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Reduced Neutralization Feasibility Study for H-Canyon Accelerated Basin De-Inventory (ABD) Program

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EXECUTIVE SUMMARY

An alternative approach to Spent Nuclear Fuel (SNF) and Nuclear Material Processing was developed for future H-Canyon (HCAN) and L-Area operations that involves a paradigm shift from current HCAN, Concentrate, Storage, and Transfer Facility (CSTF), and Defense Waste Processing Facility (DWPF) operations. The alternative, referred to as Accelerated Basin De-inventory (ABD), requires that all Domestic and Foreign Research Reactor SNF currently at the Savannah River Site (SRS) will be dissolved, stored, and then transferred to CSTF without recovery of Highly Enriched Uranium (HEU).

Concentrated nitric acid is utilized to dissolve aluminum spent nuclear fuel (ASNF) in HCAN. The vessels and piping in HCAN are fabricated from 304L stainless steel and are ideally suited to handle the acidic waste stream. However, as the waste is transferred to the CSTF and DWPF, it will contact the carbon steel waste tanks in CSTF. In order to prevent corrosion of the carbon steel, the acidic waste is neutralized (i.e., pH adjusted over 11) by the addition of sodium hydroxide (NaOH). The NaOH is added until the final solution contains 1.2 M excess -OH. Additionally, if the waste is not neutralized to a pH greater than 11, then aluminum hydroxide ($Al(OH)_3$) would form, and solids may form in the piping as it is transferred to CSTF. This document presents an analysis of the influence of reducing the excess caustic that is added to the neutralization tanks on the corrosion protection scheme primarily for the CSTF waste tanks. The implications to HCAN and DWPF were also assessed.

The following conclusions were made from the evaluation:

HCAN
- A two-fold reduction in the excess caustic added decreases the neutralized solution volume by 10%.
- The reduction in excess caustic is not expected to influence the corrosion behavior of the stainless steel equipment in HCAN.
- Freshly precipitated sludge typically has a smaller particle size and the aluminum is precipitated as gibbsite and not boehmite. The resulting slurry tends to be thicker rheologically, foamier and is more reactive than the aged sludge that it will be combined with in the CSTF.

CSTF
- Corrosion prevention in the CSTF can be managed without significant processing changes or increases in volumes.
- The ABD stream increases the amount of sodium nitrite necessary to prevent corrosion during sludge batch washing. The nitrite required, however, could be reduced by implementation of the Hanford Pitting Factor approach.
- Reducing the excess caustic requires more sodium hydroxide addition to the feed preparation tank in order to ensure aluminum dissolution.
- If a dedicated receipt tank is used for the ABD stream in CSTF, sodium nitrite inhibitor will need to be added to the tank prior to transfer of the ABD stream to ensure corrosion prevention. Less inhibitor will be required if the excess caustic concentration is maintained at 1.2 M.
- Reduced neutralization has a very minor impact on the composition of sludge after washing and isn't expected to impact rheology or settling.

DWPF
- The projected chemistry of the sludge batch feed tank in CSTF (Tank 40) after the addition of the ABD stream is not expected to change significantly. Although the ABD stream will add uranium and aluminum to Tank 40, the uranium is a very small compared to the uranium in the sludge batch and the added aluminum will be removed as part of the aluminum dissolution planned for each

future sludge batch. Therefore, the ABD stream is not anticipated to have an influence on the corrosion behavior in DWPF.

- Reduced neutralization is not expected to influence DWPF processing significantly.

To ensure waste will be processable in the tank farm and DWPF, the following is recommended:

- Actual waste testing for each sludge batch is recommended from HCAN through DWPF. This would ensure that the chemical and physical properties (rheology, settling rate, foaming) of the slurry is acceptable for transfer, mixing, and processing from HCAN through DWPF.
- Measure the rheology and settling behavior of the freshly precipitated ABD, ABD combined with sludge, and then process the sludge through prototypic Sludge Receipt and Adjustment Tank (SRAT) and Slurry Mix Evaporator (SME) cycles.
- Samples should be taken to track the poison and fissile solubility, hydrogen generation, reduction/oxidation (REDOX) and other parameters needed for processing
- Use of the Hanford Pitting Factor approach to corrosion inhibition reduces the amount of nitrite inhibitor needed during sludge batch washing.

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LIST OF ABBREVIATIONS

ABD	Accelerated Basin De-inventory
ASNF	Aluminum Spent Nuclear Fuel
CPC	Chemical Processing Cell
CSTF	Concentrate, Storage, and Transfer Facility
DWPF	Defense Waste Processing Facility
FS	Ferrous Sulfamate
HCAN	H-Canyon
HEU	Highly Enriched Uranium
HFIR	High Flux Test Reactor
HLW	High Level Waste
HM	H-Modified
LTAD	Low Temperature Aluminum Dissolution
MC&A	Material Control and Accountability
MTR	Materials Test Reactor
REDOX	Reduction/Oxidation
PUREX	Plutonium Uranium Reduction Extraction
SB	Sludge Batch
SCC	Stress Corrosion Cracking
SEHT	Strip Effluent Hold Tank
SME	Slurry Mix Evaporator
SNF	Spent Nuclear Fuel
SRAT	Slurry Receipt Adjustment Tank
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
SSRT	Sludge Solids Receipt Tank
SWPF	Salt Waste Processing Facility
TTQAP	Task Technical and Quality Assurance Plan

1.0 Introduction

An alternative approach to Spent Nuclear Fuel (SNF) and Nuclear Material Processing was developed for future H-Canyon (HCAN) and L-Area operations that involves a paradigm shift from current HCAN, Concentrate, Storage and Transfer Facility (CSTF), and Defense Waste Processing Facility (DWPF) operations.[1] The alternative, referred to as Accelerated Basin De-inventory (ABD), requires that all Domestic and Foreign Research Reactor SNF currently at the Savannah River Site (SRS) will be dissolved using limited HCAN processes in which the dissolved solution will be directly transferred to CSTF without recovery of Highly Enriched Uranium (HEU). During ABD, HCAN will dissolve 18 6.4D equivalent dissolutions batches per year and produce approximately 170,000 gallons of solution that will be sent to DWPF via CSTF. Initially, aluminum SNF (ASNF) will be processed and will focus on the High Flux Test Reactor (HFIR) and the Materials Test Reactor (MTR). ABD is currently projected to be performed after DOE approval, until approximately 2033.

Concentrated nitric acid is utilized to dissolve ASNF in HCAN. The vessels and piping in HCAN are fabricated from 304L stainless steel and are ideally suited to handle the acidic waste stream. However, as the waste is transferred to DWPF, it will contact the carbon steel waste tanks in CSTF. In order to prevent corrosion of the carbon steel, the acidic waste is neutralized (i.e., pH adjusted over 11) by the addition of sodium hydroxide (NaOH) to a minimum of 1.2 M excess hydroxide (OH). When processing ABD material, the NaOH solution volume is approximately equal to the volume of dissolver solution; reduction of the NaOH volume would allow more flexibility in H-Canyon operations. This document investigated the influence of reducing the excess caustic that is added to the neutralization tanks (i.e., reduced neutralization) on operability in the CSTF and DWPF. These were compared to the downstream implications as a result of the ABD material neutralized per the existing operating conditions (1.2 M excess OH).

The neutralization process converts the nitric acid solution into a caustic slurry since most of the dissolved metals will precipitate as hydroxide or oxide species. The solubility of these species as well as the type of solids formed during the precipitation process may be altered by a reduction in the volume of the NaOH addition. Thus, the reduction may result in changes in physical properties, such as rheology, aluminum solubility, fissile species solubility that may influence the transfers to CSTF, solids settling rates in the waste tanks, and settled solids bed properties. Downstream implications to DWPF were assessed and issues for further investigation have been identified.

The evaluation was organized by focusing on each of the three facilities, HCAN, CSTF, and DWPF separately. The focus of the HCAN was the neutralization tanks, while sludge batch (SB) washing in the feed preparation tank was the primary process for CSTF. For DWPF, the chemical processing cell and the melter are the primary considerations. For each facility, the corrosion implications for ABD will be considered followed by a discussion on the waste physical properties.

