Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy.

Disclaimer:

SRNL-STI-2008-00050

"**Accelerated Processing of SB4 and Preparation for SB5 Processing at DWPF**"

C.C. Herman

December 1, 2008

ACCELERATED PROCESSING OF SB4 AND PREPARATION FOR SB5 PROCESSING AT DWPF

C.C. Herman
Savannah River National Laboratory
Aiken, South Carolina, USA

ABSTRACT

The Defense Waste Processing Facility (DWPF) initiated processing of Sludge Batch 4 (SB4) in May 2007. SB4 was the first DWPF sludge batch to contain significant quantities of HM or high Al sludge. Initial testing with SB4 simulants showed potential negative impacts to DWPF processing; therefore, Savannah River National Laboratory (SRNL) performed extensive testing in an attempt to optimize processing. SRNL's testing has resulted in the highest DWPF production rates since start-up. During SB4 processing, DWPF also began incorporating waste streams from the interim salt processing facilities to initiate coupled operations. While DWPF has been processing SB4, the Liquid Waste Organization (LWO) and the SRNL have been preparing Sludge Batch 5 (SB5). SB5 has undergone low-temperature aluminum dissolution to reduce the mass of sludge for vitrification and will contain a small fraction of Purex sludge. A high-level review of SB4 processing and the SB5 preparation studies will be provided.

INTRODUCTION AND BACKGROUND

The DWPF's mission is to immobilize the millions of gallons of High Level Waste (HLW) that is currently in storage at the Department of Energy's Savannah River Site. The HLW consists of two fractions that must be immobilized in DWPF. The sludge fraction consists of the insoluble solids in the HLW, which contain the long-lived radionuclides and inert components such as iron and aluminum hydroxide. The salt fraction destined for treatment in the DWPF consists of Cs, actinides, and sludge solids that have been treated through salt waste processing facilities. As of August 2008, the DWPF has processed 2.6 million gallons of the HLW sludge containing 17 million curies of radioactivity and a very small percentage of the salt stream. The HLW has been immobilized in glass that has been poured in over 2500 canisters that are currently stored in glass waste storage buildings awaiting disposal in the federal repository. Approximately 35 million gallons of HLW remain for treatment.

A schematic of the SRS HLW system and treatment processes is provided as Figure 1. The HLW sludge, along with the salt cake and concentrated supernate, is stored in 48 underground carbon steel tanks. Before the sludge and salt can be treated in the DWPF, several process steps must be performed to prepare the streams for treatment. Supernate is decanted off of the tanks for treatment in the site's three evaporators, where the waste is concentrated and stored until downstream processes are available for further processing. Currently, the salt is transferred to a storage tank for subsequent treatment in the salt waste processing facilities. The sludge must be transferred into the DWPF sludge preparation tank (Tank 51) to undergo Extended Sludge Processing (ESP).

