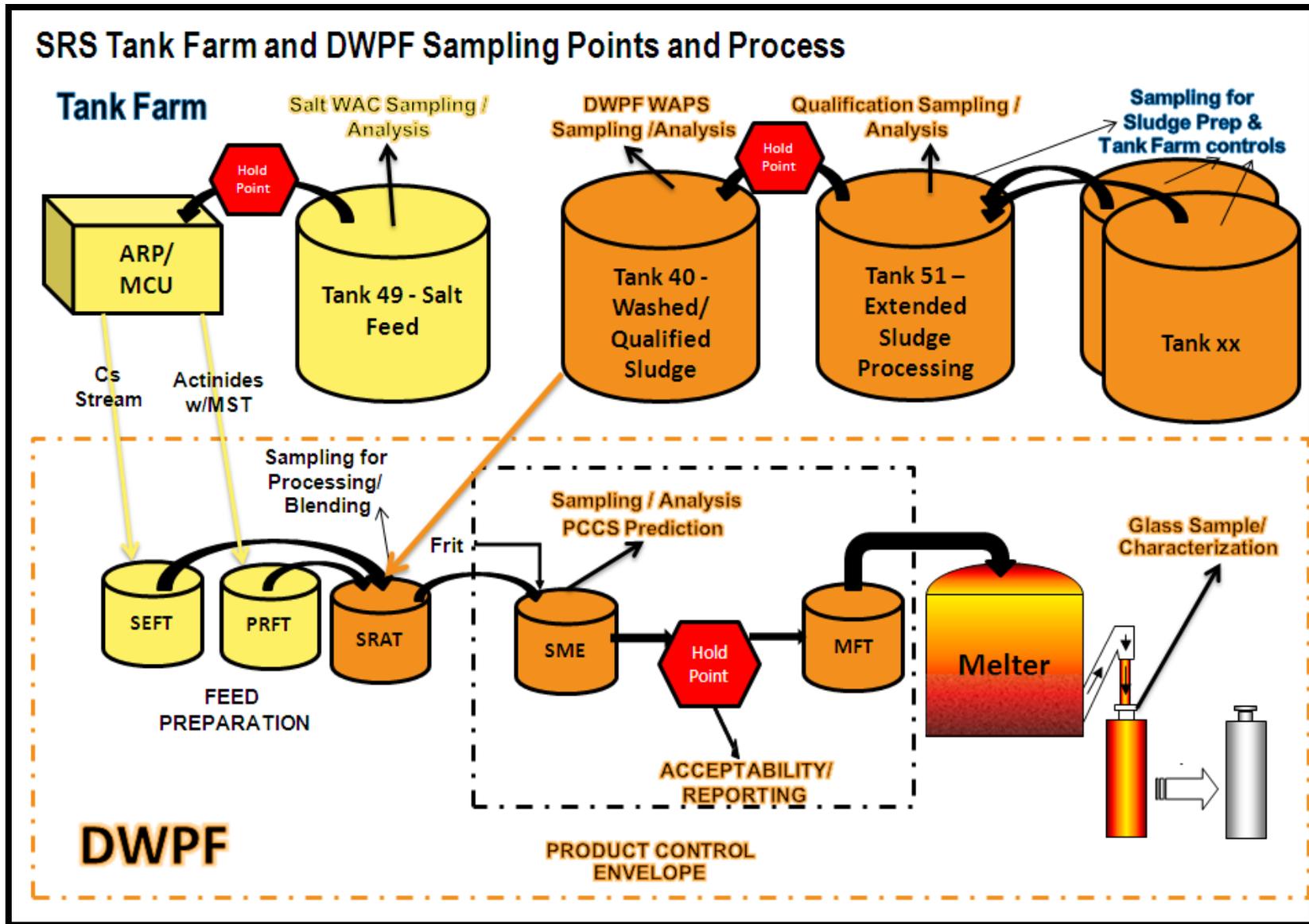


Figure 3-1. Sampling Points for DWPF Macro-Batch Strategy

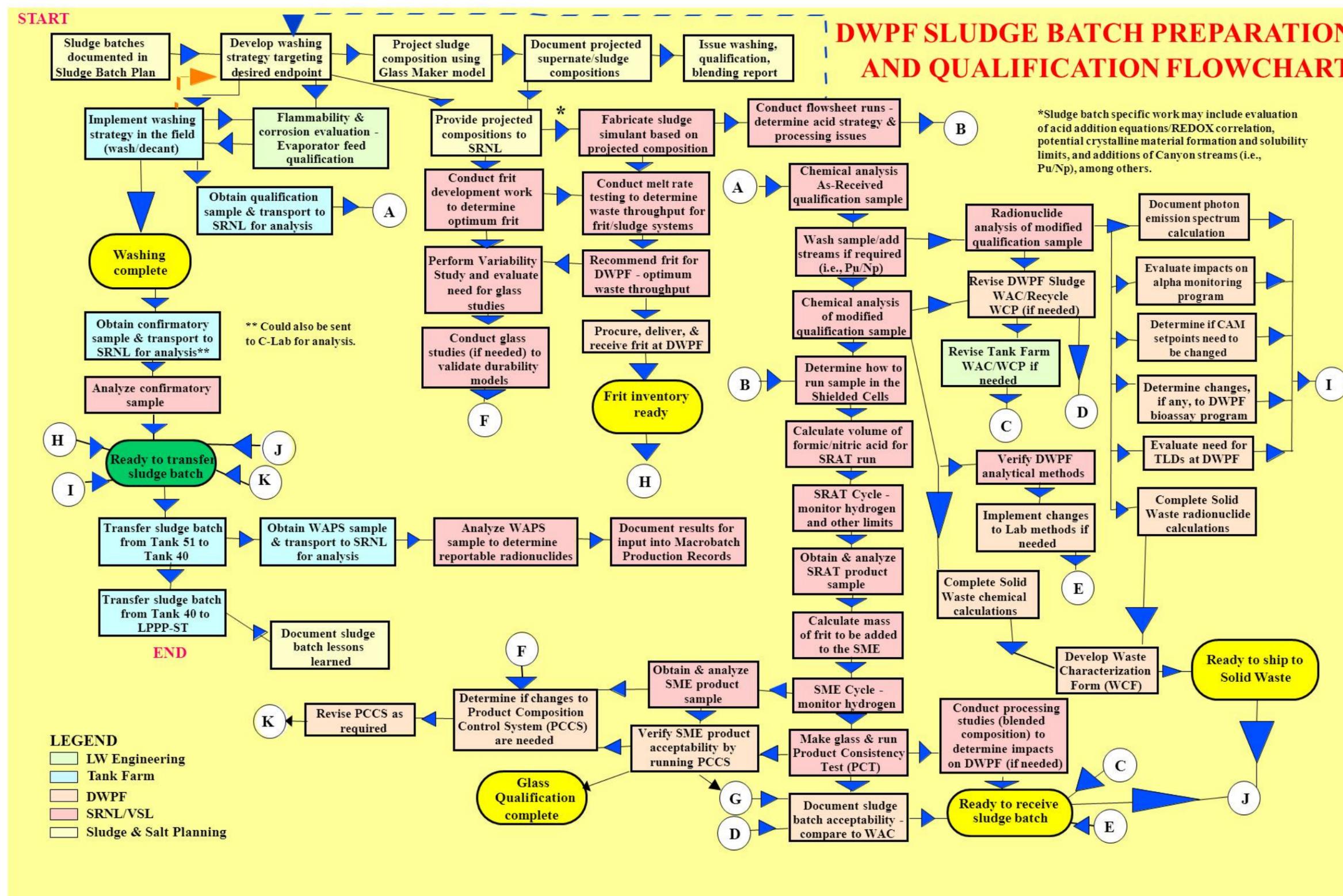


Figure 3-2. Flowchart for DWPF Sludge Batch Preparation and Qualification.