2.0 Quality Assurance

This work was requested via a Technical Task Request[2] and directed by a Task Technical and Quality Assurance Plan.[3] The functional classification of this task is Safety Significant. Requirements for performing reviews of technical reports and the extent of review are established in Manual E7, Procedure 2.60. This document, including all calculations, was reviewed by a Design Checklist. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2. All calculations, document preparation, and reviews satisfy the quality requirements for Safety Significant.

3.0 Discussion

3.1 HCAN

3.1.1 Corrosion Assessment

The acidic waste products are currently neutralized at three locations in HCAN just prior to transfer to the CSTF see Figure 3-1). Tank 8.4 primarily neutralizes high activity waste from the first cycle. Tank 9.8 previously handled low activity waste sent from the second uranium cycle and HB Line discards from the facility. Tank 16.1 is utilized for neutralization of waste from sumps, spent solvent wash and sample returns. These tanks may be used for neutralization during ABD processing. Table 3-1 summarizes the functionality of each of these tanks during the first two phases, which encompasses the dissolution of the ASNF through FY28. Additionally, for phases 2C and 2D a fourth tank, 15.3, may also be utilized for neutralization of waste from the dissolver (see Figure 3-1).

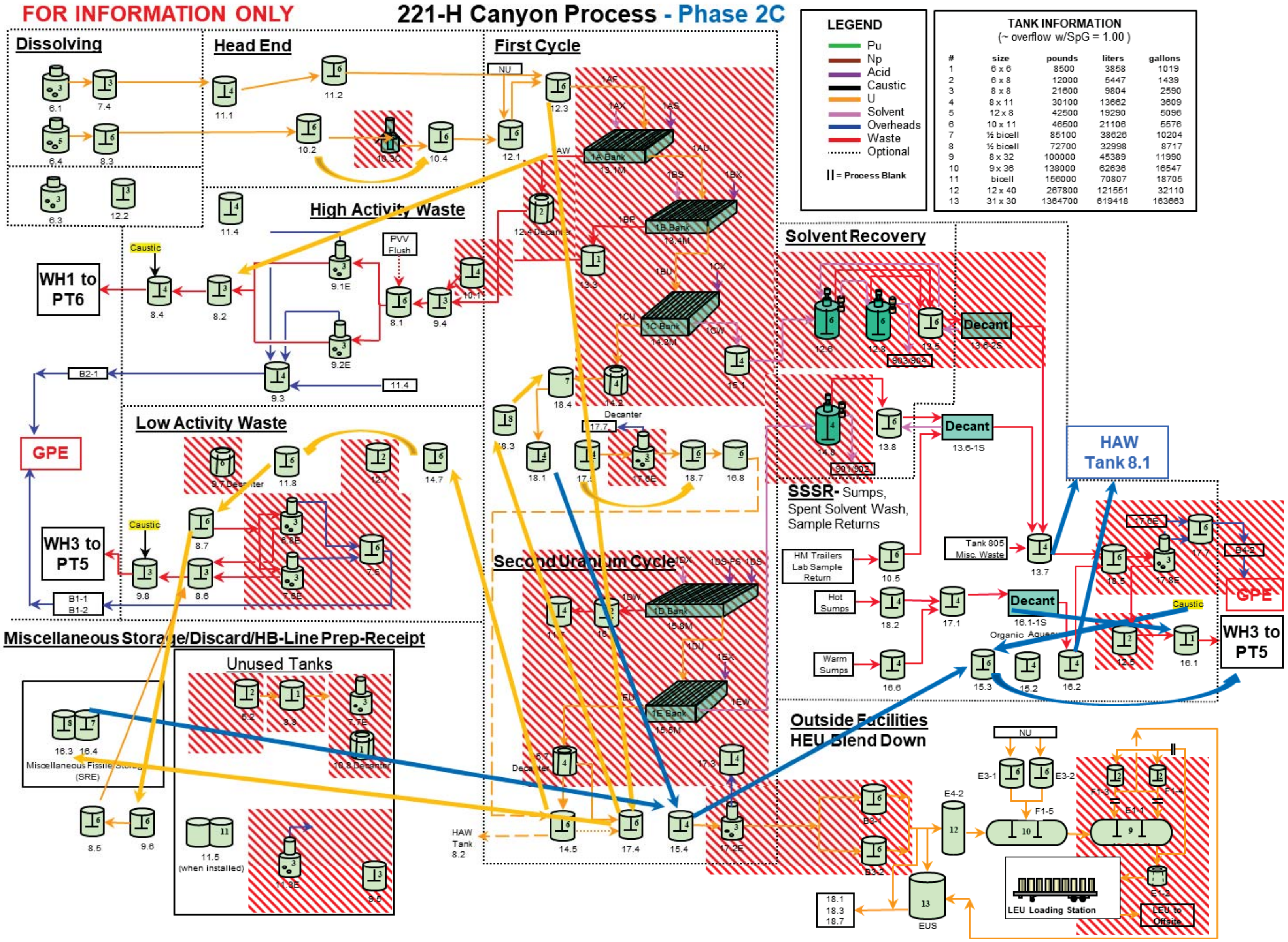
Table 3-1. Utilization of Neutralization Tanks During the First Two Phases of ABD

Phase	Tank 8.4	Tank 9.8	Tank 16.1	Tank 15.3
1	X	X	X	
2A	X	X	X	
2B	X	X	X	
2C	X	X	X	X
2D	X			X
2E	X			

An X indicates that the tank is being utilized.

The primary wetted parts of the neutralization tank are the tank walls and the internal cooling coils. The vessels were designed per ASME Sec. VIII, Div. I, while the cooling coils were designed to ASME B31.3 standards.[4] Each of these parts were constructed of 304L stainless steel and welded with either 308L or Inconel 52 filler material.[4] All tank bottoms are sloped to the front to promote drainage. Reference drawings indicate that the materials for the most recent vessels were corrosion evaluated.[5] Welds for the vessel and cooling coils were radiographed and hydrostatically tested. Chloride levels in the hydrostatic water were less than 250 ppm per the site standard.[6] The design life for a vessel was typically 20 years.[7] This information indicates that the initial design was adequate for the intended service.

The dimensions for each of the vessels and the cooling coils are shown in Table 3-2. The tanks with the thinnest walls are 9.8 and 16.1, while the tanks with the thinnest cooling coil wall piping are 9.8 and 15.3. The tanks and coils with the greater wall thickness are expected to be able to handle greater stresses and provide longer service assuming similar corrosion degradation rates.



TANK INFORMATION
(~ overflow w/SpG = 1.00)

#	size	pounds	liters	gallons
1	6 x 6	8500	3858	1019
2	6 x 8	12000	5447	1439
3	8 x 8	21600	9804	2590
4	8 x 11	30100	13662	3609
5	12 x 8	42500	19290	5096
6	10 x 11	46500	21106	5576
7	½ bicell	85100	38626	10204
8	½ bicell	72700	32998	8717
9	8 x 32	100000	45389	11990
10	9 x 36	138000	62636	16547
11	bicell	156000	70807	18705
12	12 x 40	267800	121551	32110
13	31 x 30	1364700	619418	163663

Figure 3-1. HCAN configuration for Phase 2C.

Figure 3-1 illustrates the facility changes required for the ABD process and the utilization of Tanks 8.4 and 15.3 for neutralization. The red diagonal lines indicate portions of the original HCAN process that have been eliminated.

