Flowsheet for SRS Waste Tank Heel Removal Using Oxalic Acid

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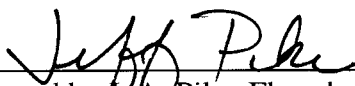
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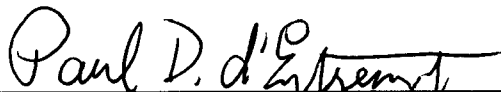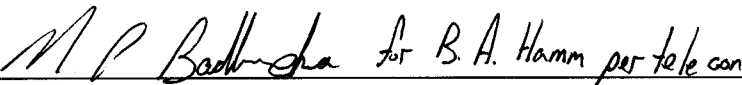
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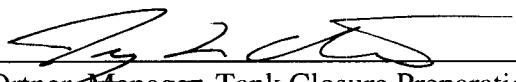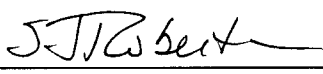
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SUMMARY

After bulk sludge removal, the remaining sludge heel from Savannah River Site (SRS) waste tanks may need to be removed to meet final tank closure requirements. Oxalic acid will dissolve most of the material in the heel, which can be pumped out of the tank. An integrated High Level Waste (HLW) system process flowsheet is presented in this report as the preferred method of disposal of the spent acid solution using existing facilities (see section 4.9.3). The preferred flowsheet includes recommended amount of oxalic acid based on sludge heel composition.

Sludge heel cleaning with oxalic acid essentially results in two streams that need to be dispositioned. The first is the neutralized supernatant liquid stream and the second is the sludge with the precipitated metal oxalate solids slurry stream. The preferred flowsheet calls for the supernatant to be added to an evaporator drop tank and subsequent disposal with the saltcake heel. The solids slurry would be added to a washed sludge batch and subsequent disposal with a sludge batch to the Defense Waste Processing Facility (DWPF).

Based on the preferred flowsheet and data from sludge batch 3 qualification tests, the following conclusions are made for planning purposes concerning the effect on DWPF:

- Sodium oxalate from the solids slurry can be added to a sludge batch without affecting the number of canisters produced.

- The feed to the SRAT can tolerate up to 26 wt% sodium oxalate in total solids.

- Increasing metal oxalate in the feed to the SRAT increases formic and nitric acid consumption, thus, increasing SRAT cycle time and altering melter redox.

- Glass quality limits the total amount of sodium in a batch without increase the number of canisters produced.

- Using past experience with sludge batch 3 to calculate a general planning guide, the maximum sodium content in a sludge batch could be 1.4 M sodium.

- If sludge processing washes the soluble sodium content to about 1 M, the sludge batch can contain about 10 wt% of total solids as sodium oxalate before increasing the number of canisters produced or changing sludge processing.

- If all of the metal oxalate becomes part of a sludge batch, about 26,000 to 38,000 kg sodium oxalate is added to the sludge batch per 5000 gallon sludge tank heel processed.

- 10 wt% sodium oxalate in total solids amounts to disposal of 1 to 6 sludge heels depending on waste type of sludge heel cleaned and specific sludge batch.

- Using past experience with sludge batch 3 qualification testing as general planning guide, feed rheology during mixing and transfer in DWPF, melter flammability, and melter feed rates remain within acceptable ranges with added sodium oxalate to a

sludge batch. Existing sludge batch qualification testing will determine any actual effects that can not be predicted based on composition estimates alone.

- Solid slurries from tank heel cleaning should be added to sludge batches in relatively small batches, i.e. bled into the DWPF feed stream at a relatively low rate.

- Solid slurry additions from heel cleaning should be included in future sludge batch planning.

The following conclusions are made concerning the effect on the Tank Farm waste storage and evaporator systems:

- Planned salt dissolution will send about 14,000 kg of dissolved sodium oxalate per 1,000,000 gallons of saltcake, all of which currently exists in the saltcake, to the salt waste processing facilities and eventually to the Saltstone Facility.

- All sodium oxalate added to an evaporator drop tank will remain in the drop tank.

- Planned bulk saltcake dissolution will remove none of the added sodium oxalate to an evaporator drop tank, thus, becoming part of the salt heel.

- Sodium oxalate in the salt heel could be dissolved at a very low total sodium concentration, but none of the existing salt waste processes include this stream as a design basis feed stream. A process will need to be developed to treat/remove the heel.

If this flowsheet is changed such that the generated solids slurry from the acid cleaning is added to an unwashed sludge batch and the liquid decant is transferred to the evaporator feed tank, then:

- Sludge processing will wash most of the sodium oxalate from the sludge batch.

- Sludge processing can tolerate sodium oxalate generated from two to three 5000-gallon sludge heel cleanings before accumulating solid sodium oxalate in the sludge batch.

- The evaporator feed tank will accumulate most of the sodium oxalate from any number of sludge heels processed and transferred into the tank.

- The sludge batch that includes the evaporator feed tank sludge will have a large amount of sodium oxalate, which may require an alternate frit formulation and, possibly, modification to the process at DWPF to avoid introducing criticality concerns with the dissolution of iron.

- After processing several sludge heels, approximately 60,000 kg of sodium oxalate will return to the evaporator feed tank when the sludge from the evaporator feed tank is washed as part of sludge processing. An alternate method of disposal would need to be used or developed.

- High sodium oxalate content in the evaporator feed tank causes excessive foaming in the evaporator pot. Current use of defoaming agents would need to be evaluated and adjusted to avoid foaming problems.

If the flowsheet is changed such that the generated solids slurry from the acid cleaning is added to an unwashed sludge batch and the liquid decant is transferred to the evaporator drop tank, then:

- Practically all the sodium oxalate remains in the drop tank as part of the salt heel.

- Dissolving and disposing of the sodium oxalate via the Saltstone Facility results in about 250,000 gallons of 0.5 M sodium feed to the Saltstone Facility per 5000 gallon sludge heel processed.

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Flowsheet for SRS Waste Tank Heel Removal Using Oxalic Acid

By J. A. Pike, N. P. Badheka, and E. T. Ketusky

1 Introduction

Waste removal from Savannah River Site (SRS) waste tanks starts with bulk waste removal. The remaining sludge heel needs to be removed to meet final tank closure requirements. One potential method of heel removal is dissolving the residual heel with oxalic acid. The spent acid solution will be sent to existing waste facilities. This report describes the process flowsheet and effects on downstream waste processing.

2 Background

2.1 Waste Generation

Since SRS began operations in the early 1950s, the Tank Farms have received and managed high-level radioactive liquid wastes generated by uranium and plutonium recovery processing. Currently 37 million gallons of high level radioactive waste are stored in 49 underground tanks in the F-and H-Areas. The Department of Energy (DOE) intends to remove these high-level waste (HLW) tanks from service as they complete their missions.

The waste from the recovery process is acidic. Immediately before transfer to a HLW tank, the acidic waste is treated with sodium hydroxide to increase pH above 12. The high pH waste form precipitates most of the dissolved metals in a sludge slurry that settles to the bottom of the receipt tank. The decanted supernate is concentrated by evaporation to produce solid salt precipitates. The resulting saltcake is later dissolved with water for further processing. Insoluble solids that settle to the bottom of the waste receipt tank are slurried using hydraulic slurrying techniques and sent to sludge processing. In sludge processing, the sludge slurry is washed with water to reduce its soluble salt content. The spent wash water from this process is returned to the tank farm for evaporation. The washed sludge is sent to the Defense Waste Processing Facility (DWPF) for vitrification.

2.2 Waste Removal

The following background on the waste removal program is substantially extracted from pertinent sections of reference 1. There are essentially seven broad functional areas that are important to the waste removal program. They are as follows:

Functional Areas

1. Bulk Salt Removal
2. Bulk Sludge Removal
3. Spray Washing (if needed)
4. Heel Removal
5. Annulus Cleaning (if needed)
6. Tank Isolation
7. Tank Closure

Each functional area is briefly discussed in the following sections.

2.2.1 Bulk Salt Removal

The saltcake consists primarily of water soluble sodium nitrate with sodium carbonate, sodium aluminate, sodium sulfate, and small amounts of several other moderate to low solubility salts such as sodium phosphate and sodium oxalate. The saltcake also contains a small amount of sludge-like material.

In the bulk salt removal program, the salt is typically dissolved with water and transferred from the tank as a concentrated solution. The majority of the salt waste contained in a tank will be removed as part of the bulk salt removal program.

Bulk salt removal will remove most of the soluble salts leaving low solubility salts and sludge-like solids as part of the salt heel.

2.2.2 Bulk Sludge Removal

Sludge is a dark brown, sticky material which forms from oxides and hydroxides of iron, aluminum, manganese and other metals. This sludge has compacted over time into a solid mass which is somewhat difficult to remove from the tanks.

In the bulk sludge removal program, centrifugal pumps (slurry pumps) are used to generate powerful jets of liquid directed out of two opposing nozzles. The fluid jets impinge upon the sludge and entrain the particles into the high-velocity jet fluid, thereby causing suspension (mixing) of the sludge. The sludge slurry is transferred from the tank using a transfer pump at a nominal rate of 100 gpm. The majority of the sludge waste contained in a tank will be removed as part of the bulk sludge removal program.

Although hydraulic slurrying is an effective waste removal method, there will still be an amount of waste which is not easily removed using this technique. This residual waste is termed the 'sludge heel'.

2.2.3 Spray Washing

The purpose of spray washing is to remove waste material from the tank walls and internal equipment. This step may be performed at any logical point in a tank treatment schedule. If sludge-like solids will be removed during spray washing, the spray washing will be performed prior to the final sludge transfer out of the tank. If the material to be removed is mainly liquid or soluble salts, spray washing will be performed before the final transfer out of the tank.

2.2.4 Heel Removal

The purpose of the heel removal program is to remove material left after the end of the bulk waste removal step and prior to the tank isolation step. Both sludge and saltcake heels may need to be cleaned.

Chemical treatment of sludge heels may be used to dissolve the remaining material with oxalic acid that can not be removed by mechanical agitation. Optionally, partial dissolution may be attempted in order to change the physical properties such as average particle size, thus, resulting in easier to slurry solids.

Saltcake heels may need additional large volume water dissolution steps to remove low solubility salts in the heel. The remaining material will likely resemble and behave like a sludge tank heel and further removal may proceed in a manner similar to sludge tank heels.

2.2.5 Annulus Cleaning

The purpose of annulus cleaning is to remove waste leaked from the tank primary to the tank secondary containment. The need for this cleaning will depend on the concentration and volume of radionuclides in the leaked material.

2.2.6 Tank Isolation

The purpose of tank isolation is to physically disconnect the tank from the tank farm so that the tank can be placed in the "removed from service" mode of operation.

2.2.7 Tank Closure

The purpose of tank closure is to fill the waste tank with a grout mixture so that it will be in a stable condition for long term monitoring.

2.3 Heel Removal Process Conditions and Options

The following sections provide a description of the various types of heel removal evolutions

and the plan or options available for each. Most of this information was extracted from pertinent sections of reference 1.

2.3.1 Salt Heel Removal

The saltcake heel after bulk salt dissolution is assumed to consist primarily of sludge-like materials with some low solubility salts. The plan for salt heel removal is to add water to the low solubility salts and allow them to dissolve. The resulting salt solution will contain relatively low total salt content and will be transferred from the tank to a down stream process. Agitation will increase the rate of salt dissolution and may be used if available. The remaining material will likely be sludge-like solids that will not dissolve in water or readily transfer out with the installed mixing and transfer equipment. The remaining heel may be processed like a sludge heel if needed to achieve tank closure requirements.

2.3.2 Mixed Salt/Sludge Heel Removal

The plan for mixed salt-sludge heel removal is to add water and dissolve the salt portion of the heel to the extent practicable. Agitation will most likely be required to mix the water and salt/sludge. The remaining salt-sludge will be processed as sludge heel material.

2.3.3 Sludge Heel Removal

There are three options for the removal of the sludge heel, as follows:

Sludge Heel Removal Option 1. Hydraulic Slurrying

The sludge could be removed using traditional hydraulic slurrying methods. Tank farm operations to enhance sludge removal include lancing with a water jet and indexing the slurry pump discharge to disrupt highly cohesive sludge mounds. These traditional methods are effective and will be considered for sludge heel removal, especially when large volumes of sludge remain after the official completion of bulk sludge removal. These methods have limitations due to internal interferences, such as cooling coils and roof support columns, and limited accessibility through existing tank riser openings.

Sludge Heel Removal Option 2. Acid Dissolution

The second option is to chemically treat the sludge heel with an acid to dissolve the sludge. This acid dissolution process uses oxalic acid to dissolve a significant amount of iron, aluminum and manganese from the sludge. Limited agitation will be required for the acid dissolution process in order to keep a supply of fresh acid in contact with the sludge surfaces.[2] The dissolved sludge in the acid solution will be transferred out of the tank using a transfer pump.

4

Acid dissolution generates a significant amount of waste solution that will have to be processed through the high level waste system. Therefore, it is beneficial to minimize the volume of acid that has to be used in the process.

Sludge Heel Removal Option 3. Combined Hydraulic Slurrying and Acid Dissolution

The third option combines the acid dissolution of the sludge with hydraulic slurrying of the sludge. This combination can be expected to be more effective than either method alone. The dissolution of the sludge can be expected to generate cracks in the surface of the sludge. The breakup of highly cohesive sludges involves a mechanism of crack propagation that can be enhanced with vigorous agitation. The dissolved sludge in the spent acid solution and the undissolved sludge that was physically incorporated into the sludge slurry will be transferred out of the tank using a transfer pump.

2.4   Acid Dissolution Process

In preparing the heel for chemical treatment, the sludge will be dewatered to the maximum extent practical. After each acid strike, the remaining heel will also be dewatered to the maximum extent practical.

3 Approach

The waste tank heel removal process is first translated to a process flowsheet description. Second, interfaces with existing processes and baseline process conditions are established. A material balance is calculated with identified baseline conditions using an Environmental Simulation Program, Version 6.7®, licensed by OLI Systems, Inc. (OLI ESP) model. The material balance will estimate the composition of the interface streams to existing processes. In order to establish relative accuracy of the model, historical data from oxalic acid cleaning of Tank 16 will be compared to a model simulation of the cleaning process.

Using the results of the process material balance, the effects on downstream processes are determined using existing process models and evaluations.

Perturbation cases to the baseline will be established and calculated to determine if

- the effluent from heel dissolution process should be added to a washed sludge batch instead of an unwashed sludge batch, and

- the dissolved sludge heel can be neutralized with existing waste supernate instead of fresh sodium hydroxide.

4 Discussion

4.1   Process Description

For the purposes of this analysis the baseline heel dissolution process consists of the following steps:[1]

1. Charge neutralization tank with caustic adequate to neutralize entire acid batch.
2. Add oxalic acid to sludge heel tank, amount determined by process conditions.
3. Add water to establish operating height.
4. Start mixing device(s) and mix tank for 3 days.
5. Turn off mixer(s) or run at slower speed.
6. Transfer oxalic acid to neutralization tank (assume downcomer injects into liquid and no additional mixing is needed).
7. Repeat steps 2 through 6 twice more.
8. Settle in neutralization tank.
9. Decant neutralization tank to evaporator feed tank.
10. Mix neutralization tank to suspend solids.
11. Transfer suspended solids to sludge wash tank.

Figure 1 shows the process flow diagram in context with downstream processes. The flow diagram is divided into segments with process models. The unique heel removal portion of the flowsheet shown in Figure 1 includes streams 1 – 4, 6 – 8, and 13. The flow diagram is divided into segments:

- Heel Removal
- Sludge Washing
- Tank Farm Evaporation
- Salt Dissolution

Existing evaporator process[3,4] and sludge washing models[5] are used to model the respective portions of the flowsheet. The unique portion of the sludge heel dissolution process is modeled using OLI ESP software, Version 6.7. Other process effects are calculated separately and included in this analysis.