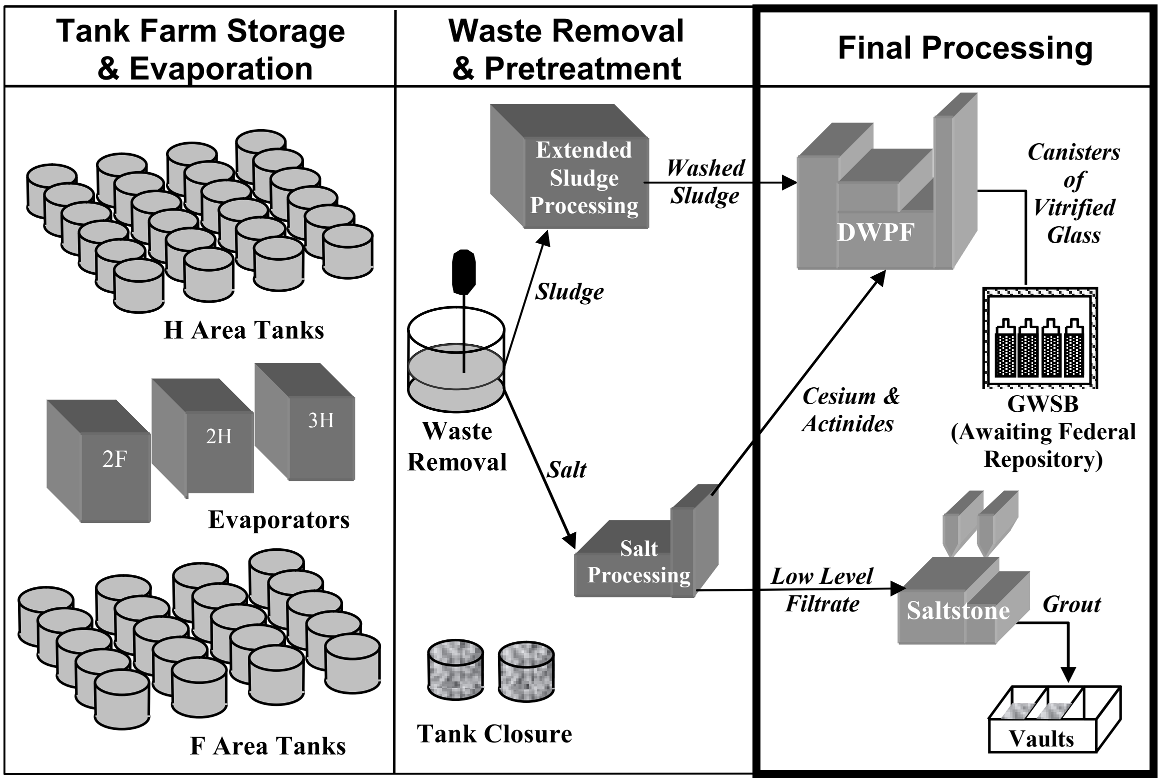

Figure 1. Flow diagram of SRS HLW Process

Sludge Processing and Qualification

Typically, sludge from more than one tank is transferred to the preparation tank to provide a blended sludge composition suitable for DWPF processing. The tanks are selected by the LWO based on necessary tank closure dates and expected sludge compositions. ESP is initiated with the introduction of inhibited water (water with a dilute concentration of sodium hydroxide and sodium nitrite) or decanting of supernate to reduce the high sodium salt content of the sludge. The iterative process is repeated until the final sodium supernate concentration target and the insoluble/total solids target are obtained. The final product constitutes a sludge batch for DWPF.

A key component of the sludge batch preparation process is the SRNL qualification testing that is performed to ensure that the sludge will meet DWPF processing and wasteform acceptance criteria. A sample of the sludge or sludges to be processed is taken early in the process and shipped to SRNL for characterization. Characterization includes the chemical constituents as well as the physical properties. This information is used to perform flowsheet testing, determine a frit for processing, and verify acceptability of the DWPF durability models over the expected glass composition region. Depending on when the sample is taken, multiple wash and decant cycles may need to be performed to complete the sludge batch preparation process. Replication of these cycles can identify potential problems with sludge settling and verify the accuracy of washing model predictions. All of this information is used by SRNL to recommend the sodium and solid target endpoints to LWO for each sludge batch.

In addition to characterization and washing steps, the radioactive sample is subjected to the chemical processing steps performed in DWPF to prepare the feed for melting. The chemical processing steps involve adding nitric and formic acids to the sludge at 93°C, heating the sludge to boiling, removing water to meet the target solids, and then boiling under reflux conditions to complete the necessary chemical reactions. 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, frit is added at the target waste loading and the slurry is boiled further to concentrate to the melter feed solids target, which is typically in the range of 45 – 50 weight percent total solids. During the SRAT and SME processes, significant chemical reactions occur and hydrogen is generated, which requires monitoring to ensure that a flammable concentration is not reached. After verification of DWPF acceptability, a portion of the SME material is used to fabricate a glass at the nominal DWPF melter temperature of 1150°C. This glass is subjected to the ASTM Product Consistency Test (PCT)[1] to ensure that its durability performance is better than the HLW Environmental Assessment (EA) benchmark glass.

To support the radioactive testing, flowsheet testing with simulants is performed to refine the washing endpoint and to define the nominal acid addition quantities for the radioactive testing. These studies are typically completed before the actual waste testing and help define the width of the processing window. For the glass formulation development and melter processing, variability studies are performed considering the nominal sludge and frit compositions. The nominal sludge and frit compositions are combined over the waste loading interval of interest (typically 28 to 42 weight percent waste loading) and uncertainty in the compositions are considered to fully bracket the composition region. Glasses are then selected for fabrication representing points within the composition region. The PCT is performed on these glasses to verify the predictability of the DWPF durability models and to verify product acceptability. However, before these studies can be initiated, the candidate frit for that sludge batch must be determined. This involves both paper studies to determine the maximum processing window and laboratory studies to measure the melt rate of the sludge and frit compositions of interest. Initial laboratory testing focuses on dried feed testing and, therefore, is not able to discern differences in feed rheology and its subsequent impact on melter feed behavior. This Melt Rate Furnace (MRF) testing does allow a comparison between frits and waste loadings to identify relative melt rates for that system. This allows fine-tuning or down-selection of the frits for slurry fed melt rate furnace (SMRF) testing, which also provides relative melt rate data for DWPF processing.