Table 3-2. Dimensions for HCAN Neutralization Vessels and Cooling Coils

	Tank			Cooling Coils	
Vessel	Diameter (ft.)	Height (ft.)	Thickness (in.)	Diameter (in.)	Schedule
8.4	8	11	0.5	2	40
9.8	8	8	0.375	2	80
16.1	6	6	0.375	2	40
15.3	10	11	0.5	2	80

ASNF fuel elements that will be dissolved during ABD process are either HFIR or MTR, which have existing dissolution flowsheets. The flowsheets use Hg, Gd, and nitric acid. Since these are both aluminum-based fuels and the chemicals for the dissolution process remain the same, the concentrations of the anions in the solution transferred to the neutralization tanks during the ABD process are assumed to be similar to that for the current HCAN stream. The primary difference is the amount of uranium, reduced dilution since 1st and 2nd cycles will not be operating, ceasing of gelatin strike, and ceasing of the addition of ferrous sulfamate (FS). Facility engineers and the waste compliance documents[8] were consulted to identify nominal concentrations for key constituents related to neutralization and corrosion of the HCAN and CSTF infrastructure. Table 3-3 contains a summary of the key corrosion constituents that are considered in the HCAN waste compliance plan, a nominal concentration, and whether they remain a concern for the ABD process. ASNF processed under ABD, with the current dissolver flowsheets, are not expected to add any new species that would create a corrosion concern to either the HCAN or CSTF infrastructure. Future ABD flowsheets that process non-ASNF may incorporate fluoride for dissolution. Once these flowsheets are developed, the influence of the fluoride on corrosion of the HCAN and CSTF infrastructure should be reviewed.

The HCAN waste compliance program[8] requires the waste solution to be neutralized to a minimum of 1.2 M excess hydroxide to ensure that the waste stream contains sufficient corrosion inhibitor to protect the carbon steel waste tanks in CSTF. Sufficient sodium hydroxide must also be added to ensure that any aluminum present in the waste forms sodium aluminate, a soluble compound. If the solution was not neutralized to a pH greater than 11, then aluminum hydroxide ($Al(OH)_3$) would form, and solids may form in the piping as it is transferred to CSTF. Therefore, the acid term, (H^+), is analyzed as total acid to pH 11. For the current process, dilution, flush and scrubber water may also be added to the neutralization tanks. The ammonia scrubber will not be utilized for ABD and the stream was not considered for these calculations. Dilution water is added only if needed to dilute a component below CSTF or Material Control and Accountability (MC&A) limits. Although dilution water may still be needed for ABD it was not considered for the base case. Flush water is necessary to remove residual concentrated caustic from the cold chemical piping and the head tank. Typically, domestic water is utilized for the flush.

The following inputs were utilized to calculate the amount of 50 wt. % caustic that need to be added to a neutralization tank.

- The specific gravity of the waste was assumed to be 1.25. This represents a nominal value as typical values range between 1.19-1.33 after a jet dilution of 4% by volume.[9]
- The specific gravity of the 50 wt. % sodium hydroxide solution will be 1.52.
- The molarity of the 50 wt. % sodium hydroxide solution will be 18.8 M.
- The line between the head tanks and the neutralized feed was flushed with 500 lbs. of water following the caustic addition.
- Domestic water has an acid normality of zero.
- The total uncertainty due to random and systematic sampling measurement error is 10.6%.

The calculation steps shown in X-CLC-H-00585[9] were followed to determine the amount of caustic added to the neutralization tank. [Note: Since this report was drafted, a new revision to this calculation was performed that reduces the amount of caustic added. However, this is not anticipated to significantly impact the conclusions of the report. Therefore, the formulas from the previous revision were utilized.] Since the impact of the reducing the excess hydroxide added was being investigated, the volume of 50 wt. % caustic added as a function of excess hydroxide as it ranges from 0.1 to 1.2 M was calculated.

Table 3-3. HCAN Corrosion Species

Corrosion Species	**Nominal Concentration (M)**	**Comments**
Total Acidity (H^+)	6.5	This value is determined by titration of a liquid sample to pH 11 in the laboratory. This value takes into consideration sulfate, nitrate and nitric acid and is necessary for the excess hydroxide calculation.
Nitrate	6.5	Nitric acid is utilized to dissolve the fuel elements. Nominal concentration as it is transferred from the dissolver to the neutralization tank; After the hydroxide is added this value decreases to between 4-5 M.
Chloride	Trace	Chlorides are not added directly to the dissolution process. There may be some trace chlorides in the sodium hydroxide that is added to the neutralization tank. Likely on the order of 100 ppm or less.
Fluoride	Trace to 0.05	Fluoride is sometimes added to complete dissolution of the aluminum fuel. This is the concentration of uncomplexed fluoride. Although more than a trace quantity, the concentration in the neutralized solution will not be significant.
Sulfate	Trace	Sulfate typically originates from ferrous sulfamate that is added as part of the extraction process. This addition will not be done during the ABD process.

Although each of the three neutralization tanks have a procedure for neutralizing waste,[10,11,12] the method is similar. The 50 wt. % caustic solution is stored in a tank located in the outdoor facility. The solution is transferred to the tank at a rate fast enough that minimizes the potential for the caustic “freezing” in the line, yet not too fast such that the heat of neutralization causes the tank temperature to rise above 60 °C. The rate is typically on the order of 15-20 lbs./min. The tank is agitated to promote complete neutralization and there are controllers to ensure that the temperature is maintained below 60 °C. At the completion of neutralization, the waste is required to cool to less than 50 °C, but not below 40 °C, before it is transferred to an CSTF pump tank en route to a waste tank destination. At this temperature, and at the expected corrosive anion species, the potential for localized corrosion, such as stress corrosion cracking (SCC), is minimal for the neutralization tank. The waste is typically steam jetted to the pump tank, which results in a volume increase, as well as dilution. The total dilution for the transfer from the neutralization tank until it reaches the waste tank was assumed to be 3% by volume for this evaluation.

A nominal batch size for Tank 8.4 of 15,500 lbs. was selected as a basis for the study. Given the assumption that the specific gravity of the waste is 1.25, this represents a volume of 1489 gallons. The necessary weight of caustic to add as a function of the excess hydroxide needed was calculated with the same methodology that is currently used for the neutralization tanks.[9] The excess hydroxide was varied from 0.1 to 1.2 M. These calculations were performed on an EXCEL spreadsheet. The results are shown in Table 3-4. The first three columns show the caustic added expressed in terms of weight and volume as a function of the excess hydroxide for the basis batch size. Column 4 shows the space that would be recovered if the excess hydroxide was reduced from 1.2 M to the specified excess hydroxide in Column 1 for each basis batch. This total volume reduction can also be estimated for an 18-month sludge batch ABD campaign. The volume of solution for each ABD campaign is estimated to be approximately 170,000 gallons or 49 of the basis batches. Column 5 illustrates the total volume recovered during an ABD campaign as a function of excess hydroxide. Finally, the volume recovered can be visualized in terms of the size of a neutralization tank. Tank 8.4 can contain up to 3809 gallons of solution. The value shown in Column 6 was calculated by dividing the volume in Column 5 by the volume in Tank 8.4. The conclusion that may be drawn is that the amount of space recovered is negligible over the duration of the ABD campaign relative to the amount of solution that is processed.

Table 3-4. Volume Recovery in HCAN as a Function of Excess Caustic Added to Neutralization Tank

Excess OH	Caustic Added (lbs)	Caustic Volume (gal)	Volume Recovered/Basis Batch (gal)	Volume Recovered/Sludge Batch Campaign (gal)	Neutralization Tank Space Saved in Terms of Tank 8.4
0.1	20,646	1,631	355	9,591	2.52
0.2	21,033	1,661	325	8,766	2.30
0.3	21,424	1,692	294	7,932	2.08
0.4	21,819	1,723	263	7,089	1.86
0.5	22,219	1,755	231	6,236	1.64
0.6	22,623	1,787	199	5,375	1.41
0.7	23,032	1,819	167	4,504	1.18
0.8	23,445	1,852	134	3,623	0.95
0.9	23,862	1,885	101	2,732	0.72
1.0	24,285	1,918	68	1,832	0.48
1.1	24,712	1,952	34	921	0.24
1.2	25,144	1,986	0	0	0.00

The amount of caustic added also affects the concentration of the nitrate present in the solution. Table 3-5 shows the nitrate concentration as a function of the excess hydroxide. The nitrate concentration decreases as the excess hydroxide increases. The third column shows the ratio of the hydroxide to nitrate. Thus, it shows the ratio of the inhibitor species to the aggressive species for carbon steel as the excess hydroxide increases. The impact of the change in this ratio on the corrosion chemistry of the sludge batch feed preparation tank in CSTF will be subsequently evaluated (see Section 3.2.1).