For this simulation, enough oxalic acid is added to the sludge heel to completely dissolve the heel to the extent practical. 100% molar excess oxalic acid is added to the sludge heel. This amount of oxalic acid creates a final solution that is likely to be concentrated enough to drive the dissolution reaction to completion within a reasonable duration.[2]
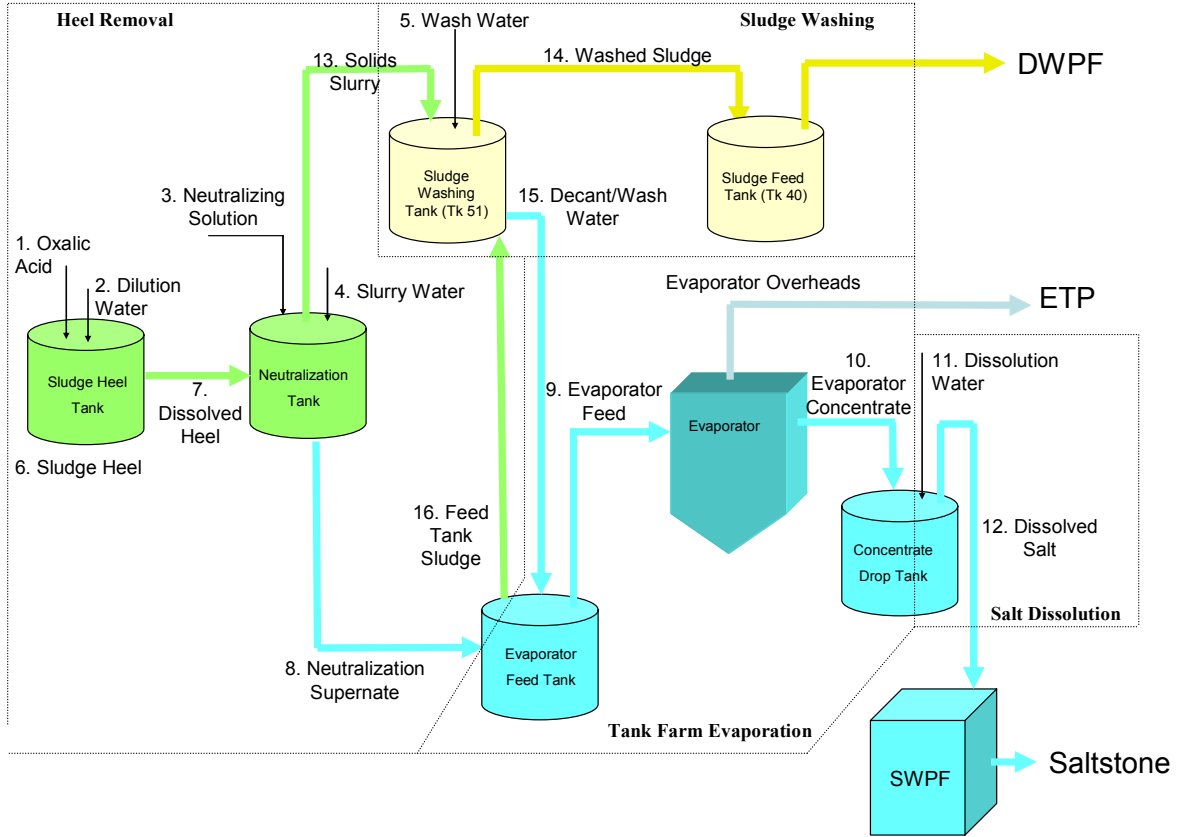
Figure 1: Heel Removal Flow Diagram

4.2   OLI ESP Estimation of Sodium Oxalate Solubility

The primary material formed using oxalic acid to clean the waste tanks will be metal oxalates, primarily sodium oxalate. Results of laboratory tests on waste simulants with sodium oxalate show how the solubility of sodium oxalate changes in different environments. Fowler ran tests where varying amounts of sodium nitrate was added to a 1 M sodium hydroxide solution.[6] An excess of sodium oxalate was then added to each solution and allowed to equilibrate. Fowler ran this test at three temperatures so the change in solubility with temperature can be estimated. Wiley ran the same tests at 21°C only, but conducted additional tests where the simulated solution consisted of sodium nitrate only.[7] Figure 2 shows Fowler's and Wiley's test results for two component simulated waste compared to an OLI ESP simulation of the same. The OLI ESP starts near 1 M total sodium since the simulated waste starts with a 1 M sodium hydroxide solution. OLI ESP consistently under predicts the solubility of sodium oxalate in these tests. Figure 3 shows Wiley's data for the sodium nitrate only tests compared to an OLI ESP simulation of the test. For the second series of test, OLI ESP also consistently under predicts the solubility of sodium oxalate. Section 4.10 includes a discussion comparing results of the OLI ESP model with historical date of oxalic acid cleaning in Tank 16.

The under prediction of sodium oxalate solubility will cause the OLI ESP model to predict that somewhat more solid sodium oxalate to precipitate in the neutralization tank. Since the solids slurry is predicted to contain a bit more sodium oxalate than would exist in reality, the amount of sodium oxalate predicted to go into a sludge batch is also slightly higher than reality. Thus, this model will conservatively estimate the magnitude of any effect on a sludge batch from each sludge heel processed.

Figure 4 shows curve fits by Kilpatrick to the results of Fowler and Wiley shown in Figure 2.[8] Figure 4 shows the data in Figure 2 plus solubility measurements by Wiley on a complex simulated waste solution with the additional components of sodium aluminate, sodium carbonate, and sodium sulfate. Figure 4 also includes test data obtained by Pareizs.[9] This last data set shows oxalate solubility in a complex simulated waste that also includes simulated sludge. The simulated supernate includes sodium salts of chloride, hydroxide, carbonate, nitrite, nitrate, and sulfate. Notice that all the data shows the sodium oxalate solubility is relatively insensitive to the anions in solution. The solubility can be estimated very well as a function of the total sodium concentration. Kilpatrick's equation 3 matches the measured data best, especially at the low sodium concentrations.
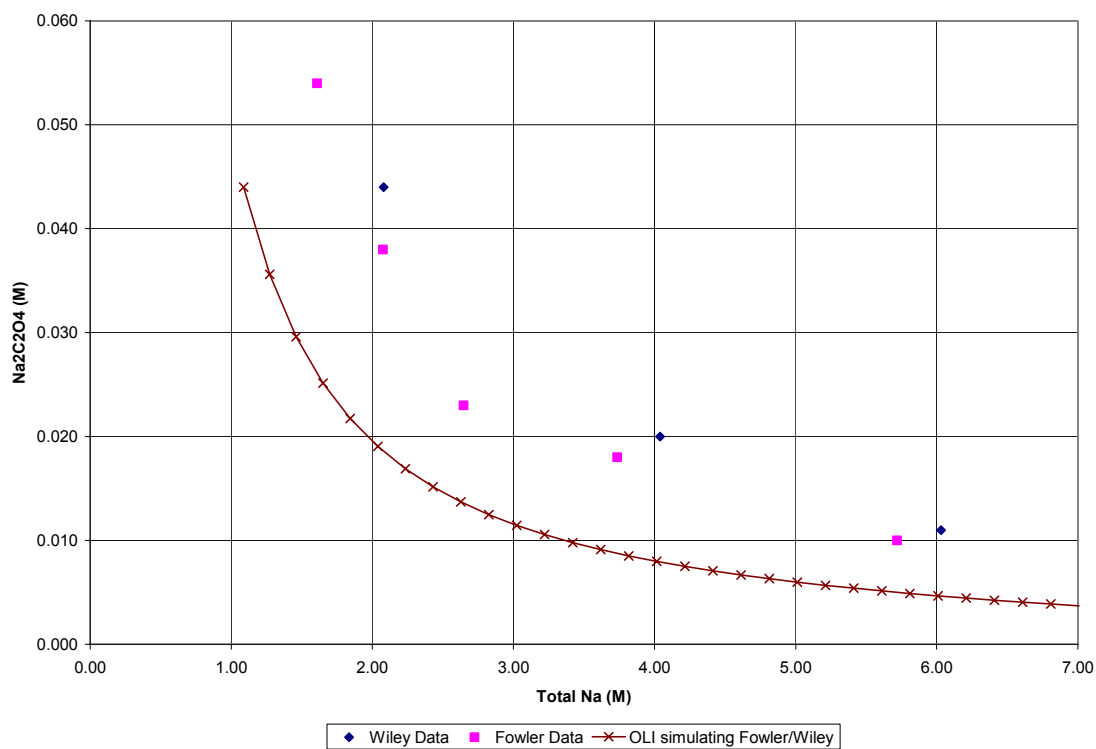
Figure 2: Oxalate Solubility in Simple $NaNO_3$-NaOH Simulated Waste
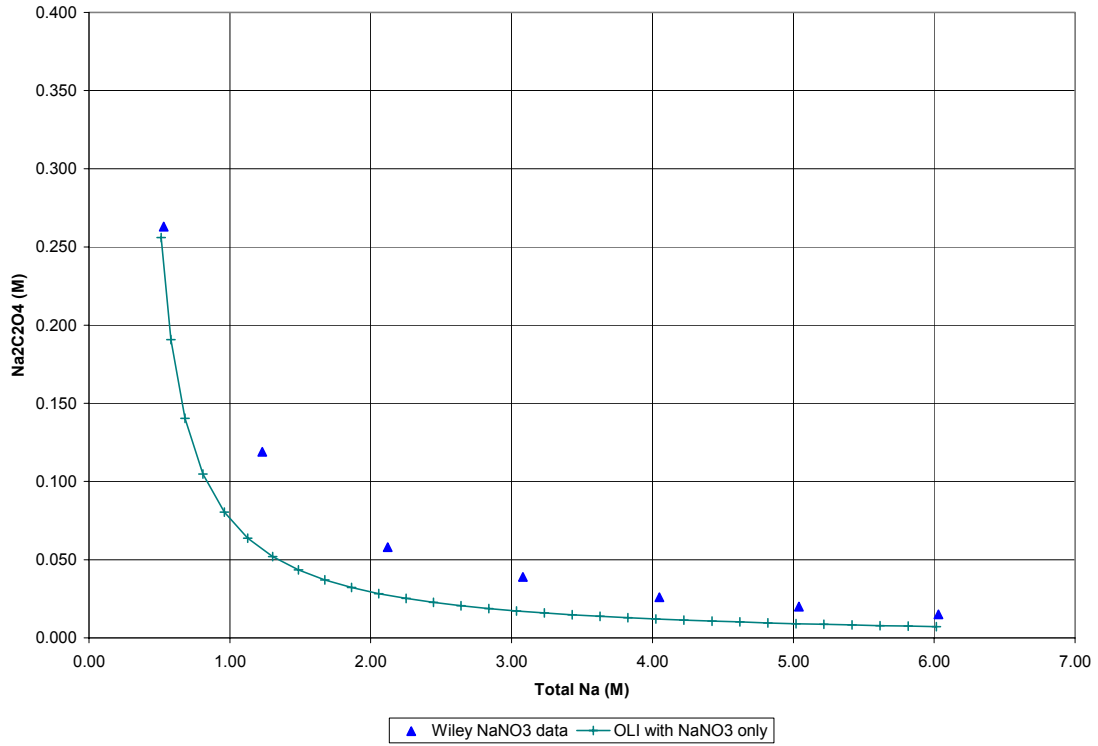
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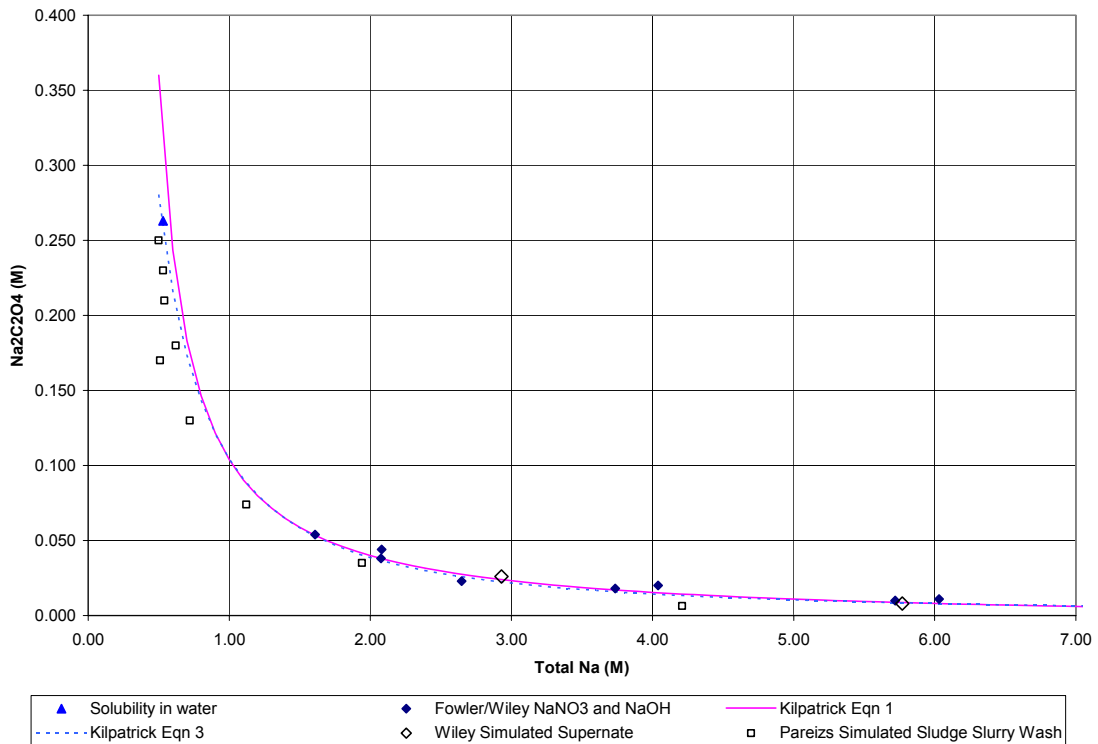
Figure 4: Oxalate Solubility Curve as a Function of Sodium Concentration

4.3 Heel Removal

4.3.1 Initial Heel Conditions

The heel dissolution process assumes that the tank has completed bulk sludge removal. The remaining heel is no greater than 5000 gallons of well-settled sludge slurry which equates to roughly 2" in Tanks 1 – 15. The flowsheet material balance tracks the movement of material by mass and estimates the resulting volume. The total quantity of solids and composition of the solids are more important than the volume of the heel. Therefore, the total sludge solids content of the 5000 gallon heel is conservatively estimated by assuming that the heel contains 40 weight % sludge solids with the remainder of the slurry consisting of a salt solution. Bulk sludge removal uses water or inhibited water such that minimal soluble salts are present in this salt solution. Inhibited water minimally consists of 0.01 M NaOH and 0.011 $NaNO_2$, which results in about 0.02 – 0.03 M total sodium salts. Thus, the heel consists primarily of 40 weight % sludge solids and water with no more than 0.1 M soluble sodium salts.

The sludge solids composition for waste Tanks 1 – 15 is based on the Waste Characterization System (WCS) version 1.5 as of September 13, 2004.[10] The composition of sludge in WCS results from a historical reconstruction from monthly data records. The records include measurements or estimates based on feed and process used of a few waste components sent to the waste tanks, namely thorium, uranium isotopes, plutonium isotopes, and iron, manganese, aluminum, and nickel as $Fe(OH)_3$, MnO_2, $NaAlO_2$, and $Ni(OH)_2$. The remaining components for each month are determined by ratio to the amount of iron reported for the month and a standard composition by waste type.

For this flowsheet, only the composition of the heel is important and not the total amount of material in each tank. In this case, the relative percentage of each waste type sent to the waste tank will be used to determine the composition of the heel. WCS reports the waste type and monthly amount of waste transferred to each tank. Table 1 shows the totals of each type and relative percentage sent to each tank. Table 2 shows composition by waste type. Table 3 shows the resulting composition of the sludge heel for each tank by combining the information in Table 1 and Table 2. Note that the sludge composition includes some soluble sodium salts. The planned initial heel removal includes substantial water contact with the heel which will reduce the soluble salts to much lower amounts. These salts are left in the estimated composition to conservatively estimate the consumption of acid during dissolution.

Table 4 shows the final composition of the 5000 gallon heel which includes the sludge solids and the slurry liquid.

