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Overview of Testing to Support Processing of Sludge Batch 4 in the Defense Waste Processing Facility

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Abstract

The Defense Waste Processing Facility (DWPF) at the Savannah River Site began processing of its third sludge batch in March 2004. To avoid a feed outage in the facility, the next sludge batch will have to be prepared and ready for transfer to the DWPF by the end of 2006. The next sludge batch, Sludge Batch 4 (SB4), will consist of a significant volume of HM-type sludge. HM-type sludge is very high in aluminum compared to the mostly Purex-type sludges that have been processed to date. The Savannah River National Laboratory (SRNL) has been working with Liquid Waste Operations to define the sludge preparation plans and to perform testing to support qualification and processing of SB4. Significant challenges have arisen during SB4 preparation and testing to include poor sludge settling behavior and lower than desired projected melt rates. An overview of the testing activities is provided.

Introduction

The DWPF has been immobilizing high-level radioactive waste in glass at the Savannah River Site since 1995. The high-level waste is stored in underground storage tanks with a capacity of one million gallons. The tanks contain varying amounts of supernate, salt solution, and sludge slurry. DWPF is currently processing the sludge slurry fraction of the waste, which must be separated and washed before any waste can be transferred to the DWPF. In some cases, multiple tanks of sludge slurry are combined in the preparation process to either obtain a blend with a favorable composition for vitrification and/or to obtain a large enough volume to allow DWPF processing for several years. The DWPF is currently processing Sludge Batch 3 (SB3), while Sludge Batch 4 (SB4) is being prepared in the Tank Farm.

SRNL participates in the preparation process by assisting with the definition of the washing endpoint and by performing the necessary research and development studies to support sludge batch qualification and DWPF processing. Definition of the washing endpoint involves determining the optimal supernate chemistry such that DWPF processing can remove the nitrite and mercury, neutralize the hydroxide, and immobilize the sodium and sulfate in glass while meeting the necessary processing, quality, and safety criteria. Each sludge batch must meet the requirements of the Waste Acceptance Product Specifications (WAPS) [1] as dictated by the qualification program outlined in the Waste Compliance Plan (WCP) [2]. Compliance must be demonstrated before the material is transferred to the DWPF feed tank. Although not specifically part of the WCP, the SRNL also performs process testing to ensure rheology characteristics and melt rate are acceptable to meet attainment goals. The following sections describe the testing to define the washing endpoint, qualify the sludge batch, and develop processing parameters.

Sludge Batch Planning and Preparation

Phase I and II Planning and Composition Projections

Planning for SB4 began in 2004, shortly after the initiation of processing of SB3 with a target readiness date of October 2006. The initial plan was to blend sludge from a high aluminum (HM) tank with sludge from three high iron (Purex) tanks. Blending was necessary to allow dilution of the HM sludge to minimize the impact on DWPF processing properties. Additionally, to accelerate tank closure, transfer of SB4 to a heel of SB3 would occur after producing the number of canisters required by the operating contract (i.e., 1100 or 1200 equivalent canisters). Table I contains the Phase I projected compositions for the major elements based on blending of the three Purex tanks and the one HM tank (SB4 only) and the compositions after blending SB4 with SB3 after producing either 1100 or 1200 equivalent canisters. The compositions represented increased concentrations of aluminum, potassium, manganese, and nickel over earlier sludge batches.

Table I. Phase I SB4 Major Element Composition Projections with Three Purex and One HM Sludge Tank (Wt% in Calcined Solids) [3]

Element	SB4 Only	SB4 Blended after 1100 Canisters	SB4 Blended after 1200 Canisters
Al	16.3	11.9	12.8
Ca	1.18	1.58	1.49
Cr	0.194	0.171	0.175
Fe	14.2	18.1	17.2
K	1.57	0.844	0.987
Mg	0.211	1.16	0.964
Mn	3.94	4.49	4.36
Na	14.7	16.2	16.2
Ni	4.57	2.90	3.22
S	0.363	0.363	0.363
Si	1.12	1.27	1.23
U	7.24	7.81	7.65
Zr	0.233	0.205	0.208

In 2005, the Tank Farm executed several sludge transfers from the HM tank to the DWPF preparation tank. More transfers than planned had to be performed due to the mounds of solids that remained in the HM tank. Sludge transfers halted when it was determined that minimal material was being recovered for the amount of water that was being added. After the fourth transfer and as part of the Tank Farm's corrosion control program, supernate samples were removed from the DWPF preparation tank at variable depths and a sludge height measurement was attempted. The samples and the height measurement indicated a discrepancy in the anticipated settled sludge height and mass. Technical meetings were held between SRNL and Liquid Waste Operations (LWO) to determine potential causes for the settling problems, and slurry samples were pulled to help in this assessment.