The primary variable that is changed during the qualification flowsheet testing is the amount and ratio of acid to add. The recommended amount is enough to complete the necessary reactions but not so much that excessive catalytic hydrogen is generated. Other process parameters that are defined include determining the time required for Hg stripping, the amount of antifoam to add, and the solids endpoint from a rheological standpoint for each process in the flowsheet. Simulant tests are used to refine these parameters and a processing window is defined for each Macro-Batch. The simulant testing also supports the recommendations for the Shielded Cells run with the qualification sample, which is a single test run to demonstrate the material is acceptable for DWPF processing and demonstrates that the Macro-Batch can be processed in the DWPF. High confidence in the recommendations for the Shielded Cells test run is necessary because of the potential schedule delay that could occur with a failed qualification test. In addition to providing an indication of the potential acid addition amount that might be necessary in DWPF, the Shielded Cells qualification provides information on both the foaming nature and rheology characteristics of the feed. This information is helpful to set the antifoam strategy and target solids endpoint for DWPF processing. Based on the combination of simulant and radioactive testing, SRNL provides a recommendation on the nominal acid addition strategy for DWPF processing, as well as the potential window for successful operation.

Some of the HM sludges produced from the H-modified canyon extraction process contain appreciable quantities of aluminum that would require extensive blending to produce an acceptable glass and/or have acceptable feed processing properties. At SRS, aluminum dissolution has been performed on two batches for DWPF processing. In both of these cases, the Al dissolution step was performed outside of the typical DWPF sludge batch qualification process (i.e., Al dissolution performed and then the qualification sample was taken). For the first batch, it was performed on a previously washed batch in Tank 51, which was then further washed to remove the added caustic. For the second batch, it was also performed in Tank 51 but on an unwashed batch, which was then washed. The Al dissolution is performed in the tank farm by adding concentrated caustic solution, heating to between 55 and 65°C, mixing for extended periods (~28 days), and then decanting the dissolved Al containing supernate to another tank. Chemical models, which have been verified with actual Al dissolution demonstrations in the SRNL Shielded Cells, are used to determine the required caustic concentration and contact time to meet the Al removal targets. Although SRNL testing has been performed on <3 L of sample, the results have been fairly consistent with Tank Farm results.

Up to this point, SRNL has not been able to define a representative simulant for performing Al dissolution. However, SRNL has been successful at defining a small-scale beaker test to determine whether the Al in the sludge behaves more like the boehmite or gibbsite phase. This information can be used to define operating parameters based on the models in a shorter time span than the full demonstration of the Al dissolution process. This test would be similar in concept to the Specification 12 testing proposed for Hanford. In order for the flowsheet testing to be completed for an Al-dissolved batch, SRNL prepares the simulant based on the post Al-dissolution composition. This results in some delays in the process since actual plant data is needed on the percentage of Al removed. If a simulant for performing aluminum dissolution could be developed, then testing of the simulant could be integrated into the qualification program to provide more representative feed for flowsheet testing as well as to support projections of the composition to be obtained after Tank Farm performance of the aluminum dissolution process. Without this simulant, only projections of composition are available and no information on the expected physical properties of the sludge are known.

The above discussions have addressed sludge-only processing or the HLW fraction of the SRS waste. When the DWPF started up, the salt waste processing facilities had not been brought on-line and the processes/flowsheets were subsequently changed. The current interim/modular processing that is being performed in the Actinide Removal Process (ARP) and Modular Caustic Side Solvent Extraction (MCU)

is similar to that which will be performed when the Salt Waste Processing Facility (SWPF) comes on line. These facilities remove Cs, Sr, actinides, and other entrained solids from the LAW fraction of the waste for processing in the DWPF. The qualification process for the LAW feed (i.e., Salt Batch) to ARP/MCU is similar in concept to the DWPF Macro-Batch strategy but the unit operations that are performed are more simplistic. Salt batches are staged in Tank 49 and the Salt Batch qualification sample can be taken from this tank or from the individual tanks and then combined for qualification. Characterization includes those parameters necessary for processing of the salt processing streams throughout the SRR liquid waste system. The demonstration of the ARP/MCU processes involves simple batch testing. For the ARP facility where the actinides, Sr, and entrained solids are removed, a known volume of waste is obtained, and an amount of a qualified batch of monosodium titanate (MST) is added. The target MST concentration is that of the actual ARP process. The “qualification” of the supplied MST by SRNL prior to use by ARP is to ensure that the quality assurance components of the MST procurement process are completed. The slurry is agitated with laboratory mixers and sampled periodically to ensure that the alpha concentration will meet the downstream WACs for LAW processing within the flowsheet duration. For MCU, the decontaminated tank waste is characterized and then tested using an extraction, scrub, and strip (ESS) protocol, which is equivalent to the solvent extraction process that would be performed in the MCU facility for Cs removal. This protocol simulates the chemistry within the solvent extraction process using typical phase ratios and measures the cesium distribution behavior. These measured distribution coefficients are compared to plant acceptance levels.

Two of the effluents from the salt processing facilities have to be processed through the DWPF CPC and include high activity (Cs) and solids containing fractions (sorbents, Sr, and actinides). The MST/sludge solids stream from ARP is added to the SRAT at boiling before the initiation of the SRAT process (i.e., before acid addition). After the stream is added, a sample is taken to determine the acid addition amounts and then typical processing is initiated. The process is depicted in Figure 3-1. Qualification of the MST/sludge solids stream for DWPF processing was performed by SRNL using simulants in flowsheet testing prior to ARP incorporation and is now only verified with a simulant run as part of the simulant flowsheet testing. The simulant flowsheet testing with bounding volumes of the stream were shown to have minimal impact on the SRAT processing chemistry and low concentrations of radioactive constituents are not believed to have an impact on processing characteristics; therefore, this strategy was considered acceptable and a radioactive demonstration with the coupled flowsheet is not performed as part of the qualification process. While chemical processing does not appear to be impacted, the stream does increase the SRAT processing time because of the additional boiling required.

The strip effluent containing Cs from the MCU process is transferred to the DWPF in small batches. These batches are stored in a hold tank until they can be transferred to the SRAT during the boiling process after all acid has been added. The stream is a dilute nitric acid stream that contains low concentrations of the removed Cs and non-recovered solvent; thus, the stream has the potential to impact the melter feed redox because of the nitrate in the stream. The Cs has no impact on the CPC flowsheet, while the residual solvent results in flammability concerns for DWPF. Flammability is primarily controlled in CPC by the addition at boiling and insurance of purge gas during static and processing conditions. This has little net impact on the SRAT processing time as the addition of MCU replaces time spent boiling under reflux conditions. As with the MST/sludge solids stream, qualification is only performed using simulant streams, which are considered adequate to bound the potential processing impacts. This was possible after sufficient flowsheet testing with simulants was performed to demonstrate that minimal impact would be realized on the flowsheet. The proposed next generation solvent has been evaluated for impacts on the DWPF and the primary concern was control of the boric acid concentration in the solvent strip. Boron is a key component of the frit used to make glass and if present in elevated concentrations would require adjustment to the frit composition.