Table 1: Waste Type by Tank

Process	Stream	PS Index	Tank														
			1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
PUREX	Low	PL	15.2%	0.0%	0.0%	0.0%	0.0%	0.0%	79.4%	70.6%	0.0%	0.0%	6.3%	0.0%	12.0%	0.0%	0.0%
PUREX	Mixed	PM	47.1%	100.0%	100.0%	6.1%	67.2%	0.0%	16.3%	14.6%	100.0%	98.3%	0.0%	16.9%	13.1%	0.0%	0.0%
PUREX	High	PH	37.7%	0.0%	0.0%	93.9%	32.8%	100.0%	4.2%	14.8%	0.0%	0.0%	0.0%	0.0%	3.3%	58.7%	0.0%
H Modified	Low	HL	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	25.9%	0.0%	57.4%	24.9%	8.7%
H Modified	Mixed	HM	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	1.7%	2.7%	0.0%	2.1%	0.0%	33.1%
H Modified	High	HH	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	65.2%	83.1%	12.1%	16.4%	58.1%

Table 2: Composition of Sludge Solids by Waste Type[10] - Major Components

Process Stream PS Index Units	H Modified High HH wt. frac.	H Modified Low HL wt. frac.	H Modified Mixed HM wt. frac.	PUREX High PH wt. frac.	PUREX Low PL wt. frac.	PUREX Mixed PM wt. frac.
Al(OH)3	67.03%	20.63%	61.98%	6.50%	13.89%	11.35%
CaC2O4	2.16%	0.00%	1.93%	0.00%	0.00%	0.00%
CaCO3	0.00%	4.55%	0.50%	2.77%	5.45%	4.53%
Ce(OH)3	0.05%	1.19%	0.18%	0.26%	0.35%	0.32%
Fe(OH)3	10.18%	46.02%	14.08%	48.52%	48.00%	48.18%
HgO	3.01%	2.15%	2.92%	0.24%	0.07%	0.13%
MnO2	2.61%	11.84%	3.61%	12.11%	4.21%	6.93%
NaCl	0.00%	1.44%	0.16%	0.21%	2.08%	1.44%
NaNO3	3.26%	0.35%	2.94%	1.34%	1.57%	1.49%
NaOH	1.35%	3.29%	1.56%	5.08%	4.69%	4.83%
Ni(OH)2	1.01%	0.68%	0.98%	5.79%	3.45%	4.25%
SiO2	4.68%	0.00%	4.17%	0.96%	1.89%	1.57%
ThO2	1.31%	0.11%	1.18%	0.08%	0.01%	0.03%
UO2(OH)2	1.25%	4.71%	1.63%	10.93%	7.79%	8.86%
Total	97.91%	96.96%	97.81%	94.77%	93.44%	93.90%

Table 3: Estimated Composition of Sludge Solids in Tank Heels - Major Components

		Tank														
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Al(OH)3	(wt %)	10.5%	12.1%	12.1%	7.2%	10.4%	6.9%	14.1%	13.3%	12.1%	13.0%	52.8%	59.0%	25.4%	20.6%	62.7%
CaC2O4	(wt %)	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	1.5%	1.8%	0.3%	0.4%	1.9%
CaCO3	(wt %)	4.3%	4.8%	4.8%	3.0%	4.2%	2.9%	5.5%	5.3%	4.8%	4.7%	1.6%	0.8%	4.1%	2.9%	0.6%
Ce(OH)3	(wt %)	0.3%	0.3%	0.3%	0.3%	0.3%	0.3%	0.4%	0.4%	0.3%	0.3%	0.4%	0.1%	0.8%	0.5%	0.2%
Fe(OH)3	(wt %)	51.3%	51.3%	51.3%	51.2%	51.3%	51.2%	51.4%	51.3%	51.3%	50.7%	22.7%	17.3%	43.4%	43.6%	15.0%
HgO	(wt %)	0.2%	0.1%	0.1%	0.2%	0.2%	0.3%	0.1%	0.1%	0.1%	0.2%	2.7%	2.6%	1.7%	1.2%	3.0%
MnO2	(wt %)	9.0%	7.4%	7.4%	12.4%	9.1%	12.8%	5.3%	6.2%	7.4%	7.3%	5.3%	3.5%	9.3%	11.0%	3.8%
NaCl	(wt %)	1.1%	1.5%	1.5%	0.3%	1.1%	0.2%	2.0%	1.8%	1.5%	1.5%	0.5%	0.3%	1.3%	0.5%	0.2%
NaNO3	(wt %)	1.5%	1.6%	1.6%	1.4%	1.5%	1.4%	1.7%	1.6%	1.6%	1.6%	2.4%	3.0%	1.1%	1.5%	3.0%
NaOH	(wt %)	5.2%	5.1%	5.1%	5.3%	5.2%	5.4%	5.1%	5.1%	5.1%	5.1%	2.1%	2.0%	3.6%	4.2%	1.6%
Ni(OH)2	(wt %)	5.0%	4.5%	4.5%	6.0%	5.0%	6.1%	3.9%	4.2%	4.5%	4.5%	1.1%	1.6%	1.8%	3.9%	1.0%
SiO2	(wt %)	1.5%	1.7%	1.7%	1.1%	1.5%	1.0%	1.9%	1.8%	1.7%	1.7%	3.4%	4.3%	1.2%	1.4%	4.2%
ThO2	(wt %)	0.0%	0.0%	0.0%	0.1%	0.0%	0.1%	0.0%	0.0%	0.0%	0.1%	0.9%	1.1%	0.3%	0.3%	1.2%
UO2(OH)2	(wt %)	10.1%	9.4%	9.4%	11.4%	10.1%	11.5%	8.6%	9.0%	9.4%	9.3%	2.7%	2.7%	5.6%	8.2%	1.7%
Total	(wt %)	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%

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Table 4: Estimated Composition of Sludge Slurry in Tank Heels

		Tank														
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Al(OH)3	(wt %)	4.2%	4.8%	4.8%	2.9%	4.1%	2.7%	5.6%	5.3%	4.8%	5.2%	21.1%	23.6%	10.2%	8.2%	25.1%
CaC2O4	(wt %)	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.6%	0.7%	0.1%	0.1%	0.8%
CaCO3	(wt %)	1.7%	1.9%	1.9%	1.2%	1.7%	1.2%	2.2%	2.1%	1.9%	1.9%	0.6%	0.3%	1.7%	1.2%	0.2%
Ce(OH)3	(wt %)	0.1%	0.1%	0.1%	0.1%	0.1%	0.1%	0.1%	0.1%	0.1%	0.1%	0.2%	0.0%	0.3%	0.2%	0.1%
Fe(OH)3	(wt %)	20.5%	20.5%	20.5%	20.5%	20.5%	20.5%	20.5%	20.5%	20.5%	20.3%	9.1%	6.9%	17.4%	17.4%	6.0%
HgO	(wt %)	0.1%	0.1%	0.1%	0.1%	0.1%	0.1%	0.0%	0.0%	0.1%	0.1%	1.1%	1.0%	0.7%	0.5%	1.2%
MnO2	(wt %)	3.6%	3.0%	3.0%	5.0%	3.7%	5.1%	2.1%	2.5%	3.0%	2.9%	2.1%	1.4%	3.7%	4.4%	1.5%
NaCl	(wt %)	0.5%	0.6%	0.6%	0.1%	0.4%	0.1%	0.8%	0.7%	0.6%	0.6%	0.2%	0.1%	0.5%	0.2%	0.1%
NaNO3	(wt %)	0.6%	0.6%	0.6%	0.6%	0.6%	0.6%	0.7%	0.7%	0.6%	0.6%	1.0%	1.2%	0.5%	0.6%	1.2%
NaOH	(wt %)	2.1%	2.1%	2.1%	2.1%	2.1%	2.1%	2.0%	2.0%	2.1%	2.0%	0.9%	0.8%	1.4%	1.7%	0.7%
Ni(OH)2	(wt %)	2.0%	1.8%	1.8%	2.4%	2.0%	2.4%	1.6%	1.7%	1.8%	1.8%	0.4%	0.6%	0.7%	1.6%	0.4%
SiO2	(wt %)	0.6%	0.7%	0.7%	0.4%	0.6%	0.4%	0.8%	0.7%	0.7%	0.7%	1.3%	1.7%	0.5%	0.6%	1.7%
ThO2	(wt %)	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.4%	0.4%	0.1%	0.1%	0.5%
UO2(OH)2	(wt %)	4.0%	3.8%	3.8%	4.6%	4.1%	4.6%	3.5%	3.6%	3.8%	3.7%	1.1%	1.1%	2.2%	3.3%	0.7%
H2O	(wt %)	60.0%	60.0%	60.0%	60.0%	60.0%	60.0%	60.0%	60.0%	60.0%	60.0%	60.0%	60.0%	60.0%	60.0%	60.0%
Total	(wt %)	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%
Sludge Solids	(wt %)	40%	40%	40%	40%	40%	40%	40%	40%	40%	40%	40%	40%	40%	40%	40%

4.3.2 Simulation Results

Table 4 shows that the heel composition for the all the F-Area waste tanks, Tanks 1 – 8, are very similar. The heel compositions in H-Area Tanks 9 – 15 exhibit some variation. The heel compositions for Tanks 8 and 11 were picked to represent the range of compositions.

The specific material balances are calculated for the following cases:

Case	Heel from Tank	Neutralization Liquid
1	8	50 wt% NaOH
2	8	supernate
3	11	50 wt% NaOH
4	11	supernate

Table 5 shows the supernate composition used for each of the cases using supernate to neutralize the oxalic acid. The acid is considered neutralized at 0.1 M free hydroxide concentration. The simulation calculated the volume needed to reach this neutralization concentration and stopped.

Table 6 and Table 8 show the material balance of the heel dissolution for these tanks using 50% NaOH solution for neutralization of the acid. Table 7 and Table 9 show the same material balance using an average waste supernate for neutralization.

Note that Table 6 through Table 9 show the added materials only, not existing tank farm material, thus, streams 9, 10, 12, 14, and 16 show only a material balance for added sodium oxalate. Stream 12 shows zero sodium oxalate transferred because none of the bulk salt dissolution removes any of the added sodium oxalate. 100% of the added sodium oxalate remains in the heel. The salt dissolution section (Section 4.6) explains this effect.

Table 5: Average Supernate Composition – Major Components[11]

Component	Average
H_2O, wt%	67.4
$NaNO_3$, wt%	15.8
NaOH, wt%	7.56
$NaNO_2$, wt%	3.09
$NaAlO_2$, wt%	2.15
Na_2SO_4, wt%	1.76
Na_2CO_3, wt%	1.41
Other salts, wt%	0.67
KOH, wt%	0.074
NH_4NO_3, wt%	2.6E-03
CsOH, wt%	1.9E-03
$Na_2U_2O_7$, wt%	6.2E-03
sludge, wt%	0.048
HgO, wt%	2.6E-03
Total, wt%	100.0
Density, kg/L	1.267

Table 6: Baseline Material Balance for Case 1

Stream Number	1	2	3	4	5	6a	6b	7a	7b
Stream	Oxalic Acid	Dilution Water	Neutralizing Solution	Slurry Water	Wash Water	Sludge Heel	Sludge Heel	Dissolved Heel	Dissolved Heel
Phase	Aqueous	Aqueous	Aqueous	Aqueous	Aqueous	Aqueous	Solid	Aqueous	Solid
Temperature (°C)	30	-	30	-	-	30	30	30	30
pH	0.7	-	17.6	-	-	13.4	-	0.7	-
Units	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac
H2O	9.20E-01	-	5.00E-01	-	9.76E-01	9.25E-01	0.00E+00	9.11E-01	0.00E+00
H2C2O4	8.00E-02	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	4.01E-02	0.00E+00
HCl	0.00E+00	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	4.58E-04	0.00E+00
HNO3	0.00E+00	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	4.76E-04	0.00E+00
Na2CO3	0.00E+00	-	0.00E+00	-	0.00E+00	3.44E-04	0.00E+00	2.14E-03	0.00E+00
NaCL	0.00E+00	-	0.00E+00	-	0.00E+00	1.23E-02	0.00E+00	0.00E+00	0.00E+00
NaNO2	0.00E+00	-	0.00E+00	-	2.41E-02	0.00E+00	0.00E+00	0.00E+00	0.00E+00
NaNO3	0.00E+00	-	0.00E+00	-	0.00E+00	1.08E-02	0.00E+00	0.00E+00	0.00E+00
NaOH	0.00E+00	-	5.00E-01	-	0.00E+00	3.44E-02	0.00E+00	0.00E+00	0.00E+00
Na2SO4	0.00E+00	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Na2C2O4	0.00E+00	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	4.42E-03	0.00E+00
Al(OH)3	0.00E+00	-	0.00E+00	-	0.00E+00	0.00E+00	1.53E-01	0.00E+00	0.00E+00
AlOOH	0.00E+00	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	3.95E-03	0.00E+00
NaAlO2	0.00E+00	-	0.00E+00	-	0.00E+00	3.29E-03	0.00E+00	0.00E+00	0.00E+00
CaC2O4	0.00E+00	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	4.08E-04	2.80E-01
CaCO3	0.00E+00	-	0.00E+00	-	0.00E+00	0.00E+00	6.18E-02	0.00E+00	0.00E+00
Ca(OH)2	0.00E+00	-	0.00E+00	-	0.00E+00	2.40E-04	0.00E+00	0.00E+00	0.00E+00
Ce2O3	0.00E+00	-	0.00E+00	-	0.00E+00	1.32E-03	0.00E+00	0.00E+00	0.00E+00
Ce2(C2O4)3	0.00E+00	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	3.76E-05	9.07E-03
Fe2(C2O4)3	0.00E+00	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	3.31E-02	0.00E+00
Fe(OH)3	0.00E+00	-	0.00E+00	-	0.00E+00	7.44E-05	5.81E-01	0.00E+00	0.00E+00
K2C2O4	0.00E+00	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
KOH	0.00E+00	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
MnC2O4	0.00E+00	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	4.55E-04	3.40E-01
Mn(OH)2	0.00E+00	-	0.00E+00	-	0.00E+00	8.83E-07	5.95E-02	0.00E+00	0.00E+00
NiC2O4	0.00E+00	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	5.71E-05	2.91E-01
NiOH2	0.00E+00	-	0.00E+00	-	0.00E+00	3.07E-07	4.54E-02	0.00E+00	0.00E+00
SiO2	0.00E+00	-	0.00E+00	-	0.00E+00	1.23E-02	0.00E+00	3.78E-03	8.00E-02
UO2C2O4	0.00E+00	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	3.78E-03	0.00E+00
UO2(OH)2	0.00E+00	-	0.00E+00	-	0.00E+00	2.66E-08	9.92E-02	0.00E+00	0.00E+00
THO2	0.00E+00	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
HGO	0.00E+00	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
TH(C2O4)2	0.00E+00	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Total (kg)	2.64E+05	0.00E+00	3.94E+04	0.00E+00	3.05E+06	1.72E+04	9.37E+03	2.88E+05	2.55E+03
Volume (gal)	6.54E+04	-	6.80E+03	-	8.00E+05	4.29E+03	7.07E+02	7.03E+04	1.08E+02
Enthalpy (cal)	-9.67E+11	-	-1.26E+11	-	-	-6.35E+10	-2.04E+10	-1.05E+12	-5.68E+09
Density (g/gal)	4.04E+03	-	5.79E+03	-	-	4.00E+03	1.33E+04	4.10E+03	2.36E+04
Oxalate ion (kg)	2.07E+04		0.00E+00			0.00E+00	0.00E+00	1.93E+04	1.48E+03

Table 6: Baseline Material Balance for Case 1 (continued)

Stream Number	8	9	10	11	12	13a	13b	14	15	16
Stream	Neutralization Supernate	Evaporator Feed	Evaporator Concentrate	Dissolution Water	Dissolved Salt	Solids Slurry	Solids Slurry	Washed Sludge	Decant/ Wash Water	Feed Tank Sludge
Phase	Aqueous	-	-	Aqueous	Aqueous	Aqueous	Solid	Slurry	Aqueous	Slurry
Temperature (°C)	30	30	30	30	30	30	30	30	30	30
pH	12.7	-	-	12.0	-	12.7	-	-	-	-
Units	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac
H2O	9.61E-01	-	-	9.99E-01	-	9.61E-01	0.00E+00	-	8.09E-01	-
H2C2O4	0.00E+00	-	-	0.00E+00	-	0.00E+00	0.00E+00	-	0.00E+00	-
HCl	0.00E+00	-	-	0.00E+00	-	0.00E+00	0.00E+00	-	0.00E+00	-
HNO3	0.00E+00	-	-	0.00E+00	-	0.00E+00	0.00E+00	-	0.00E+00	-
Na2CO3	2.07E-03	-	-	0.00E+00	-	2.07E-03	0.00E+00	-	1.01E-02	-
NaCL	7.12E-04	-	-	0.00E+00	-	7.11E-04	0.00E+00	-	2.40E-04	-
NaNO2	0.00E+00	-	-	7.50E-04	-	0.00E+00	0.00E+00	-	7.64E-02	-
NaNO3	6.23E-04	-	-	0.00E+00	-	6.22E-04	0.00E+00	-	6.98E-02	-
NaOH	4.55E-03	-	-	3.95E-04	-	4.99E-03	0.00E+00	-	1.76E-02	-
Na2SO4	0.00E+00	-	-	0.00E+00	-	0.00E+00	0.00E+00	-	3.03E-03	-
Na2C2O4	2.90E-02	1.00E+00	1.00E+00	0.00E+00	0.00E+00	2.90E-02	7.01E-01	6.10E-02	5.79E-03	1.00E+00
Al(OH)3	0.00E+00	-	-	0.00E+00	-	0.00E+00	4.15E-02	-	0.00E+00	-
AlOOH	0.00E+00	-	-	0.00E+00	-	0.00E+00	0.00E+00	-	0.00E+00	-
NaAlO2	6.55E-04	-	-	0.00E+00	-	6.55E-04	0.00E+00	-	7.60E-03	-
CaC2O4	7.62E-07	-	-	0.00E+00	-	7.61E-07	2.38E-02	1.87E-03	2.59E-07	-
CaCO3	0.00E+00	-	-	0.00E+00	-	0.00E+00	0.00E+00	-	0.00E+00	-
Ca(OH)2	0.00E+00	-	-	0.00E+00	-	0.00E+00	0.00E+00	-	0.00E+00	-
Ce2O3	7.64E-05	-	-	0.00E+00	-	7.63E-05	0.00E+00	-	0.00E+00	-
Ce2(C2O4)3	0.00E+00	-	-	0.00E+00	-	0.00E+00	0.00E+00	-	0.00E+00	-
Fe2(C2O4)3	2.55E-05	-	-	0.00E+00	-	2.54E-05	0.00E+00	1.35E-06	8.64E-06	-
Fe(OH)3	0.00E+00	-	-	0.00E+00	-	0.00E+00	1.74E-01	-	0.00E+00	-
K2C2O4	0.00E+00	-	-	0.00E+00	-	0.00E+00	0.00E+00	-	0.00E+00	-
KOH	0.00E+00	-	-	0.00E+00	-	0.00E+00	0.00E+00	-	0.00E+00	-
MnC2O4	2.78E-06	-	-	0.00E+00	-	2.78E-06	0.00E+00	1.47E-07	9.45E-07	-
Mn(OH)2	0.00E+00	-	-	0.00E+00	-	0.00E+00	1.78E-02	-	0.00E+00	-
NiC2O4	9.54E-08	-	-	0.00E+00	-	9.53E-08	0.00E+00	5.05E-09	3.24E-08	-
NiOH2	0.00E+00	-	-	0.00E+00	-	0.00E+00	1.36E-02	-	0.00E+00	-
SiO2	7.12E-04	-	-	0.00E+00	-	7.11E-04	0.00E+00	-	0.00E+00	-
UO2C2O4	1.07E-04	-	-	0.00E+00	-	1.07E-04	0.00E+00	5.68E-06	3.64E-05	-
UO2(OH)2	0.00E+00	-	-	0.00E+00	-	0.00E+00	2.88E-02	-	0.00E+00	-
THO2	0.00E+00	-	-	0.00E+00	-	0.00E+00	0.00E+00	-	0.00E+00	-
HGO	0.00E+00	-	-	0.00E+00	-	0.00E+00	0.00E+00	-	0.00E+00	-
TH(C2O4)2	0.00E+00	-	-	0.00E+00	-	0.00E+00	0.00E+00	-	0.00E+00	-
Total (kg)	1.41E+05	1.23E+03	1.23E+03	8.39E+06	-	1.57E+05	3.15E+04	4.01E+05	3.77E+05	5.06E+03
Volume (gal)	3.62E+04	-	-	2.20E+06	3.20E+06	4.02E+04	7.38E+02	5.53E+05	1.38E+06	-
Enthalpy (cal)	-5.28E+11	-	-	-	-	-5.87E+11	-7.23E+10	-	-	-
Density (g/gal)	3.91E+03	-	-	3.82E+03	-	3.91E+03	4.26E+04	-	-	-
Oxalate ion (kg)	2.70E+03	8.08E+02	8.08E+02		0.00E+00	3.01E+03	1.50E+04	1.61E+04	1.44E+03	3.32E+03