In parallel, LWO began preparing for sludge removal operations in the Purex tank containing the largest mass of sludge. As the equipment to slurry the tank contents was being inserted into the tank, a hard layer of material was encountered that could not be penetrated through the normal means of slurrying the tank or by mining with tools. The material was cored, analyzed, and determined to be predominately burkheite [4]. Due to the uncertainty on the composition of the material and on a possible means to remove this material, LWO revisited the tanks to be blended as part of SB4. It was decided that the tank containing burkheite would not be considered in the SB4 blend

New compositions were projected that included only the two Purex tanks and the already transferred HM sludge tank. In this scenario, compositions included blending with SB3 at either a 40” or 127” heel and at two different sodium molarity washing endpoints. Table II provides the projections used in Phase II testing. A comparison of the projected compositions in Table I and II shows the impact of not blending the third Purex tank. Aluminum concentration is higher in the revised projections for the sludge only and blended compositions regardless of the sodium washing endpoint, while iron, nickel, sulfur, and uranium projections are lower since these are Purex components. As expected, all of the less washed cases contained more sodium than the original projections for SB4.

Table II. Phase II SB4 Major Element Composition Projections Considering Two Purex and One HM Sludge Tank (Wt% in Calcined Solids) [5, 6]

Element	SB4 Only, 1.6 M Na	SB4 Only, 1.0 M Na	SB4 Blended with 40" SB3 Heel, 1.6 M Na	SB4 Blended with 40” SB3 Heel, 1.0 M Na	SB4 Blended with 127” SB3 Heel, 1.6 M Na	SB4 Blended with 127” SB3 Heel, 1.0 M Na
Al	17.46	19.02	15.63	16.29	13.73	14.61
Ca	1.15	1.26	1.36	1.42	1.41	1.45
Cr	0.17	0.19	0.17	0.18	0.16	0.17
Fe	12.43	13.54	14.79	15.41	15.37	15.84
K	1.74	1.89	1.41	1.47	1.15	1.24
Mg	0.20	0.22	0.64	0.66	0.84	0.83
Mn	3.16	3.44	3.68	3.83	3.74	3.87
Na	18.81	13.87	17.31	14.92	19.56	17.08
Ni	3.03	3.30	2.71	2.82	2.38	2.53
S	0.33	0.24	0.31	0.26	0.35	0.34
Si	1.18	1.28	1.27	1.32	1.24	1.29
U	5.08	5.53	5.95	6.20	6.11	6.31
Zr	0.21	0.23	0.20	0.21	0.19	0.20

Initial Sludge Sample Characterization and Settling Activities

SRNL performed characterization and settling rate investigations on the slurry samples removed from the DWPF preparation tank after all of the HM tank sludge transfers were made and before any Purex sludge was transferred. The assessment included characterization of the solid and supernate constituents, X-Ray Diffraction (XRD), Scanning Electron Microscopy, Differential Scanning Calorimetry (DSC), and particle size analyses. The solids were slightly more than anticipated based on historical data. The sludge composition was found to be consistent with other HM sludges [7]. However, all of the dried sludge solids did not dissolve when digestions were attempted for chemical characterization. XRD of the undissolved material from the digestions identified the main constituent to be boehmite (AlO(OH)) as opposed to gibbsite that is the primary Al phase usually found in sludge [5]. XRD and DSC confirmed the presence of the boehmite form of Al in the sample [8]. This phase of Al is known to present settling problems in the Al industry due to the small needle-like morphology of the crystal structure. Particle size analyses indicated the presence of small particles (nominally 2-4 • m with

90% of the particles less than ~11 • m) [6]. These small particles may also have been the result of extra shearing that occurred as a result of the multiple transfers to the DWPF preparation tank.