Table 3-5. Nitrate Concentration as a Function of the Excess Caustic Addition to the Neutralization Tank

Excess OH	$[NO_3]$ (M)	[OH] (M)	$[OH]/[NO_3]$
0.1	4.51	0.10	0.02
0.2	4.49	0.19	0.04
0.3	4.47	0.29	0.07
0.4	4.44	0.39	0.09
0.5	4.42	0.49	0.11
0.6	4.39	0.58	0.13
0.7	4.37	0.68	0.16
0.8	4.35	0.78	0.18
0.9	4.32	0.87	0.20
1.0	4.30	0.97	0.23
1.1	4.27	1.07	0.25
1.2	4.25	1.17	0.27

From this initial analysis, two conclusions were made. A decrease in the excess caustic demanded will not result in a significant volume recovery to HCAN. A large majority of the caustic that is added to the neutralization tank is required to neutralize the waste to pH 11 to ensure that aluminum will not precipitate in the transfer piping. A reduction in the amount of excess caustic will decrease the ratio of inhibitor to aggressive species for the carbon steel tanks in CSTF. However, the influence on the corrosion chemistry of the waste in the feed preparation tank will need to be evaluated for a sludge batch process.

3.2 Tank Farm Facility

3.2.1 Corrosion Assessment

Transfer from the HCAN neutralization tanks to the CSTF occurs via primarily H-pump Tank 5. For current waste transfers the waste is typically sent to Tank 39. However, ABD solutions will be transferred to a DWPF feed preparation tank, either Tank 51 or Tank 42 or to a dedicated receipt tank. Figure 3-2 shows a hypothetical process diagram for integration of the ABD stream into the feed tank sludge batch. This figure shows a draft plan for SB13, which is representative of all ABD stream integration into the CSTF flowsheet.[13] After the sludge batch is assembled in the feed preparation tank, the ABD stream will be added to the tank over a period of 18 months. Sludge batch washing will then proceed as before, with the final batch being transferred to Tank 40, the DWPF feed tank. For the dedicated receipt tank, the waste in that tank would be blended into the sludge batches at a rate to be determined by CSTF.

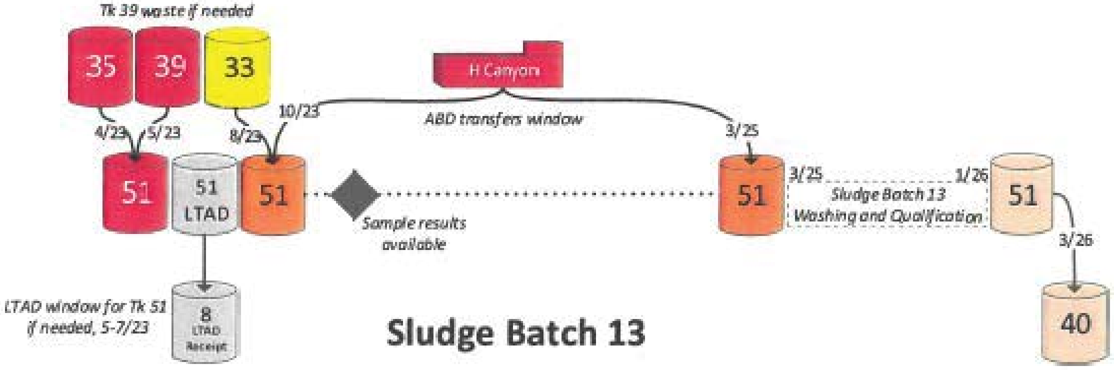


Figure 3-2. ABD integration into sludge batch feed preparation.

The pump tanks and transfer lines that are utilized between the HCAN neutralization tank and the CSTF feed preparation tank are all fabricated from corrosion evaluated 304L stainless steel. The waste from the neutralization tanks will be slightly diluted (~3 vol.%) due to the steam jet that provides the motive force for the transfer. As a result, the composition of the nitrate and hydroxide in the ABD stream are as shown in Table 3-6. The temperature of the stream will likely be less than 60 °C [8] during the time the waste is transferred in the pipes and held in the tanks. The total volume of liquid transferred during the 18-month ABD campaign as a function of the excess caustic is also displayed in the table. The volume does not increase significantly as the excess caustic concentration increases from 0.1 to 1.2 M.

The composition and temperature of this stream is similar to the waste stream that has been transferred for several years.[8] The nitrate and hydroxide present in the stream are not expected to disrupt the passive film on the stainless steel,[14] and therefore corrosion of these components is not expected to be significant throughout the ABD process. There have been no known failures of either transfer lines or pump tank infrastructure due to exposure to this type of environment.

Table 3-6. Composition of ABD Stream Transferred to the CSTF Feed Preparation Tank

Excess OH (M)	[NO_3] (M)	[OH] (M)	Total Volume (gallons)
0.1	4.51	0.10	159,231
0.2	4.49	0.19	160,081
0.3	4.47	0.29	160,940
0.4	4.44	0.39	161,808
0.5	4.42	0.49	162,686
0.6	4.39	0.58	163,573
0.7	4.37	0.68	164,470
0.8	4.35	0.78	165,378
0.9	4.32	0.87	166,295
1.0	4.30	0.97	167,222
1.1	4.27	1.07	168,161
1.2	4.25	1.17	169,109

Both feed preparation tanks, Tanks 42 and 51, are constructed of A537 carbon steel,[15] the same material as Tank 39. However, the waste chemistry in the feed preparation tank is very different than the fresh waste receiver. The waste in Tank 39 typically has a chemistry such that the total sodium concentration remains well above 6 M. The total inhibitor concentration (nitrite and hydroxide) typically remains well above 1.1 M. The effect of reducing the excess hydroxide concentration for the neutralization tanks was investigated previously.[16]

On the other hand, for the feed preparation tanks the total sodium concentration is diluted, or washed, to a final endpoint of 1 M. The dilution, or washing process, is accomplished by a sequence of alternating inhibited water additions followed by a decant of the supernate to an evaporator feed tank. In this case, the current corrosion control program requires that the waste is inhibited with a minimum nitrite concentration. [17] The minimum nitrite concentration is determined by the nitrate concentration and the temperature of the waste. The hydroxide concentration is typically maintained well above a 0.1 M during the washing sequence.

For the purpose of this investigation, personnel from CSTF were consulted to determine a representative initial chemistry (i.e., sludge batch qualification chemistry) for the feed tank prior to sludge batch washing. [18] The consensus was that the SB10 qualification chemistry for Tank 51 would be a reasonable estimate for the feed preparation tank.[19] Additionally, the amount of waste present in the tank will influence the evolution of the waste chemistry as the ABD stream is added to the feed preparation tank. Again, for the purpose of this evaluation, the present level of the waste in Tank 51 after the qualification sample was assumed to be a reasonable initial value. The composition of the corrosion species in Tank 51, the waste temperature, and the supernate volume are shown in Table 3-7.