Salt Processing Facilities and Associated DWPF Impact

To remove the salt, the salt cake is dissolved in the storage tank in preparation for treatment in one of the site's salt waste processing facilities. In the salt waste processing facilities, radionuclides (e.g., actinides, strontium, and cesium) are removed and prepared for transfer to DWPF. Removal of strontium and actinides is accomplished through the Actinide Removal Process (ARP) that entails sorption with monosodium titanate (MST). This produces a slurry that must be filtered to remove the MST and entrained sludge solids. The MST/sludge solids stream is subsequently transferred to DWPF for co-processing with the HLW sludge. Cesium removal is performed through a caustic-side solvent extraction (CSSX) process. In this process, the cesium becomes entrained in the organic solvent phase. After multiple extraction steps, the non-recovered solvent is transferred with the cesium as a dilute nitric acid stream to DWPF and the solvent is recycled. The decontaminated salt solution, on the other hand, is sent to the Saltstone Processing Facility for disposal as grout. Both of the salt treatment processes are currently being demonstrated on a pilot-scale to identify potential processing issues and to provide tank space until the larger capacity Salt Waste Processing Facility (SWPF) is brought on line.

In the DWPF, the MST/sludge solids stream is added to the SRAT at boiling to reduce the volume to be processed through the DWPF chemical process. After the stream is added, a sample is taken to determine the acid addition amounts and then typical processing is initiated. The MST/sludge solids stream itself has minimal impact on the SRAT processing chemistry, but does increase the SRAT processing time because of the additional boiling required. On the glass formulation side, more impacts are realized because of the high sodium and titanium content of the feed. The frit composition must be tolerant to significant sodium variation because in some cases none of the salt stream will be added, while in others a full tank addition may be necessary (which would be equivalent in volume to the nominal sludge processing volume). Nominally, 1500 to 2500 gallons of the stream would be processed with each SRAT batch. The titanium concentration must be considered because it is a known nucleating agent for crystals. Currently, the process is not creating a large enough volume to exceed the current 2 weight percent titania glass limit. However, once the SWPF begins processing, titania concentrations up to 6 weight percent may need to be accommodated. Due to the large volume of sample and associated radioactive dose that would be required to perform a demonstration with radioactive material, qualification is not performed on radioactive material as is done with the sludge. Qualification of the MST/sludge solids stream is performed by SRNL using simulants in flowsheet testing and surrogates in glass testing. The radioactive constituents are not believed to have a significant impact on either of these components of the qualification process and should have minimal impact on processing characteristics when the simulants are adequately formulated.

The strip effluent from the MCU process, and later the SWPF, is transferred to the DWPF in small batches. These batches are held in a hold tank until they can be transferred to the SRAT during the boiling process after all acid has been added. As with the MST/sludge solids stream, a SRAT batch can have no MCU stream or a full tank of the MCU stream (which would be equivalent in volume to the nominal sludge processing volume). The stream is a dilute nitric acid stream that contains small concentrations of the removed cesium and non-recovered solvent. In the SRAT, the stream has the potential to impact the feed redox because of the nitrate in the stream so this must be accommodated by the split of formic and nitric acids that are added at the beginning of the SRAT process. The cesium has no impact, while the residual solvent has resulted in flammability controls being implemented in DWPF to ensure that a flammable mixture was not created in the SRAT or SME cycle. Flammability is primarily controlled by the addition at boiling and insurance of purge gas during static and processing conditions. This has a net impact on the SRAT processing time, which will be further increased with the larger volume additions expected for SWPF. On the glass processing side, minimal impact is seen, as long as the redox is properly adjusted, because of the small concentration of all of the stream constituents. As with the MST/sludge solids stream, qualification is only performed using simulant streams, which are considered adequate to bound the potential processing impacts.

SLUDGE BATCH 4

Preparation of Sludge Batch 4 (SB4) was initiated in the Tank Farm in 2004 by transferring HM (high aluminum) sludge from Tank 11. The sludge exhibited settling problems soon after completion of the third transfer into the DWPF feed preparation tank (Tank 51). Good settling behavior is important during the sludge preparation process since ESP relies upon clean separation of the supernate and solids phase to remove the sodium salts during decanting and it needs to happen in a timely fashion to avoid a DWPF feed break. After completion of limited characterization of the Tank 51 samples, the settling problems were attributed to excessive shearing performed during sludge removal and the small boehmite particles that were the predominant compound in the insoluble solids.

The samples also indicated the presence of a much larger mass of sludge than originally projected. Due to the large mass of sludge solids, enhanced controls had to be enacted to ensure that hydrogen generated through reactions of the radioactive sludge components with the supernate did not result in the accumulation of a flammable concentration of hydrogen. The controls included limiting the mass to minimize the pathway for hydrogen to be released and stirring of the tank contents on a routine basis to limit accumulation. This caused problems with washing and sludge preparation, which were mitigated by performing less washing and extending the sludge preparation time. In addition, the sludge preparation plan was changed to limit the components of SB4; therefore, Purex sludge was not blended with Tank 51 resulting in a very high aluminum sludge content. The high aluminum coupled with higher sodium from limited washing created a durability issue for the glass wasteform. The combination of these two components can cause nepheline crystals to form upon slow cooling of the DWPF canister, and nepheline can have a significant impact on the product durability.

