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USE OF AN EQUILIBRIUM MODEL TO FORECAST DISSOLUTION EFFECTIVENESS, SAFETY IMPACTS, AND DOWNSTREAM PROCESSABILITY FROM OXALIC ACID AIDED SLUDGE REMOVAL IN SAVANNAH RIVER SITE HIGH LEVEL WASTE TANKS 1-15

by

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the degree of

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ABSTRACT

This thesis details a graduate research effort written to fulfil the Magister of Technologiae in Chemical Engineering requirements at the University of South Africa. The research evaluates the ability of equilibrium based software to forecast dissolution, evaluate safety impacts, and determine downstream processability changes associated with using oxalic acid solutions to dissolve sludge heels in Savannah River Site High Level Waste (HLW) Tanks 1-15.

First, a dissolution model is constructed and validated. Coupled with a model, a material balance determines the fate of hypothetical worst-case sludge in the treatment and neutralization tanks during each chemical adjustment. Although sludge is dissolved, after neutralization more is created within HLW. An energy balance determines overpressurization and overheating to be unlikely. Corrosion induced hydrogen may overwhelm the purge ventilation. Limiting the heel volume treated/acid added and processing the solids through vitrification is preferred and should not significantly increase the number of glass canisters.

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DECLARATION

I declare that this thesis does not incorporate without acknowledgement any material previously submitted for a degree or diploma in any university, and that to the best of my knowledge it does not contain any materials previously published or written by another person except where due reference is made in the text.

ACKNOWLEDGMENTS

I would like to thank my family for being an immeasurable source of strength and encouragement. Additionally, I want to thank my many colleagues throughout High Level Waste, as well as the many other people at the Savannah River Site, who helped make my effort become a reality. Distinct appreciation belongs to my mentors and supervisors, without whom, I would have never had this unique opportunity.

Ultimately, all thanks belong to God for placing these people in my life. Truly, he is the maker of all good things.

CHAPTER 1

INTRODUCTION TO THE PROBLEM

At the Savannah River Site (SRS) near Aiken, South Carolina, USA, there are approximately 36 million gallons of legacy radioactive High Level Wastes (HLW) (Burnes, 2004). The approximately 46 tanks that hold the waste are fabricated from commercially available mostly ASTM-285B carbon steel (Sunrammanian, 2005). Out of those 46 tanks, Tanks 1-15 are single containment, non-conforming tanks built in the 1950's. Some of these tanks contain sludge heels which may need to be removed as part of closure and/or as feed for vitrification (Badheka, 2003).

Since many of the tanks were built in the 1950's and are being used past their original design life, significant sludge removal and processing campaigns are scheduled. In order to process the sludge, however, it must be removed from the tanks. Currently, slurry pumps are used to mechanically remove the sludge with only varying degrees of success. To aid in the removal, the use of oxalic acid for sludge dissolution is being considered.

Because of the process complexities, as well as concern about chemical incompatibilities, only limited acid dissolution has been performed on solids within the process. The last significant solids dissolution was performed as an in-situ cleaning of an evaporator pot. Since there were significant concerns about adding acid directly to the process, an OLI© based chemical equilibrium model was used to better understand the sodium aluminosilicate-acid interactions. The use of the model proved very successful (Barnes, 2003). Additionally, both Hanford (Saito, 2002) and SRS (Pike, 2002) used OLI© based chemical equilibrium models to help forecast salt dissolution; therefore, this research investigates the use of OLI ESP© and OLI Stream Analyzer© to help understand and forecast dissolution effectiveness and potential system and process impacts associated with sludge dissolution within HLW.

Acid treatment of multiple SRS HLW tanks is being planned. Figure 1-1 shows the Sludge Dissolution via Acid Treatment Process Sketch as an overview to help provide insight to the complexity and the scope of potential system impacts.

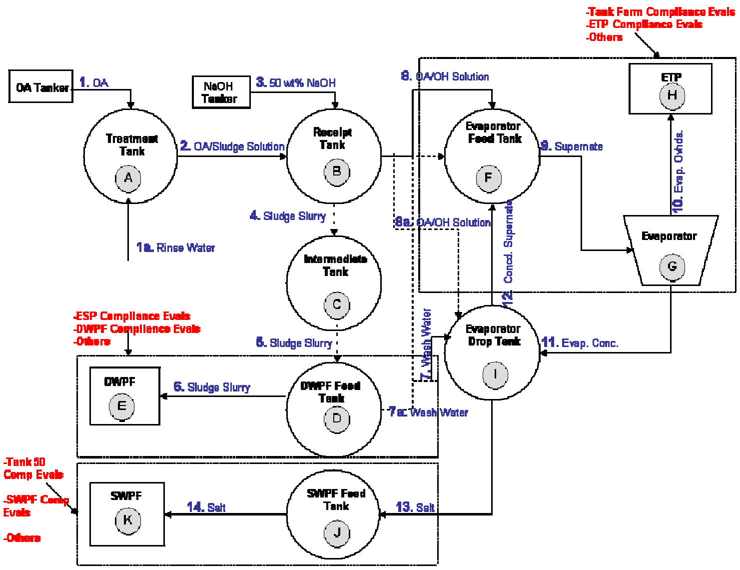


Figure 1-1 Sludge Dissolution via Acid Treatment Process Sketch

Where:

- A = approximate 1 million gallon High Level Waste (HLW) treatment tank
- B = approximate 1 million gallon HLW tank neutralization receipt tank
- C = intermediate tank if necessary to support Defence Waste Processing Facility (DWPF) extended sludge batch washing schedule
- D = DWPF feed tank, also called Extended Sludge Processing (ESP) tank, as it is used to wash sludge prior to feed to DWPF
- E = DWPF. Place where HLW sludge is vitrified in canisters to be transported for eventual disposal
- F = Evaporator feed tank
- G = Evaporator
- I = Evaporator drop tank
- J = Salt Waste Processing Facility (SWPF) feed tank
- K = SWPF is place where supernate is planned to be disposed.

Since the HLW system is a complex process as shown above in Figure 1-1, it is necessary to understand the effects that the acid additions and subsequent neutralization will have on the tank farm and on the entire HLW process. Originally, nitric acid, citric acid, and oxalic acid were identified as potential candidates to aid in the sludge removal (Hobbs, 2004). For Tanks 1-15, the considerations of nitric and citric acid were eliminated. Neither are as effective as a tank cleaning agent. Nitric acid will cause flammable gas generation issues, and citric acid will preferentially dissolve the uranium, causing potential downstream processing concerns during vitrification (Adu-Wusu, 2003, p70). The model and evaluation efforts for Tanks 1-15, as contained in this report, therefore, solely focus on the use of oxalic acid.

CHAPTER 2

LOGIC AND METHODOLOGY

2.1 Introduction to the Methodology

The subject and scope of the thesis are chosen to ensure applicability and that the outcome will provide significant yet practical value to the SRS sludge heel removal effort. Because acid dissolution represents what can be considered a new technology, many parameters were not yet identified or even considered at the initiation of this effort.

2.2 Research Efforts

As part of this research the following endeavours are performed:

- A comprehensive literature search is initiated.
- A model for the purpose of validation is built using the SRNL recipe for Purex simulant and HM simulant (Hobbs, 2004, p11-12). To validate the model's ability to estimate total wt% of sludge dissolved, initial model dissolution forecasts for simulant are compared to the SRNL measured total wt% of simulant dissolved.
- To further validate the model, model forecasts for Purex sludge and HM sludge are compared to SRNL measured sludge dissolved.
- A material balance is constructed across the treatment tank and neutralization tank evaluating effectiveness and conservatively evaluating applicable safety impacts as identified in the Documented Safety Analyses accident analyses (DSA, 2003, Chapter 3).
- The material balance is conservatively revised as necessary using "spiking of energetics" to understand the impact of using oxalic acid on energetic materials within the tank farm.
- An integrated material balance is built with the impacts to downstream processability evaluated.
- A sensitivity analysis is constructed to determine the possible effects of varying inputs.

Although the model dissolution forecasts are compared to the Tank 16 SRNL measured dissolution results, the safety impacts and downstream processability could not be formally validated beyond Tank 16. A sensitivity analysis, therefore, is developed appraising the effects of different amounts of acid and variations in the input.

Figure 2-1 pictorially shows the "Research Logic Flowsheet".

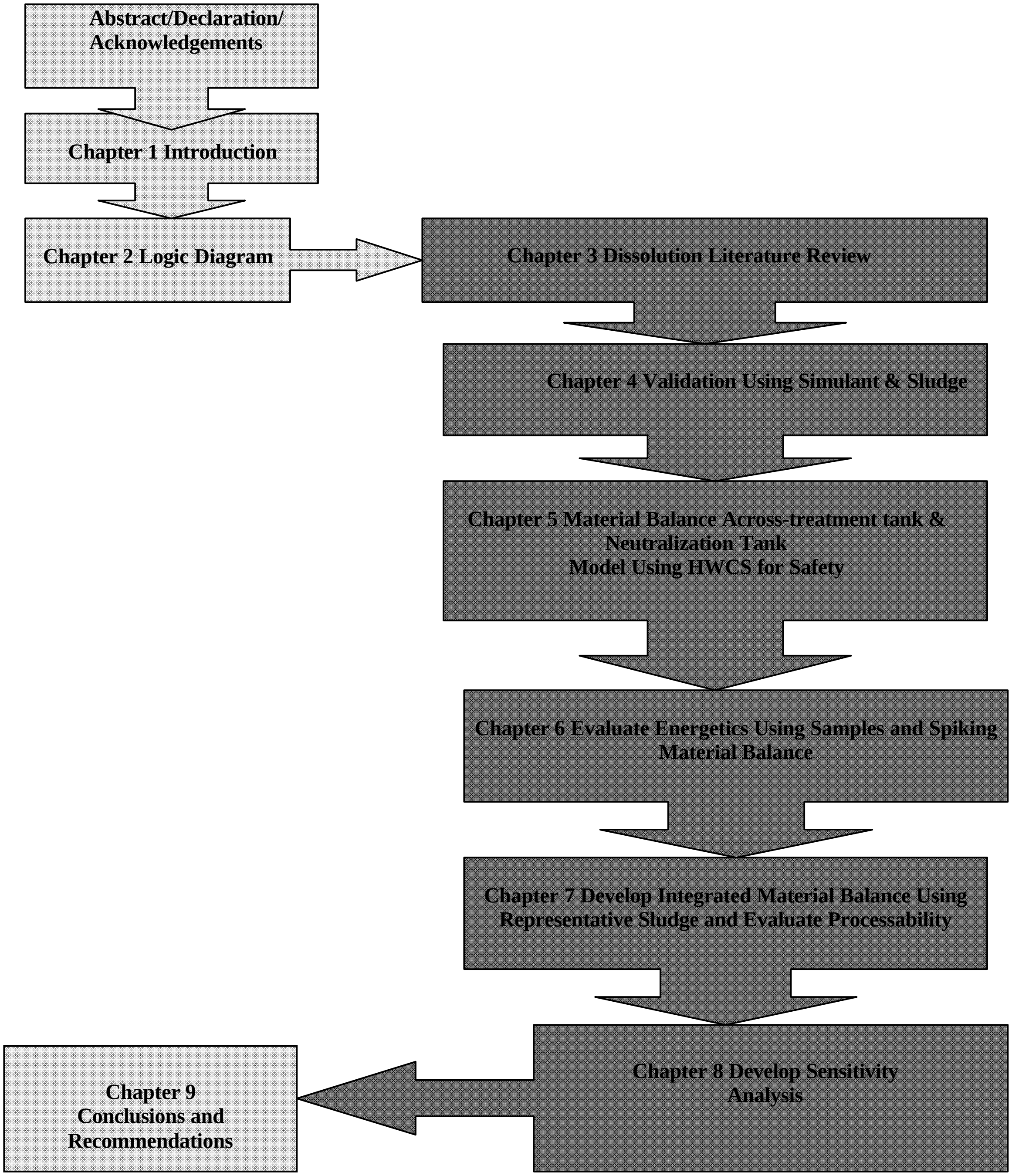


Figure 2-1 Research Logic Flowsheet/Diagram

CHAPTER 3

DISSOLUTION LITERATURE REVIEW

3.1 Introduction to Literature Review

Initially, as part of writing the research proposal, many experts were consulted to determine if the modelling of sludge dissolution with acid seemed to represent something that would have useful utility. The authorities consulted include SRS Tank Farm Engineering, SRS Liquid Waste Chemical Engineering, Planning Integration and Technology, and Savannah River National Laboratory scientists/chemists, scientists/chemists from other U.S. National Laboratories, and academia. Through these efforts, a significant amount of information was gathered.

The comprehensive literature search was conducted, considering basic chemical theory such as aqueous chemistry (Morel, 1983), electrochemical theory, basic chemical reactions (Metcalf, 1978), general acid cleaning (Wiersma, 2004), acid induced corrosion effects of acid on energetic compounds (Ketusky, 2003), and flammable gas formation reactions (Hobbs, 1999) were also used. A large part of the effort also consisted of SRS specific documents such as: High Level Waste sludge characterization (WCS, 2005); HLW process records (i.e., acid treatments of iron, aluminium and sludge compounds affecting high level waste tanks) (Cavin, 2003); and historical files from SRS HLW in-tank sludge dissolution efforts (Bradley, 1977) (Johnson, 1987) (West, 1980). Similar efforts were performed at the Hanford Site and West Valley and were also investigated (Elmore, 1996) (Flour, 2003) (Huckaby, 2004) (Gray, 1995).

The literature review shows that dissolution can be affected by four major factors: For the purpose of this effort, they are called rheology, chemistry, energy, and cleaning solution (Adu-Wusu, 2003, p5). This is illustrated as shown in Figure 3-1.

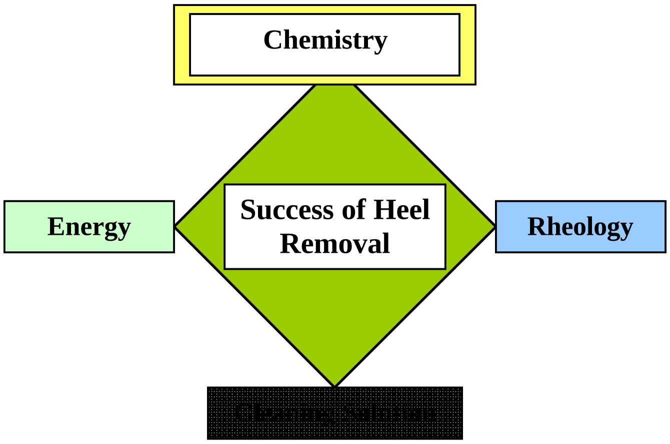


Figure 3-1 Factors Determining Sludge Heel Removal Success

Since the possible energy and rheology are indeterminate, as the pumps are mostly yet to be installed, and the rheology is poorly known, most of the literature review focuses on chemistry and dissolution.

3.2 Electrochemical Modelling

The literature reviewed shows that electrochemical modelling is extremely complex and hard to forecast in real process systems. Often the reactions behave in complex and seemingly counter-intuitive ways, introducing great risk if misapplied (Anderko, 2002, p123). Literature supplies the bulk of the theory.

3.3 Cleaning Agents

The current understanding of the chemical composition of heels includes the possibilities of aluminosilicate such as cancrinite and sodalite, hematite and boehmite (Adu-Wusu, 2003, p26, 27 28, and 30). The exact chemical composition of the sludge varies from tank to tank, and even within the tank. The chemical cleaning efficiency largely depends on the cleaning agent and the type of oxide. HLW sludge is an aggregate of the different oxides. The sludge might behave differently from the pure oxide components. This is due to the often elevated trace element contents of the oxides and the presence of other trace elements in solution that interferes with dissolution.

There are generally four types of chemical cleaning processes (surface controlled dissolution) by which inorganic oxides and hydroxides dissolve (Adu-Wusu, 2003, p51). They are:

- Reductive agents (e.g., sodium thiosulfite)
- Oxidative agents (e.g., hydrogen peroxide)
- Hydrogen ion assisted dissolution with acids (e.g., nitric acid)
- Ligands and complexing agents (e.g., organic acids like citric acid and oxalic acid)

This research was initiated to consider the effectiveness and system impacts associated with using nitric acid, oxalic acid, and citric acid; therefore, only the last two types are considered. Since these two types involve different dissolution mechanisms, different dissolution kinetics are expected. The dissolution efficiency largely depends on the type of oxide or hydroxide compound it encounters. A general rule for dissolution is, 'the farther an oxide is from a hydrated form, the longer it takes it to dissolve (Adu-Wusu, 2003, p52). For example, $Mn(OH)_2$ converts to MnC_2O_4 and $MnC_2O_4.2H_2O$ prior to the bulk dissolving. Logically, each additional step adds additional uncertainty to the dissolution kinetics.

3.4 Sludge Characterization

There is limited characterization data based on actual samples of the sludge. Additionally, even if the tanks have slurrying capabilities, they may not be mixed during sampling. Many times the sludge sample results appear to contradict the process history (Cavin, 2003) therefore, to ensure conservatism, the way in that characterization data is used within the research varies. Although largely based on the process database, the characterization data are refined within the multiple aspects of the modelling and flow sheet. Examples within this effort include the use of the process database for bulk solids (HLW, 2005), while organics are based on bounding application of sample results (Hobbs, 1999). Furthermore, laboratory simulant characterization data, such as from Hobbs (2004), simulant dissolution efforts is preferred during model validation. However, when determining the system and downstream impacts, the process database as found in the process database is preferred (HLW, 2005).

The SRNL dissolution efforts report (Hobbs, 2004) is most valuable because it focuses on the development of recipes for sludge simulants and the subsequent laboratory dissolution using oxalic acid. The use of such simulants in the laboratory helps ensure that the sludge is well characterized. Excluding any analytical uncertainty, the difference between the laboratory results and the model forecasts, are likely caused by the inaccuracies in the model and not inaccurate characterization. The SRNL measured dissolution results report (Hobbs, 2004) details the making and results of laboratory dissolution of simulants and the dissolution of HLW sludges.

The material balance across the treatment and neutralization tank (Badheka, 2003) supplies the primary input for the characterization using a Hypothetical Worst Case Sludge (HWCS). HWCS is defined as hypothetical sludge where the primary characterization constituent concentrations are bounded to negatively affect safety and process impacts. Possible safety impacts include excessive hydrogen generation from corrosion, heat generation, and overpressurization. The HWCS dissolution model is detailed in Chapter 5. Energetic compounds are discussed in Chapter 6.

The sludge and supernate characterizations are obtained from the process database as maintained in the Waste Characterization System (HLW, 2005). It represents the likely contents of Type I SRS HLW tank as modelled and considered in this effort. Possible processability impacts include effects on the evaporator, effects on saltstone, and effects on vitrification.

3.5 Acids As Cleaning Agents

Although some laboratory testing of acid as a cleaning agent for actual HLW sludge has occurred, most of the research for other non nitric/citric/oxalic acid used a simulant for the sludge. Out of the nitric, citric and oxalic acids, oxalic has most often been used on in-tank HLW sludge. One time oxalic acid was used in the 1970’s at SRS on sludge and once during 2003 at the Hanford Site. Overall, oxalic acid is the most researched cleaning agent for use on applicable HLW tank sludge (Adu-Wusu, 2003, p70).

3.5.1 Oxalic Acid

Oxalic acid has been widely tested and utilized as a sludge dissolution/cleaning agent at SRS and other US Department of Energy facilities. It use is backed by the largest body of literature (Adu-Wusu, 2003, p6).

3.5.1.1 Filter Cleaning

In literature, Poirier and Fink (Poirer, 2002) conduct a series of tests at SRNL investigating various cleaning agents for porous metal filters considered to be exposed to SRS HLW sludge. The testing showed that 4 wt% oxalic acid in a 60:1 volume ratio to both Purex and HM sludge was considered accept able for cleaning the filters. This is important since the results of the testing showed that one cleaning solution could be potentially used for the dissolution of both HM and Purex sludge. Poirer also clearly shows the following:

- Increased oxalic acid enhances sludge cleaning/dissolution.
- Increasing the concentration, temperature, and contact significantly increases the amount of sludge, including aluminium, dissolved over a given period.

3.5.1.2 Laboratory Tests Supporting Tank 16H Heel Cleaning

In the late 1970’s, Tank 16 was used for an oxalic acid cleaning/sludge removal demonstration. Prior to the demonstration, various laboratory testing was performed. Bradley and Hill (1977) reports on the series of laboratory scale tests conducted in the late 1970’s in support of oxalic acid treatment of the sludge heel in Tank 16H. Three sets of tests are reported.: They are: (1) scoping tests in laboratory with actual Tank 16H sludge; (2) short term laboratory tests of oxalic acid with simulated aluminium hydroxide, iron hydroxide, and manganese dioxide, and (3) long term laboratory tests with Tank 16H sludge.

(1) Laboratory Scoping Tests with SRS Tank 16 Sludge

For scoping tests, Bradley (1977, p8-12) details the laboratory testing mixing about 2 ml of SRS Tank 16H sludge with various cleaning agents (20 wt% glycolic, 20 wt% formic acid, 6 wt% sulfamic acid, 6 wt% citric acid, 5 wt% and 10 wt% sulphuric acid, and 8 wt% oxalic acid) at ambient temperature for 30 minutes with agitation. The scoping tests show that citric acid mixes of citric and oxalic acid and oxalic acid to have the same relative effectiveness in Tank 16 sludge dissolution.

(2) Short Term Laboratory Tests with Simulated Sludge Materials

Bradley (1977, p16) shows that short term laboratory tests of aluminium hydroxide, ferric hydroxide, and manganese dioxide were prepared and subjected to dissolution with oxalic acid. Tests varied the volume ratio of acid to sludge (10:1, 20:1, and 40:1) and the oxalic acid concentration (4 wt% and 8 wt%). The tests were conducted at 55°C. These tests were performed on only one metal oxide or hydroxide. The following conclusions are drawn from the tests.

- 8wt% oxalic acid in a 20:1 volume ratio to aluminium hydroxide is required for complete dissolution
- 8 wt% oxalic acid in a 40:1 volume ratio to ferric hydroxide is required for complete dissolution
- 8 wt% oxalic acid in a 10:1 volume ratio to ferric hydroxide yields nearly 70 % dissolution
- 8 wt% oxalic acid in a 40:1 volume ratio to manganese dioxide results in a significant amount of dissolution

It is difficult to compare the data between the tests because the experimental conditions were different. In addition, the specific sludge compounds were not given in Poirier and Fink's study (2002, p9). A seemingly contradiction in the results exists with the manganese. Poirier and Fink's study concluded that it readily dissolved, while Bradley and Hill's work concluded that it was very difficult to dissolve (1977, p18). Both sets of tests, however, generally agree that 8 wt% oxalic acid solutions in a 20:1 volume ratio with sludge will dissolve about 70 vol% of the Tank 16 sludge for up to 3-strikes with acid, after which the overall dissolution efficiency will drastically decrease.

(3) Long Term Laboratory Contact Tests with Actual Tank 16H Sludge

Reports (Adu-Wusu, 2003) (Bradley, 1977, p8) shows that tests were conducted with oxalic acid using in-tank Tank 16H sludge to examine the dissolution efficiency. Multiple step experiments with final oxalic acid to sludge volume ratios as high as 80:1 with contact times of about 1 week are conducted. Result showed that two successive strikes (2-strikes) using 8 wt% oxalic acid and an acid solution volume of 40:1 to sludge dissolved over 96 vol% of the Tank 16 sludge. Increased volumes of acid, however, did not result in additional dissolution.

3.5.1.3 Actual In-Tank Full Scale Tank 16H Results

Historic reports (Johnson, 1987) (West, 1980) detail the results of the oxalic acid treatment of on the SRS HLW Tank 16 sludge heel. The effort included two water washes, three oxalic acid washes, and a final water rinse. The effort removed 99.9% of the radioactive waste from the tank. The in-tank full scale demonstration corroborates the results of long term tests using actual Tank 16 waste sludge, as well is collaborated by the models in Chapter 5 and Chapter 7. The major difference is that Hobb's (2003) report uses a higher concentration of oxalic acid in the laboratory (8 wt%) compared to the (1 wt%) used in the SRS in-tank demonstration.

3.5.1.4 Laboratory Testing at Hanford

Tests were performed at the Hanford site using oxalic acid and actual Hanford Site Tank 241-C-106 simulant and sludge (Flour, 2003) (Huckaby, 2004). All the tests were done at approximate room temperature using 10 wt% oxalic acid. In general, the results of the testing were used as a form of validating the SRS laboratory results with 8 wt% oxalic acid solution. It was seen that the concentration of iron, and to a lesser extent aluminium and manganese increased in solution throughout the entire test period. This supports the results of the model that show Purex will dissolve faster than HM sludge. Even with increasing dissolution of the iron, aluminium, and manganese, the volume of sludge did not significantly change. It is speculated that substitution of oxalate for oxide/hydroxide in the undissolved solids were the cause of this effect (because oxalate weighs more than oxide/hydroxide). The amount of acid added at any time or over any period, does not affect the total amount of sludge dissolved. Nearly all of the gas produced is CO_2, with traces of H_2 and CH_4. The CO_2 production is used in Chapter 5 to confirm the modelling associated with flammability and gas generation. Neutralization of the spent oxalic acid with supernate and 50 wt% NaOH solution produces large volumes of easily compacted sodium oxalate. This is important since it suggests that newly formed precipitating sodium oxalate may be easily pump out of a tank, while aged sodium oxalate may be compacted and therefore, more difficult to remove.

3.5.1.5 Corrosion of Carbon Steel from Oxalic Acid

As detailed below, the references show that significant variables influencing the general corrosion rate are acid concentration, carbon content of the metal, temperature and length of exposure. These references are detailed as follows.

Ondrejcin's (1976, p2) data is largely based on coupon tests that provided part of the technical basis for chemical cleaning of Tank 16H. Wilde's data (1984, p5) is from coupon tests in support of cleaning SRS heat exchangers. Russian and SRNL data investigate the effectiveness of acid cleaning on HLW sludge (Hobbs, 2004) (Adu-Wusu, 2003). Additional literature is also obtained from studies performed at Pacific Northwest National Laboratory that supported the clean-out of HLW tanks at West Valley (Gray, 1995). All tests show that the rate for the general corrosion would be would be significantly less than 60 mil/year (Wiersma, 2004). Additionally, data shows that temperature has a strong effect on the corrosion rate. Therefore, to ensure corrosion would not be become a problem, the temperature is assumed to be bound to 50°C with assumed cooling applied as necessary.

3.5.2 Citric Acid

The use of citric acid as a sludge dissolution agent is studied in detail in a few independent efforts that were considered in this effort. Bradley and Hill (1977, p30, p61) consider citric acid in Tank 16H sludge and determine that citric acid, as a lone cleaning agent, is slightly less effective than oxalic acid. Additionally, comparison tests with simulated Tank 40H sludge and 0.5 M citric acid at ambient temperature and high solution to sludge solid ratio necessary of >60:1, shows that citric acid alone is less effective than oxalic acid (Poirer, 2002, p18).

The bulk of information for using mixtures of oxalic and citric acid, however, comes from recent tests performed by the V. G. Khlopin Radium Institute Mining Chemical Combine (MCC) and SRNL (Adu-Wusu, 2003, p54). Both groups, working in association with each other, conduct tests with simulated Purex and simulated HM sludges. Results from the two teams varied, even though the MCC scientists used simulant sludge recipes provided by SRNL. Complete dissolution of sludge solids was not achieved in any of the SRNL chemical cleaning tests, regardless of liquid to sludge ratio or sludge simulate used. Observations from the results are as follows:

- Use of citric acid did not promote uniform dissolution of neutron poisons in relation to fissile products
- Citric acid and citric acid/oxalic acid mixtures are only about as effective in dissolving sludge as oxalic acid

Since the use of citric acid would require further processing, is not compatible with DWPF (Hobbs, 2004, p27) and only as effective as oxalic acid, the use of citric acid and citric acid mixes are not modelled, and eliminated from further consideration in this research effort.

3.5.3 Nitric Acid

The use of nitric acid is almost as widely used as oxalic acid in cleaning metal surfaces at SRS. The nitric acid corrosion mechanism; therefore, has been studied for many years as documented (Adu-Wusu, 2003, p36 and p64). For both sludge and simulants, it has been shown that 4 M nitric acid performs comparably to only 4 wt% oxalic acid, significantly below the ideal strength for oxalic acid.

Tests (Hobbs, 2003, p8-10) are done which involved placing 300 mL of simulated Tank 40 sludge and 60 mL of actual Tank 8 in a beaker and adding 0.5 M, 1 M, 2 M, and 4 M nitric acid for a contact time of 1 and 8 hours in a single-strike 5:1 volume ratio. Although the anodic reaction is fairly simple, for iron being oxidized to ferrous cation (Fe^{2+}), there are a number of cathodic reactions that occur. The cathodic reduction of nitric acid likely proceeds in Reaction 3-1 to Reaction 3-4 (Adu-Wusu, 2003, .p59).

$H^+ + e^- = H$ (Reaction 3-1)
$HNO_3 + H^+ + e^- = NO_2 + H_2O$ (Reaction 3-2)
$NO_2 + e^- = NO_2^-$ (Reaction 3-3)
$H^+ + NO_2^- = HNO_2$ (Reaction 3-4)

These equations show the possibility of NOx and ammonia issues associated with the use of nitric acid. The nitrous acid (HNO_2) that is formed as is shown above regenerates NO_2 by an interaction with the nitric acid as shown in Reaction 3-5 (Adu-Wusu, 2003, p59).

$HNO_2 + HNO_3 = 2NO_2 + H_2O$ (Reaction 3-5)

Ammonia salts are also formed. The ammonia salts decompose to form N_2 and NOx compounds by Reaction 3-6 and Reaction 3-7 (Adu-Wusu, 2003, p59).

$NH_4NO_2 = N_2 + 2H_2O$ (Reaction 3-6)
$NH_4NO_3 = N_2O + 2H_2O$ (Reaction 3-7)

Thus, if nitric acid is used, the formation of NH_4, NO_2, NO, N_2O and N_2 is expected. Because of the cost, time constraints, and issues associated with introducing significant NO_X and flammable gases in Tanks 1-15, the consideration of using use of nitric acid received no further consideration.

CHAPTER 4

BASELINE OUTPUT AND VALIDATION

4.1 Introduction to Validation

The purpose of model validation is to show that the model suitably simulates actual dissolution behaviour. The validation is done by comparing model dissolution forecasts to Savannah River National Laboratory (SRNL) measured dissolution results. As part of validation, the model forecasts and the SRNL measured dissolutions must result in similar total wt% dissolved sludge values. Ideally, as part of validation the speciation capability of the model would also be validated. The ability to validate the speciation, however, is severely limited, based on the performed SRNL analyzes. Since the ability to perform laboratory dissolution is more restrictive than actual in-tank heel removal, validation using SRNL dissolutions will be conservative (i.e., Tank 16 testing showed that only 30 to 50% of the oxide matrix had to be weaken to remove the sludge from the tank)(West, 1980, p1).

Chapter 5, 6, 7 conservatively make use of the process flow diagram and the associated material balance to conservatively evaluate safety impacts and realistic estimate processability impacts. Additionally, Chapter 8 helps explain the sensitivity associated with possible variables.

Because of the need to validate the model dissolution forecasts with SRNL measured dissolutions, well characterized SRNL simulants are first used. A second step includes the validation of the model with Purex sludge and HM sludge samples. For Tank 8F Purex sludge, model dissolution forecasts results are consistent with SRNL measured dissolution results. Because the Tank 12 HM sludge sample was noted as being very dry and requiring significant amounts of (acid) solution to first re-wet (Hobbs, 2003, p25), a historic dissolution results from a non-archived sludge sample of Tank 16 is used (Bradley, 1977, p15).

4.2 Validation of Model for Simulants

Based on historical records, two streams, Purex and HM represent the SRS sludge in Tanks 1-15. Because of the need to validate model forecasts with SRNL measured dissolutions, well characterized simulants are first used as part of the validation.

Recipes for the SRNL to make Purex simulant and HM simulant are provided in literature (Hobbs, 2003, p12 and 14). Although provided as a recipe, these also characterize the contents of the simulant. The recipe/characterization for the Purex simulant and HM simulant is show in Table 4-1.

Table 4-1 Purex Simulant and HM Simulant Constituents

Constituent	Purex Simulant Recipe (mol)	HM Simulant Recipe (mol)
$Al(OH)_3$	2.21E-01	1.50E+00
$Ca_3(PO_4)_2$	1.49E-03	4.80E-05
$Fe(OH)_3$	8.37E-01	1.75E-01
$Mg(OH)_2$	2.55E-02	1.20E-02
$Mn(OH)_2$	4.70E-01	1.09E-01
$Mn_3(PO_4)_2$	1.10E-02	1.10E-02
HgO	1.85E-03	2.58E-02
$Ni(OH)_2$	8.99E-01	1.60E-02

4.2.1 SRNL Measured Dissolutions for Simulants

SRNL measured the laboratory dissolution of Purex simulant and HM simulant using 1-strike and 7-strikes of 4 wt% oxalic acid solution in 2:1 and 50:1 volume ratios to simulants. Details are recorded in the literature (Hobbs, 2003, p14) and the results are summarized in Table 4-2.

Table 4-2 SRNL Measured Dissolution Results for Purex Simulant and HM Simulant

Dissolution Scenario	Total Sludge Dissolved (wt%)	Al Dissolved (wt%)	Fe Dissolved (wt%)	Mn Dissolved (wt%)	Ni Dissolved (wt%)
1-strike @ 2:1$_{Purex}$	3.7	9.4	3.4	3.4	2.9
7-strikes @ 2:1$_{Purex}$	40.8	46.0	41.4	42.6	36.2
1-strike @ 50:1$_{Purex}$	83.7	69.2	79.8	99.1	95.3
7-strikes @ 50:1$_{Purex}$	87.2	81.8	84.4	99.1	95.3
1-strike @ 2:1$_{HM}$	1.9	0.7	1.1	8.9	10.8
7-strikes @ 2:1$_{HM}$	26.7	25.2	25.0	42.8	56.6
1-strike @ 50:1$_{HM}$	76.4	42.0	70.8	96.9	100.0
7-strikes @ 50:1$_{HM}$	81.6	60.9	77.5	97.0	100.0

Based on the SRNL measure dissolutions, Table 4-2 shows that as more oxalic acid is added, either in terms of-strikes or volume ratios, more total sludge will be dissolved.

4.2.2 Model Dissolution Forecasts for Simulants

The dissolution of Purex simulant and HM simulant corresponding to the SRNL dissolutions discussed in Section 4.2.1 are modelled (Hobbs, 2003, p12). The model dissolution forecasts for total, Al, Fe, Mn, and Ni wt% dissolved are shown in Table 4-3. In agreement with Table 4-2, 1-strike and 7-strikes of 4 wt% oxalic acid solutions in 2:1 and 50:1 volume ratios to simulant, are used.

Table 4-3 Model Forecasts for Purex Simulant and HM Simulant

Dissolution Scenario	Total Sludge Dissolved (wt%)	Al Dissolved (wt%)	Fe Dissolved (wt%)	Mn Dissolved (wt%)	Ni Dissolved (wt%)
1-strike @ 2:1$_{Purex}$	27.9	28.3	28.0	26.6	28.0
7-strikes @ 2:1$_{Purex}$	29.4	28.0	31.6	27.5	35.2
1-strike @ 50:1$_{Purex}$	57.0	83.2	100.0	26.1	28.1
7-strikes @ 50:1$_{Purex}$	73.3	100.0	100.0	26.3	28.1
1-strike @ 2:1$_{HM}$	30.4	28.4	28.1	44.4	28.0
7-strikes @ 2:1$_{HM}$	90.9	90.6	100.0	99.2	90.0
1-strike @ 50:1$_{HM}$	72.8	70.2	100.0	69.2	35.4
7-strikes @ 50:1$_{HM}$	100	100	100.0	100	100

4.2.3 Comparison of Model Dissolution Forecasts to SRNL Measured Results for Simulants

A comparison between model dissolution forecasts and the SRNL measured dissolutions for 1-strike and 7-strikes of 4 wt% oxalic acid solution, using 2:1 and 50:1 volume ratios of oxalic acid to Purex simulant and HM simulant, are shown in Table 4-4.

Table 4-4 Comparison of Model Forecasts to SRNL Measured Dissolution Results for Purex Simulant and HM Simulant

Dissolution Scenario	Results	Total Simulant Dissolved	Al Dissolved (wt%)	Fe Dissolved (wt%)	Mn Dissolved (wt%)	Ni Dissolved (wt%)
1-strike @ 2:1$_{PurexS}$	Model	27.9	28.3	28.0	26.6	28.0
	SRNL	3.7	9.4	3.4	3.4	2.9
	Fraction	7.54	3.01	8.24	7.82	9.66
7-strikes @ 2:1$_{Purex}$	Model	29.4	28.0	31.6	27.5	35.2
	SRNL	40.8	46.0	41.4	42.6	36.2
	Fraction	0.72	0.61	0.76	0.65	0.97
1-strike @ 50:1$_{Purex}$	Model	57.0	83.2	100	26.1	28.1
	SRNL	83.7	69.2	79.8	99.1	95.3
	Fraction	0.68	1.20	1.25	0.26	0.29
7-strikes @ 50:1$_{Purex}$	Model	73.3	100	100	26.3	28.1
	SRNL	87.2	81.8	84.4	99.1	95.3
	Fraction	0.84	1.22	1.18	0.27	0.29
1-strike @ 2:1$_{HM}$	Model	30.4	28.4	28.1	44.4	28.0
	SRNL	1.9	0.7	1.1	8.9	10.8
	Fraction	16.00	40.57	25.55	4.99	2.59
7-strikes @ 2:1$_{HM}$	Model	90.9	90.6	100	99.2	90.0
	SRNL	26.7	25.2	25.0	42.8	56.6
	Fraction	3.40	3.60	4.00	2.32	1.59
1-strike @ 50:1$_{HM}$	Model	72.8	70.2	100	69.2	35.4
	SRNL	76.4	42.0	70.8	96.9	100.0
	Fraction	0.95	1.67	1.41	0.71	0.35
7-strikes @ 50:1$_{HM}$	Model	100	100	100	100	100
	SRNL	81.6	60.9	77.5	97.0	100.0
	Fraction	1.23	1.64	1.29	1.03	1.00

As shown in Table 4-4, for even 1-strike at a 50:1 volume ratios of 4 wt% of oxalic acid solution to simulant, the model forecasts and the SRNL measured dissolutions result in a rough similarity between results. Starting from 1-strike at 50 for both Purex simulant and HM simulant as the amount of acid increases (from either volume ratio or total wt%) the models forecasts and the SRNL measured dissolutions more closely match. Figure 4-1 compares the Purex simulant modelled forecasts to the SRNL laboratory dissolutions for a 1-strike 4 wt% oxalic acid solution in a 50:1 volume ratio to simulant.