Table 7: Material Balance for Case 2

Stream Number	1	2	3	4	5	6a	6b	7a	7b
Stream	Oxalic Acid	Dilution Water	Neutralizing Solution	Slurry Water	Wash Water	Sludge Heel	Sludge Heel	Dissolved Heel	Dissolved Heel
Phase	Aqueous	Aqueous	Aqueous	Aqueous	Aqueous	Aqueous	Solid	Aqueous	Solid
Temperature (°C)	30	-	30	-	-	30	30	30	30
pH	0.7	-	14.7	-	-	13.4	-	0.7	-
Units	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac
H2O	9.20E-01	-	6.79E-01	-	9.76E-01	9.25E-01	0.00E+00	9.11E-01	0.00E+00
H2C2O4	8.00E-02	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	4.01E-02	0.00E+00
HCl	0.00E+00	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	4.58E-04	0.00E+00
HNO3	0.00E+00	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	4.76E-04	0.00E+00
Na2CO3	0.00E+00	-	1.42E-02	-	0.00E+00	3.44E-04	0.00E+00	2.14E-03	0.00E+00
NaCL	0.00E+00	-	0.00E+00	-	0.00E+00	1.23E-02	0.00E+00	0.00E+00	0.00E+00
NaNO2	0.00E+00	-	3.11E-02	-	2.41E-02	0.00E+00	0.00E+00	0.00E+00	0.00E+00
NaNO3	0.00E+00	-	1.59E-01	-	0.00E+00	1.08E-02	0.00E+00	0.00E+00	0.00E+00
NaOH	0.00E+00	-	7.62E-02	-	0.00E+00	3.44E-02	0.00E+00	0.00E+00	0.00E+00
Na2SO4	0.00E+00	-	1.77E-02	-	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Na2C2O4	0.00E+00	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	4.42E-03	0.00E+00
Al(OH)3	0.00E+00	-	0.00E+00	-	0.00E+00	0.00E+00	1.53E-01	0.00E+00	0.00E+00
AlOOH	0.00E+00	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	3.95E-03	0.00E+00
NaAlO2	0.00E+00	-	2.17E-02	-	0.00E+00	3.29E-03	0.00E+00	0.00E+00	0.00E+00
CaC2O4	0.00E+00	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	4.08E-04	2.80E-01
CaCO3	0.00E+00	-	0.00E+00	-	0.00E+00	0.00E+00	6.18E-02	0.00E+00	0.00E+00
Ca(OH)2	0.00E+00	-	0.00E+00	-	0.00E+00	2.40E-04	0.00E+00	0.00E+00	0.00E+00
Ce2O3	0.00E+00	-	0.00E+00	-	0.00E+00	1.32E-03	0.00E+00	0.00E+00	0.00E+00
Ce2(C2O4)3	0.00E+00	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	3.76E-05	9.07E-03
Fe2(C2O4)3	0.00E+00	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	3.31E-02	0.00E+00
Fe(OH)3	0.00E+00	-	0.00E+00	-	0.00E+00	7.44E-05	5.81E-01	0.00E+00	0.00E+00
K2C2O4	0.00E+00	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
KOH	0.00E+00	-	7.46E-04	-	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
MnC2O4	0.00E+00	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	4.55E-04	3.40E-01
Mn(OH)2	0.00E+00	-	0.00E+00	-	0.00E+00	8.83E-07	5.95E-02	0.00E+00	0.00E+00
NiC2O4	0.00E+00	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	5.71E-05	2.91E-01
NiOH2	0.00E+00	-	0.00E+00	-	0.00E+00	3.07E-07	4.54E-02	0.00E+00	0.00E+00
SiO2	0.00E+00	-	0.00E+00	-	0.00E+00	1.23E-02	0.00E+00	1.12E-04	8.00E-02
UO2C2O4	0.00E+00	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	3.78E-03	0.00E+00
UO2(OH)2	0.00E+00	-	0.00E+00	-	0.00E+00	2.66E-08	9.92E-02	0.00E+00	0.00E+00
THO2	0.00E+00	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
HGO	0.00E+00	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
TH(C2O4)2	0.00E+00	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Total (kg)	2.64E+05	0.00E+00	2.31E+05	0.00E+00	3.05E+06	1.72E+04	9.37E+03	2.88E+05	2.55E+03
Volume (gal)	6.54E+04	-	4.90E+04	-	8.00E+05	4.29E+03	7.07E+02	7.03E+04	1.08E+02
Enthalpy (cal)	-9.67E+11	-	-7.33E+11	-	-	-6.35E+10	-2.04E+10	-1.05E+12	-5.68E+09
Density (g/gal)	4.04E+03	-	4.72E+03	-	-	4.00E+03	1.33E+04	4.10E+03	2.36E+04
Oxalate ion (kg)	2.07E+04		0.00E+00			0.00E+00	0.00E+00	1.93E+04	1.48E+03

Table 7: Material Balance for Case 2 (continued)

Stream Number	8	9	10	11	12	13a	13b	14	15	16
Stream	Neutralization Supernate	Evaporator Feed	Evaporator Concentrate	Dissolution Water	Dissolved Salt	Solids Slurry	Solids Slurry	Washed Sludge	Decant/ Wash Water	Feed Tank Sludge
Phase	Aqueous	-	-	Aqueous	Aqueous	Aqueous	Solid	Slurry	Aqueous	Slurry
Temperature (°C)	30	30	30	30	30	30	30	30	30	30
pH	12.8	-	-	12.0	-	12.8	-	-	-	-
Units	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac
H2O	8.78E-01	-	-	9.99E-01	-	8.71E-01	0.00E+00	-	8.08E-01	-
H2C2O4	0.00E+00	-	-	0.00E+00	-	0.00E+00	0.00E+00	-	0.00E+00	-
HCl	0.00E+00	-	-	0.00E+00	-	0.00E+00	0.00E+00	-	0.00E+00	-
HNO3	0.00E+00	-	-	0.00E+00	-	0.00E+00	0.00E+00	-	0.00E+00	-
Na2CO3	8.11E-03	-	-	0.00E+00	-	8.07E-03	0.00E+00	-	1.00E-02	-
NaCL	4.42E-04	-	-	0.00E+00	-	4.39E-04	0.00E+00	-	2.40E-04	-
NaNO2	1.50E-02	-	-	7.50E-04	-	1.49E-02	0.00E+00	-	7.63E-02	-
NaNO3	7.69E-02	-	-	0.00E+00	-	7.65E-02	0.00E+00	-	6.97E-02	-
NaOH	4.18E-03	-	-	3.95E-04	-	1.16E-02	0.00E+00	-	1.76E-02	-
Na2SO4	8.52E-03	-	-	0.00E+00	-	8.48E-03	0.00E+00	-	3.02E-03	-
Na2C2O4	4.95E-03	1.00E+00	1.00E+00	0.00E+00	0.00E+00	4.93E-03	6.79E-01	6.31E-02	7.66E-03	1.00E+00
Al(OH)3	0.00E+00	-	-	0.00E+00	-	0.00E+00	1.45E-01	-	0.00E+00	-
AlOOH	0.00E+00	-	-	0.00E+00	-	0.00E+00	0.00E+00	-	0.00E+00	-
NaAlO2	7.74E-04	-	-	0.00E+00	-	7.70E-04	0.00E+00	-	7.59E-03	-
CaC2O4	2.15E-06	-	-	0.00E+00	-	2.14E-06	1.83E-02	1.83E-03	1.00E-06	-
CaCO3	0.00E+00	-	-	0.00E+00	-	0.00E+00	0.00E+00	-	0.00E+00	-
Ca(OH)2	0.00E+00	-	-	0.00E+00	-	0.00E+00	0.00E+00	-	0.00E+00	-
Ce2O3	4.74E-05	-	-	0.00E+00	-	4.72E-05	0.00E+00	3.17E-06	2.21E-05	-
Ce2(C2O4)3	0.00E+00	-	-	0.00E+00	-	0.00E+00	0.00E+00	-	0.00E+00	-
Fe2(C2O4)3	3.17E-05	-	-	0.00E+00	-	3.16E-05	0.00E+00	2.12E-06	1.48E-05	-
Fe(OH)3	0.00E+00	-	-	0.00E+00	-	0.00E+00	1.34E-01	-	0.00E+00	-
K2C2O4	5.31E-04	-	-	0.00E+00	-	5.28E-04	0.00E+00	3.55E-05	2.47E-04	-
KOH	0.00E+00	-	-	0.00E+00	-	0.00E+00	0.00E+00	-	0.00E+00	-
MnC2O4	1.98E-07	-	-	0.00E+00	-	1.97E-07	0.00E+00	1.32E-08	9.21E-08	-
Mn(OH)2	0.00E+00	-	-	0.00E+00	-	0.00E+00	1.37E-02	-	0.00E+00	-
NiC2O4	1.18E-07	-	-	0.00E+00	-	1.18E-07	0.00E+00	7.92E-09	5.51E-08	-
NiOH2	0.00E+00	-	-	0.00E+00	-	0.00E+00	1.04E-02	-	0.00E+00	-
SiO2	4.42E-04	-	-	0.00E+00	-	4.39E-04	0.00E+00	-	0.00E+00	-
UO2C2O4	2.28E-03	-	-	0.00E+00	-	2.26E-03	0.00E+00	1.52E-04	1.06E-03	-
UO2(OH)2	0.00E+00	-	-	0.00E+00	-	0.00E+00	0.00E+00	-	0.00E+00	-
THO2	0.00E+00	-	-	0.00E+00	-	0.00E+00	0.00E+00	-	0.00E+00	-
HGO	0.00E+00	-	-	0.00E+00	-	0.00E+00	0.00E+00	-	0.00E+00	-
TH(C2O4)2	0.00E+00	-	-	0.00E+00	-	0.00E+00	0.00E+00	-	0.00E+00	-
Total (kg)	2.77E+05	1.25E+03	1.25E+03	8.39E+06	-	2.04E+05	4.08E+04	4.10E+05	3.77E+05	3.01E+03
Volume (gal)	6.74E+04	-	-	2.20E+06	3.20E+06	4.96E+04	1.24E+03	5.53E+05	1.38E+06	-
Enthalpy (cal)	-9.73E+11	-	-	-	-	-7.17E+11	-1.03E+11	-	-	-
Density (g/gal)	4.11E+03	-	-	3.82E+03	-	4.11E+03	3.30E+04	-	-	-
Oxalate ion (kg)	1.14E+03	8.21E+02	8.21E+02		0.00E+00	8.37E+02	1.87E+04	1.70E+04	2.05E+03	1.98E+03

Table 8: Baseline Material Balance for Case 3

Stream Number	1	2	3	4	5	6a	6b	7a	7b
Stream	Oxalic Acid	Dilution Water	Neutralizing Solution	Slurry Water	Wash Water	Sludge Heel	Sludge Heel	Dissolved Heel	Dissolved Heel
Phase	Aqueous	Aqueous	Aqueous	Aqueous	Aqueous	Aqueous	Solid	Aqueous	Solid
Temperature (°C)	30	30	30	-	-	30	30	30	30
pH	0.738632	-	17.6224	-	-	11.5886	-	1.39016	-
Units	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac
H2O	9.20E-01	-	5.00E-01	-	9.76E-01	9.40E-01	0.00E+00	9.10E-01	0.00E+00
H2C2O4	8.00E-02	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	6.27E-02	0.00E+00
HCl	0.00E+00	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	8.66E-05	0.00E+00
HNO3	0.00E+00	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	5.14E-04	0.00E+00
Na2CO3	0.00E+00	-	0.00E+00	-	0.00E+00	6.20E-05	0.00E+00	4.41E-04	0.00E+00
NaCL	0.00E+00	-	0.00E+00	-	0.00E+00	3.14E-03	0.00E+00	0.00E+00	0.00E+00
NaNO2	0.00E+00	-	0.00E+00	-	2.41E-02	0.00E+00	0.00E+00	0.00E+00	0.00E+00
NaNO3	0.00E+00	-	0.00E+00	-	0.00E+00	1.57E-02	0.00E+00	0.00E+00	0.00E+00
NaOH	0.00E+00	-	5.00E-01	-	0.00E+00	1.75E-02	0.00E+00	0.00E+00	0.00E+00
Na2SO4	0.00E+00	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Na2C2O4	0.00E+00	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	1.75E-03	0.00E+00
Al(OH)3	0.00E+00	-	0.00E+00	-	0.00E+00	0.00E+00	5.88E-01	0.00E+00	0.00E+00
AlOOH	0.00E+00	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	1.13E-02	0.00E+00
NaAlO2	0.00E+00	-	0.00E+00	-	0.00E+00	4.38E-05	0.00E+00	0.00E+00	0.00E+00
CaC2O4	0.00E+00	-	0.00E+00	-	0.00E+00	4.87E-05	0.00E+00	3.96E-05	0.00E+00
CaCO3	0.00E+00	-	0.00E+00	-	0.00E+00	0.00E+00	1.66E-02	0.00E+00	0.00E+00
Ca(OH)2	0.00E+00	-	0.00E+00	-	0.00E+00	4.33E-05	0.00E+00	0.00E+00	0.00E+00
Ce2O3	0.00E+00	-	0.00E+00	-	0.00E+00	2.69E-03	0.00E+00	0.00E+00	0.00E+00
Ce2(C2O4)3	0.00E+00	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	6.07E-05	0.00E+00
Fe2(C2O4)3	0.00E+00	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	1.11E-02	0.00E+00
Fe(OH)3	0.00E+00	-	0.00E+00	-	0.00E+00	9.59E-07	2.54E-01	0.00E+00	0.00E+00
K2C2O4	0.00E+00	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
KOH	0.00E+00	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
MnC2O4	0.00E+00	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	2.79E-04	0.00E+00
Mn(OH)2	0.00E+00	-	0.00E+00	-	0.00E+00	1.03E-07	5.85E-02	0.00E+00	0.00E+00
NiC2O4	0.00E+00	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	5.11E-05	3.27E-01
NiOH2	0.00E+00	-	0.00E+00	-	0.00E+00	4.53E-09	1.11E-02	0.00E+00	0.00E+00
SiO2	0.00E+00	-	0.00E+00	-	0.00E+00	2.04E-02	0.00E+00	1.02E-04	6.73E-01
UO2C2O4	0.00E+00	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	8.99E-04	0.00E+00
UO2(OH)2	0.00E+00	-	0.00E+00	-	0.00E+00	2.69E-07	3.06E-02	0.00E+00	0.00E+00
THO2	0.00E+00	-	0.00E+00	-	0.00E+00	4.92E-14	1.11E-02	0.00E+00	0.00E+00
HGO	0.00E+00	-	0.00E+00	-	0.00E+00	3.86E-05	3.06E-02	7.63E-04	0.00E+00
THC2O42	0.00E+00	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	4.29E-04	0.00E+00
Total (kg)	3.45E+05	0.00E+00	5.21E+04	0.00E+00	3.05E+06	1.63E+04	9.39E+03	3.68E+05	1.84E+03
Volume (gal)	8.53E+04	-	9.00E+03	-	8.00E+05	4.14E+03	8.63E+02	8.94E+04	8.16E+01
Enthalpy (cal)	-1.26E+12	-	-1.67E+11	-	-	-6.07E+10	-2.84E+10	-1.35E+12	-4.53E+09
Density (g/gal)	4.04E+03	-	5.79E+03	-	-	3.95E+03	1.09E+04	4.12E+03	2.26E+04
Oxalate ion (kg)	2.69E+04		0.00E+00			5.47E-01	0.00E+00	2.61E+04	3.62E+02