The supernate in Tank 51 is currently in compliance with the corrosion control program and is inhibited by the hydroxide concentration, which is greater than 1 M. The nitrite to nitrate ratio is also noted in the table as 0.61. This ratio is less than the value of 1.66 that will be needed to inhibit the waste once washing has diluted the waste such that the hydroxide concentration is less than 1 M. This situation indicates that nitrite will need to be added to the tank during sludge batch washing. This addition is typically necessary, however, the inclusion of the ABD stream in the flowsheet will require a larger addition of nitrite than would normally is expected. Currently, the waste temperature is less than the maximum allowable temperature of 40 °C and is not anticipated to exceed this value during the ABD stream additions.[17]

Table 3-7. Current Tank 51 Conditions

Variable	Value
Hydroxide (M)	1.53
Nitrite (M)	0.36
Nitrate (M)	0.59
Nitrite/Nitrate Ratio	0.61
Volume of Supernate in Tank 51 (gallons)	500,877
Temperature of Tank 51 (°C)	33

Sludge batch washing is performed to reduce the sodium ion concentration to 1 M or less. This dilution is accomplished by a sequence of water addition/decant steps.[20] There are two significant constraints for this process. First, the hydroxide concentration must be such that the hydroxide to aluminum ratio at any stage remains greater than 10. This ratio minimizes the likelihood of precipitation of aluminum oxides/hydroxides in the feed preparation tank during the washing steps. Sodium hydroxide is added to the tank for this purpose and will most likely be added prior to the addition of the ABD stream. The second constraint is related to corrosion and requires that once the nitrate concentration and the hydroxide concentration is less than 1 M, that the nitrite to nitrate ratio be greater than 1.66. Compliance with this requirement mitigates the risk of pitting corrosion of the carbon steel, particularly near the liquid air interface region. After the ABD stream is added to the feed preparation tank, a series of water addition/decant steps are performed until the hydroxide concentration reaches approximately 1 M. At this time, nitrite is added to the tank such that the nitrite to nitrate ratio exceeds 1.66. Excess nitrite is typically added so that the ratio is approximately 1.8. After the nitrite addition, the water addition/decant steps are continued until the sodium concentration reaches the target value of 1. The tank farm operator, currently Savannah River Remediation, utilizes an EXCEL spreadsheet to estimate the quantities of hydroxide and nitrite that will be needed. [21] The spreadsheet was utilized to perform calculations to evaluate the impact of the ABD stream on the sludge batch washing process.

Table 3-8 shows the compositions for Tank 51 after the addition of the sodium hydroxide and the ABD stream to the tank, but prior to the addition of the nitrite. The most notable change is the significant decrease in the nitrite to nitrate ratio by a factor of approximately 2.1 as compared with the initial supernate in Tank 51 (see Table 3-7). Thus, the amount of nitrite to be added to Tank 51 during sludge batch washing will increase significantly as compared with the sludge batch that does not contain the ABD stream. The results in the table also demonstrate that a significant reduction in the excess caustic (0.6 vs. 1.2) has little impact on the final concentrations or volume of waste in Tank 51.

Table 3-8. Projected Tank 51 Conditions After the Completion of the ABD Transfers

Variable	0.6 M Excess Caustic Case	1.2 M Excess Caustic Case
Hydroxide (M)	1.65	1.67
Nitrite (M)	0.28	0.28
Nitrate (M)	1.28	1.28
Nitrite/Nitrate Ratio	0.22	0.22
Supernate Volume (gallons)	873,872	874,908

The compositions at the completion of SB washing were calculated. Three cases were evaluated: 1) No ABD Stream, 2) ABD stream with 0.6 M excess caustic, and 3) ABD stream with 1.2 M excess caustic. The impact of the ABD stream on sludge batch washing was evaluated by investigating the 1) decant volume to the evaporator, 2) number of decants, 3) total settle days for the solids in the tank, 4) gallons of sodium hydroxide added, 5) gallons of sodium nitrite added. Table 3-9 shows the results from the spreadsheet calculations. The results indicate that reducing the excess caustic does not have a significant influence in the overall sludge batch process. The reduction in the excess caustic resulted in a slight increase in the amount of hydroxide necessary to maintain the aluminum in solution. Alternatively, the additional amount of nitrite needed for corrosion protection decreased slightly. There was essentially no change in the other indicators.

The table also illustrates the influence of the ABD stream on sludge batch washing. The volume of waste decanted to the evaporator increased by approximately 180,000 gallons, which required one additional water add/decant step. The time for the solids to settle increased by approximately 110 days. The gallons of sodium hydroxide decreased due to the ABD stream addition, which contains excess caustic. Because of the high nitrate concentration in the ABD stream, the volume of nitrite added increased by a factor of nearly 2.5.

Table 3-9. Evaluation of the Influence of the ABD Stream on Sludge Batch Washing

	No ABD Stream Case	0.6 M Excess Caustic Case	1.2 M Excess Caustic Case
Decant Volume	1,377,389	1,666,312	1,663,341
Number of decants	12	13	13
Total settle days for the tank	196	307	303
Gallons of NaOH solution added	22,000	17,500	13,000
Gallons of $NaNO_2$ solution added	31,656	105,000	100,000

The nitrite addition was determined based on achieving a nitrite to nitrate ratio of approximately 1.8, which complies with the corrosion control requirements. The approximate final concentrations for the three evaluation cases are shown in Table 3-10. The reduction in excess caustic did not change the final chemistry of the waste in the feed preparation tank. The ABD stream did have a small influence on the waste chemistry as shown. However, as alluded to previously, the final chemistry is well inhibited.

Table 3-10. Influence of the ABD Stream on the Final Tank 51 Waste Chemistry

	No ABD Stream Case	0.6 M Excess Caustic Case	1.2 M Excess Caustic Case
Hydroxide (M)	0.45	0.28	0.29
Nitrite (M)	0.23	0.38	0.38
Nitrate (M)	0.12	0.21	0.21
Nitrite/Nitrate Ratio	1.85	1.81	1.81

The CSTF is considering a modification to the corrosion control program.[21] In 2016, the Hanford tank farm facility began considering modifying their corrosion control program to minimize conservatisms inherent to the requirements. The result was the development of a new requirement, referred to as the pitting factor, that is applicable to wastes at temperatures less than 50 °C.[22] The CSTF has applied this methodology in certain instances to assess the risk of pitting corrosion. The pitting factor is defined by Equation 1. The numerator contains the inhibitor species, while the denominator contains the aggressive species. The Hanford waste contains significant quantities of chloride and fluoride as well and are considered in the pitting factor calculation. However, the quantities of chloride and fluoride in the SRS waste are relatively low and do not have a significant impact on the pitting factor calculations for the feed preparation tank. Table 3-11 shows the corrosion control requirements for utilization of the pitting factor methodology. [23] If the pitting factor for a waste is greater than 1.2, and the nitrite concentration is greater than 0.2 M, the waste is benign with respect to pitting corrosion at temperatures less than 50 °C . This equation is valid for nitrate concentrations less than 5.5 M. The minimum nitrite concentration takes into consideration that very dilute solutions (nitrate concentrations < 0.3 M) rely on the total inhibitor present as well as a ratio of inhibitor to aggressive species for corrosion mitigation.[23] The pitting factor also addresses control for stress corrosion cracking at temperatures less than 50 °C. The minimum nitrite/nitrate ratio provides additional level of conservatism that mitigates against stress corrosion cracking of the steel.

$$Pitting\ Factor = \frac{8.06*[Hydroxide]+1.55*[Nitrite]}{[Nitrate]+16.7*[Chloride]+5.7*[Fluoride]} \qquad \text{Equation 1}$$

Table 3-11. Pitting Factor Control Limits for Pitting and Stress Corrosion Cracking

Quantity	Minimum	Maximum
Temperature, °C	--	50
Hydroxide, M	0.01	6.0
Nitrite, M	0.20	--
Nitrate, M	--	5.5
Nitrite/Nitrate Ratio	0.15	--
Pitting Factor	1.2	--

The effect of utilizing the pitting factor during sludge batch washing that includes the ABD stream was investigated with the 0.6 M and 1.2 M excess hydroxide cases. For this evaluation, the nitrite addition was reduced to 40,000 gallons or approximately the same as the addition for the no ABD stream. The amount of hydroxide added was the same as for the previously considered 0.6 M and 1.2 M excess caustic cases. Table 3-12 shows the influence on the sludge batch operation, while Table 3-13 shows the final composition and the pitting factor. Table 3-13 indicates that these cases exceed the minimum required pitting factor and the minimum nitrite concentration. The requirement for the minimum nitrite concentration is the primary factor in determining the volume of nitrite that needed to be added. However, it can be concluded from Table 3-12 that utilization of the pitting factor methodology in the future would likely make the influence of the addition of the ABD stream to the sludge batch flowsheet negligible in comparison to the current flowsheet that is under the present corrosion control program.