Settling tests confirmed a much slower settling rate than evidenced for SB3 or previous Purex sludges. Hay and Fellinger [7] performed a historical review of settling literature that indicated that the poor settling behavior may be typical for the HM sludges. A portion of the slurry sample was mixed with SB3 sludge to determine if settling rate would improve upon blending with SB3 or with other Purex sludges (as planned for SB4 preparation). The mixture showed minimal improvement in the settling rate [7]. SRNL concluded that the presence of boehmite, as opposed to gibbsite, and the small particle size distribution, along with the fact that the material was predominantly HM sludge instead of Purex sludge, contributed to the slower settling behavior experienced versus previous sludge batches [7, 8].

Due to the limited quantity of actual sludge material available, testing with a sludge simulant was performed in parallel to determine if a flocculant could be added to improve settling rate. The SB4 simulant exhibited very slow settling characteristics similar to the characteristics of the actual sludge material. This simulant was based on the expected chemical composition of SB4 washed to ~1.6 M Na and then blended with a 40" heel of SB3 (see Table II). A portion of the simulant was adjusted to the same insoluble solids concentration and sodium supernate molarity as the actual radioactive sludge sample from the DWPF preparation tank. Since the settling rate of the adjusted simulant was slower and the final settled solids volume was higher, the simulant was considered conservative for testing additives to alter the properties of the radioactive sample. Flocculating agents that were both inorganic and organic in nature were tested on the simulant. The additives were selected based on availability, and the amounts added were based on previous testing experience. Testing indicated no improvements in the settling rate or the settled solids volume [8]. A new set of additives was obtained to ensure that the use of older additives or small quantities was not biasing the results. This additional testing found only limited success and, due to the other potential problems the additive could introduce in DWPF and in implementation in the Tank Farm, was not pursued further. Therefore, SB4 planning proceeded considering the SRNL compositional and physical property data and with the assumption that settling was going to be slower than previous batches.

Phase III Planning and Projections

The higher solids reported by SRNL indicated more mass had been transferred than previously projected. The Tank Farm safety basis assumes a radiolytic hydrogen generation rate based on the radioactive content of the sludge, which in turn results in a mass limit on the amount of material that can be stored/held in a tank. The safety basis is protected by controlling the mass and performing mixing at a calculated duration to ensure that hydrogen does not accumulate above the safety basis limit. The potential to exceed the radiolytic hydrogen generation rate in a very short period of time and the concern over settling problems resulted in the need for another revision to the sludge batch preparation plan. An evaluation team was formed across departmental lines to review possible options to qualify SB4 within the time constraints.

A baseline option was selected that minimized the chances for a feed break. This option involved qualifying the material already located in the DWPF preparation tank, which was primarily HM sludge material, and then transferring enough of this material to the current DWPF feed tank containing SB3 to allow the other two Purex tanks to be transferred into the feed preparation tank while still meeting the sludge volume constraints for hydrogen generation. The transfer was planned to occur after DWPF met its canister goal for the contract period, which would mean a significant heel of SB3 material (~96") would remain to dilute the high Al content. After the transfer of the two Purex sludge tanks, the material in the DWPF preparation tank would be considered Sludge Batch 5 (SB5), and it, in turn, would be transferred to the DWPF feed tank on top of the heel of SB4. At the time, the LWO projections indicated a 6 – 8 month processing window for SB4 before SB5 would be transferred. Table III presents the projected compositions for the SB4 and SB5 material to be qualified and processed (with the SB3 or SB4 heel, respectively) for the baseline processing scenario.

Table III. Phase III SB4 and SB5 Major Element Composition Projections (Wt% in Calcined Solids) [9]

Element	SB4 Only	SB4 Blended with SB3 Heel	SB5 Only	SB5 Blended with SB4 Heel
Al	22.39	13.15	15.29	14.75
Ca	1.13	1.71	1.21	1.31
Cr	0.13	0.15	0.15	0.15
Fe	11.95	18.61	14.23	15.12
K	0.49	0.29	0.35	0.33
Mg	0.46	1.51	0.89	1.02
Mn	2.85	4.25	4.01	4.04
Na	16.66	16.40	17.88	17.84
Ni	1.04	1.24	3.10	2.68
S	0.55	0.45	0.25	0.29
Si	2.83	1.93	2.00	1.97
U	2.92	6.49	6.93	6.80
Zr	0.14	0.18	0.18	0.18

The revised composition for SB4 only indicated an even higher concentration of aluminum than the earlier projections, which would be expected given less Purex sludge. The blended SB4 projection, on the other hand, indicated a slightly lower aluminum and higher iron concentration compared to Phase III blend projections. Not too surprisingly, the SB5 compositions were close to the projections for the Phase II blends and were similar to each other. These facts will allow previous information gained on SB4 testing to be used for SB5 and will help minimize the studies (i.e., qualification versus processing) that will need to be performed for SB5.

