# HIGH LEVEL WASTE SYSTEM IMPACTS FROM ACID DISSOLUTION OF SLUDGE

by

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March 2008

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## DECLARATION

I declare that this dissertation 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.

Signature　　　　　　　　　　Date

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Edward T Kotisky 6/16/2008

Signature Date

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## ABSTRACT

### High Level Waste System Impacts from Acid Dissolution of Sludge

Currently at the Savannah River Site (SRS), there are fifteen single-shell, 3.6-million liter tanks containing High Level Waste. To close the tanks, the sludge must be removed. Mechanical methods have had limited success. Oxalic acid cleaning is now being considered as a new technology. This research uses sample results and chemical equilibrium software to develop a preferred flowsheet and evaluate the acceptability of the system impacts.

Based on modeling and testing, between 246,000 to 511,000 l of 8 wt% oxalic acid were required to dissolve a 9,000 liter Purex sludge heel. For SRS H-Area modified sludge, 322,000 to 511,000 l were required. To restore the pH of the treatment tank slurries, approximately 140,000 to 190,000 l of 50 wt% NaOH or 260,000 to 340,000 l of supernate were required.

When developing the flowsheet, there were two primary goals to minimize downstream impacts. The first was to ensure that the Resultant oxalate solids were transferred to DWPF, without being washed. The second was to transfer the remaining soluble sodium oxalates to the evaporator drop tank, so they do not transfer through or precipitate in the evaporator pot.

Adiabatic modeling determined the maximum possible temperature to be 73.5°C and the maximum expected temperature to be 64.6°C. At one atmosphere and at 73.5°C, a maximum of 770 l of water vapor was generated, while at 64.6°C a maximum 254 l of carbon dioxide were generated. Although tank wall corrosion was not a concern, because of the large cooling coil surface area, the corrosion induced hydrogen generation rate was calculated to be as high as 10,250 l/hr. Since the minimum tank purge exhaust was assumed to be 5,600 l/hr, the corrosion induced hydrogen generation rate was identified as a potential concern.

Excluding corrosion induced hydrogen, trending the behavior of the spiked constituents of concern, and considering conditions necessary for ignition, energetic compounds were shown not to represent an increased risk

Based on modeling, about 56,800 l of Resultant oxalates could be added to a washed sludge batch with minimal impact on the number of additional glass canisters produced. For each sludge batch, with 1 to 3 heel dissolutions, about 60,000 kg of sodium oxalate entered the evaporator system, with most collecting in the drop tank, where they will remain until eventual salt heel removal. For each 6,000 kg of sodium oxalate in the drop tank, about 189,000 l of Saltstone feed would eventually be produced.

Overall, except for corrosion-induced hydrogen, there were no significant process impacts that would forbid the use of oxalic acid in cleaning High Level Waste tanks.

## KEY WORDS

Dissolve
Impacts
Clean
Dissolution
Heel
Tank
Oxalic Acid
Sludge
Oxalate
High Level Waste

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## NOMENCLATURE

Bulk waste removal - Sludge removal by using only mechanical means which occurs prior to acid aided heel removal.

Case 1 – Refers to Tank 8 sludge dissolved with supernate used as the pH fix.

Case 2 – Refers to Tank 8 sludge dissolved with 50 wt% caustic used as the pH fix.

Case 3 – Refers to Tank 11 sludge dissolved with supernate used as the pH fix.

Case 4 – Refers to Tank 11 sludge dissolved with 50 wt% caustic used as the pH fix.

Corrosion – Refers to general surface corrosion.

Downstream process impacts – Potential impacts which were minimized while developing an integrated HLW system flowsheet for the dissolution of representative sludge. The impacts considered included the oxalate impacts on the evaporator system, DWPF glass production, and the quantity of oxalates that remain in the HLW system.

DWPF - Defense Waste Processing Facility – The facility that performs vitrification on High Level Waste.

DWPF sludge wash tank - This refer to the tank where sludge is washed as part of the preparation for eventual transfer to DWPF for vitrification.

Energetic compounds – At SRS the term “energetic compound” is loosely applied. It is used to refer to any compound that can potentially impact flammability. The 14 families of compounds that are considered “energetic compounds” at SRS 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, and 14) hydrogen.

Flammability impacts – Potential impacts which were evaluated based on spiking concentrations of energetic compounds and organics in a material balance across the treatment tank and pH restoration tank. The effects included the consideration of both organics and energetic compounds.

Gas generation and pressurization – Primarily refers to the water vapor, CO2 and hydrogen gases.

Heating – Refers to unacceptable temperature increases.

HLW - The High Level Waste Process in both the F-Area and H-Area tank farms, as well as DWPF.

HM sludge – Sludge waste from the Savannah River Site specific H-area modified process. Contains a larger wt% of aluminum oxides and hydroxides than iron oxides and hydroxides.

HWCS – Hypothetical Worst Case Sludge – A hypothetical sludge which contains the maximum concentration of each constituent.

Integrated flowsheet – A flowsheet whose scope includes the final fate of the oxalates.

OLI$^{©}$ - Either OLI Stream Analyzer$^{©}$ Version 1.3, or OLI ESP$^{©}$ Version 6.7 as indicated. Both are chemical thermodynamic equilibrium based software programs used in this research.

Oswald ripening process - Growth of larger solid particles from those of smaller sized ones which have a higher solubility. The smaller solid particles act as fuel for the growth of bigger solid particles. The process is commonly referred to as ‘sludge aging‘ and ‘sludge hardening.‘

Operating height – Refers to the minimum tank liquid level, normally based on pump capability, limitations, and requirements.

Oxalic acid – OA - Either 4 wt% or 8 wt% cleaning solution used to dissolve the sludge.

pH fix – Liquid which is used to pre-treat the pH restoration tank, such that excess caustic is available to restore pH. Can be either supernate of 50 wt% NaOH.

pH restoration tank – Tank in which the liquid is returned to the normal operating pH.

pH restoration tank decanter – A separator block in the OLI ESP© dissolution model that is used to separate liquids from solids. Required as part of the unit operations of the OLI ESP© dissolution model.

Pump down level – The liquid level which remains in the tank after the maximum liquid is removed, based on pump limitations.

Pump tank – Approximately 20,000 to 40,000-liter tanks in which waste is passed through as part of waste receipts and waste transfers.

Purex – Sludge waste from the Purex process that contains a larger wt% of iron oxides and hydroxides than the aluminum oxides and hydroxides.

Resultant liquid - Available pH restored supernate after some fraction is used to transfer the Resultant oxalate solids. Does not include the aqueous fraction of the Resultant oxalate slurry.

Resultant oxalate slurry – The Resultant oxalate solids, plus aqueous used to transfer the solids, that are sent to DWPF.

Safety impacts - Potential impacts which were evaluated based on using Hypothetical Worst Case Sludge (HWCS). The impacts could be, corrosion, temperature, gas generation, and pressurization.

Saltcake - Bulk quantities of salt that are already in a solid matrix.

Simulant – Non-radioactive sludge made for the sole purpose of laboratory testing.

Sludge heel – Refers to the remaining 19,000 l of sludge remaining in a tank after bulk waste removal.

Sludge Receipt Adjustment Tank – SRAT – Part of the DWPF process, where sludge is adjusted for processing.