Glass Formulation and Melt Rate Observations

SRNL performed glass formulation testing to define a frit composition that would provide a reasonable operating window from a waste loading and processing perspective while also ensuring product durability. This testing concluded that increasing the B_2O_3 concentration in the frit could suppress the formation of nepheline in the SB4 system.[2] The testing also showed that the implementation of the nepheline constraint previously developed by Li et. al.[3] could adequately prevent the use of a glass formulation that was susceptible to nepheline formation. As an added benefit, increasing the B_2O_3 concentration was also shown to have a positive impact on melt rate and throughput.[4] This finding was equally important since initial SB4 melt rate testing had little success in finding a frit that would provide melt rate that was considered acceptable for DWPF processing.[5,6]

However, shortly after SRNL recommended the use of Frit 503, whoich appeared to have a throughput equivalent to that seen for the Sludge Batch 3 (SB3)-Frit 418 system[4], the LWO had to change the final composition of SB4. A confirmation sample of SB4 taken from Tank 51 near the end of sludge preparation indicated rheological properties that exceeded the transfer pump criteria. To solve this problem and to help increase the total solids content of the sludge in the DWPF feed tank (Tank 40, which would eventually be a blend of SB3 and the material qualified as SB4 in Tank 51 to be called SB4), supernate from Tank 40 was transferred to Tank 51. The net effect was a decrease in the total sodium content of the feed. This change could not be accommodated with Frit 503. Therefore, Frit 418 was recommended for initial processing due to the long lead times needed for frit procurement and the need for a SRNL variability study to verify the durability performance of the frit and sludge combination. Frit 418 satisfied these criteria since it was already being used for SB3 processing and had previously been tested in a variability study with SB4 using a wide compositional uncertainty region[7]. Therefore, DWPF initiated SB4 processing with Frit 418. Shortly after SB4 startup, SRNL performed additional melt rate testing with additional high boron containing frits with lower sodium content than Frit 503. The goal was to take advantage of the suppression of nepheline formation and the increased melt rate seen with the higher boron containing frits. Of these selected frits, Frit 510 provided an optimized melt rate in MRF testing and a reasonable operating window. Frit 510 was subsequently tested in the SMRF and shown to have an increased throughput compared to the

Frit 418 – SB4 system.[8] See Table I for the composition of the frits recommended for SB4 processing.

Table I. Frit Compositions for DWPF Processing

Frit #	B_2O_3 wt%	Li_2O wt%	Na_2O wt%	SiO_2 wt%
418	8	8	8	76
503	14	8	4	74
510	14	8	8	70

Initial DWPF throughput with the SB4-Frit 418 system was slower than that seen for the SB3-Frit 418 system. Waste loading was limited to ~34% in DWPF due to rheological properties of the sludge and slow throughput seen with the SB4 system. Canister pour times were near 30 hours per can with significant increases seen when the waste loading was increased. Feed rates were limited to ~0.5 gallons per minute, which was equivalent to the feed rate with SB3 at the end of processing. Once DWPF implemented Frit 510, DWPF increased their melter feed rates to upwards of 0.9 gallons per minute, which is near the upper limit of feeding capacity. While these high feed rates were utilized, pouring of DWPF canisters was accomplished in ~20 hours. This pour rate was the highest achieved in DWPF since startup and approached the design basis of the melter. However, waste loadings were still limited to ~34% since this appeared to provide the optimal throughput. Therefore, DWPF production verified the trends seen in the SRNL MRF and SMRF testing with regards to the frit composition.

Additional processing issues plagued SB4 due to leaking slurry pumps in the DWPF feed tank. This caused the feed to become diluted resulting in slower chemical processing since additional boiling to concentrate the feed was required. This caused a reduction in the melter feed and production rates because of the dilute feed being fed to the melter. To alleviate this problem, two decants of supernate were performed to concentrate the solids. However, before these decants could be performed, SRNL had to perform testing to ensure that these decants could be accommodated since sodium would be removed from the glass and the processing window might need adjustment due to the change in feed chemistry. SRNL flowsheet testing demonstrated minimal impact[9,10], but glass formulation assessments indicated a slight decrease in processing window with each decant[10,11]. To mitigate the decreases in the processing window and melt rate, sodium hydroxide was added to the feed tank to increase the Na_2O in the sludge by 3 weight percent on a calcined sludge oxide basis. Since the completion of the decants and sodium hydroxide addition, some of the processing rates have been recovered in the DWPF such that feed preparation remains the processing constraint in the facility.