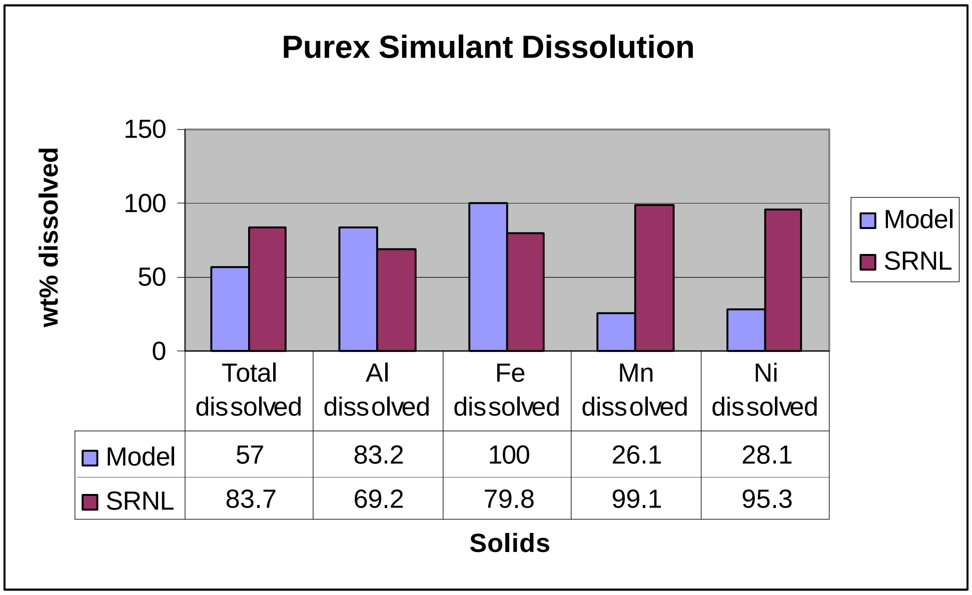
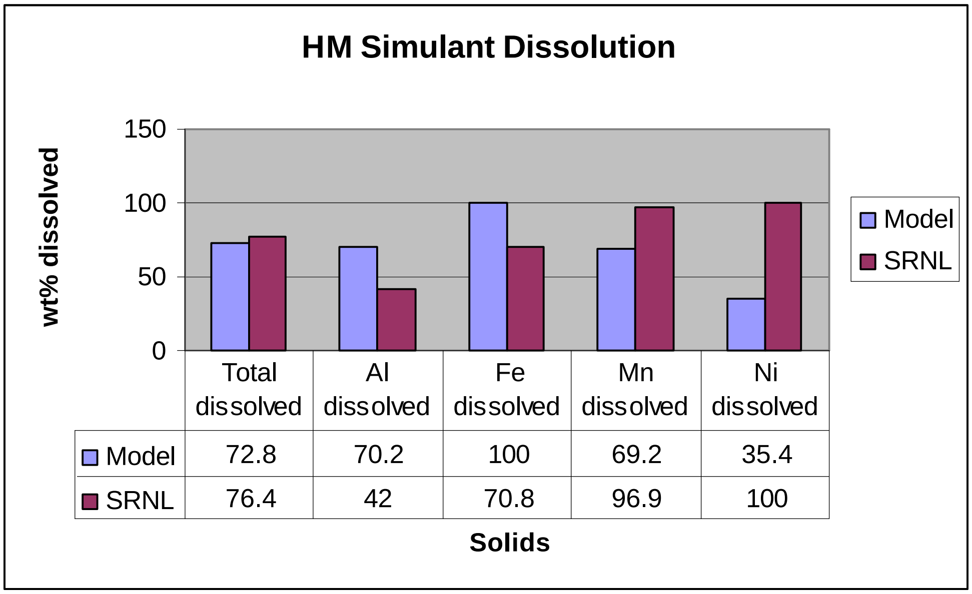


Figure 4-1 Model Dissolution Forecasts vs. SRNL Measured Dissolution Results for Purex Simulant

The 1-strike 4 wt% oxalic acid solution in a 50:1 volume ratio to Purex simulant appears to be within 33% of the SRNL dissolution. Upon closer observation, however, the wt% aluminium and iron are overestimated, while the manganese and nickel are underestimated. The difference between the forecast and the SRNL measured results can most likely be attributed to the re-precipitation of manganese and nickel as newly formed oxalate compounds within the model. The fate of the $Al(OH)_3$, $Fe(OH)_3$, $Mn(OH)_2$, and $NI(OH)_2$ are quantified in Appendix 2, Table A2-1.

Figure 4-2 compares the HM simulant modelled dissolution forecasts to the SRNL laboratory dissolutions for a 1-strike 4 wt% of oxalic acid solution in a 50:1 volume ratio to HM simulant.



	Total dissolved	Al dissolved	Fe dissolved	Mn dissolved	Ni dissolved
Model	72.8	70.2	100	69.2	35.4
SRNL	76.4	42	70.8	96.9	100

Figure 4-2 Model Dissolution Forecasts vs. SRNL Measured Dissolution Results for HM Simulant

Although the 1-strike 4 wt% 50:1 oxalic acid ratio to HM simulant model could be considered to approximate the total sludge wt% dissolved, the modelled wt% dissolved for nickel and manganese are significantly less than the SRNL measured wt% dissolved. The difference between the model forecasts and the SRNL measured dissolution results could most likely be attributed to the re-precipitation of manganese and nickel as newly formed oxalate compounds within the model. The fate of the $Al(OH)_3$, $Fe(OH)_3$, $Mn(OH)_2$, and $NI(OH)_2$ are quantified in Appendix 2, Table A2-2.

At best, a model forecasted 1-strike of 4 wt% 50:1 volume ratio of oxalic acid to sludge dissolution would match a SRNL measured dissolution of Purex simulant and HM simulant. Since the relative wt% of manganese and wt% nickel are lower in actual Purex sludge and HM sludge than in the simulants, comparison of the model dissolution forecasts to laboratory measured results for the actual Purex sludge and actual HM sludge result in closer similarities.

4.3 Validation of Model for Sludge

Previously taken Tank 8 Purex sludge and Tank 12 HM sludge samples were archived in the laboratory and available for dissolution tests. The Tank 12 sample, however, was extremely dried out, and therefore, discounted from modelling consideration (i.e., ~65 vol% liquid required for OLI© modelling) (Hobbs, 2005, p25).

4.3.1 SRNL Measured Dissolutions of Tank 8 Purex Sludge

Table 4-5 shows the characterization of the Tank 8 sludge.

Table 4-5 Tank 8 Purex Sludge Constituents

Constituent	Tank 8 Purex Sludge (mol)
$Al(OH)_3$	3.59E-01
$Ca_3(PO_4)_2$	6.66E-03
$Fe(OH)_3$	2.00E+00
$Mg(OH)_2$	0.00E+00
$Mn(OH)_2$	2.60E-01
$Mn_3(PO_4)_2$	6.09E-03
HgO	3.03E-03
$Ni(OH)_2$	2.01E+00

The SRNL laboratory dissolution of Tank 8 Purex sludge for 1-strike of 4 wt% oxalic acid solution using a 50:1 volume ratio of oxalic acid to simulant was performed. Details are recorded (Hobbs, 2003, p33), and the results are summarized in Table 4-6.

Table 4-6 SRNL Measured Dissolutions for Tank 8 Purex Sludge

Dissolution Scenario	Total Sludge Dissolved (wt%)
1-strike @ $50:1_{Purex}$	69

4.3.2 Modelling Dissolution Forecasts for Tank 8 Purex Sludge

The dissolution of Tank 8 Purex sludge corresponding to the SRNL dissolution discussed in Section 4.3.1 is modelled. The OLI Stream Analyzer© Tank 8 Purex sludge dissolution forecasts for total weight dissolved are shown in Table 4-7.

Table 4-7 Model Dissolution Forecasts for Tank 8 Purex Sludge

Dissolution Scenario	Total Sludge Dissolved (wt%)
1-strike @ $50:1_{\text{Purex}}$	87

As shown in Table 4-7, the model dissolution forecasts that not all of the Tank 8 Purex sludge will dissolve.

4.3.3 Forecast vs. SRNL Measured Dissolution Results for Tanks 8 Purex Sludge

A comparison between the model dissolution forecast and the SRNL measured dissolution results for 1-strike of 4 wt% oxalic acid solution using a 50:1 volume ratio of oxalic acid to sludge, for Tank 8 Purex sludge is shown in Table 4-8.

Table 4-8 SRNL Measured Dissolution Results vs. Model Dissolution Forecast for Tank 8 Purex Sludge

Dissolution Scenario	Results	Total Sludge Dissolved (wt%)
1-strike @ $50:1_{\text{Purex}}$	Model	87
	SRNL	69
	Fraction	1.26

As shown in Table 4-8, the model dissolution forecast of the Tank 8 Purex 1-strike of 4 wt% oxalic acid solutions for a volume ratio of 50:1 acid to sludge, results in an over–estimate of total dissolution. Figure 4-3 graphically compares the Tank 8 Purex sludge dissolution forecast to the SRNL measured dissolution results.

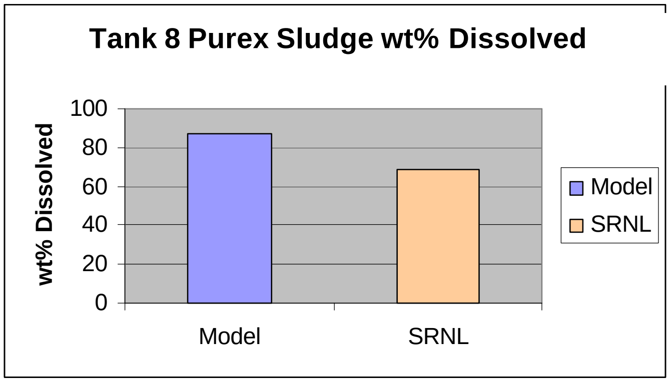


Figure 4-3 Forecasts vs. SRNL Measured Dissolution Results f Tank 8 Purex Sludge

As shown in Figure 4-3, the Tank 8 Purex sludge dissolution using a 1-strike of 4 wt% oxalic acid solution in a volume ratio of 50:1 oxalic acid solution to sludge results in only a slight under-estimate compared to the SRNL measured dissolution results.

Overall, based on the comparisons of the Purex simulant and the Tank 8 Purex sludge model dissolution forecasts to the SRNL measured dissolutions, the model is assumed to be validated for both Purex simulant and Purex sludge.

4.3.4 Historic Measured Dissolutions of Tank 16 HM Sludge Dissolution

In the late 1970's a demonstration was performed on Tank 16 prior to its retirement. The purpose of the demonstration was to access waste removal effectiveness of different processes, including acid cleaning (West, 1980, p1). Although the SRS waste has aged, the fact remains that as part of the evaluation for closure, acid dissolution was tested in the laboratory, used in the HLW tank, and eventually declared successful for sludge dissolution (West, 1980). Table 4-9 shows the characterization of the Tank 16 sludge.

Table 4-9 Tank 16 HM Sludge Constituents

Constituent	Tank 16 HM Sludge (mol)
$Al(OH)_3$	6.86E-01
$Fe(OH)_3$	1.75E+00
$Mn(OH)_2$	3.27E-01
$Mn_3(PO_4)_2$	1.10E-02
HgO	6.45E-02
$Ni(OH)_2$	1.02E-01

4.3.5 SRNL Measured Dissolution of Tank 16H Sludge

The SRNL laboratory dissolution of Tank 16 HM sludge using a 20:1 acid to sludge volume ratio for 2-strikes of 8 wt% oxalic acid are recorded in the referenced literature (West, 1980, p8). The results are summarized in Table 4-10.

Table 4-10 SRNL Dissolution Results for Tank 16 HM Sludge

Dissolution Scenario	Total Sludge Dissolved (wt%)
2-strikes @ 20:1HM	95

4.3.6 Model Dissolution Forecasts for Tank 16H HM Sludge

The dissolution of Tank 16 HM sludge corresponding to the SRNL dissolution discussed in Section 4.4.1 is modelled. The OLI Stream Analyzer© Tank 16. HM sludge dissolution forecasts for total weight dissolved are shown in Table 4-11.

Table 4-11 Model Dissolution Forecast for Tank 16 HM Sludge

Dissolution Scenario	Total Sludge Dissolved (wt%)
2-strikes @ 20:1HM	80

4.3.7 Comparison of Forecast to SRNL Measured Dissolution Results for Tank 16H Sludge

The comparison between the SRNL results and the OLI modelled results for Tank 16 HM sludge dissolution are shown in Table 4-12.

Table 4-12 SRNL Dissolution Results vs. Model Dissolution Results For Tank 16 HM Sludge

Dissolution Scenario	Results	Total Sludge Dissolved (wt%)
2-strikes @ 20:1$_{\text{HMS}}$	Model	80
	SRNL	95
	Fraction	84

As shown in Table 4-12, the 2–strikes of 8 wt% oxalic acid solutions in volume ratios of 20:1 results in a slight under-estimate. This is also shown graphically in Figure 4-4.

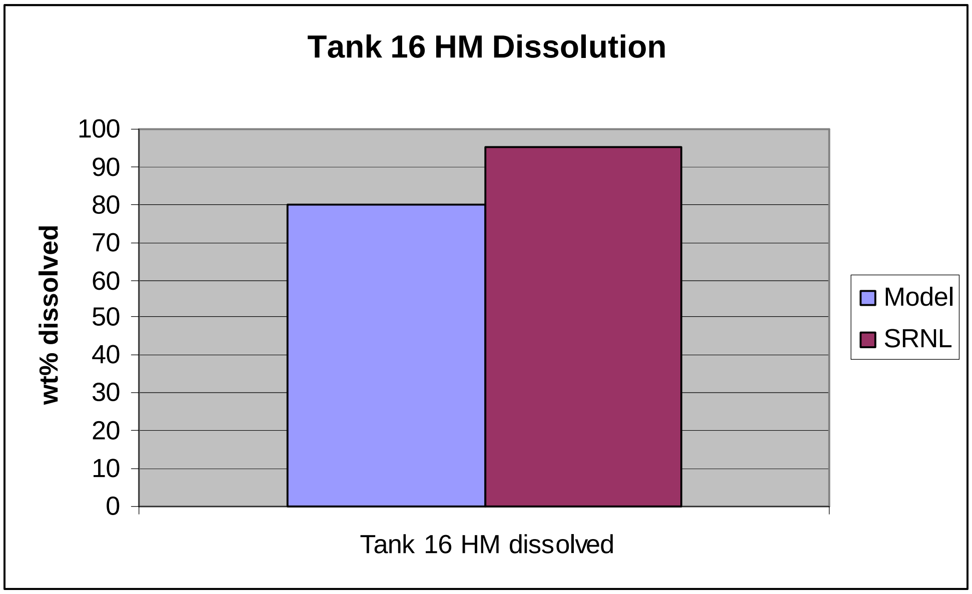


Figure 4-4 Forecast vs. SRNL Measured Dissolution Results for Tank 16 HM Sludge

Based on the similarity between the Tank 16 SRNL Measured Dissolution Results for Tank 16 Sludge and the model forecast, the model is considered to represent an approximate be validated for total wt% of HM sludge dissolved.

4.4 Conclusion on Validation

In this chapter as part of validation we have compared the Purex simulant model, the HM simulant model, the Tank 8 Purex sludge model, and the Tank 16 HM sludge model with the corresponding SRNL dissolutions for total wt% of the sludge dissolved. For validation, purposes only the total wt% dissolved could be for sludge, since laboratory analyses only record total wt% dissolved. All of the models performed within relative close comparisons with the SRNL dissolution results, without any simulant differences greater than 32% and sludge differences greater than 26%. Refer to Table 4-13.

Table 4-13 Summary of Model Forecast vs. SRNL Measured Dissolution

Dissolution Scenario	Solute	Results	Total Dissolved (wt%)
1-strike @ 50:1$_{\text{Purex}}$	Simulant	Model SRNL Fraction	57.0 83.7 0.68
1-strike @ 50:1$_{\text{HM}}$	Simulant	Model SRNL Fraction	72.8 76.4 0.95
1-strike @ 50:1$_{\text{Purex}}$	Tank 8 Sludge	Model SRNL Fraction	87 69 1.26
2-strikes @ 20:1$_{\text{HM}}$	Tank 16 Sludge	Model SRNL Fraction	80 95 0.84

As we see in Table 4-4, as more acid is used, the model forecast and SRNL measured dissolution results are comparable. Based on literature (Adu-Wusu, 2003, p71) a 3-strike of 8 wt% oxalic acid solution in volume ratios of 20:1 to sludge is recommended.

As part of the sensitivity analyses discussed further in Chapter 8, the dissolution effectiveness, safety and processability impacts associated of adding varying amounts of acid are combined and expressed in terms of total mass (kg).

CHAPTER 5

SAFETY IMPACTS

5.1 Introduction to Material Balance and Safety Impacts

The purpose of this chapter is to:

- develop a limited material balance across only the treatment and neutralization tanks from the dissolution of hypothetical worst case sludge (HWCS)
- to forecast dissolution and safety impacts on the treatment tank and on the neutralization tank from an oxalic acid aided sludge heel removal effort in an SRS HLW Tank 1 through 15.

The recommended cleaning solution consists of a 3-strike 8 wt% oxalic acid solution in a volume ratio of 20:1 oxalic acid solution to sludge (Adu-Wusu, 2003, p71.) The model, however, requires significantly less acid. As part of this chapter, a Hypothetical Worst Case Sludge (HWCS) is first defined, the material balance developed, and the dissolution and the safety impacts evaluated.

Since the validation in Chapter 4 is limited to evaluating the total sludge wt% dissolved, when evaluating potential safety impacts (originating from the developed material balance), bounding assumptions are applied to help ensure validity.

Effects on energetic compounds (not including hydrogen from corrosion) are outside the scope of this chapter, as Chapter 6 specifically addresses energetic compounds. Chapter 7 contains an integrated process flow sheet where downstream processability impacts are evaluated. Chapter 8 contains a sensitivity analysis to evaluate and compared the impact of using varying amounts (i.e., strikes, wt%, and volume ratio are simply combined and expressed in terms for mass, kg) of oxalic acid.

5.2 Hypothetical Worst Case Sludge

Because there is a myriad of potential compounds and complexes that may exist in HLW, the process database (HLW, 2005) uses a single-species approach in defining the contents of the sludge. In this approach, single representative species are used to primarily account for each of the contained species. It is assumed that programs such as OLI© can then be used to better characterize the specific constituents in the tanks. Although the characterization database must be carefully used, it is extremely beneficial since it enables initial forecasts on effectiveness, safety, and processability to be made, such that resources (e.g., new sampling) can be allocated to only those activities where success seems plausible.

Because of the complexity associated with characterization, much of the operational activities in HLW rely on the process database. The contents of the sludge as contained in the process database consider (HLW, 2005).

1. Radionuclides:
   Thorium, Uranium, Neptunium, Plutonium, Tritium, Caesium, C-14, Co-60, Se-79, Y-90, Nb-94, Tc-99, Ru-106, Rh-106, Sb-125, Sn-126, I-129, Ba-137m, Ce-144, Pr-144, Pm-147, Eu-154, Am-241, Am-242m, Am-244, Cm-245.

2. Chemical Compounds:
   $Al(OH)_3$, $BaSO_4$, $Ca_3(PO)_4$, CaC_2O_4, CaF_2, $CaSO_4$, $Ce(OH)_3$, $Co(OH)_3$, $Cr(OH)_3$, $Cu(OH)_2$, $Fe(OH)_3$, HgO, KNO_3, $La(OH)_3$, $Mg(OH)_2$, MnO_2, Na_2SO_4, Na_3PO_4, NaCl, NaF, NaI, $NaNO_3$, NaOH, $Ni(OH)_2$, $PbCO_3$, $PbSO_4$, $Pr(OH)_3$, RuO_2, SiO_2, $SrCO_3$, ThO_2, TiO_2, $UO_2(OH)_2$, $Zn(OH)_2$, $Zr(OH)_2$.

The process database, however, is not a complete database, as its uncertainty definitively exceeds the tolerance needed to quantify organic and ammonia contents. To ensure data is not inappropriately applied organic and ammonia compounds are therefore not recorded in the database. On a mass basis, the quantity of organics and ammonia compounds required to have a significant impact on flammability are very small. Generally, sample results show that organic and ammonia concentrations within the tanks are near or less than the lower levels of detectability (Swingle, 1999) (Britt, 2003) (Hobbs, 1999). Organics and ammonia can not be quantified using the process database, nor this material balance, but are addressed separately as part of Chapter 6.

Initially when attempting to determine what "sludge" would look like for the model input, all of the transfers to Tanks 1-15 were listed, and a worst case transfer of each constituent is defined. Since, approximately 65 vol% must be water for OLI© to work (Badheka, 2003, p117); the solids were too concentrated for the OLI© electrolyte chemistry model to work, resulting in the software "timing out."

The strategy that was eventually implemented was to consider the metal constituents of the transfers accounting for approximately 90% of the mass (Badheka, 2003). This is in accordance with the validation in Chapter 4, where the metals accounting for approximately 90% of the mass were used. Additionally, those constituents, which could contribute to safety impacts (i.e., excessive temperature, over pressurization, and hydrogen generation from corrosion), were considered. Table 5-1 compares the constituents in HWCS, Purex simulant, HM simulant, Tank 8 Purex sludge, and Tank 16 HM sludge.

Table 5-1 Constituents Considered in Modelling

Constituent	HWCS	Purex Simulant	HM Simulant	Tank 8 Purex Sludge	Tank 16 HM Sludge
AgOH	X				
$Al(OH)_3$	X	X	X	X	X
CaC_2O_4	X				
$CaCO_3$	X				
$Ca(PO)_4$		X	X	X	
$Fe(OH)_3$	X	X	X	X	X
HgO	X	X	X	X	X
KNO_3	X				
$Mg(OH)_2$		X	X	X	
$Mn(OH)_2$	X	X	X	X	X
NaCl	X				
$NaNO_3$	X				
NaOH	X				
$Ni(OH)_2$	X	X	X	X	X
$PbCO_3$	X				
SiO_2	X				
$UO_2(OH)_2$	X				
$SrCO_3$	X				
$Pu(OH)_4$	X				

As seen in Table 5-1, HWCS includes the metal oxides included in the Chapter 4 validation, as well as various other constituents. The HWCS bounding sludge transfers to Tanks 1-15 are shown in Table 5-2.

Table 5-2 Tank 1-15 Bounding Sludge Constituents in Transfers

Tank	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Const.	(kg)														
AgOH	1.15E-3	1.90E-3	1.71E-3	5.32E-4	1.47E-3	2.83E-4	3.73E-3	2.01E-3	1.81E-3	1.53E-3	0.00E+0	3.12E-4	2.01E-4	2.68E-4	0.00E+0
$Al(OH)_3$	9.66E-2	3.78E-2	3.74E-2	7.90E-2	4.67E-2	1.18E-1	1.79E-1	1.73E-1	3.62E-2	3.85E-2	4.27E-1	4.01E-1	2.14E-1	1.47E-1	5.31E-1
CaC_2O_4	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	2.46E-2	2.31E-2	6.15E-3	4.53E-3	2.22E-2
$CaCO_3$	2.26E-2	3.28E-2	2.96E-2	1.59E-2	2.83E-2	1.08E-2	6.46E-2	3.30E-2	3.14E-2	2.65E-2	1.26E-2	5.41E-3	4.26E-2	1.61E-2	7.17E-3
$Fe(OH)_3$	2.73E-2	3.49E-1	3.16E-1	2.52E-1	3.37E-1	1.90E-1	6.54E-1	3.27E-1	3.34E-1	2.82E-1	2.43E-1	1.66E-1	4.66E-1	2.60E-1	1.77E-1
HGO	9.18E-4	9.30E-4	8.43E-4	1.17E-3	1.12E-3	9.48E-4	6.72E-4	7.32E-4	8.95E-4	7.54E-4	4.03E-2	3.23E-2	2.70E-2	9.96E-3	3.43E-2
KNO_3	3.02E-3	4.78E-3	4.32E-3	1.63E-3	3.85E-3	9.70E-4	9.06E-3	5.02E-3	4.58E-3	3.87E-3	3.03E-3	3.16E-3	2.69E-3	1.62E-3	2.57E-3
$Mn(OH)_2$	1.37E-1	2.88E-1	3.11E-1	7.67E-2	7.60E-2	4.48E-2	3.62E-2	3.04E-2	2.66E-1	3.47E-1	2.90E-2	1.21E-1	6.01E-2	2.50E-1	4.08E-2
NACL	6.02E-3	1.04E-2	9.37E-3	2.09E-3	7.77E-3	8.06E-4	2.15E-2	1.13E-2	9.99E-3	8.42E-3	4.00E-3	1.73E-3	1.33E-2	2.62E-3	2.28E-3
$NANO_3$	8.22E-3	1.08E-2	9.81E-3	7.10E-3	1.02E-2	5.25E-3	1.45E-2	1.03E-2	1.03E-2	8.75E-3	3.83E-2	3.67E-2	1.36E-2	1.22E-2	3.42E-2
NAOH	2.78E-2	3.50E-2	3.16E-2	2.62E-2	3.42E-2	2.00E-2	4.86E-2	3.25E-2	3.35E-2	2.83E-2	2.46E-2	2.02E-2	3.64E-2	2.60E-2	1.91E-2
$Ni(OH)_2$	8.78E-2	6.20E-2	6.12E-2	1.29E-1	7.64E-2	1.35E-1	5.73E-3	3.10E-2	5.93E-2	6.29E-2	3.62E-3	2.13E-2	1.06E-2	5.73E-2	1.63E-4
$PBCO_3$	1.50E-3	1.22E-3	1.11E-3	2.28E-3	1.78E-3	1.92E-3	1.02E-4	7.40E-4	1.16E-3	9.90E-4	1.80E-4	2.02E-4	7.82E-4	1.91E-3	1.03E-4
SiO_2	7.83E-3	1.14E-2	1.03E-2	5.50E-3	9.84E-3	3.76E-3	1.72E-2	1.15E-2	1.09E-2	9.19E-3	1.24E-1	5.21E-2	1.46E-2	1.34E-2	4.84E-2
$UO_2(OH)_2$	1.23E-1	4.55E-2	5.81E-2	1.50E-1	1.32E-1	1.78E-1	5.04E-2	1.19E-1	6.66E-2	6.33E-2	1.87E-3	1.38E-2	1.65E-2	6.78E-2	3.15E-4
$SrCO_3$	1.13E-3	1.22E-3	1.10E-3	1.33E-3	1.37E-3	1.07E-3	1.07E-3	1.01E-3	1.16E-3	9.81E-4	8.48E-4	8.80E-4	7.33E-4	1.20E-3	7.24E-4
$Pu(OH)_4$	2.00E-4	2.39E-4	1.47E-4	1.45E-4	1.38E-4	2.83E-4	3.73E-3	2.01E-3	1.81E-3	1.53E-3	3.39E-4	3.12E-4	2.01E-4	2.68E-4	0.00E+0
Total Solids	7.98E-1	8.94E-1	8.84E-1	7.52E-1	7.69E-1	7.13E-1	8.71E-1	7.90E-1	8.69E-1	8.84E-1	9.11E-1	9.04E-1	9.26E-1	8.74E-1	9.25E-1

Note: MnO_2 was not available in the model, therefore $Mn(OH)_2$ was used in its place with no correction since the 2xH does not significantly change the value.

Since transfers vary in size, the values contained in Table 5-2 need to be normalized for comparative purposes. To normalized data for comparative purposes, each constituent mass was divided by the total mass (horizontal row) of the considered tank. This is shown in Table 5-3.

Table 5-3 Normalization of Sludge Mass

Tank	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	MAX
Const	(kg/kg_{total})															
AgOH	1.44E-3	2.12E-3	1.93E-3	7.08E-4	1.91E-3	3.97E-4	4.28E-3	2.55E-3	2.08E-3	1.73E-3	0.00E+0	3.45E-4	2.17E-4	3.07E-4	0.00E+0	4.28E-3
$Al(OH)_3$	1.21E-1	4.23E-2	4.23E-2	1.05E-1	6.07E-2	1.66E-1	2.06E-1	2.19E-1	4.16E-2	4.35E-2	4.69E-1	4.44E-1	2.31E-1	1.68E-1	5.74E-1	5.74E-1
CaC_2O_4	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	2.70E-2	2.55E-2	6.64E-3	5.18E-3	2.40E-2	2.70E-2
$CaCO_3$	2.83E-2	3.67E-2	3.35E-2	2.11E-2	3.68E-2	1.52E-2	7.42E-2	4.18E-2	3.61E-2	3.00E-2	1.38E-2	5.98E-3	4.60E-2	1.84E-2	7.75E-3	7.42E-2
$Fe(OH)_3$	3.42E-2	3.90E-1	3.57E-1	3.35E-1	4.38E-1	2.66E-1	7.51E-1	4.14E-1	3.84E-1	3.19E-1	2.67E-1	1.84E-1	5.03E-1	2.98E-1	1.91E-1	7.51E-1
HGO	1.15E-3	1.04E-3	9.54E-4	1.55E-3	1.45E-3	1.33E-3	7.71E-4	9.27E-4	1.03E-3	8.53E-4	4.42E-2	3.57E-2	2.92E-2	1.14E-2	3.71E-2	4.42E-2
KNO_3	3.79E-3	5.35E-3	4.89E-3	2.17E-3	5.00E-3	1.36E-3	1.04E-2	6.35E-3	5.27E-3	4.38E-3	3.33E-3	3.50E-3	2.91E-3	1.85E-3	2.78E-3	1.04E-2
$Mn(OH)_2$	1.72E-1	3.22E-1	3.52E-1	1.02E-1	9.88E-2	6.29E-2	4.16E-2	3.85E-2	3.06E-1	3.93E-1	3.18E-2	1.34E-1	6.49E-2	2.86E-1	4.41E-2	3.93E-1
NACL	7.54E-3	1.16E-2	1.06E-2	2.78E-3	1.01E-2	1.13E-3	2.47E-2	1.43E-2	1.15E-2	9.52E-3	4.39E-3	1.91E-3	1.44E-2	3.00E-3	2.47E-3	2.47E-2
$NANO_3$	1.03E-2	1.21E-2	1.11E-2	9.44E-3	1.32E-2	7.37E-3	1.66E-2	1.31E-2	1.19E-2	9.90E-3	4.20E-2	4.06E-2	1.47E-2	1.40E-2	3.70E-2	4.20E-2
NAOH	3.48E-2	3.92E-2	3.58E-2	3.49E-2	4.45E-2	2.80E-2	5.58E-2	4.12E-2	3.85E-2	3.20E-2	2.70E-2	2.24E-2	3.93E-2	2.97E-2	2.07E-2	5.58E-2
$Ni(OH)_2$	1.10E-1	6.93E-2	6.92E-2	1.72E-1	9.94E-2	1.89E-1	6.58E-3	3.93E-2	6.82E-2	7.11E-2	3.97E-3	2.36E-2	1.15E-2	6.56E-2	1.76E-4	1.89E-1
$PBCO_3$	1.88E-3	1.37E-3	1.25E-3	3.03E-3	2.31E-3	2.69E-3	1.17E-4	9.37E-4	1.34E-3	1.12E-3	1.98E-4	2.23E-4	8.44E-4	2.18E-3	1.11E-4	3.03E-3
SiO_2	9.81E-3	1.27E-2	1.16E-2	7.32E-3	1.28E-2	5.28E-3	1.97E-2	1.45E-2	1.25E-2	1.04E-2	1.36E-1	5.76E-2	1.58E-2	1.53E-2	5.23E-2	1.36E-1
$UO_2(OH)_2$	1.54E-1	5.09E-2	6.57E-2	2.00E-1	1.72E-1	2.50E-1	5.79E-2	1.51E-1	7.66E-2	7.16E-2	2.05E-3	1.53E-2	1.78E-2	7.76E-2	3.40E-4	2.50E-1
$SrCO_3$	1.41E-3	1.36E-3	1.24E-3	1.77E-3	1.78E-3	1.50E-3	1.23E-3	1.28E-3	1.34E-3	1.11E-3	9.31E-4	9.74E-4	7.92E-4	1.37E-3	7.83E-4	1.78E-3
$Pu(OH)_4$	2.51E-4	2.67E-4	1.66E-4	1.93E-4	1.80E-4	1.38E-4	1.55E-4	2.33E-4	8.75E-5	2.14E-4	3.72E-4	3.55E-4	8.86E-5	3.25E-4	2.05E-4	3.72E-4
Total Solids	1.00E+0	1.00E+0	1.00E+0	1.00E+0	1.00E+0	1.00E+0	1.00E+0	1.00E+0	1.00E+0	1.00E+0	1.00E+0	1.00E+0	1.00E+0	1.00E+0	1.00E+0	

The “MAX kg/kg_{total}” Column in Table 5-3 is multiplied by the concentration of dry solids in a gallon of sludge. For conservatism 1.12 kg_{total}/gal is used, except for plutonium in which 1.32 kg_{total}/gal is used for conservatism. Additionally, to convert to a “per sludge heel,” the concentration per gallon is multiplied by the assumed 5,000 gallon heel size as shown in Equation 5-1.

$$\text{Mass} = \text{MAX kg/kg}_{total} \ \times \ \text{concentration of solids} \ \times \ \text{volume} \qquad \text{(Eq. 5-1)}$$

Where:

- Volume = 5,000 gal
- Mass = kg of constituent solids per 5,000 gallons of sludge
- MAX kg/kg_{total} = value from Table 5-3
- Concentration of dry solids in 1 gallon of heel = conservatively assumed to be approx. 1.12kg/gal, except for plutonium which is assumed to be 1.32 kg/gal .

Table 5-4 shows the mass of each constituent in the 5,000 gallon HWCS heel used in the modelling.

Table 5-4 Bounding HWCS Heel

AgOH	$Al(OH)_3$	CaC_2O_4	$CaCO_3$	$Fe(OH)_3$	HgO	KNO_3	$Mn(OH)_2$	NaCl	$NaNO_3$	NaOH	$Ni(OH)_2$	$PbCO_3$	SiO_2	$UO_2(OH)_2$	$SrCO_3$	$Pu(OH)_4$
(kg)																
24	3200	150	420	4200	250	59	2300	140	240	320	1100	17	690	1400	10	2.46

5.3 Supernate in Neutralization Tank

The supernate characterization data is also taken from the process database (HLW, 2005). The choice of data is limited to the currently proposed receipt tanks and Tank 33, based on the potential for transfers. The data is shown in Table 5-5.

Table 5-5 Supernate Characterization

Tank	Ag	Al	CO_3	C_2O_4	Fe	Hg	Mn	Ni	NO_2	NO_3	NaOH
	(kg/gal)										
8	1.14E-05	2.59E-01	3.18E-02	2.60E-03	1.06E-04	1.14E-04	3.19E-06	1.14E-05	4.79E-01	4.69E-01	Used 0.65
13	1.51E-07	3.81E-01	3.41E-02	2.27E-03	6.76E-05	7.57E-05	2.61E-06	9.48E-06	5.29E-01	5.28E-01	Used 0.65
33	1.51E-07	1.08E-01	4.54E-02	2.27E-03	6.76E-05	7.57E-05	3.22E-06	1.15E-05	4.70E-01	3.76E-01	Used 0.65
Max	1.14E-05	3.81E-01	4.54E-02	2.60E-03	1.06E-04	1.14E-04	3.22E-06	1.15E-05	5.29E-01	5.28E-01	Used 0.65

The values were converted to the simplest compounds of OH^-, except for NaOH that was based on maintaining the corrosion control program. For 5,000 gallons the model input is shown in Table 5-6.

Table 5-6 Model Input for 5,000 gallons of Bounding Supernate

AgOH	$Al(OH)_3$	Na_2CO_3	HgC_2O_4	$Fe(OH)_3$	HgO	$Mn(OH)_2$	$Ni(OH)_2$	HNO_2	$NaNO_3$	NaOH
(kg)										
1.74E+00	5.50E+03	5.23E+02	1.87E+01	1.01E+00	7.70E+00	2.61E-02	9.06E-02	2.70E+03	9.76E+03	3.25E+03

5.4 Material and Energy Balance

The purpose of the material balance is to estimate the contents in the treatment tank and neutralization tank throughout each evolution of the treatment.

5.4.1 HWCS Material Balance

The material balance for the three acid strikes is shown in Figure 5-1.