Sludge - Metal oxides and hydroxides that have precipitated in the high pH solution. Also contains interstitial supernate unless designated as “dry sludge.”

SRNL – Savannah River National Laboratory - The United States Department of Energy National Laboratory located at the Savannah River Site.

SRS – Savannah River Site - Near Aiken South Carolina, location of the tanks and High Level Waste process.

Strike – Refers to the contact of the sludge or simulant with the acid.

Supernate - The soluble or supernatant (i.e., liquid) fraction of the waste.

SVAs – Sensitivity and Variability Analyses.

SWPF – Salt waste processing facility - The facility where supernate and dissolved salt disposed.

System impacts – Refers to the combined safety impacts (i.e., impacts on corrosion, temperature, gas generation, and pressurization), flammability impacts (i.e., impacts on the energetic compounds and the organics), and the downstream process impacts (i.e., oxalate impacts on the evaporator system, DWPF glass production, and the quantity of oxalates that remain in the HLW system).

Treat tank - Treatment tank – Tank which is cleaned using acid.

Vitrification - The term applied to the glass encapsulation process for disposal of High Level Waste.

# 1 PROBLEM STATEMENT AND NEED FOR SLUDGE HEEL DISSOLUTION

At the Savannah River Site (SRS) near Aiken, South Carolina, there are approximately 136 million l of legacy, Cold War generated, highly radioactive, alkaline High Level Wastes (HLW) (Barnes, *et al,* 2003:6). The approximately 46 tanks that hold the waste are fabricated from mostly commercially available ASTM-285B carbon steel (Sunrammanian & Wiersma, 2005:1). Out of those 46 tanks, Tanks 1-15 are single containment, non-conforming tanks built mostly in the 1950's. Some of these tanks contain sludge heels that need to be removed as part of closure and/or as feed for vitrification (Badheka & Ketusky, 2003:1).

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 have been scheduled. In order to process the sludge, it first must be removed from the tanks. The sludge, however, has aged and hardened via a form of the Oswald ripening process. Internal obstructions (*e.g.,* cooling coils) and the hardening have hindered the success of slurry pumps. To aid in the removal, the use of oxalic acid for sludge dissolution is being considered (United States Department of Energy, 2002:53784).

Because of the unique system and 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 software proved very successful (Barnes, *et al,* 2003). Additionally, both Hanford (Saito, 2002) and SRS (Pike, 2002), the two largest U.S. repositories of alkaline High Level Waste, used OLI© based chemical equilibrium software to help forecast salt dissolution. This research, used OLI Environmental Simulation Program (ESP)© and OLI Stream Analyzer© to help understand and forecast sludge dissolution effectiveness and the potential system impacts associated with sludge dissolution within HLW.

Dissolution of sludge heels using acid treatment of multiple SRS HLW tanks is planned. Figure 1-1 shows the sludge dissolution process diagram as an overview and provides insight to the complexity and scope of potential system impacts.

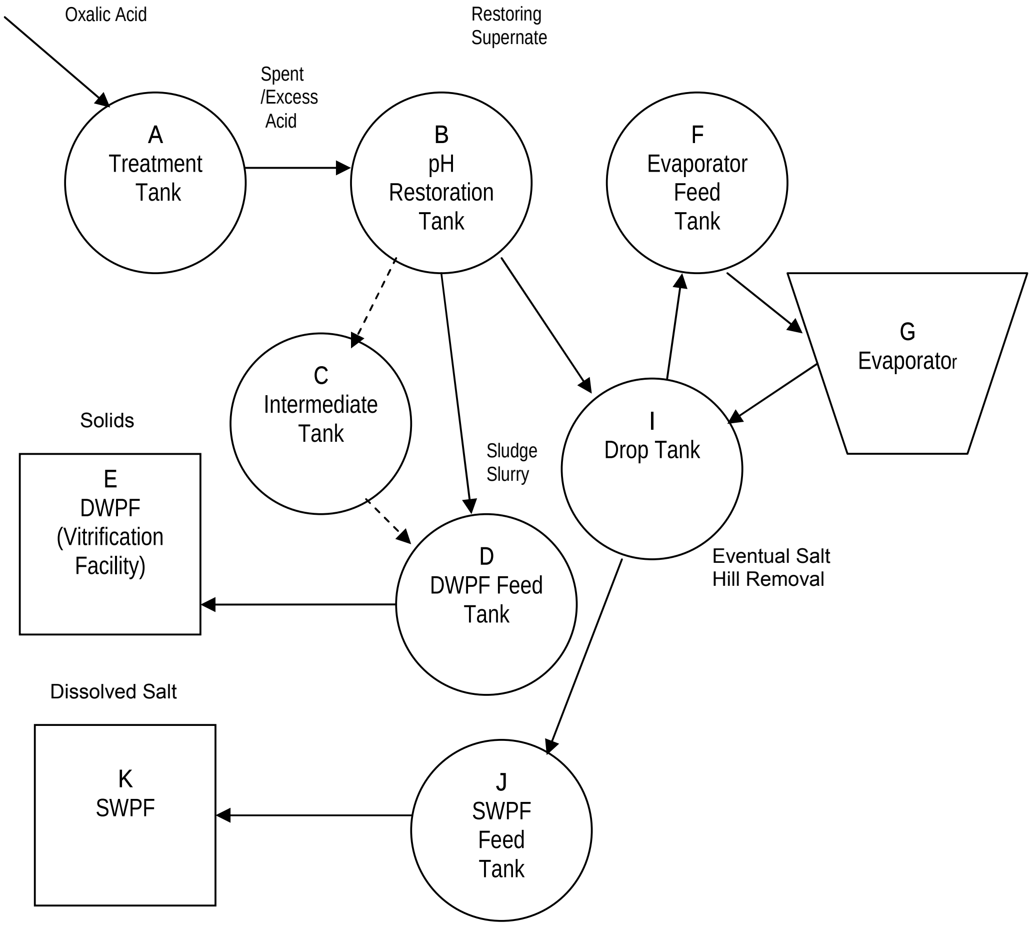


**Figure 1-1 Oxalic acid sludge heel dissolution process sketch**

Where:

A = Approximately 3.8 million liter treatment tank

B = Approximately 3.8 million liter pH restoration tank

C = Intermediate tank, if necessary, to support the vitrification schedule

D = Defense waste processing facility (DWPF) feed tank, as it is used to wash sludge prior to feed to DWPF (*i.e.*, vitrification)

E = DWPF is the facility 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 the facility where supernatant and dissolved salt are currently planned to be disposed of

Since the HLW system is a complex process as, shown in Figure 1-1, it is necessary to understand the effects that the acid additions and chemical adjustments would have on the HLW system.

Besides the effectiveness in dissolving sludge, the system impacts considered were safety, flammability, and downstream process impacts. For the purpose of this research, corrosion, temperature, gas generation (including corrosion induced hydrogen) and pressurization were termed safety impacts. The effects on energetic compounds and organics were termed flammability, while Resultant oxalate impacts on evaporator system, DWPF glass production, and the quantity of oxalates that remained in the HLW system were termed downstream process impacts.

# 2 LOGIC AND RESEARCH METHODOLOGY

## 2.1 Introduction to the Methodology

The subject and scope of the research was chosen to ensure applicability and provide significant, yet practical value to the SRS sludge heel removal efforts.