Salt Processing Impacts

Transfers of the MST/sludge solids stream from the ARP facility were initiated to DWPF in the spring of 2008. The need to process this stream through the SRAT resulted in longer processing times for the feed preparation system, which in turn impacted the melter processing. With the high throughputs seen with Frit 510, the feed preparation process became the rate limiting step in the facility for the first time since startup. No other significant impacts have been seen with processing of the MST/sludge solids stream in DWPF.

Only small quantities of the MCU stream have been transferred to the DWPF facility. Therefore, its true impact cannot yet be assessed. However, simulants from the MCU facility have been processed through the DWPF to ensure that the transfer lines, hold tanks, and flammability controls are adequately operating. The true impact of this stream will not likely be known until the start of Sludge Batch 5 processing when higher volumes are processed in the facility.

SLUDGE BACTH 5

To try to broaden the operating window, reduce the sludge mass going to DWPF, and potentially improve processing for Sludge Batch 5, LWO decided to perform low temperature aluminum dissolution on the sludge remaining in Tank 51 after transfers were made for SB4. The decision was made before the high throughput data was obtained from DWPF processing with Frit 510. However, even with these high processing rates, it was believed that the potential for mass reduction (reduced canister production) and increased waste loading were sufficient reasons to pursue this technology. After completion of the aluminum dissolution process, the remaining sludge was blended with the Purex sludge previously selected for blending with SB4 (as stated above, this Purex sludge could not be blended with SB4 because the mass was too high). In addition, excess plutonium that had been dissolved and neutralized was transferred to Tank 51 for disposition as part of SB5. Upon completion of the qualification of SB5, the plan was to blend the SB5 material with the remaining SB4 heel in Tank 40 such that the blend would be processed as SB5. Final preparation of SB5 is underway in the Tank Farm and a sample will be used to confirm that the target composition has been met and to determine the target insoluble solids target to ensure acceptable rheology is obtained before the sludge is transferred.

Al Dissolution of Tank 51 Sludge

The goal of the low temperature aluminum dissolution process is to use caustic to dissolve the aluminum from the insoluble solids fraction of the sludge, whereby it becomes soluble in the supernate phase that can be decanted from the insoluble solids. In the Tank Farm, tankers of 50% sodium hydroxide were added to the remaining SB4 sludge in Tank 51 over a 4 week period. The slurry containing the sodium hydroxide was then mixed at a temperature between 55 - 65°C. The slurry pumps in Tank 51 provided mixing as well as the necessary heat to maintain the tank temperature over 46 days. After this period, the insoluble solids were allowed to settle for 29 days before the supernate was decanted to another HLW tank for treatment through the SWPF at a later date. Based on analyses of the sludge before and after dissolution, ~ 60% of the aluminum was removed through the dissolution process.[12] The oxide composition of the primary sludge components before (equivalent to the SB4 qualification material) and after the aluminum dissolution process are shown in Table II. The SB4 composition after blending with the SB3 heel (SB4 processing composition) and the washed SB5 qualification sample composition (post aluminum dissolution and Purex blending) are also given in Table II for comparison. The Tank 51 composition after aluminum dissolution is very high in sodium concentration because of the significant amount of sodium hydroxide that is added to perform aluminum dissolution. The impact of washing on the SB5 qualification sample is evident by the dramatic reduction in Na_2O concentration, while the impact of the Purex sludge addition on the Tank 51 sample both before and after aluminum dissolution is evident by the increase in Fe_2O_3 and U_3O_8 concentration.

Table II. Oxide Compositions of SB4 and SB5 Sludges of Interest

Oxide	Tank 51 before Aluminum Dissolution[13] (SB4 as Qualified)	SB4 as Processed (Blended with SB3 Heel)[14]	Tank 51 after Aluminum Dissolution[15]	Washed SB5 Qualification Sample[16]
Al_2O_3	42.9	24.1	20.6	20.6
CaO	1.65	2.64	1.30	2.24
Fe_2O_3	15.2	27.4	11.31	28.6
MgO	0.71	2.60	0.532	1.23
MnO_2	3.98	6.73	2.88	7.08
Na_2O	28.5	19.9	55.27	25.1
NiO	1.19	1.53	0.781	3.64
SiO_2	1.35	2.57	0.924	2.42
U_3O_8	2.80	8.38	2.03	7.72

Sludge Preparation Challenges

A 3-L sample of the post aluminum dissolution sludge blended with the Purex sludge material was taken to perform sludge batch qualification in the SRNL Shielded Cells. Approximately half of the plutonium was already in the sample at the time it was pulled. Since the qualification sample was taken very early in the sludge preparation process, the planned washing and concentration steps needed to be mimicked on the qualification sample. This included 6 washes with one being supernate material from Tank 40, 7 decants, and 1 plutonium stream/chemical addition. Performance of these process steps would result in a sludge with a final supernate concentration of roughly 1 M sodium and an insoluble solids concentration of approximately 10.5 weight percent. As part of the SRNL testing, chemical and physical behavior of the sludge was monitored throughout the processing steps to ensure that the final sludge would meet acceptable processing behaviors and to provide guidance to the Tank Farm on the effectiveness of their models for predicting sludge chemistry.

