FLOWSHEET FOR ALUMINUM REMOVAL FROM SLUDGE BATCH 6

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December 2008

SRNL

DISCLAIMER

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SUMMARY

Samples of Tank 12 sludge slurry show a substantially larger fraction of aluminum than originally identified in sludge batch planning. The Liquid Waste Organization (LWO) plans to formulate Sludge Batch 6 (SB6) with about one half of the sludge slurry in Tank 12 and one half of the sludge slurry in Tank 4. LWO identified aluminum dissolution as a method to mitigate the effect of having about 50% more solids in High Level Waste (HLW) sludge than previously planned. Previous aluminum dissolution performed in a HLW tank in 1982 was performed at approximately 85°C for 5 days and dissolved nearly 80% of the aluminum in the sludge slurry. In 2008, LWO successfully dissolved 64% of the aluminum at approximately 60°C in 46 days with minimal tank modifications and using only slurry pumps as a heat source. This report establishes the technical basis and flowsheet for performing an aluminum removal process in Tank 51 for SB6 that incorporates the lessons learned from previous aluminum dissolution evolutions.

For SB6, aluminum dissolution process temperature will be held at a minimum of 65°C for at least 24 days, but as long as practical or until as much as 80% of the aluminum is dissolved.

As planned, an aluminum removal process can reduce the aluminum in SB6 from about 84,500 kg to as little as 17,900 kg with a corresponding reduction of total insoluble solids in the batch from 246,000 kg to 131,000 kg. The extent of the reduction may be limited by the time available to maintain Tank 51 at dissolution temperature. The range of dissolution in four weeks based on the known variability in dissolution kinetics can range from 44 to more than 80%. At 44% of the aluminum dissolved, the mass reduction is approximately ½ of the mass noted above, i.e., 33,300 kg of aluminum instead of 66,600 kg. Planning to reach 80% of the aluminum dissolved should allow a maximum of 81 days for dissolution and reduce the allowance if test data shows faster kinetics. 47,800 kg of the dissolved aluminum will be stored in Tank 8 and 21,000 kg will be stored in saltcake via evaporation. Up to 77% of the total aluminum planned for SB6 may be removed via aluminum dissolution.

Storage of the aluminum-laden supernate in Tank 8 will require routine evaluation of the free hydroxide concentration in order to maintain aluminum in solution. Periodic evaluation will be established on concurrent frequency with corrosion program samples as previously established for aluminum-laden supernate from SB5 that is stored in Tank 11.

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LWO	Liquid Waste Organization
LTAD	Low Temperature Aluminum Dissolution
DWPF	Defense Waste Processing Facility
SPF	Saltstone Processing Facility
SWPF	Salt Waste Processing Facility
SB5	Sludge Batch 5
SB6	Sludge Batch 6
ARP	Actinide Removal Process
MCU	Modular Caustic-side Solvent Extraction Unit
WCS	Waste Characterization System
HLW	High Level Waste

1 INTRODUCTION

Samples of Tank 12 sludge slurry show a substantially larger fraction of aluminum than originally identified in sludge batch planning. The Liquid Waste Organization (LWO) plans to formulate Sludge Batch 6 (SB6) with about one half of the sludge slurry in Tank 12 and one half of the sludge slurry in Tank 4. Tank 12 sludge contains a high aluminum content that was selected as candidate sludges for aluminum dissolution.[1] The current plan includes dissolving and removing a significant portion of the aluminum before mixing the Tank 12 sludge slurry with other waste that constitutes the sludge batch. This report establishes the technical basis and flowsheet for performing an aluminum removal process in Tank 51 for SB6 that incorporates the lessons learned from previous aluminum dissolution evolutions.

2 BACKGROUND

An evaluation of sludge mass remaining in the High Level Waste (HLW) Tank Farms shows about 50% more solids in the sludge than previously estimated.[2] The new estimate will affect the estimated life cycle cost and schedule for HLW disposition. Consequently, Washington Savannah River Company chartered a LWO Technology Development team to evaluate techniques to mitigate these life cycle impacts. The Technology Development Team focused on three areas: reducing the sludge mass, new melter technology, and DWPF flowsheet improvements.

One promising mitigation option was aluminum dissolution, which offers the potential for significantly reducing the quantity of sludge solids sent to the DWPF, thus, reducing the number of canisters produced. Aluminum adversely affects sludge slurry rheology and glass viscosity, and adds to overall waste vo1ume. Aluminum is dissolved from sludge waste into the supernate by treatment with caustic at moderate to high temperatures, where it is subsequently removed by decantation and water washing.

As part of Sludge Batch 5 (SB5) preparation, the LWO successfully completed a low cost version of an aluminum dissolution process in Tank 51 with minimal tank modification. The process, dubbed Low Temperature Aluminum Dissolution (LTAD), was a variation of the baseline aluminum dissolution process operating at a temperature of 55 – 65°C rather than up to 90°C. This variation used the existing slurry pumps as the primary source of heat to warm the tank and maintain temperature. This process temperature was well within all existing safety limits for operating the waste tank, thus, required no special modification. The effect of lower temperature substantially increases the time required to dissolve the aluminum. In a 46 day dissolution cycle at process temperature, about 64% of the aluminum dissolved verses nearly 80% at 85°C in less than 5 days in 1982.[3] The reduction in aluminum mass in SB5 from LTAD directly reduced the total estimated canister production by 92 canisters at 34% waste loading.[4]

Aluminum solids in the sludge are believed to be present primarily in three forms – aluminum trihydrate or gibbsite, alumina monohydrate or boehmite, and aluminosilicate. With caustic treatment, the gibbsite form dissolves readily at the relatively low dissolving temperatures possible in the waste tanks. The boehmite form dissolves much more slowly and is somewhat less soluble than gibbsite. In addition to chemical form, the physical forms of the boehmite and gibbsite particles in the sludge slurry have an effect on the rate of dissolution, especially the specific surface area of aluminum exposed to the dissolving solution. The aluminosilicate has such low solubility in waste slurries that it is generally considered insoluble.

Equation (1) shows a kinetic model developed for dissolving aluminum from SRS sludge that is based on dissolution test data, in tank demonstration data, and literature data.[5] The rate model is based on dissolving boehmite, which is believed to be the slowest dissolving form of aluminum in the waste.

(1) $\quad t = \dfrac{\alpha F(wf, \alpha)}{(\eta^0 \gamma_\pm^{1/2} A)\sqrt{C_{OH}^0}} \, e^{\frac{14800}{T}}$

where

$\quad$ t = Dissolution time, hr

$F(wf, \alpha) = \dfrac{1}{\sqrt{\alpha(\alpha\text{-}1)}} \, Ln \left| \dfrac{(\sqrt{\alpha} - \sqrt{\alpha-1})(\sqrt{\alpha\text{-}1+wf} + \sqrt{\alpha-1})}{(\sqrt{\alpha} + \sqrt{\alpha-1})(\sqrt{\alpha\text{-}1+wf} - \sqrt{\alpha-1})} \right|$

$\quad \alpha$ = Mole ratio at initial conditions of free OH ion in the liquid phase relative to Al in the solid phase, dimensionless

$\quad C_{OH}^0$ = Initial liquid phase concentration of free OH ion in molal units, gmol/kg water

$\quad$ T = Dissolution operating temperature, K

$\quad$ wf = Weight fraction of initial Al remaining in solids at the conclusion of the dissolution process, dimensionless

$\quad \eta^0$ = the initial specific surface area of aluminum hydroxide solids, m^2/gmol Al

$\quad \gamma_\pm$ = Constant defined in the batch dissolution model development equivalent to variation of $_{25}a_{NaOH}$, activity of NaOH in water at 25°C, with free OH molality for the liquid phase where $_{25}a_{NaOH} \sim \gamma_\pm C_{OH}$, dimensionless.

$\quad$ A = Boehmite dissolution reaction pre-exponential rate constant, mol Al-m^{-2}-hr^{-1}-(mol OH/kg water)$^{1/2}$

The rate equation is based on a number of simplifying assumptions, including:

- Sufficient solids and liquid mixing is provided,
- Aluminum hydroxide solids are primarily present in the form of boehmite,
- The dissolution endpoint composition is selected such that the solubility limit does not influence the dissolution rate at the dissolution operating temperature,
- The change in liquid phase water mass is negligible over the dissolution time period,
- The operating temperature is constant over the dissolution time period, and
- The liquid phase sodium hydroxide activity is approximately proportional to the molal concentration of free hydroxide ion in solution.

The rate equation is applicable for hydroxide ion concentrations less than 6.8 M. A shift in reaction order occurs above this concentration and the rate equation would be expected to over-estimate times to dissolve aluminum while the liquid phase is at free hydroxide ion concentration greater than 6.8 M.

The group of constants, $(\eta^0 \gamma_\pm^{1/2} A)$, was fitted to simulated and real waste dissolution data. To best represent SRS waste, the recommended constant to apply was 2E15. One might note that the group of constants contains the initial specific surface area of aluminum hydroxide. Little or no data is available to determine the specific surface area. However, the value is a constant for any given dissolution and may vary some from batch to batch. Therefore, application of this fitted parameter includes the assumption that the specific surface area is about the same from batch to batch. Considering that the targeted sludge for aluminum dissolution all originated from the same process in H-Area, the aluminum particles in the sludge are likely to be similar from batch to batch.

Testing with Tank 12 sludge at 60°C shows most of the aluminum dissolved in 10 days.[6] This test implied that dissolution could be relatively quick, but the fraction of gibbsite in Tank 12 sludge was not determined. Gibbsite dissolution rate is faster than boehmite under identical conditions. Furthermore, dissolution rates in laboratory testing appear to be substantially faster than observed in a waste tank. In preparation for aluminum dissolution for SB5, a laboratory simulation of the dissolution process was performed on a sample of sludge slurry from SB5 at 55°C. The laboratory testing simulating SB5 dissolution showed that the dissolution rate observed in the laboratory tests was much faster than predicted by this equation. When compared to the observations of dissolution in Tank 51, the laboratory dissolution test reached the same extent of dissolution in the first 10 days as was observed in the first 20 days in Tank 51.[3] The dissolution rate observed in Tank 51 was still faster than predicted by the model.

Inherent in this equation is the assumption that the reaction rate is limited by the chemical reaction rate at the surface of the particle. Dissolution of aluminum from SB5 was about 3.5 times faster than predicted, most likely because the specific surface area was larger than suggested by the fitted value for ($\eta^0 \gamma_\pm^{1/2}$ A). Since there was inadequate data to change the value for the rate constant, the conclusion from the dissolution experience on SB5 recommended continued use of the same rate constant until additional data is available to adequately account for particle characteristics.

3 APPROACH

The flowsheet and parameters were modeled after the flowsheet for LTAD. The aluminum-laden supernate is destined for Tank 8 in this case.

The initial conditions in Tank 51 for aluminum dissolution for SB6 assume a small heel from SB5 preparation. The SB5 heel composition is estimated from composition projections after preparation is complete.

The estimation or projection of the composition of the sludge slurry from Tank 12 is much more complicated than estimating the composition for SB5 since the actual sludge slurry to be processed has not yet been transferred to Tank 51. Samples from Tank 12 are planned, but limited data is available to use for this estimate. The liquid phase is estimated based on the historical record of Tank 12 and estimated changes to the composition due to the effects of evaporation, carbon dioxide absorption from the atmosphere, and radiolysis of sodium nitrate. In addition, the compositions of the solutions added to Tank 12 used to slurry the waste are included in the material balance to estimate the Tank 12 sludge slurry composition. The solids phase other than aluminum is practically inert relative to aluminum dissolution, so the aluminum content of the solids is based on sample data.

The composition of Tank 8 is estimated by samples of waste similar to what is expected to remain in the heel.

Tank 24 composition is based on the best available sample data.

Tank 4 sludge slurry composition is based on existing projections of the composition at the end of waste removal.

The process parameters are then determined based on the estimated composition of the sludge slurry. OLI Stream Analyzer[tm] is used to estimate the solubility of aluminum in order to refine the preliminary process parameters for Tank 12 sludge slurry.[7] Using the dissolution rate model for estimating duration, the target process temperature is determined by balancing the target extent of dissolution with time available to

perform dissolution. The range of aluminum predicted to dissolve is then determined by the known variation in parameters.

A material balance is produced using the identified conditions and at the maximum extent of aluminum dissolution anticipated. The maximum extent of dissolution is used to demonstrate the conditions necessary to store the aluminum-laden decant in Tank 8 without precipitating aluminum. In addition, the process conditions generated will maximize the extent of aluminum dissolved for any dissolution time less than necessary to reach the maximum.   The material balance will be used to estimate the composition of the interface streams to feed existing processes.

4   DISCUSSION

4.1   Tank 51 Dissolution Process Description

For the purposes of this flowsheet the dissolution process consists of the following steps. Procedure requirements will be further detailed in an Operations Plan.

1. Valve out cooling water to Tank 51.
2. Unload 50% sodium hydroxide solution to Tank 51 via HPT 7 and HPT 8.
3. Use slurry pumps to mix Tank 51 periodically during the batch transfers of caustic from HPT 7 and HPT 8 to Tank 51.
4. Use slurry pumps to increase slurry temperature in Tank 51 and maintain the temperature as necessary. A supplemental heater may be used if installed. If necessary, cooling coils may be used to avoid exceeding the upper operating temperature limits.
5. Periodically mix tank for number of days available. Supernate analysis results will indicate the rate and extent of dissolution, and be used to finalize the dissolution time to be allotted.
6. Turn off slurry pumps.
7. Settle for as long as allowable by the Q-Time program for a maximum decant to Tank 8.
8. Decant the maximum amount of aluminum-laden supernate to decant storage tank, Tank 8.
9. Start SB6 washing prior to the planned receipt of sludge from F-Area Tank Farm (Tank 4).
10. Proceed with SB6 preparation by transferring sludge slurry from F-Area Tank Farm (Tank 4) and Pu waste receipts from H Canyon, as planned.
11. Continue washing SB6 for preparation as feed to DWPF.
12. Store aluminum-laden supernate for feed to the Salt Waste Processing Facility (SWPF) or any other salt waste process installed in the future.

Figure 1 shows the process flow diagram in context with downstream processes.