Qualification and Processing Studies

Analytical Method Development

The analytical laboratory in DWPF performs routine analyses to support production and to provide the necessary data for the WAPS [1]. Any new methods that are precipitated by changes in the sludge batch must be identified and implemented in DWPF before acceptance of the sludge batch. Therefore, testing is performed in SRNL on the actual qualification sample to confirm that the existing DWPF methods will provide adequate results.

Initial characterization indicated potential problems with digesting the boehmite phase of the aluminum in the sludge. In DWPF, a cold chemistry method is used to characterize the sludge processed in the Sludge Receipt and Adjustment Tank (SRAT), while a sodium peroxide/ hydroxide (Na_2O_2/NaOH) and mixed acid digestion are used to prepare the product sample from the Slurry Mix Evaporator (SME). The cold chemistry method involves a room temperature HF-HNO_3 acid dissolution, so is considered less aggressive than other digestion methods. The Na_2O_2/NaOH digestion method was shown to be adequate in the characterization discussed above, but the cold chemistry method was not tested. Implementation of the Na_2O_2/NaOH digestion method for the SRAT sample would require an additional digestion to be performed so that the sodium concentration in the sample could be measured. Thus, a two-step method would be required for SB4 instead of the one method currently being used, which could increase DWPF analytical lab turn-around time. As part of the program to evaluate DWPF analytical methods, the Hg analysis method was also tested since initial analyses of SB4 indicated a very high concentration of mercury. Obtaining an accurate Hg concentration is important in DWPF because Hg must be steam stripped from the sludge to <0.45 wt% in the total solids to meet acceptance criteria.

Analytical Development initiated evaluation of the DWPF characterization methods using SB4 simulants and then applied the findings to the actual radioactive sludge sample. The primary focus was the digestion methods for the slurry samples and Hg analyses on the sludge and the SRAT product. For the digestions, testing involved the use of high aluminum standards and boehmite so that the thoroughness of the digestions could be verified. The cold chemistry and Na_2O_2/NaOH methods were used to digest the slurry sample. Initial results by Click [10] indicated that cold chemistry method did not provide complete digestion for the sludge. While the amount of non-dissolved material was very small, a statistically significant difference existed between the methods. Therefore, SRNL has recommended both methods be used for SRAT product analyses in the qualification testing, while the traditional methods will be used for the SME product analyses (Na_2O_2/NaOH and mixed acid), as well as a one step method being proposed by Coleman. DWPF methods for mercury analyses have provided acceptable results to date.

Simulant Development

Each batch of sludge to be qualified is slightly different from a chemical and physical property standpoint. SRNL develops simulants to match the projected compositions to determine processing behavior and provide recommendations for the qualification run performed with actual sludge material. Two different simulant types have been used for SB4. For Phase I testing, two generic sludges (sludge B and C) fabricated at the Clemson Environmental Technologies Laboratory were blended with additional trim chemicals to match the projected sludge composition. This simulant exhibited rapid settling, which was much different than the radioactive sludge, and appeared to behave differently from a chemical reaction perspective when subjected to the DWPF chemical processing cycles. Therefore, alternative simulant production methods were pursued.

This second simulant attempted to match the chemical and physical properties of the SB4 composition projection for the “1.6M Na – Blended with 40” SB3 heel” in Table II. The sludge was fabricated by co-precipitating the metal nitrates, washing the precipitated solids until the target nitrate concentration was met, and adding soluble species to meet the target supernate chemistry. The washing step was performed in parallel with a concentration step using a 3-disc SpinTek rotary filter. Details of the preparation can be found by Herman, et al. [11]. The simulant matched the chemical composition, but was very thick and could not be concentrated to the target total solids. The simulant had a yield stress of 31 Pa and a consistency of 13 cP [11] at 17.8 wt% total solids, which was higher than the radioactive sludge samples. The sludge had a slightly higher particle size distribution (i.e., median particle size of 11 •m before washing and 8 •m after washing) and contained some of the same compounds (e.g., boehmite) as the radioactive sample [11]. As will be discussed in the next subsection, the simulant better represented the chemical reactions that had been previously seen for other sludge batches during DWPF chemical processing. Although this sludge simulant had some promising properties, the high yield stress prevented this sludge from being used in all of the SRNL testing and additional changes to the simulant preparation method were pursued.