From the very beginning of processing of the sludge in the Tank Farm, problems were experienced with support equipment and with physical behavior of the sludge. Problems included limitations on the evaporator capacity due to the high hydroxide content of the feed, increased radiolytic hydrogen generation, and poor settling behavior. This resulted in changes to the sludge preparation plan on several occasions. In addition, SRNL testing showed that the insoluble solids might be slightly higher than projected due to the precipitation of some of the soluble species and sodium could be more effectively removed than the washing model indicated. The higher solids are advantageous from a DWPF processing perspective since it requires less evaporation in the facility during either the feed preparation or melter processing steps, while the lower sodium provides more flexibility to find a larger glass composition operating window. In the end, SRNL completed 5 washes of the qualification sample with one being a sample of Tank 40 supernate, addition of a plutonium stream and cold chemicals to properly balance the corrosion chemistry, and 6 decants to obtain an insoluble solids concentration of 11.3 weight percent. Therefore, SRNL recommended that a wash/decant cycle be eliminated and a higher solids endpoint targeted, which had the potential to reduce the preparation time by up to 1 month and would save valuable tank space. The primary oxide components of the SB5 qualification sample are shown in Table II.

Chemical Processing Cell Demonstrations

As discussed above, a routine step in the qualification process is demonstration of the chemical process cell SRAT and SME cycles. For SB5, a new challenge was introduced since the sludge simulant did not adequately represent the dissolved aluminum behavior. More specifically, the soluble aluminum hydroxide phase that was known to be present in the radioactive sludge could not be adequately represented by the aluminum hydroxide chemical that was added to the sludge simulant upon final trimming. The difference manifested itself in the acid demand for base equivalents when a titration or hydroxide measurement was performed. This made estimating the required acid challenging for the qualification run in the Shielded Cells. Testing with the simulant at several acid addition levels was performed. From this series of tests, a recommended acid addition amount was provided and was based on acceptable processing to meet DWPF defined objectives. Although no blended runs with radioactive sludge were planned, simulant testing was still necessary to ensure that a processing recommendation could be made to DWPF. Similar acid stoichiometric factors were used in the blend series testing; however, more problems were experienced with mercury reduction, which is one of the primary goals of the SRAT. As part of the flowsheet testing, a run where a simulant of the MST/sludge solids stream and the MCU strip effluent stream was added was also performed at the nominal acid stoichiometry. Minimal impact to processing was seen from these additions.[17]

When the testing was performed in the Shielded Cells, three processing problems were identified during demonstration of the SRAT cycle. Although below the DWPF process limits, significant hydrogen was generated, which was above the levels seen in the simulant runs. The sludge exhibited foaming throughout the process demonstration requiring the addition of multiple doses of antifoam above that typically required in DWPF processing. Finally, the rheology of the SRAT product was above DWPF design limits and yield stress was higher than before the start of processing, which is counterintuitive to the SRAT cycle goals. Although multiple problems were experienced in the SRAT demonstration, the SRAT chemical reaction requirements were met and all of the SME cycle parameters were met after diluting the SRAT product at the start of testing and adding antifoam with each frit or water addition.

An additional flowsheet demonstration will be performed with a 3-L sample taken from Tank 51. The original intent of this sample was to confirm the SB5 washing endpoint. However, a neptunium stream will now be added to the confirmation sample to qualify the stream for addition in Tank 40 since the decision to disposition this stream through DWPF was not made early enough to include it in the SB5 qualification process. As part of this second demonstration, the solids concentration target will be reduced slightly to try to alleviate the foaming and poor rheological properties seen in the first demonstration. It is anticipated that the lower solids targets should alleviate some of the rheological problems and may decrease the hydrogen generation rate. Once this test is completed, an updated recommendation will be made on the processing parameters to be used in DWPF.

Glass Formulation Challenges

Frit selection for SB5 was made more difficult due to uncertainty over the final composition of the SB5 sludge. This was partially driven by the performance of low temperature aluminum dissolution for the first time and the need to decant SB4-Tank 40 to concentrate the solids (which provided uncertainty in the composition to be blended with Tank 51). However, the problem was compounded by the typical uncertainty associated with the composition of a new sludge being blended (Purex-Tank 7 in this case) and definition of the final washing endpoint. To attempt to accommodate all of this uncertainty, several projections of the potential sludge composition were provided both for the material as prepared in Tank 51 (SB5 qualification) and after blending with Tank 40. The blended compositions addressed uncertainty in the heel mass that would remain in Tank 40 for blending with SB5.