The HLW Tank Farms has limited volume for storing the aluminum-laden supernate generated from the aluminum dissolution process. Tank 8 is used to store the aluminum-laden supernate from this process, because Tank 8 has space available that cannot be used for bulk sludge storage. The supernatant is stored without mixing with other supernates to avoid inadvertent reprecipitation of the aluminum. However, if supernate is transferred into or left in Tank 8 before transfer from Tank 51, the blended liquid needs to be evaluated for the risk of precipitating aluminum and chemical adjustments made to the blending supernate, if necessary, before mixing the liquids. The aluminum-laden supernate may be purposely blended at any time for salt waste processing and final disposition at the SPF.
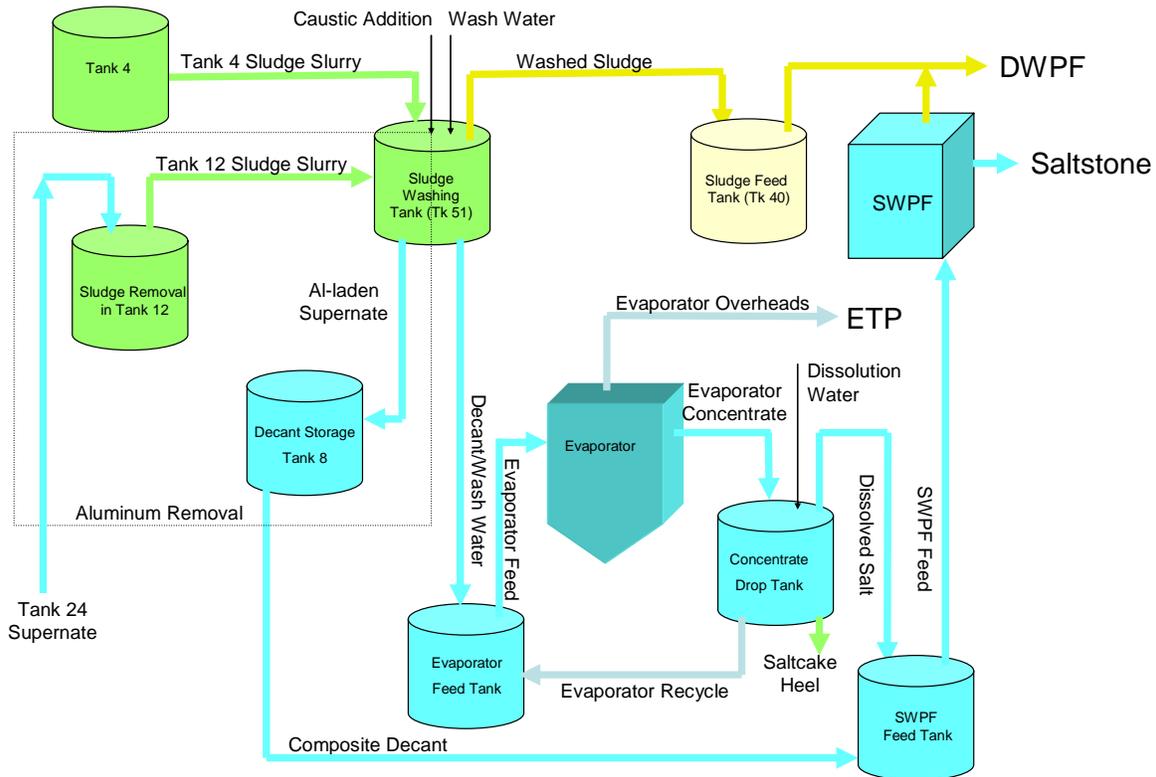
Figure 1: Aluminum Removal Flow Diagram for Sludge Batch 6

4.2   Selecting Process Conditions

4.2.1   Initial Process Conditions

Primarily, SB6 will consist of about half of the sludge slurry in Tank 12 and half of the sludge slurry in Tank 4. Only the high aluminum content slurry from Tank 12 will be included in this aluminum dissolution process. Other sludge slurry or additions may be added to the sludge batch, but after aluminum dissolution, thus, not affecting the composition for the dissolution process. The heel from SB5 in Tank 51 is anticipated to be about 7". The start of aluminum dissolution will consist of the sludge slurry from Tank 12 combined with the heel remaining in Tank 51 from SB5 preparation.

4.2.1.1   Tank 12 Composition

The composition of the sludge in Tank 12 consists of two parts, a solid phase and a liquid phase. The composition of the solid phase is discussed in Section 4.2.1.1.5. The liquid phase composition is estimated by analyzing the transfer and sample history of the tank.

Tank 12 last received a transfer of waste in June 1973.[8] Supernate was transferred from the tank in April 1976 and again in September 1978. The remaining liquid was allowed to concentrate by natural evaporation of water via the tank ventilation. Around March 1983, the liquid level and solids level was

approximately the same. However, significant rain water in-leakage restored a liquid layer in May 1984. The water evaporated and the liquid level generally fell below the top of the solids level again by February 1985. Water likely continued to evaporate until the water vapor pressure of the supernate was reduced to match the average water vapor pressure in the atmosphere. The evaporation rate slowed down as the liquid phase composition approached this point. Further complicating the chemistry in the liquid phase is the fact that carbon dioxide from the atmosphere is absorbed in the supernate, depleting the free hydroxide until the pH is in equilibrium with the saturation concentration of carbonates. Furthermore, nitrates in the liquid are converted to nitrites by radiolysis. Liquid was added to the tank between November 2004 and January 2005 in preparation of waste removal. Additional liquid was added to the tank by two supernate transfers from Tank 51 in April and May 2008.

The liquid phase composition is determined first by estimating the likely composition of the supernate after the last waste transfer into the tank in 1973. Then, the liquid composition after the last transfer in 1978 is adjusted for evaporation and carbon dioxide absorption. Some salts in solution will precipitate as water evaporates. The liquid phase is then adjusted for the liquid additions in 2004, followed by another concentration step for a short period of evaporation, and finally by adjusting for the supernate transfers. In order to determine if all of the salt precipitated will redissolve with the liquid additions, salt precipitation and dissolution is evaluated by using OLI Stream Analyzer[tm] to simulate evaporation.

Table 1 and Table 2 summarize Tank 12 transfer and sample history since the last transfer into Tank 12. Ideally, the sample data could be used to establish a trend for composition changes expected, but the limited supernate sample data varies considerably without establishing a distinct trend. The sample variability is consistent with what would be expected from single determinations from dip samples.[9] In addition, the 1984 sample is likely dilute due to the rain water intrusion. If a trend could be established, the data could then be used to estimate the composition after the last transfer out Tank 12 and composition changes calculated to account for changes since the transfer. Without an established trend, the average of the four samples taken between 1975 and 1981 is used to estimate the actual composition after the last transfer out of the tank in 1978.

Table 1: Historical Summary of Tank 12 Since Last Waste Receipt

June 1973	Last received waste[10]
April 1975	Supernate sampled[11]
April 1976	Transferred 242,000 gallons of supernate from Tank 12[10]
September 1978	Transferred 107,000 gallons of supernate from Tank 12 to Tank 13[10]
December 1978	Supernate sampled[11]
April 1980	Supernate sampled[11]
September 1981	Supernate sampled[11]
March 1983	Supernate fell below sludge solids surface[10]
May 1984	Rain water in-leakage[12] (17,000 gallons based on monthly increase in liquid level)[10]
November 1984	Supernate sampled[11]
February 1985	Supernate sample attempted, but vial was empty[11]
February 1985	Supernate fell below sludge solids surface (based on lack of liquid for sampling)[10]
November 2004 – January 2005	Initial "rewetting" solution added[13]
April 2008	Transfer from Tank 51 to Tank 12[14]
May 2008	Transfer from Tank 51 to Tank 12[14]

Table 2: Tank 12 Supernate Sample Data Since Last Waste Receipt

Sample Date	Average (1975-1981 samples)	02/28/85	11/29/84	09/10/81	04/01/80	12/18/78	04/16/75
Liquid Phase							
Specific Gravity	-	EMPTY VIAL	1.3680	1.4400	1.2000	-	-
Concentration in M:							
Na^+ (estimated from charge balance)	7.21		-	-	-	-	-
NO_2^-	1.60		0.386	2.30	1.20	1.70	1.20
NO_3^-	2.61		0.415	3.10	2.90	1.45	3.00
OH^-	1.42		0.610	1.30	1.50	1.50	1.40
Cl^-	-		-	-	-	-	-
SO_4^-	0.300		-	-	-	0.300	-
F^-	-		-	-	-	-	-
CO_3^{-2}	0.300		-	-	-	0.300	-
AlO_2^-	0.370		-	-	-	0.300	0.440
$C_2O_4^{-2}$	-		-	-	-	-	-
PO_4^{-3}	< 0.01		-	-	-	<0.01	-
Gross Gamma (Ci/gal)	-		-	-	-	-	-

4.2.1.1.1   Tank 12 Supernate Concentration Due to Evaporation

Monthly report data can be used to estimate the evaporation rates in tanks in a similar manner as Pike used in 1993[15]. Long periods of relatively quiescent times between transfers provide a reasonable length of time to average over several seasons and small, periodic maintenance flush water additions. Figure 2 graphically shows the monthly report data for the tank volumes and temperatures.
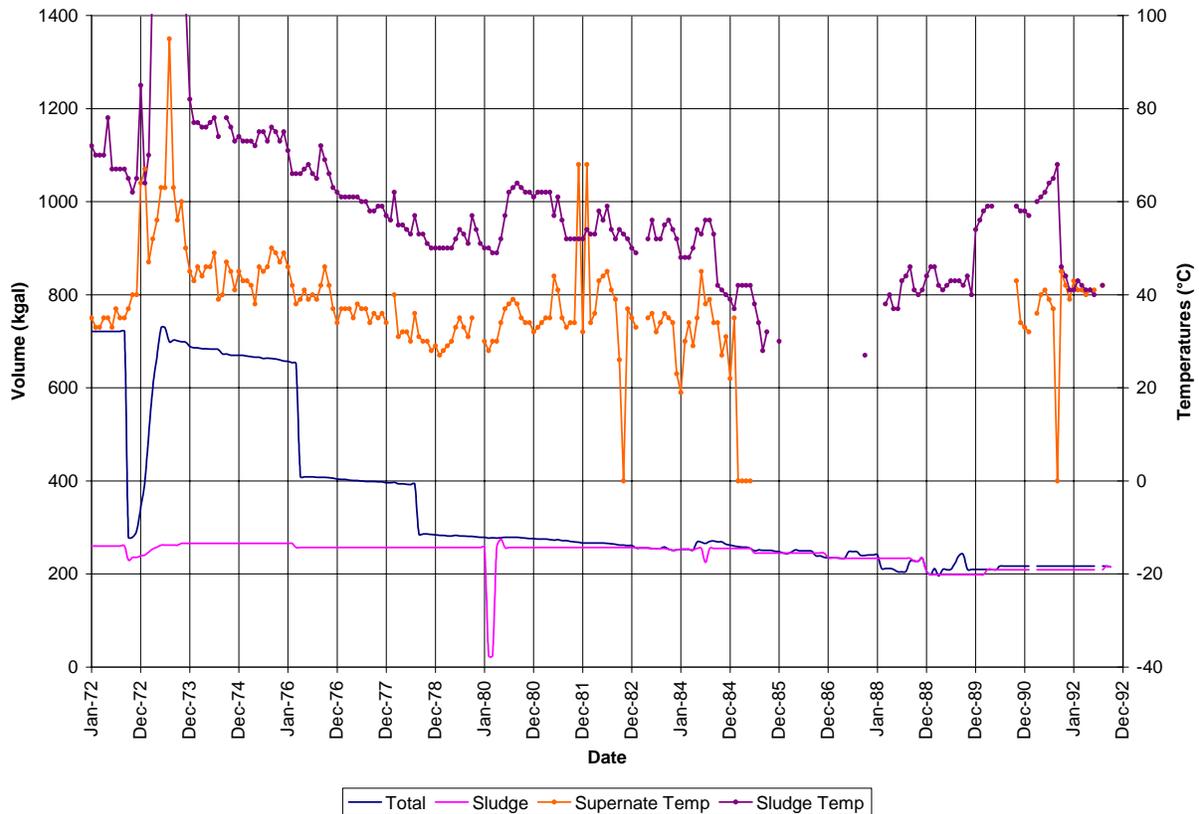
Figure 2: Tank 12 Volume and Temperature Data from Monthly Reports

Table 3 shows the evaporation rates estimated between transfers out of the tank. One might note that the evaporation rate appears to be decreasing as expected. However, once the liquid level falls below the surface, there's no way to track the changes. If one assumes that the evaporation rate maintains at a constant rate after the liquid level falls below the solids surface, then evaporation occurred at the volumetric equivalent rate of 2.1 inches per year until liquid addition in November 2004. 46.5" or 126,000 gallons of water is estimated to have evaporated since the last transfer, leaving 120,000 gallons of the equivalent original solution in the tank (note that 120,000 gallons in 176,000 gallons determined just before rewetting is not, in any way, "dry"). Since only water is removed due to evaporation, the concentration of the salts in solution actually increases inversely to the water content of the supernate.

Table 3: Tank 12 Evaporation Rates

From	To	Evaporation (inches/year)
9/1978	1/1983	2.1
4/1976	8/1978	2.7
2/1974	3/1976	6.0

4.2.1.1.2 Absorption of Carbon Dioxide

Carbon dioxide was measured at 361 ppm in H-Area.[16] Between the last transfer out of the tank in 1978 and liquid addition in 2004, 26.2 years at an estimated nominal 300 scfm ventilation rate, Tank 12 supernate was exposed to 1.1 million moles of carbon dioxide. With an exposed liquid surface, practically all the carbon dioxide is absorbed by the liquid. However, it's not known how the rate is affected once the liquid surface falls below the top of the solids. Some amount of liquid is always wicking up to the surface of the solids. The water content of the solids increases with distance from the surface of the solids layer until the pores in the solids layer are completely full, thus, identifying the interstitial liquid level.