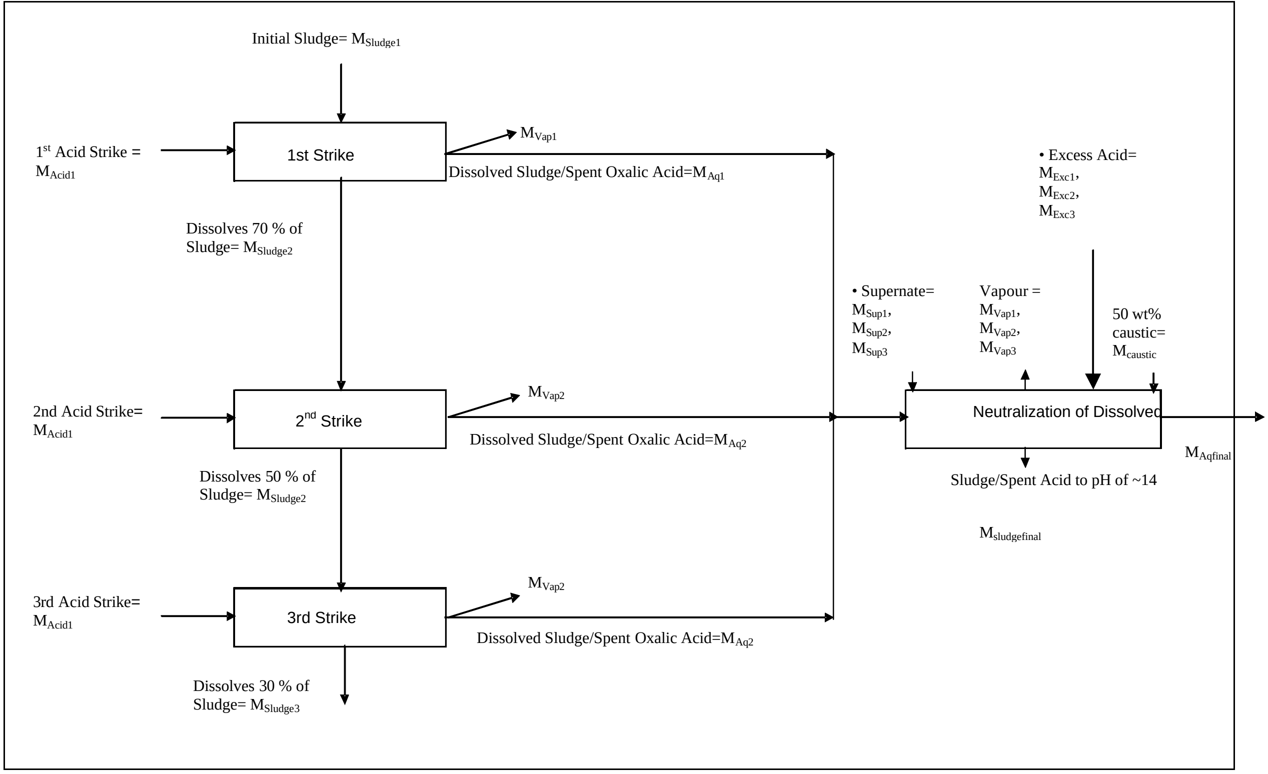


Figure 5-1 Treatment and Neutralization (Limited) Tank Material Balance

Initially, the oxalic acid solution (M_{AcidN}) will be added to the HWCS heel ($M_{SludgeN}$), mixed, and allowed to come to equilibrium. The resultant chemistry is made up of 3 parts (solid = $M_{SludgeN+1}$, liquid = M_{AqN}, and gas = M_{VapN}) based on their physical phase. This is shown by Equation 5-2.

$$M_{AcidN} + M_{SludgeN} = M_{SludgeN+1} + M_{AqN} + M_{VapN} \qquad \text{(Eq. 5-2)}$$

Where:

- "N" = Acid strike number (i.e., 1st-strike, 2nd-strike, or 3rd-strike)
- $M_{SludgeN}$ = Sludge at the beginning of strike "N"
- $M_{SludgeN+1}$ = Sludge remaining in the treatment tank after strike "N"
- M_{AqN} = Aqueous that results from strike "N" and is made from dissolved sludge/reacted acid and will be transferred to the neutralization tank
- M_{VapN} = Vapour that will be released from the treatment tank after strike "N"
- M_{AcidN} = Acid Need for desired dissolution in Strike "N"

This equation does not include unreacted acid, M_{ExcN}; therefore, to show unreacted acid in the system we can add it both sides as shown in Equation 5-3.

$$M_{ExcN} + M_{AcidN} + M_{SludgeN} = M_{SludgeN+1} + M_{AqN} + M_{VapN} + M_{ExcN} \qquad \text{(Eq. 5-3)}$$

Where:

- M_{ExcN} = Excess acid that does not react in the treatment tank, but passes through the system until reacting in the neutralization tank

For the 3-strikes in the treatment tank this is expressed as Equation 5-4.

$$M_{Sludge1} + \sum_{N} M_{Acid} + \sum_{N} M_{Excess} = M_{Sludge4} + \sum_{N} M_{Aq} + \sum_{N} M_{Vap} + \sum_{N} M_{Exc} \qquad \text{(Eq. 5-4)}$$

M_{Vap1}, M_{Vap2}, and M_{Vap3} are released to the atmosphere from the treatment tank. $M_{Sludge4}$ is the remaining sludge heel, while M_{Aq1}, M_{Aq2}, M_{Ag3}, M_{Exc1}, M_{Exc2}, and M_{Exc3} are added to the neutralization tank.

The neutralization tank is initially assumed to have a heel of 10,000 gallons of supernate (M_{Snate1}) and be pre-treated with a heel of 50 wt% NaOH solution, $M_{Caustic}$ to ensure corrosion control. It should be noted that large additions of 50 wt% caustic are normal evolutions evaluated to be acceptable as part of maintaining the corrosion control program. The material balance for the neutralization tank is shown as Equation 5-5.

$$M_{Snate1} + M_{Caustic} + \sum_N M_{Aq} + \sum_N M_{Exc} = \sum_N M_{Prec} + \sum_N M_{gas} + M_{Snate2} \quad \text{(Eq. 5-5)}$$

Where:

- M_{Snate1} = Initial supernate in neutralization tank
- $M_{Caustic}$ = Estimated caustic pre-added to the neutralization tank to ensure pH remains within corrosion control program
- $\sum M_{Aq} = M_{Aq1} + M_{Aq2} + M_{Aq3}$ = Dissolved sludge/spent acid each added individually transferred from treatment tank to neutralization tank
- $\sum M_{Exc} = M_{Exc1} + M_{Exc2} + M_{Exc3}$ = Unspent acid added during strikes, but does not react in system until reaching neutralization tank. Each excess transferred with corresponding aqueous (i.e., M_{Ag1}+M_{Exc1} transferred from treatment tank, M_{Acid2} added to treatment tank and mixed, then M_{Ag2}+M_{Exc2} transferred out of treatment tank to neutralization tank)
- $\sum M_{Prec} = M_{Prec1} + M_{Prec2} + M_{Prec3}$ = Precipitate that forms in neutralization tank after transfers from treatment tank
- $\sum M_{Gas} = M_{Gas1} + M_{Gas2} + M_{Gas3}$ = Neutralization vapour produced from aqueous and excess acid of strike transferred into the neutralization tank
- $M_{SnateEnd}$ = End Aqueous in the neutralization tank after $\sum M_{Aq}$ and $\sum M_{Exc}$ additions to neutralization tank and reactions complete

5.4.2 Modelling Input and Assumptions

1. For speciation, the amount of oxalic acid to be added is based on obtaining 70 vol%, 50 vol% and 30 vol% as determined by using OLI Stream Analyzer$^{©}$. Literature (Adu-Wusu, 2003, p71) recommends that 8 wt% oxalic acid solutions in volume ratios of 20:1 acid to sludge be used to dissolve the sludge. The excess acid will be assumed to not to react, but pass through the system with the aqueous until finally reacting within the neutralization tank.

2. No corrosion inhibitors will be required to be added to the treatment tank during acid cleaning or post acid cleaning. Currently, since the treatment tank will be closed, without significant process changes/requirements, no additional NaOH will be added to the treatment tank.

3. Salt/supernate is removed prior to acid heel dissolution, based on space availability and ease of separation. The minimum pump down level is assumed to be 5,000 gallons. At the minimum pump down level, the tank will initially contain the 5,000 gallon heel of HWCS, and 70 vol% of which is assumed to be interstitial liquid, which has been rinsed down to mostly water.

4. Acid can contact the sludge, based on the fact that the surface of the sludge after bulk removal should be relatively uniform. Additionally, adequate time will be allowed for the reactions to come to equilibrium.

5. Oxalic acid vapours are minimized for the material balance. Bounding calculations based on an energy balance are used to calculate input for overpressurization concerns.

6. Small additions, round offs, and speciation simplification based on perceived process, risk importance, and over-all concentration are acceptable based on the likelihood that they are within the uncertainty. This includes the interstitial liquid since the volume is very small compared to the volume of the acid solution.

7. Solids carryover is considered negligible for the speciation and are not factored into the model (i.e., currently without knowing the pumping capabilities of the system, only dissolved solids are considered to be transferred in the mass balance. Furthermore, this is outside the scope of the material balance).

8. The maximization of enthalpy, temperature, gas generation, and dissolution are considered independent and therefore can be independently maximized. Such an approach is conservative.

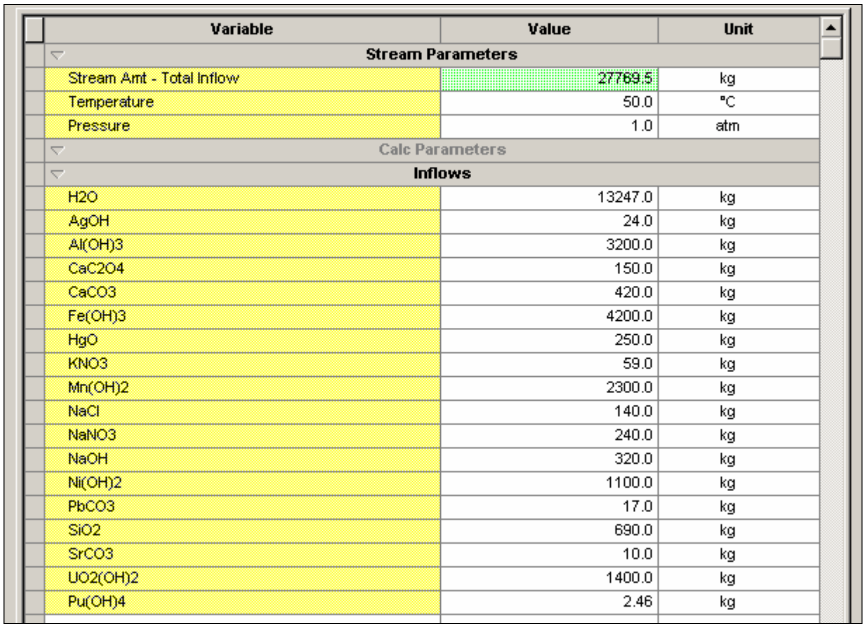
9. The HWCS volume when acid heel dissolution begins is limited to about 5,000 gallons.

Based on size of tanks, and the fact that no significant temperature changes are expected, modelling is performed isothermically, assuming the HLW tanks are at 50ºC. When added, the oxalic acid solution and the 50 wt% sodium hydroxide solution are at 25ºC.

5.4.3 Material Balance Modelling

5.4.3.1 $M_{Sludge1}$

The input for the initial 5,000 gallon $M_{Sludge1}$ uses Table 5-4 and is shown in Figure 5-2. In addition to HWCS the interstitial liquid is assumed to be water and occupies 70 vol% of the sludge.



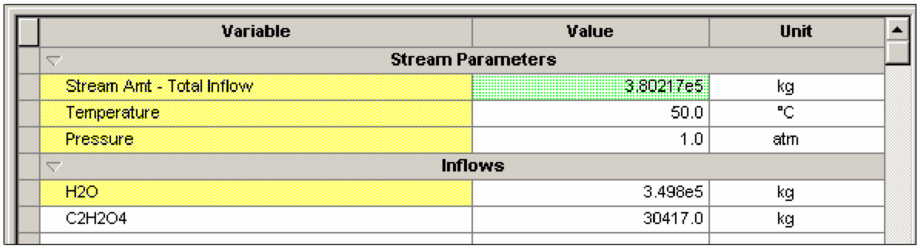
Variable	Value	Unit
Stream Parameters		
Stream Amt - Total Inflow	27769.5	kg
Temperature	50.0	°C
Pressure	1.0	atm
Calc Parameters		
Inflows		
H2O	13247.0	kg
AgOH	24.0	kg
Al(OH)3	3200.0	kg
CaC2O4	150.0	kg
CaCO3	420.0	kg
Fe(OH)3	4200.0	kg
HgO	250.0	kg
KNO3	59.0	kg
Mn(OH)2	2300.0	kg
NaCl	140.0	kg
NaNO3	240.0	kg
NaOH	320.0	kg
Ni(OH)2	1100.0	kg
PbCO3	17.0	kg
SiO2	690.0	kg
SrCO3	10.0	kg
UO2(OH)2	1400.0	kg
Pu(OH)4	2.46	kg

Figure 5-2 HWCS Input

The white background cells under inflow are manually entered, whereas, the green, Stream amount is automatically calculated by OLI Stream Analyzer©. The "Output" (not shown) estimates the mass of the solids as 14,523 kg having a volume of 5,678 litres.

5.4.3.2 M_{Acid1}, M_{Exc1}

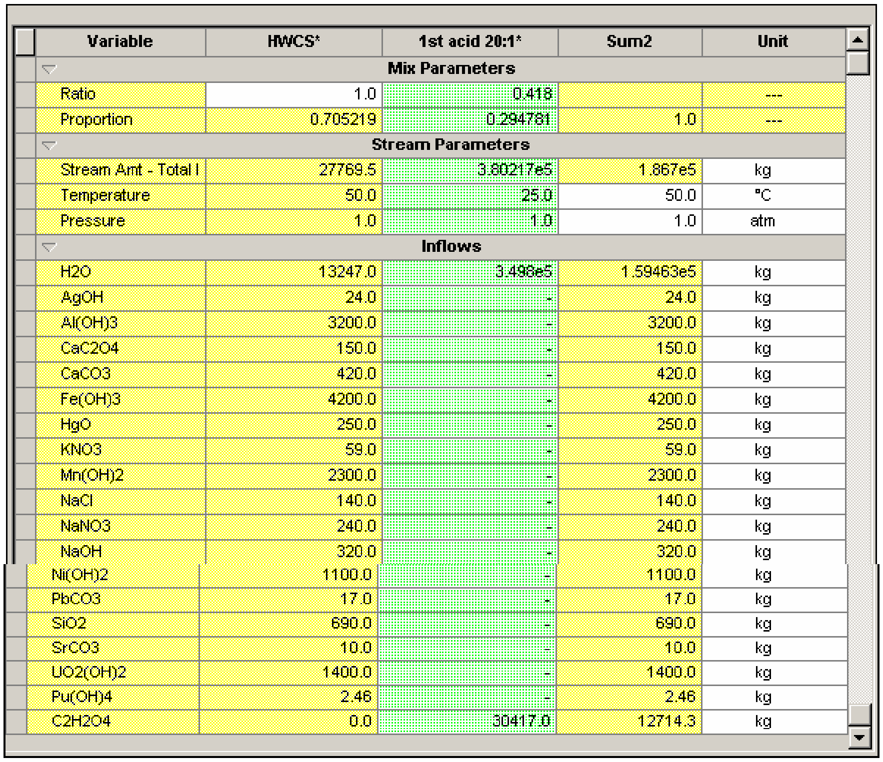
Literature (Adu-Wusu, 2003, p70) recommends that 8 wt% of a 20:1 volume ratio be added to result in 70 vol% of the sludge heel dissolved. This amount of acid is shown in Figure 5-3.



Variable	Value	Unit
Stream Parameters		
Stream Amt - Total Inflow	3.80217e5	kg
Temperature	50.0	°C
Pressure	1.0	atm
Inflows		
H2O	3.498e5	kg
C2H2O4	30417.0	kg

Figure 5-3 Literature Recommended Amount of Acid for First-Strike

Through trial and error, enough 8 wt% oxalic acid solution is added to dissolve 70 vol% of the 5,678 litres and result in approximately 1,703 litres. This value is M_{Acid1}. M_{Acid1} equals 0.418 multiplied by the literature recommended amount of acid. In Figure 5-4, the literature recommended amount of acid is put into the model with a ratio of 0.418 to equal M_{Acid1}. While M_{Exc1} equals 0.582 multiplied by the literature recommended amount of acid. The inputs to the 1st-strike are shown in Figure 5-4.



Variable	HWCS*	1st acid 20:1*	Sum2	Unit
Mix Parameters				
Ratio	1.0	0.418		---
Proportion	0.705219	0.294781	1.0	---
Stream Parameters				
Stream Amt - Total I	27769.5	3.80217e5	1.867e5	kg
Temperature	50.0	25.0	50.0	°C
Pressure	1.0	1.0	1.0	atm
Inflows				
H2O	13247.0	3.498e5	1.59463e5	kg
AgOH	24.0	-	24.0	kg
Al(OH)3	3200.0	-	3200.0	kg
CaC2O4	150.0	-	150.0	kg
CaCO3	420.0	-	420.0	kg
Fe(OH)3	4200.0	-	4200.0	kg
HgO	250.0	-	250.0	kg
KNO3	59.0	-	59.0	kg
Mn(OH)2	2300.0	-	2300.0	kg
NaCl	140.0	-	140.0	kg
NaNO3	240.0	-	240.0	kg
NaOH	320.0	-	320.0	kg
Ni(OH)2	1100.0	-	1100.0	kg
PbCO3	17.0	-	17.0	kg
SiO2	690.0	-	690.0	kg
SrCO3	10.0	-	10.0	kg
UO2(OH)2	1400.0	-	1400.0	kg
Pu(OH)4	2.46	-	2.46	kg
C2H2O4	0.0	30417.0	12714.3	kg

Figure 5-4 Input to First-Strike

5.4.3.3 M_{Aq1}, M_{Exc1}, M_{Vap1}, $M_{Sludge2}$

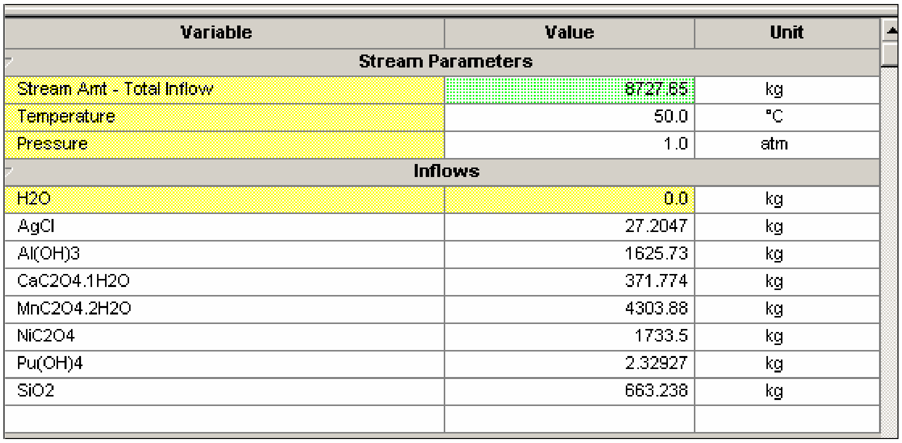
The output from the first-strike is shown in Table 5-7.

Table 5-7 Output from the First-Strike of Acid

Constituents	**Aqueous (kg)**	**Excess Acid (kg)**	**Vapour (kg)**	**Solid (kg)**
	(M_{Aq1})	**(M_{Exc1})**	**(M_{Vap1})**	**($M_{Sludge2}$)**
H_2O	1.63E+05	=0.582 x 3.50E5	4.47E+00	0.00E+00
$Al(OH)_3$	0.00E+00		0.00E+00	1.63E+03
CaC_2O4	3.62E+02		0.00E+00	0.00E+00
SiO_2	2.68E+01		0.00E+00	6.63E+02
$Pu(OH)_4$	0.00E+00		0.00E+00	2.33E+00
$C_2H_2O_4$	2.48E+03	=0.582 x 3.04E5	0.00E+00	0.00E+00
$Ag_2C_2O_4$	3.61E-01		0.00E+00	0.00E+00
$AgCl$	0.00E+00		0.00E+00	2.72E+01
$Al(NO_3)_3$	2.42E+02		0.00E+00	0.00E+00
$AlCl_3$	9.80E+01		0.00E+00	0.00E+00
$CaC_2O_4.1H_2O$	1.10E+03		0.00E+00	0.00E+00
CO_2	0.00E+00		0.00E+00	3.72E+02
$Fe_2(C_2O_4)_3$	1.13E+02		7.79E+01	0.00E+00
HCl	7.38E+03		0.00E+00	0.00E+00
HgC_2O_4	0.00E+00		9.81E-11	0.00E+00
$HgCl_2$	3.33E+02		0.00E+00	0.00E+00
HNO_3	0.00E+00		7.45E-05	0.00E+00
$K_2C_2O_4$	0.00E+00		8.19E-09	0.00E+00
MnC_2O_4	4.85E+01		0.00E+00	0.00E+00
$MnC_2O_4.2H_2O$	2.59E+02		0.00E+00	0.00E+00
$Na_2C_2O_4$	0.00E+00		0.00E+00	4.30E+03
$NaALO_2$	8.86E+02		0.00E+00	0.00E+00
NiC_2O_4	7.44E+00		0.00E+00	1.73E+03
PbC_2O_4	1.88E+01		0.00E+00	0.00E+00
$Pu(C_2O_4)_2$	1.76E-01		0.00E+00	0.00E+00
$SiCl_4$	0.00E+00		1.47E-68	0.00E+00
SrC_2O_4	1.19E+01		0.00E+00	0.00E+00
$UO_2C_2O_4$	1.65E+03		0.00E+00	0.00E+00

M_{Exc1} must be hand calculated since it was restricted from the input in order to keep it from reacting within the treatment tank.

The aqueous, $M_{Aq1,}$ and excess acid, M_{Exc1}, from the first-strike are transferred to the neutralization tank, while the vapour $M_{Vap1}$is released to the atmosphere. The sludge solids, $M_{Sludge2}$ remain in the treatment tank. After each dissolution, the remaining sludge may be flushed. Flushing will lower the ionic strength of the remaining interstitial solution within the treatment tank. The interstitial liquid, however, is not considered significant within the model, since the volume is very small compared to the amount of acid solution to be added. Solids are assumed not to carry over**.** Spent acid/dissolved sludge and unspent acid, M_{Aq1}, M_{Exc1} are transferred to the neutralization tank, with the solids remaining. The software's capability to separate each phase is used to separate the liquid fraction from the solids, and the solids become input to the second-strike. Refer to Figure 5-5.

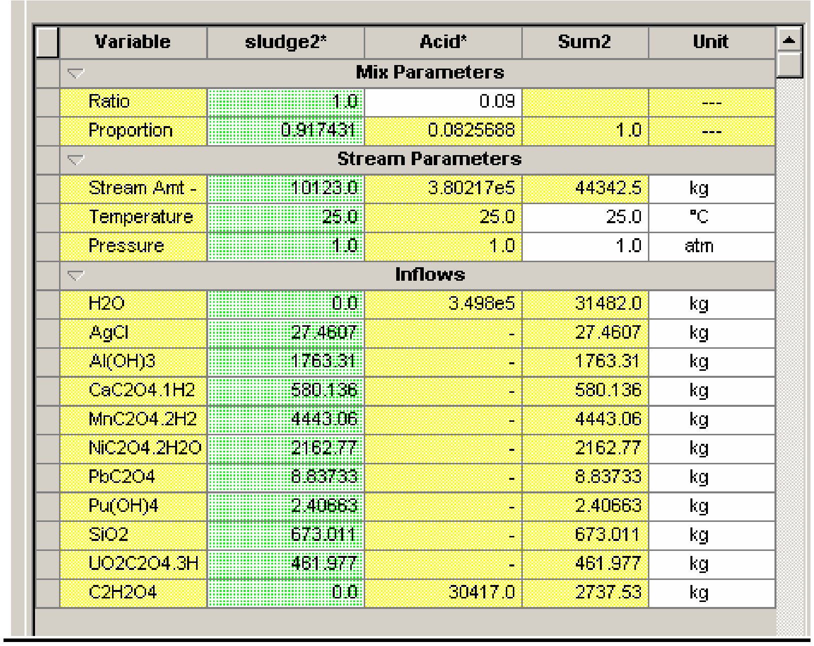


Variable	Value	Unit
Stream Parameters		
Stream Amt - Total Inflow	8727.65	kg
Temperature	50.0	°C
Pressure	1.0	atm
Inflows		
H2O	0.0	kg
AgCl	27.2047	kg
Al(OH)3	1625.73	kg
CaC2O4.1H2O	371.774	kg
MnC2O4.2H2O	4303.88	kg
NiC2O4	1733.5	kg
Pu(OH)4	2.32927	kg
SiO2	663.238	kg

Figure 5-5 Solids After First-Strike of Acid

5.4.3.4 M_{Acid2}, M_{Exc2}

The literature recommended amount of 8 wt% oxalic acid solution, to result in a 50 vol% dissolution for the second strike is a 0.3 fraction of the initial acid. Using trial and error it is determined that only 0.3 of the initial 0.3 fraction is required for the model to dissolve 50 vol% of the sludge; therefore, $M_{Acid2} = 0.3 \times 0.3 \times M_{Acid1}$). Refer to Figure 5-6.



Variable	sludge2*	Acid*	Sum2	Unit
Mix Parameters				
Ratio	1.0	0.09		---
Proportion	0.917431	0.0825688	1.0	---
Stream Parameters				
Stream Amt -	10123.0	3.80217e5	44342.5	kg
Temperature	25.0	25.0	25.0	°C
Pressure	1.0	1.0	1.0	atm
Inflows				
H2O	0.0	3.498e5	31482.0	kg
AgCl	27.4607	-	27.4607	kg
Al(OH)3	1763.31	-	1763.31	kg
CaC2O4.1H2	580.136	-	580.136	kg
MnC2O4.2H2	4443.06	-	4443.06	kg
NiC2O4.2H2O	2162.77	-	2162.77	kg
PbC2O4	8.83733	-	8.83733	kg
Pu(OH)4	2.40663	-	2.40663	kg
SiO2	673.011	-	673.011	kg
UO2C2O4.3H	461.977	-	461.977	kg
C2H2O4	0.0	30417.0	2737.53	kg

Figure 5-6 Input to Second-Strike

5.4.3.5 M_{Aq2}, M_{Exc2}, M_{Vap2}, M_{Solid3}

M_{Exc2} is based on (1-0.3) multiplied by the initial acid required. Table 5-8 shows the output of the second acid strike, where M_{Exc2} is excess and must be hand entered, so as not to react until reaching the neutralization tank.

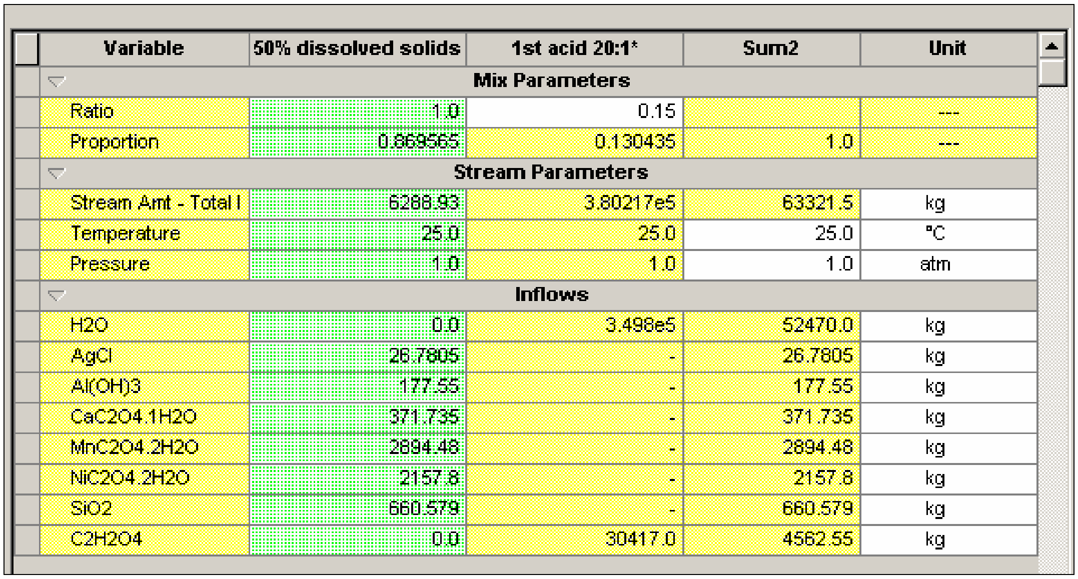
Table 5-8 Output from the Second-Strike of Acid

Constituents	Aqueous (kg)	Excess Acid (kg)	Vapour (kg)	Solid (kg)
	(M_{Aq2})	**(M_{Exc2})**	**(M_{Vap2})**	**($M_{Sludge3}$)**
H_2O	3.17E+04	=0.7x1.05E+05	0.00E+00	0.00E+00
AgCl	4.24E-01		0.00E+00	2.68E+01
$Al(OH)_3$	0.00E+00		0.00E+00	1.78E+02
$CaC_2O_4.1H_2O$	0.00E+00		0.00E+00	3.72E+02
$MnC_2O_4.2H_2O$	0.00E+00		0.00E+00	2.89E+03
NiC_2O_4	1.19E+00		0.00E+00	0.00E+00
SiO_2	2.66E+00		0.00E+00	6.61E+02
$C_2H_2O_4$	2.74E+03	=0.7x9125.1	0.00E+00	0.00E+00
AlO(OH)	1.11E+03		0.00E+00	0.00E+00
CaC_2O_4	3.44E-02		0.00E+00	0.00E+00
MnC_2O_4	1.13E+03		0.00E+00	0.00E+00
$Pu(C_2O_4)_2$	0.00E+00		0.00E+00	2.16E+03

After the second-strike, the aqueous and excess acid solutions are transferred to the neutralization tank, and the vapour is released to the atmosphere. The solids remain within the treatment tank. The interstitial liquid, although 70 vol% of the sludge, is considered to be negligible compared to M_{Acid2}. The sludge is again treated with oxalic acid.

5.4.3.5 $M_{Sludge3}, M_{Acid3}$

The third-strike of oxalic acid is estimated to dissolve 30 vol% of the sludge. This time the literature[8] recommended amount of 8 wt% oxalic acid is equal to that required based on modelling trials. M_{Acid3} is expressed in terms of M_{Acid1} for convenience. The input for the third-strike is shown in Figure 5-7.



Variable	50% dissolved solids	1st acid 20:1*	Sum2	Unit
Mix Parameters				
Ratio	1.0	0.15		---
Proportion	0.869565	0.130435	1.0	---
Stream Parameters				
Stream Amt - Total I	6288.93	3.80217e5	63321.5	kg
Temperature	25.0	25.0	25.0	°C
Pressure	1.0	1.0	1.0	atm
Inflows				
H2O	0.0	3.498e5	52470.0	kg
AgCl	26.7805	-	26.7805	kg
Al(OH)3	177.55	-	177.55	kg
CaC2O4.1H2O	371.735	-	371.735	kg
MnC2O4.2H2O	2894.48	-	2894.48	kg
NiC2O4.2H2O	2157.8	-	2157.8	kg
SiO2	660.579	-	660.579	kg
C2H2O4	0.0	30417.0	4562.55	kg

Figure 5-7 Input to Third-Strike

5.4.3.6 M_{Aq3}, M_{Exc3}, M_{Vap3}, $M_{Sludge\ 4}$

The output from the third strike and the excess acid are shown in Table 5-9.

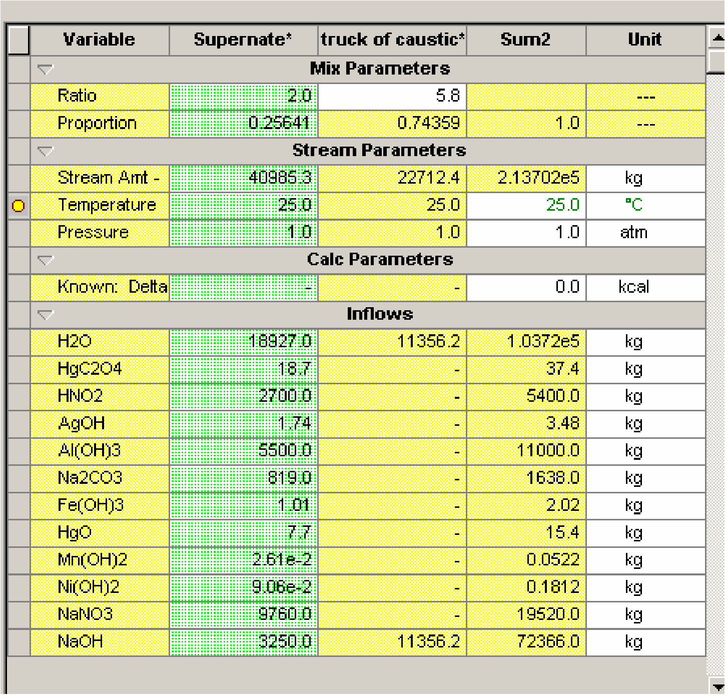
Table 5-9 Output from the Third-Strike of Acid

Constituents	Aqueous (kg)	Excess Acid (kg)	Vapour (kg)	Solid (kg)
	M_{Aq3}	M_{Exc3}	M_{Vap3}	$M_{Sludge4}$
H_2O	5.25E+04	=0.15x3.80E5	0.00E+00	0.00E+00
AgCl	1.75E-01		0.00E+00	2.66E+01
$CaC_2O_4.1H_2O$	0.00E+00		0.00E+00	3.65E+02
$MnC_2O_4.2H_2O$	0.00E+00		0.00E+00	2.87E+03
$NiC_2O_4.2H_2O$	0.00E+00		0.00E+00	2.16E+03
SiO_2	5.97E+00		0.00E+00	6.55E+02
$C_2H_2O_4$	4.56E+03	=0.15x30417	0.00E+00	0.00E+00
AlO(OH)	1.37E+02		0.00E+00	0.00E+00
CaC_2O_4	6.31E+00		0.00E+00	0.00E+00
MnC_2O_4	1.69E+01		0.00E+00	0.00E+00
NiC_2O_4	1.48E+00		0.00E+00	0.00E+00

Again the aqueous and excess acid are transferred out, the vapour is released to the atmosphere, and 6,076 kg of solids remain. Since 70-50-30 vol% is assumed to be dissolved, the sludge heel in the treatment tank decreased from a volume of 5,000 gallons to a resulting volume of 525 gallons or 1,987 litres.

5.4.3.7 M_{Snate1}, $M_{Caustic}$

The neutralization tank is assumed to initially contain 100,000 gallons of supernate and is pre-charged with caustic to ensure that it will remain within the corrosion control program. The input to the neutralization tank is shown in Figure 5-8.



Variable	Supernate*	truck of caustic*	Sum2	Unit
Mix Parameters				
Ratio	2.0	5.8		---
Proportion	0.25641	0.74359	1.0	---
Stream Parameters				
Stream Amt -	40985.3	22712.4	2.13702e5	kg
Temperature	25.0	25.0	25.0	°C
Pressure	1.0	1.0	1.0	atm
Calc Parameters				
Known: Delta	-	-	0.0	kcal
Inflows				
H2O	18927.0	11356.2	1.0372e5	kg
HgC2O4	18.7	-	37.4	kg
HNO2	2700.0	-	5400.0	kg
AgOH	1.74	-	3.48	kg
Al(OH)3	5500.0	-	11000.0	kg
Na2CO3	819.0	-	1638.0	kg
Fe(OH)3	1.01	-	2.02	kg
HgO	7.7	-	15.4	kg
Mn(OH)2	2.61e-2	-	0.0522	kg
Ni(OH)2	9.06e-2	-	0.1812	kg
NaNO3	9760.0	-	19520.0	kg
NaOH	3250.0	11356.2	72366.0	kg

Figure 5-8 Input to Initial Pre-charged Neutralization Tank

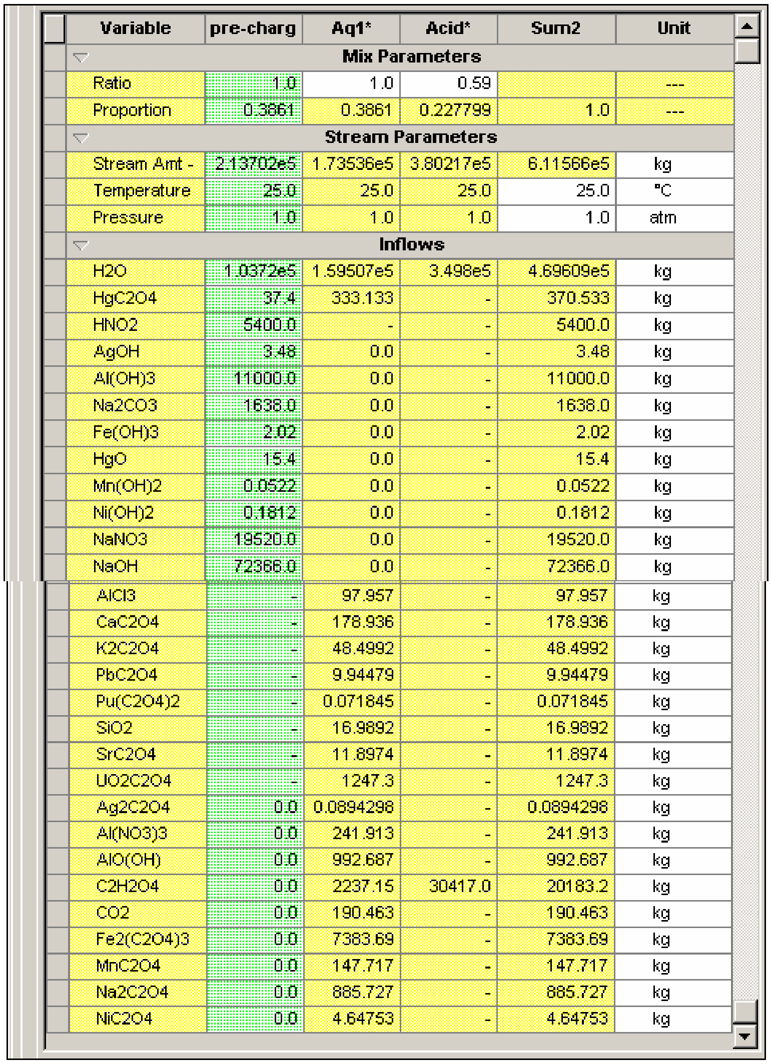
The output of the addition of caustic to supernate is shown in Table 5-10.

Table 5-10 Results of Caustic Addition to Supernate Heel

Constituents	Aqueous (kg)	Vapour (kg)	Solid (kg)
H_2O	1.11E+05	0.00E+00	0.00E+00
AgOH	3.48E+00	0.00E+00	0.00E+00
Na_2CO3	1.64E+03	0.00E+00	0.00E+00
$Fe(OH)_3$	2.02E+00	0.00E+00	0.00E+00
HgO	4.35E+01	0.00E+00	0.00E+00
$Mn(OH)_2$	5.22E-02	0.00E+00	0.00E+00
$Ni(OH)_2$	1.81E-01	0.00E+00	0.00E+00
$NaNO_3$	1.86E+04	0.00E+00	8.73E+02
NaOH	6.21E+04	0.00E+00	0.00E+00
$Na_2C_2O_4$	8.18E-01	0.00E+00	1.65E+01
$NaAlO_2$	1.16E+04	0.00E+00	0.00E+00
$NaNO_2$	7.92E+03	0.00E+00	0.00E+00

5.4.3.8 M_{Aq1}, M_{Exc1}

M_{Aq1} and M_{Exc1} are added to the neutralization tank as shown in Figure 5-9. M_{Exc1} is calculated based on M_{Acid1} + M_{Exc1}=Recommended amount of acid to be added based on literature.