While the discussion above has focused on the Tank Farm and DWPF processing that is performed with each batch, another aspect of the qualification is the characterization of the chemical and radioactive constituents and physical properties of the Macro-Batch. As with the WTP, the DWPF has a WAC that the salt (LAW) and sludge (HLW) Macro-Batch must meet before it can be received into the facility. The WAC is updated with each salt and sludge batch and includes those parameters that must be controlled to meet waste form repository requirements, safety basis limits, or design basis criteria. The SRS has learned over the years that WAC criteria should be set as either a target or limit and need to be criteria that can be definitively met. With regards to the target or limit, targets are more aligned with processing criteria, while limits are typically tied to safety basis or waste form criteria. One obvious difference with WTP WAC criteria is the particle size limit proposed for WTP. Early characterization and well-defined testing were performed at SRS to provide a potential particle size range for the sludge components. For SRS, the frit is the largest particle that is processed in DWPF and can be up to 178 μm . The testing for DWPF considered both the sludge and frit range and frit particle size was shown to be most limiting. If new information was to be gained that larger particle sizes would be processed in DWPF, then additional testing would need to be performed to determine the impact on criteria such as mixing and sampling. The latest revision to the DWPF WAC is given as Reference 22 and contains both targets and limits. To minimize the number of analyses performed in DWPF, the washed qualification sample undergoes extensive chemical and radionuclide characterization to determine the WAPS reportable chemical constituents and a preliminary list of radionuclide components. The radioactive constituents are used mainly by DWPF to protect the safety basis for the facility, provide adequate monitoring for the constituents of concern, and to complete certification of the solid waste stream for that batch. The results from the chemical constituent analyses, on the other hand, identify the elements that need to be measured and reported in DWPF, which reduces turn-around time in DWPF through minimization of the number of analyses.

3.2 Waste Form Qualification Strategy

As mentioned above, the DWPF qualification process is slightly different than the waste feed qualification process for WTP because of the focus on the waste form acceptance for DWPF during the sludge batch or Macro-Batch qualification process. Two primary studies are currently required to qualify the Macro-Batch for DWPF with respect to the glass waste form: (1) a variability study and (2) fabrication of the qualification glass in the SRNL Shielded Cells facility. Additional studies are performed to provide an optimal processing window and to verify the glass solubility limits.

The DWPF glass algorithms (referred to as the Product Composition Control System (PCCS)²³) play an integral role in the Macro-Batch qualification process and are used to predict various process and product performance properties of the glass waste form. The durability models embedded in PCCS are used to predict the Product Consistency Test (PCT)²⁴ response based on glass composition. The objective of the variability study is to determine the applicability of the correlation between PCT results and the chemical composition for that batch. If the correlation does not apply over the entire range of compositions, then the DWPF would constrain the process to operate only within the region over which the correlation does apply or a new correlation would be developed for that batch. If a new correlation were needed, data generated during the variability study would be used to develop the new correlation.¹⁹ Durability is assessed against the benchmark Environmental Assessment (EA) glass.²⁵ For Hanford, a similar goal exists to develop correlations across the entire anticipated compositional range. Given the complexity and potential range of compositions anticipated for Hanford, it may be more practical to develop correlations for certain waste types or composition ranges. This would be similar in concept to the variability study but could be performed early in the process and the composition range verified with each batch.

For the DWPF, the glass compositional region is defined by three inputs:

- the sludge and salt waste composition;
- the frit composition; and
- the waste loading.

The sludge waste composition is based on the measured washed qualification sample composition, while the salt composition is based on the projected bounding composition of the salt streams. The frit composition is determined from model assessments of the glass composition window with an array of frit compositions. The nominal blending of the sludge, salt, and frit at a range of waste loadings provides the anticipated glass composition window. For sludge, the typical waste loading range considered is 28 to 60 wt% on a sludge oxides basis. The salt components contribute only a minor amount to the waste loading and the operating window is defined by the projected salt composition and a bounding volume contribution to the process batch (which is typically one full Precipitate Reactor Feed Tank and Strip Effluent Feed Tank). Calculations of the glass composition are performed over this range and then the assessment uses the same models as those in DWPF's PCCS and considers the model uncertainty and error in the analytical measurements. SRNL recommends the specific frit composition for each Macro-Batch based on this assessment and the ability to procure the frit in time for DWPF production. This combination of information is used to project the potential glass composition window for that Macro-Batch and the assessment of the applicability of the durability models to that window constitutes the variability study. If insufficient data is available in that window, glasses are fabricated and subjected to durability testing to validate the models.

In addition to the glass variability study, a glass sample is produced from the qualification sample and is subjected to durability testing. The glass sample is fabricated from the Shielded Cells processed feed and a frit that is projected to produce an acceptable glass. The composition of the glass is measured and the analytical results are used to predict the properties of the glass. This single data point provides additional confidence that the glass to be processed in DWPF will be acceptable

Finally, the last type of studies that may be performed are crucible melts to determine glass solubility limits. It is known that the anion species of SRS waste have solubility limits that are dependent on the glass composition. Therefore, for each batch of feed that is processed through the DWPF, solubility limits will be tested if the composition will be approaching the limits. This testing has mainly focused on sulfate for DWPF since the sludge contribution typically approaches the glass solubility limits.

The discussion in this section has focused on the glass processing/formulation activities that are performed as part of the qualification process. Additional requirements of the waste form qualification strategy are satisfied through sampling in the DWPF feed tank (Tank 40), in the DWPF process vessels, and from the DWPF pour stream. These sample points are depicted in Figure 3-1. The WAPS require the waste form producer to report the inventory of radionuclide constituents projected through 1100 years. DWPF meets this requirement by analyzing a sample from the Tank Farm (Tank 40) and scaling the radionuclides to a reportable element that is measured for each melter feed batch. This minimizes the number of radionuclide analyses that are performed, which are often time consuming measurements. This is possible for the DWPF because Tank 40 is well mixed and the uncertainty has been quantified.

As planned at WTP, the DWPF measures the composition of each melter feed batch to determine the glass composition. This measurement is performed on a sample taken from the DWPF SME, and PCCS is used to project the properties of the glass that will be produced. The feed is not moved forward to the melter feed tank until its acceptability has been demonstrated. This process was demonstrated to be acceptable in the DWPF qualification runs.

The final step in the qualification process for the Macro-Batch is to obtain a glass pour stream sample for characterization and testing. A glass pour stream sample is taken from each Macro-Batch and is

transferred to the SRNL Shielded Cells. Reportable constituents are measured on this glass sample and compared to those identified in the qualification process and from the Tank 40 WAPS sample. The durability is measured on this glass through the performance of the PCT and the results are compared to the PCCS durability projections. The data from the pour stream samples taken to date have not identified any new reportable constituents and have confirmed the glass acceptability. Thus, the adequacy of the DWPF glass product control program has been demonstrated routinely and these confirmation samples may not be necessary any longer.