Table 3-12. Evaluation of the Influence of the ABD Stream on Sludge Batch Washing with Pitting Factor

	No ABD Stream Case	0.6 M Excess Caustic Case	1.2 M Excess Caustic Case
Decant Volume	1,377,389	1,415,173	1,421,276
Number of decants	12	13	13
Total settle days for the tank	196	296	294
Gallons of NaOH solution added	22,000	17,500	13,000
Gallons of $NaNO_2$ solution added	31,656	40,000	35,000

Table 3-13. Influence of the ABD Stream on the Final Tank 51 Waste Chemistry with Pitting Factor

	0.6 M Excess Caustic Case	1.2 M Excess Caustic Case
Hydroxide (M)	0.39	0.4
Nitrite (M)	0.25	0.22
Nitrate (M)	0.3	0.3
Pitting Factor	11.8	11.9

The final tank to consider for CSTF is the DWPF feed tank, Tank 40. The composition in this tank becomes essentially the composition of the feed preparation tank at the completion of sludge batch washing. Thus, this tank will be in compliance with the present corrosion control program as well as for the program with pitting factor methodology. For the evaluation, the final composition of Tank 51 for the 0.6 M excess caustic was compared with the average composition of Tank 40 over the past 20 years it has been in service as the DWPF feed tank (see Table 3-14). The difference between the average and the projected composition of Tank 40 with ABD is essentially negligible. Thus, no change in the corrosion behavior of the tank would be anticipated due to addition of ABD to the CSTF flowsheet.

Finally, a dedicated receipt tank in CSTF would mitigate operational delays in HCAN and provide additional storage space for dissolved SNF.[1] Without a dedicated receipt tank, HCAN may be limited to only dissolving 14 batches/yr versus 18 batches/yr and have a one-month time frame to transfer the entire ABD batch directly to the sludge batch. The receipt tank concept is viable; however, the tank will need to be pre-conditioned with nitrite inhibitor in order to ensure that the tank contents meet the corrosion control program.

Table 3-14. Comparison of Average Tank 40 Composition with Anticipated Tank 40 Composition with ABD

	Average Tank 40 Composition Since 2001	0.6 M Excess Caustic Case with ABD	1.2 M Excess Caustic Case with ABD
Hydroxide (M)	0.21	0.25	0.26
Nitrite (M)	0.30	0.36	0.36
Nitrate (M)	0.12	0.20	0.20
Nitrite/Nitrate Ratio	2.50	1.8	1.8

To evaluate how much nitrite would be needed to pre-condition the supernate in the dedicated receipt tank such that the solution will be in compliance with the corrosion control program after the transfer of the ABD stream, the 0.6 M and 1.2 M excess caustic cases were investigated. The volume and concentration of the ABD stream for both cases were obtained from Table 3-6. Table 3-15 shows the final supernate concentrations for the key corrosion components after the addition of 40 wt. % sodium nitrite additions were made for corrosion inhibition. Sufficient nitrite was added so that for each case the inhibitor concentration exceeded the requirement by 10-20%.The results from the table indicate that the dedicated feed tank would need approximately 18,000 gallons of 40 wt. % sodium nitrite for each 18-month of 0.6 M excess caustic ABD addition in order comply with the corrosion control requirements, while only 3000 gallons of 40 wt.% nitrite would be sufficient with a 1.2 M excess caustic. Thus, for a dedicated tank, the amount of inhibitor addition is clearly minimized by maintaining the excess caustic at 1.2 M.

Table 3-15. Evaluation of Nitrite Addition for Dedicated CSTF Receipt Tank

Excess Hydroxide (M)	40 wt.% Nitrite volume added (gal)	Final Concentrations in Dedicated Tank Following Nitrite Addition		
		Nitrate (M)	Nitrite (M)	Hydroxide (M)
0.6	18,000	3.95	0.73	0.52
1.2	3,000	4.17	1.15	0.13

3.2.2 Waste Chemistry and Properties

In addition to the concern that reduced neutralization will accelerate corrosion, the chemical and physical properties of the slurry have a significant influence on slurry rheology and particle settling. A typical sludge batch will have approximately ten settling periods, so a slow settling sludge can significantly slow the preparation of a sludge batch. So, the potential changes to the waste chemistry and properties as they influence the processes in CSTF will be summarized in this section.

3.2.2.1 Chemical and Physical Differences of Freshly Precipitated Sludge

The bulk of the high-level waste (HLW) in the SRS waste tanks was produced between 1954 and 1992, when the last production reactor was permanently shut down. As a result, much of the HLW has been in storage for 30-65 years.

Fresh sludge is coprecipitated by adding sodium hydroxide to a very acidic nitric acid and metal nitrate solution. Most of the metals precipitate as insoluble solids in the slurry, which is a mixture of hydrous metal oxide phases (containing metals (M) such as iron, aluminum, manganese and uranium), amorphous metal hydroxides $M(OH)_x$(am) or hydrous metal oxides MO_x (am,hyd).[24] The freshly precipitated sludge usually contains small particles, typically 2 microns and smaller. Two studies[25,26] looked at impact of parameters such as initial metal nitrate solution molarity and final free hydroxide molarity on particle size. These small particles can make the slurry rheologically thicker, increase foaminess, and are more reactive than larger particles.

During the decades of storage, Ostwald ripening has and will continue to transform the metal oxides MO_x (am,hyd) to a more crystalline form of metal oxides, MO_x (c). Ostwald ripening changes both the particle size and the reactivity of the insoluble metal oxides and hydroxides as the Ostwald ripening leads to larger particles and less reactive metal oxides as the slurry ages. In general, the slurry becomes thinner rheologically as the particle size increases.[27] In addition, fine particles produce more foam during evaporation and more air entrainment during mixing than larger particles.[28] Additionally, as the rheology of the systems moves from smaller particles to larger particles with Ostwald ripening, the system rheology can be greatly impacted.[29]

3.2.2.2 Processing Implications of Chemical and Physical Differences Due to Reduced Neutralization

As was discussed previously, reduced neutralization would lead to less free hydroxide in the freshly precipitated slurry that will be produced from ABD. The ABD slurry will be transferred to a sludge preparation tank, where it will be blended with sludge from other HLW tanks. The addition of the ABD slurry will increase the nitrate concentration in the tank. Also, additional nitrite will be added to comply with current corrosion control requirements.

Because the resulting mixture is high in aluminum, additional sodium hydroxide will be added to dissolve as much aluminum as feasible. Note the additional sodium hydroxide mass added is much higher than the sodium hydroxide saved by the reduced neutralization.[30] Low temperature Aluminum Dissolution (LTAD) will take place in Tank 42 or 51, the two sludge preparation tanks. During LTAD, aluminum is slowly dissolved, and the soluble aluminum can be removed through washing and decanting. The removal of 20-80% of the aluminum lowers the number of canisters that will be produced from that sludge batch. The resulting washed slurry has a fairly low yield stress (2.5 Pa) but a high plastic viscosity (27 cP) leading to a slurry that likely will settle slowly.[31]

After the LTAD processing is complete, the sludge will be washed from 4-8 M Na to reach the washed sludge supernate Na target, typically about 1 M. Because of the large addition of sodium hydroxide for LTAD processing, the nitrate and nitrite are a smaller fraction of the anions compared to the free hydroxide.

The presence of slurry from ABD will likely have only a minor impact on slurry rheology and settling time because it is a minor fraction of the sludge insoluble solids mass. In addition, the freshly precipitated aluminum in the ABD slurry is predominantly gibbsite and not boehmite as it won't have had as much time for Ostwald ripening. Gibbsite is much easier to dissolve than Boehmite in a caustic solution[32] so likely will have a higher Al dissolution efficiency.