Early in this research, acid dissolution represented a new technology; consequently, many parameters were not yet identified or formally documented.

## 2.2 Research Approach/Design

The research design was based on extending the available acid dissolution sample results. OLI© software was used because it predicts final chemical outcomes. The goal of this research was to use OLI© software to determine if acid solutions could be used to effectively aid in sludge heel dissolution without causing any unacceptable impacts on the following:

1) Safety (*i.e.*, corrosion rates, heating, gas generation, and pressure).
2) Flammability (*i.e.*, energetic compounds and organics).
3) Downstream process impacts (*i.e.*, oxalate effects on the evaporator, DWPF glass production, and remaining oxalates in the tank farm).

Sensitivity and Variability Analyses (SVAs) were not used to evaluate all of the impact parameters because during the research it was determined that the "acceptability" of the parameters were poorly defined. SVAs could only be determined if the acceptability of the parameters were quantitatively based. Instead, almost all of the safety, flammability, and downstream process impact parameters were qualitatively based. To meet the intent of the research, therefore, instead of building SVAs into each aspect of the evaluation, SVAs limited to dissolution and precipitation were developed only after all other evaluations were complete.

In summary, as part of the research, the following evaluations were performed:

1) The software's ability to forecast dissolution effectiveness.
2) The effect on the general corrosion rate.
3) The effect on heating (*i.e.*, temperature).
4) The effect on gas generation (including corrosion induced hydrogen) and tank pressure.
5) The effects on flammability, which includes energetic compounds and organics.
6) A preferred flowpath was developed based on limiting the downstream process impacts from the oxalates.

In addition, after all other evaluations were complete, limited sensitivity and variability analyses were performed for dissolution and precipitation.

### 2.3 Research Efforts

As part of this research, the following were performed:

1) A comprehensive literature search was initiated.

2) For determining the software's acceptability to predict effects from cleaning, forecasted dissolutions for Purex simulant, Purex sludge, HM simulant, and HM sludge were compared to SRNL measured dissolutions.

3) A material balance was constructed across the treatment tank and pH restoration tank, conservatively allowing the effects on the corrosion rate, heating, gas generation (including corrosion induced hydrogen) and pressure to be evaluated (*i.e.*, safety impacts).

4) The material balance was conservatively revised by "spiking the energetics" to understand the effects of using oxalic acid on the energetic compounds and organics within the tank farm (*i.e.,* flammability).

5) An integrated flowsheet was built which minimized the Resultant oxalate impacts on the evaporator system; minimized the effects on DWPF glass production; and minimized the quantity of oxalates that remain in the HLW system (*i.e.,* downstream process impacts).

6) In addition, after all other evaluations were complete, SVAs were developed for dissolution and precipitation.

# 3 SLUDGE HEEL DISSOLUTION LITERATURE REVIEW

## 3.1 Introduction

Initially, as part of writing the research proposal, many experts were consulted to determine if the modeling of sludge dissolution with acid seemed useful to SRS. The authorities consulted included Savannah River Site (SRS) Tank Farm Engineering, SRS Liquid Waste Chemical Engineering, Planning Integration and Technology, and Savannah River National Laboratory (SRNL) scientists, scientists and 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 and basic chemical reactions (Metcalf, *et al,* 1978). General acid cleaning (Wiersma, 2004), acid induced corrosion, effects of acid on energetic compounds (Ketusky, 2004), and flammable gas formation reactions (Hobbs,1999) were also investigated. A large part of the effort consisted of reviewing SRS specific documents such as: the High Level Waste characterization database (HLW, 2005); HLW process records (*i.e.*, acid treatments of iron, aluminum and sludge compounds affecting high level waste tanks) (Cavin & Crumm, 2003); and historical files from SRS HLW in-tank sludge dissolution efforts (Bradley & Hill, 1977; Johnson, 1987; West, 1980). Similar tank cleaning efforts that were performed at the Hanford Site and West Valley were also investigated (Elmore, 1996; Fluor Hanford, 2003; Huckaby, *et al*, 2004; Gray & Westerman, 1995).

The literature review showed that the success of sludge heel removal would be affected by four major factors (Adu-Wusu, *et al,* 2003:25). For the purpose of this effort, they are referred to as rheology, chemistry, energy, and cleaning agent. Refer to Figure 3-1.

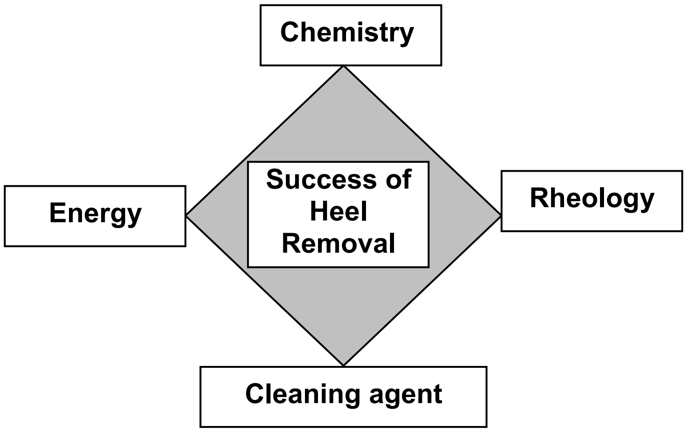


**Figure 3-1 Factors determining sludge heel removal success**

Since the possible energy and rheology are indeterminate, as the pumps are not yet installed, and the rheology is poorly known, most of the initial literature review focused on different cleaning solutions and energy addition methods.

### 3.2 Electrochemical Modeling

Literature supplied the bulk of the theory. The literature review showed that electrochemical modeling was extremely complex and hard to forecast in real process systems. Often chemical reactions behave in complex and seemingly counter-intuitive ways, introducing great risk if misapplied (Anderko, 2002:3).

### 3.3 Cleaning Agents

The understanding of the chemical composition of the sludge heels included the possibilities of aluminosilicate such as cancrinite and sodalite, hematite and boehmite (Adu-Wusu, *et al,* 2003:26-30). The exact chemical composition of the sludge varies from tank to tank and even within the tank.

The chemical cleaning efficiency would largely depend on the cleaning agent and the type of oxide. As HLW sludge is an aggregate of the different oxides and hydroxides, the sludge, almost assuredly, would behave differently from the pure oxide components. This different behavior would be due, in part, to the trace concentrations of other materials contained with the oxides and hydroxides.

There are generally four types of chemical cleaning processes (surface controlled dissolution) by which inorganic oxides and hydroxides dissolve. They are as follows:

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

The review also showed that the dissolution efficiency largely depended on the type of oxide or hydroxide compound encountered. A general rule for dissolution is that "the farther an oxide is from a hydrated form, the longer it takes it to dissolve" (Adu-Wusu, *et al*, 2003:26). 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 was limited characterization data based on actual SRS sludge analytical analyses. Additionally, the sludge may not be representative. That is, even in the tanks with slurrying capabilities, the tanks may not have been adequately mixed during sampling. Many times the sludge sample results appeared to contradict the process history (Cavin & Crumm, 2003:5); therefore, to ensure conservatism, characterization data from the process database was used as the baseline.

In use, the characterization data were refined within the different aspects of the research. Examples within this research included the use of Hypothetical Worst Case Sludge based on the process database to determine safety impacts, while flammability outcomes were determined based on grossly spiking the energetic compounds and organics far in excess of possible quantities.