After the last transfer out of Tank 12 in 1978, 105.5" or 286,000 gallons of waste remained containing an estimated 316,000 kg of sludge solids. Assuming a nominal sludge solid density of 2.40 kg/L, the total liquid volume was 251,000 gallons. At the average hydroxide concentration, Tank 12 contained a total of 1.4 million moles of free hydroxide. Therefore, Tank 12 has been exposed to nearly twice as much carbon dioxide as needed to completely deplete Tank 12 of free hydroxide. Note that carbon dioxide absorption progresses to an equilibrium near pH of 9-10. Therefore, it's likely that most if not all the free hydroxide was converted to carbonate and the hydroxide and carbonate are at or near equilibrium with the atmosphere. Further neutralization of metal hydroxides in the sludge solids may have occurred, converting the metal hydroxides to metal carbonates, but no further hydroxide depletion is assumed in this estimate.

4.2.1.1.3 Radiolysis of Nitrate

The conversion of nitrate to nitrite by radiolysis was measured in a waste tank at the rate of 4.9E-11 moles/L/BTU of fission product heat.[17] In order to estimate the total conversion of nitrate, the cumulative fission product heat generated between the 1978 transfer and the 2004 liquid addition needs to be estimated. The rate of fission product heat was tracked in monthly reports until the mid-1990's. For the purposes of estimating the cumulative energy, periodic sampling of the heat generation rate was extracted from the monthly record and is shown in Table 4 and graphically in Figure 3. The rate of heat generation decreases as a unique function of the mixture of radio isotopes in the sludge waste and does not fit a function for a single average decay half life. For simplicity, the total decay heat was determined by numerically integrating the reported heat generation rate over time. The rate for each month between each extracted point is estimated by interpolation. Decay heat rate after the last reported rate is determined by linear extrapolation of the last two points. The cumulative decay heat is approximately 4.0E10 BTU, thus, the total nitrate to nitrite conversion is 2.0 moles/L.

Table 4: Tank 12 Radiolytic Decay Heat Rate

Date	Radiolytic Decay Heat Rate (BTU/hr)	Reference	Page
Feb-74	1,181,000	Works Technical Department Report for February 1974, DPSP 74-1-2, Redacted Version	74
May-74	982,000	Works Technical Department Report for May 1974, DPSP 74-1-5, Redacted Version	85
Jul-74	879,534	Works Technical Department Report for July 1974, DPSP 74-1-7, Redacted Version	74
Oct-74	758,600	Works Technical Department Report for October 1974, DPSP 74-1-10, Redacted Version	69
Jan-75	665,303	Works Technical Department Report for January 1975, DPSP 75-1-1, Redacted Version	78
Dec-75	461,300	Works Technical Report for December 1975, DPSP 75-1-12, Redacted Version	S-46
Sep-76	348,300	Works Technical Report for September 1976, DPSP 76-1-9, Redacted Version	63
Jan-79	250,000	Waste Management Programs Report for January 1979, DPSP 79-21-1	25
Dec-80	229,400	Waste Management Programs Report for December 1980, DPSP 80-21-12	25
Dec-92	167,700	High Level Waste Engineering Monthly Data Record, WSRC-RP-92-78-12B, December 1992	12
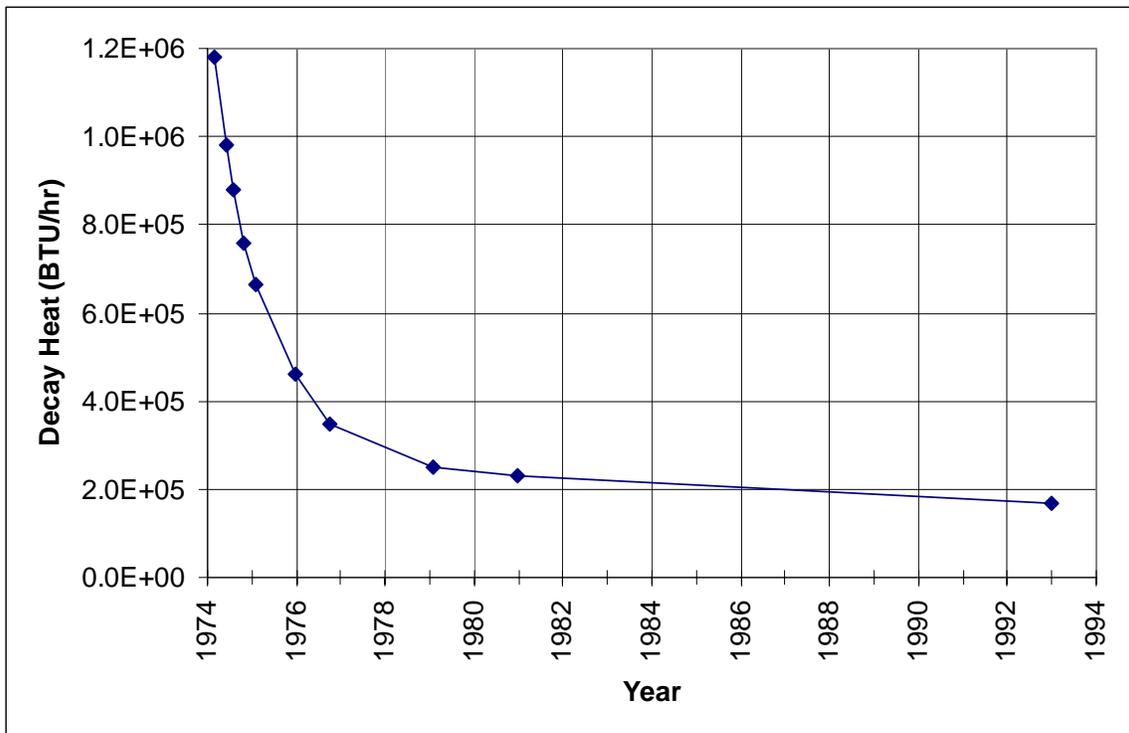
Figure 3: Tank 12 Radiolytic Decay Heat Estimation

4.2.1.1.4 Estimating Liquid Phase Composition

After evaporation, carbon dioxide absorption, and nitrate conversion, the apparent composition of the liquid phase is shown in Table 6. This composition is not at equilibrium and will precipitate $2Na_2SO_4 \cdot Na_2CO_3$ (a carbonate-sulfate double salt), sodium carbonate monohydrate, and possibly a small amount of gibbsite. For this material balance, the extent of any precipitation was determined after accounting for the liquid additions.

Table 6 completes the material balance for Tank 12 up to the time sludge removal started. After liquid addition in 2004, some evaporation occurred. The apparent evaporation rate was 2.9 inches per year based on the waste level in Tank 12 before the supernate transfers from Tank 51. This evaporation rate was very similar to the rates observed in the tank before the liquid level fell below the solids surface as shown in Table 3.

After the transfers from Tank 51 to Tank 12, the reel tape was out of service for maintenance and put back in service indicating a somewhat lower level. The new level may be a result of recalibration, actual level change due to liquid "soaking" into the sludge layer, or evaporation. Regardless, the change was treated as evaporation since a volume reduction in the interstitial liquid by evaporation had to occur for any liquid to absorb into the sludge layer and the volume reduction was not previously accounted. The composition as of 6/30/2008 in the last column of Table 6 was used as the initial composition in Tank 12 for the aluminum dissolution material balance.

The final liquid composition is still not below saturation relative to $2Na_2SO_4 \cdot Na_2CO_3$, sodium carbonate monohydrate, and gibbsite. A relatively small volume of salt crystals remain in the waste. The aluminum dissolution material balance uses the apparent composition in order to account for the relative fraction of salt crystals carried in the slurry transfer to Tank 51.

The final estimate for Tank 12 initial composition is shown in Table 10.

4.2.1.1.5 Estimating Solid Phase Composition

The solids phase consists primarily of metal oxides and hydroxides that remain practically insoluble during aluminum dissolution. A small amount of mercury will dissolve with the aluminum, significantly increasing the mercury in solution, but the amount is small relative to the quantity of mercury in the sludge solids.[3] As such all the components other than aluminum may be treated as inert mass and only the components associated with aluminum will change during dissolution. Therefore, only the aluminum content of the solid phase is tracked rigorously.

The aluminum content of the sludge is estimated from a recent sample of partially mixed sludge slurry in Tank 12. Table 5 shows the metals analysis for the Tank 12 sludge slurry sample and an estimate of the composition of the insoluble solids relative to an assumed solids species. The solids species were picked to be consistent with the LWO Waste Characterization System (WCS).[14] However, WCS shows several forms of calcium and all the calcium is assumed to be in the form of calcium carbonate, the most likely form as predicted using OLI Stream Analyzer[tm]. A few of the measured metals do not have equivalent solids tracked in WCS. Since these metals were measured at very low concentrations, they are assumed to make no significant contribution to the total mass and no equivalent compound assumed.

After conversion to the assumed chemical species, the composition was normalized to 100%.

Table 5: Aluminum Content Estimate of Tank 12 Sludge Solids

Metals Analysis in Total Solids[18]			Metals as Converted to Assumed Insoluble Species			
Constituent	MW (g/mole)	Mean Concentration Mass % of TS	Assumed Insoluble Chemical Species	MW (g/mole)	Mass % of IS	Normalized Mass % of IS
Al	27	10	AlOOH*	60.0	96	78.065
Ag	107.9	0.0023	AgOH	124.9	0.0143	0.0117
B		0.009	None			
Ba	137.3	0.013	$BaSO_4$	233.4	0.119	0.0972
Ca	40.1	0.22	$CaCO_3$	100.1	2.96	2.41
Ce	140.1	0.021	$Ce(OH)_3$	191.1	0.154	0.126
Cr	52	0.036	$Cr(OH)_3$	103.0	0.384	0.314
Cu	63.6	0.01	$Cu(OH)_2$	97.6	0.0827	0.0675
Fe	55.6	1.0	$Fe(OH)_3$	106.6	10.3	8.43
Hg	200.5	0.39	HgO	216.5	2.27	1.85
K		0.12	Assumed all soluble			
La	138.9	0.011	$La(OH)_3$	189.9	0.0811	0.0661
Mg	24.3	0.21	$Mg(OH)_2$	58.3	2.72	2.22
Mn	54.9	0.47	MnO_2	86.9	4.01	3.27
Mo		0.0073	None			
Na		30	Assumed all soluble			
Ni	58.7	0.12	$Ni(OH)_2$	92.7	1.02	0.833
Pd		0.0018	None			
Ru	101.1	0.022	RuO_2	133.1	0.156	0.127
Rh		0.0047	None			
Si	28.1	0.04	SiO_2	60.1	0.461	0.376
Sr	87.6	0.0069	$SrCO_3$	147.6	0.0627	0.0511
Th	232	0.23	ThO_2	264	1.41	1.15
Ti	47.9	0.0029	TiO_2	79.9	0.0261	0.0213
U	238	0.027	$UO_2(OH)_2$	304.0	0.186	0.152
Zn	65.4	0.014	$Zn(OH)_2$	99.4	0.115	0.0936
Zr	91.2	0.044	$ZrO(OH)_2$	125.2	0.326	0.266
Total		44.0			122.6	100.0

* Aluminum concentration in insoluble solids was determined by subtracting the contribution of aluminum from the dissolved solids from the total solids.

Mass percent in insoluble solids was calculated by the following conversion:

$$\%_{IS\text{-Compound}} = \%_{TS\text{-Element}} \cdot MW_{Compound} / MW_{Element} \cdot \%_{TS} / \%_{IS}$$

where

MW = molecular weight in g/mole,
$\%_{IS}$ = mass percent of insoluble solids in slurry, i.e., those solids not in the liquid phase of the sample, 7.2%,[19]
$\%_{TS}$ = mass percent of total solids in slurry, 38.8%,[19]
$\%_{IS\text{-Compound}}$ = mass percent of compound in the insoluble solids, and
$\%_{TS\text{-Element}}$ = mass percent of element in the total solids.

A portion of the aluminum is in the dissolved solids such that the calculation includes the removal of soluble aluminum before converting as follows:

$$\%_{IS\text{-Compound}} = (\%_{TS\text{-Element}} \cdot \rho_{slurry} \cdot \%_{TS} - [Al] \cdot MW_{Element} / 1000 \text{ ml/L}) / (\rho_{slurry} \cdot \%_{IS}) \cdot MW_{Compound} / MW_{Element}$$

where

ρ_{slurry} = density of slurry, g/ml, 1.35,[19] and
[Al] = concentration in supernate, M, 0.39.[20]

Table 6: Tank 12 Composition Estimate

Date	Sep-78					11/7/04 - 1/6/05			4/6/2008	5/5/2008			6/30/2008
Description	Inventory After Last Transfer Out	Estimated Evaporative Losses	Tank 12 After Evaporative Loss	Tank 12 After CO2 Absorbtion	Tank 12 After NO3 Conversion	Rewetting Solution	Evaporative Loss After Rewet	Tank 12 After Evaporation	Transfer A from Tank 51	Transfer B from Tank 51	Tank 12 after Transfers	Water Evaporation	Tank 12 after Evaporation
Tank Level, in	105.5		59.0	59.0	59.0		4.3	66.6			116.9		109.8
Total Volume, gal	286,000	126,000	160,000	160,000	160,000	58,300	37,600	181,000	32,100	88,700	317,000	22,300	298,000
wt% Insoluble Solids											18.1%		19.0%
Total Mass, kg		477,000							143,000	386,000	1,747,000	84,400	1,663,000
Liquid Phase													
Volume, gal	251,000	126,000	125,000	125,000	125,000	58,300	37,600	146,000	32,100	88,700	282,000	22,300	263,000
Sp G	-	1.000	-	-	-	-	-	-	1.179	1.151	1.341	1.000	1.354
Mass of liquid, kg	-	477,000	-	-	-	-	-	-	143,336	386,287	1,431,679	84,414	1,347,264
Al, kg	9,490	-	9,490	9,490	9,490	-	-	9,490	1,040	2,380	12,900	-	12,900
Concentration in M:													
Na+	7.21	-	14.53	14.53	14.53	3.50	-	13.87	3.92	3.30	8.75	-	9.39
NO2-	1.60	-	3.21	3.21	5.17	1.20	-	4.91	0.410	0.376	2.71	-	2.90
NO3-	2.61	-	5.24	5.24	3.29	1.10	-	3.26	0.410	0.351	1.84	-	1.98
OH-	1.43	-	2.86	-	-	1.20	-	0.480	2.35	1.93	1.12	-	1.20
Cl-	-	-	-	-	-	-	-	-	0.0017	0.0015	0.0014	-	0.0015
SO4-	0.300	-	0.602	0.602	0.602	-	-	0.517	0.0236	0.0213	0.277	-	0.297
F-	-	-	-	-	-	-	-	-	0.0054	0.0048	0.0044	-	0.0047
CO3-2	0.300	-	0.602	2.033	2.033	-	-	1.74	0.313	0.265	1.02	-	1.09
AlO2-	0.370	-	0.743	0.743	0.743	-	-	0.637	0.319	0.263	0.45	-	0.48
C2O4-2	-	-	-	-	-	-	-	-	0.0035	0.0036	0.0031	-	0.0034
PO4-3	< 0.01	-	0.020	0.020	0.020	-	-	0.017	0.0010	0.0009	0.0093	-	0.0100
K+	-	-	-	-	-	-	-	-	0.0081	0.0068	0.0031	-	0.0033
Solid Phase													
Sludge Solids Volume, gal	34,800	-	34,800	34,800	34,800	-	-	34,800	-	-	34,800	-	34,800
Saltcake Volume, gal	-	-	-	-	-	-	-	-	-	-	-	-	6,058
Sp G (bulk-hydrated)	2.40	-	2.40	2.40	2.40	-	-	2.40	-	-	2.40	-	2.40
Saltcake Density, kg/L	-	-	-	-	-	-	-	-	-	-	-	-	2.51
Mass of Insoluble Solids,													
. kg, dried solids	316,000	-	316,000	316,000	316,000	-	-	316,000	-	-	316,000	-	316,000
wt% Al in insoluble solids	35.1%	-	35.1%	35.1%	35.1%	-	-	35.1%	-	-	35.1%	-	35.1%
Al, kg (as elemental Al)	110,900	-	110,900	110,900	110,900	-	-	110,900	-	-	110,900	-	110,900
Other Components, kg	205,000	-	205,000	205,000	205,000	-	-	205,000	-	-	205,000	-	205,000