Table 8: Baseline Material Balance for Case 3 (continued)

Stream Number	8	9	10	11	12	13a	13b	14	15	16
Stream	Neutralization Supernate	Evaporator Feed	Evaporator Concentrate	Dissolution Water	Dissolved Salt	Solids Slurry	Solids Slurry	Washed Sludge	Decant/ Wash Water	Feed Tank Sludge
Phase	Aqueous	-	-	Aqueous	Aqueous	Aqueous	Solid	Slurry	Aqueous	Slurry
Temperature (°C)	30	-	-	-	-	30	30	-	-	-
pH	12.6632	-	-	12	-	12.6632		-	-	-
Units	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac
H_2O	9.62E-01	-	-	9.99E-01	-	9.62E-01	0.00E+00	-	8.08E-01	-
$H_2C_2O_4$	0.00E+00	-	-	0.00E+00	-	0.00E+00	0.00E+00	-	0.00E+00	-
HCl	0.00E+00	-	-	0.00E+00	-	0.00E+00	0.00E+00	-	0.00E+00	-
HNO_3	0.00E+00	-	-	0.00E+00	-	0.00E+00	0.00E+00	-	0.00E+00	-
Na_2CO_3	4.25E-04	-	-	0.00E+00	-	4.25E-04	0.00E+00	-	1.00E-02	-
NaCL	1.34E-04	-	-	0.00E+00	-	1.34E-04	0.00E+00	-	2.40E-04	-
$NaNO_2$	0.00E+00	-	-	7.50E-04	-	0.00E+00	0.00E+00	-	7.63E-02	-
$NaNO_3$	6.68E-04	-	-	0.00E+00	-	6.68E-04	0.00E+00	-	6.97E-02	-
NaOH	4.42E-03	-	-	3.95E-04	-	4.59E-03	0.00E+00	-	1.76E-02	-
Na_2SO_4	0.00E+00	-	-	0.00E+00	-	0.00E+00	0.00E+00	-	3.03E-03	-
$Na_2C_2O_4$	3.06E-02	1.00E+00	1.00E+00	0.00E+00	0.00E+00	3.06E-02	7.67E-01	8.76E-02	7.66E-03	1.00E+00
$Al(OH)_3$	0.00E+00	-	-	0.00E+00	-	0.00E+00	1.37E-01	-	0.00E+00	-
AlOOH	0.00E+00	-	-	0.00E+00	-	0.00E+00	0.00E+00	-	0.00E+00	-
$NaAlO_2$	6.12E-04	-	-	0.00E+00	-	6.11E-04	0.00E+00	-	7.59E-03	-
CaC_2O_4	7.35E-07	-	-	0.00E+00	-	7.35E-07	0.00E+00	5.14E-08	3.22E-07	-
$CaCO_3$	0.00E+00	-	-	0.00E+00	-	0.00E+00	0.00E+00	-	0.00E+00	-
$Ca(OH)_2$	0.00E+00	-	-	0.00E+00	-	0.00E+00	0.00E+00	-	0.00E+00	-
Ce_2O_3	1.15E-04	-	-	0.00E+00	-	1.15E-04	0.00E+00	8.03E-06	5.03E-05	-
$Ce_2(C_2O_4)_3$	0.00E+00	-	-	0.00E+00	-	0.00E+00	0.00E+00	-	0.00E+00	-
$Fe_2(C_2O_4)_3$	2.37E-05	-	-	0.00E+00	-	2.37E-05	0.00E+00	1.66E-06	1.04E-05	-
$Fe(OH)_3$	0.00E+00	-	-	0.00E+00	-	0.00E+00	6.15E-02	-	0.00E+00	-
$K_2C_2O_4$	0.00E+00	-	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	0.00E+00	-
KOH	0.00E+00	-	-	0.00E+00	-	0.00E+00	0.00E+00	-	0.00E+00	-
MnC_2O_4	3.56E-06	-	-	0.00E+00	-	3.56E-06	0.00E+00	2.49E-07	1.56E-06	-
$Mn(OH)_2$	0.00E+00	-	-	0.00E+00	-	0.00E+00	1.42E-02	-	0.00E+00	-
NiC_2O_4	8.90E-08	-	-	0.00E+00	-	8.90E-08	0.00E+00	6.23E-09	3.91E-08	-
NiOH2	0.00E+00	-	-	0.00E+00	-	0.00E+00	2.71E-03	-	0.00E+00	-
SiO_2	8.69E-04	-	-	0.00E+00	-	8.69E-04	0.00E+00	-	0.00E+00	-
$UO_2C_2O_4$	1.21E-06	-	-	0.00E+00	-	1.21E-06	0.00E+00	8.47E-08	5.31E-07	-
$UO_2(OH)_2$	0.00E+00	-	-	0.00E+00	-	0.00E+00	7.45E-03	-	0.00E+00	-
THO_2	4.83E-14	-	-	0.00E+00	-	4.83E-14	2.71E-03	-	0.00E+00	-
HGO	3.83E-05	-	-	0.00E+00	-	3.83E-05	7.07E-03	-	0.00E+00	-
THC_2O_42	0.00E+00	-	-	0.00E+00	-	0.00E+00	0.00E+00	-	0.00E+00	-
Total (kg)	1.93E+05	1.23E+03	1.23E+03	8.39E+06	-	1.91E+05	3.83E+04	3.69E+05	3.77E+05	7.55E+03
Volume (gal)	4.93E+04	-	-	2.20E+06	3.20E+06	4.90E+04	8.51E+02	5.52E+05	1.38E+06	-
Enthalpy (cal)	-7.20E+11	-	-	-	-	-7.15E+11	-9.62E+10	-	-	-
Density (g/gal)	3.91E+03	-	-	3.82E+03	-	3.91E+03	4.50E+04	-	-	-
Oxalate ion (kg)	3.87E+03	8.08E+02	8.08E+02		0.00E+00	3.85E+03	1.93E+04	2.12E+04	1.90E+03	4.96E+03

Table 9: Material Balance for Case 4

Stream Number	1	2	3	4	5	6a	6b	7a	7b
Stream	Oxalic Acid	Dilution Water	Neutralizing Solution	Slurry Water	Wash Water	Sludge Heel	Sludge Heel	Dissolved Heel	Dissolved Heel
Phase	Aqueous	Aqueous	Aqueous	Aqueous	Aqueous	Aqueous	Solid	Aqueous	Solid
Temperature (°C)	30	-	30	-	-	30	30	30	30
pH	0.7	-	14.7	-	-	11.6		1.4	
Units	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac
H2O	9.20E-01	-	6.79E-01	-	9.76E-01	9.40E-01	0.00E+00	9.10E-01	0.00E+00
H2C2O4	8.00E-02	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	6.27E-02	0.00E+00
HCl	0.00E+00	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	8.66E-05	0.00E+00
HNO3	0.00E+00	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	5.14E-04	0.00E+00
Na2CO3	0.00E+00	-	1.42E-02	-	0.00E+00	6.20E-05	0.00E+00	4.41E-04	0.00E+00
NaCL	0.00E+00	-	0.00E+00	-	0.00E+00	3.14E-03	0.00E+00	0.00E+00	0.00E+00
NaNO2	0.00E+00	-	3.11E-02	-	2.41E-02	0.00E+00	0.00E+00	0.00E+00	0.00E+00
NaNO3	0.00E+00	-	1.59E-01	-	0.00E+00	1.57E-02	0.00E+00	0.00E+00	0.00E+00
NaOH	0.00E+00	-	7.62E-02	-	0.00E+00	1.74E-02	0.00E+00	0.00E+00	0.00E+00
Na2SO4	0.00E+00	-	1.77E-02	-	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Na2C2O4	0.00E+00	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	1.75E-03	0.00E+00
Al(OH)3	0.00E+00	-	0.00E+00	-	0.00E+00	0.00E+00	5.78E-01	0.00E+00	0.00E+00
AlOOH	0.00E+00	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	1.13E-02	0.00E+00
NaAlO2	0.00E+00	-	2.17E-02	-	0.00E+00	4.38E-05	0.00E+00	0.00E+00	0.00E+00
CaC2O4	0.00E+00	-	0.00E+00	-	0.00E+00	4.88E-05	1.64E-02	3.96E-05	2.13E-01
CaCO3	0.00E+00	-	0.00E+00	-	0.00E+00	0.00E+00	1.63E-02	0.00E+00	0.00E+00
Ca(OH)2	0.00E+00	-	0.00E+00	-	0.00E+00	4.33E-05	0.00E+00	0.00E+00	0.00E+00
Ce2O3	0.00E+00	-	0.00E+00	-	0.00E+00	2.69E-03	0.00E+00	0.00E+00	0.00E+00
Ce2(C2O4)3	0.00E+00	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	6.07E-05	2.44E-02
Fe2(C2O4)3	0.00E+00	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	1.11E-02	0.00E+00
Fe(OH)3	0.00E+00	-	0.00E+00	-	0.00E+00	9.59E-07	2.49E-01	0.00E+00	0.00E+00
K2C2O4	0.00E+00	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
KOH	0.00E+00	-	7.46E-04	-	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
MnC2O4	0.00E+00	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	2.79E-04	4.84E-01
Mn(OH)2	0.00E+00	-	0.00E+00	-	0.00E+00	1.03E-07	5.76E-02	0.00E+00	0.00E+00
NiC2O4	0.00E+00	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	5.11E-05	9.10E-02
NiOH2	0.00E+00	-	0.00E+00	-	0.00E+00	4.53E-09	1.10E-02	0.00E+00	0.00E+00
SiO2	0.00E+00	-	0.00E+00	-	0.00E+00	2.04E-02	0.00E+00	1.02E-04	1.88E-01
UO2C2O4	0.00E+00	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	8.99E-04	0.00E+00
UO2(OH)2	0.00E+00	-	0.00E+00	-	0.00E+00	2.69E-07	3.01E-02	0.00E+00	0.00E+00
THO2	0.00E+00	-	0.00E+00	-	0.00E+00	4.93E-14	1.10E-02	0.00E+00	0.00E+00
HGO	0.00E+00	-	0.00E+00	-	0.00E+00	3.86E-05	3.01E-02	7.63E-04	0.00E+00
TH(C2O4)2	0.00E+00	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	4.29E-04	0.00E+00
Total (kg)	3.45E+05	0.00E+00	3.09E+05	0.00E+00	3.05E+06	1.72E+04	9.39E+03	3.68E+05	1.84E+03
Volume (gal)	8.53E+04	-	6.55E+04	-	8.00E+05	4.14E+03	8.63E+02	8.94E+04	8.16E+01
Enthalpy (cal)	-1.26E+12	-	-9.80E+11	-	-	-6.07E+10	-2.84E+10	-1.35E+12	-4.53E+09
Density (g/gal)	4.04E+03	-	4.72E+03	-	-	3.95E+03	1.09E+04	4.12E+03	2.26E+04
Oxalate ion (kg)	2.69E+04		0.00E+00			5.75E-01	1.06E+02	2.61E+04	9.42E+02

Table 9: Material Balance for Case 4 (continued)

Stream Number	8	9	10	11	12	13a	13b	14	15	16
Stream	Neutralization Supernate	Evaporator Feed	Evaporator Concentrate	Dissolution Water	Dissolved Salt	Solids Slurry	Solids Slurry	Washed Sludge	Decant/ Wash Water	Feed Tank Sludge
Phase	Aqueous	-	-	Aqueous	Aqueous	Aqueous	Solid	Slurry	Aqueous	Slurry
Temperature (°C)	30	-	-	-	-	30	30	-	-	-
pH	12.8	-	-	12.0	-	12.8		-	-	-
Units	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac
H2O	8.78E-01	-	-	9.99E-01	-	8.71E-01	0.00E+00	-	7.63E-02	-
H2C2O4	0.00E+00	-	-	0.00E+00	-	0.00E+00	0.00E+00	-	0.00E+00	-
HCl	0.00E+00	-	-	0.00E+00	-	0.00E+00	0.00E+00	-	0.00E+00	-
HNO3	0.00E+00	-	-	0.00E+00	-	0.00E+00	0.00E+00	-	0.00E+00	-
Na2CO3	7.26E-03	-	-	0.00E+00	-	7.23E-03	0.00E+00	-	1.00E-02	-
NaCL	8.18E-05	-	-	0.00E+00	-	8.15E-05	0.00E+00	-	2.40E-04	-
NaNO2	1.53E-02	-	-	7.50E-04	-	1.53E-02	0.00E+00	-	7.63E-02	-
NaNO3	7.89E-02	-	-	0.00E+00	-	7.85E-02	0.00E+00	-	6.97E-02	-
NaOH	4.13E-03	-	-	3.95E-04	-	1.16E-02	0.00E+00	-	1.76E-02	-
Na2SO4	8.74E-03	-	-	0.00E+00	-	8.70E-03	0.00E+00	-	3.02E-03	-
Na2C2O4	5.44E-03	1.00E+00	1.00E+00	0.00E+00	0.00E+00	5.42E-03	7.11E-01	9.63E-02	7.66E-03	1.00E+00
Al(OH)3	0.00E+00	-	-	0.00E+00	-	0.00E+00	2.18E-01	-	0.00E+00	-
AlOOH	0.00E+00	-	-	0.00E+00	-	0.00E+00	0.00E+00	-	0.00E+00	-
NaAlO2	7.53E-04	-	-	0.00E+00	-	7.50E-04	0.00E+00	-	7.59E-03	-
CaC2O4	2.24E-06	-	-	0.00E+00	-	2.23E-06	6.73E-03	9.49E-04	1.33E-06	-
CaCO3	0.00E+00	-	-	0.00E+00	-	0.00E+00	0.00E+00	-	0.00E+00	-
Ca(OH)2	0.00E+00	-	-	0.00E+00	-	0.00E+00	0.00E+00	-	0.00E+00	-
Ce2O3	7.03E-05	-	-	0.00E+00	-	6.99E-05	0.00E+00	6.66E-06	4.17E-05	-
Ce2(C2O4)3	0.00E+00	-	-	0.00E+00	-	0.00E+00	0.00E+00	-	0.00E+00	-
Fe2(C2O4)3	3.09E-05	-	-	0.00E+00	-	3.08E-05	0.00E+00	2.93E-06	1.84E-05	-
Fe(OH)3	0.00E+00	-	-	0.00E+00	-	0.00E+00	4.47E-02	-	0.00E+00	-
K2C2O4	5.44E-04	-	-	0.00E+00	-	5.42E-04	0.00E+00	5.16E-05	3.23E-04	-
KOH	0.00E+00	-	-	0.00E+00	-	0.00E+00	0.00E+00	-	0.00E+00	-
MnC2O4	1.92E-07	-	-	0.00E+00	-	1.91E-07	0.00E+00	1.82E-08	1.14E-07	-
Mn(OH)2	0.00E+00	-	-	0.00E+00	-	0.00E+00	1.04E-02	-	0.00E+00	-
NiC2O4	1.15E-07	-	-	0.00E+00	-	1.15E-07	0.00E+00	1.09E-08	6.84E-08	-
NiOH2	0.00E+00	-	-	0.00E+00	-	0.00E+00	1.97E-03	-	0.00E+00	-
SiO2	5.32E-04	-	-	0.00E+00	-	5.29E-04	0.00E+00	-	0.00E+00	-
UO2C2O4	5.30E-04	-	-	0.00E+00	-	5.28E-04	0.00E+00	5.02E-05	3.15E-04	-
UO2(OH)2	0.00E+00	-	-	0.00E+00	-	0.00E+00	0.00E+00	-	0.00E+00	-
THO2	3.71E-14	-	-	0.00E+00	-	3.70E-14	1.97E-03	-	0.00E+00	-
HGO	3.08E-05	-	-	0.00E+00	-	3.06E-05	5.06E-03	-	0.00E+00	-
TH(C2O4)2	0.00E+00	-	-	0.00E+00	-	0.00E+00	0.00E+00	-	0.00E+00	-
Total (kg)	3.67E+05	9.90E+02	9.90E+02	8.39E+06	-	2.60E+05	5.21E+04	3.69E+05	3.77E+05	3.90E+03
Volume (gal)	8.93E+04	-	-	2.20E+06	3.20E+06	6.33E+04	1.52E+03	5.52E+05	1.38E+06	-
Enthalpy (cal)	-1.29E+12	-	-	-	-	-9.14E+11	-1.39E+11	-	-	-
Density (g/gal)	4.11E+03	-	-	3.82E+03	-	4.11E+03	3.43E+04	-	-	-
Oxalate ion (kg)	1.48E+03	6.50E+02	6.50E+02		0.00E+00	1.04E+03	2.46E+04	2.33E+04	2.00E+03	2.56E+03

4.4   Sludge Washing

Sludge batch 4 is used as an example sludge batch for the material balance in this section.[5] Assuming that the slurry from heel removal is added to the sludge washing tank at the beginning of the sludge batch, the decanted liquid from sludge transfers and washing will remove some oxalate from the sludge batch. The sludge washing targeted a total sodium concentration of 1 M. Washing to the same sodium concentration, the effect on sludge washing is shown in Table 10. Nearly all of the added sodium oxalate from one dissolved heel will be washed out of the sludge batch.