When evaluating the acceptability of the software, simulant recipes were used in addition to the real sludge sample results to ensure adequate characterization, thereby potentially eliminating some uncertainty. When determining the system impacts, however, the process database was used because it enabled hypothetical worst case, spiked, and realistic assessments to be developed.

The 2004 SRNL measured dissolution report (Hobbs, *et al,* 2004) was most valuable because it focused on the development of simulant recipes and the characterization of sludge, while also containing the resultant dissolution data. The use of simulants helped to ensure that the solids to be dissolved were well characterized. Excluding any dissolution uncertainty, any difference between the laboratory results and the forecasts would likely be caused by the inaccuracies in the software, and not by inaccurate characterization. Although the 2004 SRNL measured dissolution report (Hobbs, *et al,* 2004) details the making and dissolution of simulant, it also contains similar data for select HLW sludge dissolutions.

The material balance across the treatment tank and pH restoration tank (Badheka & Ketusky, 2003) supplied the primary input to evaluate the safety impacts using a Hypothetical Worst Case Sludge (HWCS). HWCS was defined as hypothetical sludge where constituent concentrations were maximized so that the most negative safety-affecting conditions could occur. Safety impacts include excessive corrosion rates, unacceptable heating, excessive gas generation (including hydrogen generation), and tank pressurization.

The flammability impacts were evaluated based on use of a similar material balance, grossly spiking the quantities of energetic compounds and organics, and observing the forecasted behavior.

The sludge and supernate (*i.e.*, supernatant) characterizations were obtained from the process database as maintained in the waste characterization system (HLW, 2005). This characterization represented the likely contents of the SRS HLW Tanks 1-15, considered in this dissertation.

### 3.5 Acids as Cleaning Agents

Although some laboratory testing of acid as a cleaning agent for actual HLW sludge has been performed, most of the research for using nitric/citric/oxalic acid was based on using simulant for the sludge. Out of the nitric, citric and oxalic acids, oxalic acid was the only acid ever actually used on in-tank HLW sludge heel removal. More specifically, oxalic acid was used once in the 1970’s, on in-tank SRS sludge. Additionally, oxalic acid was once used during 2003 at the United States Department of Energy Hanford Site (Fluor Hanford, 2003).

Overall, based on the literature review, it became apparent that oxalic acid was the most researched cleaning agent for use on cleaning SRS HLW sludge tanks.

### 3.5.1 Oxalic acid

Oxalic acid has been widely tested and utilized as a sludge dissolution/cleaning agent at SRS and other U.S. Department of Energy facilities. Its use was backed by the largest body of literature (Adu-Wusu, *et al,* 2003:6).

Poirier and Fink (2002) conducted a series of tests at SRNL investigating various cleaning agents on porous metal filters considered to be exposed to SRS HLW sludge. The testing showed that an approximate 4 wt% oxalic acid in a 60:1 volume ratio to both Purex and HM sludge was acceptable for cleaning the metal filters. The results of this test were important, as they concluded that one cleaning solution could potentially be used for the dissolution of both HM and Purex sludge. The testing (Poirier & Fink, 2002) also showed the following:

1) Increasing the oxalic acid concentration significantly increased the volume of sludge dissolved over a given period.
2) Increasing the temperature and contact with the sludge increased the volume of sludge dissolved over a given period.

In the late 1970's, Tank 16, containing small quantities of HM sludge from various tanks, was used for an oxalic acid/sludge dissolution cleaning demonstration. Prior to the demonstration, laboratory testing was performed. Three sets of tests were conducted in the late 1970's in support of the Tank 16 cleaning demonstration (Bradley & Hill, 1977). The tests were as follows:

1) Scoping tests in laboratory with actual Tank 16 sludge.
2) Short term laboratory tests using oxalic acid with aluminum hydroxide, iron hydroxide, and manganese dioxide simulant.
3) Long term laboratory tests with Tank 16 sludge.

<u>Laboratory scoping tests with SRS Tank 16 sludge</u> - Bradley and Hill (1977:6-15) performed laboratory testing, mixing about 2 ml of SRS Tank 16 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% sulfuric acid, and 8 wt% oxalic acid) for 30 minutes at ambient temperature with agitation. These test results concluded that oxalic

acid/citric acid mixes and oxalic acid had the same relative effectiveness in dissolving Tank 16 sludge.

Short term laboratory tests with simulant - Bradley and Hill (1977:15-21) also showed the results of short-term laboratory tests of aluminum hydroxide, ferric hydroxide, and manganese dioxide simulant subject to dissolution with oxalic acid.

The tests varied the volume ratio of acid to simulant (10:1, 20:1, and 40:1) and the acid concentration (4 wt% and 8 wt%) and conducted all of the tests at 55°C. The following conclusions were drawn from the tests:

1) 8 wt% oxalic acid in a 20:1 volume ratio to aluminum hydroxide was required for complete dissolution.
2) 8 wt% oxalic acid in a 40:1 volume ratio to ferric hydroxide was required for complete dissolution.
3) 8 wt% oxalic acid in a 10:1 volume ratio to ferric hydroxide yielded nearly 70 vol% dissolution.
4) 8 wt% oxalic acid in a 40:1 volume ratio to manganese dioxide resulted in a significant amount of dissolution.

The shortfall of these short-term simulant tests was that the dissolution of only one metal oxide or hydroxide was considered at a time.

Long term laboratory contact tests with actual Tank 16 sludge – West (1980:4-10) documented oxalic acid dissolution tests using Tank 16 sludge, which examined the dissolution efficiency. Multiple step experiments with oxalic acid to sludge volume ratios as high as 80:1 with contact times of about 1 week were conducted. Results showed that two successive strikes, using 8 wt% oxalic acid, and an acid to sludge volume ratio of 40:1, dissolved over 96 vol% of the Tank 16 sludge. Increased volumes of acid, however, did not necessarily result in additional dissolution.

It was difficult to compare the data between the three sets of tests because the experimental conditions were different. In addition, the specific sludge compounds were not given in Poirier and Fink's study (2003).

Between the tests, an apparent contradiction existed with the dissolution of manganese. Poirier and Fink (2003) concluded that manganese readily dissolves, while Bradley and Hill (1977) concluded that it is very difficult to dissolve. Both sets of tests, however, generally agreed that 8 wt% oxalic acid solutions in a 20:1 volume ratio with sludge dissolved about 70 vol% of sludge for up to three strikes with acid. After the third strike, the overall dissolution efficiency for the acid drastically decreased.

Reports by Johnson (1987) and West (1980) detailed the results of the oxalic acid treatment 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 demonstration collaborated the results of the long-term laboratory tests using actual Tank 16 waste sludge.

The major difference between the in-field demonstration and laboratory testing, was that laboratory testing used higher concentrations of oxalic acid (*i.e.,* generally 4 to 8 wt%) compared to the in-field SRS Tank 16 demonstration (*i.e.*, one of the strikes was at 1 wt%).

<u>Laboratory testing at Hanford</u> - Laboratory tests were documented for the Hanford site using oxalic acid, simulant, and actual Hanford site Tank 241-C-106 sludge (Fluor Hanford, 2003; Huckaby, *et al,* 2004). The tests were done using 10 wt% oxalic acid.