4.2.1.2   Tank 51 Composition

Tank 51 is expected to have an 8" heel after preparation of sludge slurry for SB5. The initial composition shown in Table 10 was derived from the estimated composition after completion of sludge washing based the composition data from the waste qualification sample[21, 22] taken before washing was complete. The value for the aluminum content in insoluble solids can be derived from sample data as follows:

Solids per liter of supernate = 1 L · 1.19 kg/L · 19.32 wt% dissolved solids = 0.230 kg solids/L

Aluminum in supernate: 7340 mg/kg supernate · 1.19 kg supernate/L / 1000 mg/g = 8.7346 g Al/L

Weight fraction Al in supernate solids: 8.7346 g Al/L · 1 kg/1000 g / 0.230 kg solids/L = 0.0380

Material balance per unit mass of slurry:

(6.18 wt% Al in total solids) · (23.61 wt% total solids in slurry) = (3.80 wt% Al in supernate solids) · (18.3 wt% soluble solids in slurry) + (x wt% Al in insoluble solids) · (5.31 wt% insoluble solids in slurry)

Solving for x = 14.4 wt% Al in insoluble solids.

4.2.1.3   Tank 8 Composition

Tank 8 is expected to contain a heel as low as 2" before the transfer of aluminum-laden supernate into the tank for interim storage. Sludge waste was already removed from Tank 8 and is functioning as interim storage for waste removal activities in F-Tank Farm. Specifically, Tank 8 receives bulk supernate transfers from Tank 7 where the waste is sampled to qualify the waste for feed to the evaporator and is then transferred from Tank 8 to the evaporator feed tank. This sequence of transfers and sampling is planned to repeat at least 3 more times before aluminum-laden supernate will be transferred to Tank 8. As such, the composition of the heel in Tank 8 will be very difficult to predict. Considering that the heel is relatively small compared to the aluminum-laden supernate planned to be transferred into Tank 8, the effect of the heel will be small. Therefore, the composition is approximated from a similar solution rather than estimating the composition from a detailed material balance after a complex series of transfers, chemical additions, and reactions for the source of the supernate in Tank 7.

Tank 7 will receive spent oxalic acid cleaning solution from Tank 5 and Tank 6 and waste removal solutions from Tank 18 and Tank 19. Tank 8 received a transfer from Tank 7 on July 3, 2008, that consisted of neutralized and spent oxalic acid heel cleaning solutions. The composition of the liquid after the Tank 7 to Tank 8 transfer is used to estimate the composition of the heel. The supernate sample results from samples taken from Tank 8 shortly after the Tank 7 transfer are shown in Table 7.

Table 7: Recent Tank 8 Sample Data[23]

Date	Average	07/09/08 Sample from surface (125.3")	07/09/08 Sample from 6" from bottom
Sp G	1.2353	1.2152	1.2554
Concentration in M:			
Na^+ (estimated from charge balance)	4.83		
NO_2^-	0.91	0.82	1.00
NO_3^-	0.93	0.82	1.03
OH^-	1.83	1.88	1.77
Cl^-	0.0073	0.0081	0.0064
SO_4^-	0.0631	0.0483	0.0779
F^-	-	-	-
CO_3^{-2}	0.378	0.317	0.439
AlO_2^-	0.235	0.230	0.240
$C_2O_4^{-2}$	0.0101	0.0115	0.0087
PO_4^{-3}	0.0069	0.0075	0.0062
Gross Gamma (Ci/gal)	2.34	2.34	-

4.2.1.4 Tank 24 Composition

Tank 24 supernate is planned for use in waste removal of Tank 12. Using an existing supernate rather than inhibited water reduces the amount of new water added to the tank farm which ultimately reduces the load on the evaporator. The supernate used in Tank 12 waste removal becomes the sludge interstitial liquid in Tank 51 for aluminum dissolution. The Tank 24 supernate contains free hydroxide and sodium salts that will supplement the caustic addition to Tank 51 for aluminum dissolution. The low aluminum content of the Tank 24 supernate is preferred over most existing supernates that contain significantly higher aluminum concentrations.

Samples of the existing Tank 24 supernate provide minimal data. Additional sample data can be obtained by tracing the history of the liquid to the origins of the liquid and extracting the closest sample data before transferring to Tank 24. Table 8 shows the history of transfers for the current supernate in Tank 24. The original source came from Tanks 38 and 43, but was first transferred into Tank 49 before transfer to Tank 24. No samples were taken from the liquid as it resided in Tank 49. A sample was taken from Tank 38 less than 10 days before the transfer from Tank 38 to Tank 49 as shown in Table 9. Part of the supernate came from Tank 43. However, the closest sample before the transfer from Tank 43 was about 2 months before in July and has minimal composition data. Comparison of the composition to the sample taken in May and October, shows the composition appears consistent with minimal changes, thus, the additional compositional data from these samples were averaged with the July sample to approximate the composition of the Tank 43 liquid. The composition of the liquid transferred into Tank 49 and eventually transferred to Tank 24 is then calculated by volume averaging the concentrations of the supernates from Tank 43 and Tank 38. Note that the supernate will be slightly diluted from the minimal heels in Tank 49 and again in Tank 24. The samples from Tank 24 show slight dilution for nitrate and nitrate and good agreement for specific gravity, but disproportionately low hydroxide concentration. Regardless, the estimated composition is formed by combining the Tank 24 sample data with the estimated transferred supernate. The minor constituents, potassium, oxalate, and phosphate, have no data available for estimating concentration and are ignored.

Table 8: Historical Summary of Tank 24 Supernate

June 23, 2004	Tank 49 is emptied of existing liquid by transfer to Tanks 42 and 35
September 1, 2004	41,700 gallons of Tank 43 supernate is transferred into Tank 49
October 28, 2004	293,000 gallons of Tank 38 superante is transferred into Tank 49
November 16, 2004	421,000 gallons of Tank 38 superante is transferred into Tank 49
March 1, 2005	Tank 24 emptied of existing supernate by transfer to Tanks 21 and 22
March 1, 2005 – April 19, 2005	784,000 gallons of Tank 49 supernate is transferred into Tank 24, effectively leaving Tank 49 empty.

Table 9: Tank 24 Supernate Composition Estimate

	Tank 24 Estimate	Tank 24 Samples				Estimate of Supernate Transferred to Tank 24	Tank 38	Tank 43			
Sample Date		12/4/08	12/12/07	12/12/06	12/19/05		10/19/04	Sample Average	10/19/04	07/27/04	05/09/04
Volume (gal)	-	-	-	-	-	756,000	714,300	41,800	-	-	-
Sp G	1.361	1.346	1.373	1.341	1.383		1.377	1.299	1.305	1.287	1.304
Concentration in M:											
NO_2^-	1.72	1.89	1.83	1.48	1.69	2.12	2.15	1.60	1.38	1.83	1.59
NO_3^-	2.05	2.10	2.12	1.98	2.01	2.45	2.49	1.70	1.58	1.81	1.71
OH^-	4.85	4.80	4.74	4.18	5.70	6.98	7.09	5.15	5.18	5.12	5.14
Cl^-	0.0060	-	-	-	< 0.0021	0.0060		< 0.0060		-	< 0.0060
SO_4^-	0.017	0.017	-	-	0.0165	0.017	0.018	0.012	0.011	-	0.012
F^-	0.011	-	-	-	-	0.011		< 0.011		-	< 0.011
CO_3^{-2}	0.266	-	-	-	-	0.266	0.251	0.509	0.877	-	0.140
AlO_2^-	0.12	0.12	-	-	-	0.057	0.060	0.010	-	-	0.010
$C_2O_4^{-2}$	-	-	-	-	-	-	-	-	-	-	-
PO_4^{-3}	0.00061	0.00061	-	-	-	-	-	-	-	-	-
K^+	-	-	-	-	-	-	-	-	-	-	-
Si	0.0036	0.0036	-	-	-	0.0055	0.0054	0.0077	0.0046	-	0.0107

4.2.1.5 Tank 4 Composition

The total mass and aluminum content of the sludge solids in Tank 4 is based on the WCS using dial-up factors.[2] Half of this amount is slated for inclusion in SB6.

The supernate composition of Tank 4 is estimated from the latest historical samples from Tank 4 and Tank 8, and material balances for transfers between those tanks, dilution, evaporation, and burkeite dissolution in Tank 4. The following sequence outlines the calculation resulting in the calculated initial supernate composition:

1. A Tank 4 supernate sample from 11/20/01 provided an initial $[PO_4^{-3}]$ of less than 0.0053 M, an initial $[C_2O_4^{-2}]$ of less than 0.0058, and an initial $[F^-]$ of less than 0.0053.

2. Supernate analysis results from a Tank 4 VDS sample pulled on 5/12/05 provided an initial $[K^+]$ of 0.065 M, $[AlO_2^-]$ of 0.180 M, and a $[CO_3^{-2}]$ of 0.510 M.[24]

3. An initial decant of supernate was made from Tank 4 to Tank 8, followed by a series of four inhibited water additions, each of which was followed by a decant to Tank 33.[25] Material balances were used to account for the dilution in Tank 4 and for the assumed uniform dissolution of the 6 inch burkeite layer. This provided updated estimates for concentrations of the species mentioned above.

4. Between April and September of 2007, a series of Tank 8 supernate transfers were made into Tank 4. That supernate receipt was a combination of the above supernate from Tank 4, and the previous contents of Tank 8. The supernate in Tank 8 prior to the receipt of supernate from Tank 4 was characterized for the above species using Tank 8 samples:

Sample	Analysis	Concentration (M)
1/17/07	$[AlO_2^-]$	0.217
1/17/07	$[C_2O_4^{-2}]$	0.016
10/18/06	$[CO_3^{-2}]$	0.521
10/18/06	$[PO_4^{-3}]$	0.0078

    The results of the 10/18/06 sample were adjusted for apparent evaporation in Tank 8 over an extended period of time, to a $[CO_3^{-2}]$ of 0.548 M and a $[PO_4^{-3}]$ of 0.0082 M, respectively. Minor Tank 8 supernate species $[F^-]$ and $[K^+]$ were estimated at 0.012 M and 0.033M, respectively, from earlier samples and a more convoluted historical transfer accounting.

5. The current Tank 4 supernate composition estimate was obtained by material balance for the combination of the estimated Tank 4 and Tank 8 supernate compositions, and from two Tank 4 supernate samples as follows:

Sample	Analysis	Result
7/14/08	Sp.G.	1.321
7/14/08	$[NO_2^-]$	1.66 M
7/14/08	$[NO_3^-]$	1.86 M
7/14/08	$[OH^-]$	1.44 M
1/14/08	$[SO_4^{-2}]$	0.225 M
1/14/08	$[Cl^-]$	0.016 M

6. The Tank 4 slurry composition to be transferred to Tank 51 is estimated by assuming a single transfer, and accounting for enough additional water such that the transfer slurry (50% of the Tank 4 insoluble solids) matches an estimated specific gravity of 1.25, in accordance with the operating conditions of the Tank 4 submersible mixer pumps.

Table 10 summarizes the estimated initial conditions of Tanks 4, 8, 12, 24, and 51 at the start of aluminum dissolution.

Table 10: Initial Composition Estimates for Aluminum Dissolution of Sludge Batch 6

	Tank 4 Slurry	Tank 24 Supernate	Tank 8	Tank 12	Tank 51
Initial Tank Level (in)	-	-	4.0	109.8	8.0
Liquid Volume (gal)	-	-	10,800	263,000	28,100
Sludge Solids Volume (gal)	-	-	-	34,800	1,510
Insoluble Solids (kg)	50,500	-	-	316,000	13,700
wt% Insoluble Solids	2.70	0	0	17.9	11.58
Specific Gravity	1.234	1.361	1.235	1.354	1.044
Concentration in M:					
Na^+	4.85	9.33	4.83	9.39	1.00
NO_2^-	1.21	1.72	0.91	2.90	0.233
NO_3^-	1.35	2.05	0.93	1.98	0.096
OH^-	1.05	4.85	1.83	1.20	0.460
Cl^-	0.012	0.0060	0.0073	0.0015	0.0040
SO_4^-	0.16	0.017	0.0631	0.297	0.0053
F^-	0.0035	0.011	-	0.0047	0.0016
CO_3^{-2}	0.39	0.266	0.378	1.10	0.066
AlO_2^-	0.11	0.12	0.235	0.483	0.061
$C_2O_4^{-2}$	0.0039	-	0.0101	0.0034	0.0010
PO_4^{-3}	0.0032	0.00061	0.0069	0.0100	0.00034
K^+	0.036	-	-	0.0033	0.0020

4.2.2 Plutonium Waste Stream Receipts

Two campaigns of plutonium waste stream receipts into Tank 51 during SB6 preparation are planned. The first campaign volume and composition are based on existing characterization data.[26] The quantity and composition of the second, larger campaign has not been determined. In order to account for the effect on SB6 preparation, the total quantity of waste transferred into Tank 51 is assumed to correspond to 55 kg of plutonium. The composition is assumed to be the same as described for the SB5 Plutonium Discards received during SB5 preparation.[27]

4.2.3 Chemical Process Requirements

LWO Planning, Integration, and Technology conducted a process study to determine process parameters that would result in removing 75% of the aluminum from the sludge slurry of the six target tanks.[28] The method developed from this process study is applied to this flowsheet in order to determine dissolution conditions.