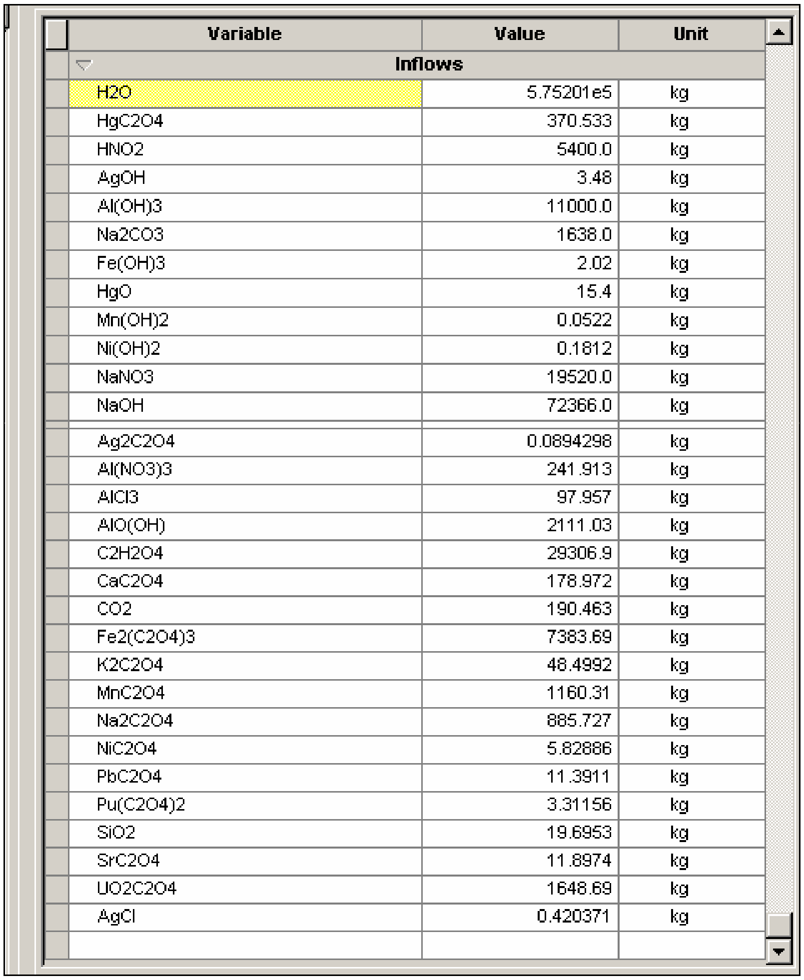


Variable	pre-charg	Aq1*	Acid*	Sum2	Unit
Mix Parameters					
Ratio	1.0	1.0	0.59		---
Proportion	0.3861	0.3861	0.227799	1.0	---
Stream Parameters					
Stream Amt -	2.13702e5	1.73536e5	3.80217e5	6.11566e5	kg
Temperature	25.0	25.0	25.0	25.0	°C
Pressure	1.0	1.0	1.0	1.0	atm
Inflows					
H2O	1.0372e5	1.59507e5	3.498e5	4.69609e5	kg
HgC2O4	37.4	333.133	-	370.533	kg
HNO2	5400.0	-	-	5400.0	kg
AgOH	3.48	0.0	-	3.48	kg
Al(OH)3	11000.0	0.0	-	11000.0	kg
Na2CO3	1638.0	0.0	-	1638.0	kg
Fe(OH)3	2.02	0.0	-	2.02	kg
HgO	15.4	0.0	-	15.4	kg
Mn(OH)2	0.0522	0.0	-	0.0522	kg
Ni(OH)2	0.1812	0.0	-	0.1812	kg
NaNO3	19520.0	0.0	-	19520.0	kg
NaOH	72366.0	0.0	-	72366.0	kg
AlCl3	-	97.957	-	97.957	kg
CaC2O4	-	178.936	-	178.936	kg
K2C2O4	-	48.4992	-	48.4992	kg
PbC2O4	-	9.94479	-	9.94479	kg
Pu(C2O4)2	-	0.071845	-	0.071845	kg
SiO2	-	16.9892	-	16.9892	kg
SrC2O4	-	11.8974	-	11.8974	kg
UO2C2O4	-	1247.3	-	1247.3	kg
Ag2C2O4	0.0	0.0894298	-	0.0894298	kg
Al(NO3)3	0.0	241.913	-	241.913	kg
AlO(OH)	0.0	992.687	-	992.687	kg
C2H2O4	0.0	2237.15	30417.0	20183.2	kg
CO2	0.0	190.463	-	190.463	kg
Fe2(C2O4)3	0.0	7383.69	-	7383.69	kg
MnC2O4	0.0	147.717	-	147.717	kg
Na2C2O4	0.0	885.727	-	885.727	kg
NiC2O4	0.0	4.64753	-	4.64753	kg

Figure 5-9 First Addition of Spent Acid Plus Excess Acid to Neutralization Tank

5.4.3.9 M_{Aq2}, M_{Exc2}

M_{Aq2} and M_{Exc2} are added to the neutralization tank as shown in Figure 5-10.

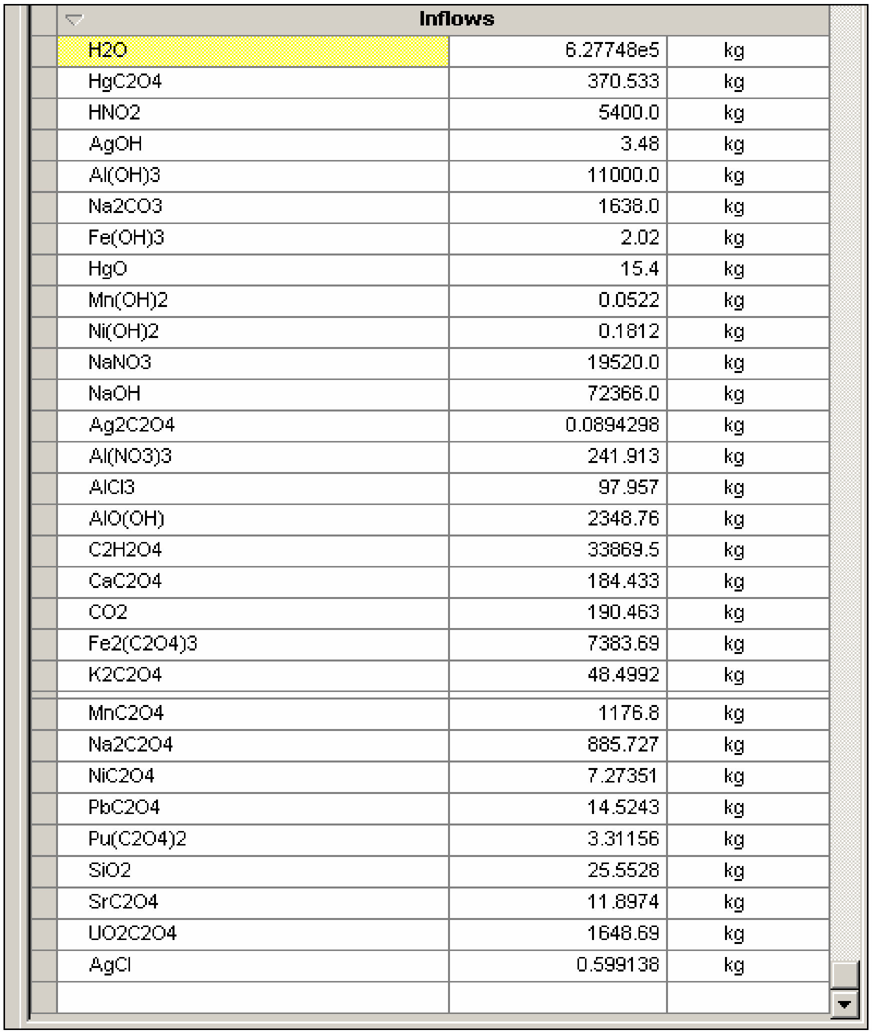


Variable	Value	Unit
Inflows		
H2O	5.75201e5	kg
HgC2O4	370.533	kg
HNO2	5400.0	kg
AgOH	3.48	kg
Al(OH)3	11000.0	kg
Na2CO3	1638.0	kg
Fe(OH)3	2.02	kg
HgO	15.4	kg
Mn(OH)2	0.0522	kg
Ni(OH)2	0.1812	kg
NaNO3	19520.0	kg
NaOH	72366.0	kg
Ag2C2O4	0.0894298	kg
Al(NO3)3	241.913	kg
AlCl3	97.957	kg
AlO(OH)	2111.03	kg
C2H2O4	29306.9	kg
CaC2O4	178.972	kg
CO2	190.463	kg
Fe2(C2O4)3	7383.69	kg
K2C2O4	48.4992	kg
MnC2O4	1160.31	kg
Na2C2O4	885.727	kg
NiC2O4	5.82886	kg
PbC2O4	11.3911	kg
Pu(C2O4)2	3.31156	kg
SiO2	19.6953	kg
SrC2O4	11.8974	kg
UO2C2O4	1648.69	kg
AgCl	0.420371	kg

Figure 5-10 Second Addition of Spent Acid Plus Excess Acid to Neutralization Tank

5.4.3.10 M_{Aq3}, M_{Exc3}

M_{Aq3} and M_{Exc3} are added to the neutralization tank as shown in Figure 5-11.



Inflows		
H2O	6.27748e5	kg
HgC2O4	370.533	kg
HNO2	5400.0	kg
AgOH	3.48	kg
Al(OH)3	11000.0	kg
Na2CO3	1638.0	kg
Fe(OH)3	2.02	kg
HgO	15.4	kg
Mn(OH)2	0.0522	kg
Ni(OH)2	0.1812	kg
NaNO3	19520.0	kg
NaOH	72366.0	kg
Ag2C2O4	0.0894298	kg
Al(NO3)3	241.913	kg
AlCl3	97.957	kg
AlO(OH)	2348.76	kg
C2H2O4	33869.5	kg
CaC2O4	184.433	kg
CO2	190.463	kg
Fe2(C2O4)3	7383.69	kg
K2C2O4	48.4992	kg
MnC2O4	1176.8	kg
Na2C2O4	885.727	kg
NiC2O4	7.27351	kg
PbC2O4	14.5243	kg
Pu(C2O4)2	3.31156	kg
SiO2	25.5528	kg
SrC2O4	11.8974	kg
UO2C2O4	1648.69	kg
AgCl	0.599138	kg

Figure 5-11 Third Addition of Spent Acid Plus Excess Acid to Neutralization Tank

5.4.3.11 Combined Output in Neutralization Tank

Table 5-11 shows the combined output in the neutralization tank. Both the aqueous and solids will remain in the tank, while the solids will be released to the atmosphere.

Table 5-11 Combined Output in the Neutralization Tank

Constituents	Aqueous (kg)	Vapour (kg)	Solid (kg)
	M_{Snate2}	$\sum M_{gas}$	$\sum M_{Prec}$
H_2O	6.45E+05	0.00E+00	0.00E+00
$K_2C_2O_4$	4.85E+01	0.00E+00	0.00E+00
$Na_2C_2O_4$	2.20E+03	0.00E+00	5.91E+04
$Al(OH)_3$	0.00E+00	0.00E+00	9.25E+03
Na_2CO_3	1.90E+03	0.00E+00	0.00E+00
$Fe(OH)_3$	9.62E+01	0.00E+00	4.11E+03
HgO	2.14E+01	0.00E+00	2.72E+02
$Mn(OH)_2$	5.81E+00	0.00E+00	8.66E+02
$Ni(OH)_2$	7.17E-01	0.00E+00	5.85E+00
$NaNO_3$	1.98E+04	0.00E+00	0.00E+00
NaOH	2.88E+04	0.00E+00	0.00E+00
Ag_2CO_3	0.00E+00	0.00E+00	4.46E+00
Ag_2O	2.41E-01	0.00E+00	0.00E+00
$CaC_2O_4.1H_2O$	0.00E+00	0.00E+00	4.15E+02
$CaCl_2.CaO$	2.67E+00	0.00E+00	0.00E+00
Na_2SiO_3	7.19E+01	0.00E+00	0.00E+00
$NaALO_2$	5.20E+03	0.00E+00	0.00E+00
NaCl	1.27E+02	0.00E+00	0.00E+00
$NaNO_2$	7.92E+03	0.00E+00	0.00E+00
PbO	1.42E+01	0.00E+00	0.00E+00
$Pu(OH)_4$	0.00E+00	0.00E+00	2.46E+00
$SrCl_2$	6.74E-01	0.00E+00	0.00E+00
$SrCO_3$	0.00E+00	0.00E+00	9.37E+00
$UO_2(OH)_2$	0.00E+00	0.00E+00	1.40E+03
UO_2Cl_2	6.56E-01	0.00E+00	0.00E+00

By comparing the solids originally in the tank, $M_{Sludge1}$ = 27,769.5 kg – 13,296.0 kg = 14,474 kg to the final total, $\sum M_{Prec} + M_{Sludge4}$ = 74,913 kg + 6,584 kg = 81,497 kg , we can approximate increase in the original solids by a factor of greater than 5; therefore, although oxalic acid will help remove sludge heels from tanks destined to be closed, it can significantly increase the volume of solids within the system.

5.4.4 Energy Balance

Energy balances are used to calculate the bounding temperature changes associated with heel removal in the treatment tank and the caustic adjustments in the neutralization tank. Since 3-strikes will occur, only the bounding cases are analyzed.

In order to calculate the amount of maximum heat gained by adding 8 wt% oxalic acid in a 20:1 ratio with 5,000 gallons of sludge, an energy balance was performed using Equation 5-6. The initial temperature will be 25°C for the oxalic acid solution and 50°C for the sludge.

$$E_{Sludge1} + E_{Acid} + E_{HeatRxn} = E_{Dissolved} \qquad \text{(Eq. 5-6)}$$

Where:

- $E_{initialsludge}$ = Energy of the sludge going to equilibrium
- E_{acid} = Energy of 8 wt% oxalic acid
- $E_{HeatRxn}$ = Energy gained by the reaction of sludge to acid
- $E_{100\%Dissolved}$ = Energy required to dissolve 100% of the sludge

To calculate the maximum heat gained by adding spent solution and excess acid to a pre-charged neutralization tank of 50 wt%, an energy balance is performed using Equation 5-7. The initial temperature will be 25°C for the caustic and 50°C for the spent solution and excess acid. Conservatively, caustic is simply assumed to be added to unspent oxalic acid. The formula for the addition of caustic into the oxalic acid summarized in Equation 5-7.

$$E_{Acid} + E_{NaOH} + E_{Neutralization} + E_{Dilution} = E_{pH=14} \qquad \text{(Eq. 5-7)}$$

Where:

- $E_{oxalicacid}$ = Energy of 100,000 gallons of 8 wt% oxalic acid
- E_{NaOH} = Energy of 50 wt% NaOH required to neutralize the oxalic acid
- $E_{pH,14}$ = Overall energy required to neutralize the oxalic acid
- $E_{HeatRxn}$ = Energy gained by the reaction of oxalic acid to caustic
- $E_{Dilution}$ = Energy change by the dilution of NaOH

5.4.5 Temperature Modelling

The maximum temperature associated with each evolution above is calculated using OLI Stream Analyzer© as an enthalpy change, but setting the change to zero, hence calculating temperature. The calculated temperatures are shown in Table 5-12.

Table 5-12 Treatment Tank and Neutralization Tank Temperatures

Step in Treatment Process	Temperature (°C)	• Temperature from previous step (• °C)
$T_{Sludge1}$ = Initial sludge heel temperature	50	NA
T_{Acid} = Initial Temperature of acid when added to tank	25	NA
T_1 = Resultant Temperature from first-strike	39.90	+14.9
T_2 = Resultant Temperature from second strike	30.81	-9.09
T_3 = Resultant Temperature from third strike	25	-5.81
$T_{supernate}$ = Neutralization supernate heel temperature	25	NA
$T_{caustic}$ = Temperature of caustic	25	NA
$T_{pre\text{-}charge}$ = Temperature of pre-charged tank	30.55	+30.55
$T_{Aq1\&excess}$ = Temperature after aqeous1 & excess added to Neutralization Tank	64.62	+34.07
$T_{Aq2\&excess}$ = Temperature after aqeous2 & excess added to Neutralization Tank	63.48	-1.14
$T_{Aq3\&excess}$ = Temperature after aqeous2 & excess added to Neutralization Tank	62.97	-0.51

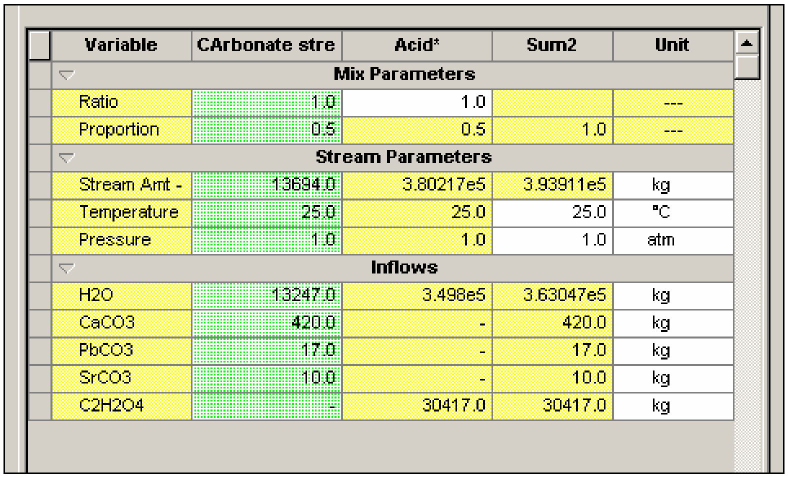
If 100,000 gallons of 8 wt% oxalic acid are is added to the 5,000 gallon HWCS, the resultant temperature is 32.67°C, slightly less than T_1. If none of the acid reacts, and 100,000 gallons of 8 wt% oxalic acid are combined with the 5.8 trucks of caustic, the resulting temperature is 73.46°C. Although this value (73.46°C) is larger than the maximum shown in Table 5-12, it is highly unlikely.

5.5 Maximum Vapour Generated

Based on the quantity of inflows and the kinetics of the reaction, although 7 types of vapours form, only 2 species of vapour are shown to be generated in sufficient quantities to potentially result in overpressurization. They are CO_2 vapour and H_2O vapour.

5.5.1 Maximum CO_2

In order to maximize the amount of CO_2 and H_2O released as a gas, 100,000 gallons of oxalic acid was allowed to react with all of the carbonate that was present in the inflow as shown in Figure 5-12.



Variable	CArbonate stre	Acid*	Sum2	Unit
Mix Parameters				
Ratio	1.0	1.0		---
Proportion	0.5	0.5	1.0	---
Stream Parameters				
Stream Amt -	13694.0	3.80217e5	3.93911e5	kg
Temperature	25.0	25.0	25.0	°C
Pressure	1.0	1.0	1.0	atm
Inflows				
H2O	13247.0	3.498e5	3.63047e5	kg
CaCO3	420.0	-	420.0	kg
PbCO3	17.0	-	17.0	kg
SrCO3	10.0	-	10.0	kg
C2H2O4	-	30417.0	30417.0	kg

Figure 5-12 Input to Maximum CO_2 Model

The maximum temperature was calculated in Section 5.4.5 to be 64.62°C. The maximum gas generated was determined using the gas fraction function of OLI©. The vapour output is determined to be 253 litres. Although this is a conservative assumption, it allows for the CO_2 and H_2O production to be maximized.

The reaction of acid and the carbonate in the sludge cannot be modelled because the CO_2 is not released as a gas, but instead reacts with the solid/aqueous and is not released.

5.5.2 Maximum H_2O

The reaction of an acid plus a base results in a salt and water. Reacting an acid plus a base therefore, will result in the maximum amount of H_2O vapour formed. The change in temperature is first calculated by setting the enthalpy change to zero, and then using that temperature to calculate the litres of gas formed. This calculation adds 100,000 gallons of 8 wt% oxalic acid to 17,400 litres of 50 wt% NaOH and calculates 768 litres of gas at 73.46°C.

5.5.3 Hydrogen Induced Corrosion

If slurry pumps are utilized in the treatment tanks, it will ensure that the oxalic acid is evenly distributed throughout the sludge; therefore, enhancing the dissolution process. The slurry pumps will erode away the sludge as the acid decreases the strength of the bonds binding the sludge particles. During this process, radiolysis of the acidic solution and corrosion of the carbon steel components in the treatment tanks upon contact with the acidic solution will result in hydrogen generation. As part of this research, the corrosion of the carbon steel components in the treatment tank upon contact with the oxalic acid is considered.

Figure 5-13 provides laboratory measured corrosion rates for representative carbon steel coupons in a 4 wt% and 8 wt% oxalic acid solution (Wiersma, 2004, p43).

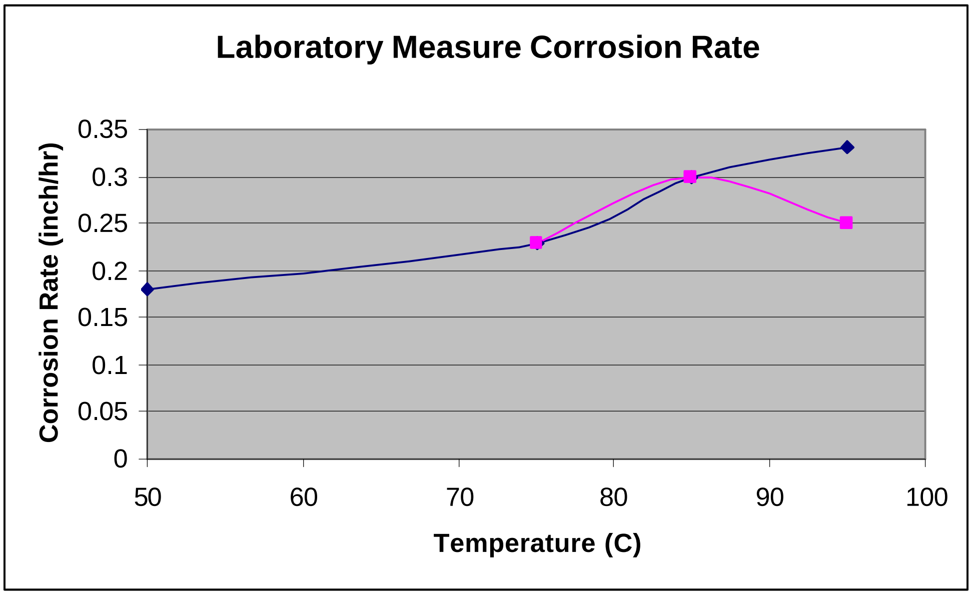


Figure 5-13 SRNL Laboratory Measured Corrosion Rates for Oxalic Acid Exposed Steel

Since the maximum temperature is calculated above as 73.46°C, we can estimate the bounding corrosion rate as 0.23 inches/hour, the volumetric flowrate of carbon steel consumed can be calculated using Equation 5-8 (Lang, 2004, p11).

$$V_{es} = \text{Corrosion Rate (ft/day)} \times \text{Surface Area (ft}^2\text{)} \qquad \text{(Eq. 5-8)}$$

Where:

- V_{cs} = volumetric flow rate of carbon steel consumed per time (ft^3/day)
- Corrosion rate of carbon steel in 8 wt% oxalic acid =

  (0.23E-05 in/hr) x (24hr/day) x (1ft/12inch) = 0.6E-5 ft/day

The surface area of the carbon steel is bound by 14,739 ft^2 (Phillips, 2004, p20). The amount of carbon steel consumed and hydrogen produced can be determined by Reaction 5-1 and Reaction 5-2 which occur from hydrogen generation due to corrosion of carbon steel.

$$2Fe^{\circ} + 6H^{+} \bullet 2Fe^{+3} + 3H_2 \qquad \text{(Reaction 5-1)}$$

$$Fe^{o} + 2H^{+} \bullet Fe^{+2} + H_2 \qquad \text{(Reaction 5-2)}$$

The molar flow rate of carbon steel consumed is calculated using Equation 5-9 and Equation 5-10.

$$m_{cs} = \frac{V_{cs} \bullet_{cs}}{MW_{cs}} \text{ x } 28{,}317 \text{ cm}^3/\text{ft}^3 = 5.86\text{E+07 cm3/ft3} \qquad \text{(Eq. 5-9)}$$

$$m_{H2} = m_{es}(n_{H2}/n_{es}) \qquad \text{(Eq. 5-10)}$$

Where:

- V_{es} = volumetric flow rate of carbon steel consumed per time (ft^3/day)
- $\bullet_{es}$ = density of carbon steel (grams/ml) = 7.83 g/ml
- m_{es} = molar flow rate of carbon steel consumed (mol/day)
- MW_{es} = molecular weight of carbon steel (grams/mol) = 55.82 grams
- m_{H2} = molar flow rate of hydrogen produced (mol/day)
- n_{H2} = moles of hydrogen produced (mol)=

  = 1.5 mol (from Reaction 1) + 1 mol (from Reaction 2)
- n_{es} = moles of carbon steel consumed (mol)

  = 1 mole (from Reaction 1 and Reaction 2)

The volumetric flow rate of hydrogen generated due to corrosion of carbon steel can be determined by Equation 5-11.

$$V_{H2} = \frac{(m_{H2}RT)}{P} \text{ x } (\text{day}/24\text{hr}) \text{ x } (35.3145 \text{ ft}^3/\text{m}^3) \qquad \text{(Eq. 5-11)}$$

Where:

- m_{H2} = molar flow rate of hydrogen produced (mol/day)
- V_{H2} = Hydrogen generation rate due to corrosion (ft^3/hr)
- R = 8.314 (m^3-Pa/mol-K)
- T = 346.6 K
- P = 101,325 Pa

V_{H2} = 362 ft^3/hr

The bounding hydrogen generation rate from corrosion can be conservatively approximated as 362 ft^3/hr, which may require further evaluation/ventilation upgrades.

5.6 Conclusion on Material Balance and Safety Impacts Determination

Based on the conservative modelling, acid aided heal removal should reduce the heel size by a factor of ten, while increasing the overall solids in the system by a factor of greater than five. The modelling also shows that over-pressurization and overheating should not be significant concerns. The maximum gas volume in the treatment tank will be 253 litres at the maximum calculated temperature of 64.62°C. The maximum calculated gas in the neutralization tank at the maximum calculated temperature will be 768 litres at 73.46°C. Corrosion induced hydrogen generation from the cooling coil corrosion is determined to be a potential concern at 362 ft^3/hr and therefore requires further evaluation and/or ventilation upgrades.

CHAPTER 6

ENERGETIC COMPOUNDS

6.1 Introduction to Energetic Compound Impacts Determination

The purpose of this chapter is to determine the impacts on energetic compounds associated with using oxalic acid solution to dissolve sludge heels in SRS HLW tanks.

This chapter is different from Chapter 5, because the process database is not generally designed to characterize and/or quantify energetic compounds. Instead, each family of energetic compounds must be individually evaluated and where necessary, sample data and "spiking" the material balance is performed as available. The spiked material balance contained in Appendix 3 does not represent projected quantities of material (or all of the energetic compounds), but instead introduces significantly inflated quantities to clearly identify behaviour and other characteristics of interest.

Literature (Hobbs, 1999) shows that identified energetic compounds in the SRS HLW tanks can be grouped into 14 families. They are:

1. metal fulminates
2. metal azides
3. metal NOx compounds
4. metal amine complexes
5. metal cynides/cyanates
6. metal acetylides
7. nitrate/oxalate mixtures
8. metal oxalates
9. peroxides
10. metal halogenates and halogens
11. metal nitrides
12. ammonia compounds
13. organics
14. hydrogen gas

Although 14 families have been identified in the SRS HLW, all 14 of the families may not be applicable or impacted when using oxalic acid and subsequent activities to aid in SRS HLW Tanks 1-15 sludge heel removal.

6.2 Initial Chemistry

The liquid contained within the treatment tank, immediately prior to beginning oxalic acid aided heel removal, will have a low ionic strength, since the vast majority of the soluble constituents will have been washed out during the previous bulk waste removal activities.

During the acid-strikes, the sludge heel will undergo dissolution, with solids, aqueous, and vapours possibly being formed. The spike tank, at the time of each acid addition, is envisioned to be well agitated and in contact with the sludge for a period of about 2 weeks for each strike. In all cases, the spent, dissolved sludge solution and any unspent acid will be transferred to the neutralization tank.

Since the neutralization tank will continue to be operated, it will be pre-charged with supernate and or sodium hydroxide to ensure the overall pH does not enter the acidic regime (i.e., pH will remain greater than 7) (Badheka, 2003, p80). Vapours are potentially generated, while solid precipitates will form.

6.2.1 Recent Receipts and Transfers

High Level Waste (HLW) originates from separations, decontamination facilities, analytical laboratories, Research and Development laboratories, and Defence Waste Processing Facility (DWPF). Historically, separations produced most of the sludge (volume). Tanks 1-15 have not received solids since the early 1980’s, and therefore have been aged (HLW, 2005).

The term “transfers” in Table 6-1 refers to supernate transfers from tank to tank, whereas “receipts” in Table 6-2 refers to receiving waste solids from separations. As such, solubles are tracked in Table 6-1, and solids are tracked under Table 6-2.

Table 6-1 Post 1979 Supernate Transfers

Yr.	Tank	Source	Size (1E+4 gal)	Description
1998	2	NA	2	BEARING SEAL WATER ADDED
1985	2	NA	2	FLUSH WATER
1985	2	NA	3	SALT MINING WATER
1989	2	NA	7	REEL TAPE CALIBRATION/REPLACEMENT OR INVENTORY
1985	3	NA	2	REEL TAPE CALIBRATION/REPLACEMENT OR INVENTORY
1985,19	4	NA	4, 0.1	REELTAPE CALIBRATION/REPLACEMENT OR INVENTORY CHANGE
1995	4	NA	0.4	THERMAL EXPANSION
2000	5	22	30	SUPERNATE
1992	6	NA	20	REEL TAPE CALIBRATION/REPLACEMENT OR INVENTORY
2000	6	22	30	SUPERNATE
1980	7	242-1F	1	OVER SPEC
1980	7	NA	3	MISC ADDITION/TRANSFER
1980	7	10	10	CONCENTRATED SUPERNATE
1980	7	18	100	DIISOLVED SALT
1980	7	33	10	CONCENTRATED SUPERNATE
1980	7	8	100	SUPERNATE
1980	7	4	3	SUPERNATE
1981	7	242-1F	2	OVER SPEC
1981	7		0.8	FDB-1 CATCH TANK TRANSFER
1981	7	8	20	SUPERNATE
1981	7	18	200	SALT TRANSFER
1981	7	26	200	CONCENTRATED SUPERNATE
1982	7	242-1F	0.8	OVER SPEC
1982	7	18	60	SALT TRANSFER
1982	7	26	40	SUPERNATE
1983	7	NA	30	CONCENTRATED SUPERNATE
1983	7	26	200	CONCENTRATED SUPERNATE
1983	7	242-1F	3	OVER SPEC
1984	7	26	20	FLUSH
1984	7	NA	6, 2	FLUSH + CATCH TANK
1986	7	NA	2@6	UNEXPLAINED INCREASE/DECREASE OR INVENTORY ADJ.&
1990	7	NA	2@3	THERMAL EXPANSION
1992	7	NA	4@.1	REEL TAPE ERROR + THERMAL /TRANSFER
1994	7	NA	2@.1	INTERAREA FLUSH TRANSFER
1980	9	NA	0.3	FLUSH WATER
1981	9	NA	1	COOLING COIL WATER LEAK-CHROMATE WATER
1982	9	NA	1, 0.1	REELTAPE CALIBRATION/REPLACEMENT OR INVENTORY CHANGE
1980	10	23	30	MISC ADDITION/TRANSFER
1983	10	NA	10	REELTAPE CALIBRATION/REPLACEMENT OR INVENTORY CHANGE
1985	10	NA	7	SALT MINING, REEL TAPE, NAOH, PT-4
1986	10	NA	7	REEL TAPE CALIBRATION/REPLACEMENT OR INVENTORY
1989	10	NA	2	REEL TAPE CALIBRATION/REPLACEMENT OR INVENTORY
1982	11	NA	0.9	TANK INLEAKAGE FROM RAIN STORM
1983	11	NA	.01	TANK INLEAKAGE FROM RAIN STORM
1984	11	NA	0.3	TANK INLEAKAGE FROM RAIN STORM
1984	11	NA	3	TANK INLEAKAGE FROM RAIN STORM
1984	11	NA	0.7	REEL TAPE CALIBRATION/REPLACEMENT OR INVENTORY

(Continued)

(Continuation of Table 6-1)

Year	Tank	Source	Size (1E+4 gal)	Description
1986	11	NA	0.3	TANK INLEAKAGE FROM RAIN STORM
1992	11	NA	0.2	RAIN WATER
1995	11	NA	1	EVAPORATION
1984	12	NA	0.4	TANK INLEAKAGE FROM RAIN STORM
1989	12	NA	0.4	REELTAPE CALIBRATION/REPLACEMENT OR INVENTORY
1992	12	NA	0.1	REELTAPE CALIBRATION/REPLACEMENT OR INVENTORY
1980	13	NA	0.7	FLUSH WATER
1981	13	11,22	7	SUPERNATE
1981	13	32	70	SUPERNATE
1980	13	21	40	SUPERNATE
1980	13	242-1H	10	OVERSPEC
1982	13	31,29	2@30	CONCENTRATED SUPERNATE
1982	13	10	30	SALT TRANSFER
1982	13	35	100	SUPERNATE
1982	13	30	30, 80	CONCENTRATED SUPERNATE
1981	13	37, 36	500, 700	CONCENTRATED SUPERNATE
1983	13	NA	6	FLUSH WATER
1983	13	NA	3	WATER AND OXALIC ACID
1985	13	24	1	TANK 42 HOT WATER RINSE
1983	13	242-1H	4	OVERSPEC
1986	13	33	10	SUPERNATE
1986	13	22	30	SUPERNATE
1985	13	NA	3	FLUSHES
1986	13	32	80	SUPERNATE
1987	13	NA	1	DECON WATER
1987	13	35	50	SUPERNATE
1985	13	37	600	CONCENTRATED SUPERNATE
1985	13	30	200	SUPERNATE
1985	13	36	400	CONCENTRATED SUPERNATE
1980	15	16	200	WASH WATER
1982	15	NA	30	BEARING SEAL WATER ADDED

As shown in the last column of Table 6-1, Tanks 1-15 are recorded as not receiving DWPF recycle. Entries shown are for sources of supernate received into Tanks 1-15 since 1980. The Tanks 1, 8, and 14 are not shown in Table 6-1 because they have not received supernate transfers since 1980. The limited solids received in Tanks 1-15 since 1980 are shown in Table 6-2. (Note: Tanks 4, 8, 11, and 15 were the only tanks out of Tanks 1-15 which received any solids since the beginning of 1980).

Table 6-2 Post 1979 Waste Receipts into Tanks 1-15

Year	Tank	Size (1E+04 gal)	Campaign	Stream
1980	4	2.5E+5	PUREX	F-HHW
1980	8	1.1E+6	PUREX	F-LHW
1981	11	2.6E+5	HM	H-LHW
1980	15	6.0E+3	HM	H-HHW

Table 6-2 shows the last Tank 1-15 solid receipts as being no later than 1981 (HLW, 2005). Since DWPF was not yet operational, Tanks 1-15 did not receive DWPF recycle, and therefore DWPF organics are not a concern. This aging ensures that volatile organics no-longer represent a flammability concern (Britt, 2003, p42).

Table 6-3 summarizes the applicable organics and chemicals identified in literature, as potentially being present in Tanks 1-15 (Hobbs, 1999).

Table 6-3 Miscellaneous Organics and Chemicals

PARENT	CONSTITUENT	FORMULA
Ammonia	Ammonia/Ammonium ion Hydrazine Hydroxylamine	NH_3/NH_4 N_2H_4 NH_2OH
Dodecane	Dodecane	$C_{12}H_{26}$
TBP	Tri-n-butyl phosphate (tributyl phosphate) Di-n-butyl phosphate Mono-n-butyl phosphate n-Butanol	$(CH_3[CH_2]_3O)_3PO$ $C_8H_{18}O_4P_1$(1 neg. charge) $C_4H_9O_4P_1$(2 neg charge) $C_4H_{10}O$
Acid	Gluconic Acid Ascorbic Acid	$C_6H_{12}O_7$ $C_6H_8O_7$
Resins	Ion-exchange Resins	$(C_8H_8)n$
CST	Polydimethylsiloxane	$(C_2H_6OSi)n$
Defoamers	Hydrogenated tallow glycerides Ethylene glycol (1,2-ethanediol) Methylcellulose 2,4,7,9-tetramethyl-5 -decyne-4,7-diol	NA $C_2H_6O_2$ CH_4OxUnspecified $C_{14}H_{26}O_2$ Siloxanes

6.3 Acidic Chemistry Qualitative Assessment

Eventually during waste removal, solids will become harder and harder to remove, and oxalic acid will be required to dissolve the solids. The oxalic acid additions to the tank will, at a minimum, change the chemistry. Temperatures may slightly increase from exothermic reactions. The maximum temperature for either the treatment tank or the neutralization tank because of corrosion is recommended to be controlled to approximately 50°C. The impacts to the known 14 families of energetic materials in SRS HLW tanks are investigated below.

6.3.1 Metal Fulminates

The first family of energetic compounds considered are metal fulminates. Metal fulminates are compounds similar to $XC_2N_2O_2$, where “x” represents a metal and $C_2N_2O_2$ is fulminate. Generally metal fulminates form in two steps. In the first step, the metal is nitrated with an excess of nitric acid. Refer to Equation 6-1.

$$X + 3OHNO_2 \bullet \quad xNO_3 + OHNO_3 + NO_2 \qquad \text{(Eq. 6-1)}$$

As shown in the material balance contained in Appendix 3, the overall moles of NO_3^- and NO_2^- will decrease as part of the bulk waste and acid treatment activities. Table 6-4 summarizes the expected change to the overall quantities of NO_3^- and NO_2^-.