In the Hanford testing, even with increasing dissolution of the iron, aluminum, and manganese, the volume of sludge did not significantly change. In the testing, this was speculated to be the result of substitution of oxalate for oxide/hydroxide in the solids (Huckaby, *et al,* 2004:20). That is, the overall weight did not change even with decreasing volume, because the Resultant oxalate weighed more than the original oxide/hydroxide. Nearly all of the gas produced in the Hanford testing was $CO_2$, with traces of $H_2$ and $CH_4$.

The Hanford testing also showed that restoring the pH of the spent acid/excess acid with HLW supernate and a 50 wt% NaOH solution produced large volumes of easily compacted sodium oxalate. Although large volumes of sodium oxalate solids were generated, the tests suggested that the newly formed sodium oxalate precipitate could be easily pumped out of a tank, while aged sodium oxalate may be hardened and, therefore, more difficult to remove.

Corrosion of carbon steel from oxalic acid – Based on the literature review, acid concentration, the carbon content of the metal, temperature, and exposure duration greatly influenced the corrosion (Adu-Wusu, *et al,* 2003:6).

Ondrejcin's (1976) corrosion testing was based largely on coupon tests that provided part of the technical basis used for the chemical cleaning of Tank 16. The Wilde, *et al* (1984) data was from coupon tests supporting the cleaning of SRS nuclear reactor heat exchangers.

Tests performed by the V. G. Khlopin Radium Institute Mining Chemical Combine (MCC) and summarized by SRNL (Adu-Wusu, *et al*, 2003:15-30) and SRNL tests (Hobbs, *et al,* 2004) were also used to investigate the effectiveness of oxalic acid dissolution of HLW sludge. Studies performed at Pacific Northwest National Laboratory that supported the clean-out of HLW tanks at West Valley (Gray & Westerman, 1995) were also reviewed.

The tests showed that the rate for the general corrosion would be significantly less than 1.52 mm/year (Wiersma, 2004:23). Additionally, data showed that the temperature had a strong effect on the corrosion rate.

### 3.5.2 Citric acid

The use of citric acid as a sludge dissolution agent was studied during the 1970's. Bradley and Hill (1977:30&61) considered the use of citric acid for Tank 16 sludge. They determined that citric acid, as a lone cleaning agent, was slightly less effective than oxalic acid. Additionally, comparison tests with simulated Tank 40 sludge and 0.5 M citric acid at ambient temperatures, and 60:1 volume ratios of acid solution to sludge, showed that citric acid was less effective than oxalic acid (Poirier & Fink, 2002:14).

The bulk of information on citric acid and oxalic/citric acid mixes, however, came from recent tests performed by the V. G. Khlopin Radium Institute Mining Chemical Combine (MCC) as summarized by SRNL (Adu-Wusu, *et al*, 2003:55-61) and testing by SRNL (Hobbs, *et al,* 2004). Both groups, working together, conducted tests with Purex and HM simulant. Results from the two teams varied, even though the MCC scientists used simulant recipes provided by SRNL. The conclusions from the testing were as follows:

1) Use of citric acid did not promote the uniform dissolution of neutron poisons in relation to fissile products.
2) Even under the best conditions, citric acid and citric acid/oxalic acid mixtures were only about as effective in dissolving sludge as oxalic acid.

Since the use of citric acid would require further processing, as it is not compatible with DWPF (Hobbs, *et al,* 2004:27), and it was determined to have an effectiveness less than or equal to oxalic acid, the use of citric acid and oxalic/citric acid mixes were eliminated from further consideration.

### 3.5.3 Nitric acid

The use of nitric acid has been used for cleaning metal surfaces at SRS.

The nitric acid corrosion mechanism has been studied for many years (Adu-Wusu, *et al*, 2003:36&64). For both sludge and simulants, it was shown that 4 M nitric acid performed comparably to 4 wt% oxalic acid, while the ideal strength for oxalic acid dissolution based on SRNL studies, as discussed above, was determined to be somewhere in the range between 4 wt% to 8 wt%.

Tests, (Hobbs, *et al,* 2004:8-10) which involved placing 300 ml of Tank 40 simulant and 60 ml of actual Tank 8 sludge in a beaker, were done, while 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 with an acid to sludge volume ratio of 5:1.

Although the anodic reaction is simple for iron to be oxidized to ferrous cation ($Fe^{+2}$), there are a number of cathodic reactions that occur. The possible cathodic reduction of nitric acid is shown by Reactions 3-1 through 3-4 (Adu-Wusu, *et al,* 2003:59).

$$H^{+} + e^{-} \rightarrow H \qquad \text{(Reaction 3-1)}$$

$$HNO_3 + H^{+} + e^{-} \rightarrow NO_2 + H_2O \qquad \text{(Reaction 3-2)}$$

$$NO_2 + e^{-} \rightarrow NO_2^{-} \qquad \text{(Reaction 3-3)}$$

$H^{+} + NO_2^{-} \rightarrow HNO_2$ (Reaction 3-4)

These equations make obvious that $NO_x$ and ammonia issues would be associated with the use of nitric acid. The nitrous acid ($HNO_2$) that would be formed would regenerate $NO_2$ by an interaction with the nitric acid as shown in Reaction 3-5 (Adu-Wusu, *et al*, 2003:59).

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

Ammonia salts would also be formed. The ammonia salts would likely decompose to form $N_2$ and $NO_x$ compounds by Reaction 3-6 and Reaction 3-7 (Adu-Wusu, *et al,* 2003:59).

$NH_4NO_2 \rightarrow N_2 + 2H_2O$ (Reaction 3-6)

$NH_4NO_3 \rightarrow N_2O + 2H_2O$ (Reaction 3-7)

Thus, if nitric acid is used, the formation of $NH_4$, $NO_2$, NO, $N_2O$ and $N_2$ would be expected. Because of the cost, time constraints, and issues associated with introducing significant $NO_x$ gases into Tanks 1-15, the consideration of using nitric acid in the near future, was considered implausible.

### 3.6 Research after the Literature Review

Based on the literature review, it was concluded that there was a significant amount of information about the general behavior of oxalic acidic dissolution of metal oxides and hydroxides. However, as discussed in Section 3.5.1, much of the information conflicted with other sources of information, and much of the data between the tests could not be compared. Additionally, except for Tank 16, no in-tank dissolutions of SRS HLW sludge have been performed.

Based on past SRS experience, the results of the literature review, the results of a few proof-in-principle tests (Refer to Appendix 1, Sections A1.1), and published results from other simulators (Refer to Appendix 1, Sections A1.2), the OLI© software was considered a candidate to be used in evaluating the system impacts.

For this research, the software's ability to forecast oxalic acid dissolution of sludge was evaluated by comparing the forecasted dissolution results for both simulant and sludge to SRNL measured dissolution results. The results are summarized in Chapter 4.

As shown in Chapter 5, a dissolution model was created using Hypothetical Worst Case Sludge (HWCS) and a material balance. With the material balance and HWCS, the safety impacts (*i.e.*, corrosion, temperature, gas generation, and pressurization) were evaluated.

Since very small concentrations (*i.e.*, less than process database concentrations) of energetic compounds and organics have a significant impact on the flammability, the affects were evaluated by "spiking" constituent concentrations and tracking their behavior. This spiking and tracking to understand behavior, was performed as part of Chapter 6.