Without any additional constraints, the dissolution conditions chosen allow for the dissolution of up to 80% of the aluminum and for these solids to remain completely soluble at or below 20°C. This condition minimizes the risk of precipitation of aluminum when Tank 51 sludge slurry is transferred into Tank 8. The Tank 51 temperature is expected to be between 20 and 25°C during washing.

Figure 4 shows aluminum solubility at various temperatures. Isotherms are plotted for every 5°C generated from OLI Stream Analyzer[tm] based the supernate chemistry after aluminum dissolution and dilution caused by bearing water leakage or flushing. The dotted red line shows the aluminum solubility

estimated at 25°C for SB5 aluminum dissolution for comparison. Starting salt content of the SB5 supernate was substantially lower than planned for SB6. The operating conditions of the process are represented by connected red dots that meet the dissolution conditions outlined above. Using the initial conditions from section 4.2.1, the sludge slurry transferred from Tank 12 contains about 6.7 gal of liquid/kg of aluminum. At the start of dissolution, the hydroxide concentration in Tank 51 needs to be about 5.3 M or greater as indicated by the point labeled "0% Dissolved". This hydroxide concentration produces approximately 9:2 molar ratio of hydroxide to aluminum. About 102,000 gallons of 50 wt% caustic (19.1 M hydroxide) needs to be added to Tank 51 as shown in Section 4.7. Note that the caustic addition estimate is based on projections of the dissolution condition. The caustic addition estimate should be considered as the minimum caustic needed and is dependent on the actual composition of the waste slurry transferred from Tank 12, especially if more water is added to Tank 12 than expected during waste removal. Added water effectively reduces the starting free hydroxide concentration and ionic strength of the solution, potentially resulting in higher caustic demand to meet the same process conditions.

A sufficient margin below saturation of aluminum in Tank 8 supernate will be required throughout the time the solution is stored. At 80% dissolution of aluminum, the free hydroxide ion concentration will be adequate to maintain aluminum in solution as indicated by the point labeled "Tk 8 After Trans." in Figure 4. Some additional caustic may be needed during storage depending on total time stored in Tank 8. Section 4.8.2.1 discusses the potential caustic additions needed for Tank 8.
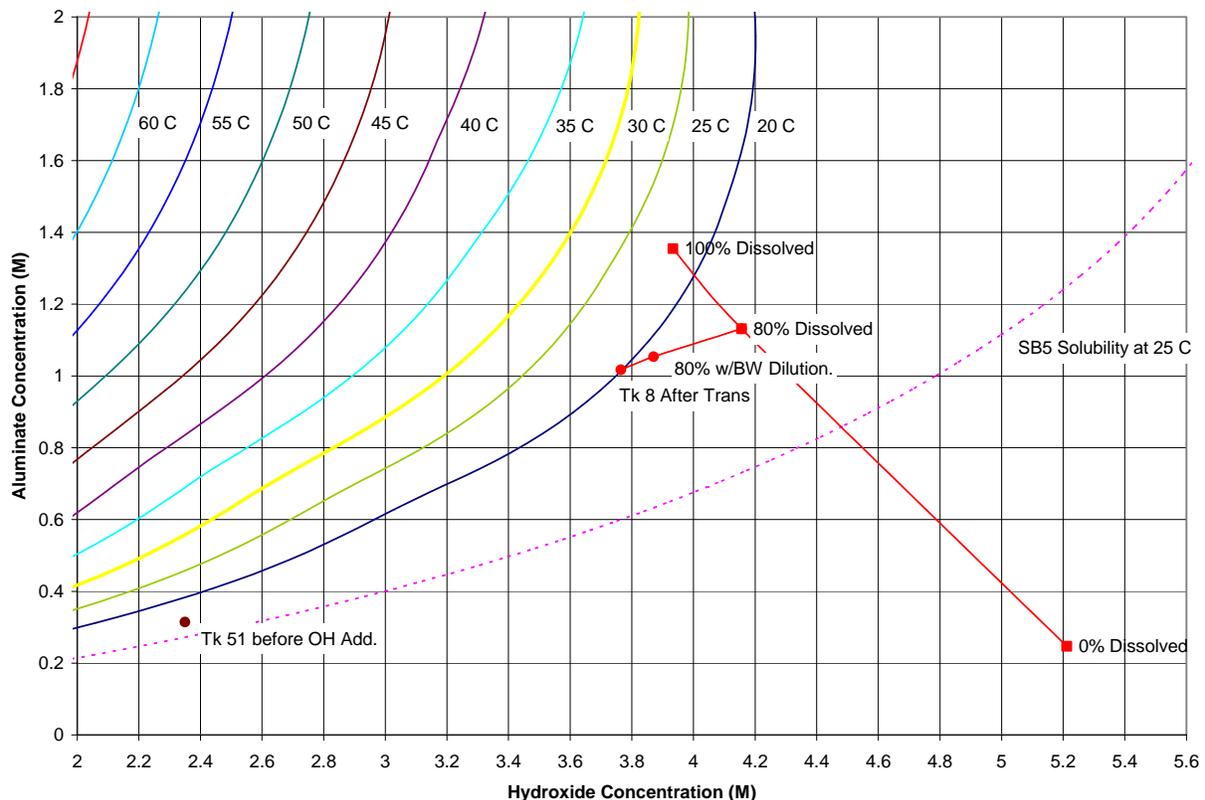
Figure 4: Dissolution Conditions for Sludge Batch 6
(based on gibbsite solubility)

The high aluminum content of the leaching solution will precipitate aluminum when diluted. In order to prevent precipitation during washing, the first two wash water additions will need to be supplemented with adequate caustic to prevent precipitation. Figure 5 shows the approximate concentrations of the wash solutions superimposed on the same aluminum solubility curves shown in Figure 4, but for a lower range of hydroxide concentrations. Each wash composition is represented by a red square along a curve representing the washing conditions for the entire sludge batch preparation plan. With each wash water dilution, the solubility curves will tend to shift to the right, i.e., aluminum becomes progressively less soluble, but this set of isotherms provides a reasonable estimate of solubility, particularly in the first wash which affects most of the dissolved aluminum remaining in Tank 51. The first wash water addition includes adequate hydroxide for 1.2 M hydroxide concentration. The second water addition is in the form of dilution water in Tank 4 to create a slurry that can be pumped between F-Tank Farm and H-Tank Farm. Adequate caustic should be added to Tank 51 to compensate for the dilution effect before the transfer from Tank 4 to equate to 1.0 M hydroxide concentration in the water addition. These concentrations are adequate to minimize the risk of precipitation relative to the initial dissolution conditions, but ionic strength of the solution is diluted as well as the free hydroxide concentration, further reducing aluminum solubility. The aluminum solubility at the specific composition of each wash water batch will need to be calculated to provide the most accurate results.
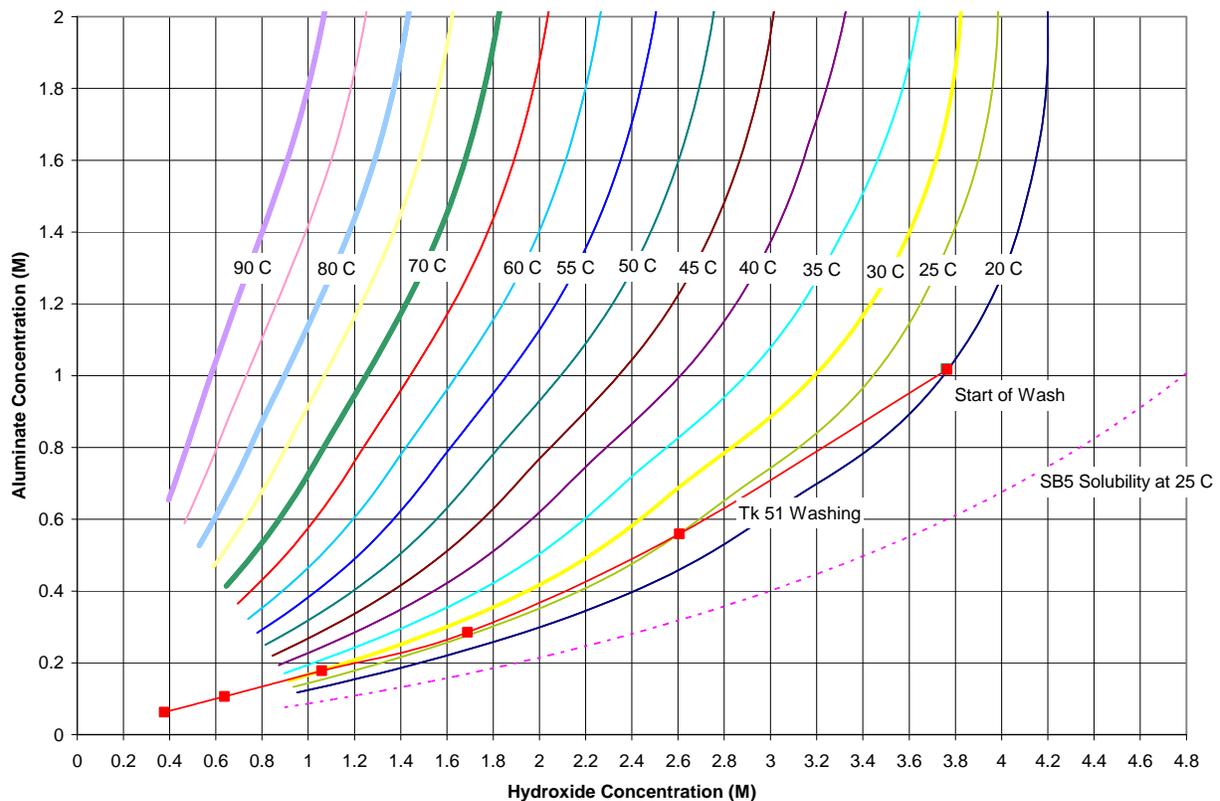
**Figure 5: Sludge Washing Conditions for Sludge Batch 6
(based on gibbsite solubility)**

The first wash solution will still contain substantial aluminum and is desirable to transfer to Tank 8. Current plans include transfer of the first wash solution to Tank 8. The mixture in Tank 8 as shown in the material balance in Section 4.7 is at or above saturation at less than 28°C. To prevent precipitation down to 20°C, hydroxide concentration will need to be maintained above 4.0 M. About 18,000 gallons of

50wt% caustic would be needed for this. The need for caustic addition will need to be evaluated to prevent precipitation of aluminum after actual results of dissolution are known. The first wash decant would be transferred to the 3H evaporator system if not sent to Tank 8.

4.3   Temperature Change in Tank 51 Due to Caustic Addition

Dilution of caustic in Tank 51 is strongly exothermic which tends to increase liquid temperature and the dissolution reaction is endothermic which tends to decrease liquid temperature. Since the dissolution reaction is slow relative to the rate of transfer of hydroxide solution into Tank 51, the reaction will tend to slowly absorb the heat generated from the initial heat generated from dilution. The caustic solution transfer from HPT-7 and HPT-8 will occur in small batches, 3000 gal each, over approximately 3 weeks. The duration of each transfer will be short. The dissolution reaction will continue for many days after the last transfer is complete. The maximum temperature increase expected is estimated using OLI Stream Analyzer^{tm}. The planned caustic addition combined with the composition of the liquid shown in Section 4.7 results in a 10°C increase. The temperature of the tank contents will be closely monitored during the transfer and subsequent dissolution process.

4.4   Process Cycle Time

Table 11 outlines the process steps and estimated time required to complete each step. The basis for the settling time is discussed in Section 4.6.

Table 11: Process Cycle Time (with no down time)

Step	Time (days)
Add caustic to Tank 51 via HPT-7 and HPT-8 (108,000 gallons = 36 3000-gallon trucks @ 3 per day).	12
Use slurry pumps to increase tank temperature and maintain.	N/A
Mix tank for number of days available (duration currently scheduled).	28
Turn off slurry pumps to allow settling.	N/A
Settle for 30 days.	30
Decant aluminum-laden supernate to decant storage tank, Tank 8. (350,000 gal @ 50 gpm)	5
Total Cycle Time in Tank 51	**75 days**

Note that caustic additions are planned for normal facility 4 day work week and no more than 12 per week. Accounting for weekends, the caustic addition may take about 18 calendar days to complete. Adding 2 week ends results in a total cycle time of about 81 days. The remaining operations can occur without breaks.

Note that the time for mixing the tank is not optimal, but reflects scheduled days available. Section 4.5 discusses optimal time for completing aluminum dissolution.

4.5   Extent of Aluminum Dissolved

4.5.1   Caustic Dissolution Kinetics

Gibbsite and boehmite are common forms of aluminum in HLW sludge. Boehmite is the thermodynamically favored form of aluminum such that gibbsite will tend to convert to boehmite over time. Given that the last waste receipt to Tank 12 was from June 1973, much of the aluminum is likely to be boehmite as was the case in Tank 11.[29] Consistent with the strategy developed for aluminum dissolution[28] all the aluminum is assumed to be the form of boehmite.

The model was solved numerically to determine fraction dissolved with time. At 70°C, 85 days are required to achieve 80% dissolution. At 75°C, 46 days are required. The result for 28 days shows 42% of the aluminum dissolves at 70°C and 63% at 75°C. If the dissolution rate turns out to be as fast as the sludge slurry from Tank 11, 80% dissolution can be achieved in 24 days at 70°C. The amount dissolved is sensitive to the temperature. Maintaining the waste as warm as practical during the dissolution cycle will dissolve the most aluminum. For this material balance, the maximum of 80% dissolved is carried throughout in order to identify adequate process conditions to achieve the most dissolution possible. 55% dissolution of the aluminum is a reasonable nominal expectation if the time is not available to reach 80% dissolution, with a total potential range from 40 – 80%.