Table 6-4 Estimated Normalized Abundance of NO_2^- and NO_3^- During Acid Cleaning

Stage	**% Total (% mol)**	**Aqueous (% of initial mol)**	**Vapour (% of initial mol)**	**Solid (% of initial mol)**
Pre-bulk waste removal	~5000	~5000	NA	NA
Initial	100	100	0	0
70% Dissolution	100	100	<1.5E-8	0
50% Dissolution	0	0	0	0
30% Dissolution	0	0	0	0
Supernate add*	~5000	~5000	0	0
Caustic add	~5000	~5000	0	0

Note: Supernate addition reflects an increase because of the soluble NO_2^- and NO_3^- in supernate.*

Besides nitrates, alcohol {i.e., organics having–OH} is also needed to form heavy metal fulminate. The nitrated metal and excess acid would be added to the alcohol, such as ethanol, forming metal fulminate. Refer to Equation 6-2.

$$XNO_3 + HNO_3 + C_2H_6O \bullet \quad X(ONC)_2 \qquad \text{(Eq. 6-2)}$$

Alcohols are not used in bulk quantities within the tank farm and are only present in trace amounts as a result of laboratory operations and decomposition of tri-n-butyl phosphate {i.e., $(CH_3[CH_2]_3O)_3PO$} and other organics. Methanol {i.e., CH_4O} and isopropanol {i.e., C_3H_8O} are two of the more likely impurities that could help form alcohols. For example, Monosodium Titinate (MST) slurries, prepared and submitted by vendors, have been analyzed to contain <0.1 by volume alcohols (Hobbs, 1999, p23).

Silver fulminate {i.e., $Ag_2C_2N_2O_2 \bullet Hf=+180$ Kjoule/mole} and mercury fulminate {i.e., $HgC_2N_2O_2 \bullet Hf=+200$ Kjoule/mole} are two energetics which potentially raise the most concern as they are used in explosives and blasting caps. Reports show that mercury fulminate decomposes when in a gamma field (Ketusky, 2005, p31). Recent studies further detail these phenomena as the mercury fulminate transforming into a less energetic form when in a gamma field. In a 1 M sodium hydroxide solution and a 1 Rad/hr gamma field, the mercury fulminate would completely decompose. Any silver fulminate and mercury fulminate; therefore, should have already decomposed.

Modelling in Appendix 3 shows that mercury fulminate, silver fulminate, and fulminating silver are not expected to form since after bulk waste removal, the sludge is nitrogen depleted and no significant means is available as part of oxalic acid additions. It is expected that there should be no increase in the possibility of explosive events from fulminates due to the activities and subsequent activities associated with the oxalic acid aided heel removal.

6.3.2 Metal Azides

Metal azides are compounds in the form of XNy, where “X” represents the metal and “y” represents the nitrogen. The formation of metal azides were considered as a result of a reported explosive event that occurred in the 1970’s. The incident was associated with dried waste deposits in a feed jet enclosure. It occurred shortly after receiving waste from the flushing of silver coated saddles in separations.

Hydrazoic acid {i.e., HN_3 • Hf=+328 Kjoule/mole} is reported to be dangerously explosive with a minimum explosive concentration of about 17 wt% in aqueous solutions. If within the HLW, this acid would easily react with the excess sodium to result in sodium azide {i.e., NaN_3 • Hf=+93 Kjoule/mole}. Electropositive metal azides are not as energetic and decompose at temperatures only above 300ºC. These metal azides, however, can easily react to form heavy metal azides. Heavy metal azides such as silver {i.e., AgN_3 • Hf =+376 Kjoule/mole}, and mercury {i.e., $Hg_3(N_2)_3$} • Hf=+590 Kjoule/mole} are reported to be explosive and have been used in detonation assemblies (Walker, 1999, p12).

As shown in Table 6-4, the initial sludge would be nitrogen depleted. Additionally HN_3 is extremely soluble and would be quickly removed even prior to the start of oxalic acid cleaning. Because of solubility, even if present, hydrazoic acid would remain in solution, while the heavy metals would remain mostly at the bottom of the tank. It is then concluded that there is no likely mechanism in which heavy metal azides could be formed in the waste tanks.

6.3.3 NOx Compounds

Although NO_x compounds are compounds that may include nitrites and nitrates, there are also many other different NxOx anions. Some reported explosive NOx compounds include methylcellulose, salts of Millon's base (i.e., $(HOHg)_2NH_2OH$}, lead hyponitrite {i.e., PbN_2O_2}, silver hyponitrite {i.e., $Ag(NO)_3$ • Hf=-124 Kjoule/mole}, and nitrate salts {e.g., $NaNO_3$}.

The only identified source of cellulosic materials into the tank farm is from Antifoam B Emulsion (l-5% methylcellulose {i.e., CH_4OxUnspecified}. It is used to minimize foaming in HLW evaporators. The quantity of methylcellulose added to the tank farm is very small. No incidents of uncontrolled reactions have been reported during evaporator operations and laboratory evaluations using this defoamer (Hobbs, 1999, p15). The nitration of cellulose occurs only under strongly acidic conditions and elevated temperatures >160ºC (Hobbs, 1999, p21). In the HLW tanks, cellulose will decompose during storage due to radiolysis and alkaline hydrolysis (Hobbs, 1999, p21). As part of oxalic acid cleaning, the temperatures during acid heel dissolution will be maintained at approximately 50ºC to minimize corrosion.

In the HLW tanks, nitrate is reduced by radiolysis to nitrite, and thus, lower oxidation state nitrogen-oxygen compounds such as hyponitrite {NO} may be produced radio lytically. Mercury, lead, and silver are all present in SRS waste, and thus, hyponitrite salts with these metals are conceivable.

Since the solubility of NO_3^- and NO_2^- approach 90 gram/100 gram of water at 25°C, most should be removed as part of bulk waste removal (Britt, 2003, p26). Since Pb, Ag, and Hg are generally insoluble, the heavy metals would be among the last materials to go into solution. Section 6.3.1 shows that the NO_2^- and NO_3^- would be depleted when the acid spikes begin; therefore, the increase in energetic additional NOx compounds forming above routine HLW conditions is extremely low (Hobbs, 1992, p14).

6.3.4 Metal Amine Complexes

Amine complexes {~a compound derived from NH_4 by replacing H with hydrocarbon radicals} of metals containing oxyanion ligands {~a polyatomic atom that has a "-" charge & contains O} have been reported to be explosive and exhibit moderate to strong shock sensitivity[16]. These compounds are particularly hazardous because of the presence of both the fuel (amine) and the oxidant (i.e., oxyanion ligand) in the same compound. SRS waste generally contains two species for forming complexes of this type: metal ions, and oxyanions {e.g. nitrate, nitrite, and sulphate} and potentially, ammonia. However, based on the age of the waste, the ammonia would no-longer be present (Hobbs, 1992, p28).

Metal ions that are present in SRS waste and conceivably form amine complexes, including copper, chromium, cobalt, mercury, palladium, silver, and zinc complexes. Preparation of metal-amine complexes is generally carried out in concentrated ammonium hydroxide {i.e., NH_4OH} solution or liquid ammonia. Because of the age of the waste in Tanks 1-15, as well as the fact that it is being evaluated after post bulk waste removal, ammonia and ammonium hydroxide concentrations are very low. Table 6-4 above, additionally shows the decrease in NO_2^- and NO_3^- during the oxalic acid aided heel removal. Appendix 3 also shows the decrease in other spiked oxyanion ligands during the oxalic acid aided heel removal effort. It is then concluded that the production of amine complexes would not increase.

6.3.5 Cyanate and Cyanides

Metal cyanides {i.e., xCN} and metal cyanates {i.e., xOCN} are often endothermic, but at elevated temperatures can undergo violent exothermic oxidations and release significant amounts of energy. Solid potassium cyanide {i.e., $K(CN)_2$ • Hf=-8.4 Kjoule/mole}, and mercury cyanide {i.e., $Hg(CN)_2$ • Hf=+264 Kjoule/mole} explode when heated (Swingle, 2004). Mercury cyanate {i.e., $Hg(OCN)_2$} explodes when crushed. Endothermic compounds such as cadmium cyanide {i.e., $Cd(CN)_2$ • Hf=+267 Kjoule/mole} and nickel cyanide {i.e., $Ni(CN)_2$} can decompose explosively (Swingle, 2004, p11).

Potassium, nickel, and mercury are known components of SRS HLW; however, there is no significant source of cyanide and cyanate within the tank farm (Britt, 2003, p23). Appendix 3 contains a spike of $Ni(CN)_2$ and $Hg(OCN)_2$ to show how cyanides and cyanate will behave during the oxalic acid aided heel removal effort. It should be noted that cyanide has not been detected in SRS HLW, although in 1986, analysis of a Tank 50H sample indicated a cyanide concentration of 3.6 ppm. Review of the sample analysis indicates that the positive result for cyanide was an artefact of the experimental procedure (Hobbs, 1999, p21). Since oxalic acid cleaning will not introduce cyanides or cyanates, there will be no additional risk from cyanides or cyanates during the oxalic acid cleaning.

6.3.6 Metal Acetylides

Literature (Hobbs, 1999, p13) indicates that acetylenic glycol or similar material would be required to produce acetylide. Based solely on the presence of copper, silver, and mercury in HLW, copper acetylide can be considered potentially present in SRS HLW. CuCHO has a solubility of 12.5g/100g of water at 25°C, requiring an impact as low as 2E-09 Kjoule to explode . Silver acetylide {AgCHO} is a more powerful detonator than Cu, and it explodes when heated to 120-140°C. Mercury acetylide { $Hg(CHO)_2$} is both shock and heat sensitive. Temperatures during the use of oxalic acid and subsequent neutralization will not get than large approx. 75ºC as shown in Chapter 5.

Acetylene and terminal alkynes react with metal ions in solid/vapour reaction or in non aqueous solvents to produce metal acetylides. If a terminal hydrogen atom is not present, no reaction occurs. Radiolytic and chemical decomposition of the acetylenic glycol could produce acetylene, other terminal alkynes, methyl isobutyl ketone and low molecular weight alcohols.

Metal acetylides react with water to produce the alkyne and the corresponding metal hydroxide. The high water content in the waste prevents the accumulation of metal acetylides in the bulk of the waste. Additionally acetylene and terminal alkenes are spiked into the sludge in Appendix 3. Appendix 3 shows that the formation of metal acetylides are not preferred.

Strict controls are placed on the precursors, and thus, there is no identified mechanism for the formation and accumulation of metal acetylides; therefore, this class of explosive compounds is not a hazard in the tank farm. Oxalic acid heel dissolution will not introduce any of the precursor materials.

6.3.7 Nitrate/Oxalate Mixtures

The reaction of sodium nitrate with sodium oxalate is considered a potentially uncontrollable reaction. The basis is that current documentation shows this mixture as extremely exothermic and with the potential to generate large amounts of gas/heat if left uncontrolled (Hobbs, 1999, p7).

From literature (Hobbs, 1999, p4), differential thermal analyses of mixtures of sodium nitrate, sodium nitrite and sodium oxalate indicate that both endothermic and exothermic reactions start at about 150ºC. Endothermic reactions initiate from about 160ºC to 315ºC, while a single exothermic reaction is initiated in the range from 375ºC to 450ºC. Calculations in Chapter 5 show that temperatures will not get this high during oxalic acid treatment or during subsequent neutralization.

Table 6-4 summarizes the expected change to the overall quantities of NO_3^- and NO_2^- during oxalic acid heel removal based on OLI© modelling. Sodium nitrate has a solubility of about 90g/100g water at 25°C, while sodium oxalate has a solubility of about 3.5g/100g of water 25°C, meaning that the nitrates and nitrites would be depleted as the oxalates build-up in the bottom of the tank. The oxalic acid addition, therefore, will not increase the probability of a nitrate/oxalate explosive event.

6.3.8 Oxalates

As oxalic acid is added to the spike tank, oxalates will increase, not only in the spike tank, but throughout all of HLW. Historically, during sludge removal from Tank 16, a special procedure using oxalic acid assisted in removing the final amount of sludge. Under acidic conditions, mercury oxides and silver oxides can react with oxalic acid to produce insoluble mercury oxalate and silver oxalate. When relatively dry, silver oxalate and mercury oxalates are reported to be weakly explosive, at a minimum temperature of 130ºC (Hobbs, 1999, p8). Experimental testing indicated that neither compound ignites by an electric arc when dispersed in air. Explosions occur only when the materials are confined or dry and in a pure form. Since the temperatures will be maintained at approximately 50ºC, and the heel will remain wet, mercury and silver oxalates will not present an explosion hazard during oxalic acid cleaning.

6.3.9 Peroxides

Peroxides {i.e., similar to X_2O_2} are highly reactive molecules due to the presence of an oxygen–oxygen linkage. Under activating conditions, the oxygen–oxygen bond may form highly reactive free radicals. These highly reactive radicals can be used to initiate polymerization or curing. Consequently, organic peroxides are used as initiators for free-radical polymerization, curing agents for resins, and cross-linking agents for elastomers and polyethylene. There are three possible types of peroxide explosion hazards in HLW. They are:

1) peroxide/organic mixtures
2) organic peroxides
3) metal peroxides

Radiolytic generation of peroxide is well known in aqueous solutions. The radiolytic generation rate for peroxide varies slightly with pH, decreasing slightly in alkaline solutions as compared to acidic solutions. Hydroxyl radical scavengers such as chloride, bromide, iodide, and nitrite, decrease the rate of peroxide formation (Hobbs, 1999, p6). As a gas, oxygen and hydrogen will quickly recombine with hydrogen peroxide to form water.

Because of the high water content of SRS waste, the heavy metal peroxides {e.g., Ag_2O • Hf=-11 Kjoule/mole, CdO • Hf=-289 Kjoule/mole, and Hg_2O • Hf=-91 Kjoule/mole} are not stable and significant quantities are not produced. Potassium peroxide {K_2O_2 • Hf=-425 Kjoule/mole} requires cold temperatures (<10ºC) to remain stable in aqueous solutions. Since SRS waste storage conditions are at higher temperatures ($\geq$25ºC), it is clear, based on Chapter 5, potassium peroxide would immediately decompose.

Sodium peroxide {i.e., Na_2O_2 • Hf=-450 Kjoule/mole} is fairly stable in solution, but can crystallize from aqueous solutions. It is considered a dangerous fire and explosion risk when in contact with water, alcohols, acids, powdered metals, and organic materials. However, transition metal ions {e.g., Fe, Mn, Cu, Co, and Ni} are known to catalyze the decomposition of sodium peroxide. Since these metals are required to be present in SRS waste and sludge for nuclear criticality control (and also shown in Appendix 3, Table 3-1), it is unlikely that appreciable quantities of sodium peroxide form and crystallize in the tank farms as the result of acid heel dissolution.

Because of the low organic content of the waste, organic peroxides do not present a safety hazard in tank farm operations. Organic peroxides are conceivably produced in waste by the reaction of organics with oxygen-containing radicals {e.g., OH^-} or the combination of two alkoxide radicals {e.g., RO^-}. These types of radicals are well known products produced by the radiolysis of water and alcohol solutions. However, the concentration of organics in the waste is very low, and as a result, the concentration of organic peroxides generated by either of these pathways is also very low.

Heavy metal peroxides {e.g., Ag_2O • Hf=-11 Kjoule/mole; CdO • Hf=-258 Kjoule/mole; Hg_2O • Hf=-91 Kjoule/mole; and Zn_2O • Hf=-351 Kjoule/mole} are not stable in water. Because of the high water content of SRS waste, the heavy metal peroxides are not stable, and significant quantities are not produced. Potassium peroxide {K_2O_2} requires cold temperatures (<10ºC) to remain stable in aqueous solutions. Since SRS waste storage conditions are at higher temperatures ($\geq$25ºC), as calculated in Chapter 5, potassium peroxide {K_2O_2} would quickly decompose.

Table 6-5 Properties of Some SRS Peroxides (based 25°C in water or indicated)

Constituent	Formula	Molecular Weight	Density (g/cm^3)	Melting Point (°C)	Boiling Point (°C)	Solubility in 100 parts solvent (g/100 g solv.)
Barium peroxide	BaO_2	169.33	4.96	450 d	$-O_2$, 800	1.5 aq
Calcium peroxide	CaO_2	72.08	2.92	explodes 275		sl s aq; s acids
Hydrogen peroxide	H_2O_2	34.01	1.4630	-0.43	152	misc aq; s alc, eth
Lithium peroxide	Li_2O_2	45.88	2.31	d > 195 to Li_2O		
Magnesium peroxide	MgO_2	56.30	~3.0	d 100		s acids
Sodium peroxide	Na_2O_2	77.98	2.805	675	d	v s aq (dec)
Strontium peroxide	SrO_2	119.62	4.78	215 d		0.018^{20} aq; d hot aq
Uranium peroxide 2-water	$UO_4\ 2H_2O$	338.06		d 90-195 to U_2O_7 (slow)	d >200 to UO_2	d by HCl
Zinc peroxide	ZnO_2	97.39	1.57	d >150	explodes 212	d (slow) aq; dilute acids (d)

6.3.10 Halogens and Metal Halogenates

The halogen family of elements, as found on the periodic table, are fluorine (F), chlorine (Cl), bromine (Br), iodine (I), and astatine (At). Although chloride is present in HLW only as an impurity, it has been hypothesized that chlorate can be produced during oxalic acid cleaning.

Since halogen compounds are generally highly soluble, most will be removed as part of bulk waste removal. Any remaining will most likely be restricted to those that react with silver, such as highly insoluble, AgCl or CCL. If the chloride, or halogen becomes available and oxygenated, it will become highly soluble in water. In water, chlorine dioxide will decompose. Since it has been shown that even dry sludge contains significant interstitial liquid concentration/accumulation will not occur. The solubility Cl^- throughout the dissolution process is shown in Table 6-6.

Table 6-6 Estimated Normalized Abundance of Cl^- During Acid Cleaning

Stage	% Total (% mol)	Aqueous (% of initial mol)	Vapour (% of initial mol)	Solid (% of initial mol)
Pre-bulk waste removal	100	100	NA	NA
Initial	100	100	0	0
70% Dissolution	100	85	<1E-1	7.9
50% Dissolution	7.9	0.3	0	7.6
30% Dissolution	7.6	0.1	0	7.5
Supernate add*	93	93	0	0
Caustic add	~93	~93	0	0

Note: Supernate add reflects an increase because of the soluble Cl^- in supernate.*

Iodine and the other halogens are fission products in spent fuel. Most are removed by scrubbing the off-gases from fuel dissolution. Silver iodide is removed from the saddles with acid flushes. A small amount of the fission product iodine is reduced to iodide and travels through fuel processing operations and is received with the waste. The acidic solutions made alkaline with sodium hydroxide are sent to the tank farms.

Transfers of flushes from the iodine reactors to the tank farm were stopped in 1970's. Only small amounts of iodide have been added to the waste since 1970 (HLW, 2005). Additionally, a vast majority of the iodine in the tanks will remain soluble. Literature (Knovel, 2003) shows that the solubility is 29g/L at 25ºC in water. Because of bulk waste removal, little iodine will remain within the tank for acid heel dissolution. Consequently, conditions within tank farm facilities prevent the production or accumulation of these compounds in sufficiently large enough quantities to be an explosion hazard. The iodine behaviour can be better understood by spiking the material balance and tracking its fate as summarized in Table 6-7.

Table 6-7 Estimated Normalized Abundance of I^- During Acid Cleaning

Stage	% Total (% mol)	Aqueous (% of initial mol)	Vapour (% of initial mol)	Solid (% of initial mol)
Pre-bulk waste removal	100	100	NA	NA
Initial	100	100	0	0
70% Dissolution	100	85	<1E-1	7.9
50% Dissolution	7.9	0.3	0	7.6
30% Dissolution	7.6	0.1	0	7.5
Supernate add*	93	93	0	0
Caustic add	~93	~93	0	0

Note: Supernate add reflects an increase because of the soluble I^- in supernate.*

Approximately 50 kg of silver was sent into Tank 13 from the flushing of silver coated saddles from separations. This occurred between November 1969 to May 1970. From Tank 13, the waste was transferred into Tank 21, which was the 1H Evaporator Feed Tank. A total of about 2 million gallons of waste transferred into Tank 21 from Tank 13 during this period. A total of about 3 million gallons of waste is processed through the Evaporator, producing slightly less than 1 million gallons of concentrate in Tank 10. After cooling, approximately 30,000 gallons of saltcake crystallized. After cooling, the concentrated supernate was transferred from Tank 10 into Tank 11, Tank 14, and Tank 16 (HLW, 2005).

During May and the remainder of 1970, an effort was made to mix the concentrated silver containing waste with other waste to dilute the silver content. Multiple waste transfers were made to Tanks 11, 13, 14, 15, and 16 to dilute the silver content. During this time an approx. 2 million gallons of waste, that contained only trace silver, was transferred into the 1H Evaporator system from the Receipt Basin for Offsite Fuels and Tank 12. Also, the saltcake produced between November 1969 and May 1970 was dissolved and mixed with the other concentrated supernate (HLW, 2005).

For F-Area the primary source of silver was the iodine reactors. From July 1956 to October 1970, a total of 300 kg of silver was transferred into Tank 7. No incidents of popping noises have ever been reported with waste transferred into this tank or processed through the 2F evaporator. In the H-Area part of the tank farm, the silver containing waste was diluted with other waste that contained no more than trace amounts of silver (HLW, 2005).

The output of the OLI© model, as shown in Table 6-8, forecasts that as dissolution begins, all of the insoluble (post first-strike) Cl^- associated with the Ag^+ will form solids. Refer to Table 6-8.

Table 6-8 Ag^+ and Cl^- Ion Balance from Material Balance

Ion	Initial Aqueous (Mole)	Initial Solid (Mole)	Post Aqueous (Mole)	Post Solid (Mole)
Ag (+)	0.8	208.9	11.1	198.5
Cl (-)	4615.2	0.0	4416.9	198.5

Although the results above do not preclude the formation of AgCl, since the available silver is significantly less than that used in studies, and the chloride is predominately soluble, the possible formation of AgCl should be bound by that of the studies.

Halo-nitrogen compounds such as nitrogen tri-iodide {i.e., NI_3 • Hf=-144 Kjoule/mole} and nitrogen trichloride {i.e., NCl_3 = +230 Kjoule/mole}, and halo-oxygen compounds such as chlorine dioxide {i.e., ClO_2 • Hf=+100 Kjoule/mole} & dichloride heptaoxide {i.e., Cl_2O_7 • Hf = +270 Kjoule/mole} are known to be potentially explosive (KNOVEL, 2003).

Nitrogen trichloride and nitrogen tri-iodide are formed by reacting an ammonium halide with a halogen gas (KNOVEL, 2003). Traces of halogen gas must be present during chemical separations for these compounds to be formed. Gases expected from acid cleaning include primarily CO_2, H_2, potentially NOx, sulphates, and some low concentrations of acids. Since the halogen concentration is maintained very low and the tank vapour space is purged, any halogen gases would be quickly purged prior to building up to flammable concentrations.

Dichloride heptaoxide {i.e., Cl_2O_7 • Hf=+238 Kjoule/mole} is normally produced by the dehydration of perchloric acid {i.e., $HClO_4$ • Hf=+8.36 Kjoule/mole} (KNOVEL, 2003). Perchlorates are not used as process chemicals at SRS, and the formation of appreciable amounts of perchlorates has been deemed not possible based on thermodynamics. Additionally, since even “dry sludge tanks” contained at least 50 vol% interstitial liquid, dehydration of perchloric acid, if present, is highly unlikely. Therefore, oxalic acid dissolution is deemed not to increase the risk of halo-nitrogen and halo-oxygen explosive events.

6.3.11 Metal Nitrides

Metal nitrides of concern consist of primarily silver (e.g., Ag_3N) and mercury nitrides (e.g., HgN). As discussed previously, silver and mercury additions to the tank farm have been limited. The fate of nitrogen throughout the oxalic acid aided heel removal effort is detailed in Table 6-9.

Table 6-9 Estimated Normalized Abundance of Nitrides

Stage	% Total (% mol)	Aqueous (% of initial mol)	Vapour (% of initial mol)	Solid (% of initial mol)
Pre-bulk waste removal	100	100	NA	NA
Initial	100	100	0	0
70% Dissolution	100	99.9	<1E-1	0
50% Dissolution	0	0	0	0
30% Dissolution	0	0	0	0
Supernate add*	~5000	~5000	0	0
Caustic add	~5000	~5000	0	0

Note: Supernate add reflects an increase because of the soluble N^- in supernate.*

As can be seen from Table 6-9, any metal nitrides will quickly decrease during the oxalic acid aided heel removal effort, even potentially creating NOx emissions. The material balance contained in Appendix 3 is additionally spiked to confirm that because of solubility nitrides, and they quickly exit the system.

6.3.12 Ammonia Compounds

Based on the aging studies of organics and ammonia compounds and the process history, any ammonia compounds, precursors, or decomposition products should be long gone prior to acid being added to the tank. Nitrogen and hydrogen at elevated temperatures can produce ammonia, but most of the soluble nitrogen has been previously washed away. Ammonia concentrations and nitrides, post acid additions, are therefore not anticipated to exist in explosive quantities.

Additionally, it is important to note that ammonia salts are generally soluble. The solubility of ammonia in water at 25ºC is about 77 mg/L at 1 atm. Its boiling point is -33°C, while its melting point is -77.7°C. Its heat of vaporization is +23 Kjoule/mole. Its auto ignition temperature is 104°C. Its critical temperature of 133°C is easily exceeded in fires. The lower flammability limit is 16 vol%, while the upper is 25% (Knovel, 2003).

A lingering presence of ammonia can be discounted since the NH_4 would quickly evaporate based on partial pressure. Literature (Knovel, 2003) estimates the partial pressures of ammonia (with Na^+=6.2 moles/l and OH^-=1.7 moles/l; similar to routine non-evaporator system tank farm conditions) at various temperatures. Refer to Table 6-10.

Table 6-10 Partial Pressures of Ammonia (with 6.2 [Na^+], 1.7 [OH^-]**)**

	Liquid Phase Ammonia Concentrations				
Ammonia Concentration (wt%)	3.85	1.27	0.834	0.0841	0.0417
Ammonia Concentration (molality)	3.54	1.14	7.43E-01	7.43E-2	3.68E-02
Temp. (°C)	**K_h**	**Partial Pressure of Ammonia in Vapour Phase (atm)**			
25	23.91	1.48E-01	4.75E-02	3.11E-02	1.54E-03
30	19.68	1.80E-01	5.77E-02	3.78E-02	1.87E-03
40	13.56	2.61E-01	8.38E-02	5.48E-02	2.72E-03
50	9.55	3.70E-01	1.19E-01	7.78E-02	3.86E-3
56.96	7.68	4.61E-01	1.48E-01	9.68E-01	4.80E-03
70	5.02	7.05E-01	2.26E-01	1.48E-01	7.34E-03

Where, K_h represents Henry's Law Constant

It has been estimated that up to 90 wt% of ammonia would be from the decomposition of the hydrazine {i.e., N_2H_4 • Hf=+149 Kjoule/mole} and hydroxylamine {i.e., NH_3O • Hf=-114 Kjoule/mole} which entered the tank farms from the separations process (Knovel, 2003). Besides ammonia, ammonium nitrate {i.e., NH_4NO_3 • Hf=-184 Kjoule/mole}, ammonium nitrite {i.e., NH_4NO_2 • Hf=+116 Kjoule/mole}, and ammonia/air mixtures are well-documented explosive compounds (Knovel, 2003). In the separation facilities, hydrazine and hydroxylamine are used as chemical reductants (i.e., materials that accept electrons). During processing, excess hydrazine and hydroxylamine are destroyed by chemical reactions with nitrate and nitrite. Both hydrazine & hydroxylamine are considered soluble. The solubility for hydrazine and hydroxylamine (in water at 25°C) are shown in Table 6-11 (Knovel, 2003).

Table 6-11 Properties of Hydrazine and Hydroxylamine (in Water)

Name	**Formula**	**Mol. Weight**	**Specific Gravity**	**Melting Point**	**B.P.**	**Solubility in 0°C water**	**Solubility in 100°C water (g/100g H_2O)**
hydrazine	N_2H_4	32.05	1.01	1.4	113.5	soluble in all proportions	soluble in all proportions
hydroxylamine	NH_2OH	33.03	1.358°	34	56.5 Hg mm	NH_2OH	33.03

Hydrazine can be dissolved with oxygen as shown in Reaction 6-3.

$N_2H_4 + O_2$ à $2H_2O + N_2$ (Reaction 6-3)

Hydrazine, however has two possible ways to produce a significant amount of ammonia as shown below in Reaction 6.4 and 6.5.

$3N_2H_4 \rightarrow 4NH_3 + N_2$ (Reaction 6-4)

$2N_2H_4 \rightarrow H_2 + N_2 + 2NH_3$ (Reaction 6-5)

Hydroxylamine possible reaction pathways are pH dependent. In an alkaline solution the reaction pathway is shown in Reaction 6-6 (Hobbs, 1999).

$3NH_3O \rightarrow NH_3 + N_2 + 3H_2O$ (Reaction 6-6)

In an acidic solution the hydroxylamine reaction pathway is shown in Reaction 6-7.

$4NH_3O \rightarrow N_2O + 2\,NH_3 + 3H_2O$ (Reaction 6-7)

Hydrolysis and radiolysis of the hydrazine and hydroxylamine can also indirectly produce various gases including NO_X gases, nitrogen, ammonia and even hydrogen gas. Since hydrazine and hydroxylamine are mostly volatized with the partial pressure of hydrazine at roughly 0.066 atm, the precursor, $Ag(NH_3)_2$ could most likely could not be created with the normal ammonia decay (Hobbs, 2002, p23).

6.3.13 Organics

The possible miscellaneous organics and chemicals introduced into Tanks 1-15 have been previously shown in Table 6-3. Because of the age of both the supernate and sludge contained in Tanks 1-15, volatile organics would have long ago decomposed (Britt, 2003, p5). A review of the SRNL analysis of samples, taken as part of the organic Potential Inadequacy of Safety Analysis (PISA) resolution effort, demonstrated that the concentrations of volatile organics, along with hydrogen and NH_3, do not pose a flammability hazard (Britt, 2003). With all factors being equal, since the waste in Tanks 1-15 has been aged since the 1980's, it can be ascertained that even with acid treatment of Tanks 1-15, there will be a lower risk of explosion than that currently accepted.

Since oxalic acid is also an organic, its net effect should also be considered. Since the heat of formation for oxalic acid is -822 Kjoule/mole, while for sodium oxalate the heat of formation is -1318 Kjoule/mole (Knovel, 2003) one could predict that both would not have a significant impact on energetics. The energy of combustion and the energy of formation for the Tank 1-15 organics are shown in Table 6-12.

Table 6-12 Energy of Combustion of Organics

Constituent	Formula	Heat of Combustion	Heat of Formation
Oxalic acid	$(COOH)_2$	119 Kjoule/mole	-822 Kjoule/mole
Dodecane	$C_{12}H_{26}$	7514 Kjoule/mole	+28.1 Kjoule/mole
Tri-n-butyl phosphate	$(CH_3[CH_2]_3O)_3PO$		
Di-n-butyl phosphate	$C_8H_{18}O_4P_1$(1 neg. charge)		
Mono-n-butyl phosphate	$C_4H_9O_4P_1$(2 neg charge)		
n-Butanol	$C_4H_{10}O$	2456 Kjoule/mole	-2746 Kjoule/mole
Gluconic acid	$C_6H_{12}O_7$		-1587 Kjoule/mole
Ascorbic acid	$C_6H_8O_7$		-731 Kjoule/mole
Ion-exchange resins	(C_8H_8)n	4219 Kjoule/mole	+213 Kjoule/mole
Polydimethylsiloxane	(C_2H_6OSi)n		
Hydrogenated tallow	NA		
Ethylene glycol (1,2-	$C_2H_6O_2$	1058 Kjoule/mole	-304 Kjoule/mole
Methylcellulose	CH_4OxUnspecified		
2,4,7,9-tetramethyl-5 -			
	Siloxanes		

As seen in Table 6-12, dodecane has the largest heat of combustion/lowest positive net of formation. Dodecane, because of its very low very pressure {0.33 mmHg at 20°C}, is removed by separation evaporators prior to its discharge to HLW. Based on the modelling of evaporation of organic liquids, any paraffin that reaches the tank farm will persist in the tank farms for less than a few months (Britt, 2003, p42). Since Tanks 1-15 have not received fresh waste since the mid 1980's, any dodecane or volatile decomposition products are considered to have long ago evaporated.

Tri-n-butyl phosphate could hypothetically reach the tank farm dissolved or entrained in the aqueous waste. Any TBP that reaches alkaline tanks would have been slowly hydrolyzed by the following reactions (Hobbs, 1999, p20).

$(C_4H_9O)_3PO + OH^-$ à $(C_4H_9O)_2PO_2^- + C_4H_9OH$ (Reaction 6-8)

$(C_4H_9O)_2PO_2^- + OH^-$ à $(C_4H_9O)PO_3^{2-} + C_4H_9OH$ (Reaction 6-9)

$(C_4H_9O)_2 PO_3^{2-} + OH^-$ à $PO_4^{3-} + C_4H_9OH$ (Reaction 6-10)

Hydrolysis and radiolysis of the TBP produces di-n-butyl phosphate {i.e., $(C_8H_{19}O_4)PO$}, mono-n-butyl phosphate {i.e., $(C_4H_{10}O_4)P$}, as well as carbon dioxide and inorganic phosphates. N-butanol is also a decomposition product of TBP. Because of the age of the wastes, any remaining TBP or volatile decomposition products are considered to have mostly evaporated and would not affect Tank 1-15 (Britt, 2003, p42).

Gluconic acid {i.e., $C_6H_{12}O_7$ • Hf=-1587 Kjoule/mole} was used briefly in the separation facilities during the late 1950's, and has not been used since that time. Ascorbic acid, {i.e., $C_3H_8O_6$ • Hf=-731 Kjoule/mole}, is sometimes still used in the separation facilities for actinide valence adjustment. Gluconic & ascorbic acids hydrolyze rapidly in both acidic and basic solutions. Hydrolysis products include oxalic acid {i.e., $(COOH)_2$ • Hf=-822 Kjoule/mole} and smaller organic acids. Further hydrolytic and radiolytic reactions with the organic acids produce various gasses including carbon dioxide (Knovel, 2003). Based on the age of the wastes in Tanks 1-15, any gluconic or ascorbic acids introduced into the tanks, as well as any associated decomposition products are considered to have decomposed long ago.

Both anion and cation ion exchange resins were historically used in the separation facilities. Most of the resins contained polymeric backbones made of polystyrene and/or styrene-di-vinylbenzene co-polymers. Process records show that the majority of the resins were definitively digested in alkaline permanganate prior to being transferred to the tank farms. About 15 wt% of the resins, however, may have been sent to the tank farms in the undigested form (Britt, 2003, p32). The permanganate digestion breaks down the resin into short chains that contain alcohol and carboxylic acid {i.e., COOH}. Depending on the length of the chain, the resulting fragments may be soluble in aqueous solution. Radiolysis will also contribute to the breakdown of the resins, eventually forming small organic molecules of hydrogen, carbon dioxide, and ammonia (Camaioni, 1999). Based on the age of the wastes in Tanks 1-15, any resin introduced into the tanks is considered to have decomposed and no-longer represent an explosive hazard.

As previously discussed, vapour & liquid samples were taken from pump tanks HTP-5 & FTP-3, as well as HLW Tanks 38, 43, 26, 33 and 46. Vapour samples taken from HTP-5 and FTP-3 exhibited trace amounts of organics that were several orders of magnitude below levels that could potentially represent flammability concerns. These liquid samples were taken at/and below the surface of the waste (Swingle, 1999, p17). Vapour sampling revealed that for Tanks 1-15 organic explosives are not considered to be a potential flammability concern.

Red oil is produced when organics enter vessels containing uranyl nitrate solutions that are heated to relatively high temperatures (Robinson, 2003, p3-3). Based on industry locations where red oil has been found, the organic materials are generally TBP, diluents, and associated decomposition products. Since red oil is not explosive at temperatures, less than 130°C and the sludge temperature during heel removal will be maintained at less than 100°C, red oil does not form an explosive concern (Robinson, 2003, p3-3).

High Level Waste stored at the SRS is considered to contain only small amounts of organic compounds. Based on the process records of organic compounds received in the tank farms through 1984, a Total Organic Carbon (TOC) concentration in the waste, assuming a perfect blend, is calculated to be about 2,000 ppm (Britt, 2003). The actual concentration, however, is much lower than this due to radiolytic and chemical decomposition. Analysis of two active current sludge tanks closest to the organic processes indicated a (TOC) total organic carbon content of about 85 ppm and 220 ppm. The TOC in Tanks 1-15, considering the 20^+ years of aging, will be significantly less (Britt, 2003, p52).

6.3.14 Hydrogen

Hydrogen is generated either radiolytically or chemically. With the HLW Tanks, radiolytic hydrogen generation rate, X, is calculated using Equation 6-3 (Davis, 2004, p12).

$$X = \frac{R_{B/G}H_{B/G} + R_a H_a}{10^6} \qquad \text{(Eq. 6-3)}$$

Where:

$R_{B/G}$ = amount of hydrogen generated per 10^6 BTU of heat added from beta or gamma decay

$H_{B/G}$ = heat generated by beta and gamma decay

R_a = amount of hydrogen generated per 10^6 BTU of heat added from alpha decay

H_a = heat generated by alpha decay

The values $R_{B/G}$ and R_a are dependent on the concentration of nitrate and nitrite in the waste and are given by Equation 6-4 and Equation 6-5.

$$Ra = 134.7 - 82.3x(NO_{eff})^{1/3} - 13.6x(NO_{eff})^{2/3} + 11.8x(NO_{eff}) \qquad \text{(Eq. 6-4)}$$

$$R_{B/G} = 48.36 - 52.78x(NO_{eff})^{1/3} + 14.1x(NO_{eff})^{2/3} + 0.572x(NO_{eff}) \qquad \text{(Eq. 6-5)}$$

Where:

NO_{eff} = the nitrate concentration plus one half the nitrite concentration

Since nitrates and nitrites are very soluble {i.e., $NaNO_2$ has a solubility of about 85g/100g water at 25ºC, while $NaNO_3$ has a solubility of about 90g/100g of water at 25°C, they will largely be washed out as part of bulk waste removal (prior to the actual oxalic acid additions). Since the solubilities for NO_3^{-1} and NO_2^{-1} are very similar, the detailed OLI Stream Analyzer© outputs can be used to estimate the decrease of any initial nitrates or nitrates contained in the in material balance. Table 6-4 contained in Section 6.3.1 show the relative percent decrease in NO_2^{-1} and NO_3^{-1} as part of cleaning the tank. As can be seen in Table 6-4 both NO_2^{-1} and NO_3^{-1} are highly soluble and many will be washed out during treatment.