Using representative sludge, a preferred process flowsheet was developed which minimized the downstream process impacts. The downstream process impacts evaluated included the effect of oxalate impacts on evaporator, the effects of oxalates on DWPF glass production, and the quantity of oxalates that remain in the HLW system. The development of a preferred flowsheet to minimize these impacts is discussed in Chapter 7.

SVAs were then developed for the possible dissolution and precipitation variations of input. The results are summarized in Chapter 8.

Chapter 9 contains general conclusions from the research.

# 4 SOFTWARE'S ABILITY TO FORECAST DISSOLUTION

## 4.1 Introduction to the Software's Acceptability

This chapter evaluates the acceptability of the OLI$^{©}$ software to forecast dissolution.

The acceptability of the OLI$^{©}$ software was evaluated by comparing available documented Savannah River National Laboratory (SRNL) measured simulant and sludge dissolutions to OLI$^{©}$ forecasted dissolutions. The types of solids considered in the dissolution comparisons included Purex and HM simulant, as well as Purex and HM sludge.

Purex is associated with running a Purex separation campaign, and is indicated by a high iron to aluminum ratio, while H-Area Modified (HM) is specific to SRS, as is indicated by a high aluminum to iron ratio.

Because of the need to evaluate the dissolution forecasting ability of the software with measured dissolutions, the results from simulants, whose constituents were well known, were first compared. Since, however, the results from simulant can be misleading, as any test with simulant is only as good as the simulant, a second part of the effort included using both HM and Purex sludge.

## 4.2 Software Specifics

As discussed in Chapter 1, although seen as one software program, two related OLI$^{©}$ software programs, which use the same software engine and result in the same forecasted values, were used.

OLI Stream Analyzer$^{©}$ and OLI ESP$^{©}$ are related steady state chemical thermodynamic equilibrium software programs, as they use the same software engine and databank.

The software engine is based on the combined chemical thermodynamic modeling work of Helgeson, Pitzer, Zemaitis, Bromely, Miesner, and others and was refined over a 25-year period. The software is supported by a very extensive thermodynamic databank for 79 inorganic elements and more than 3,000 organic molecules (OLI systems, 2004:12).

OLI Stream Analyzer$^{©}$ is a Windows$^{©}$ based program that was used to forecast dissolution effectiveness (Section 4.3), determine safety impacts (Chapter 5), determine the flammability impacts (Chapter 6), and develop the SVAs (Chapter 8). The advantage of using OLI Stream Analyzer$^{©}$ was that it allowed multiple streams to be quickly combined (*i.e.,* as mixer blocks) estimating either the resultant chemistry or temperature changes.

The second program used, OLI ESP$^{©}$, is not Windows$^{©}$ based, but is FORTRAN$^{©}$ based. It is ideally suited for developing multi-unit operations and was used to develop the preferred flowsheet (Chapter 7).

### 4.2.1 Equilibrium theory

Chemical thermodynamic equilibrium software programs do not consider kinetics, but are based on the assumption that chemical reactions occur to completion, or more specifically that reactions occur until all of the free energy is accounted for. The free energy relates the effects of the combination of heat, entropy, temperature, and pressure. The free energy change 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 4-1.

$$\Delta G = \Delta G^{o} + RT(\ln Q) \qquad \text{(Equation 4-1)}$$

Where:

$\Delta G$ = free energy (kj)

$\Delta G^{o}$= standard-state free energy of reaction (kj)

$T$ = temperature (K)

$R$ = gas constant= 8.21E-3 kj/K-mol

*ln Q* = natural log of the reaction quotient

At equilibrium ($\Delta G$=0) 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 4-2.

$$\sum \Delta Gproduct - \sum \Delta Greact = 0 \qquad \text{(Equation 4-2)}$$

The key to thermodynamic equilibrium is that each of 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 4-3.

$$\sum \Delta G_{Right} - \sum \Delta G_{Left} \qquad \text{(Equation 4-3)}$$

Knowing that the Gibbs free energies are equal, the software could discern when the reactions would reach thermodynamic equilibrium.

In this case, the thermodynamic equilibriums and sludge dissolutions had the same starting and stopping points. By comparing the final solids volume, therefore, to the original solids volume, the volume percent dissolved was determined (OLI Systems, 2004:79&80).

### 4.2.2 Software databank

The OLI's$^{©}$ dissolution databank, which is provided with the software, is based upon published experimental solubility data. The software uses data regression wherever possible, and only estimates and extrapolates as required when determining equilibrium. The software provides general dissolution modeling capability for almost any aqueous chemical mixture entered into the databank within the temperature, pressure, and ionic strength range (OLI Systems, 2004:3).

At the time of the research, the databank contained thermodynamic, transport, and physical properties for 79 inorganic elements, including actinides, heavy, and precious metals and their associated aqueous species. The databank also included over 3,000 organics, including electrolytes, chelates, and organo-metallic species (OLI Systems, 2004:6).

In general, accurate and reliable dissolution simulation is possible if the appropriate solubility data is in the databank. Since the primary Purex and HM constituents are of common industrial interest, the solubility data was contained in the databank.

### 4.3 Dissolution Model

The unique portion of the sludge heel dissolution process, function 1, was modeled using OLI Stream Analyzer©. Figure 4-1 is a schematic of the model.

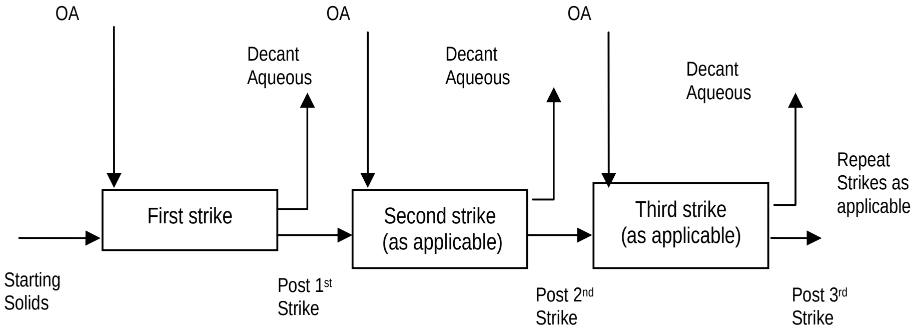


**Figure 4-1 Dissolution Model**

<u>First strike</u>

The first strike combined the oxalic acid (OA) and sludge solids. The oxalic acid stream had a starting temperature of 30°C, a pressure of 1 atm, and had a composition of either 4 wt% or 8 wt% oxalic acid, as applicable. The starting solids were either sludge or simulant.

The dissolution estimate was performed as an isothermal calculation with a final temperature of 30°C. The resultant aqueous was decanted off, and the resultant solids were measured**.** The solids were fed into the next strike tank, and the process was repeated for the appropriate number of strikes.

### 4.4 Measured vs Forecasted Dissolutions

As detailed in the process database (HLW, 2005), SRS tanks 1-15 contain Purex and HM sludge. Because of the need to evaluate the software's ability to forecast sludge dissolution with laboratory measured tests, the results from simulants were first compared.

### 4.4.1 Recipes for simulants

Recipes for the SRNL to make the Purex and HM simulant for dissolution studies were provided in Hobbs, *et al*, (2004:12&14). The recipes are shown in Table 4-1.