4.0 Potential Hanford WTP Strategies

Given the higher total volume of Hanford waste, the greater vitrification facility design throughput, and large number of campaigns that are anticipated for the WTP, qualifying as large a campaign as possible has benefit to the overall mission. Another goal is to develop a strategy to provide better assurance of meeting the WTP WAC while also providing more processing flexibility. As discussed in Section 1.0, risks have been identified in the ability to homogeneously mix and representatively sample the campaign feed³, which would increase the uncertainty associated with the sample analyses and in defining the processing parameters. The benefits of achieving these goals could include reducing the total number of campaign qualifications required and minimizing the composition and process variability through the WTP.

With these goals in mind and with the DWPF Macro-Batch strategy as a reference case, SRNL assessed the existing WTP waste feed qualification program and Tank Farm staging strategies for potential improvements. Generally speaking, two types of strategies evolved. The first considered the baseline assumptions for the WTP processing facilities using the current Tank Farm limitations. The second strategy considered improvements or changes to these assumptions, as well as potential changes to the baseline flowsheet, to improve the chances of success. This strategy set considered the design and construction of a Tank Waste Characterization and Staging Facility. The objective of the facility is to provide the Tank Farms with the capability to stage, mix, and blend tank waste to allow the delivery of a consistent, certifiable, and compatible waste feed to the WTP. Presumably, this facility would be similar in functional concept to the ESP tanks used to feed DWPF (Tank 51 and Tank 40 discussed above). Consideration was also given to incorporating some of the aspects of the waste form qualification process into the Tank Farm to minimize the variability and sample analyses in the vitrification facilities.

4.1 Incorporation of a Macro-Batch Strategy in the WTP Baseline

The baseline waste feed qualification and acceptance program for WTP was described in Section 2.0 and included the TOC plans for staging, sampling, and transferring the campaign batches. The primary objectives of this program are to demonstrate compliance with the WAC, determine waste processability, and demonstrate unit operations at a laboratory scale. Risks to acceptability and successful implementation of this program, as compared to the DWPF Macro-Batch qualification strategy, include: limitations of mixing/blending capability of the Tank Farm; the complexity of unit operations (i.e., multiple chemical and mechanical separations processes) involved in the WTP pretreatment qualification process; the need to account for effects of blending of LAW and HLW streams, as well as a recycle stream, within the PT unit operations; and the reliance on only a single set of unit operations demonstrations with the radioactive qualification sample. This later limitation is further complicated because of the 180-day completion requirement for all of the necessary waste feed qualification steps.

To improve the chances of success of the qualification program and subsequent processing in the WTP with the baseline flowsheet, several changes are recommended and are depicted in the flowchart in Figure 4-1. The new processing steps are indicated with a bolded outline and striped interior patterns in the flowchart. Two of the items in this figure were present in the original flowchart (Figure 2-3) but the responsible organizations have changed to include the use of the national laboratories in the assessments as is done at the DWPF. At a high level, the changes include:

- Sampling and characterization of the individual tanks to be staged with a view to WTP feed qualification,
- Initiation of qualification activities earlier in the staging process to optimize the campaign composition including use of the national laboratories in the process,
- Incorporation of simulant studies to understand the parameters of importance and define the parameters to be tested with the waste feed qualification sample, and

- Evaluation of alternative processes/equipment demonstrations to define unit operations parameters.

How these changes are already used at the DWPF and how they could be applied at WTP will be discussed below. In some cases, the changes are closely tied together so discussion of the changes will in some cases overlap.

The first change would be accomplished by taking samples during retrieval of the individual Single Shell Tanks (SST) or DSTs that will be blended/staged to produce the WTP staged feed campaign. Although Hanford has a Best Basis Inventory (BBI) that estimates each tank's contents and composition, SRS experience has shown that layering does occur in the tanks and that surprises can occur when sampling/retrieving the tanks compared to projections in the inventory system. An example at SRS was the high levels of both sulfate and nickel in Tank 4, which were mitigated through the washing and blending strategy. Washing reduced the overall sulfate level, while blending took advantage of the ability to split the contents of Tank 4 into two sludge batches to bring the total concentration to a more acceptable level for glass processing. Having these early samples allowed SRS the flexibility to accommodate these higher than anticipated components in the sludge. In the case of Hanford, many of the samples that formed the basis for the BBI were core samples and not slurried samples of the entire tank contents so uncertainties in the compositions should be anticipated. It is recognized that the new samples may also not represent a well-mixed or slurried tank but the insight provided to batch planning has typically been invaluable in the SRS system. Currently, process control samples will be taken during the preparation process and these slurried samples could be taken at the same time or instead of the process control samples. Given the concern with both rheology and particle size for Hanford waste, insight would be gained on these properties earlier in the preparation process so additional time would be available to develop an approach to mitigate any issues. This will be especially important with the 180-day completion time requirement for the waste feed qualification program and because of the anticipated composition variation of the different Hanford wastes. Further benefit is gained when this information is used to smart blend (i.e., intentional blending strategy where blending of HLW feed is based on the composition of waste⁴) or to select processing strategies for that campaign and begin qualification activities with simulants.

For the DWPF qualification, individual tank samples are used to update Macro-Batch composition projections, and initiation of qualification activities begin at this point in the process. Currently for WTP, qualification activities would not commence until the operational plan for the campaign is finalized. For the DWPF qualification, several spreadsheets and models have been developed by SRNL since DWPF start-up to allow assessment of the impact on waste composition from different blending and washing scenarios. These assessments start for SRS during the annual System Planning process and begin for the individual batch preparation process as soon as the tanks to be dispositioned are identified. The resulting compositions can be used in glass composition window assessments or flowsheet assessments with simulants. This set of feedback assessments allow for optimization of the overall system process (Tank Farm washing, DWPF melter feed processing, and DWPF glass processing window), and the same type of spreadsheets and/or assessments could be implemented at Hanford to initiate qualification activities earlier, optimize processing, and improve throughput. The change in Hanford logic is depicted in Figure 4-1 as a feed loop ("Optimization of Campaign Composition") that brings in all relevant organizations to perform optimization as new information is gained.

To be successful with developing these assessment tools, a thorough understanding of the parameters of importance for WTP processing needs to be established. In the DWPF, this was accomplished over several years of lab and pilot-scale processing with simulants over a wide range of waste compositions and at production scale with simulants and radioactive material. For both the melter feed processing and melter processing aspects in DWPF, critical operating parameters were established before the start of qualification runs and included parameters such as operating temperature, acid addition rates, boil-up rates, target nitrite destruction and Hg concentration, and melter feed rate. Control of these parameters was shown to produce acceptable processing and products. However, chemical reactions occur during the process and the key reaction sequences needed to be established to allow identification of the analytes of importance. Once the reactions were established, the required information to control the process for each batch could be defined. For the CPC melter feed processing, the total acid to be added, the split of the formic and nitric acid to control glass redox, and the concentration endpoint to provide acceptable rheology are determined for each batch. To resolve the first two needs, analyses of the sludge is used with the reaction equations and lab-scale demonstrations to confirm acceptable processing. Rheology, on the other hand, requires measurement of the slurry products and is not a predictable result. Even after direct measurement, the exact yield stress or consistency value will likely be different than that in actual plant processing because of slight differences in the full-scale production processes and the associated impact on the property. However, the data does provide a target and relevant trends for plant processing.