The projections were holistically reviewed and then composition groupings were developed with uncertainty around the sodium concentration. Sodium concentration represented the greatest uncertainty because it was the component most strongly impacted by the washing endpoint and decisions on decanting the Tank 40 supernate. To provide the most flexibility and accommodate this large uncertainty, Frit 418 that had been used in initial processing of SB4 and to increase throughput for SB3 was recommended for initial SB5 processing.[18] This frit was used in a variability study to ensure that DWPF's durability model would adequately predict the performance of the DWPF glass over the anticipated compositional range when subjected to the ASTM PCT[1]. Glass performance data from this testing demonstrated that the models were acceptable. Included in the glass variability assessment were options to include up to half a tank volume of the MST/sludge solids stream.

Frit 418 was sufficiently robust that it also could be processed with the SB5 material before blending with SB4. Therefore, it was used as the frit in the SME testing of the qualification sample. A glass was fabricated from the SME product and was subjected to the ASTM PCT[1]. The data indicated that the glass was more durable than the EA glass and its durability performance was predictable by the DWPF product and process control models.

While Frit 418 provides tremendous compositional flexibility for SB5 processing, it may not be the best frit for optimal throughput in DWPF. Due to the delays in receiving the qualification sample and the numerous changes in the sludge preparation plan, melt rate testing to support the development of a frit that would optimize throughput for SB5 could not be developed in time to procure frit for DWPF and/or complete the variability study. Therefore, additional testing is currently underway to determine if another frit can be identified that exhibits enhanced throughput over Frit 418 with SB5. Once the melt rate testing is completed, a recommendation will be made to DWPF on the path forward for proceeding.

CONCLUSIONS

Each sludge batch that is qualified for DWPF continues to present new challenges that must be overcome. SRNL has worked successfully with DWPF to overcome these challenges as they have arisen during the sludge preparation or qualification processes. For Sludge Batch 4, problems with sludge preparation, glass acceptability, and melter processing were identified early on in the preparation process. These problems were attributed to the high aluminum content and particular compound in the HM sludge that was SB4. After performing testing to understand the potential processing issues, SRNL was able to recommend a frit that not only suppressed nepheline formation (therefore increasing glass durability) but also provided the highest throughputs seen in DWPF since startup. The higher throughputs were accomplished even with a dilute feed that required additional chemical processing time to accommodate the actinides and sludge solids from the interim salt processing facilities.

For Sludge Batch 5, low temperature aluminum dissolution was successfully performed to remove a significant mass of the insoluble solids destined for DWPF immobilization. After demonstration of this process, similar challenges to SB4 were realized and identified. These challenges were enhanced by the need to understand the behavior of the aluminum hydroxide component that had become soluble during the dissolution process, which included uncertainty in the final composition to be processed. Currently, SRNL is completing most of the testing and/or documenting the results of testing needed to support SB5 qualification. DWPF should initiate processing of SB5 in November 2008. When processing is initiated, Frit 418 will be used and will continue to be used unless a more optimized frit is identified in SRNL melt rate testing that will be performed in late 2008.

ACKNOWLEDGEMENTS

Testing reported was performed under the auspices of contract DE-AC09-96SR18500 between the Department of Energy and the Washington Savannah River Company. Qualification studies for both sludge batches were performed by J. Pareizs, C. Bannochie, D. Click, K. Zeigler, D. Lambert, B. Pickenheim, S. Reboul, N. Bibler, and Shielded Cells' facility personnel. Chemical processing studies for both sludge batches were performed by M. Stone, D. Lambert, D. Koopman, B. Pickenheim, M. Barnes, M. Williams, and technical analysts assigned to the Process Science & Engineering Section of the Environmental & Chemical Processing Technology directorate of the SRNL. Glass formulation and melt rate assessment studies for the sludge batches was supported by D. Peeler, T. Edwards, M. Smith, K. Fox, D. Miller, T. Jones, F. Raszewski, and technical analysts assigned to the Process Science & Engineering Section. Analytical characterization was supported by D. Best, W. Riley, technical analysts assigned to the Process Science & Engineering Section, and the Analytical Development organization of SRNL.

REFERENCES

[1] American Society of Testing Materials, Standard Test Methods for Determining Chemical Durability of Nuclear Waste Glasses: The Product Consistency Test (PCT), ASTM C-1285-2002 (2002).