3.3 DWPF

3.3.1 Corrosion Assessment

The materials of construction for the DWPF are primarily 304L stainless steel and a nickel-based alloy, C-276. The facility receives waste from Tank 40 and then acidifies the waste in the Chemical Process Cell (CPC) before sending the sludge slurry/glass frit mixture to the melter for vitrification. Given that the Tank 40 DWPF chemistry is not significantly altered from the previous 20 years of service, the influence of the ABD stream on the corrosion of DWPF materials is expected to be minimal. This conclusion is expected to be valid for both the formic acid and the glycolic acid flowsheets.[33]

3.3.2 Waste Chemistry and Properties

As was discussed in the section on Waste Chemistry and Properties (section 3.2.2), the addition of the ABD slurry is expected to have minor changes on the chemistry and rheology of the washed sludge that will be fed to DWPF. This section will discuss implications of the ABD slurry on DWPF processing and will also recommend testing that will be needed to ensure the sludge containing the ABD slurry can be processed in the Sludge Receipt and Adjustment Tank (SRAT) and Slurry Mix Evaporator (SME) in DWPF and can be fed to the melter.

Because each sludge batch is distinctly different due to changes in composition and particle size, each sludge batch is qualified prior to use in DWPF. A flowsheet and a frit are developed for each sludge batch using modeling, simulant testing[34] and actual waste testing.[35] Each future sludge batch is expected to use modeling, simulant testing and actual waste testing to develop the optimum frit for glass processing and quality along with sludge processing in the CPC. Modeling and testing need to be completed using predicted, simulant and actual waste sludge containing ABD sludge to ensure the sludge can be efficiently and safely processed in DWPF.

3.3.2.1 Chemistry Changes in Processing Sludge in DWPF

Future processing in DWPF is expected to include the processing of washed sludge along with two streams from the Salt Waste Processing Facility (SWPF), namely the Sludge Slurry Receipt Tank (SSRT) and Strip Effluent Hold Tank (SEHT) using the nitric-glycolic acid flowsheet.[36]

Chemical processing in the CPC involves the blending of the sludge, SSRT, and SEHT together with nitric acid, glycolic acid and frit. Evaporation of the slurry is needed to remove the excess water added with each stream and to minimize the water in the DWPF melter feed. Nitric and glycolic acid is added to achieve the following processing objectives:

- Reduce the slurry pH from ~13 to ~5 using both an oxidizing and reducing acid
    - Destroy nitrite (leads to NO, NO_2 and N_2O generation)
    - Destroy carbonate (leads to CO_2 generation)
    - Reduce HgO to Hg^0
    - Reduce MnO_2 from Mn^{4+} to Mn^{2+}
    - Thin the slurry rheologically by dissolving and complexing metals (Mn)
    - Produce a melter feed that is Reduction/Oxidation (REDOX) balanced
- Remove water from the slurry through evaporation
    - Maintain maximum freeboard in processing vessels
    - Minimize water fed to the melter
    - Remove mercury from slurry by steam stripping

The chemistry of the nitric-glycolic acid flowsheet has been studied in over 100 experiments. A document summarizing the chemistry during CPC processing was issued, including the equations for anion destruction needed for predicting nitrate, nitrite, glycolate, oxalate and oxalate conversion needed for predicting the REDOX of the melter feed.[37] SRNL has developed an acid calculation spreadsheet, which is used for performing these predictions using the CPC chemistry equations. This spreadsheet was used in this analysis based on the predicted composition of the SB11 Tank 40 slurry after washing, with and without added ABD slurry. In addition, there was a prediction for washed Tank 40 slurry with added ABD slurry if produced at 0.6 and 1.2 M supernate sodium endpoints. The predicted composition of the Tank 40 washed sludge fed to DWPF is summarized in Table 3-16.

The bottom of Table 3-16 summarizes the supernate density, supernate anion, and supernate cation chemistry. Because aluminum will be removed first through the LTAD process, then the slurry will be washed down to the 1 M supernate sodium target, the supernate portion of the three scenarios is almost identical. As a result, the CPC acid demand for free hydroxide and carbonate will be almost identical.

The primary differences in the resulting sludges in Table 3-17 is that sludges with ABD will have a 10% higher volume, an insoluble solids mass about 7% higher and a total solids mass about 10% higher. There is really no difference between the two slurries produced targeting 0.6 and 1.2 M Na. As a result, the discussions below will focus on the difference in processing due to the increased insoluble solids in the slurry with ABD.

The ABD slurry is chemically very similar to the sludge in the SRAT sludge tanks. In other words, the ABD slurry, like SRS sludge, will be high in sodium, aluminum, manganese, uranium, nickel and magnesium. Most of the insoluble solids are inert during CPC processing so they are not reduced or dissolved by nitric and glycolic acid addition. The main exception is manganese, which can be easily reduced due to the glycolic acid addition. Although the two slurries are chemically very similar, the fresh precipitation of manganese from the ABD slurry, assuming Mn is used as a neutron poison, is more reactive than Mn that has been in storage for decades. The result is that the addition of nitric and glycolic acid may lead to faster and more extensive dissolution of Mn from the ABD slurry than the Mn from the aged sludge. Since the ABD slurry makes up less than 10% of the insoluble solids, there won't be a change unless Mn is used as the neutron poison. Testing is planned to determine whether Gd is a better poison for DWPF than Mn.[38] Note that the data in Table 3-17 uses the data from Table 3-16 converted to the inputs expected by the DWPF Acid Calculation Spreadsheet.

The composition of the SRAT product, as predicted by the DWPF Acid Calculation Spreadsheet, is summarized in Table 3-18. Note that the final composition of both the 0.6 M and 1.2 M Na cases are nearly identical so the reduced neutralization has essentially no impact on the composition of the SRAT product in DWPF.

Table 3-16. Projected Composition of SB10 Tank 40 Feed to DWPF

Added ABD?	**No**	**Yes**	**Yes**
ABD Wash Endpoint	**NA**	**0.6 M Na**	**1.2 M Na**
Supernate volume (gal)	758,000	760,000	760,000
sludge volume (gal)	46,300	51,300	51,400
Total Slurry volume (gal)	804,000	812,000	811,000
Total Volume (L)	3,043,000	3,072,000	3,070,000
Total Mass (kg)	3,276,000	3,345,000	3,344,000
Mass Total solids (kg)	459,000	534,000	536,000
Mass Insoluble Solids (kg)	286066	346,962	349,006
Total Solids (wt. %)	14.02	15.97	16.02
Insoluble solids (wt. %)	8.73	10.37	10.44
Slurry density (kg/L)	1.0765	1.0887	1.0893
Supernate density (kg/L)	1.0426	1.0416	1.0417
Supernate Na^+ (M)	0.9892	0.9899	0.9897
Supernate K^+ (M)	0.0017	0.0011	0.0011
Supernate NO_2^- (M)	0.2387	0.3665	0.3627
Supernate NO_3^- (M)	0.1267	0.2001	0.2005
Supernate OH^- (M)	0.3934	0.2551	0.2582
Supernate Cl^- (M)	0.0011	0.0008	0.0008
Supernate SO_4^{-2} (M)	0.0174	0.0115	0.0115
Supernate F^- (M)	0.0008	0.0006	0.0006
Supernate CO_3^{-2} (M)	0.0568	0.0441	0.0441
Supernate AlO_2^{-2} (M)	0.0430	0.0291	0.0292
Supernate $C_2O_4^{-2}$ (M)	0.0105	0.0086	0.0087
Supernate PO_4^{-3} (M)	0.0004	0.0003	0.0003

Table 3-17. SRAT Conditions and Analyses

Parameter	0.6 M Na	1.2 M Na
Volume [gal]	7,638	7,638
Slurry density [g/mL]	1.089	1.089
Dried Solids [wt. %]	15.97	16.02
Base Equivalents [eq/L]	0.255	0.258
Nitrite [ppm]	15,487	15,318
Mercury [ppm]	2,339	2,319
Manganese [wt. % solids]	4.43	4.40
TIC [ppm]	487	486
Formate [ppm]	0	0
Glycolate [ppm]	0	0
Nitrate [ppm]	11,396	11,413
Oxalate [ppm]	695	2,359
Carbon [ppm solids]	0	0

Table 3-18. SRAT Product Analyses for REDOX

SRAT Product	0.6 M Na	1.2 M Na
Nitrate	35,300 ppm	35,500 ppm
Glycolate	19,900 ppm	19,900 ppm
Oxalate	238 ppm	331 ppm
Formate	548 ppm	548 ppm
Nitrite	0 ppm	0 ppm
Manganese	8,670 ppm	8,620 ppm
Mercury in SRAT Product at target	985 ppm	988 ppm

3.3.2.2 Rheology Implications of Reduced Neutralization

Rheology is a physical property of slurry simulants and actual waste, which is studied to ensure the slurry can be pumped and mixed as needed for processing. The particle size, particle morphology, particle distribution, and particle to particle interactions all impact the settling and rheology of the slurry.[39] The rheology of both simulants and actual waste has been extensively studied.[40] Typically, the actual waste is thicker rheologically than chemical simulants used in SRNL testing.