As discussed in Chapter 5, under acidic conditions, corrosion of the carbon steel tank is postulated to become the overwhelming source of hydrogen, masking a relative small increase from the nitrate and nitrite reduction. Since the hydrogen from acid induced corrosion is currently not considered in the safety basis, changes will be required to the basis to ensure that the risk does not increase.

6.4 Conclusion on Energetic Compound Impacts Determination

Hydrogen will effectively show an increased generation rate as part of the oxalic acid aided heel removal effort. Hydrogen is evaluated under the Documented Safety Analyses (DSA, 2003, Chapter 3), and as part of the revision to allow oxalic acid aided heel removal, corrosion induced hydrogen will have to be evaluated and be shown to be acceptable. No other increase in energetic compounds is expected.

CHAPTER 7

DOWNSTREAM PROCESSABILITY

7.1 Introduction to Downstream Processability Determination

Using OLI ESP$^{©}$, an integrated HLW process flow sheet, is constructed to simulate the dissolution of a 5,000 gallon heel of representative sludge material. This chapter is different from that used in Chapter 5, as it focused on a material balance across the tank, whereas this chapter focuses on a material balance across a much larger part of the HLW process. Chapter 7 intends to provide an evaluation of process impacts. Chapter 5 focuses on treatment tank and neutralization tank safety analyses concerns, and hence uses Hypothetical Worst Case Sludge to bound any potential concerns, whereas, Chapter 7 focuses on the downstream processability concerns, and hence uses representative sludge slurry.

In this chapter, two different cases are evaluated. They are:

- If effluent from heel dissolution process should be added to a washed sludge batch for DWPF feed instead of an unwashed sludge batch

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

For the purposes of Chapter 8, the Tank 1-15 heel dissolution process has the following refinements:

- Tank 8 characterization data from the process database and Tank 12 characterization data from the process database is used
- Water is added to establish operating heights
- Neutralized spent acid is decanted to the evaporator feed or drop tank
- The neutralization tank will be mixed to suspend solids
- The resultant sodium oxalate is transferred to the DWPF sludge wash tank

The flow diagram is divided into segments with process models. The unique heel removal portion of the flow sheet shown in Figure 7-1 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 (Hang, 2002) (Koffman, 2002) and sludge washing models (Lillistan, 2004) are used to model the respective portions of the flow sheet. Other process effects are calculated separately and are included in this analysis.

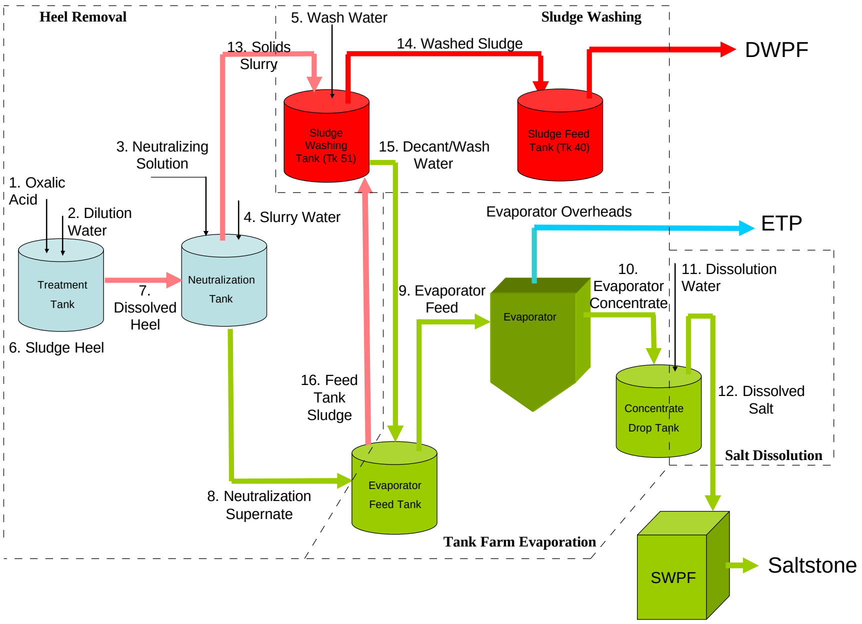


Figure 7-1 Heel Removal Flow Diagram

7.2 Sodium Oxalate Solubility

The primary material formed using oxalic acid to clean the waste tanks has been determined as demonstrated in Chapter 5, to be metal oxalates and sodium oxalate. Figure 7-2 shows measured solubility of sodium oxalate for both simulants and HLW (Fowler, 1980) (Wiley, 1978). The figure also shows the results of several other estimation methods (Kilpatrick, 1984).

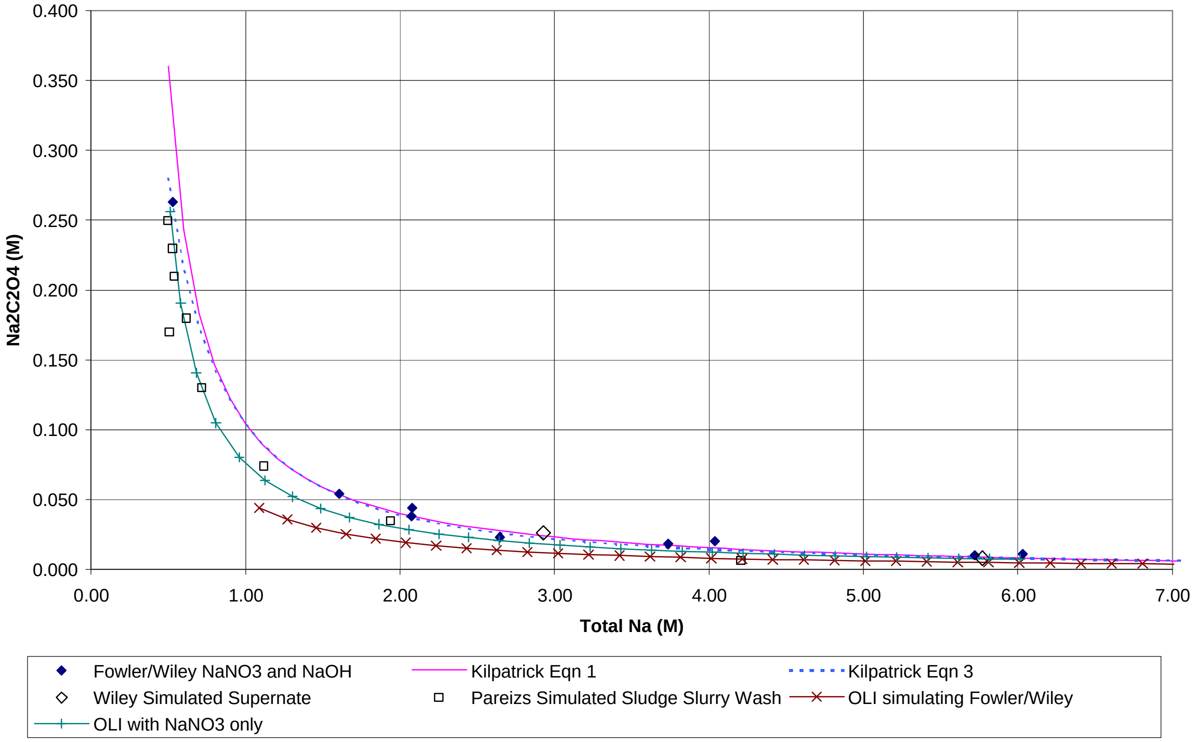


Figure 7-2 Oxalate Solubility Curve as a Function of Sodium Concentration

Note that the supernate simulants used by Fowler and Wiley, containing only sodium nitrate and sodium hydroxide, are represented in solid symbols. The open symbols represent more complex multi-component supernate simulants. The lines represent various estimation methods. Two empirical data fits by Kilpatrick are shown, as well as two calculation using OLI ESP©. Based on the results, it can be seen that the OLI© based model only slightly under-predicts the oxalate solubility.

7.3 Heel Removal

The heel dissolution process assumes that the tank has completed bulk sludge removal, and as a result underwent significant washing. The remaining heel in the treated tank is no greater than 5,000 gallons of sludge slurry, which equates to roughly 2 inches of sludge slurry in Tanks 1-15. In addition, bulk sludge removal uses inhibited water to establish the minimum operating level. This ensures that minimal soluble salts are present in the heel. Inhibited water in the process minimally consists of 0.01 to 1 M NaOH and 0.011 M $NaNO_3$, which results in about 0.02-0.03 M total sodium salts. The heel, therefore, consists primarily of sludge solids and water with no more than 0.1 M of soluble sodium salts.

The sludge solids composition for waste Tanks 1-15 is taken from the process database (HLW, 2005). Since representative sludge is used in this chapter, only the composition is important and not the total amount of material in each tank. For this chapter it is reasoned that the relative percentage of each type of waste sent to the waste tank will more accurately reflect composition of the heel. The process database reports the waste type and monthly amount of waste transferred to each tank. Table 7-1 shows the totals of each type and relative percentage sent to each tank. Table 7-2 shows the composition by waste type. Table 7-3 shows the resulting composition of the sludge heel for each tank by combining the information in Table 7-1 and 7-2. Note that the sludge composition includes some soluble sodium salts. The planned initial heel removal includes substantial water contact with the heel that will reduce the soluble salts to much lower amounts. These salts, however, are left in the estimated composition to conservatively estimate the consumption of acid during dissolution.

Table 7-1 Waste Type For Tanks 1-15

	Tank														
Stream	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**
Purex Low (%)	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 (%)	47.1	100	100	6.1	67.2	0.0	16.3	14.6	100	98.3	0.0	16.9	13.1	0.0	0.0
Purex High (%)	37.7	0.0	0.0	93.9	32.8	100	4.2	14.8	0.0	0.0	0.0	0.0	3.3	58.7	0.0
HM Low (%)	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
HM Mixed (%)	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
HM High (%)	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 7-2 Composition of Sludge Solids by Waste Type

Constituents	**HM High (wt%)**	**HM Low (wt%)**	**HM Mixed (wt%)**	**PUREX High (wt%)**	**PUREX Low (wt%)**	**PUREX Mixed (wt%)**
$Al(OH)_3$	67	20.6	62.0	6.50	13.9	11.4
$CaC2O_4$	2.2	0.0	1.9	0.0	0.0	0.0
$CaCO_3$	0.0	4.6	0.5	2.8	5.5	4.5
$Ce(OH)_3$	0.1	1.2	0.2	0.3	0.4	0.3
$Fe(OH)_3$	10.2	46.0	14.1	48.5	48.0	48.2
HgO	3.0	2.2	2.9	0.2	0.1	0.1
MnO_2	2.6	11.8	3.6	12.1	4.2	6.9
NaCl	0.0	1.4	0.2	0.2	2.1	1.4
$NaNO_3$	3.3	0.4	2.9	1.3	1.6	1.5
NaOH	1.4	3.3	1.6	5.1	4.7	4.8
$Ni(OH)_2$	1.0	0.7	1.0	5.8	3.5	4.3
SiO_2	4.7	0.0	4.2	1.0	1. 9	1.6
ThO_2	1.3	0.1	1.2	0.1	0.0	0.0
$UO_2(OH)_2$	1.3	4.7	1.6	10.9	7.8	8.9
Total	97.9	97.0	97.8	94.8	93.4	93.9

Note: Plutonium and Strontium considered in HWCS are a very small fraction of the total waste and are not considered in evaluating downstream processability.

Table 7-3 Estimated Composition of Sludge Solids in Tank Heels

Constituent	Tank														
	1 (wt%)	2 (wt%)	3 (wt%)	4 (wt%)	5 (wt%)	6 (wt%)	7 (wt%)	8 (wt%)	9 (wt%)	10 (wt%)	11 (wt%)	12 (wt%)	13 (wt%)	14 (wt%)	15 (wt%)
$Al(OH)_3$	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
CaC_2O_4	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
$CaCO_3$	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
$Ce(OH)_3$	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
$Fe(OH)_3$	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	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
MnO_2	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	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
$NaNO_3$	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	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
$Ni(OH)_2$	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
SiO_2	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
ThO_2	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
$UO_2(OH)_2$	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	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100

Table 7-4 Estimated Composition of Sludge Slurry in Tank Heels

	Tank														
Constituen	1 (wt%)	2 (wt%)	3 (wt%)	4 (wt%)	5 (wt%)	6 (wt%)	7 (wt%)	8 (wt%)	9 (wt%)	10 (wt%)	11 (wt%)	12 (wt%)	13 (wt%)	14 (wt%)	15 (wt%)
$Al(OH)_3$	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
CaC_2O_4	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
$CaCO_3$	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
$Ce(OH)_3$	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
$Fe(OH)_3$	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	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
MnO_2	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	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
$NaNO_3$	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	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
$Ni(OH)_2$	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
SiO_2	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
ThO_2	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
$UO_2(OH)_2$	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
H_2O	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
Total	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Total	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40
slurry sp.g.	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2
solids/L slurry (kg/L)	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48

As can be seen above, the heel composition for Tanks 1-8 are very similar. The heel compositions in Tanks 9-15 show some variation. The heel compositions for Tanks 8 and 11 were picked to represent the base case. Table 7-5 shows the different cases which will be considered in the material balance.

Table 7-5 Material Balance Cases Considered

Case	Heel from Tank	Neutralization Liquid	Decant to Evaporator Feed or Drop Tank
1	8	50 wt% NaOH	Feed
2	8	supernate	Feed
3	11	50 wt% NaOH	Feed
4	11	supernate	Feed

Table 7-6 shows the assumed supernate composition used to neutralize the oxalic acid. The acid is considered neutralized at 0.1 M free hydroxide concentration (i.e., a pH of 12 and a pH of 14 representing the difference between being within the corrosion control program and targeted pH when adding caustic). The simulation calculated the volume needed to reach the neutralization concentration. Table 7-7 and Table 7-9 show the material balance of the heel dissolution for these tanks using 50 wt% NaOH solution for neutralization of the acid. Table 7-8 and Table 7-10 show the same material balance using an average supernate for neutralization.

Note that 7-7 through 7-10 show the added materials only, not necessarily 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 salt dissolution dissolves any of the added sodium oxalate. That is, 100% remains in the heel.

Table 7-6 Supernate Composition

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 7-7 Baseline Material Balance for Case 1
(Tank 8 Purex Neutralized with NaOH)

	1	2	3	4	5	6a	6b	7a	7b
Stream	Oxalic Acid	Dilution Water	Supernate	Slurry Water	Wash Water	sludge heel	sludge heel	TTslurry	TTslurry
Phase	Aqueous	-	Aqueous	-		Aqueous	Solid	Aqueous	Solid
Temperature, C	30	Aqueous	30	Aqueous	Aqueous	30	30	30	30
Pressure, atm	1	-	1	-		1	1	1	1
pH	0.738632	-		-		13.414		0.655618	
Total mol	1.37E+07	0.00E+00	1585450	0.00E+00	0.00E+00	909256	89039	14782500	17793
Flow Units	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac
H_2O	0.92	-	5.00E-01	-	9.76E-01	9.25E-01	0.00E+00	9.11E-01	0.00E+00
$H_2C_2O_4$	0.07999997	-	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	4.58E-04	0.00E+00
HNO_3		-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	4.76E-04	0.00E+00
Na_2CO_3		-	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	1.23E-02	0.00E+00	0.00E+00	0.00E+00
$NaNO_2$		-	0.00E+00	-	2.41E-02	0.00E+00	0.00E+00	0.00E+00	0.00E+00
$NaNO_3$		-	0.00E+00	-	0.00E+00	1.08E-02	0.00E+00	0.00E+00	0.00E+00
NaOH		-	5.00E-01	-	0.00E+00	3.44E-02	0.00E+00	0.00E+00	0.00E+00
Na_2SO_4		-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
$Na_2C_2O_4$		-	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	1.53E-01	0.00E+00	0.00E+00
AlOOH		-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	3.95E-03	0.00E+00
$NaAlO_2$		-	0.00E+00	-	0.00E+00	3.29E-03	0.00E+00	0.00E+00	0.00E+00
CaC_2O_4		-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	4.08E-04	2.80E-01
$CaCO_3$		-	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	2.40E-04	0.00E+00	0.00E+00	0.00E+00
Ce_2O_3		-	0.00E+00	-	0.00E+00	1.32E-03	0.00E+00	0.00E+00	0.00E+00
$Ce_2(C_2O_4)_3$		-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	3.76E-05	9.07E-03
$Fe_2(C_2O_4)_3$		-	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	7.44E-05	5.81E-01	0.00E+00	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	0.00E+00
MnC_2O_4		-	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	8.83E-07	5.95E-02	0.00E+00	0.00E+00
NiC_2O_4		-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	5.71E-05	2.91E-01
$Ni(OH)_2$		-	0.00E+00	-	0.00E+00	3.07E-07	4.54E-02	0.00E+00	0.00E+00
SiO_2		-	0.00E+00	-	0.00E+00	1.23E-02	0.00E+00	3.78E-03	8.00E-02
$UO_2C_2O_4$		-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	3.78E-03	0.00E+00
UO_2OH_2		-	0.00E+00	-	0.00E+00	2.66E-08	9.92E-02	0.00E+00	0.00E+00
Total g	2.64E+08	0.00E+00	3.94E+07	0.00E+00	3.05E+09	1.72E+07	9.37E+06	2.88E+08	2.55E+06
Volume, gal	65401.9	-	6800.003	-	800,000	4292.983	707.0119	70269.8	107.8953
Enthalpy, cal	-9.67E+11	-	-1.26E+11	-	-	-6.35E+10	-2.04E+10	-1.05E+12	-5.68E+09
Density, g/gal	4040.282	-	5791.942	-	-	4.00E+03	1.33E+04	4.10E+03	2.36E+04

(continued)

(Continuation of Table 7-7)

	8	9	10	11	12	13a	13b	14	15	16
Stream	RTsupernate	Evaporator Feed	Evaporator Concentrate	Dissolution Water	Dissolved Salt	RTsolids	RTsolids	Washed Sludge	Decant/Wash Water	Feed Tank Sludge
Phase	Aqueous	-	-	-	-	Aqueous	Solid	-	-	-
Temperature, C	30	-	-	-	-	30	30	-	-	-
Pressure, atm	1	30	30	30	30	1	1	30	30	30
pH	12.6922	-	-	12	-	12.6922		-	-	-
Total mol	7603220	-	-	-	-	8.46E+06	251314	-	-	-
Flow Units	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac
H_2O	9.61E-01	-	-	9.99E-01	-	9.61E-01	0.00E+00	-	8.09E-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	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	-
$NaNO_2$	0.00E+00	-	-	7.50E-04	-	0.00E+00	0.00E+00	-	7.64E-02	-
$NaNO_3$	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	-
Na_2SO_4	0.00E+00	-	-	0.00E+00	-	0.00E+00	0.00E+00	-	3.03E-03	-
$Na_2C_2O_4$	2.90E-02	1.00E+00	1.00E+00	0.00E+00	0.00E+00	2.90E-02	7.01E-01	5.51E-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	-
$NaAlO_2$	6.55E-04	-	-	0.00E+00	-	6.55E-04	0.00E+00	-	7.60E-03	-
CaC_2O_4	7.62E-07	-	-	0.00E+00	-	7.61E-07	2.38E-02	-	0.00E+00	-
$CaCO_3$	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	7.64E-05	-	-	0.00E+00	-	7.63E-05	0.00E+00	-	0.00E+00	-
$Ce_2(C_2O_4)_3$	0.00E+00	-	-	0.00E+00	-	0.00E+00	0.00E+00	-	0.00E+00	-
$Fe_2(C_2O_4)_3$	2.55E-05	-	-	0.00E+00	-	2.54E-05	0.00E+00	-	0.00E+00	-
$Fe(OH)_3$	0.00E+00	-	-	0.00E+00	-	0.00E+00	1.74E-01	-	0.00E+00	-
$K_2C_2O_4$	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	2.78E-06	-	-	0.00E+00	-	2.78E-06	0.00E+00	-	0.00E+00	-
$Mn(OH)_2$	0.00E+00	-	-	0.00E+00	-	0.00E+00	1.78E-02	-	0.00E+00	-
NiC_2O_4	9.54E-08	-	-	0.00E+00	-	9.53E-08	0.00E+00	-	0.00E+00	-
$Ni(OH)_2$	0.00E+00	-	-	0.00E+00	-	0.00E+00	1.36E-02	-	0.00E+00	-
SiO_2	7.12E-04	-	-	0.00E+00	-	7.11E-04	0.00E+00	-	0.00E+00	-
$UO_2C_2O_4$	1.07E-04	-	-	0.00E+00	-	1.07E-04	0.00E+00	-	0.00E+00	-
UO_2OH_2	0.00E+00	-	-	0.00E+00	-	0.00E+00	2.88E-02	-	0.00E+00	-
Total g	1.41E+08	1.23E+06	1.23E+06	8.39E+09	-	1.57E+08	3.15E+07	4.01E+08	3.77E+08	5.06E+06
Volume, gal	36162	-	-	2,200,000	3,200,000	40237.12	738.4035	552,738	1,377,000	-
Enthalpy, cal	-5.27817E+11	-	-	-	-	-5.87E+11	-7.23E+10	-	-	-
Density, g/gal	3909.799	-	-	3817.8	-	3.91E+03	4.26E+04	-	-	-

Table 7-8 Material Balance for Case 2
(Tank 8 Purex Neutralized with Supernate)

	1	2	3	4	5	6a	6b	7a	7b
Stream Name	Oxalic Acid	Dilution Water	Neutralization Solution	Slurry Water	Wash Water	Sludge Heel	Sludge Heel	Dissolved Heel	Dissolved Heel
OLI Stream	Oxalic Acid	-	Supernate	-		sludge heel	sludge heel	TTslurry	TTslurry
Phase	Aqueous	Aqueous	Aqueous	Aqueous	Aqueous	Aqueous	Solid	Aqueous	Solid
Temperature, C	30	-	30	-		30	30	30	30
pH	0.738632	-		-		13.4139		0.655625	
Total mol	1.37E+07	0.00E+00	9.88E+06	0.00E+00	0.00E+00	909256	89038.9	1.48E+07	17792.5
Flow Units	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac
H_2O	0.92	-	6.79E-01	-	9.76E-01	9.25E-01	0.00E+00	9.11E-01	0.00E+00
$H_2C_2O_4$	0.07999997	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	4.01E-02	0.00E+00
HCl	0	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	4.58E-04	0.00E+00
HNO_3	0	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	4.76E-04	0.00E+00
Na_2CO_3	0	-	1.42E-02	-	0.00E+00	3.44E-04	0.00E+00	2.14E-03	0.00E+00
NaCL	0	-	0.00E+00	-	0.00E+00	1.23E-02	0.00E+00	0.00E+00	0.00E+00
$NaNO_2$	0	-	3.11E-02	-	2.41E-02	0.00E+00	0.00E+00	0.00E+00	0.00E+00
$NaNO_3$	0	-	1.59E-01	-	0.00E+00	1.08E-02	0.00E+00	0.00E+00	0.00E+00
NaOH	0	-	7.62E-02	-	0.00E+00	3.44E-02	0.00E+00	0.00E+00	0.00E+00
Na_2SO_4	0	-	1.77E-02	-	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
$Na_2C_2O_4$	0	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	4.42E-03	0.00E+00
				-					
$Al(OH)_3$	0	-	0.00E+00	-	0.00E+00	0.00E+00	1.53E-01	0.00E+00	0.00E+00
AlOOH	0	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	3.95E-03	0.00E+00
$NaAlO_2$	0	-	2.17E-02	-	0.00E+00	3.29E-03	0.00E+00	0.00E+00	0.00E+00
CaC_2O_4	0	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	4.08E-04	2.80E-01
$CaCO_3$	0	-	0.00E+00	-	0.00E+00	0.00E+00	6.18E-02	0.00E+00	0.00E+00
$Ca(OH)_2$	0	-	0.00E+00	-	0.00E+00	2.40E-04	0.00E+00	0.00E+00	0.00E+00
Ce_2O_3	0	-	0.00E+00	-	0.00E+00	1.32E-03	0.00E+00	0.00E+00	0.00E+00
$Ce_2(C_2O_4)_3$	0	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	3.76E-05	9.07E-03
$Fe_2(C_2O_4)_3$	0	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	3.31E-02	0.00E+00
$Fe(OH)_3$	0	-	0.00E+00	-	0.00E+00	7.44E-05	5.81E-01	0.00E+00	0.00E+00
$K_2C_2O_4$	0	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
KOH	0	-	7.46E-04	-	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
MnC_2O_4	0	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	4.55E-04	3.40E-01
$Mn(OH)_2$	0	-	0.00E+00	-	0.00E+00	8.83E-07	5.95E-02	0.00E+00	0.00E+00
NiC_2O_4	0	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	5.71E-05	2.91E-01
$Ni(OH)_2$	0	-	0.00E+00	-	0.00E+00	3.07E-07	4.54E-02	0.00E+00	0.00E+00
SiO_2	0	-	0.00E+00	-	0.00E+00	1.23E-02	0.00E+00	1.12E-04	8.00E-02
$UO_2C_2O_4$	0	-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	3.78E-03	0.00E+00
UO_2OH_2	0	-	0.00E+00	-	0.00E+00	2.66E-08	9.92E-02	0.00E+00	0.00E+00
Total g	2.64E+08	0.00E+00	2.31E+08	0.00E+00	3.05E+09	1.72E+07	9.37E+06	2.88E+08	2.55E+06
Volume, gal	65,402	-	49,000	-	800,000	4,293	707	70,270	108
Enthalpy, cal	-9.67E+11	-	-7.33E+11	-	-	-6.35E+10	-2.04E+10	-1.05E+12	-5.68E+09
Density, g/gal	4040.282	-	4721.201	-	-	3999.816	1.33E+04	4.10E+03	23616.19

(continued)

(Continuation of Table 7-8)

	8	9	10	11	12	13a	13b	14	15	16
Stream Name	Neutralization Supernate	Evaporator Feed	Evaporator Concentrate	Dissolution Water	Dissolved Salt	Solids Slurry	Solids Slurry	Washed Sludge	Decant/Wash Water	Feed Tank Sludge
OLI Stream	RTsupernate	-	-	-	-	RTsolids	RTsolids	-	-	-
Phase	Aqueous	-	-	-	-	Aqueous	Solid	-	-	-
Temperature, C	30	30	30	30	30	30	30	30	30	30
pH	12.7934	-	-	12	-	12.7934		-	-	-
Total mol	1.39E+07	-	-	-	-	1.03E+07	349678	-	-	-
Flow Units	wtfrac					wtfrac	wtfrac			
H_2O	8.78E-01	-	-	9.99E-01	-	8.71E-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	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	-
$NaNO_2$	1.50E-02	-	-	7.50E-04	-	1.49E-02	0.00E+00	-	7.63E-02	-
$NaNO_3$	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	-
Na_2SO_4	8.52E-03	-	-	0.00E+00	-	8.48E-03	0.00E+00	-	3.02E-03	-
$Na_2C_2O_4$	4.95E-03	1.00E+00	1.00E+00	0.00E+00	0.00E+00	4.93E-03	6.79E-01	6.77E-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	-
$NaAlO_2$	7.74E-04	-	-	0.00E+00	-	7.70E-04	0.00E+00	-	7.59E-03	-
CaC_2O_4	2.15E-06	-	-	0.00E+00	-	2.14E-06	1.83E-02	-	0.00E+00	-
$CaCO_3$	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	4.74E-05	-	-	0.00E+00	-	4.72E-05	0.00E+00	-	0.00E+00	-
$Ce_2(C_2O_4)_3$	0.00E+00	-	-	0.00E+00	-	0.00E+00	0.00E+00	-	0.00E+00	-
$Fe_2(C_2O_4)_3$	3.17E-05	-	-	0.00E+00	-	3.16E-05	0.00E+00	-	0.00E+00	-
$Fe(OH)_3$	0.00E+00	-	-	0.00E+00	-	0.00E+00	1.34E-01	-	0.00E+00	-
$K_2C_2O_4$	5.31E-04	-	-	0.00E+00	-	5.28E-04	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	1.98E-07	-	-	0.00E+00	-	1.97E-07	0.00E+00	-	0.00E+00	-
$Mn(OH)_2$	0.00E+00	-	-	0.00E+00	-	0.00E+00	1.37E-02	-	0.00E+00	-
NiC_2O_4	1.18E-07	-	-	0.00E+00	-	1.18E-07	0.00E+00	-	0.00E+00	-
$Ni(OH)_2$	0.00E+00	-	-	0.00E+00	-	0.00E+00	1.04E-02	-	0.00E+00	-
SiO_2	4.42E-04	-	-	0.00E+00	-	4.39E-04	0.00E+00	-	0.00E+00	-
$UO_2C_2O_4$	2.28E-03	-	-	0.00E+00	-	2.26E-03	0.00E+00	-	0.00E+00	-
UO_2OH_2	0.00E+00	-	-	0.00E+00	-	0.00E+00	0.00E+00	-	0.00E+00	-
Total g	2.77E+08	1.25E+06	1.25E+06	8.39E+09	-	2.04E+08	4.08E+07	4.10E+08	3.77E+08	3.01E+06
Volume, gal	67,364	-	-	2,200,000	3,200,000	49,640	1,236	553,236	1,377,000	-
Enthalpy, cal	-9.73E+11	-	-	-	-	-7.17E+11	-1.03E+11	-	-	-
Density, g/gal	4113.416	-	-	3817.8	-	4113.416	33040.95	-	-	-

Table 7-9 Baseline Material Balance for Case 3
(Tank 11 HM Neutralized with NaOH)

	1	2	3	4	5	6a	6b	7a	7b
Stream	Oxalic Acid	Dilution Water	Supernate	Slurry Water	Wash Water	Sludge Heel	Sludge Heel	TTslurry	TTslurry
Phase	Aqueous	-	Aqueous	-		Aqueous	Solid	Aqueous	Solid
Temperature, C	30	Aqueous	30	Aqueous	Aqueous	30	30	30	30
pH	0.738632	-		-		11.5886		1.39016	
Total mol	17901400	0.00E+00	2098390	0.00E+00	0.00E+00	870546	103816	18949900	13964.9
Flow Units	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac
H_2O	0.9199997	-	5.00E-01	-	9.76E-01	9.40E-01	0.00E+00	9.10E-01	0.00E+00
$H_2C_2O_4$	0.08000027	-	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	8.66E-05	0.00E+00
HNO_3		-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	5.14E-04	0.00E+00
Na_2CO_3		-	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	3.14E-03	0.00E+00	0.00E+00	0.00E+00
$NaNO_2$		-	0.00E+00	-	2.41E-02	0.00E+00	0.00E+00	0.00E+00	0.00E+00
$NaNO_3$		-	0.00E+00	-	0.00E+00	1.57E-02	0.00E+00	0.00E+00	0.00E+00
NaOH		-	5.00E-01	-	0.00E+00	1.75E-02	0.00E+00	0.00E+00	0.00E+00
Na_2SO_4		-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
$Na_2C_2O_4$		-	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	5.88E-01	0.00E+00	0.00E+00
AlOOH		-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	1.13E-02	0.00E+00
$NaAlO_2$		-	0.00E+00	-	0.00E+00	4.38E-05	0.00E+00	0.00E+00	0.00E+00
CaC_2O_4		-	0.00E+00	-	0.00E+00	4.87E-05	0.00E+00	3.96E-05	0.00E+00
$CaCO_3$		-	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	4.33E-05	0.00E+00	0.00E+00	0.00E+00
Ce_2O_3		-	0.00E+00	-	0.00E+00	2.69E-03	0.00E+00	0.00E+00	0.00E+00
$Ce_2(C_2O_4)_3$		-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	6.07E-05	0.00E+00
$Fe_2(C_2O_4)_3$		-	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	9.59E-07	2.54E-01	0.00E+00	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	0.00E+00
MnC_2O_4		-	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	1.03E-07	5.85E-02	0.00E+00	0.00E+00
NiC_2O_4		-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	5.11E-05	3.27E-01
$Ni(OH)_2$		-	0.00E+00	-	0.00E+00	4.53E-09	1.11E-02	0.00E+00	0.00E+00
SiO_2		-	0.00E+00	-	0.00E+00	2.04E-02	0.00E+00	1.02E-04	6.73E-01
$UO_2C_2O_4$		-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	8.99E-04	0.00E+00
UO_2OH_2		-	0.00E+00	-	0.00E+00	2.69E-07	3.06E-02	0.00E+00	0.00E+00
ThO_2		-	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	3.86E-05	3.06E-02	7.63E-04	0.00E+00
$Th(C_2O_4)_2$		-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	4.29E-04	0.00E+00
Total g	3.45E+08	0.00E+00	5.21E+07	0.00E+00	3.05E+09	1.63E+07	9.39E+06	3.68E+08	1.84E+06
Volume, gal	85279.01	-	9000.003	-	800,000	4136.593	863.4177	89443.95	81.58614
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

(continued)

(Continuation of Table 7-9)

	8	9	10	11	12	13a	13b	14	15	16
Stream	RTsupernate	Evaporator Feed	Evaporator Concentrate	Dissolution Water	Dissolved Salt	RTsolids	RTsolids	Washed Sludge	Decant/Wash Water	Feed Tank Sludge
Phase	Aqueous	-	-	-	-	Aqueous	Solid	-	-	-
Temperature, C	30	-	-	-	-	30	30	-	-	-
pH	12.6632	-	-	12	-	12.6632		-	-	-
Total mol	10365200	-	-	-	-	10294200	317721	-	-	-
Flow 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	7.96E-02	7.20E-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	-	0.00E+00	-
$CaCO_3$	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	-	0.00E+00	-
$Ce_2(C_2O_4)_3$	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	-	0.00E+00	-
$Fe(OH)_3$	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	-
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	-	0.00E+00	-
$Mn(OH)_2$	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	-	0.00E+00	-
$Ni(OH)_2$	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	-	0.00E+00	-
UO_2OH_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	-
$Th(C_2O_4)_2$	0.00E+00	-	-	0.00E+00	-	0.00E+00	0.00E+00	-	0.00E+00	-
Total g	1.93E+08	1.23E+06	1.23E+06	8.39E+09	-	1.91E+08	3.83E+07	3.69E+08	3.77E+08	7.38E+06
Volume, gal	49317.25	-	-	2,200,000	3,200,000	48979.9	850.6423	552,000	1,377,000	-
Enthalpy, cal	-7.20E+11	-	-	-	-	-7.15E+11	-9.62E+10	-	-	-
Density, g/gal	3.91E+03	-	-	3817.8	-	3.91E+03	4.50E+04	-	-	-

Table 7-10 Material Balance for Case 4 (Tank 11 HM Neutralized with Supernate)

	1	2	3	4	5	6a	6b	7a	7b
Stream	Oxalic Acid	Dilution Water	Supernate	Slurry Water	Wash Water	sludge heel	sludge heel	TTslurry	TTslurry
Phase	Aqueous	-	Aqueous	-		Aqueous	Solid	Aqueous	Solid
Temperature, C	30	Aqueous	30	Aqueous	Aqueous	30	30	30	30
pH	0.738632	-		-		11.5886		1.39017	
Total mol	1.79E+07	0.00E+00	1.32E+07	0.00E+00	0.00E+00	870546	103816	1.89E+07	13964.8
Flow Units	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac
H_2O	0.9199997	-	6.79E-01	-	9.76E-01	9.40E-01	0.00E+00	9.10E-01	0.00E+00
$H_2C_2O_4$	0.0800003	-	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	8.66E-05	0.00E+00
HNO_3		-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	5.14E-04	0.00E+00
Na_2CO_3		-	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	3.14E-03	0.00E+00	0.00E+00	0.00E+00
$NaNO_2$		-	3.11E-02	-	2.41E-02	0.00E+00	0.00E+00	0.00E+00	0.00E+00
$NaNO_3$		-	1.59E-01	-	0.00E+00	1.57E-02	0.00E+00	0.00E+00	0.00E+00
NaOH		-	7.62E-02	-	0.00E+00	1.74E-02	0.00E+00	0.00E+00	0.00E+00
Na_2SO_4		-	1.77E-02	-	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
$Na_2C_2O_4$		-	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	5.78E-01	0.00E+00	0.00E+00
AlOOH		-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	1.13E-02	0.00E+00
$NaAlO_2$		-	2.17E-02	-	0.00E+00	4.38E-05	0.00E+00	0.00E+00	0.00E+00
CaC_2O_4		-	0.00E+00	-	0.00E+00	4.88E-05	1.64E-02	3.96E-05	2.13E-01
$CaCO_3$		-	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	4.33E-05	0.00E+00	0.00E+00	0.00E+00
Ce_2O_3		-	0.00E+00	-	0.00E+00	2.69E-03	0.00E+00	0.00E+00	0.00E+00
$Ce_2(C_2O_4)_3$		-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	6.07E-05	2.44E-02
$Fe_2(C_2O_4)_3$		-	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	9.59E-07	2.49E-01	0.00E+00	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		-	7.46E-04	-	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
MnC_2O_4		-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	2.79E-04	4.84E-01
$MnOH_2$		-	0.00E+00	-	0.00E+00	1.03E-07	5.76E-02	0.00E+00	0.00E+00
NiC_2O_4		-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	5.11E-05	9.10E-02
$Ni(OH)_2$		-	0.00E+00	-	0.00E+00	4.53E-09	1.10E-02	0.00E+00	0.00E+00
SiO_2		-	0.00E+00	-	0.00E+00	2.04E-02	0.00E+00	1.02E-04	1.88E-01
$UO_2C_2O_4$		-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	8.99E-04	0.00E+00
UO_2OH_2		-	0.00E+00	-	0.00E+00	2.69E-07	3.01E-02	0.00E+00	0.00E+00
ThO_2		-	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	3.86E-05	3.01E-02	7.63E-04	0.00E+00
$Th(C_2O_4)_2$		-	0.00E+00	-	0.00E+00	0.00E+00	0.00E+00	4.29E-04	0.00E+00
Total g	3.45E+08	0.00E+00	3.09E+08	0.00E+00	3.05E+09	1.72E+07	9.39E+06	3.68E+08	1.84E+06
Volume, gal	85279.01	-	65499.91	-	800,000	4.14E+03	8.63E+02	8.94E+04	81.58508
Enthalpy, cal	-1.26E+12	-	-9.80E+11	-	-	-6.07E+10	-2.84E+10	-1.35E+12	-4.53E+09
Density, g/gal	4040.282	-	4721.277	-	-	3.95E+03	1.09E+04	4.12E+03	22612.79

(continued)

(Continuation of Table 7-10)

	8	9	10	11	12	13a	13b	14	15	16
Stream	RTsupernate	Evaporator Feed	Evaporator Concentrate	Dissolution Water	Dissolved Salt	RTsolids	RTsolids	Washed Sludge	Decant/Wash Water	Feed Tank Sludge
Phase	Aqueous	-	-	-	-	Aqueous	Solid	-	-	-
Temperature, C	30	-	-	-	-	30	30	-	-	-
pH	12.7833	-	-	12	-	12.7833		-	-	-
Total mol	1.85E+07	-	-	-	-	1.31E+07	454647	-	-	-
Flow Units	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac	wtfrac
H_2O	8.78E-01	-	-	9.99E-01	-	8.71E-01	0.00E+00	-	7.63E-02	-
$H_2C_2O_4$	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	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	-
$NaNO_2$	1.53E-02	-	-	7.50E-04	-	1.53E-02	0.00E+00	-	7.63E-02	-
$NaNO_3$	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	-
$Na_2C_2O_4$	5.44E-03	1.00E+00	1.00E+00	0.00E+00	0.00E+00	5.42E-03	7.11E-01	1.00E-01	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	-
$NaAlO_2$	7.53E-04	-	-	0.00E+00	-	7.50E-04	0.00E+00	-	7.59E-03	-
CaC_2O_4	2.24E-06	-	-	0.00E+00	-	2.23E-06	6.73E-03	-	0.00E+00	-
$CaCO_3$	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	7.03E-05	-	-	0.00E+00	-	6.99E-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	-
$Fe_2(C_2O_4)_3$	3.09E-05	-	-	0.00E+00	-	3.08E-05	0.00E+00	-	0.00E+00	-
$Fe(OH)_3$	0.00E+00	-	-	0.00E+00	-	0.00E+00	4.47E-02	-	0.00E+00	-
$K_2C_2O_4$	5.44E-04	-	-	0.00E+00	-	5.42E-04	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	1.92E-07	-	-	0.00E+00	-	1.91E-07	0.00E+00	-	0.00E+00	-
$MnOH_2$	0.00E+00	-	-	0.00E+00	-	0.00E+00	1.04E-02	-	0.00E+00	-
NiC_2O_4	1.15E-07	-	-	0.00E+00	-	1.15E-07	0.00E+00	-	0.00E+00	-
$Ni(OH)_2$	0.00E+00	-	-	0.00E+00	-	0.00E+00	1.97E-03	-	0.00E+00	-
SiO_2	5.32E-04	-	-	0.00E+00	-	5.29E-04	0.00E+00	-	0.00E+00	-
$UO_2C_2O_4$	5.30E-04	-	-	0.00E+00	-	5.28E-04	0.00E+00	-	0.00E+00	-
UO_2OH_2	0.00E+00	-	-	0.00E+00	-	0.00E+00	0.00E+00	-	0.00E+00	-
THO_2	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	-
$Th(C_2O_4)_2$	0.00E+00	-	-	0.00E+00	-	0.00E+00	0.00E+00	-	0.00E+00	-
Total g	3.67E+08	9.90E+05	9.90E+05	8.39E+09	-	2.60E+08	5.21E+07	3.69E+08	3.77E+08	3.90E+06
Volume, gal	89272.5	-	-	2,200,000	3,200,000	63281.39	1515.492	552,000	1,377,000	-
Enthalpy, cal	-1.29E+12	-	-	-	-	-9.14E+11	-1.39E+11	-	-	-
Density, g/gal	4113	-	-	3817.8	-	4113	34348.81	-	-	-

7.5 Sludge Washing

For this material balance, sludge batch 4 is used for an example. 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 less than 1.0 M. Assuming the same target is acceptable; the effect on sludge washing is shown in Table 7-11. Nearly all of the added sodium oxalate from one dissolved heel will be washed out of the sludge batch.