With no changes to the sludge wash batches, 60,500 kg of sodium oxalate could be added to the sludge batch before residual solid sodium oxalate would remain with the sludge slurry after the final planned wash. The total sodium concentration would be approximately 1.0 M. The total sodium oxalate from one 5000 gallon F-Area sludge heel would be about 27,000 to 29,000 kg. The total sodium oxalate from on one 5000 gallon H-Area sludge heel would be about 35,000 to 38,000 kg. Among the cases examined, 2 to 3 dissolved 5000 gallon heels of sludge could be sent to sludge washing before either sodium oxalate would accumulate in the solids or wash water batches would increase in size or number to achieve the same washing goal.

In contrast, if the dissolved 5000 gallon heel is added to the washed sludge batch, all the sodium oxalate would become part of the final batch. The sodium oxalate amounts to about 67 to 75 wt% of the total solids added to the sludge batch. The remainder consists primarily of metal hydroxides, oxides and other metal oxalates formed from dissolution of the heel. For illustration of the effect on a sludge batch, the final sodium oxalate from one heel dissolution from Case 4 would equate to 7.3 wt% of total solids in the sludge slurry for sludge batch 4. The sodium concentration in solution would still be about 1.0 M, but the total sodium in the slurry would increase substantially, by 13,200 kg.

Note that this discussion assumes no reaction of the sodium oxalate when mixed with the sludge batch. Thermodynamically, formation of iron and manganese oxalates are favored as observed in stream 13 and shown in Table 6 through Table 9. However, the reaction occurs between ions in solution rather than solid compounds. The aqueous concentrations of metals are very small in the sludge slurry liquid and the oxalate is sparingly soluble, so that ionic concentrations of potential reactants are low. In turn, the low concentration of reactants in solution means that the driving potential for the reaction is low. In other words, the rate of reaction will be very slow. The sodium product of the reaction is soluble sodium salts, primarily sodium hydroxide, which would readily wash out of the sludge slurry. If these reactions occur to any appreciable extent before washing the sludge batch, then the amount of metal oxalates will increase and the amount of sodium oxalate will decrease. The total sodium will decrease because more soluble sodium will wash out. If these reactions occur in the washed sludge batch, the free hydroxide will tend to increase and the total sodium will remain unchanged.

Table 10: Sodium Oxalate Balance for Sludge Washing

	Heel Slurry	After Decant-51-1	After Decant 51-2	After Decant 51-3	After Decant 51-4	After Decant 51-5	Total to Evaporator System
Case 1							
[Na+] (M)		3.46	2.85	1.58	1.09	1.00	
Volume (gal)		350,000	350,000	350,000	250,000	77,000	
Sodium Oxalate Solid (kg)	22,000	19,500	13,000	-	-	-	
Sodium Oxalate in Solution (kg)	4,570	3,450	5,140	9,450	5,680	4,710	
Total (kg)	26,600	23,000	18,200	9,450	5,680	4,710	21,800
Concentration Sodium Oxalate (M)		0.0203	0.0268	0.0492	0.0297	0.0247	
Case 2							
[Na+] (M)		3.46	2.85	1.58	1.09	1.00	
Volume (gal)		350,000	350,000	350,000	250,000	77,000	
Sodium Oxalate Solid (kg)	27,700	21,700	15,200	-	-	-	
Sodium Oxalate in Solution (kg)	1,010	3,450	5,140	10,600	6,360	5,280	
Total (kg)	28,700	25,100	20,400	10,600	6,360	5,280	23,500
Concentration Sodium Oxalate (M)		0.0203	0.0268	0.0552	0.0333	0.0277	
Case 3							
[Na+] (M)		3.46	2.85	1.58	1.09	1.00	
Volume (gal)		350,000	350,000	350,000	250,000	77,000	
Sodium Oxalate Solid (kg)	29,100	27,900	21,400	3,440	-	-	
Sodium Oxalate in Solution (kg)	5,850	3,450	5,140	12,000	9,290	7,710	
Total (kg)	34,900	31,300	26,600	15,400	9,300	7,700	27,200
Concentration Sodium Oxalate (M)		0.0203	0.0268	0.0626	0.0485	0.0404	

Table 10: Sodium Oxalate Balance for Sludge Washing (continued)

	Heel Slurry	After Decant-51-1	After Decant 51-2	After Decant 51-3	After Decant 51-4	After Decant 51-5	Total to Evaporator System
Case 4							
[Na+] (M)		3.46	2.85	1.58	1.09	1.00	
Volume (gal)		350,000	350,000	350,000	250,000	77,000	
Sodium Oxalate Solid (kg)	37,000	31,300	24,900	6,900	-	-	
Sodium Oxalate in Solution (kg)	1,420	3,450	5,140	12,000	11,400	9,450	
Total (kg)	38,400	34,800	30,000	18,900	11,400	9,450	29,000
Concentration Sodium Oxalate (M)		0.0203	0.0268	0.0626	0.0595	0.0495	

4.5 Tank Farm Evaporation

The material balance is calculated using the tank farm evaporator model for 242-16H (commonly referred to as the 2H evaporator) with an example recent starting condition used for process planning.[12] Table 11 shows the feed tank initial composition. Table 12 shows the results for transferring one liquid decant from heel dissolution to the evaporator feed tank for each case.

The evaporator model results indicate that only a relatively small amount of sodium oxalate will be fed to the evaporator and subsequently to the drop tank. About 1000 to 1200 kg move from the feed tank to the drop tank during the simulated 3000 hours of operation. Figure 5 and Figure 6 show example evaporator model results for case 2. The amount of sodium oxalate in the evaporator feed decreases to the point that the remaining sodium oxalate in the feed tank does not practically change. The concentration in the aqueous phase decreases due to the increase in total sodium concentration or ionic strength. By inference, more sodium oxalate will transfer to the drop tank with each large transfer of fresh, relatively dilute, waste into the feed tank. If no additional sodium oxalate is added to the feed tank, the remaining oxalate will eventually be deposited in the drop tank. However, the feed tank contains a sludge layer at the bottom. If the evaporator feed tank continues to receive waste with sludge solids, the precipitated sodium oxalate is covered by the added sludge, thus, slowing the effective transfer from the feed tank to the drop tank. In addition, the precipitated sodium oxalate could settle into the sludge layer, especially a relatively low solids density material at the top of the sludge layer, which would tend to inhibit further dissolution by covering the solids.

If stream 8, neutralization supernate, is added to the evaporator drop tank, most of sodium oxalate will remain with the saltcake. The high sodium concentration inherently present in

the drop tank will cause nearly all the oxalate to precipitate. Recycling from the evaporator drop tank to the evaporator feed tank will not cause significant precipitation in the feed tank because the relatively low sodium oxalate concentration in the recycle is diluted with existing supernate in the feed tank.

Table 11: Evaporator Feed Tank Initial Composition[12]

Chemical Compound	Feed Tank (M)
$NaNO_3$	1.82
$Na_2CO_3.H_2O$	0.0876
$NaNO_2$	1.69
$NaAlO_2 \cdot 2H_2O$	0.114
$Na_2C_2O_4$	0.00619
Na_2SO_4	0.0239
NaCl	0.00348
NaF	0.00579
NaOH	4.71
Na_3PO_4	0.00651
Na_2SiO_3	0.00784

Stream 15, the decant stream from sludge washing, will simply add additional sodium oxalate directly to the solids layer of the feed or drop tank. If added to the feed tank, large quantities of sodium oxalate will accumulate in the sludge layer. The sodium oxalate will move back to the sludge wash tank when the appropriate sludge batch calls for the feed tank sludge. A large portion will return to the evaporator feed tank via the sludge washing process as shown in an earlier section. As noted earlier, if more residual than the amount from 2 or 3 heel dissolutions have accumulated in the evaporator feed tank, about 60,000 kg of sodium oxalate, then all the sodium oxalate above this threshold will become part of the washed sludge slurry. A quantity less than this amount will tend to remain or return to the feed tank and remain until heel removal is performed in the feed tank.

Up to this point, evaporator operability is not considered. Past experience includes a large amount of heat exchanger flush solution from Building 105-C that was added to Tank 7. This solution contained sodium oxalate from the flush solutions used. Immediately after the supernate from Tank 7 was transferred to the evaporator feed tank, the 242-F evaporator operation experienced an increase in descaling frequency and an abrupt increase in gamma activity in the overheads. Samples of the scale showed primarily sodium sulfate and sodium oxalate with minor amounts of carbonate, iron, aluminum and manganese. The high activity was attributed to an increase in foaming during startup after each descale.[13] The combined problem significantly decreased attainment. From this experience, high sodium oxalate concentration in the evaporator feed would likely result in higher descaling frequencies. An evaluation and adjustment of defoaming agent usage rates in the evaporator will likely avoid the foaming problems experienced in the past.

Table 12: Sodium Oxalate Balance for the Evaporator Model Runs

	Case 1		Case 2		Case 3		Case 4	
	$Na_2C_2O_4$ (kg)	(% of added)	$Na_2C_2O_4$ (kg)	(% of added)	$Na_2C_2O_4$ (kg)	(% of added)	$Na_2C_2O_4$ (kg)	(% of added)
Started in Feed Tank	2940	-	2890	-	2917	-	2670	-
Started in Drop Tank	1100	-	1140	-	1115	-	1370	-
Added to Feed Tank	4110	-	1370	-	5893	-	2000	-
Remains in Feed Tank	5940	73%	3100	15%	7666	81%	3700	52%
Remains in Drop Tank	2250	28%	2390	91%	2343	21%	2360	50%
Transferred to Drop Tank	1150	-	1250	-	1230	-	990	-
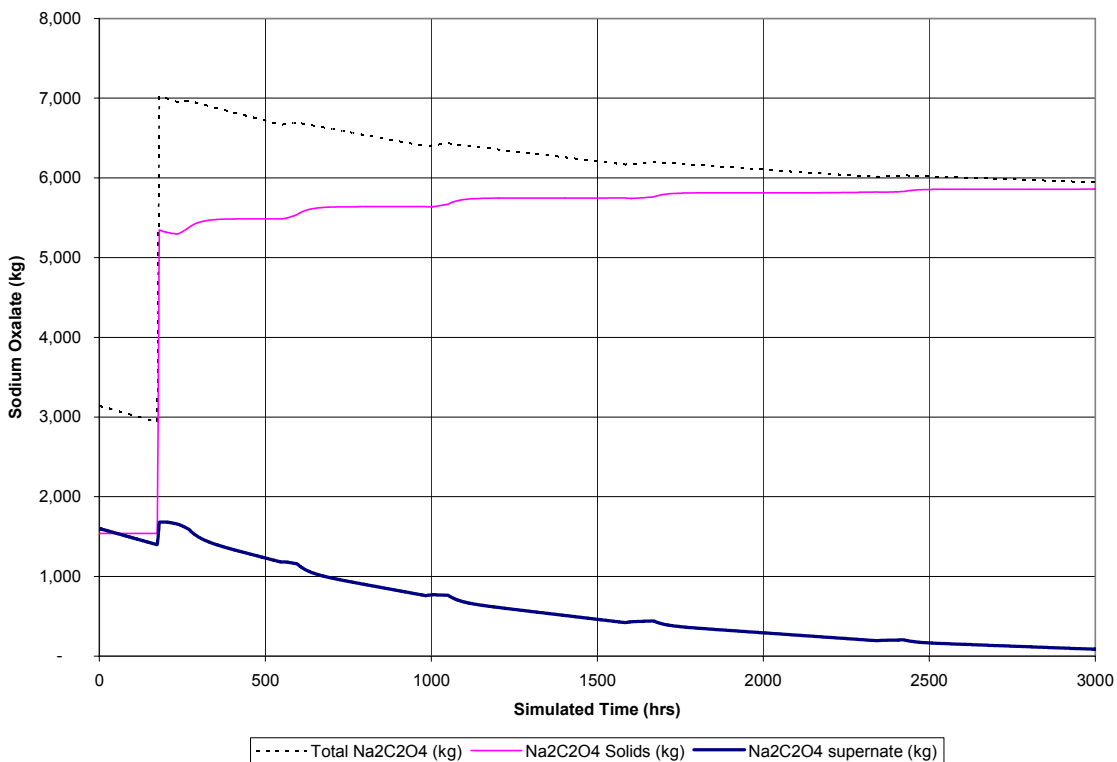
Figure 5: Sodium Oxalate in Evaporator Feed Tank with Stream 8 Added to the Feed Tank for Case 2
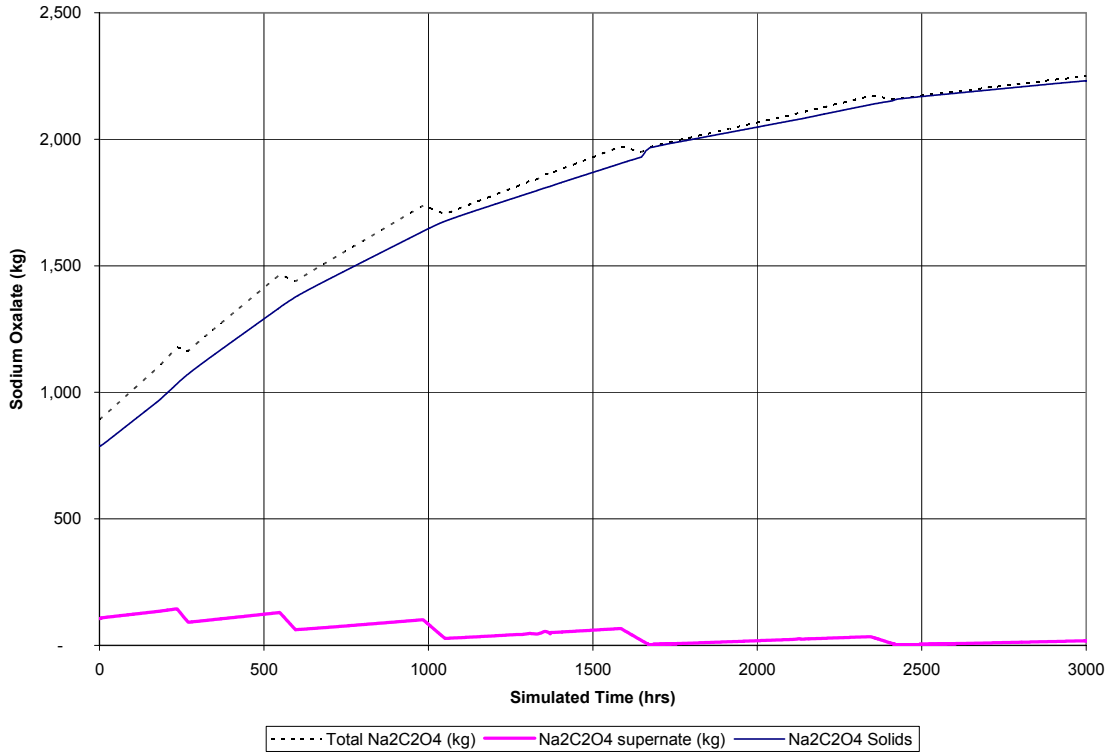
Figure 6: Sodium Oxalate in Evaporator Drop Tank with Stream 8 Added to the Feed Tank for Case 2

4.6   Salt Dissolution

About 2.2 gal of water will be added to each gallon of saltcake to produce about 3.2 gallons of feed solution at a total sodium concentration of 6.4 M. In a salt tank with nominally 1 million gallons of saltcake, about 3.2 million gallons of dissolved salt solution will be created to feed the salt process. At 6.4 M sodium, sodium oxalate has a total solubility of

$$\text{Maximum}[\text{Na}_2\text{C}_2\text{O}_4] = \text{T} \cdot \left(0.00159 \cdot \text{I}^{-1.444}\right) + \left(0.0723 \cdot \text{I}^{-1.424}\right)$$

where

    T = temperature in Celsius, and
    I = total sodium concentration in molarity.

Assuming 30°C and 6.4 M total sodium concentration, the saturation level of sodium oxalate is about 0.0084 M. At this saturation concentration, the total oxalate dissolved would be as much as 13,600 kg or 30,000 lb of sodium oxalate. If the saltcake contains more sodium oxalate, the additional oxalate would make up part of the relatively insoluble or low solubility heel.