4.6   Process Constraints and Assumptions

Other than physical limitations, the process is constrained by maximum temperature allowed in Tank 51 and the amount of time allowed for sludge settling prior to each decant. Assumptions for each of these constraints are identified in separate sections below along with assumptions related to the material balance. Any assumptions applied to initial composition and conditions are detailed in Section 4.2.1.

4.6.1   Tank Temperature

The constraints and assumptions that tank temperature limits are as follows:

- After caustic addition, the corrosion control program will limit tank temperature to less than 100°C for the liquid and sludge slurry. The tank wall will be limited to 95°C.[30]

- A requisite quantity of sodium nitrite is added during washing before the hydroxide supernate concentration drops below 1.0 M.[30]

- Vapor load at process temperatures remains within the capacity of the ventilation system.

4.6.2   Settling Time Allowance

The following must be completed within the available quiescent time in Tank 51 specified per the Flammability Control Program criteria:[31]

- Settling prior to decant of supernate from Tank 51,
- turbidity height measurement,
- decant jet repositioning,
- decant transfer, and

- initiation of slurry pump to reset the quiescent time clock.

The constraints and assumptions that drive settling time and quiescent time management are as follows:

- Available settling time is calculated from the quiescent time less 7 days. The 7 days is an allowance for turbidity check, jet positioning, decant, and initiation of slurry pump run.

- 50% flammable gas retention is assumed for conditions where the sludge is projected to settle to less than 90" height in 20 days. This is in accordance with the Flammability Control Program.[31]

- 100% flammable gas retention is assumed for before aluminum dissolution and when settling from a very high initial slurry height, such that a sludge height of less than 90" in 20 days is not expected.

- Initial sludge and supernate radiolytic heats, are based on the WCS.[14]

4.6.3   Settling

The rate of change to the level of sludge solids drives the maximum size of a decant within the constraint of the available quiescent time. The constraints and assumptions that drive settling are as follows:

- Tank 51 solids settling rates are projected from historical observation of SB4 and SB5 settling in Tank 51.

- Pre-dissolution sludge is projected to settle like Sludge Batch 4 sludge and pre-dissolution SB5 sludge,[32] adjusting for the projected solids mass.

- Post-dissolution sludge settling behavior is projected from SB5 post-dissolution settling results as follows:

    The SB5 post-dissolution sludge was modeled by empirically adjusting the sludge mass input of the pre-dissolution model to match observed behavior of the SB5 post dissolution sludge.

    The actual mass reduction by dissolution of SB5 per analyses was compared to the "apparent" mass reduction that satisfied the settling model. The ratio of these two masses was applied to the planned SB6 dissolved mass, in order to obtain an adjusted mass input value for the SB6 post dissolution settling model.

- Tank 4 sludge settling is modeled using the historical settling model for PUREX sludge slurry.[33] An "infinite settled height" input to the model was estimated by assuming that the sludge mass in Tank 4 will settle to a compaction of 280 g solids per liter of settled slurry in 20 days.

- The settling of the combined post-dissolution sludge and Tank 4 sludge was modeled by assuming that the two sludge slurries behave independently, and using a technique described in reference 32.

4.6.4   Material Balance Assumptions and Constraints

The constraints and assumptions that apply to the material balance and are not identified elsewhere are as follows:

- Sludge additions to Tank 51 include approximately 56% of the sludge in Tank 12, and 50% of the sludge in Tank 4.

- Sludge solids are assumed to have a density of 2.4 g/ml. This assumption is used to estimate supernate volumes within a sludge slurry.

- Tank 12 maximum fill limit is 120 inches.

- Liquid transfers into Tank 12 are limited to allow for 5" operating margin below the maximum fill limit.

- Tank 51 waste level is limited to 12" below the high level liquid conductivity probe set point. The set point will be altered as necessary to maintain adequate quiescent time.

- A 12 inch separation between the decanting jet and the measured turbidity level is maintained during initial decant to Tank 8 and the final wash decant, based on Reference [34]

- A 24 inch separation between the decanting jet and the measured turbidity level is maintained during other decants to the evaporator systems.

- The first wash decant volume to Tank 8 is 150,000 gallons.

- The second wash decant volume to the 3H Evaporator system is 120,000 gallons.

- Wash decants after the first two are sent to the 2F Evaporator system.

- The first decant to the 2F Evaporator system is 300,000 gallons.

- Decants to the 2F Evaporator after the first decant are limited by the time estimated to process the previous decant. The decant limit is estimated as follows:
    - The initial decant fills the feed tank
    - Subsequent decant fills the volume recovered by evaporation since the last decant.
    - The time for processing is estimated as four days longer than the settling time of immediately before the planned decant, i.e., the time between decants is estimated as the settling time plus 4 days.
    - The 2F evaporator is assumed to process 7,020 gallons (2 inches) per day.

- Slurry transfers from Tank 12 are 8.0 wt% insoluble solids.

- The Tank 4 sludge removal for SB6 is accomplished in a single transfer after dilution with water to dilute the slurry specific gravity to 1.25.

- The washing end point is assumed to be 1.0 M sodium in the supernate. The end point will change as detailed characterization data becomes available and DWPF flowsheet testing is completed.

4.7   Material Balance

A material balance for the aluminum dissolution process using the process parameters outlined above is shown in Table 12. The material balance includes the composition of the SB6 slurry, the number of decants, and the size of decants needed to complete the batch washing in Tank 51. The washing projection was performed by using a series of sequential material balances in Excel spreadsheet form to describe the steps for stepwise dilution, settling, and decanting of the supernate from the resultant slurry until the target feed composition for DWPF is reached. The same process is used in preparing the sludge batch plan. The following key points result from the material balance:

1. Incorporating aluminum dissolution into SB6 preparation at the maximum extent of dissolution results in 130,000 kg of washed insoluble sludge solids in Tank 51, at an insoluble solids concentration of approximately 11 wt%. In comparison, the SB6 base case (without aluminum dissolution) results in 244,000 kg of insolubles.

2. Washing of SB6 with aluminum dissolution requires an initial decant from Tank 51 to remove aluminum-laden supernate. In this study, a single initial decant volume was maximized at 354,000 gallons. However, this decant should be as large as possible. Maximizing the decant:

   - reduces the potential for aluminum reprecipitation in SB6,
   - reduces the subsequent degree of washing needed, and
   - marginally improves washing efficiency.

   Washing efficiency marginally improves because the proportion of nitrites and nitrates increases relative to hydroxide in the supernate, suppressing hydrogen generation and incrementally increasing available settling times. In addition, less hydroxide is needed in the wash water to minimize reprecipitation.

3. The level in Tank 8 after the post-dissolution decant is about 135".

4. Continued storage of the aluminum-laden supernate will require monitoring of the anion concentrations to assure hydroxide concentration is maintained such that the aluminum remains in solution.

Salient streams from Table 12 are depicted in Figure 6, which summarizes the material balance. This material balance includes the downstream impacts of sludge washing, but does not include any impact on DWPF or the evaporator. Existing evaporator processes[35,36] can be used to model the respective portions of the flowsheet. Figure 6 summarizes the overall material balance for aluminum.

Water additions from miscellaneous flushes are not accounted in this material balance; however, the additions are not expected to have a significant effect. An allowance for slurry pump bearing water leakage is included at a nominal rate of 1200 gallons per day for a total of 40 days which allows for an additional 12 day buffer beyond what is scheduled. The buffer was added to provide a small amount of conservatism in the composition estimate relative to aluminum solubility after aluminum dissolution. The leak rate is based on the rate observed during the last 12 days of running pumps during dissolution on SB5, which was 1140 gallons per day.

Table 12: Material Balance
(assuming 80% of the aluminum dissolves)

Tank 12 Sludge Slurry Transfer to Tank 51

Stream No	1	2	3	4	5	6	7	8	9	10	11	12	13
Description	Initial Tank 51 Inventory	Pu Transfers to Tank 51	Tank 51 Inventory After Pu Transfer	Initial Tank 12 Inventory	Tank 12 to 51 Transfer A	Tank 12 Inventory After Transfer A	Tank 51 Inventory After Tk 12 Transfer A	Water Addition to Tank 12	Tank 24 to Tank 12 Transfer	Tank 12 Inventory After Tank 24 Transfer	Tank 12 to 51 Transfer B	Tank 12 Inventory After Transfer B	Tank 51 Inventory After Tk 12 Transfer B
Tank Level, in	8.0		9.1	109.8		49.7	54.5			115.0		30.9	119.7
Total Volume, gal	28,100	3,500	31,900	298,000	163,000	135,000	191,000	20,000	157,000	312,000	228,000	83,700	420,000
wt% Insoluble Solids	11.58%	1.51%	10.34%	18.99%	8.00%	30.92%	8.32%	0.00%	0.00%	14.67%	8.00%	30.93%	8.14%
Total Mass, kg	119,000	16,700	135,000	1,663,000	866,000	798,000	1,001,000	76,000	807,000	1,680,000	1,192,000	489,000	2,192,000
Liquid Phase													
Volume, gal	26,600	3,470	30,300	263,000	155,000	108,000	182,000	20,000	157,000	285,000	218,000	67,000	400,000
Sp G	1.044	1.250	1.058	1.354	1.354	1.354	1.332	1.000	1.361	1.331	1.331	1.331	1.328
Mass of liquid, kg	105,000	16,400	121,000	1,347,000	796,000	551,000	918,000	76,000	807,000	1,434,000	1,096,000	338,000	2,014,000
Al, kg	166	0.0	166	12,900	7,640	5,290	7,810	0	1,922	7,210	5,510	1,700	13,316
Concentration in M:													
Na+	1.00	4.58	1.40	9.39	9.39	9.39	8.25	0.00	9.33	8.69	8.69	8.69	8.47
NO2-	0.23	0.003	0.20	2.90	2.90	2.90	2.51	0.00	1.72	2.05	2.05	2.05	2.25
NO3-	0.096	3.35	0.47	1.98	1.98	1.98	1.77	0.00	2.05	1.88	1.88	1.88	1.82
OH-	0.46	1.20	0.54	1.20	1.20	1.20	1.12	0.00	4.85	3.13	3.13	3.13	2.21
Cl-	0.0040	0.004	0.0039	0.0015	0.0015	0.0015	0.0019	0.00000	0.00600	0.00387	0.00387	0.00387	0.0030
SO4-	0.0053	0.00182	0.0049	0.30	0.30	0.30	0.25	0.000	0.017	0.12	0.12	0.12	0.18
F-	0.0016	0.013	0.0029	0.0047	0.0047	0.0047	0.0045	0.0000	0.0111	0.0079	0.0079	0.0079	0.0063
CO3-2	0.066	0.00283	0.058	1.09	1.09	1.09	0.94	0.000	0.266	0.56	0.56	0.56	0.73
AlO2-	0.061	0.000	0.054	0.48	0.48	0.48	0.42	0.000	0.120	0.25	0.25	0.25	0.33
C2O4-2	0.0010	0.0000	0.0009	0.0034	0.0034	0.0034	0.00302	0.0000	0.0000	0.0013	0.0013	0.0013	0.0021
PO4-3	0.00034	0.0000	0.00030	0.0100	0.0100	0.0100	0.0086	0.00000	0.00061	0.0041	0.0041	0.0041	0.0061
K+	0.0020	0.0000	0.0018	0.0033	0.0033	0.0033	0.0031	0.0000	0.0000	0.0012	0.0012	0.0012	0.0021
Solid Phase													
Volume, gal	1,510	28	1,540	34,800	7,620	27,100	9,160	0	0	27,100	10,492	16,600	19,700
Sp G (bulk-hydrated)	2.40	2.40	2.40	2.40	2.40	2.40	2.40	2.40	2.40	2.40	2.40	2.40	2.40
Mass of Insoluble Solids, kg, dried solids	13,700	251	14,000	316,000	69,200	247,000	83,200	0	0	247,000	95,300	151,000	179,000
wt% Al in insoluble solids	14.4%	0.0%	14.1%	35.1%	35.1%	35.1%	31.6%	0.0%	0.0%	35.1%	35.1%	35.1%	33.5%
wt% as Al(OH)3 in insoluble solids	41.6%	0.0%	40.9%	101%	101%	101%	91%	0.0%	0.0%	101%	101%	101%	97%
wt% as AlO(OH) in insoluble solids	32.0%	0.0%	31.4%	78.1%	78.1%	78.1%	70.2%	0.0%	0.0%	78.1%	78.1%	78.1%	74.4%
Al, kg (as elemental Al)	1,980	0	1,980	111,000	24,300	87,000	26,300	0	0	87,000	33,500	53,100	59,800
Other than Al Components, kg	11,800	251	12,000	205,000	44,900	160,000	56,900	0	0	160,000	61,800	98,000	119,000
Max Settling Time (days)	-		-		-		-		-		-		-

Note: Yellow blocks indicate initial conditions/inputs to the material balance calculation. Blue headers highlight columns specific to Tank 51.