WTP needs to complete the process of establishing the parameters of importance for their processes either through a review of existing data or the performance of additional testing to validate these parameters. A key step in this process is to demonstrate that the parameters are the same or of a similar magnitude with radioactive and simulant samples, while a key consideration is to determine whether the parameters can be established with lab-scale equipment, since this will be the primary means for determining the processing parameters for the campaign. Part of this effort will be accomplished during the development of the unit operations equipment for Phase 2 of the Hanford Waste Feed Qualification Program⁶. As an example, this was accomplished at SRS by scaling the 11,000 gallon SRAT/SME in DWPF to 1 and 3-L vessels for lab-scale testing. During flowsheet evaluations, the equipment design and processing parameters for the lab-scale testing were intentionally designed to ensure that the chemistry of the process is being studied versus attempting to scale physical parameters such as mixing and heat transfer. When specific issues with physical conditions are noted (such as air entrainment or coil fouling), dedicated testing is performed with test apparatus specifically designed to evaluate the physical phenomenon. To gain this information, a review of existing data and testing, as well as understanding of the range of waste parameters to be expected and the level of importance of those parameters, will need to be combined with the design of the qualification equipment. If WTP can define the parameters of importance, then simulant testing should be possible earlier in the qualification process (during the staging of the waste or earlier with relevant projections of the waste chemical and physical properties) and would provide a definition of the operating window possible for the feed and a better chance of success for the qualification demonstration.

Currently, WTP plans to design and scale all equipment and parameters for the waste feed qualification demonstration as it is currently envisioned in PT. Simpler systems to demonstrate these functions would make qualification more efficient. This practice has been taken advantage of primarily for LAW processing at SRS. To mimic the process steps during the salt batch qualification, MST is added with the salt (LAW) to a beaker that is thoroughly mixed to replicate ARP conditions and the supernate is separated from the MST. The alpha removed supernate is then added to a beaker with the MCU solvent and the extraction, scrub, and strip steps are replicated using vigorous mixing and separation. However, in order to accomplish this simplification and incorporate simulant studies during the waste feed qualification process, a thorough understanding of the parameters relevant to processing and of those that can be replicated with simulants is necessary. A processing window or range of acceptable processing parameters for the unit operations could then be established for the campaign as opposed to only testing

one processing point in unit operations testing with the radioactive qualification sample. The process to develop an operating window has been shown to be very effective in DWPF pretreatment processing (CPC), but the value was mostly realized after processing issues were experienced in DWPF during Sludge Batch 2 processing. It is now an integral part of the qualification process and begins early in the process to identify issues early so they can be resolved.

Depending on the width of the operational/processing window that is established, it could have ramifications to the Tank Farm mixing protocol. If a fairly wide range is available, more uncertainty can be tolerated in the reported constituents or properties of the qualification sample, which may directly correlate with the extent of mixing. For the DWPF, potential variation in the elemental constituents and physical properties were established through Tank 51 sampling before the start-up of DWPF. Samples were taken on different days after thoroughly mixing the tanks and the relative standard deviation ranged from 5 to 36% for the major elements (Al, Fe, Mg, Mn, Ni, and U) with all error sources considered for tank sampling. Other samples have been taken from Tank 51 and 40 after different mixing times to demonstrate the minimum mixing time required with the four pumps to obtain consistent samples (see reference 26 for an example). Evaluations have also been performed since radioactive start-up to show the consistency of the composition of Tank 40 in transfers to the DWPF receipt tank (SRAT). Since start-up, the variation for the major elements has typically been on the order of 3 to 13% relative standard deviation. See reference 21 for further discussion on these areas. The same type of information is needed on the WTP staging tanks to determine how effective mixing is from a chemical composition standpoint for PT processing. The error sources need to be established and should include analytical and sampling sources. WTP has begun the process of identifying some of these error sources with the DQO process¹².

The changes outlined above would provide more assurance of successful processing in the WTP. They could be implemented individually or as a whole to increase the chances of success with qualification of the campaign feed and with processing of the Hanford baseline flowsheet. A summary of the steps of the qualification process including the recommended changes is provided in Table 4-1. This process as depicted in Figure 4-1 would place the current baseline WTP process more in line with the DWPF Macro-Batch strategy.

Table 4-1. Proposed Changes to the Waste Feed Qualification Program with the Hanford Baseline Flowsheet

Program Step	Existing Step	Proposed Change	Risks Mitigated or Reduced
Sampling and characterization of the tanks comprising the campaign with a view to WTP feed qualification	Includes sampling for process control in the Tank Farm	Add chemical and physical property analyses of waste as tanks are being retrieved	Actual waste data would <ul style="list-style-type: none"> • Inform the blending process and allow for intentional blending to optimize the feed composition • Allow flowsheet and glass formulation assessments of the campaign earlier in the process • Provide flexibility to accommodate unanticipated components in the waste • Increase the chance of success with the 180-day completion time requirement for the waste feed qualification sample
Assessment and optimization of the campaign composition and processing targets (e.g., washing and AI dissolution point)	Includes evaluations using current Hanford system models	Develop and use simplified composition assessments to optimize the glass formulation and flowsheet	<ul style="list-style-type: none"> • Allows for optimization of the overall system process to improve throughput • Initiates qualification processes earlier to increase chance of success of 180-day qualification time period • Provides an operating window to provide more flexibility given tank farm mixing/blending limitations
Performance of simulant studies to determine the WTP flowsheet operating parameters	Plan does not involve simulant studies for qualification	<ul style="list-style-type: none"> • Determine parameters of importance as they relate to bench-scale testing with a radioactive sample • Perform flowsheet studies with HLW simulant to define the processing window • Determine if simpler systems can be identified for unit operations testing 	Providing an operating window as opposed to a single processing point will provide more flexibility given <ul style="list-style-type: none"> • Tank farm mixing/blending limitations • Complexity of PT unit operations (multiple chemical and mechanical separation processes) • Inclusion of recycle streams and different blends with HLW and LAW campaigns in PT flowsheet • Single run performed with the qualification sample in a constrained time frame
Sampling and characterization of the waste feed qualification sample	Step has some uncertainty on effectiveness of mixing and representativeness of sampling	<ul style="list-style-type: none"> • Gather information on effectiveness of mixing with respect to chemical composition uncertainty • Quantify sampling uncertainty with mixing information considered • Use information from the initial sample characterization to feed optimization studies 	<ul style="list-style-type: none"> • Quantifying the uncertainty associated with the chemical composition early in the process will allow its impact on processing to be determined and will allow the number of samples and required analyses to be defined early in the process instead of changing for each batch as currently envisioned • Using initial information on the sample to tailor the campaign processing parameters will provide a more optimized WTP process
Performance of unit operations testing with the radioactive sample	Perform single run using scaled equipment	Select the qualification run parameters based on simulant testing and using simplified equipment if parameters can be defined to simplify the radioactive apparatus	Performing simulant studies to provide a range of operating parameters will <ul style="list-style-type: none"> • Increase the chance of success during the qualification demonstration • Provide the opportunity to optimize processing or identify potential processing issues in the WTP facility

4.2 Macro-Batch Strategy Using a TWCSF or Baseline Flowsheet Modifications

While the section above includes some changes to the qualification process, no equipment changes would be required to the Hanford Baseline Flowsheet. If new equipment or flowsheet changes were to be incorporated in the Hanford Flowsheet, then the qualification program could be closer aligned with the DWPF Macro-Batch strategy. An enhanced strategy would include the changes in the previous section, as well as the changes discussed here.