**Table 4-1 Purex and HM simulant recipes**

| **Constituent** | **Purex simulant** | **HM simulant** |
|---|---|---|
| | **(mole)** | |
| $Al(OH)_3$ | 2.21E-1 | 1.50E+0 |
| $Ca_3(PO_4)_2$ | 1.49E-3 | 4.80E-5 |
| $Fe(OH)_3$ | 8.37E-1 | 1.75E-1 |
| $Mg(OH)_2$ | 2.55E-2 | 1.20E-2 |
| $Mn(OH)_2$ | 4.70E-1 | 1.09E-1 |
| $Mn_3(PO_4)_2$ | 1.10E-2 | 1.10E-2 |
| HgO | 1.85E-3 | 2.58E-2 |
| $Ni(OH)_2$ | 8.99E-1 | 1.60E-2 |

### 4.4.2 Measured simulant dissolutions

SRNL measured the laboratory dissolution of Purex simulant and HM simulant using one acid strike and seven acid strikes of 4 wt% oxalic acid solution in 2:1 and 50:1 volume ratios of acid solution to simulant. The dissolution results were recorded in the literature (Hobbs, *et al*, 2004:14) and are summarized in Table 4-2.

**Table 4-2 Measured Purex and HM simulant dissolutions**

| **Scenario** | **Total** | **Al** | **Fe** | **Mn** | **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 |
| 7 strikes @ $50:1_{HM}$ | 81.6 | 60.9 | 77.5 | 97.0 | 100 |

Based on the SRNL measured dissolutions, Table 4-2 shows that both a 1 strike @ 2:1 and a 7 strike @ 2:1 volume ratio of 4 wt% oxalic acid did not dissolve a significant amount of sludge, while a 1 strike @ 50:1 and a 7 strike @ 50:1 was more successful. Overall, the simulant testing showed that as more oxalic acid was used, in terms of either strikes or volume ratios, more sludge was dissolved.

### 4.4.3 Forecasted simulant dissolutions

Using the same acid strength and volume of acid to sludge ratios, OLI Stream Analyzer© was used to forecast the dissolutions.

The forecasted results for the simulants are shown in Table 4-3.

**Table 4-3 Forecasted Purex and HM simulant dissolutions**

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

### 4.4.4 Measured vs forecasted simulant dissolutions

The measured and forecasted dissolutions were compared using Equation 4-1.

$$\%DIFF = \frac{Forecasted\ \ wt\% - Measured\ \ wt\%}{Measured\ \ wt\%}\,x\ \ 100\% \qquad \text{(Equation 4-1)}$$

Where:

%DIFF = percent difference between the forecasted wt% dissolved and the SRNL measured wt% dissolved (%), where “+” means the forecasted values were in excess of measured values, and “-“

means the forecasted values were deficient from the measured values (%)

Forecasted wt% = OLI$^{©}$ forecasted wt% dissolved (wt%)

Measured wt% = measured SRNL wt% dissolved (wt%)

The comparisons between the measured and forecasted values are shown in Table 4-4.

**Table 4-4 Forecasted vs Measured Purex and HM simulant dissolutions**

| Scenario | Method | Total | Al | Fe | Mn | Ni |
|---|---|---|---|---|---|---|
| | | (wt%) | | | | |
| 1 strike @ 2:1$_{\text{Purex}}$ | Forecasted | 27.9 | 28.3 | 28.0 | 26.6 | 28.0 |
| | Measured | 3.7 | 9.4 | 3.4 | 3.4 | 2.9 |
| | %DIFF | +6540 | +2011 | +7235 | +6824 | +8655 |
| 7 strike @ 2:1$_{\text{Purex}}$ | Forecasted | 29.4 | 28.0 | 31.6 | 27.5 | 35.2 |
| | Measured | 40.8 | 46.0 | 41.4 | 42.6 | 46.2 |
| | %DIFF | -27.9 | -39.1 | -23.7 | -35.4 | -23.8 |
| 1 strike @ 50:1$_{\text{Purex}}$ | Forecasted | 57.0 | 83.2 | 100 | 26.1 | 28.1 |
| | Measured | 83.7 | 69.2 | 79.8 | 99.1 | 95.3 |
| | %DIFF | -31.9 | +20.2 | +25.3 | -73.7 | -70.5 |
| 7 strikes @ 50:1$_{\text{Purex}}$ | Forecasted | 73.3 | 100 | 100 | 26.3 | 28.1 |
| | Measured | 87.2 | 81.8 | 84.4 | 99.1 | 95.3 |
| | %DIFF | -15.9 | +22.2 | +18.4 | -73.5 | -70.5 |
| 1strike @ 2:1$_{\text{HM}}$ | Forecasted | 30.4 | 28.4 | 28.1 | 44.4 | 28.0 |
| | Measured | 1.9 | 0.7 | 1.1 | 8.9 | 10.8 |
| | %DIFF | +1500 | +3957 | +2455 | +80. | +159 |
| 7 strikes @ 2:1$_{\text{HM}}$ | Forecasted | 90.9 | 90.6 | 100 | 99.2 | 90.0 |
| | Measured | 26.7 | 25.2 | 25.0 | 42.8 | 56.6 |
| | %DIFF | +240 | +259 | +300 | +132 | +59.0 |
| 1 strike @ 50:1$_{\text{HM}}$ | Forecasted | 72.8 | 70.2 | 100 | 69.2 | 35.4 |
| | Measured | 76.4 | 42.0 | 70.8 | 96.9 | 100 |
| | %DIFF | -4.7 | +67.1 | +41.2 | -28.5 | -64.6 |
| 7 strikes @ 50:1$_{\text{HM}}$ | Forecasted | 100 | 100 | 100 | 100 | 100 |
| | Measured | 81.6 | 60.9 | 77.5 | 97.0 | 100 |
| | %DIFF | +22.5 | +64.2 | +29.0 | +3.1 | 0 |

As shown in Table 4-4, for “1 strike @ 50:1 of 4 wt% oxalic acid,” the difference between the forecasted and measured total wt% dissolved for both Purex and HM were approximately -32% and -4.7 %, respectively.

For Purex the wt% aluminum and iron were overestimated by +20 wt% to +25 wt%, while the manganese and nickel were vastly underestimated by -74 wt% and -71 wt.

Since the software is equilibrium based, the forecasted dissolution included re-precipitation of manganese and nickel, as newly formed oxalate precipitation. During laboratory measured dissolutions, however, the amount of time allowed for the kinetics did not support re-precipitation. The behaviors of $Al(OH)_3$, $Fe(OH)_3$, $Mn(OH)_2$, and $Ni(OH)_2$ for Purex sludge are further evaluated in Appendix 2, Table A2-1.

For Purex, the -32% difference was initially considered to be far from an ideal comparison between the software's ability to forecast dissolution and the laboratory measured results. Based on literature, an acceptable comparison between measured dissolutions was generally assumed to be $\leq \pm 25$ %. With the overall uncertainty associated with HLW, depending on the potential system impacts, differences as high as 40% have been deemed acceptable (Adu-Wusu, *et al*, 2003: 3).