There are three places that slurry rheology is important. First, the freshly precipitated slurry in HCAN must be thin enough rheologically that the slurry can be transferred from HCAN to a sludge tank in the Tank Farm. Second, the slurry rheology must be thin enough and the solids settle fast enough during LTAD and sludge washing that it can be mixed and washed effectively and later transferred to Tank 40, the Low Point Pump Pit Sludge Tank and the SRAT. Third, the slurry is chemically treated in DWPF to thin the slurry to allow maximum concentration of feed for the DWPF melter. The rheology of the slurry in DWPF must be thin enough to allow good mixing in the processing vessels so that the slurry can be sampled and transferred as needed.

Because simulant rheology predictions for the waste have been poor throughout the life of DWPF, it is recommended to measure the rheology of radioactive waste and not rely solely on simulants for rheology predictions. The best way to ensure the rheology is acceptable is to complete the processing steps outlined above and measure the rheology after each step using samples of tank waste in the SRNL shielded cells.

An alternate is for the Tank Farm to provide a sample from the sludge preparation tank or Tank 40 after washing is complete. However, a Tank 40 sample will not ensure that the HCAN rheology is acceptable or the rheology and settling during LTAD and sludge washing is acceptable.
Assuming that Gd is used as the neutron poison to protect the waste in HCAN, the Tank Farm and DWPF (as requested in a Task Technical Request[41]), it is unlikely that the reduced neutralization in HCAN will have any influence on the rheology of the slurry in HCAN, in the Tank Farm or in DWPF. This is because Gd is a much more effective neutron poison (Mn:U-235≥ 70:1, Gd:U-235 ≥ 1:1)[42,43] and very little is needed as a poison. If future sludge batch testing identifies any rheology issues, the preparation of the slurry in HCAN, the LTAD and sludge washing or the processing in DWPF can be modified to ensure effective processing for future sludge batches.

If manganese or iron is used as the neutron poison to protect the waste in DWPF, a large addition of manganese or iron may be needed.[42,43] This large addition will not only increase the mass of insoluble solids that will be processed in DWPF, but it also has a potential to negatively alter the rheology of the slurry and the particle settling. Radioactive waste testing from HCAN to DWPF should be performed to ensure the waste can be mixed, transferred and processed through DWPF.

3.3.2.3 Other Processing Implications of Reduced Neutralization

Foaming is another physical property that might impact processing in DWPF. Foam can be formed during periods of high gas generation (during or just after acid addition or during boiling) in the SRAT or SME. Foaming in DWPF is not caused by the presence of a surfactant, but by uniformly sized small particles stabilizing the foam bubbles.[44] Like rheology, there is more foaming during processing of radioactive waste than in processing with simulants. Antifoam is added during processing to control the foam. Antifoam performance has been problematic due to chemical destruction of the antifoam during processing steps where the pH is not 6.5-7.5.[45] A new antifoam has been recommended to DWPF because of its superior performance across the wide pH range of processing in DWPF (pH 4.5-13)[46] and may mitigate any increase in foaminess due to the ABD slurry addition. It is unlikely that the reduced neutralization in HCAN will have any influence on foaminess in DWPF.

3.3.2.4 Recommended Testing

Actual waste testing for each sludge batch is recommended from HCAN through DWPF. This testing would ensure that the chemical and physical properties of the slurry (rheology, settling rate, foaming) are acceptable for transfer, mixing, and processing from HCAN through DWPF. It is recommended to measure the rheology and settling behavior of the freshly precipitated ABD, ABD combined with sludge, and then process the sludge through prototypic SRAT and SME cycles. Samples should be taking to track the poison and fissile solubility, hydrogen generation, and other parameters needed for processing.

4.0 Conclusions

The purpose of the reduced neutralization investigation was to allow HCAN processing flexibility, while not negatively influencing the overall flowsheet (CSTF and DWPF) from the standpoint of either corrosion control protection or waste chemistry properties. The following conclusions were made from the evaluation:

HCAN

- A two-fold reduction in the excess caustic added decreases the NaOH neutralization volume by 10%.
- The reduction in excess caustic is not expected to alter the corrosion behavior of the stainless steel equipment in HCAN.
- Freshly precipitated sludge typically has a smaller particle size and the aluminum is precipitated as gibbsite and not boehmite. The resulting slurry tends to be thicker rheologically, foamier and more reactive than the aged sludge that it will be combined with in the CSTF.

CSTF

- Corrosion prevention in the CSTF can be managed without significant processing changes or increases in volumes.
- The ABD stream increases the amount of sodium nitrite necessary to prevent corrosion during sludge batch washing. The nitrite required however, could be reduced by implementation of the Hanford Pitting Factor approach.
- Reducing the excess caustic requires more sodium hydroxide addition to the feed preparation tank to ensure aluminum dissolution.
- If a dedicated receipt tank is used for the ABD stream in CSTF, sodium nitrite inhibitor will need to be added to the tank prior to transfer of the ABD stream to ensure corrosion prevention. Less inhibitor will be required if the excess caustic concentration is maintained at 1.2 M.

DWPF

- The projected chemistry of sludge batch feed tank in CSTF, Tank 40, after the addition of the ABD stream is not expected to change significantly. Therefore, the ABD stream is not anticipated to have an influence on the corrosion behavior in DWPF.
- Use of Gd instead of Mn as the DWPF poison will have a bigger influence on SRAT processing as much less added Gd is needed than Mn.
- Reduced neutralization is not expected to alter DWPF processing significantly.

In summary, the reduction in excess caustic may be managed in a way that does not significantly impact the corrosion scheme for the facilities; however, the amount of caustic that is added does not significantly change by reducing the excess caustic. The evaluation did emphasize the benefit of utilizing the Hanford Pitting Factor corrosion scheme for managing corrosion control in the CSTF. Similarly, when considering the impact on the physical properties of the waste, a reduction in the excess caustic may be manageable at the CSTF source. However, it is possible that the volume of caustic necessary for a downstream facility is far greater than the volume recovered in HCAN. It is clear from this evaluation that the benefits of reducing the excess caustic in HCAN will need to be balanced with the benefits of adding caustic downstream.

5.0 Recommendations

In order to ensure waste will be processable in the tank farm and DWPF, the following is recommended

- Radioactive waste testing for each sludge batch is recommended from HCAN through DWPF. This would ensure that the chemical and physical properties (rheology, settling rate, foaming) of the slurry is acceptable for transfer, mixing, and processing from HCAN through DWPF.
- Measure the rheology and settling behavior of the freshly precipitated ABD, ABD combined with sludge, and then process the sludge through prototypic SRAT and SME cycles.
- Samples should be taking to track the poison and fissile solubility, hydrogen generation, REDOX and other parameters needed for processing.
- Use of Gd as poison adds less mass, requires less NaOH neutralization and results in lower volume of waste.
- Use of Hanford Pitting Factor approach to corrosion inhibition reduces the amount of nitrite inhibitor needed during sludge batch washing.

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