With no changes to the sludged 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 final planned wash. The total sodium concentration would be approximately 1.0 M. At this hypothesized maximum capacity, the total oxalate in the sludge batch would be about 23,000 kg. This translates to 4.7 wt% of total solids. Among the cases examined, 2 to 3 dissolved heels 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 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 other metal oxalates formed from dissolution of the heel. The final sodium oxalate from one heel dissolution from case 4 would equate to 7.3 wt%. The sodium concentration in solution would still be about 1.0 M, but the total sodium in the slurry would increase substantially, by about 13,200 kg.

Thermodynamically, the formation of iron, manganese, and aluminium oxalates are favoured as observed in stream 13; however, the reaction occurs in solution. The concentrations of metals in solution are very small, and the oxalate is sparingly soluble, so that the driving potential for the reaction is low. In other words, the rate of reaction will be very slow. The 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 sodium concentration will remain unchanged.

Table 7-11 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
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)	22,000	15,900	9,490	-	-	-	
Sodium Oxalate in Solution (kg)	1,010	3,450	5,140	7,600	4,570	3,790	
Total (kg)	23,000	19,400	14,600	7,600	4,570	3,790	19,200
Concentration Sodium Oxalate (M)		0.0203	0.0268	0.0396	0.0239	0.0199	
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	
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	

7.6 Tank Farm Evaporation

The material balance is calculated using expected starting conditions based on assumed current process parameters. Table 7-12 shows the feed tank initial feed tank composition. Table 7-13 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 1,000 to 1,200 kg move from the feed tank to the drop tank during the simulated 3,000 hours of operation. Table 7-14 and Table 7-15 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 practically does not change. The concentration in the aqueous phase decreases due to the increase in total sodium concentration or ionic strength. Additionally, 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 tank, the remaining oxalate will eventually be deposited into the drop tank. The bottom of the feed tank, however, contains a sludge layer. When the precipitated sodium oxalate settles into the sludge layer, the sludge will tend to inhibit further dissolution by coating the solids, thus, slowing the effective transfer from the feed tank to the drop tank.

If the stream 8 is added to the evaporator drop tank, practically all the sodium oxalate will remain with the saltcake. The high sodium concentration perpetually present in the drop tank will cause nearly all the oxalate to precipitate.

Table 7-12 Evaporator Feed Tank Initial Composition

Chemical Compound	Feed Tank (M)
$NaNO_3$	1.82
$Na_2CO_3{\cdot}H_2O$	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 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 be moved back to the sludge wash tank when the appropriate sludge batch calls for the feed tank sludge. A large portion will return to the feed tank via the sludge washing process as discussed in Section 7.5.

As noted earlier, if more than 2 or 3 heel dissolutions are accumulated in the evaporator feed tank, (i.e., 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 60,000 kg will tend to remain in the feed tank until eventual heel removal in the feed tank.

Table 7-13 Sodium Oxalate Balance for the Evaporator

Location	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	-

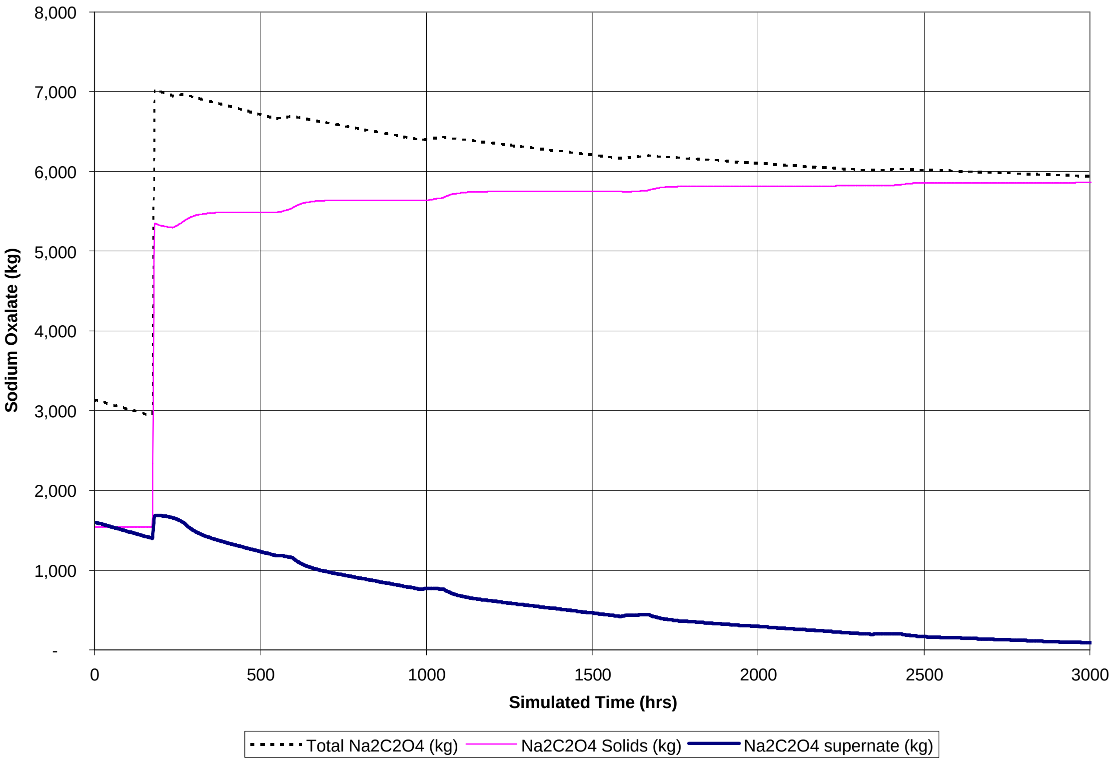


Figure7-3 Sodium Oxalate in Evaporator Feed Tank with Stream 8 Added to the Feed Tank for Case 2

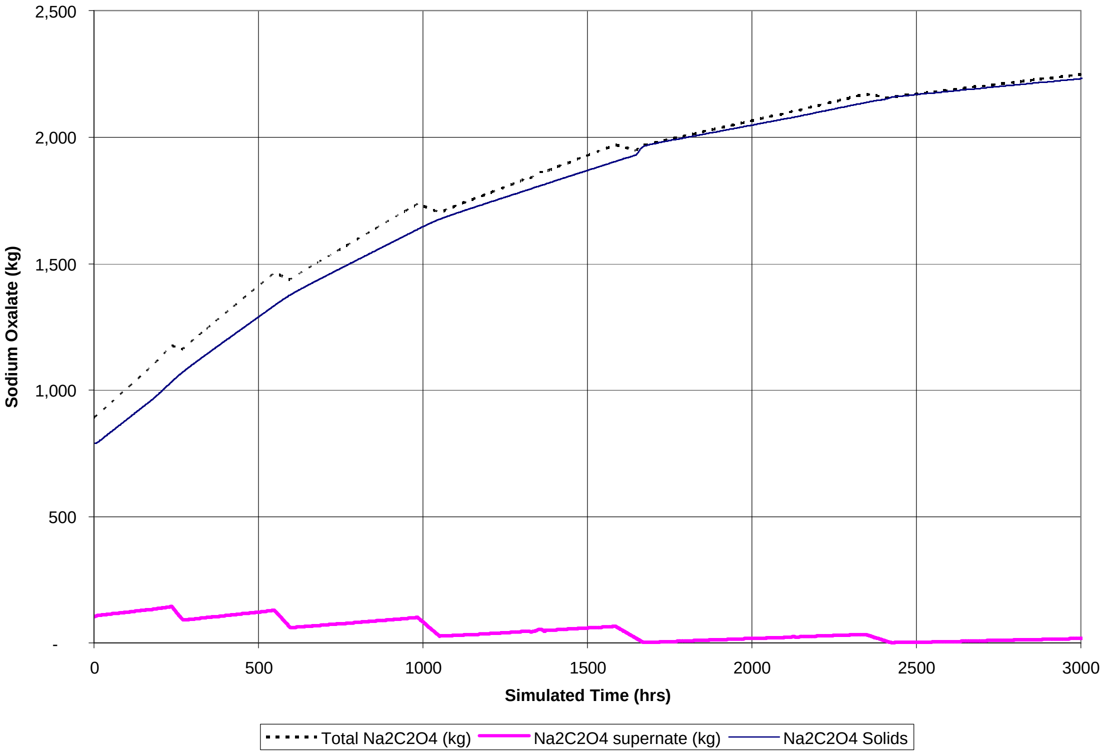


Figure 7-4 Sodium Oxalate in Evaporator Drop Tank with Stream 8 Added to the Feed Tank for Case 2

7.7 Salt Dissolution

About 2.2 gallons 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 as shown in Equation 7-1.

$$\text{Maximum}[\text{Na}_2\text{C}_2\text{O}_4] = \text{T} \cdot \left(0.00159 \cdot \text{I}^{-1.444}\right) + \left(0.0723 \cdot \text{I}^{-1.424}\right) \qquad \text{(Eq. 7-1)}$$

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. 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 certain tanks with existing saltcake at low oxalate content, sodium oxalate could be added to the saltcake with no impact to the residual. Refer to Table 7-14.

Table 7-14 Average Saltcake Composition

Chemical Compound	Saltcake (wt%)
$NaNO_3$	86
$Na_2CO_3.H_2O$	5.7
$NaNO_2$	0.82
$NaAlO_2 \cdot 2H_2O$	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

7.8 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. There are no existing plans will remove solid heels after bulk salt removal. The planned ARP/MCU or the SWPF 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 assumed to be well within the Waste Acceptance Criteria (WAC) for the saltstone facility.

7.9 Vitrification

SRNL studied the effect of substantial sodium oxalate in sludge batch 3 on the Defence Waste Processing Facility (DWPF) vitrification process. The tests were completed for sodium oxalate at 2.96, 5.74, 8.37 and 13.21 wt% of total solids. These studies show the DWPF Sludge Receipt and Adjustment Tank (SRAT) is affected as follows.

- Negligible amounts of iron and gadolinium become soluble with sodium oxalate at 5.74 wt% of total solids
- Iron becomes 10 times more soluble when sodium oxalate increases to 8.37 wt% or 13.21 wt% of total solids.
- Gadolinium becomes completely soluble at 13.21 wt% sodium oxalate
- Sodium oxalate mitigates the release of hydrogen.

- More acid is required for 5.74 wt% or higher sodium oxalate to complete nitrite destruction, which implies slightly longer cycle times for the SRAT.

If the sodium oxalate content is kept < 6 wt%, solubility of iron and gadolinium is kept low enough to be negligibly affected. This amounts to about 150,000 kg of sodium oxalate being acceptable in sludge batch 3.

Glass processing studies to determine acceptability of sludge batch 3, with elevated sodium oxalate concentrations, shows mixed results. The process is highly influenced by the choice of the glass frit used to vitrify the waste. The study demonstrates a 5% increase in the number of canisters with moderate sodium oxalate content of about 3 wt% verses no sodium oxalate. The additional sodium in the sludge slurry is offset by the slightly higher waste loading. At nearly 6 wt% sodium oxalate, the frit formulation must be changed to remain acceptable with no practical change in canisters produced due to increased waste loading. A 8.37 wt% sodium oxalate represents 50% more oxalate than 5.74 wt% and results in 28% increase in canisters. Using sludge batch 4 for an example, a 28% increase would change the net canisters predicted from 505 canisters to 646. This estimate is only a guide to the magnitude of the change. A specific frit optimization study and batch qualification analysis will identify more precise effects. In order to process higher sodium oxalate concentrations, new frit formulations would need to be implemented. Refer to Table 7-15.

Table 7-15 Effect of Sodium Oxalate in Sludge Batch 3 on Production at DWPF

Sodium Oxalate (wt%)	Frit	Limitation	% Waste Oxide Loading (Includes Oxalate)	Canisters Produced	Notes
0	320	Liquidus	36.5	560	
0	202	High Viscosity			No acceptable blend
2.96	320	Low Viscosity	38.1	589	
2.96	202	High Viscosity	31.5	712	Frit 320 is better when most of the oxalate has been removed.
5.74	320	Durability			No acceptable blend
5.74	202	Liquidus	44.2	553	
8.37	202	Durability	37.0	714	
10.86	202	Durability			No acceptable blend

- All residual transfers to the drop tank, including any sludge washing decants, will result in a large salt heel after bulk salt removal that consists mostly of sodium oxalate. A process needs to be developed to treat/remove the heel.

- Planned salt dissolution will send no more than 14,000 kg of dissolved sodium oxalate per 1,000,000 gallons of saltcake to the salt waste processing and eventually to the Saltstone Facility.

7.10 Effect on Waste Processing and Recommended Flowsheet

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

7.10.1 Neutralized Supernate

The neutralized supernate will eventually be sent to the evaporator system. The liquid may be sent to either the evaporator feed or drop tank. If this liquid is sent to the evaporator feed tank, most of the sodium oxalate will precipitate and remain in the feed tank, as shown in Section 7.6. Effectively, the sodium oxalate will build up in the sludge layer of the feed tank. This 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 need to 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 as additional saltstone. This is discussed in Section 7.7. The additional amount of sodium oxalate in the feed stream to the Saltstone Facility 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.

7.10.2 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 7.5. 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 7.8.

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.

7.10.3 Recommended Process Flowsheet

Figure 7-5 shows the process flow sheet after including the preferred process choices discussed above. Note that the amount of oxalic acid recommended for use in this process is expected to achieve complete dissolution of all reactive sludge species with a 100% molar excess. For a 5,000 gallon F-Area sludge heel, 65,000 gallons of 8 wt% acid is used and 85,000 gallons for a 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 Section 7.5.

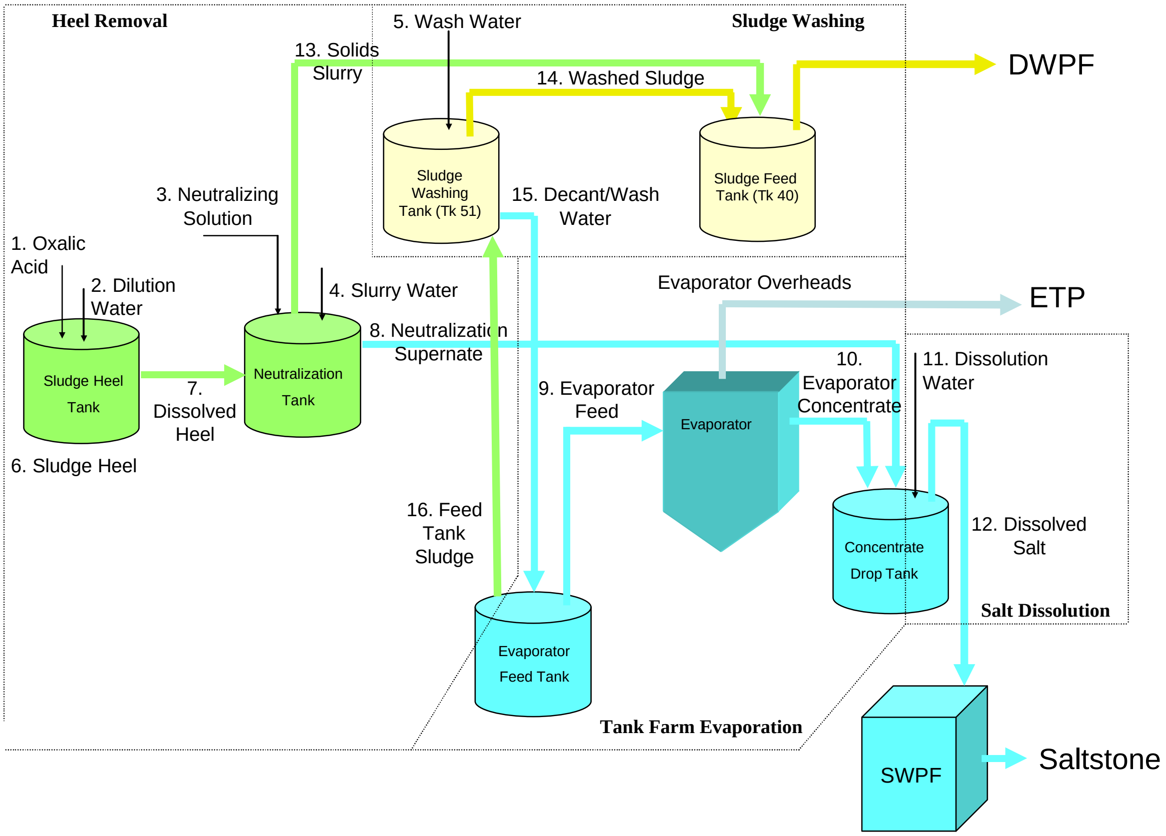


Figure 7-5 Recommended Heel Removal Flow Diagram

7.11 Model vs. Historical Experience of Cleaning Tank 16

In order to ensure flow sheet and model validation, historical data from oxalic acid cleaning of Tank 16 is compared to a model of the acid cleaning process. Table 7-16 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 7-17. Table 7-18 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 7-18 highlights one important aspect about using equilibrium models to forecast dissolution results; that is, the model forecasts 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 aluminium 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 7.2 shows that OLI ESP© has a predilection to under-predict solubility, the forecasted concentrations are adequate when compared to field measured data. This is consistent with the overall determination of the Chapter 4 validation.

Table 7-16 Sequence of Events for Tank 16 Acid Cleaning

Acid Wash Cycle 1
3,500 gallon heel to treat with oxalic acid
Sprayed about 37,000 gal of water at 90ºC 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 90ºC – 41,596 gallons total water added to tank
Slurry pumps started when pump volutes became submerged
Agitate for 2 days
22,937 gallons seal water from pumps added to tanks – total water added
Transfer to Tank 21, 4,503 gallons 50% wt% NaOH added to HPT-4 to neutralize > pH 12
3,500 gallon heel remained after transfer
Acid Wash Cycle 2
Sprayed 41,000 gal of water at 90°C through Riser 1
Sprayed 1,800-2,000 gallons of 4 wt% oxalic acid at 90°C through each of 5 spray risers – 9,865 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 wt% NaOH added to HPT-4 to neutralize > pH 12
2,800 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 5,797 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 wt% 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 hematite (Fe_2O_3) and boehmite ($Al_3O_3\ H_2O$)", but not quantified.

Table 7-17 Tank 16 Sludge Composition

Constituent	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	100*

Does not add to 100% because of rounding

Table 7-18 Comparison of Measured Values and Heel Dissolution Model Results

			Concentration in Aqueous Phase								Total Concentration in Slurry		
	density (kg/L)	Vol % solids	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

7.10 Conclusion on Processability Impacts

Sludge heel cleaning with oxalic acid essentially results in two streams that need to be dispositioned. The first is the neutralized supernate liquid stream, and the second is the sludge with the precipitated metal oxalate solids slurry stream. The preferred flow sheet calls for the supernate 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 flowsheets Case 2 and Case 4 include recommended amount of oxalic acid based on sludge stream composition.

Based on the preferred flow sheet 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.
- Glass quality limits the total amount of sodium in a batch without increasing 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 without further studies is 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 5,000 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.
- 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.

CHAPTER 8

SENSITIVITY ANALYSIS

8.1 Introduction to Sensitivity

A sensitivity analysis varies model input parameters over a reasonable range (range of uncertainty in values of model parameters) and observes the relative change in model results. The purpose of the sensitivity analysis is to demonstrate the sensitivity of the model simulations to uncertainty in input. Forecasts based on an insensitive model, will show similar outcomes regardless of variations in the input, and hence, have a predictable outcome. Alternately, sensitive models will have a less predictable outcome.

The defined processing flowpath from Chapter 7 is summarized in Figure 8-1.

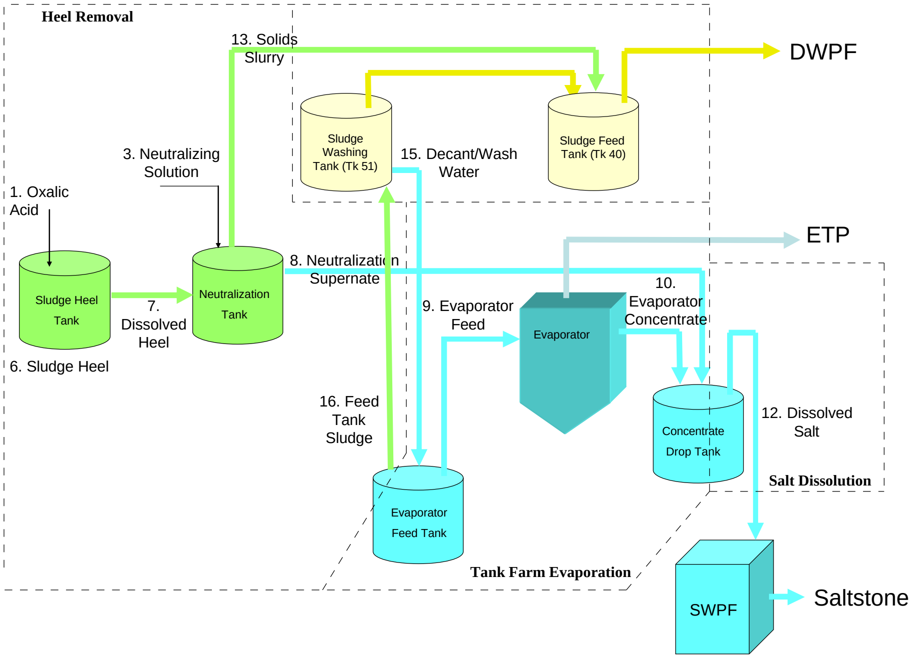


Figure 8-1 Defined Flow Path Summery

For both Purex heel dissolution and HM heel dissolution, so as to maximize the available HLW tank space, readily available supernate will be used to neutralize the spent oxalic acid. To help ensure sodium oxalate solids do not build up within the system, the precipitated solids (stream 13) will be added to a washed sludge batch, while the neutralized supernate (stream 8) will be added to the drop tank.

The defined material balance for the Tank 8 Purex sludge heel dissolution is considered to be mathematically presented in Table 7-8, while for the Tank 11 HM case, the defined processing plan is presented in Table 7-10. Table 8-1 and Table 8-2 summarize Table 7-8 and 7-10, and show where variability/sensitivity can be addressed.

Table 8-1 Defined Purex Heel Dissolution Flowpath for Tank 8 Sludge Heel

	1	6a	6b	3	7a	7b	8
Stream Name	Oxalic Acid	Sludge Heel	Sludge Heel	Neutralization Solution	Dissolved Heel	Dissolved Heel	Neutralized Supernate
OLI Stream	Oxalic Acid	Sludge Heel	Sludge Heel	Supernate	TT Slurry	TT Slurry	Supernate
Phase	Aqueous	Aqueous	Solid	Aqueous	Aqueous	Solid	Aqueous
Temperature(°C)	30	30	30	30	30	30	30
Total mol	13.7E+6	909.3E+3	89.0E+3	9.9E+6	14.8E+6	17.8E+3	13.9E+6
Flow Units	kg	kg	kg	kg	kg	kg	kg
H_2O	242.9E+3	15.9E+3	000.0E+0	157.0E+3	262.4E+3	000.0E+0	243.2E+3
$H_2C_2O_4$	21.1E+3	000.0E+0	000.0E+0	000.0E+0	11.5E+3	000.0E+0	000.0E+0
HCL	000.0E+0	000.0E+0	000.0E+0	000.0E+0	131.9E+0	000.0E+0	000.0E+0
HNO_3	000.0E+0	000.0E+0	000.0E+0	000.0E+0	137.1E+0	000.0E+0	000.0E+0
Na_2CO_3	000.0E+0	5.9E+0	000.0E+0	46.6E+0	616.3E+0	000.0E+0	2.2E+3
NaCl	000.0E+0	211.6E+0	000.0E+0	000.0E+0	000.0E+0	000.0E+0	122.4E+0
$NaNO_2$	000.0E+0	000.0E+0	000.0E+0	7.2E+3	000.0E+0	000.0E+0	4.2E+3
$NaNO_3$	000.0E+0	185.8E+0	000.0E+0	36.7E+3	000.0E+0	000.0E+0	21.3E+3
NaOH	000.0E+0	591.7E+0	000.0E+0	17.6E+3	000.0E+0	000.0E+0	1.2E+3
Na_2SO_4	000.0E+0	000.0E+0	000.0E+0	4.1E+3	000.0E+0	000.0E+0	2.4E+3
$Na_2C_2O_4$	000.0E+0	000.0E+0	000.0E+0	000.0E+0	1.3E+3	000.0E+0	1.4E+3
$Al(OH)_3$	000.0E+0	000.0E+0	14.3E+3	000.0E+0	000.0E+0	000.0E+0	000.0E+0
AlOOH	000.0E+0	000.0E+0	000.0E+0	000.0E+0	1.1E+3	000.0E+0	000.0E+0
$NaAlO_2$	000.0E+0	56.6E+0	000.0E+0	50.1E+3	000.0E+0	000.0E+0	214.4E+0
CaC_2O_4	000.0E+0	000.0E+0	000.0E+0	000.0E+0	117.5E+0	714.0E+0	595.6E-3
$CaCO_3$	000.0E+0	000.0E+0	579.0E+0	000.0E+0	000.0E+0	000.0E+0	000.0E+0
$Ca(OH)_2$	000.0E+0	4.1E+0	000.0E+0	000.0E+0	000.0E+0	000.0E+0	000.0E+0
Ce_2O_3	000.0E+0	22.7E+0	000.0E+0	000.0E+0	000.0E+0	000.0E+0	13.2E+0
$Ce_2(C_2O_4)_3$	000.0E+0	000.0E+0	000.0E+0	000.0E+0	10.8E+0	23.1E+0	000.0E+0
$Fe_2(C_2O_4)_3$	000.0E+0	000.0E+0	000.0E+0	000.0E+0	9.5E+3	000.0E+0	8.8E+0
$Fe(OH)_3$	000.0E+0	1.3E+0	5.4E+3	000.0E+0	000.0E+0	000.0E+0	000.0E+0
$K_2C_2O_4$	000.0E+0	000.0E+0	000.0E+0	000.0E+0	000.0E+0	000.0E+0	147.1E+0
KOH	000.0E+0	000.0E+0	000.0E+0	176.5E+0	000.0E+0	000.0E+0	000.0E+0
MnC_2O_4	000.0E+0	000.0E+0	000.0E+0	000.0E+0	131.0E+0	867.0E+0	54.8E-3
$Mn(OH)_2$	000.0E+0	15.2E-3	557.5E+0	000.0E+0	000.0E+0	000.0E+0	000.0E+0
NiC_2O_4	000.0E+0	000.0E+0	000.0E+0	000.0E+0	16.4E+0	742.1E+0	32.7E-3
$Ni(OH)_2$	000.0E+0	5.3E-3	425.4E+0	000.0E+0	000.0E+0	000.0E+0	000.0E+0
SiO_2	000.0E+0	211.6E+0	000.0E+0	000.0E+0	32.3E+0	204.0E+0	122.4E+0
$UO_2C_2O_4$	000.0E+0	000.0E+0	000.0E+0	000.0E+0	1.1E+3	000.0E+0	631.6E+0
UO_2OH_2	000.0E+0	457.5E-6	929.5E+0	000.0E+0	000.0E+0	000.0E+0	000.0E+0
Total kg	264.0E+3	17.2E+3	9.4E+3	231.0E+3	288.0E+3	2.6E+3	277.0E+3

(Continued)

Table 8-1 Continued

	9	10	11	12	13a	13b	14	15	16
Stream Name	Evap Feed	Evap Conc	Dissolution Water	Dissolved Salt	Solids Slurry	Solids Slurry	Washed Sludge	Decant Wash Water	Feed Tank Storage
OLI Stream					RT Solids	RT Solids			
Phase					Aqueous	Solid			
Temperature (°C)	3.00E+01	3.00E+01	3.00E+01	3.00E+01	3.00E+01	3.00E+01	3.00E+01	3.00E+01	
Total mol			1.20E+01		1.03E+07	3.50E+05			
Flow Units	kg	kg	kg	kg	kg	kg	kg	kg	kg
H_2O			8.38E+06		1.78E+06	0.00E+00		3.05E+08	
$H_2C_2O_4$			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	
HNO_3			0.00E+00		0.00E+00	0.00E+00		0.00E+00	
Na_2CO_3			0.00E+00		1.65E+03	0.00E+00		3.77E+06	
NaCl			0.00E+00		8.96E+04	0.00E+00		9.05E+04	
$NaNO_2$			6.29E+03		3.04E+03	0.00E+00		2.88E+07	
$NaNO_3$			0.00E+00		1.56E+04	0.00E+00		2.63E+07	
NaOH			3.31E+03		2.37E+03	0.00E+00		6.64E+06	
Na_2SO_4			0.00E+00		1.73E+03	0.00E+00		1.14E+06	
$Na_2C_2O_4$	1.00E+00	1.00E+00	0.00E+00	0.00E+00	1.01E+03	2.77E+04	2.78E+04	2.89E+06	1.00E+00
$Al(OH)_3$			0.00E+00		0.00E+00	5.92E+03		0.00E+00	
AlOOH			0.00E+00		0.00E+00	0.00E+00		0.00E+00	
$NaAlO_2$			0.00E+00		1.57E+02	0.00E+00		2.86E+06	
CaC_2O_4			0.00E+00		4.37E+00	7.47E+02		0.00E+00	
$CaCO_3$			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	
Ce_2O_3			0.00E+00		9.63E+00	0.00E+00		0.00E+00	
$Ce_2(C_2O_4)_3$			0.00E+00		0.00E+00	0.00E+00		0.00E+00	
$Fe_2(C_2O_4)_3$			0.00E+00		6.45E+00	0.00E+00		0.00E+00	
$Fe(OH)_3$			0.00E+00		0.00E+00	5.47E+03		0.00E+00	
$K_2C_2O_4$			0.00E+00		1.08E+02	0.00E+00		0.00E+00	
KOH			0.00E+00		0.00E+00	0.00E+00		0.00E+00	
MnC_2O_4			0.00E+00		4.02E-02	0.00E+00		0.00E+00	
$Mn(OH)_2$			0.00E+00		0.00E+00	5.59E+02		0.00E+00	
NiC_2O_4			0.00E+00		3.81E-02	0.00E+00		0.00E+00	
$Ni(OH)_2$			0.00E+00		0.00E+00	4.24E+02		0.00E+00	
SiO_2			0.00E+00		8.96E+01	0.00E+00		0.00E+00	
$UO_2C_2O_4$			0.00E+00		4.61E+02	0.00E+00		0.00E+00	
UO_2OH_2			0.00E+00		0.00E+00	0.00E+00		0.00E+00	
Total kg	1.25E+03	1.25E+03	8.39E+06	3.20E+03	2.04E+05	4.08E+04	4.10E+05	3.77E+08	3.01E+03

Table 8-2 Defined HM Heel Dissolution Flowpath for Tank 11 Sludge Heel

	1	6a	6b	3	7a	7b	8
Stream Name	Oxalic Acid	Sludge Heel	Sludge Heel	Neutralization Solution	Dissolved Heel	Dissolved Heel	Neutralized Supernate
OLI Stream	Oxalic Acid	Sludge Heel	Sludge Heel	Supernate	TT Slurry	TT Slurry	Supernate
Phase	Aqueous	Aqueous	Solid	Aqueous	Aqueous	Solid	Aqueous
Temperature (°C)	30	30	30	30	30	30	30
Total mol	17.9E+3	909.3E+3	89.0E+3	9.9E+6	14.8E+6	17.8E+3	13.9E+6
Flow Units	kg	kg	kg		kg	kg	kg
H_2O	317.4E+3	16.2E+3	000.0E+0	207.3E+3	334.9E+3	000.0E+0	322.2E+3
$H_2C_2O_4$	27.6E+3	000.0E+0	000.0E+0	000.0E+0	23.1E+3	000.0E+0	000.0E+0
HCL	000.0E+0	000.0E+0	000.0E+0	000.0E+0	31.9E+0	000.0E+0	000.0E+0
HNO_3	000.0E+0	000.0E+0	000.0E+0	000.0E+0	189.2E+0	000.0E+0	000.0E+0
Na_2CO_3	000.0E+0	1.1E+0	000.0E+0	4.4E+3	162.3E+0	000.0E+0	2.7E+3
NaCl	000.0E+0	54.0E+0	000.0E+0	000.0E+0	000.0E+0	000.0E+0	30.0E+0
$NaNO_2$	000.0E+0	000.0E+0	000.0E+0	9.6E+3	000.0E+0	000.0E+0	5.6E+3
$NaNO_3$	000.0E+0	270.0E+0	000.0E+0	49.1E+3	000.0E+0	000.0E+0	29.0E+3
NaOH	000.0E+0	299.3E+0	000.0E+0	23.5E+3	000.0E+0	000.0E+0	1.5E+3
Na_2SO_4	000.0E+0	000.0E+0	000.0E+0	5.5E+3	000.0E+0	000.0E+0	3.2E+3
$Na_2C_2O_4$	000.0E+0	000.0E+0	000.0E+0	000.0E+0	644.0E+0	000.0E+0	2.0E+3
$Al(OH)_3$	000.0E+0	000.0E+0	5.4E+3	000.0E+0	000.0E+0	000.0E+0	000.0E+0
AlOOH	000.0E+0	000.0E+0	000.0E+0	000.0E+0	4.2E+3	000.0E+0	000.0E+0
$NaAlO_2$	000.0E+0	753.4E-3	000.0E+0	6.7E+3	000.0E+0	000.0E+0	276.4E+0
CaC_2O_4	000.0E+0	839.4E-3	154.0E+0	000.0E+0	18.0E+0	391.9E+0	822.1E-3
$CaCO_3$	000.0E+0	000.0E+0	153.1E+0	000.0E+0	14.6E+0	000.0E+0	000.0E+0
$Ca(OH)_2$	000.0E+0	744.8E-3	000.0E+0	000.0E+0	000.0E+0	000.0E+0	000.0E+0
Ce_2O_3	000.0E+0	46.3E+0	000.0E+0	000.0E+0	000.0E+0	000.0E+0	25.8E+0
$Ce_2(C_2O_4)_3$	000.0E+0	000.0E+0	000.0E+0	000.0E+0	000.0E+0	44.9E+0	000.0E+0
$Fe_2(C_2O_4)_3$	000.0E+0	000.0E+0	000.0E+0	000.0E+0	22.3E+0	000.0E+0	11.3E+0
$Fe(OH)_3$	000.0E+0	16.5E-3	2.3E+3	000.0E+0	4.1E+3	000.0E+0	000.0E+0
$K_2C_2O_4$	000.0E+0	000.0E+0	000.0E+0	000.0E+0	000.0E+0	000.0E+0	199.6E+0
KOH	000.0E+0	000.0E+0	000.0E+0	230.5E+0	000.0E+0	000.0E+0	000.0E+0
MnC_2O_4	000.0E+0	000.0E+0	000.0E+0	000.0E+0	102.7E+0	890.6E+0	70.5E-3
$Mn(OH)_2$	000.0E+0	1.8E-3	540.9E+0	000.0E+0	000.0E+0	000.0E+0	000.0E+0
NiC_2O_4	000.0E+0	000.0E+0	000.0E+0	000.0E+0	18.8E+0	167.4E+0	42.2E-3
$Ni(OH)_2$	000.0E+0	779.2E-12	103.3E+0	000.0E+0	000.0E+0	000.0E+0	000.0E+0
SiO_2	000.0E+0	350.9E+0	000.0E+0	000.0E+0	37.5E+0	345.9E+0	195.2E+0
$UO_2C_2O_4$	000.0E+0	000.0E+0	000.0E+0	000.0E+0	330.8E+0	000.0E+0	194.5E+0
UO_2OH_2	000.0E+0	4.6E-3	282.6E+0	000.0E+0	000.0E+0	000.0E+0	000.0E+0
ThO_2	000.0E+0	848.0E-12	103.3E+0	000.0E+0	000.0E+0	000.0E+0	13.6E-9
HgO	000.0E+0	663.9E-3	282.6E+0	000.0E+0	280.8E+0	000.0E+0	11.3E+0
$Th(C_2O_4)_2$	000.0E+0	000.0E+0	000.0E+0	000.0E+0	157.9E+0	000.0E+0	000.0E+0
Total kg	345.0E+3	17.2E+3	9.4E+3	309.0E+3	368.0E+3	1.8E+3	367.0E+3