The first option would involve the use of a TWCSF. The TWCSF would contain several large tanks (though smaller than the existing DSTs) for receiving, staging, mixing, and blending Tank Farm waste. The tanks and associated mixing systems would be designed to adequately mix and sample the waste contents to provide more representative samples and consistent feed campaigns to the WTP facilities for processing. This option would be similar in concept to the role of ESP at SRS or Tanks 51 and 40, which are used for blending, staging, and feeding of DWPF. If successfully implemented, this option should minimize the variation seen between HLW transfers for a HLW campaign and provide more consistent processing in PT. Development of the TWCSF design should include the selection of the proper size and number of pumps and associated sampling systems to demonstrate the extent of mixing. As with the SRS Tank Farm, it is anticipated that with multiple tanks available, the tanks could be in various stages of processing (i.e., one being prepared, one feeding the facility, etc.). The primary advantage of the incorporation of the TWCSF in the baseline is the ability to mix and blend the materials to be processed. This well-mixed feed would provide better assurance that the parameters selected in the unit operations demonstrations of the waste feed qualification program will be applicable to radioactive operations. It might also allow for some of the parameters required for waste form reporting to be measured on the qualification sample particularly for LAW versus on process batches of melter feed. At SRS, the reportable wastefrom radionuclides are measured from a sample taken in the Tank Farm for both the sludge (HLW) and salt (LAW) streams to DWPF. This minimizes the number of samples that have to be analyzed and minimizes the number of analyses that are performed within DWPF. The challenge at Hanford will be estimating the radionuclide partitioning if the waste is processed through the PT since a portion will go to LAW and a portion to HLW. The different sampling points for the Hanford process are depicted in

Figure 4-2. Figure 4-3 depicts a flowchart of some of the potential processing scenarios with this option. New or changed process steps in the flowchart are shown by bolded outlines and striped interior patterns.

Another available option with the TWCSF would be for preconditioning the waste that does not meet existing WAC action limits. Preconditioning could include particle size reduction/solids segregation to minimize the chances of large particles being transferred to the Pretreatment facility and/or causing line pluggage in the system. Options have also been discussed for chemical treatment to reduce the density of some of the waste particles. These options or steps are not performed at SRS as there has been no evidence of large or highly dense particles in samples to date or evidence of the particles causing problems in DWPF processing. Preconditioning could be very similar to the processes used at SRS to prepare sludge for processing in the DWPF. These processes could include washing and concentration and/or performance of Al-dissolution. The advantage of these later preconditioning options is that the need for processing through PT is mitigated but construction modifications would still be required to incorporate the Direct Feed to HLW options. If PT processing is avoided for HLW, then some of the waste form acceptance qualification or compliance requirements could be accommodated with the qualification sample since no other process steps would be required before sending the feed to the HLW facility. This could dramatically reduce the number of samples to be analyzed for the HLW facility because of the larger volume of consistent composition feed material now being transferred. In all of these cases, the existing WAC for transfers would need to be reviewed and updated to reflect the WTP Flowsheet change.

Although the primary advantage of the TWCSF is for processing of HLW, other baseline flowsheet modifications are currently being considered for LAW processing. Direct LAW options should consider the blending of supernates that might be more problematic for glass processing (i.e., minimize anion concentrations to avoid exceeding glass solubility limits) and will be coupled with at-tank or in-tank treatment options for the LAW. The at-tank or in-tank treatment would involve ion exchange processing to remove the Cs and filtration to remove any solids; thereby avoiding the Pretreatment facility for processing.

Options that would alter the baseline WTP flowsheet and potentially use the TWCSF are depicted in Figure 4-4. New or changed process steps in the flowchart are shown by bolded outlines and striped interior patterns. In Figure 4-4, the process steps in the flowchart default to Figure 4-3 if the Pretreatment Facility is used for processing instead of Direct LAW or HLW options.

Implementation of the options discussed here has the potential to provide better assurance that staged waste will meet WAC criteria and processing constraints especially when coupled with the strategies outlined in Section 4.1. For any of the processes that implement changes to the flowsheet and feed directly to the vitrification facilities, the complexity of the waste feed qualification program is reduced because the number of unit operations is reduced. A summary of the steps of the qualification process including the recommended changes is provided in Table 4-2. The timing of the qualification sample would depend on the preconditioning steps that are performed in the TWCSF. As an example, if only washing of the sludge will be performed, the qualification sample could be taken before qualification is complete. However, other preconditioning steps (e.g. particle size reduction, solids segregation, Al dissolution) would affect properties in the WAC and would therefore need to be taken after preconditioning is performed. This process would be more in line with the DWPF Macro-Batch strategy as well as some of the DWPF Tank Farm sludge preparation steps.

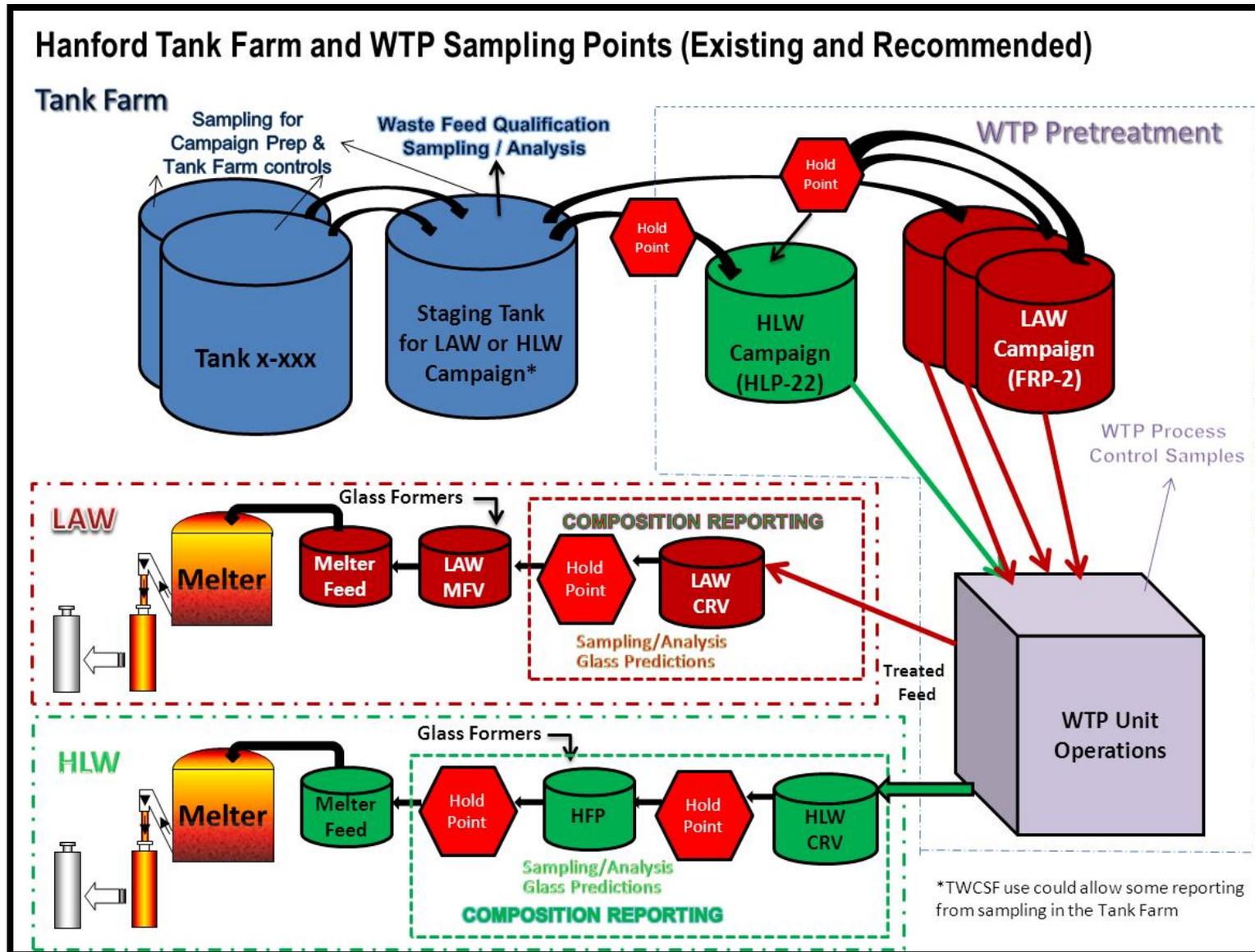


Figure 4-2. Sampling Points for Hanford Waste Feed Qualification and Product Acceptance