The team shifted its focus to the latest projection for SB4, which involved the projections given in Table III. To aid in the simulant development, the rheology was measured on both the as-received radioactive sample and on a radioactive sample adjusted to the target washing endpoint. Measurements by Hansen indicated that the yield stress was ~3 Pa on the as-received sample at ~24% total solids and ~11 Pa after washing to an ~1M Na end point with a slurry at ~17% total solids [12].

Several attempts were made to produce a large batch of the "SB4 Blended with SB3 Heel" given in Table III. However, all attempts resulted in a very thick simulant being fabricated. Therefore, the team decided to produce a simulant that was a blend of the generic B&C simulants from Clemson and the thick simulant that had been washed using the rotary microfilter. Only minor trim chemical additions were necessary. This simulant had a yield stress that more closely matched the radioactive sludge yield stress measurements and was used in melt rate testing discussed in the subsection below. At the same time, the simulant development team also had to produce a small batch of the "SB4 Only" composition given in Table III. This simulant was necessary to determine the processing parameters for the qualification testing with the radioactive sample. Fabrication of this simulant was easily accomplished.

DWPF Chemical Process Flowsheet Testing

The DWPF chemical process cell involves a two step process to prepare the sludge for feeding to the DWPF melter. The first step is performed in the SRAT and involves the destruction of nitrite, reduction of mercury and manganese, neutralization of carbonate, and adjustment of rheology for down-stream processing. The SRAT process involves the addition of nitric and formic acids at 93ºC and then heating of the slurry to boiling to complete chemical reactions and to concentrate the slurry. The reaction of the noble metals in the sludge with the formic acid results in the generation of hydrogen. To allow safe processing, DWPF maintains the hydrogen concentration below 25% of the hydrogen lower flammability limit. Before proceeding to the next processing step, DWPF performs analyses on the SRAT product to ensure that both nitrite and mercury are below their acceptance limits. Once this is verified, the SRAT product is transferred to the SME. In the SME, glass frit is added of the desired composition and at the target amount to meet the glass composition target. Additional concentration is performed to obtain a melter feed that is in the 45 to 50 wt% total solids range. Hydrogen generation is also monitored in the SME, and the SME product is characterized to ensure that an acceptable glass will be produced before transferring to the melter feed tank.

SRNL performs simulant flowsheet tests involving both SRAT and SME cycles to help determine the washing (sludge preparation) endpoint, the recommended processing strategy for the qualification run, and the DWPF processing strategy. Bounding testing has been completed with the Phase I (blended after 1200 canisters) and Phase II (~1.6M Na - Blended with 40" SB3 heel) composition projections. Phase I testing used a conservative level of noble metals, two different washing endpoints, and a mercury concentration up to 1 wt% in the total solids. A suitable operating window was found and the impact of mercury on the hydrogen generation rate was demonstrated [13]. However, some of the chemical reactions occurring during the SRAT processing were not consistent with reactions seen in previous sludge batch simulant and radioactive demonstrations. In addition, significant problems with sludge settling were seen resulting in non-representative feed being processed in a couple of the runs [13]. These problems, combined with the changes in sludge batch preparation strategy, resulted in the need for additional simulant testing. The Phase II testing involved two SRAT cycles and one SME cycle. A lower and upper bound acid addition level were tested based on Phase I testing. Equivalent concentrations of noble metals and mercury were used. The two SRAT cycles produced acceptable results. The SRAT products were combined to perform a SME cycle. Increased hydrogen was generated in the SME cycle but the concentration was still below DWPF acceptance limits. Once again, the SME product was very thick and exhibited a yield stress above DWPF limits at both 45 and 50 wt% total solids and 35 and 43% waste loading [14].

Simulant flowsheet testing has been performed by Koopman, Lambert, and Barnes to determine the parameters for SB4 qualification testing. Mercury reduction to DWPF limits was difficult in these runs, so additional boiling was recommended for the qualification run with actual waste. Due to the changes in the composition projections (see discussion on Phase III), additional testing will be necessary to determine the processing parameters for the material to be processed in DWPF. The testing will use updated noble metals and mercury concentrations based on the qualification sample characterization. As part of the testing, SRNL will provide DWPF with rheology curves as a function of acid addition level and total solids to allow DWPF to adjust processing parameters as necessary should problems be encountered with the actual SB4 material. Insight into the need for this additional information will be gained as rheology data is obtained on the radioactive qualification sample.