Table 12: Material Balance (continued)
(assuming 80% of the aluminum dissolves)

Aluminum Dissolution

Stream No	14	15	16	17	18	19	20	21	22	23	24	25	26	27
Description	Tank 24 to 12 Transfer	Tank 12 Inventory After Tk 24 Transfer	Tank 12 to 51 Transfer C	Tank 12 Inventory After Transfer C	Tank 51 Inventory After Tk 12 Transfer C	Caustic Addition to Tank 51	Tank 51 Inventory After Caustic Addition	Tank 51 Inventory After Aluminum Dissolution	Pump Bearing Water Leakage into Tank 51	Tank 51 Inventory After Bearing Water Leakage	Decant Tank 51 to Tank 8	Tank 51 Inventory After Decant to Tk 8	Initial Tank 8 Inventory	Tank 8 Inventory After Decant from Tank 51
Tank Level, in		60.0		47.4	129.7		163.3	164.7		176.8		73.1	4.0	140.0
Total Volume, gal	78,900	163,000	35,000	128,500	455,000	108,000	573,000	578,000	48,000	620,000	364,000	257,000	10,800	379,000
wt% Insoluble Solids	0.00%	16.89%	8.00%	19.18%	8.13%	0.00%	6.43%	2.59%	0.00%	2.44%	0.00%	5.75%	0.00%	0.00%
Total Mass, kg	407,000	896,000	184,000	712,000	2,376,000	629,000	3,005,000	3,005,000	182,000	3,187,000	1,870,000	1,352,000	50,700	1,921,000
Liquid Phase														
Volume, gal	78,900	146,000	33,400	113,500	434,000	108,000	552,000	570,000	48,000	612,000	364,000	248,000	10,800	379,000
Sp G	1.361	1.339	1.339	1.339	1.329	1.539	1.346	1.358	1.000	1.342	1.358	1.358	1.235	1.337
Mass of liquid, kg	407,000	744,000	169,000	575,000	2,183,000	629,000	2,812,000	2,928,000	182,000	3,109,000	1,870,000	1,275,000	50,700	1,921,000
Al, kg	968	2,670	610	2,073	13,900	0	13,900	65,900	0	65,900	39,200	26,700	260	39,400
Concentration in M:														
Na+	9.33	9.04	9.04	9.04	8.51	19.5	10.14	9.82	0.021	9.15	9.15	9.15	4.83	8.91
NO2-	1.72	1.87	1.87	1.87	2.22	0.00	1.75	1.69	0.011	1.58	1.58	1.58	0.91	1.54
NO3-	2.05	1.97	1.97	1.97	1.83	0.00	1.44	1.40	0.00	1.30	1.30	1.30	0.93	1.27
OH-	4.85	4.06	4.06	4.06	2.35	19.1	5.21	4.16	0.010	3.87	3.87	3.87	1.83	3.76
Cl-	0.00600	0.00502	0.00502	0.00502	0.0031	0.43	0.087	0.085	0.00	0.079	0.079	0.079	0.007	0.076
SO4-	0.017	0.065	0.065	0.065	0.17	0.00	0.14	0.13	0.00	0.12	0.12	0.12	0.063	0.12
F-	0.0111	0.0096	0.0096	0.0096	0.0066	0.00	0.0052	0.0050	0.00	0.0047	0.0047	0.0047	-	0.0045
CO3-2	0.266	0.40	0.40	0.40	0.71	0.00	0.56	0.54	0.00	0.50	0.50	0.50	0.378	0.49
AlO2-	0.120	0.179	0.179	0.179	0.31	0.00	0.25	1.13	0.00	1.05	1.05	1.05	0.235	1.02
C2O4-2	0.0000	0.0006	0.0006	0.0006	0.0019	0.00	0.0015	0.0015	0.00	0.0014	0.0014	0.0014	0.0101	0.0016
PO4-3	0.00061	0.0022	0.0022	0.0022	0.0058	0.00	0.0046	0.0044	0.00	0.0041	0.0041	0.0041	0.0069	0.0042
K+	0.0000	0.0006	0.0006	0.0006	0.0020	0.00	0.0015	0.0015	0.00	0.0014	0.0014	0.0014	-	0.0013
Solid Phase														
Volume, gal	0	16,600	1,620	15,000	21,300	0	21,300	8,560	0	8,560	0	8,560	0	0
Sp G (bulk-hydrated)	2.40	2.40	2.40	2.40	2.40	2.40	2.40	2.40	2.40	2.40	2.40	2.40	2.40	2.40
Mass of Insoluble Solids, kg, dried solids	0	151,000	14,700	137,000	193,000	0	193,000	77,800	0	77,800	0	77,800	0	0
wt% Al in insoluble solids	0.0%	35.1%	35.1%	35.1%	33.6%	0.0%	33.6%	16.7%	0.0%	16.7%	0.0%	16.7%	0.0%	0.0%
wt% as Al(OH)3 in insoluble solids	0.0%	101%	101%	101%	97%	0.0%	97%	48.2%	0.0%	48.2%	0.0%	48.2%	0.0%	0.0%
wt% as AlO(OH) in insoluble solids	0.0%	78.1%	78.1%	78.1%	74.7%	0.0%	74.7%	37.1%	0.0%	37.1%	0.0%	37.1%	0.0%	0.0%
Al, kg (as elemental Al)	0	53,100	5,170	48,000	64,900	0	64,900	13,000	0	13,000	0	13,000	0	0
Other than Al Components, kg	0	98,000	9,500	89,000	128,000	0	128,000	64,800	0	64,800	0	64,800	0	0
Max Settling Time (days)	-				-		-	-	-	-	-	-	-	-

Table 12: Material Balance (continued)
(assuming 80% of the aluminum dissolves)

	Pu Addition		Wash 1					Tank 4 Sludge Slurry Transfer to Tank 51						
Stream No	28	29	30	31	32	33	34	35	36	37	38	39	40	41
Description	Second Pu Transfers from 221-H to Tank 51	Tank 51 Inventory After Pu Addition	Inhibited Water Addition	Tank 51 Inventory After IW Addition	Decant A Tank 51 to Tank 8	Tank 8 Inventory After Decant from Tank 51	Tank 51 Inventory After Decant to Tank 8	Tank 4 Sludge Slurry Transfer to Tank 51	Dilution and Flush Water in Trans. from Tank 4	Tank 51 Inventory After Tank 4 Transfer	Decant B Tank 51 to 3H Evap System	Tank 51 Inventory After Decant to 3H Evap System	Decant C Tank 51 to 2F Evap System	Tank 51 Inventory After Decant to 2F Evap System
Tank Level, in		80.9		135.9			93.2			223.2		189.0		103.5
Total Volume, gal	24,100	284,000	193,000	477,000	150,000	525,000	327,000	396,000	60,000	783,000	120,000	663,000	300,000	363,000
wt% Insoluble Solids	2.33%	5.48%	0.00%	3.61%	0.00%	0.00%	5.23%	2.70%	0.00%	3.59%	0.00%	4.23%	0.00%	7.59%
Total Mass, kg	119,000	1,471,000	758,000	2,229,000	688,000	2,609,000	1,541,000	1,875,000	234,000	3,650,000	549,000	3,101,000	1,374,000	1,728,000
Liquid Phase														
Volume, gal	23,800	275,000	193,000	468,000	150,000	525,000	318,000	391,000	60,000	769,000	120,000	649,000	300,000	349,000
Sp G	1.286	1.335	1.037	1.212	1.212	1.314	1.212	1.234	1.030	1.209	1.209	1.209	1.209	1.209
Mass of liquid, kg	116,000	1,390,000	758,000	2,149,000	688,000	2,609,000	1,460,000	1,825,000	234,000	3,519,000	549,000	2,970,000	1,374,000	1,597,000
Al, kg	67	26,800	0	26,800	8,600	48,000	18,200	4,220	0	22,400	3,500	18,900	8,750	10,170
Concentration in M:														
Na+	5.457	8.72	1.211	5.62	5.62	8.05	5.62	4.85	1.00	4.87	4.87	4.87	4.87	4.87
NO2-	0.013	1.42	0.011	0.84	0.84	1.35	0.84	1.21	0.00	0.96	0.96	0.96	0.96	0.96
NO3-	4.100	1.53	0.00	0.90	0.90	1.18	0.90	1.35	0.00	1.06	1.06	1.06	1.06	1.06
OH-	1.200	3.59	1.200	2.61	2.61	3.47	2.61	1.05	1.00	1.69	1.69	1.69	1.69	1.69
Cl-	0.016	0.072	0.00	0.043	0.043	0.067	0.043	0.012	0.00	0.024	0.024	0.024	0.024	0.024
SO4-	0.00060	0.11	0.00	0.065	0.065	0.105	0.065	0.16	0.00	0.110	0.110	0.110	0.110	0.110
F-	0.0631	0.0097	0.00	0.0057	0.0057	0.0049	0.0057	0.0035	0.00	0.0041	0.0041	0.0041	0.0041	0.0041
CO3-2	0.000	0.45	0.00	0.27	0.27	0.43	0.27	0.39	0.00	0.31	0.31	0.31	0.31	0.31
AlO2-	0.027	0.95	0.00	0.56	0.56	0.90	0.56	0.11	0.00	0.29	0.29	0.29	0.29	0.29
C2O4-2	0.0067	0.0018	0.00	0.0011	0.0011	0.0015	0.0011	0.0039	0.00	0.0024	0.0024	0.0024	0.0024	0.0024
PO4-3	0.0076	0.0044	0.00	0.0026	0.0026	0.0037	0.0026	0.0032	0.00	0.0027	0.0027	0.0027	0.0027	0.0027
K+	0.031	0.0039	0.00	0.0023	0.0023	0.0016	0.0023	0.036	0.00	0.019	0.019	0.019	0.019	0.019
Solid Phase														
Volume, gal	304	8,870	0	8,870	0	0	8,870	5,560	0	14,400	0	14,400	0	14,400
Sp G (bulk-hydrated)	2.40	2.40	2.40	2.40	2.40	2.40	2.40	2.40	2.40	2.40	2.40	2.40	2.40	2.40
Mass of Insoluble Solids, kg, dried solids	2,762	80,600	0	80,600	0	0	80,600	50,500	0	131,000	0	131,000	0	131,000
wt% Al in insoluble solids	0.0%	16.1%	0.0%	16.1%	0.0%	0.0%	16.1%	7.0%	0.0%	12.6%	0.0%	12.6%	0.0%	12.6%
wt% as Al(OH)3 in insoluble solids	0.0%	46.6%	0.0%	46.6%	0.0%	0.0%	46.6%	20.3%	0.0%	36.4%	0.0%	36.4%	0.0%	36.4%
wt% as AlO(OH) in insoluble solids	0.0%	35.8%	0.0%	35.8%	0.0%	0.0%	35.8%	15.6%	0.0%	28.0%	0.0%	28.0%	0.0%	28.0%
Al, kg (as elemental Al)	0	13,000	0	13,000	0	0	12,990	3,550	0	16,500	0	16,500	0	16,500
Other than Al Components, kg	2,760	67,600	0	67,600	0	0	67,576	47,000	0	114,600	0	114,600	0	114,600
Max Settling Time (days)		-	-	-	-	-	-	-	-	-	-	-	-	-

Table 12: Material Balance (continued)
(assuming 80% of the aluminum dissolves)