Table 8-2 Continued

	9	10	11	12	13a	13b	14	15	16
Stream Name	Evap Feed	Evap Conc	Dissolution Water	Dissolved Salt	Solids Slurry	Solids Slurry	Washed Sludge	Decant Wash Water	Feed Tank Storage
OLI Stream					RT Solids	RT Solids			
Phase					Aqueous	Solid			
Temperature (°C)	30	30	30	30	30	30	30	30	
Total mol			1.20E+01		1.03E+07	3.50E+05			
Flow Units	kg	kg	kg	kg	kg	kg	kg	kg	kg
H_2O			8.38E+06		2.26E+05	0.00E+00		2.88E+07	
$H_2C_2O_4$			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	
HNO_3			0.00E+00		0.00E+00	0.00E+00		0.00E+00	
Na_2CO_3			0.00E+00		1.88E+03	0.00E+00		3.77E+06	
NaCl			0.00E+00		2.12E+01	0.00E+00		9.05E+04	
$NaNO_2$			6.29E+03		3.98E+03	0.00E+00		2.88E+07	
$NaNO_3$			0.00E+00		2.04E+04	0.00E+00		2.63E+07	
NaOH			3.31E+03		3.02E+03	0.00E+00		6.64E+06	
Na_2SO_4			0.00E+00		2.26E+03	0.00E+00		1.14E+06	
$Na_2C_2O_4$	1.00E+00	1.00E+00	0.00E+00	0.00E+00	1.41E+03	3.70E+04	1.00E-01	2.89E+06	1.00E+00
$Al(OH)_3$			0.00E+00		0.00E+00	1.14E+04		0.00E+00	
AlOOH			0.00E+00		0.00E+00	0.00E+00		0.00E+00	
$NaAlO_2$			0.00E+00		1.95E+02	0.00E+00		2.86E+06	
CaC_2O_4			0.00E+00		5.80E-01	3.51E+02		0.00E+00	
$CaCO_3$			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	
Ce_2O_3			0.00E+00		1.82E+01	0.00E+00		0.00E+00	
$Ce_2(C_2O_4)_3$			0.00E+00		0.00E+00	0.00E+00		0.00E+00	
$Fe_2(C_2O_4)_3$			0.00E+00		8.01E+00	0.00E+00		0.00E+00	
$Fe(OH)_3$			0.00E+00		0.00E+00	2.33E+03		0.00E+00	
$K_2C_2O_4$			0.00E+00		1.41E+02	0.00E+00		0.00E+00	
KOH			0.00E+00		0.00E+00	0.00E+00		0.00E+00	
MnC_2O_4			0.00E+00		4.97E-02	0.00E+00		0.00E+00	
$Mn(OH)_2$			0.00E+00		0.00E+00	5.42E+02		0.00E+00	
NiC_2O_4			0.00E+00		2.99E-02	0.00E+00		0.00E+00	
$Ni(OH)_2$			0.00E+00		0.00E+00	1.03E+02		0.00E+00	
SiO_2			0.00E+00		1.38E+02	0.00E+00		0.00E+00	
$UO_2C_2O_4$			0.00E+00		1.37E+02	0.00E+00		0.00E+00	
UO_2OH_2			0.00E+00		0.00E+00	0.00E+00		0.00E+00	
ThO_2			0.00E+00		9.62E+00	1.03E+02			
HgO			0.00E+00		7.96E+00	2.64E+02			
$Th(C_2O_4)_2$			0.00E+00		2.26E+06	0.00E+00			
Total kg	9.90E+02	9.90E+02	8.39E+06		2.60E+05	5.21E+04	3.69E+05	3.77E+08	3.90E+06

8.2 Sensitivity

As previously stated in Chapter 7, Tanks 1-9 have the same relative distribution, whereas the distributions in Tanks 10-15 vary. Using the OLI Stream Analyzer© and OLI ESP© survey functions, a sensitivity analyses was performed for single constituents using a minimum of ten intervals of varying applicable increments. Table 8-3 shows modelled Purex Sludge dissolution sensitivity to individual variations in sludge constituents.

Table 8-3 Sensitivity of Dissolution to Purex Sludge Slurry Variations

Constituent	Baseline Mass (kg/ 5K gallon Heel)	± • Baseline Mass (kg) ±• Remaining Total Solids Mass(kg)	Visual Constant Linear Range (kg)
$Al(OH)_3$	1,430	100 / 6.7	1,000-2,000
$Fe(OH)_3$	5,444	100:/ 5.7	1,000-8,000
$Mn(OH)_2$	558	100 /181	200-700
$Ni(OH)_2$	425	100 / 193	100-600
$UO2(OH)_2$	929.5	100 / 1.5	700-1,200
SiO2	211.6	100 / 94	150-250
$CaCO_3$	579	100 / 294	200-700
Ce_2O_3	22.7	100 / 57	15-30

Based on Table 8-3 changes in carbonate mass have the biggest impact on Purex sludge dissolution, while dissolution is not as sensitive to small mass changes in $Al(OH)_3$ and $Fe(OH)_3$. Table 8-4 shows the variation in HM Sludge dissolution based on changes to individual constituent mass.

Table 8-4 Sensitivity of Dissolution to HM Sludge Slurry Variations

Constant	Baseline Mass (kg/ 5K gallon Heel)	± • Constituent Mass (kg) ±• Remaining Total Solids Mass(kg)	Visual Constant Linear Range (kg)
$Al(OH)_3$	5,521	100 / 0.8.	3,000-6,000
$Fe(OH)_3$	2,385	100 / 0.8	1,000-3,000
$Mn(OH)_2$	549	100 / 184	200-700
$Ni(OH)_2$	104.2	100 /192	75-150
$UO_2(OH)_2$	287.3	100 / 4	200-350
SiO_2	332.5	100 / 91	300-400
$CaCO_3$	579	100 / 464	500-600
Ce_2O_3	115.9	100 / 50	75-150
$NaNO_3$	186	100 / 0	100-250
NaOH	225.9	100 / 12	125-225
ThO_2	104.2	100 / 0.1	NA
HgO	287.3	100 / 0	200-300

Based on Table 8-4 changes in carbonate mass also have the biggest impact on HM sludge dissolution, while $Al(OH)_3$ and $Fe(OH)_3$ appear to be among the least sensitive.

Using variations in quantities of oxalic acid and the 5,000 gallon Purex baseline characterization, the oxalic acid is varied and the remaining sludge heel is calculated in Table 8-5.

Table 8-5 Effect of Varying Oxalic Acid on Initial 5,000 Gallon Purex Sludge Heel Dissolution

Oxalic Acid (kg)	Strike Tank Solids Heel Remaining (kg)
5,000	7.81E+03
10,000	3.74E+03
15,000	2.65E+03
20,000	2.75E+03
25,000	2.79E+03
30,000	2.80E+03
35,000	2.80E+03
40,000	5.41E+03
45,000	1.28E+04
50,000	2.01E+04
55,000	2.74E+04
60,000	3.48E+04
65,000	4.21E+04
70,000	4.95E+04

In Table 8-5 we see that adding continual amounts of oxalic acid for Purex sludge dissolution will eventually cause excessive quantities of oxalate solids to form. For HM sludge dissolution, this is shown in Table 8-6.

Table 8-6 Effect of Varying Oxalic Acid on Initial 5,000 Gallon HM Sludge Heel Dissolution

Oxalic Acid (kg)	Strike Tank Solids Heel Remaining (Gallon)
5000	1.03E+04
10,000	4.84E+03
15,000	1.81E+03
20,000	1.94E+03
25,000	1.93E+03
30,000	1.91E+03
35,000	1.30E+04
40,000	2.91E+04
45,000	4.53E+04
50,000	1.03E+04
55,000	4.84E+04
60,000	1.81E+04
65,000	1.94E+04
70,000	1.93E+04

Based on the individual constituent variations in Table 8-3 and Table 8-4, the change in the neutralization tank sludge mass is shown in Table 8-7 and Table 8-8.

Table 8-7 Sensitivity of Precipitate Mass to Purex Sludge Slurry Variations

Constituent	Mass (kg/per 5K gallon Heel)	± Strike Tank Mass Variation (kg)	± Neutralization Tank Mass Variation (kg)
$Al(OH)_3$	1,430	100	109
$Fe(OH)_3$	5,444	100	102
$Mn(OH)_2$	558	100	125
$Ni(OH)_2$	425	100	138
$UO2(OH)_2$	929.5	100	6
SiO2	211.6	100	0.0
$CaCO_3$	579	100	240*
Ce_2O_3	22.7	100	18
$NaNO_3$	186	100	6
NaOH	592	100	1.4

Note: *Model does not account for the CO_2 that is expected to be given as a gas.

Table 8-8 Sensitivity of Precipitate Mass to HM Sludge Slurry Variations

Constituent	Mass (kg/per 5K gallon Heel)	± Strike Tank Mass Variation (kg)	± Neutralization Tank Mass Variation (kg)
$Al(OH)_3$	5,521	100	99
$Fe(OH)_3$	2,385	100	99
$Mn(OH)_2$	549	100	129
$Ni(OH)_2$	104.2	100	138
$UO_2(OH)_2$	287.3	100	6
SiO_2	332.5	100	NA
$CaCO_3$	579	100	414*
Ce_2O_3	115.9	100	28
$NaNO_3$	186	100	5
ThO_2	104.2	100	100
HgO	287.3	100	96

Note: *Model does not account for the CO_2 that is expected to be given as a gas.

From Table 8-7 and Table 8-8, it can be estimated that for every additional 100 kgs of metal added in the feed stream, roughly an additional 100 kgs of metal precipitate result and be fed to DWPF. Mn and Ni form hydrated solids; however, thereby increasing the total solids disproportionately.

Based on the variations in the amount of oxalic acid used, the impact to the neutralization tank is shown in Table 8-9 and Table 8-10.

Table 8-9 End Effect On Neutralization Tank of Varying Oxalic Acid in Purex Sludge Dissolution

Oxalic Acid Added (kg)	Supernate Added to System (Gallons)	Neutralization Tank Heel Solids(kg)
10,000	62,500	1.83E+04
15,000	125,000	2.58E+04
20,000	187,500	3.24E+04
25,000	250,000	3.41E+04
30,000	312,500	2.28E+04
35,000	375,000	2.46E+04
40,000	437,500	2.57E+04
45,000	500,000	2.57E+04
50,000	562,500	2.57E+04
55,000	625,000	2.57E+04
60,000	687,500	2.58E+04
65,000	750,000	2.58E+04
70,000	812,500	2.58E+04

Table 8-10 End Effect On Neutralization Tank of Varying Oxalic Acid in HM Sludge Dissolution

Oxalic Acid (kg)	Supernate Added to System (Gallons)	Neutralization Tank Heel Solids (kg)
10,000	62,500	1.76E+04
15,000	125,000	2.48E+04
20,000	187,500	3.12E+04
25,000	250,000	4.13E+04
30,000	312,500	4.35E+04
35,000	375,000	2.91E+04
40,000	437,500	2.91E+04
45,000	500,000	2.91E+04
50,000	562,500	2.91E+04
55,000	625,000	2.91E+04
60,000	687,500	2.92E+04
65,000	750,000	2.92E+04
70,000	812,500	2.92E+04

8.2 Conclusion About Sensitivity

Generally, variations in the quantity of metal oxides, will cause similar variations in the sludge feed to DWPF. Assuming adequate time has been allowed for all acid to react, adding more acid will not result in an additional amount of sludge dissolved, but will result in more solids. If significantly large amounts of excess acid is added, solids will begin to form in the strike tank, while there will be no visible increase in formed solids in the neutralization tank.

Overall, we can conclude that both the Purex and HM models are rather insensitive to single limited variations in constituent mass.

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APPENDICES

APPENDIX 1
PROOF-IN-PRINCIPLE

A1.1 Modelling Theory

The free energy relates the effects of the combination of heat, entropy, temperature, and pressure. Gibbs free energy also allows one to determine under what conditions the reaction will proceed, in what direction the reaction will occur, and the position of equilibrium. The free energy can be expressed as Equation A1-1.

$$G_i = G_i^o + RT(\bullet_i m) \qquad \text{(Eq. A1-1)}$$

Where:
- T = Temperature (Kelvin)
- R = Gas constant
- $\bullet_I$ = activity coefficient which captures departure from ideality
- m = concentration unit molarity

At equilibrium, when the reactants and products are at the same temperature and pressure, the sum of the free energy of the products equals the sum of the Gibbs Free Energy of the reactants. Refer to Equation A1-2.

$$\bullet\, \Delta G_{product} - \bullet\, \Delta G_{react} = 0 \qquad \text{(Eq. A1-2)}$$

The key to thermodynamic equilibrium is that the phases must be in equilibrium; that is, the species on the left-hand side of the reaction must be equal to the total Gibbs Free Energy on the right hand side of the reaction. Refer to Equation A1-3.

$$\Delta G_{right}=\Delta G_{left} \qquad \text{(Eq. A1-3)}$$

Knowing that the Gibbs Free Energies are equal enables the model to discern when the reaction reaches thermodynamic equilibrium. In this case, thermodynamic equilibriums and sludge dissolutions are considered to have the same starting and stopping points. By comparing the initial mass volume, therefore, to the original volume, we can determine the percent dissolved.

The OLI's© dissolution databank used is based upon published experimental solubility data. The software model uses data regression wherever possible, and only estimates and extrapolates as required when determining equilibrium. The software therefore provides general dissolution modelling capability for almost any aqueous chemical mixture entered into the databank within the temperature, pressure, and ionic strength range.

The databank contains thermodynamic, transport, and physical properties for 79 inorganic elements (including actinides, heavy, and precious metals) and their associated aqueous species. The databank also includes over 3000 organics (including electrolytes, chelates and organo-metallic species).

Accurate and reliable dissolution simulation is possible if solubility data exists for the chemical system. Since the primary sludge contents are of common industrial interest, most of the data is readily available. If commercial data is not adequate, but believed to be important, laboratory dissolution studies could be performed and added to the databank as necessary. Although for other reasons, the fact remains that several such research efforts are ongoing for secondary constituents.

A1.2 Comparisons with Literature

Although approved models have been constructed using OLI© for HLW salt dissolution models, the general potential validity of the OLI© software is initially tested using a proof in principle method. This test is for casual observers. This is necessary since many individuals not familiar with the OLI© software question the breadth of its database and its over-all acceptability. The purpose of the test is only to show potential acceptability as formal validation, sensitivity, and bounding analyses, and to ensure the applicability of this effort.

To perform the proof in principle, the calculated OLI Stream Analyzer© equilibrium constants (k_{sp} values) for manganese and iron are compared to referenced equilibrium constants found from literature (Badheka, 2003, p81). The first example considered is the dissolution of $Mn(OH)_2$, which is shown as Equation A1-4.

$$Mn(OH)_2 \bullet \quad Mn^{+2} + (OH)^{-1} \qquad \text{(Eq. A1-4)}$$

OLI predicts the pk_{sp} value as 1.4345E-13, where $k_{sp} = -\log(pk_{sp})$.

For the dissolution of $Mn(OH)_2$ in water,

$$K_{sp,Mn(OH)_2} = -\log(1.4345e-13)$$
$$K_{sp,Mn(OH)_2} = 12.8433$$

From Badheka (2003, p81), $Mn(OH)_2$ has a k_{sp} value of 12.72.
Another example is Iron(III) hydroxide, which from literature[9], has a k_{sp} value of 38.55. According to OLI Stream Analyzer, Iron(III) Hydroxide has a k_{sp} value of 37.5 which again is considered to be within reasonable limits.

For species that may have several complexes that are soluble in water, refer to Equation A1-5,

$pK_{sp} = pK_1 * pK_2 * pK_3 * pK_n$ (Eq. A1-5)

where K_1, K_2, K_3, and K_n are the equilibrium constants for each of the complexes, and K_n represents the equilibrium constant for the *nth* complex that is formed. An example is for $Al(OH)_3$. Refer to Equation A1-6 through A1-9.

$Al(OH)_3 \bullet \ Al^{3+} + (OH)^{-1}$ $k_1 = 2.0962\ e^{-9}$ (Eq. A1-6)
$Al(OH)_3 \bullet \ Al(OH)_2^{+1} + (OH)^{-1}$ $k_2 = 2.4768e^{-9}$ (Eq. A1-7)
$Al(OH)_3 \bullet \ Al(OH)^{2+} + (OH)_2^{-1}$ $k_3 = 1.0382e^{-9}$ (Eq. A1-8)
$Al(OH)_3 \bullet \ Al(OH)_4^{-1} + (OH)^{-1}$ $k_4 = 7.2826e^{-8}$ (Eq. A1-9)

Applying the equation for several species that are soluble to the complexes that $Al(OH)_3$ produces in water yields Equations A1-10 and A1-11.

$k_{sp} = 2.0962e^{-9}\ \text{x}\ 2.4768\ e^{-9}\ \text{x}\ 1.0382e^{-9}\ \text{x}\ 7.2826\ e^{-8}$ (Eq. A1-10)
$k_{sp} = 3.9255e^{-34}$ (Eq. A1-11)

From this, the k_{sp} value of $Al(OH)_3$ is 33.406. From Badheka (2003, p81) the solubility product constant is found to be 32.89, once again yielding close similarity in the values. Therefore, it is concluded that for the proof in principle tests, the software may provide adequate approximations for $k_{sp.}$

A1.3 Comparisons with Other Simulators

Literature (Barnes, 2002, p5) shows that a detailed comparison for the Aspen Plus© databank and the OLI© databank has been performed for SRS HLW as part of modelling concerns associated with the SRS evaporators. The results of the detailed comparison show that the forecasted behaviour of the metal oxides using either Aspen Plus© or OLI© are similar.

APPENDIX 2
VALIDATION MISCELLANEOUS

A2.1 Fate of the Metals

As shown in Chapter 4, the iron oxides will readily dissolve, while, aluminium, manganese, and nickel will not. To demonstrate the behaviour, using a 1-strike of a 50:1 volume ratio of 4 wt% oxalic acid to Purex simulant, Table A2-1, shows the fate of the iron, aluminium, manganese and nickel oxides.

Table A2-1 Fate of Four Metal Oxides in Purex Simulant Dissolution

Initial Compound	(% moles)	Final Compound	Aqueous (% moles)	Solid (% moles)
$Fe(OH)_3$	100	FeC_2O_4	100	0
$Al(OH)_3$	100	$Al(OH)_3$	0	23
		$AlO(OH)$	65	0
		$AlPO_4$	0	12
$Mn(OH)_2$	100	MnC_2O_4	4	0
		$MnC_2O_4.2H_2O$	0	96
$Ni(OH)_2$	100	NiC_2O_4	<1	>99

As noted, manganese and nickel form mostly insoluble oxalate compounds.

Table A2-2, shows the fate of the iron, aluminium, manganese and nickel oxides for a similar 1-strike of a 50:1 volume ratio of 4 wt% oxalic acid solution to HM simulant.

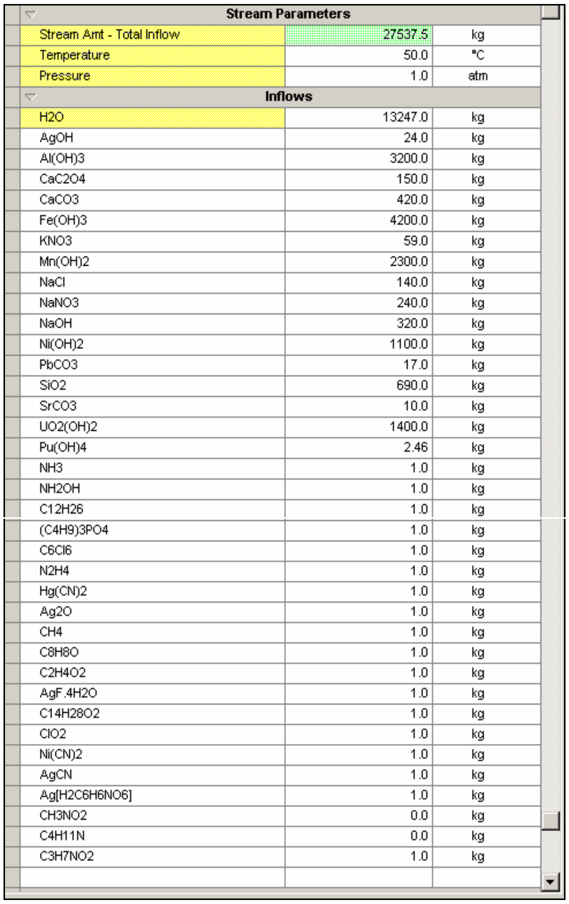
Table A2-2 Fate of Four Metal Oxides in HM Simulant Dissolution

Initial Compound	(% moles)	Final Compound	Aqueous (% moles)	Solid (% moles)
$Fe(OH)_3$	100	FeC_2O_4	100	0
$Al(OH)_3$	100	$Al(OH)_3$	0	40
		$AlO(OH)$	60	0
$Mn(OH)_2$	100	MnC_2O_4	45	0
		$MnC_2O_4.2H_2O$	0	55
$Ni(OH)_2$	100	NiC_2O_4	10	90

As noted, manganese and nickel form mostly insoluble oxalate compounds.

APPENDIX 3
SPIKED MATERIAL BALANCE

Figure A3-1 shows the input used in calculating the spiked material balance.



Stream Parameters		
Stream Amt - Total Inflow	27537.5	kg
Temperature	50.0	°C
Pressure	1.0	atm
Inflows		
H2O	13247.0	kg
AgOH	24.0	kg
Al(OH)3	3200.0	kg
CaC2O4	150.0	kg
CaCO3	420.0	kg
Fe(OH)3	4200.0	kg
KNO3	59.0	kg
Mn(OH)2	2300.0	kg
NaCl	140.0	kg
NaNO3	240.0	kg
NaOH	320.0	kg
Ni(OH)2	1100.0	kg
PbCO3	17.0	kg
SiO2	690.0	kg
SrCO3	10.0	kg
UO2(OH)2	1400.0	kg
Pu(OH)4	2.46	kg
NH3	1.0	kg
NH2OH	1.0	kg
C12H26	1.0	kg
(C4H9)3PO4	1.0	kg
C6Cl6	1.0	kg
N2H4	1.0	kg
Hg(CN)2	1.0	kg
Ag2O	1.0	kg
CH4	1.0	kg
C8H8O	1.0	kg
C2H4O2	1.0	kg
AgF.4H2O	1.0	kg
C14H28O2	1.0	kg
ClO2	1.0	kg
Ni(CN)2	1.0	kg
AgCN	1.0	kg
Ag[H2C6H6NO6]	1.0	kg
CH3NO2	0.0	kg
C4H11N	0.0	kg
C3H7NO2	1.0	kg

Figure A3-1 Input of Miscellaneous Chemicals and Organics into Spiked Material Balance

As an element balance, TableA3-1 shows the fate of the organics and other energetic chemicals added.

Table A3-1 Fate of Organics and Energetic Materials

First Strike						
	Spiked Aqueous % mol	**Spiked Vapour % mol**	**Spiked Solid % mol**	**Actual Aqueous % mol**	**Actual Vapour % mol**	**Actual Solid % mol**
AG(+1)	15.70%	0.00%	84.30%	0.31%	0.00%	99.69%
AL(+3)	46.63%	0.00%	53.37%	44.90%	0.00%	55.10%
C(+4)	71.41%	28.59%	0.00%	100.00%	0.00%	0.00%
C12H26	0.99%	99.01%	0.00%	0.00%	0.00%	0.00%
CA(+2)	42.98%	0.00%	57.02%	26.03%	0.00%	73.97%
CH4	10.98%	89.02%	0.00%	0.00%	0.00%	0.00%
CL(-1)	92.38%	0.00%	7.62%	92.00%	0.00%	8.00%
CL6BENZEN	100.00%	0.00%	0.00%	0.00%	0.00%	0.00%
CN(-1)	100.00%	0.00%	0.00%	0.00%	0.00%	0.00%
Cl(+4)	94.80%	5.20%	0.00%	0.00%	0.00%	0.00%
DLALANN(-1)	100.00%	0.00%	0.00%	0.00%	0.00%	0.00%
F(-1)	100.00%	0.00%	0.00%	0.00%	0.00%	0.00%
FE(+3)	100.00%	0.00%	0.00%	100.00%	0.00%	0.00%
H(+1)	99.05%	0.00%	0.95%	98.73%	0.00%	1.27%
HDROXAMN(0)	100.00%	0.00%	0.00%	0.00%	0.00%	0.00%
HG(+2)	100.00%	0.00%	0.00%	100.00%	0.00%	0.00%
K(+1)	100.00%	0.00%	0.00%	100.00%	0.00%	0.00%
MEFORMATE	97.21%	2.79%	0.00%	0.00%	0.00%	0.00%
MN(+2)	5.76%	0.00%	94.24%	4.00%	0.00%	96.00%
N(+5)	100.00%	0.00%	0.00%	100.00%	0.00%	0.00%
N(-2)	100.00%	0.00%	0.00%	0.00%	0.00%	0.00%
N(-3)	100.00%	0.00%	0.00%	0.00%	0.00%	0.00%
NA(+1)	100.00%	0.00%	0.00%	100.00%	0.00%	0.00%
NI(+2)	0.51%	0.00%	99.49%	0.27%	0.00%	99.73%
NTA(-3)	100.00%	0.00%	0.00%	0.00%	0.00%	0.00%
O(-2)	98.42%	0.03%	1.55%	98.09%	0.00%	1.91%
OXALAT(-2)	71.72%	0.00%	28.28%	70.09%	0.00%	29.91%
PB(+2)	98.89%	0.00%	1.11%	52.95%	0.00%	47.05%
Pu(+4)	3.17%	0.00%	96.83%	2.17%	0.00%	97.83%
SI(+4)	3.22%	0.00%	96.78%	2.46%	0.00%	97.54%
SR(+2)	100.00%	0.00%	0.00%	100.00%	0.00%	0.00%
STYRENOX	99.90%	0.10%	0.00%	0.00%	0.00%	0.00%
TBP	100.00%	0.00%	0.00%	0.00%	0.00%	0.00%
TEDEAC(-1)	100.00%	0.00%	0.00%	0.00%	0.00%	0.00%
U(+6)	94.28%	0.00%	5.72%	75.65%	0.00%	24.35%

(Continued)

(Continuation of Table A3-1)

Second Strike						
AG(+1)	1.60%	0.00%	98.40%	1.53%	0.00%	98.47%
AL(+3)	85.21%	0.00%	14.79%	82.47%	0.00%	17.53%
CA(+2)	0.01%	0.00%	99.99%	0.01%	0.00%	99.99%
CL(-1)	1.60%	0.00%	98.40%	1.53%	0.00%	98.47%
CL6BENZEN	0.01%	0.00%	99.99%			
H(+1)	96.41%	0.00%	3.59%	28.53%	0.00%	71.47%
MN(+2)	28.57%	0.00%	71.43%	0.07%	0.00%	99.93%
NI(+2)	0.07%	0.00%	99.93%	94.93%	0.00%	5.07%
O(-2)	95.04%	0.00%	4.96%	53.50%	0.00%	46.50%
OXALAT(-2)	53.53%	0.00%	46.47%	16.37%	0.00%	83.63%
PB(+2)	16.39%	0.00%	83.61%	100.00%	0.00%	0.00%
Pu(+4)	100.00%	0.00%	0.00%	0.40%	0.00%	99.60%
SI(+4)	0.40%	0.00%	99.60%	100.00%	0.00%	0.00%
U(+6)	100.00%	0.00%	0.00%	100.00%	0.00%	0.00%
Third Strike						
AG(+1)	0.66%	0.00%	99.34%	0.66%	0.00%	99.34%
AL(+3)	100.00%	0.00%	0.00%	100.00%	0.00%	0.00%
CA(+2)	0.01%	0.00%	99.99%	1.07%	0.00%	98.93%
CL(-1)	0.46%	0.00%	99.54%	0.66%	0.00%	99.34%
CL6BENZEN	0.66%	0.00%	99.34%	0.00%	0.00%	0.00%
H(+1)	94.93%	0.00%	5.07%	97.93%	0.00%	2.07%
MN(+2)	30.68%	0.00%	69.32%	0.65%	0.00%	99.35%
NI(+2)	0.03%	0.00%	99.97%	0.08%	0.00%	99.92%
O(-2)	94.03%	0.00%	5.97%	97.18%	0.00%	2.82%
OXALAT(-2)	42.68%	0.00%	57.32%	60.37%	0.00%	39.63%
PB(+2)	24.39%	0.00%	75.61%	42.39%	0.00%	57.61%
SI(+4)	3.46%	0.00%	96.54%	0.87%	0.00%	99.13%

(Continued)

(Continuation of Table A3-1)

Neutralization						
AG(+1)	68.80%	0.00%	31.20%	68.80%	0.00%	31.20%
AL(+3)	26.49%	0.00%	73.51%	0.00%	0.00%	100.00%
C(+4)	99.32%	0.00%	0.68%	99.32%	0.00%	0.68%
C12H26	100.00%	0.00%	0.00%	0.00%	0.00%	0.00%
CA(+2)	0.43%	0.00%	99.57%	0.00%	0.00%	0.00%
CH4	100.00%	0.00%	0.00%	0.00%	0.00%	0.00%
CL(-1)	100.00%	0.00%	0.00%	100.00%	0.00%	0.00%
CL6BENZEN	0.13%	0.00%	99.87%	0.00%	0.00%	0.00%
CN(-1)	100.00%	0.00%	0.00%	100.00%	0.00%	0.00%
Cl(+4)	100.00%	0.00%	0.00%	100.00%	0.00%	0.00%
DLALANN(-1)	100.00%	0.00%	0.00%	0.00%	0.00%	0.00%
F(-1)	100.00%	0.00%	0.00%	100.00%	0.00%	0.00%
FE(+3)	0.93%	0.00%	99.07%	0.93%	0.00%	99.07%
H(+1)	99.15%	0.00%	0.85%	99.15%	0.00%	0.85%
HDROXAMN(0)	100.00%	0.00%	0.00%	0.00%	0.00%	0.00%
HG(+2)	55.54%	0.00%	44.46%	55.54%	0.00%	44.46%
K(+1)	100.00%	0.00%	0.00%	100.00%	0.00%	0.00%
MEFORMATE	100.00%	0.00%	0.00%	0.00%	0.00%	0.00%
MN(+2)	0.35%	0.00%	99.65%	0.35%	0.00%	99.65%
N(+3)	100.00%	0.00%	0.00%	100.00%	0.00%	0.00%
N(+5)	100.00%	0.00%	0.00%	100.00%	0.00%	0.00%
N(-2)	100.00%	0.00%	0.00%	100.00%	0.00%	0.00%
N(-3)	100.00%	0.00%	0.00%	100.00%	0.00%	0.00%
NA(+1)	54.53%	0.00%	45.47%	54.53%	0.00%	45.47%
NI(+2)	4.76%	0.00%	95.24%	4.76%	0.00%	95.24%
NTA(-3)	100.00%	0.00%	0.00%	0.00%	0.00%	0.00%
O(-2)	98.34%	0.00%	1.66%	98.34%	0.00%	1.66%
OXALAT(-2)	5.53%	0.00%	94.47%	5.53%	0.00%	94.47%
PB(+2)	100.00%	0.00%	0.00%	100.00%	0.00%	0.00%
Pu(+4)	0.00%	0.00%	100.00%	0.00%	0.00%	100.00%
SI(+4)	100.00%	0.00%	0.00%	100.00%	0.00%	0.00%
SR(+2)	2.55%	0.00%	97.45%	0.00%	0.00%	100.00%
STYRENOX	100.00%	0.00%	0.00%	0.00%	0.00%	0.00%
TBP	100.00%	0.00%	0.00%	0.00%	0.00%	0.00%
TEDEAC(-1)	100.00%	0.00%	0.00%	0.00%	0.00%	0.00%
U(+6)	0.05%	0.00%	99.95%	0.05%	0.00%	99.95%

As seen in 1st-strike, more vapours are given off if organics and miscellaneous vapours are present, as expected. Notably, metals will also behave somewhat differently with organics.

Although outside the scope of this Appendix, it is noteworthy that generally the more organics present, the more metals will become soluble as acid is added.

APPENDIX 4
DOWNSTREAM PROCESSING MODELING SPECIFICS

A4.1 Heel Process Model Description

The unique portion of the sludge heel dissolution process is modelled using OLI ESP©

Figure A4-1 is a schematic of the OLI ESP© model.

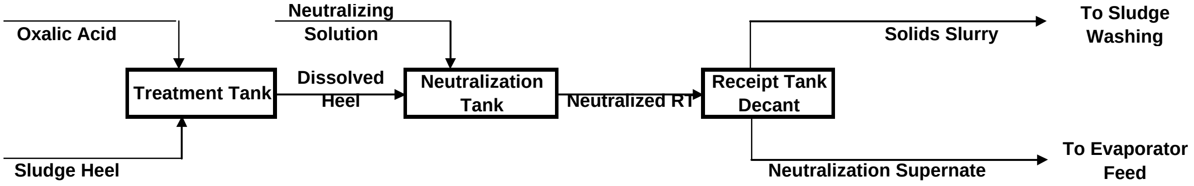


Figure A4-1 Schematic of the Sludge Heel Dissolution Process

A4.1.1 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, a pressure of 1 atm, and has a composition that is 8 wt% 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 Tables 7-3 through 7-5.

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.

A4.1.2 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 wt% caustic (50 wt% NaOH and 50 wt% H_2O) or average supernate, as defined in Table 7-6.

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

A4.1.3 Neutralization tank Decant

The **Neutralization 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 wt% solids.

At this point, the unique portion of 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.

A4.2 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 are shown in Table A4-1[44].

Table A4-1 Oxalic Acid Reactions with Sludge Components

Rxn #	Reactants	Products
1	$2AlOOH + 3H_2C_2O_4$	$Al_2(C_2O_4)_3 + 4H_2O$ (Al^{+3} also appears in solution)
2	$2Al(OH)_3 + 3H_2C_2O_4$	$Al_2(C_2O_4)_3 + 6H_2O$
3	$FeO + H_2C_2O_4$	$FeC_2O_4 + H_2O$
4	$Fe(OH)_3 + 3/2H_2C_2O_4$	$FeC_2O_4 + CO_2 + 3H_2O$ (ferrihydrite reaction)
5	$FeOOH + 3/2H_2C_2O_4$	$FeC_2O_4 + CO_2 + 2H_2O$ (goethite reaction)
6	$Fe_2O_3 + 3H_2C_2O_4$	$Fe_2(C_2O_4)_3 + 3H_2O$ (hematite reaction)
7	$Fe_3O_4 + 4H_2C_2O_4$	$Fe_2(C_2O_4)_3 + FeC_2O_4 + 4H_2O$ (magnetite reaction)
8	$Fe_2O_3 + 2H_2C_2O_4$	$2Fe(C_2O_4)_3 + H_2O + O_2$ (complexing)
9	$MnO + H_2C_2O_4$	$Mn(C_2O_4)_3 + \frac{1}{2} O_2$ (complexing)
10	$Mn_2O_3 + 2H_2C_2O_4$	$2Mn(C_2O_4) + 2H_2O + \frac{1}{2}O_2$
11	$Mn_3O_4 + 3H_2C_2O_4$	$3Mn(C_2O_4) + 3H_2O + \frac{1}{2}O_2$
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) + $CO_2 + H_2O$

SRS sludge waste consists primarily of two types, HM and Purex. The HM sludge is higher in aluminium, and the Purex is higher in iron. The primary components of each sludge type, as well as the relative ratio of oxalic acid consumed, are shown in Table A4-1 through A4-3. Table A4-4 shows the equivalent composition and ratios for Tank 16 sludge specifically. 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 A4-2 Amount of Oxalic Acid Needed to React with Components of 1 kg of HM Sludge

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 A4-3 Amount of Oxalic Acid Needed to React with Components of 1 kg of PUREX Sludge

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 A4-4 Amount of Oxalic Acid Needed to React with Components of 1 kg of Tank 16 Sludge

Constituent	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