Redox Studies

An integral part of the acid addition strategy and the chemical processing that is performed in the DWPF is to adjust the melter feed to a redox ratio (i.e., Fe^{2+}/• Fe) that will provide acceptable processing in the DWPF. Redox is controlled by reducing the manganese in the sludge and by adjusting the formic to nitric acid ratio to obtain a Fe^{2+}/• Fe of 0.2. If the feed is overly oxidized, foaming could occur in the melter; whereas, overly reduced feed could result in the precipitation of metals that could shorten the life of the melter. The redox correlation is verified with each sludge batch. For SB4, higher concentrations of redox sensitive components (e.g., nickel and manganese) and lower concentrations of iron, along with preliminary melt rate testing indicated a potential redox problem.

Several glass crucible melts were made by Jantzen and Stone to determine the glass redox ratio of fabricated melter feed. The studies also involved adding different types and amounts of reductants (e.g., sugar, coal, oxalate) to determine their effectiveness and the ability to model their behavior. For SB3, a new redox correlation was implemented that modeled the behavior of coal, sugar, and oxalate [15] and was, therefore, used to predict the behavior of the additives. The initial review of the existing glass redox data and the new SB4 data indicated appreciably higher concentrations of manganese relative to the other sludge components. Jantzen also discovered historical data to indicate that manganese may be converting to the +7 valence state; thereby releasing more oxygen in the melter. If this reaction is considered and the manganese term is adjusted, the data for SB4 was more predictable with the SB3 redox correlation as demonstrated on recently fabricated melt rate testing feed. The final studies are being completed to verify the manganese reactions and then the redox correlation will be recommended for DWPF implementation.

Glass Formulation Assessments

SRNL uses the projected sludge compositions to determine the potential glass formulation operating window. This window is highly dependent on the frit and waste loading interval that is selected for the particular sludge batch. For SB4, Peeler and Edwards [16 - 19] have considered a wide range of frit compositions and waste loadings. Examples include the addition of calcium and vanadium to increase sulfate solubility, iron to change melt rate or redox, and boron or lithium additions to increase melt rate. One problem that has been unique to SB4, as compared to other sludge batches, is the potential for formation of nepheline crystals upon glass cooling. Nepheline has been shown to have a detrimental impact on glass durability and, thus, should be avoided when practical. The nepheline discriminator developed by Li [20] has been used in SB4 glass formulation studies to assess sludge and frit compositions. The SB4 studies have shown that the discriminator can adequately predict the nepheline formation potential. [21, 22] Peeler and Edwards [18, 19] have also shown that judicial selection of the frit can move the operating window away from the nepheline formation area to systems that are bounded by the typical DWPF processing constraints (e.g., liquidus temperature). Several candidate frits with reasonable operating windows have been identified.

SRNL will use the most up to date composition projections, the latest target blend date and information from melt rate testing to select the potential glass operating window for the variability study. The variability study is necessary to demonstrate that the durability model accurately predicts the leaching performance for the sludge batch.

Melt Rate Testing

Melt rate testing is an integral part of the frit selection process to provide a frit that will maximize DWPF throughput. At SRNL, both slurry fed melt rate (SMRF) testing and dry fed melt rate (MRF) testing are used to predict the melt rate or waste throughput for a particular sludge and frit combination. Extensive MRF testing has been performed with SB4 simulants representing the Phase I through III blend projections. Initial Phase I data indicated a significantly decreased melt rate compared to SB3 regardless of the frit or waste loading tested [23]. This same behavior was seen when the SMRF test was performed, but was amplified to some degree by the overly oxidizing nature of the feed [24]. The initial results were a significant concern and prompted exploration of new frit compositions to try to improve melt rate. As the frits were developed, MRF testing was performed using the latest simulant available and promising results were seen. Three frits were selected for additional SMRF testing. The frits included 418 (the SB3 frit), 425 (a higher Na frit), and 503 (a high B frit), while the sludge composition targeted the Phase III blended feed composition. Unfortunately, the simulant was still too thick to run at the desired 50 wt% total solids target. Thus, the simulant had to be run at only 45 wt% total solids and with additional formic acid added to meet the pumping criteria for the SMRF. The data from this set of testing showed significant improvements in melt rate, but, due to the thick nature of the sludge, translation to a DWPF throughput rate could not be made. Measurements of the glass redox indicated that the Fe^{2+}/• Fe ratio was within the target range [25]. Once the final composition projection is made for SB4 and the acid addition strategy for the CPC is made, MRF testing will be performed to define the waste throughput curves for SB4.