Average saltcake solids contain about 0.45 wt. % sodium oxalate as shown in Table 13. In 1,000,000 gallons of saltcake with an average solids specific gravity of 2.3 and typical solid void fraction of 0.40, the saltcake already contains about 23,500 kg of sodium oxalate. Therefore, on average, all added sodium oxalate to the saltcake will become part of the low solubility salt heel. In tanks with existing saltcake at very low oxalate content, sodium oxalate could be added to the saltcake with no impact to salt dissolution or the resulting salt heel after dissolution. None were identified in this analysis, but insufficient chemical characterization data is available to determine if any salt tanks exist with low enough oxalate content.

Table 13: Average Saltcake Composition[14]

Chemical Compound	Saltcake (wt%)
$NaNO_3$	86
$Na_2CO_3.H_2O$	5.7
$NaNO_2$	0.82
$NaAlO_2·2H_2O$	2.2
$Na_2C_2O_4$	0.45
Na_2SO_4	2.9
$NaCl$	0.0068
NaF	0.17
$NaOH$	0.73
Na_3PO_4	0.59

This material can be processed into a final waste form by several methods. Though not proven, dissolving the sodium oxalate with water, filtering the solution at the Salt Waste Processing Facility (SWPF) or similar, and feeding the filtrate to the Saltstone facility is possible. The following discussion estimates the effective increase salt heel size, total amount of additional low concentration salt solution that would be sent to the Saltstone facility, and estimates the cost to produce the additional grout.

Sodium oxalate will saturate water at about 0.26 M concentration which is about 0.52 M total sodium concentration. The largest amount of sodium oxalate sent to an evaporator system from the four cases is Case 3 at 33,000 kg. Assuming that the precipitated sodium oxalate contains an average bulk void volume of 40% and the crystalline density is 2.34 g/ml[15], then the low solubility salt heel increases by about 6,200 gallons. At least 250,000 gallons of water is needed to dissolve this added heel. If the salt is dissolved with inhibited water, 280,000 gallons of inhibited water is needed. At $3 per additional gallon to process this solution through the Saltstone facility[16], the additional cost to process the resulting salt heel from dissolving one 5000 gallon sludge heel is about $750,000 to $850,000.

Since the Saltstone facility was not designed for this feed solution, an alternate formulation for grout needs to developed and tested. The characteristics of the salt heel need to be determined in order to determine if more than filtration of sludge-like solids from the

dissolved heel is needed to remove radionuclides that exceed the Saltstone facility feed limits.

4.7   Salt Processing and Saltstone

All the dissolved sodium oxalate will pass through salt processing with the other soluble sodium salts to the Saltstone facility. About 13,600 kg of sodium oxalate is expected to be sent to salt processing per 1,000,000 gallons of saltcake processed. No existing plans will move the solid heel after bulk salt removal to any salt process. The planned Actinide Removal Process, the Modular Solvent Extraction, or the Salt Waste Processing Facility will pass the sodium oxalate in its entirety to the Saltstone facility where it will be incorporated into a final solid waste form. The concentrations of sodium oxalate are well within the Waste Acceptance Criteria for the Saltstone facility, 1200 mg/L as C_2O_4.[17] See the previous section for a discussion about processing the salt heel.

4.8   Vitrification

The potential effects of sodium oxalate are divided into three broad divisions: sludge receipt and adjustment tank (SRAT) process, melter behavior, and glass performance.

The Savannah River National Laboratory (SRNL) studied the effect of substantial sodium oxalate in sludge batch 3 on the Defense Waste Processing Facility (DWPF) vitrification process. These tests indicate the nature of the effect on future batches, but testing of each specific batch blend will be needed to confirm expectations. The tests results are expressed in terms relative to the maximum amount of sodium estimated to be in sludge batch 3. Table 14 shows the conversion of relative percent sodium oxalate to weight percent in the simulated feeds tested.

Table 14: Sodium Oxalate Content for Sludge Batch 3 Testing

wt% Sodium Oxalate in Total Solids	% Washed Out	% Remaining
	Relative to Total Estimated Sodium Oxalate in Tank 7	
14%	75	25
26%	50	50
34%	25	75
46%	-25	125

These studies show the SRAT is affected as follows:[18,19]

- negligible amounts of iron and gadolinium become soluble with sodium oxalate at 26 wt% of total solids,

- iron becomes 10 times more soluble when sodium oxalate increases to 34 wt% or 46 wt% of total solids, but 95% of the iron remains insoluble,

- gadolinium, which was added as the canyon neutron poison for the Pu stream in sludge batch 3, becomes completely soluble at 34 wt%,

- sodium oxalate mitigated the release of hydrogen, and

- more acid is required with increasing sodium oxalate concentration to complete nitrite destruction, which implies slightly longer cycle times for the SRAT.

If the sodium oxalate content is kept below 26 wt% of total solids, the solubility of iron and gadolinium is kept low enough to be negligibly affected. This amounts to about 150,000 kg of sodium oxalate for sludge batch 3.

Process studies to determine melter behavior and glass acceptability of sludge batch 3 with elevated sodium oxalate concentrations shows mixed results. In order to verify acceptability of feed material to DWPF, melter behavior such as melt rate has only been demonstrated with bench scale testing of simulants. Acceptability testing is needed before finalizing any addition of sodium oxalate to any sludge batch.

Glass performance predictive tools based on composition are relatively well developed. Several variations of frit compositions were examined for sludge batch three to determine the acceptability of a large amount of sodium oxalate in the batch.[20] Using these studies, an estimate of the total oxalate that can be reasonably added to a sludge batch is determined.

All metal oxalates entering the DWPF process end up as metal oxides in the final glass product. The oxalate reacts to form carbon dioxide which leaves DWPF in the off-gas system. In terms of glass performance and acceptability, solid sodium oxalate adds to soluble sodium salts to increase total sodium content in the feed material. Results of the frit variation studies show that acceptable glass can be made from frit 418 and sludge batch 3 at 35% sludge loading in the glass. The studies show higher waste loadings are acceptable, but DWPF process issues such as melt rate constrain waste loading such that maximum loadings are difficult to achieve. Current processing of sludge batch 3 demonstrates that acceptable glass can be made with a total sodium content of the composite frit-sludge mixture. Projecting that similar total sodium content can be made acceptable in future sludge batches, then some of the sodium provided from the frit can be lowered to allow an increase in the sodium allowed in the sludge. The lowest sodium containing frit that has been easily produced contains 25.0% less sodium than frit 418. Assuming all this sodium is now provided by the sludge, the total possible sodium content of the sludge increases 17.4 %. Sludge batch 3 contains a total sodium content of 1.192 M at a specific gravity of 1.064 and 17.5 wt% insoluble solids slurry.[21,22] The measured sodium content is 13.2 wt% of total solids.[23] The increase would allow as much as 15.5 wt% sodium in the total solids or bulk sodium content in the same slurry of 1.40 M. If sludge washing still removes the soluble salt content down to 1.0 M sodium, sodium oxalate can be added to the sludge up to an equivalent 0.40 M sodium or 0.20 M sodium oxalate. This equates to about 9.3 wt% of total solids in the slurry which is well within the demonstrated acceptability for processing within the SRAT. In fact, considerably more sodium oxalate could be added if more soluble sodium salts are removed from the sludge by washing. Adding sodium oxalate in this manner does not result in a net increase of canister produced at DWPF relative to sludge only.

The waste slurry from sludge heel cleaning will need to be included in planning for each sludge batch. In addition, the affects on feed rheology during mixing and transfer in DWPF and during melter feeding would also have to be understood for the sludge batch. These parameters were not qualified during sludge batch 3 testing.

4.9   Effect on Waste Process Strategy and Recommended Flowsheet

Sludge heel cleaning with oxalic acid essentially results in two streams that need to be dispositioned. The first is the neutralized supernatant liquid, stream 8, and the second is the sludge with the precipitated sodium oxalate solids slurry, stream 13. Each stream is discussed below.

4.9.1   Neutralized Supernatant Liquid

The neutralized supernatant liquid will eventually be sent to the evaporator system. The liquid may be sent to the evaporator feed or drop tank. If this liquid is sent to the evaporator feed tank, Section 4.5 shows that most of the sodium oxalate precipitates and remains in the feed tank. Effectively, sodium oxalate builds up in the sludge layer of the feed tank and could become unmanageable for sludge blending.

If sent to the drop tank, practically all the sodium oxalate remains in the drop tank. All the added oxalate becomes part of the saltcake heel after bulk salt removal and will be processed with the solid salt/sludge. Potentially, all the low solubility salts and sodium oxalate remaining could be dissolved and processed through the SWPF or similar with final disposition as additional saltstone as discussed in Section 4.7. The additional amount of sodium oxalate in the feed stream to Saltstone will have only a small impact on the volume of Saltstone produced. About 6,000 kg of sodium oxalate per sludge heel dissolved could be in this stream and would generate about 50,000 gallons of additional dilute saltstone feed.

Given the additional potential operational problems with sending this stream to the evaporator feed tank, the preferred option is to send this stream to any evaporator drop tank, including salt tanks that are not currently active evaporator drop tanks.

4.9.2   Solids Slurry

The solids slurry will be sent to DWPF for incorporation into a glass waste form. This stream may be sent to either the sludge washing tank or the DWPF feed tank. If the solids slurry is sent the sludge washing tank, solids slurry from two to three sludge heels could be added and practically all the sodium oxalate would be washed out of the batch with no effect on the sludge batch as discussed in Section 4.4. All the sodium oxalate would end up in the evaporator system with significant impact to the salt heel removal and final disposal at the Saltstone Facility as discussed in Section 4.7.

The second option is to wash the sludge first to a low enough sodium level, and then to add the solids slurry to the batch. This will result in all of the insoluble sludge solids and metal

oxalates being sent to DWPF. Given the experience with sludge batch 3, considerable sodium oxalate could be added to a batch with negligible difference to the process or canisters produced as long as the addition is included in batch planning and qualification testing. Testing shows that processing in the SRAT can readily tolerate 26 wt% sodium oxalate of total solids, glass performance tests could limit the tolerance to 10 wt%, more or less depending on the amount of sludge batch washing. Sludge batch qualification testing with more alternate frit formulations might loosen this constraint.

Given that DWPF can readily accommodate only a small increase in sodium oxalate concentration (about 10 wt %), the preferred option is to add the solids slurry to the sludge feed tank and feed it to DWPF at a small, steady rate. This will prevent having to deal with a sludge with a significantly larger sodium oxalate concentration at some future date.

4.9.3 Recommended Process Flowsheet

Figure 7 shows the process flowsheet after including the preferred process choices discussed above. Note that the amount of oxalic acid recommend for use in this process is expected to achieve complete dissolution of all reactive sludge species with a 100% molar excess. For a 5000 gallon F-Area sludge heel, 65,000 gallons of 8 wt% acid is used and 85,000 gallons for an 5000 gallon H-Area sludge heel. This might vary somewhat for other H-Area tanks that are not calculated in the cases due to some composition variations identified in Table 4.
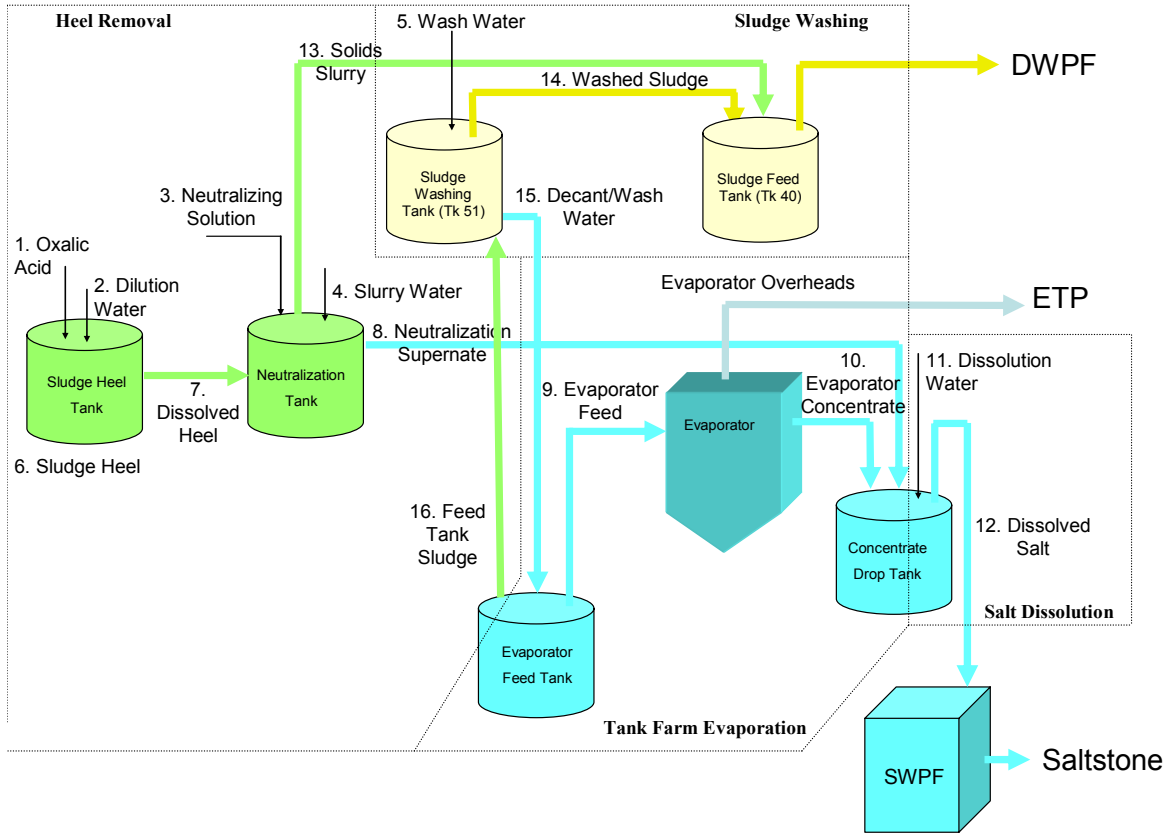
Figure 7: Recommended Heel Removal Flow Diagram

4.10 Evaluation of Model verses Historical Experience of Cleaning Tank 16

In order to establish relative accuracy of the model, historical data from oxalic acid cleaning of Tank 16 will be compared to a model simulation of the acid cleaning process. Table 15 shows the sequence of events with data needed to create the model inputs for streams 1, 2, and 3. Stream 6 is defined by the data shown in Table 16. Table 17 shows the output for stream 7 in contrast with the sample data obtained in Tank 16 after each wash cycle. Sample data was not available to compare the results of stream 13 or stream 8.

Table 17 highlights one important aspect about using equilibrium models to predict results, that is, the model predicts a complete dissolution on the first wash cycle, but significant amount of solids still existed as demonstrated in the measured total metals content. The relatively constant iron concentration implies dissolution of iron in wash cycles after the first. The model shows the total concentration of all metals as decreasing by dilution effects only in each subsequent batch. The measured aluminum and manganese appear to follow a similar trend, but the actual values and measured values differ considerably, perhaps because some solids are dissolving or the analytical/sample variance in measured values is very high.

The model very closely tracks the total soluble oxalate concentration. Although the information presented on solubility test solutions in Section 4.2 shows that OLI ESP has a propensity to under predict solubility, the predicted concentrations are adequate when compared to field measured data.

Table 15: Sequence of Events for Tank 16 Acid Cleaning[24]

Acid Wash Cycle 1
    3500 gallon heel to treat with oxalic acid
    Sprayed about 37,000 gal of water at 90 C through Riser 1
    Add 12,611 gallons of 4 wt% oxalic acid at 90 C directly to heel
    Flushed with 4,500 gallons of water at 90 C – 41,596 gallons total water added to tank
    Slurry pumps started when volutes became submerged
    Agitate for 2 days
    22,937 gallons seal water from pumps added to tanks – total water added
    Transfer to Tank 21, 4503 gallons 50% NaOH added to HPT-4 to neutralize > pH 12
    3500 gallon heel remained after transfer
Acid Wash Cycle 2
    Sprayed 41,000 gal of water at 90 C through Riser 1
    Sprayed 1800-2000 gallons of 4 wt% oxalic acid at 90 C through each of 5 spray risers – 9865 gal total
    Flushed with 5400 gallons of water – 46,477 gallons total water added to tank
    Slurry pumps started when volutes became submerged
    Agitate for 40 hours
    27,220 gallons seal water from pumps added to tanks – total water added
    Transfer to Tank 21, 2473 gallons of 50% NaOH added to HPT-4 to neutralize > pH 12
    2800 gallon heel remained after transfer
Acid Wash Cycle 3
    Sprayed 9,000-12,000 gallons of 4 wt% oxalic acid at 90 C through each of 5 spray risers – 50,545 gallons total
    Flushed with 5797 gallons of water
    Slurry pumps started when volutes became submerged
    Agitate for 48 hours
    27,220 gallons seal water from pumps added to tanks – total water added
    Transfer to Tank 22, 50% NaOH added to HPT-4 to neutralize > pH 12
    3,675 gallon heel remained after transfer
After Wash Cycle 3
    About 100 gallons of material remained in a pile
    Material was sampled but data not reported completely - radionuclides reported, chemistry stated to be "mostly hematitie (Fe_2O_3) and boehmite ($Al_3O_3\ H_2O$)", but not quantified.