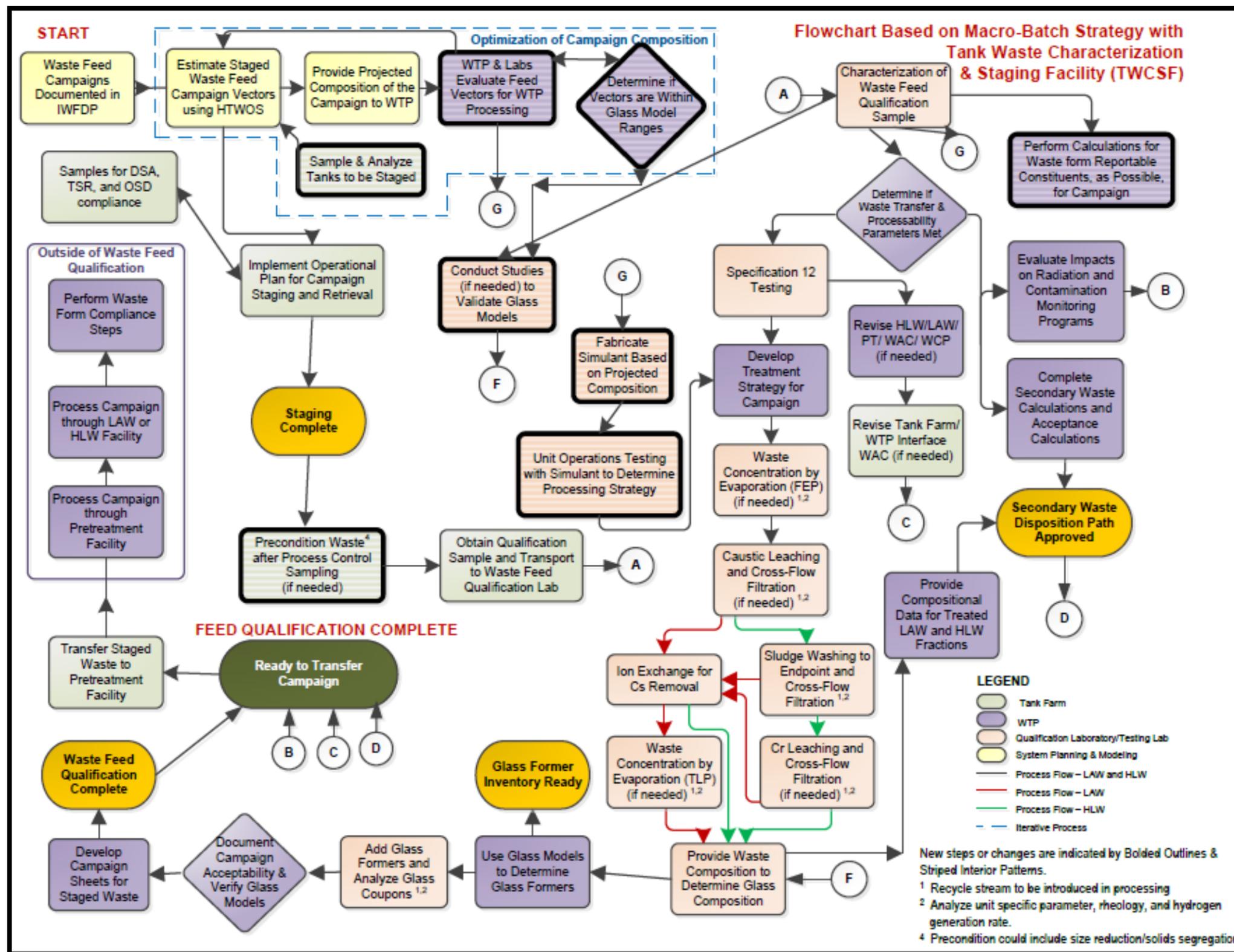


Figure 4-3. Flowchart for Hanford Macro-Batch Strategy Using a TWCSF and the Baseline Flowsheet