Characterization and Testing of the Radioactive Qualification Sample

Typically, the qualification sample is used to characterize the sludge, wash/prepare the sludge to match the Tank Farm endpoint, perform a laboratory-scale SRAT/SME cycle, and fabricate a glass from the SME product to measure glass durability. A 3-liter qualification sample was pulled and shipped to SRNL in January 2006.

Characterization of the sludge commenced upon receipt. Initial characterization included the chemical constituents and the solids content. With the exception of the slightly higher insoluble solids data, results were similar to earlier results reported by Hay and Fellinger [7]. Due to settling problems seen in the field, SRNL mimicked the plant preparation steps. The goal was to determine whether the settling rate or sludge rheology would change as washing proceeded. The SRNL plan was to perform four washes with inhibited water to reduce the sodium and soluble anion concentrations and perform five decants to remove the supernate and concentrate the slurry. Samples were taken throughout the washing cycle to verify supernate chemistry and for rheology measurements. Before the last wash and decant could be performed, however, limited supernate data became available that indicated that washing was proceeding better than planned and more soluble species had been removed than projected by the LWO washing spreadsheet. The data also indicated a potential formation of insoluble solids that had not been previously observed.

At that point, slurry samples were submitted for characterization to determine the reactions that had occurred during washing, and rheology measurement were performed to ensure that the sludge was not becoming too viscous at the higher than planned insoluble solids. Measurements by Hansen indicated a high yield stress (~30 Pa) at the SRNL endpoint (one wash/decant less than originally targeted) so additional measurements were performed as a function of the insoluble solids to determine the optimal concentration endpoint. The data indicated acceptable rheology at an insoluble solids <13% or at one less decant. Therefore, SRNL added the last decanted supernate back to the sample. This sludge was characterized to provide SRAT receipt results so the SRAT, SME, and glass testing could proceed.

Since SB4 will not actually be processed as qualified (i.e., it will be blended with a heel of SB3) and rheology issues have been identified, processing studies with the blend will be performed once the qualification work is completed. The focus will be to identify the anticipated rheological properties at different stages in the DWPF process. These studies were performed for SB3 and helped identify processing issues of the combined sludge batches.

Summary and Path Forward

The next sludge batch to be processed in DWPF, Sludge Batch 4, has presented several technical challenges, which SRNL has worked with Liquid Waste Operations to solve. The high aluminum sludge had slower settling behavior than anticipated and non-predictable behavior upon washing. SRNL is continuing to investigate the reactions that occurred during washing to help plan future strategies for sludge washing. For simulant development, significant rheological challenges were experienced. At this point, it is not known whether the behavior was an artifact of simulant production or the high aluminum/low iron content of the sludge. Once radioactive testing is complete, SRNL programs will be updated to accommodate the challenge. For DWPF implementation, SRNL will provide rheology curves as a function of the total solids in the sludge and for different acid addition levels to help DWPF select an optimal processing range.

The high aluminum content also presented challenges for glass formulation and melter processing. When combined with the high sodium content of the sludge as a result of minimizing washing, the potential for nepheline formation upon canister cooling was greatly increased. To minimize the chance of nepheline formation and its detrimental impact on glass durability, alternative frits were developed to provide a reasonable operating window. Fortunately, these alternative frits had a positive impact on melt rate as well. Since it is anticipated that future sludge batches may also contain high levels of aluminum, SRNL will continue melt rate testing to improve throughput for these sludges in DWPF.

The qualification and processing studies with actual SB4 material will be completed in the summer. The data from the radioactive and the simulant testing will then be reviewed and recommendations on processing of SB4 in DWPF will be finalized. After sludge preparation is completed in the Tank Farm, SNRL will verify the washing endpoint. Once all criteria are met, SB4 will be transferred to DWPF. A sample of the sludge from the DWPF feed tank and a glass sample from the DWPF melter will be pulled for characterization by SRNL to meet the WAPS requirements. At the same time, SRNL will be performing qualification work for sludge batch 5 so it can be transferred as soon as possible to allow waste removal and tank closure operations to continue in the Tank Farm.

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