Table 16: Tank 16 Sludge Composition[25]

	wt%
AlO_2^-	16
Fe^{3+}	40
MnO_2	16
Na^+	20
SO_4^{2-}	1.1
Si^{4+}	2
Ba^{2+}	1
Ca^{2+}	1
Ce^{4+}	1
Hg^{2+}	2.5
UO_2^{2+}	0.4
Total	101

Table 17: Comparison of Measured Values and Heel Dissolution Model Results[24,26]

	density (kg/L)	Vol % solids	Concentration in Aqueous Phase								Total Concentration in Slurry		
			NO3- (M)	NO2- (M)	Free OH- (M)	C2O4-- (M)	Fe (M)	Mn (M)	Al (M)	H+ (M)	Fe (M)	Mn (M)	Al (M)
Measured Values													
Sludge heel	1.01	3.1	0.055	0.0018	<1e-4	NM	NM	NM	NM	NM	NM	NM	NM
acid wash 1	1.02	<0.5	0.025	NM	NM	0.051	0.0040	NM	0.021	0.029	0.017	0.0099	0.004
acid wash 2	1.03	0.6	0.0060	NM	NM	0.048	0.0057	0.00044	0.0033	0.054	0.011	0.00065	0.0072
acid wash 3	1.02	<0.5	0.0028	NM	NM	0.31	0.040	0.000074	0.0046	0.49	0.076	0.0007	0.0059
Calculated Model Results													
acid wash 1	-	-	-	-	-	0.070	0.016	0.0040	0.0060	0.074	0.016	0.0040	0.0060
acid wash 2	-	-	-	-	-	0.058	0.00051	0.00013	0.0014	0.11	0.00051	0.00013	0.0014
acid wash 3	-	-	-	-	-	0.29	0.000023	0.0000060	0.000064	0.57	0.000023	0.0000060	0.000064

5   Conclusions

Sludge heel cleaning with oxalic acid essentially results in two streams that need to be dispositioned. The first is the neutralized supernatant liquid stream and the second is the sludge with the precipitated metal oxalate solids slurry stream. The preferred flowsheet (see section 4.9.3) calls for the supernatant to be added to an evaporator drop tank and subsequent disposal with the saltcake heel. The solids slurry would be added to a washed sludge batch and subsequent disposal with a sludge batch to the DWPF. The preferred flowsheet includes recommended amount of oxalic acid based on sludge heel composition.

Based on the preferred flowsheet and data from sludge batch 3 qualification tests, the following conclusions are made concerning the effect on DWPF:

- Sodium oxalate from the solids slurry can be added to a sludge batch without affecting the number of canisters produced.

- The feed to the SRAT can tolerate up to 26 wt% sodium oxalate in total solids.

- Increasing metal oxalate in the feed to the SRAT increases formic and nitric acid consumption, thus, increasing SRAT cycle time and altering melter redox.

- Glass quality limits the total amount of sodium in a batch without increase the number of canisters produced.

- Using past experience with sludge batch 3 to calculate a general planning guide, the maximum sodium content in a sludge batch could be 1.4 M sodium.

- If sludge processing washes the soluble sodium content to about 1 M, the sludge batch can contain about 10 wt% of total solids as sodium oxalate before increasing the number of canisters produced or changing sludge processing.

- If all of the metal oxalate becomes part of a sludge batch, about 26,000 to 38,000 kg sodium oxalate is added to the sludge batch per 5000 gallon sludge tank heel processed.

- 10 wt% sodium oxalate in total solids amounts to disposal of 1 to 6 sludge heels depending on waste type of sludge heel cleaned and specific sludge batch.

- Using past experience with sludge batch 3 qualification testing as general planning guide, feed rheology during mixing and transfer in DWPF, melter flammability, and melter feed rates remain within acceptable ranges with added sodium oxalate to a sludge batch. Existing sludge batch qualification testing will determine any actual effects that can not be predicted based on composition estimates alone.

- Solid slurries from tank heel cleaning should be added to sludge batches in relatively small batches, i.e. bled into the DWPF feed stream at a relatively low rate.

- Solid slurry additions from heel cleaning should be included in future sludge batch planning.

The following conclusions are made concerning the effect on the Tank Farm waste storage and evaporator systems:

- Planned salt dissolution will send about 14,000 kg of dissolved sodium oxalate per 1,000,000 gallons of saltcake, all of which currently exists in the saltcake, to the salt waste processing facilities and eventually to the Saltstone Facility.

- All sodium oxalate added to an evaporator drop tank will remain in the drop tank.

- Planned bulk saltcake dissolution will remove none of the added sodium oxalate to an evaporator drop tank, thus, becoming part of the salt heel.

- Sodium oxalate in the salt heel could be dissolved at a very low total sodium concentration, but none of the existing salt waste processes include this stream as a design basis feed stream. A process will need to be developed to treat/remove the heel.

If this flowsheet is changed such that the generated solids slurry from the acid cleaning is added to an unwashed sludge batch and the liquid decant is transferred to the evaporator feed tank, then:

- Sludge processing will wash most of the sodium oxalate from the sludge batch.

- Sludge processing can tolerate sodium oxalate generated from two to three 5000-gallon sludge heel cleanings before accumulating solid sodium oxalate in the sludge batch.

- The evaporator feed tank will accumulate most of the sodium oxalate from any number of sludge heels processed and transferred into the tank.

- The sludge batch that includes the evaporator feed tank sludge will have a large amount of sodium oxalate, which may require an alternate frit formulation and, possibly, modification to the process at DWPF to avoid introducing criticality concerns with the dissolution of iron.

- After processing several sludge heels, approximately 60,000 kg of sodium oxalate will return to the evaporator feed tank when the sludge from the evaporator feed tank is washed as part of sludge processing. An alternate method of disposal would need to be used or developed.

- High sodium oxalate content in the evaporator feed tank causes excessive foaming in the evaporator pot. Current use of defoaming agents would need to be evaluated and adjusted to avoid foaming problems.

If the flowsheet is changed such that the generated solids slurry from the acid cleaning is added to an unwashed sludge batch and the liquid decant is transferred to the evaporator drop tank, then:

- Practically all the sodium oxalate remains in the drop tank as part of the salt heel.

- Dissolving and disposing of the sodium oxalate via the Saltstone Facility results in about 250,000 gallons of 0.5 M sodium feed to the Saltstone Facility per 5000 gallon sludge heel processed.

6 Open Technical Issues

The following items remain as open technical issues:

- A process will need to be developed to treat/remove the salt heel that contains low solubility sodium oxalate.

- An alternate method of disposal would need to be used or developed to dispose of about 60,000 kg of sodium oxalate if the generated solids slurry from the acid cleaning is added to an unwashed sludge batch and the liquid decant is transferred to the evaporator feed tank.

- If the generated solids slurry from the acid cleaning is added to an unwashed sludge batch and the liquid decant is transferred to the evaporator feed tank, current use of defoaming agents would need to be evaluated and adjusted to avoid foaming problems.

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23 C. J. Bannochie, J. M. Pareizs, and D. C. Koopman, "Sludge Batch 2/3 Blend SRAT Cycle in the SRNL Shielded Cells", WSRC-TR-2004-00097, Rev. 0, May 2004, p. 8.

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25 R. F. Bradley and A. J. Hill, Jr., "Chemical Dissolving of Sludge from a High Level Waste Tank at the Savannah River Plant", DP-1471, March 1977.

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A.1   Heel Process Model Description

The unique portion of the sludge heel dissolution process is modeled using OLI ESP software, Version 6.7. Figure A.1 is a schematic of the OLI ESP model.
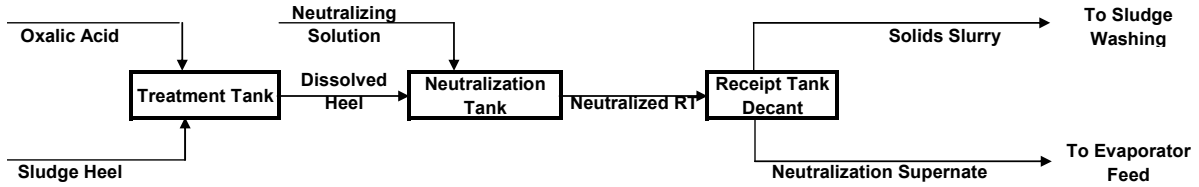
Figure A.1. Schematic of the Sludge Heel Dissolution Process.

A.1.1   Treatment Tank

The Treatment Tank is designed as a Mixer Block. Two streams enter the mixer block: **Oxalic Acid** and **Sludge Heel**. The oxalic acid stream has an initial starting temperature of 30°C, pressure of 1 atm, and has a composition that is 8 weight percent oxalic acid. The amount of oxalic acid required is dependent on the type of waste being dissolved. For the expected composition of sludge heels in Tanks 1-15, refer to Table 4 of Section 4.3.1.

This calculation is performed as an *isothermal calculation* with a final temperature of 30°C. The resultant stream is named **Dissolved Heel**. This stream is fed into the next block, the **Neutralization Tank**, where neutralization of the dissolved heel is performed.

A.1.2   Neutralization Tank

The **Neutralization Tank** is also designed as a Mixer Block. Two streams enter into this block, **Dissolved Heel** and **Neutralizing Solution**. The stream **Neutralizing Solution** can represent either 50 weight percent caustic (50 weight percent NaOH and 50 weight percent H_2O) or average supernate, as defined in Table 5.

This calculation is performed as an *isothermal calculation* with a final temperature of 30°C. The resultant stream from the Receipt Tank is called the **Neutralized RT**. This stream is fed into a Separate Block named **Receipt Tank Decant**.

A.1.3   Receipt Tank Decant

The **Receipt Tank Decant** is a Separate block. The resultant stream from the **Neutralization Tank** Mixer block is fed into this block so that the majority of the liquid can be separated from the solids. The stream name of the solids is called **Solids Slurry** while the liquid has a stream name of **Neutralization Supernate**.   The calculation is performed as an *entrainment calculation* such that the stream **Solids Slurry** contains 16.7 weight percent solids.

At this point, the unique portion of the model, the sludge heel dissolution model is completed. The stream **Neutralization Supernate** is then ran through the existing evaporator process model, while the stream **Solids Slurry** is ran through the existing sludge washing model.

A.2   Dissolution Chemistry

The reactions of oxalic acid with sludge are dependent upon the chemical species of the various elements that make up the sludge (and therefore vary by sludge type). Reactions for dissolution of some of these substances with oxalic acid and nitric acid are shown in Table A.1 and Table A.2.[1]

Table A.1: Oxalic Acid Reactions with Sludge Components[2]

Rxn #	Reactants	Products
1	$2\ AlOOH + 3\ H_2C_2O_4$	$Al_2(C_2O_4)_3 + 4\ H_2O$ (Al^{+3} also appears in solution)
2	$2\ Al(OH)_3 + 3\ H_2C_2O_4$	$Al_2(C_2O_4)_3 + 6\ H_2O$
3	$FeO + H_2C_2O_4$	$FeC_2O_4 + H_2O$
4	$Fe(OH)_3 + 3/2\ H_2C_2O_4$	$FeC_2O_4 + CO_2 + 3\ H_2O$ (ferrihydrite reaction)
5	$FeOOH + 3/2\ H_2C_2O_4$	$FeC_2O_4 + CO_2 + 2\ H_2O$ (goethite reaction)
6	$Fe_2O_3 + 3\ H_2C_2O_4$	$Fe_2(C_2O_4)_3 + 3\ H_2O$ (hematite reaction)
7	$Fe_3O_4 + 4\ H_2C_2O_4$	$Fe_2(C_2O_4)_3 + FeC_2O_4 + 4\ H_2O$ (magnetite reaction)
8	$Fe_2O_3 + 2\ H_2C_2O_4$	$2\ Fe(C_2O_4)_3 + H_2O + O_2$ (complexing)
9	$MnO + H_2C_2O_4$	$Mn(C_2O_4)_3 + \frac{1}{2}\ O_2$ (complexing)
10	$Mn_2O_3 + 2\ H_2C_2O_4$	$2\ Mn(C_2O_4) + 2\ H_2O + \frac{1}{2}\ O_2$
11	$Mn_3O_4 + 3\ H_2C_2O_4$	$3\ Mn(C_2O_4) + 3\ H_2O + \frac{1}{2}\ O_2$
12	$H_2C_2O_4 + NaNO_2 + \frac{1}{2}\ O_2$	$NO + NaNO_3 + 2CO + H_2O$
13	$H_2C_2O_4 + Na_2CO_3$	$Na_2C_2O_4$ (soluble) $+ CO_2 + H_2O$

Table A.2: Nitric Acid Reactions with Sludge Components[3]

Rxn #	Reactants	Products
14	$AlOOH + 3\ HNO_3$	$Al^{3+} + 3\ NO_3^- + 2\ H_2O$
15	$Al(OH)_3 + 3\ HNO_3$	$Al^{3+} + 3\ NO_3^- + 3\ H_2O$
16	$Fe_2O_3 + 6\ HNO_3$	$2\ Fe^{3+} + 6\ NO_3^- + 3\ H_2O$ (complexing)
17	$FeO + 2\ HNO_3$	$Fe^{2+} + 2\ NO_3^- + H_2O$
18	$Fe(OH)3 + 3\ HNO_3$	$Fe^{3+} + 3\ NO_3^- + 3\ H_2O$ (ferrihydrite reaction)
19	$FeOOH + 3\ HNO_3$	$Fe^{3+} + 3\ NO_3^- + 2\ H_2O$ (goethite reaction)
20	$Fe_2O_3 + 6\ HNO_3$	$2\ Fe^{3+} + 6\ NO_3^- + 3\ H_2O$ (hematite reaction)
21	$Fe_3O_4 + 8\ HNO_3$	$2\ Fe^{3+} + Fe^{2+} + 8\ NO_3^- + 4\ H_2O$ (magnetite reaction)
22	$Mn_2O_3 + 6\ HNO_3$	$2\ Mn^{3+} + 6\ NO_3^- + 3\ H_2O$
23	$Mn_3O_4 + 8\ HNO_3$	$2\ Mn^{3+} + Mn^{2+} + 8\ NO_3^- + 4\ H_2O$

SRS sludge waste consists primarily of two types, HM and Purex. The HM sludge is higher in aluminum and the Purex is higher in iron. The primary components of each sludge type are shown in Table A.3 and A.4 as well as the relative ratio of oxalic acid consumed per mass of sludge slurry.[1] Table A.5 shows the equivalent composition and ratios for Tank 16 sludge specifically.[4] These data range from 0.4 to 8 moles of acid per kg of sludge slurry. The ratio of acid consumed per mass of sludge slurry is highly dependent on solids concentration measured or assumed in the sludge slurry.

Table A.3: Amount of Oxalic Acid Needed to React with Components of 1 kg of HM Sludge[3]

Assumed Species	Grams	Moles of Oxalic acid needed
$Al(OH)_3$	330	6.3
Fe_2O_3	41	0.5
MnO	19	0.3
NiO	5	0.1
HM sludge	1000	7.2

Table A.4: Amount of Oxalic Acid Needed to React with Components of 1 kg of PUREX Sludge[5]

Assumed Species	Grams	Moles of Oxalic acid needed
$Al(OH)_3$	3	0.06
Fe_2O_3	19	0.24
MnO	3.7	0.05
NiO	3.8	0.05
PUREX sludge	1000	0.4

Table A.5: Amount of Oxalic Acid Needed to React with Components of 1 kg of Tank 16 Sludge[6]

	MW (g/mole)	wt%	Moles per 1 kg of sludge solids	Moles of Oxalic acid
AlO_2^-	59	16	2.71	4.07
Fe^{3+}	56	40	7.14	7.14
MnO_2	87	16	1.84	1.84
Na^+	23	20	8.70	4.35
SO_4^{2-}	96	1.1	0.11	
Si^{4+}	28	2	0.71	1.43
Ba^{2+}	137	1	0.07	0.07
Ca^{2+}	40	1	0.25	0.25
Ce^{4+}	140	1	0.07	0.14
Hg^{2+}	201	2.5	0.12	0.12
UO_2^{2+}	270	0.4	0.01	0.04
Total		101	21.75	19.46

solids wt%:	40%
slurry sp.g.	1.2
wt solids per L slurry	0.48 kg
moles reactive sludge per kg slurry	8.70
moles OA reacted	7.78

A.3 References

1. Kofi Adu-Wusu, et. el., "Waste Tank Heel Chemical Cleaning Summary", WSRC-TR-2003-00401, Rev. 0, September 9, 2003.

2. Kofi Adu-Wusu, et. el., p. 48.

3. Kofi Adu-Wusu, et. el., p. 49.

4. R. F. Bradley and A. J. Hill, Jr., "Chemical Dissolving of Sludge from a High Level Waste Tank at the Savannah River Plant", DP-1471, March 1977.

5. Kofi Adu-Wusu, et. el., p. 50.

6. R. F. Bradley and A. J. Hill, Jr., p. 8.