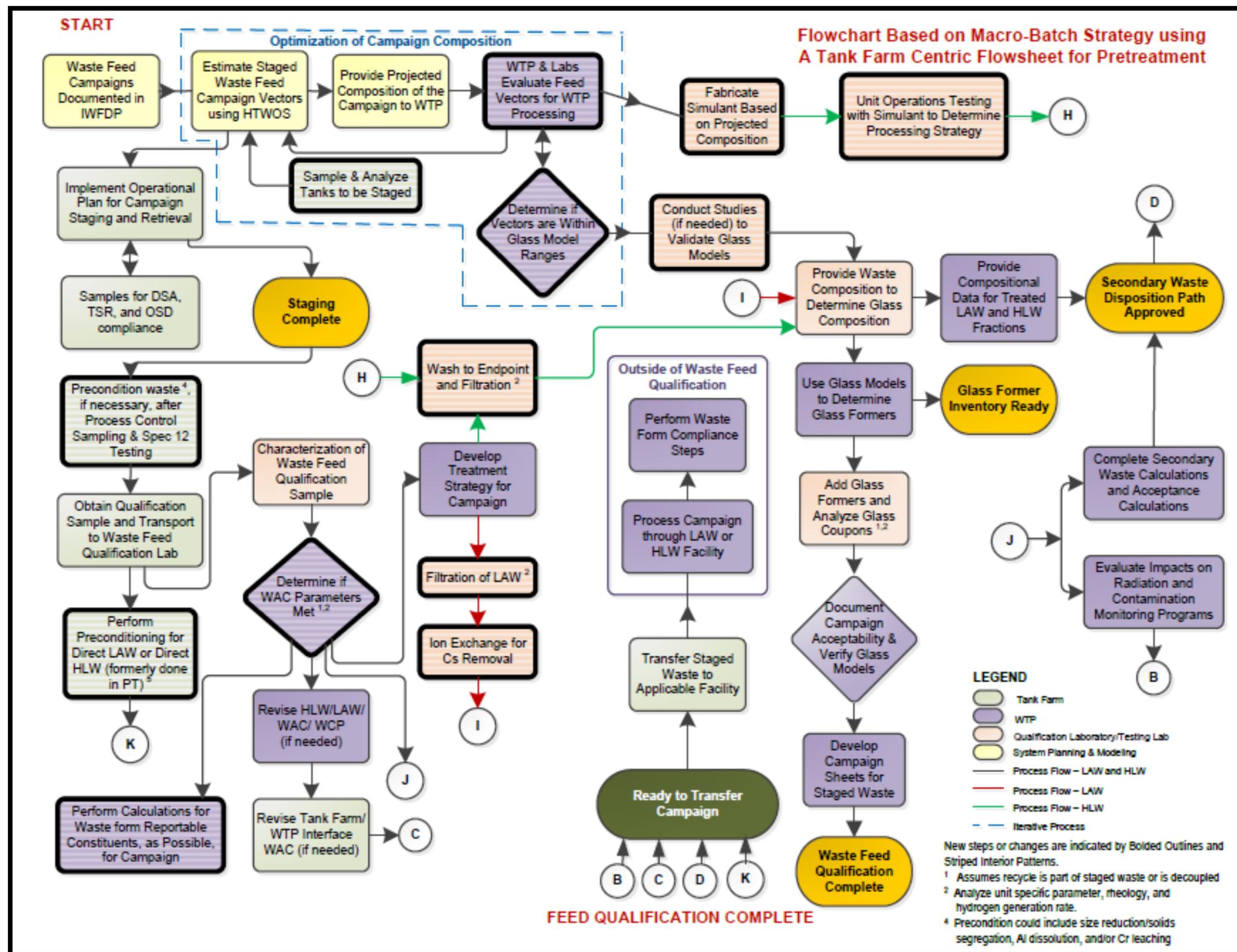


Figure 4-4. Flowchart for Hanford Based on Macro-Batch Strategy using a Tank Farm Centric Flowsheet.

Table 4-2. Proposed Changes to the Waste Feed Qualification Program with the TWCSF and/or Baseline Flowsheet Modifications

Program Step	Existing Step	Proposed Change	Risks Mitigated or Reduced
Sampling and characterization of the tanks comprising the campaign with a view to WTP feed qualification	Includes sampling for process control in the Tank Farm	Add chemical and physical property analyses of waste as tanks are being retrieved	Actual waste data would <ul style="list-style-type: none"> • Inform the blending process and allow for intentional blending to optimize the feed composition • Allow flowsheet and glass formulation assessments of the campaign earlier in the process • Provide flexibility to accommodate unanticipated components in the waste • Increase the chance of success with the 180-day completion time requirement for the waste feed qualification sample
Assessment and optimization of the campaign composition and processing targets (e.g., washing and AI dissolution point)	Includes evaluations using current Hanford system models	Develop and use simplified composition assessments to optimize the glass formulation and flowsheet	<ul style="list-style-type: none"> • Allows for optimization of the overall system process to improve throughput • Initiates qualification processes earlier to increase chance of success of 180-day qualification time period • Provides an operating window to provide more flexibility given tank farm mixing/blending limitations
Staging and blending of the campaign in the TWCSF	Waste is staged in existing tanks with less efficient mixing bringing into question the sample representativeness	The TWCSF would be designed to adequately mix and sample the waste	More representative samples and consistent feed campaigns would be provided to the WTP facilities for processing, which would provide more consistent processing in PT
Sampling and characterization of the waste feed qualification sample if preconditioning is not performed;	Step has some uncertainty on effectiveness of mixing and representativeness of sampling for current baseline	<ul style="list-style-type: none"> • Information would be available on effectiveness of mixing with respect to chemical composition uncertainty • Sampling uncertainty could be quantified with mixing information considered • Use information from the initial sample characterization to feed optimization studies 	<ul style="list-style-type: none"> • Quantifying the uncertainty associated with the chemical composition early in the process will allow its impact on processing to be determined and will allow the number of samples and required analyses to be defined early in the process instead of changing for each batch as currently envisioned • Using initial information on the sample to tailor the campaign processing parameters will provide a more optimized WTP process
Preconditioning of the batch as warranted followed by sampling and characterization for waste feed qualification	No preconditioning is planned	<ul style="list-style-type: none"> • Preconditioning to reduce particle size, segregate solids, and/or reduce particle density • Initiation of HLW processing steps such as washing and/or leaching 	<ul style="list-style-type: none"> • Minimize the chances of large particles being transferred to and/or causing line pluggage in PT • Removes the need to process all streams through PT • Potential to bring samples for waste form reporting requirements earlier in the process on a larger and more homogenous batch; thereby eliminating analytical samples

**Table 4-2. Proposed Changes to the Waste Feed Qualification Program with the TWCSF and/or Baseline Flowsheet Modifications
(Continued)**

Program Step	Existing Step	Proposed Change	Risks Mitigated or Reduced
Performance of simulant studies to determine the WTP flowsheet operating parameters	Plan does not involve simulant studies for qualification	<ul style="list-style-type: none"> • Determine parameters of importance as they relate to bench-scale testing with a radioactive sample • Perform flowsheet studies with HLW simulant to define the processing window • Determine if simpler systems can be identified for unit operations testing 	Providing an operating window as opposed to a single processing point will provide more flexibility given <ul style="list-style-type: none"> • Complexity of PT unit operations (multiple chemical and mechanical separation processes) • Inclusion of recycle streams and different blends with HLW and LAW campaigns in PT flowsheet • Single run performed with the qualification sample in a constrained time frame
Performance of unit operations testing with the radioactive sample	Perform single run using scaled equipment	Select the qualification run parameters based on simulant testing and using simplified equipment if parameters can be defined to simplify the radioactive apparatus	Performing simulant studies to provide a range of operating parameters will <ul style="list-style-type: none"> • Increase the chance of success during the qualification demonstration • Provide the opportunity to optimize processing or identify potential processing issues in the WTP facility
Sampling and characterization of the preconditioned feed as necessary to confirm the endpoint	Currently performed on as staged feed with no pre-conditioning	Precondition steps would be performed, qualification studies started, and then endpoint confirmed with another sample from the Tank Farm	Confirmation validates that assumptions made about preconditioning are valid and that qualification testing results are applicable

5.0 Conclusions and Recommendations

An evaluation has been completed of the existing waste feed qualification strategy for Hanford based on experience from the DWPF waste qualification program. Recommendations have been provided for implementation at Hanford based on the successful Macro-Batch qualification strategy utilized at SRS to reduce the risk of processing upsets or the production of an unacceptable staged waste campaign in the WTP. Considerations included the baseline WTP process, as well as options involving Direct HLW and LAW processing, and the potential use of a TWCSF.

The primary recommendations/changes include the following:

- Collection and characterization of samples from the tanks to be processed during the staging process;
- Initiation of qualification activities earlier in the staging process to optimize the campaign composition through evaluation from both a processing and glass composition perspective;
- Definition of the parameters that are important for processing in the WTP facilities (unit operations) across the anticipated range of wastes and as they relate to qualification-scale equipment;
- Performance of limited testing with simulants ahead of the waste feed qualification sample demonstration as needed to determine the available processing window for that campaign; and
- Demonstration of sufficient mixing in the staging tank to show that the waste qualification sample chemical and physical properties are representative of the transfers to be made to WTP.

For the options using the TWCSF, the staging tank would be the purpose built TWCSF for mixing and representative sampling. Process flowcharts for these processing options have been provided in this report.

While these recommendations are an extension of the existing WTP waste feed qualification program, they are more in line with the processes currently performed for SRS. These processes have been shown to offer flexibility for processing at SRS, having identified potential processing issues ahead of the qualification or facility processing, and having provided opportunity to optimize waste loading and throughput in the DWPF.

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