[2] K. Fox, T. Edwards, D. Peeler, D. Best, I. Reamer, and R. Workman, Durability and Nepheline Crystallization Study for High Level Waste (HLW) Sludge Batch 4 (SB4) Glasses Formulated with Frit 503, WSRC-STI-2006-00009, Washington Savannah River Company, Aiken, South Carolina (2006).

[3] H. Li, P. Hrma, J. Vienna, M. Qian, Y. Su, and D. Smith, Effects of Al_2O_3, B_2O_3, Na_2O, and SiO_2 on Nepheline Formation in Borosilicate Glasses: Chemical and Physical Correlations, *Journal of Non-Crystalline Solids*, **331**, 202-216 (2003).

[4] M. Smith, M. Stone, T. Jones, D. Miller, P. Burket, and D. Immel, Sludge Batch 4 Melt Rate Furnace and Slurry-Fed Melt Rate Furnace Tests with Frits 418, 425, and 503**,** WSRC-STI-2006-00015, Washington Savannah River Company, Aiken, South Carolina (2006).

[5] M. Smith and D. Miller, Initial SB4 Melt Rate Furnace Testing, WSRC-TR-2005-00339, Washington Savannah River Company, Aiken, South Carolina (2005).

[6] M. Smith, T. Jones, D. Miller, and M. Stone, SB4 SMRF Runs with Frits 418 and 320, WSRC-TR-2005-00569, Washington Savannah River Company, Aiken, South Carolina (2005).

[7] K. Fox, T. Edwards, D. Peeler, D. Best, I. Reamer, and R. Workman, High Level Waste (HLW) Sludge Batch 4 (SB4) Variability Study, WSRC-STI-2006-00204, Washington Savannah River Company, Aiken, South Carolina (2006).

[8] M. Smith, T. Jones, and D. Miller, Sludge Batch 4 Baseline Melt Rate Furnace and Slurry-Fed Melt Rate Furnace Tests with Frits 418 and 510, WSRC-STI-2007-00450, Washington Savannah River Company, Aiken, South Carolina (2007).

[9]D. Koopman, D. Best, and M. Williams, Impact of SB4 Tank 40 Decant and ARP/MCU Additions with/without Added Caustic on DWPF CPC Performance, WSRC-STI-2008-00147, Washington Savannah River Company, Aiken, South Carolina (2008).
[10]F. Raszewski, M. Stone, T. Edwards, and D. Peeler, The Impact of a Second Tank 40 Decant on the Frit 510 – Sludge Batch 4 System: Projected Operating Windows and Chemical Process Cell Processing, WSRC-TR-2008-00141, Washington Savannah River Company, Aiken, South Carolina (2008).
[11]F. Raszewski, T. Edwards, and D. Peeler, The Impact of a Tank 40H Decant on the Projected Operating Windows for SB4 and Glass Selection Strategy in Support of the Variability Study, WSRC-STI-2008-00017, Washington Savannah River Company, Aiken, South Carolina (2008).
[12]J. Pike, Evaluation of Low Temperature Aluminum Dissolution in Tank 51, SRNS-STI-2008-00021, Savannah River Nuclear Solutions, Aiken, South Carolina (2008).
[13]J. Pareizs, C. Bannochie, D. Click, E. Hansen, D. Lambert, and M. Stone, Washing and Demonstration of the DWPF Flowsheet in the SRNL Shielded Cells Using Post Aluminum Dissolution Tank 51 Sludge Slurry, WSRC-STI-2008-00086, Washington Savannah River Company, Aiken, South Carolina (2008).
[14]C. Bannochie, Tank 40 Final SB4 Chemical Characterization Results, WSRC-STI-2007-00674, Washington Savannah River Company, Aiken, South Carolina (2008).
[15]M. Hay and D. McCabe, Characterization of Tank 11H and Tank 51H Post Aluminum Dissolution Process Samples, WSRC-STI-2008-00227, Washington Savannah River Company, Aiken, South Carolina (2008).
[16]C. Bannochie, J. Pareizs, and H. Ajo, Sludge Batch 5 Acceptance Evaluation: Chemical Characterization of the Tank 51 SB5 Qualification Sample Prepared at SRNL, SRNL-PSE-2008-00125, Savannah River National Laboratory, Aiken, South Carolina (2008).
[17]D. Lambert, M. Stone, B. Pickenheim, D. Best, and D. Koopman, Sludge Batch 5 Simulant Flowsheet Studies, SRNS-STI-2008-00024, Savannah River Nuclear Solutions, Aiken, South Carolina (2008).
[18]K. Fox, T. Edwards, and D. Peeler, Recommended Frit Composition for Initial Sludge Batch 5 Processing at the Defense Waste Processing Facility, WSRC-STI-2008-00338, Washington Savannah River Company, Aiken, South Carolina (2008).