Description	Wash 2				Wash 3				Wash 4				Wash 5			
Stream No	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57
	Inhibited Water Addition	Tank 51 Inventory After IW Addition	Decant D Tank 51 to 2F Evap System	Tank 51 Inventory After Decant to 2F Evap System	Inhibited Water Addition	Tank 51 Inventory After IW Addition	Decant E Tank 51 to 2F Evap System	Tank 51 Inventory After Decant to 2F Evap System	Inhibited Water Addition	Tank 51 Inventory After IW Addition	Decant F Tank 51 to 2F Evap System	Tank 51 Inventory After Decant to 2F Evap System	Inhibited Water Addition	Tank 51 Inventory After IW Addition	Decant G Tank 51 to 2F Evap System	Tank 51 Inventory After Decant to 2F Evap System
Tank Level, in		163.3		101.3		166.4		98.4		165.4		98.4		126.0		84.3
Total Volume, gal	210,000	573,000	218,000	356,000	228,000	584,000	238,000	345,000	235,000	580,000	235,000	345,000	97,000	442,000	146,000	296,000
wt% Insoluble Solids	0.00%	5.20%	0.00%	8.24%	0.00%	5.34%	0.00%	8.85%	0.00%	5.53%	0.00%	9.10%	0.00%	7.25%	0.00%	10.62%
Total Mass, kg	795,000	2,523,000	932,000	1,591,000	865,000	2,456,000	973,000	1,482,000	890,000	2,372,000	931,000	1,441,000	367,000	1,808,000	574,000	1,234,000
Liquid Phase																
Volume, gal	210,000	559,000	218,000	341,000	228,000	570,000	238,000	331,000	235,000	566,000	235,000	331,000	97,000	428,000	146,000	281,000
Sp G	1.000	1.130	1.130	1.130	1.000	1.078	1.078	1.078	1.000	1.046	1.046	1.046	1.000	1.035	1.035	1.035
Mass of liquid, kg	795,000	2,392,000	932,000	1,460,000	865,000	2,324,000	973,000	1,351,000	890,000	2,241,000	931,000	1,310,000	367,000	1,677,000	574,000	1,103,000
Al, kg	0	10,170	3,960	6,210	0	6,210	2,600	3,610	0	3,610	1,500	2,110	0	2,110	720	1,390
Concentration in M:																
Na+	0.021	3.05	3.05	3.05	0.972	2.21	2.21	2.21	0.021	1.30	1.30	1.30	0.021	1.01	1.01	1.01
NO2-	0.011	0.60	0.60	0.60	0.962	0.75	0.75	0.75	0.011	0.44	0.44	0.44	0.011	0.34	0.34	0.34
NO3-	0.00	0.66	0.66	0.66	0.00	0.40	0.40	0.40	0.00	0.23	0.23	0.23	0.00	0.18	0.18	0.18
OH-	0.010	1.06	1.06	1.06	0.010	0.64	0.64	0.64	0.010	0.38	0.38	0.38	0.010	0.29	0.29	0.29
Cl-	0.00	0.015	0.015	0.015	0.00	0.0088	0.0088	0.0088	0.00	0.0052	0.0052	0.0052	0.00	0.0040	0.0040	0.0040
SO4-	0.00	0.069	0.069	0.069	0.00	0.041	0.041	0.041	0.00	0.024	0.024	0.024	0.00	0.019	0.019	0.019
F-	0.00	0.0026	0.0026	0.0026	0.00	0.00154	0.00154	0.00154	0.00	0.00090	0.00090	0.00090	0.00	0.00069	0.00069	0.00069
CO3-2	0.00	0.19	0.19	0.19	0.00	0.11	0.11	0.11	0.00	0.07	0.07	0.07	0.00	0.05	0.05	0.05
AlO2-	0.00	0.18	0.18	0.18	0.00	0.11	0.11	0.11	0.00	0.06	0.06	0.06	0.00	0.05	0.05	0.05
C2O4-2	0.00	0.00153	0.00153	0.00153	0.00	0.00091	0.00091	0.00091	0.00	0.00053	0.00053	0.00053	0.00	0.00041	0.00041	0.00041
PO4-3	0.00	0.0017	0.0017	0.0017	0.00	0.00101	0.00101	0.00101	0.00	0.00059	0.00059	0.00059	0.00	0.00046	0.00046	0.00046
K+	0.00	0.0119	0.0119	0.0119	0.00	0.0071	0.0071	0.0071	0.00	0.0042	0.0042	0.0042	0.00	0.0032	0.0032	0.0032
Solid Phase																
Volume, gal	0	14,400	0	14,400	0	14,400	0	14,400	0	14,400	0	14,400	0	14,400	0	14,400
Sp G (bulk-hydrated)	2.40	2.40	2.40	2.40	2.40	2.40	2.40	2.40	2.40	2.40	2.40	2.40	2.40	2.40	2.40	2.40
Mass of Insoluble Solids, kg, dried solids	0	131,000	0	131,000	0	131,000	0	131,000	0	131,000	0	131,000	0	131,000	0	131,000
wt% Al in insoluble solids	0.0%	12.6%	0.0%	12.6%	0.0%	12.6%	0.0%	12.6%	0.0%	12.6%	0.0%	12.6%	0.0%	12.6%	0.0%	12.6%
wt% as Al(OH)3 in insoluble solids	0.0%	36.4%	0.0%	36.4%	0.0%	36.4%	0.0%	36.4%	0.0%	36.4%	0.0%	36.4%	0.0%	36.4%	0.0%	36.4%
wt% as AlO(OH) in insoluble solids	0.0%	28.0%	0.0%	28.0%	0.0%	28.0%	0.0%	28.0%	0.0%	28.0%	0.0%	28.0%	0.0%	28.0%	0.0%	28.0%
Al, kg (as elemental Al)	0	16,500	0	16,500	0	16,500	0	16,500	0	16,500	0	16,500	0	16,500	0	16,500
Other than Al Components, kg	0	114,600	0	114,600	0	114,600	0	114,600	0	114,600	0	114,600	0	114,600	0	114,600
Max Settling Time (days)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Note: Stream 46 includes a sodium nitrite addition to the wash water. Streams 30 and 36 include a sodium hydroxide addition to the wash water.
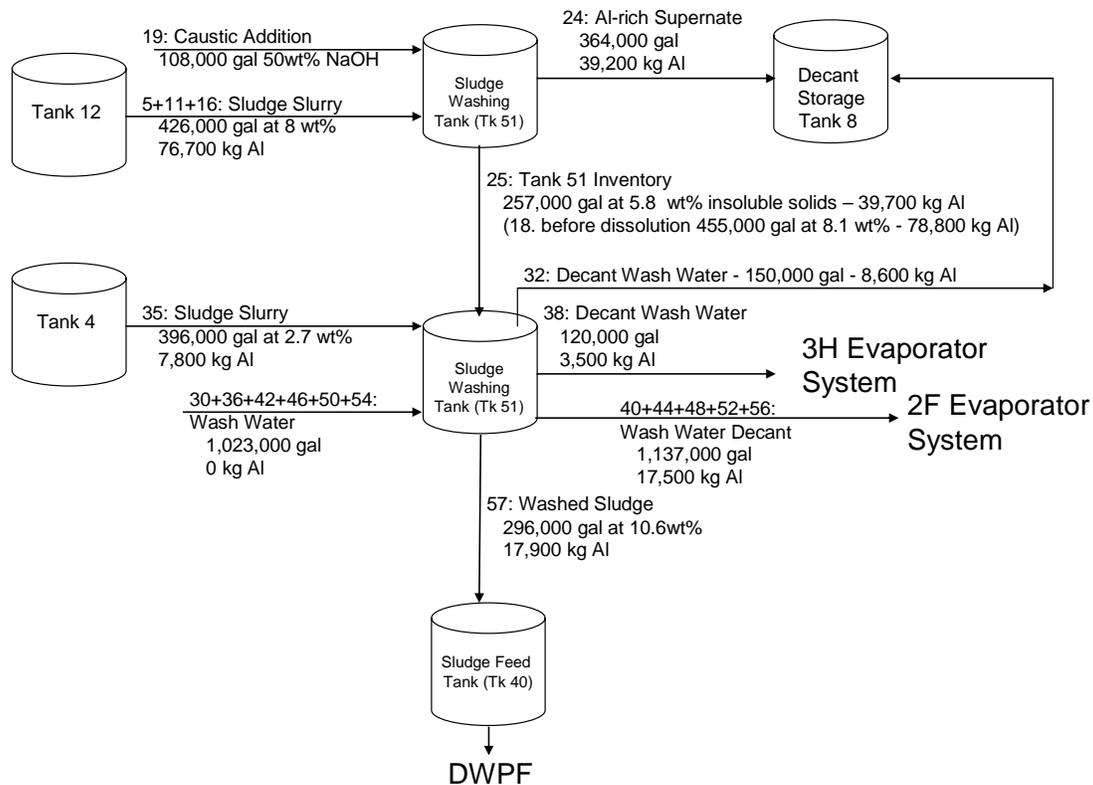
Figure 6: Aluminum Balance for Aluminum Dissolution in Tank 51

4.8   Downstream Process Impacts

4.8.1   Impact on Saltstone Production Facility

The aluminum-laden supernate decanted to Tank 8 is stored until fed to a salt waste treatment process such as the SWPF. The decontaminated salt solution will then be processed at the SPF. Table 13 shows the composition of the aluminum-laden supernate as estimated for storage in Tank 8 and after dilution to 5.6 M total sodium for comparison to the projected feed to the Saltstone Production Facility (SPF) from various salt processes and the estimated average composition of all soluble salt waste in the tank farms. The aluminum-laden supernate after dilution to 5.6 M total sodium is:

- near average relative to free hydroxide concentrations,
- lower relative to average sodium nitrate concentrations,
- higher relative to average sodium nitrite, and sodium carbonate, and
- well above average aluminum concentrations.

Only the aluminum concentration is higher than most any other stream intended for salt waste processing. The high aluminum concentrations result from dissolving aluminum from a sludge slurry with

exceptionally high aluminum content. It is likely that this stream can be blended with other waste supernates such that the aluminum concentration in the actual batch sent to salt waste processing is closer to average.[3] High aluminum concentration in salt solution was identified in simulant testing to effect grout formation. Some of the effects were beneficial to processing and some were detrimental, so specific blend testing will likely be needed for salt waste processing. Since this risk exists in a large portion of the planned feed to the SWPF, the risk will need to be managed as part of the waste acceptance program for SWPF.

Table 13: Ionic Concentration Data in Molarity for Al-Laden Supernate Stored in Tank 8 Compared to SWPF and SPF Estimated Feed Streams

Ion		Na^+	K^+	Cs^+	OH^-	NO_3^-	NO_2^-	$Al(OH)_4^-$	Al (as metal)	CO_3^{-2}	SO_4^{-2}	Cl^-	F^-	PO_4^{-3}
Estimated Tank 8 Composition		8.1	0.0016	-	3.5	1.2	1.4	0.9	-	0.43	0.11	0.067	0.0049	0.0037
Estimated Tank 8 Composition (adjusted to 5.6 M		5.6	0.0011	-	2.4	0.82	0.94	0.63	-	0.30	0.073	0.047	0.0034	0.0026
Tank 11 Sample After LTAD[(Hay)]		4.17	0.0033	-	3.10	0.18	0.33	0.39	-	0.098	0.017	0.030	< 0.026	< 0.013
Bench-Scale Test Data[(Reboul)]		5.1	-	-	3.80	0.22	0.42	0.36	-	-	0.021	< 0.034	< 0.064	0.001
Initial Life Cycle Feed for SWPF[(Dimenna)]	Min	5.8	0.0059	-	1.21	0.57	0.065	0.061	-	0.011	0.014	-	-	0.002
	Max	6.9	0.051	-	5.03	3.41	1.21	0.47	-	1.98	1.61	-	-	0.016
Standard Simulated Salt Waste[(Walker)]	Average	5.6	0.015	1.40E-04	1.91	2.14	0.52	0.31	-	0.16	0.15	0.025	0.032	0.01
	High OH	5.6	0.03	3.70E-04	3.05	1.1	0.74	0.27	-	0.17	0.03	0.01	0.01	0.008
	High NO3	5.6	0.0041	1.40E-04	1.17	2.84	0.37	0.32	-	0.16	0.22	0.04	0.05	0.01
Integrated Flowsheet Attainment Study[(Elder)]	Min	5.6	0.0050	2.69E-05	0.42	1.41	0.12	0.032	0.023	0.097	0.029	0.00080	0.00018	0.0080
	Max	5.6	0.037	2.56E-04	3.37	4.25	0.54	0.36	0.11	0.24	0.085	0.0059	0.0030	0.017
DDA and ARP/MCU Feed Basis[(Drumm)]	DDA	3.4	-	-	0.47	2.24	0.12	0.037	-	0.15	0.048	0.0012	0.0061	-
	ARP/MCU	5.7	-	-	1.21	3.44	0.33	0.022	-	0.19	0.065	0.0018	0.012	-
SPF Feed Stream Data from Spaceman Plus from:[(Pike 2007)]	DDA Min	2.76	0.0037	6.56E-10	0.24	1.58	0.0049	0.013	0.024	0.074	0.013	0.0005	0.0001	0.004
	DDA Max	3.56	0.016	1.27E-05	0.70	2.49	0.22	0.12	0.059	0.19	0.056	0.0035	0.0087	0.010
	ARP/MCU Min	4.96	0.0005	1.21E-06	0.13	1.25	0.076	0.0025	0.012	0.10	0.015	0.0006	0.0022	0.0057
	ARP/MCU Max	6.67	0.023	5.94E-05	2.85	5.42	0.79	0.13	0.145	0.28	0.109	0.0029	0.0196	0.019
	SWPF Min	5.25	0.011	1.29E-04	1.43	1.55	0.29	0.057	0.008	0.088	0.040	0.0023	0.0006	0.0049
	SWPF Max	5.26	0.029	2.27E-04	2.83	2.97	0.58	0.15	0.069	0.16	0.065	0.0045	0.0024	0.012
Tank 25 Salt Dissolution Flowsheet Adjusted to 5.6 M Total Na[(Pike 2005)]	High Na	5.6	-	-	1.65	2.11	0.33	0.36	-	0.45	0.088	0.0044	0.032	0.0084
	Low Na	5.6	-	-	0.39	4.42	0.081	0.087	-	0.13	0.13	0.0011	0.016	0.029

Note that the references on the table are as follows: Reboul is reference 37, Dimenna is reference 38, Hay is reference 39, Walker is reference 40, Elder is reference 41, Drumm is reference 42, Pike 2007 is reference 43, and Pike 2005 is reference 44.

4.8.2 Impact on F-Tank Farm

4.8.2.1 Tank 8

By design, the aluminum concentration in the initial decant liquid is projected at roughly the solubility of aluminum in Tank 8 at 20°C per calculation by OLI Steam Analyzer[tm] as shown in Figure 4. The current plan includes transferring the first wash decant to Tank 8. If the dissolution process achieves the maximum extent of dissolution expected, 80%, then NaOH would need to be added directly to Tank 8 to avoid precipitation of aluminum during storage. The size of the caustic addition depends on the margin necessary for storage.

Aluminum solubility decreases with decreasing hydroxide concentration. One known mechanism for hydroxide depletion is by absorption of carbon dioxide from the tank vapor space. The depletion rate depends on the ventilation rate of the waste tank. Assuming a ventilation rate of 300 scfm, the maximum hydroxide depletion rate is 0.02 M/year for the projected 525,000 gallon transfer to Tank 8 based on an average atmospheric carbon dioxide concentration of 316 ppm.[45] The depletion rate is very slow and will

need to be monitored for the duration of storage to avoid precipitating solids. After 6 years of storage, the hydroxide concentration could drop from 3.47 to 3.34 M where the aluminum solubility drops to 0.69 M at 20°C. The minimum hydroxide concentration that needs to be maintained depends on the success of the dissolution process. If 80% of the aluminum dissolves, the hydroxide concentration should be maintained at or above 4.0 M. This value will be evaluated based on the actual results. The corrosion chemistry program already provides adequate sampling for monitoring purposes. Aluminate ion analysis will need to be added to the analytical request for these samples as was done for the aluminum-laden supernate stored in Tank 11 from SB5.

Note that the first wash decant solution is currently shown to be transferred to Tank 8 and is included in the evaluation above. As noted earlier, the mixture in Tank 8 as shown in the material balance in Section 4.7 is at or above saturation at less than 28°C, thus, the solution is already above saturation at 3.47 M hydroxide. To prevent precipitation down to 20°C, about 18,000 gallons of 50wt% caustic would be needed to increase the hydroxide concentration to 4.0 M. Therefore, additional caustic would be needed to maintain some marginal allowance for depletion due to carbon dioxide absorption. The first wash decant would be transferred to the 3H evaporator system if not sent to Tank 8, thus, eliminating the precipitation issue with the mixed solutions.

5 CONCLUSIONS

About 80% of the insoluble solids in Tank 12 sludge slurry are aluminum compounds, most likely boehmite. An aluminum dissolution process can dissolve up to 80% of the aluminum, dramatically reducing the total amount of insoluble solids in the slurry.

As planned, an aluminum removal process can reduce the aluminum in SB6 from about 84,500 kg to as little as 17,900 kg with a corresponding reduction of total insoluble solids in the batch from 246,000 kg to 131,000 kg. The extent of the reduction may be limited by the time available to maintain Tank 51 at dissolution temperature. The range of dissolution in four weeks based on the known variability in dissolution kinetics can range from 44 to more than 80%. At 44% of the aluminum dissolved, the mass reduction is approximately ½ of the mass noted above, i.e., 33,300 kg of aluminum instead of 66,600 kg. Planning to reach 80% of the aluminum dissolved should allow a maximum of 81 days for dissolution and reduce the allowance if test data shows faster kinetics. 47,800 kg of the dissolved aluminum will be stored in Tank 8 and 21,000 kg will be stored in saltcake via evaporation. Up to 77% of the total aluminum planned for SB6 may be removed via aluminum dissolution.

Storage of the aluminum-laden supernate in Tank 8 will require routine evaluation of the free hydroxide concentration in order to maintain aluminum in solution. Periodic evaluation will be established on concurrent frequency with corrosion program samples as previously established for aluminum-laden supernate from SB5 that is stored in Tank 11.

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