Since the difference between the forecasted and measured dissolutions were larger than 25%, the possible effects on the safety impacts, flammability impacts, and downstream process impacts were evaluated. They were appraised as follows:

1) Since safety impacts, evaluated in Chapter 5, are based on Hypothetical Worst Case Sludge, it was concluded that there would be no safety impacts.

2) Since the flammability impacts, evaluated in Chapter 6, are based on grossly spiking the energetic compounds and organics, it was concluded that there would be no significant flammability impacts.

3) Using the preferred flowsheet contained in Chapter 7 and Tables 8-3 through 8-8, which showed the effects of additional solids and unspent acid, it was concluded that there would be no significant downstream processing impacts.

Additionally, since complete dissolution would not be required for effective tank cleaning, and the over-all uncertainty of the process is large, the -32% difference between the forecasted and measured values was deemed tentatively acceptable.

For HM simulant, the difference between the software forecasted values and the SRNL measured dissolution results was approximately -5 wt%. As with the Purex simulant, this difference could also be attributed to the software's equilibrium re-precipitation of manganese and nickel as newly formed oxalate compounds. The behavior of the $Al(OH)_3$, $Fe(OH)_3$, $Mn(OH)_2$, and $Ni(OH)_2$ for HM simulant are further discussed and quantified in Appendix 2, Table A2-2.

### 4.4.5 Sludge characterization

Previously taken Tank 8 Purex sludge and Tank 12 HM sludge samples were archived in the laboratory and used for dissolution testing. The Tank 12 sample, however, was extremely dry. As noted, an approximate 65 vol% liquid was determined to be required to effectively run OLI© (Badheka & Ketusky, 2003:4).

In the late 1970's a demonstration was performed on Tank 16 prior to its retirement. The purpose of the demonstration was to assess waste removal effectiveness of different processes, including acid cleaning (West, 1980:1). Although the test was done more than two decades ago, the fact remains that as part of the evaluation for closure, acid dissolution was tested in the laboratory, used in a HLW tank, and eventually declared successful for sludge heel dissolution (West, 1980).

Since laboratory measured dissolution results from Tank 16 HM sludge were available, and the Tank 16 HM results were non-archived (i.e., not dried out), the Tank 16 results were believed to more accurately reflect expected behavior. The Tank 16 sludge dissolution results were used to evaluate the dissolution of HM sludge.

Table 4-5 shows the characterization of the Tank 8 sludge and the Tank 16 sludge.

**Table 4-5 Tank 8 and Tank 16 sludge constituents**

| Constituent | Tank 8 Purex sludge | Tank 16 HM sludge |
|---|---|---|
| | (mole) | |
| $Al(OH)_3$ | 3.6E-1 | 6.9E-1 |
| $Ca_3(PO4)_2$ | 6.7E-3 | 0 |
| $Fe(OH)_3$ | 2.0E+0 | 1.8E+0 |
| $Mg(OH)_2$ | 0 | 0 |
| $Mn(OH)_2$ | 2.6E-1 | 3.3E-1 |
| $Mn_3(PO_4)_2$ | 6.1E-3 | 1.1E-2 |
| HgO | 3.0E-3 | 6.5E-2 |
| $Ni(OH)_2$ | 2.0E+0 | 1.0E-1 |

### 4.4.6 Measured vs forecasted sludge dissolutions

The SRNL laboratory dissolution of Tank 8 Purex sludge for one strike of 4 wt% oxalic acid solution using a 50:1 volume ratio of oxalic acid to sludge was measured and compared to the OLI$^©$ forecasted Tank 8 Purex sludge dissolution (Hobbs, *et al*, 2004:6). The percent difference was calculated using Equation 4-1, contained in Section 4.3.4. A similar comparison between the forecasted and the measured dissolution with a two strike 8 wt% oxalic acid solution using a 20:1 volume ratio of acid to Tank 16 HM sludge was also performed (West, 1980). Refer to Table 4-6.

**Table 4-6 Forecasted vs measured sludge dissolutions**

| Scenario | Result | Total sludge dissolved (wt%) |
|---|---|---|
| Tank 12<br>1 strike @ $50:1_{Purex}$<br>(4 wt% OA) | Forecasted | 87 |
| | Measured | 69 |
| | %DIFF | +20 |
| Tank 16<br>2 strike @ $20:1_{HM}$<br>(8 wt% OA) | Forecasted | 80 |
| | Measured | 95 |
| | %DIFF | -19 |

As shown in Table 4-6, the Tank 12 Purex forecast resulted in an approximate 20 wt% over-estimate of the total wt% dissolved. Three known factors that contributed to the difference were as follows:

1) Tank 8 sample first had to be significantly re-wet with the acid before dissolution occurred (Hobbs, *el at*., 2004:35).
2) Since the sludge was radioactive, but no radionuclides were recorded in the characterization, the characterization obviously was not all-inclusive.
3) The software forecast was based upon reaching chemical equilibrium, whereas the measured SRNL results were dependent upon the allowed reaction time and the kinetics.

Also, as shown in Table 4-6, the Tank 16 HM forecast underestimated the wt% dissolved by approximately -19 wt%. Two potentially factors that contributed to the difference for HM sludge were the same as the last two for Tank 8 sludge.

For both Purex sludge and HM sludge the difference was considered to be acceptable based on the fact that for measured dissolutions with $\leq$ ±25 wt%, the difference would assumedly to be acceptable (Adu-Wusu, *et al*, 2003:3).

## 4.5 Conclusion on Software's Acceptability

For Purex sludge, HM sludge, and HM simulant the differences between the forecasted and measured wt% dissolved were less or equal to 20%. Using the same criteria as for evaluating laboratory measured dissolution values; they were considered acceptable (Adu-Wusu, *et al*, 2003:3).

Although the difference between the forecasted wt% dissolved and the measured weight % dissolved for Purex simulant was -32%, based on the high uncertainty of the process, as well as the minimal system impacts caused by the difference, it was deemed tentatively acceptable pending the results of further SRNL simulant dissolutions. In the past, under similar conditions, differences as high as 40% were considered acceptable (Adu-Wusu, *et al*, 2003:3).

A summary of the percent differences between the forecasted total wt% dissolved and the SRNL measured wt% dissolved are shown in Table 4-7.

**Table 4-7 Summary between forecasted and measured dissolutions**

| Scenario | Material | Forecasted wt% dissolved |
|---|---|---|
| 1 strike @ 50:1$_{\text{Purex}}$ (4 wt% OA) | Purex simulant | 32% less than the measured wt% dissolved |
| 1 strike @ 50:1$_{\text{HM}}$ (4 wt% OA) | HM simulant | 5% less than the measured wt% dissolved |
| 1 strike @ 50:1$_{\text{Purex}}$ (4 wt% OA) | Tank 8 Sludge | 20% greater than the measured wt% dissolved |
| 2 strikes @ 20:1$_{\text{HM}}$ (8 wt% OA) | Tank 16 Sludge | 20% greater than the measured wt% dissolved |

Based on literature (Adu-Wusu, *et al*, 2003:71), three strikes of 8 wt% oxalic acid solution in volume ratios of 20:1 oxalic acid solution to sludge were recommended for SRS HLW sludge heel removal. Based on Table 4-4 contained in Section 4.3.4, as more acid is used, the difference between the forecasted and measured values further converges.

# 5 CORROSION, HEATING, GAS GENERATION, AND PRESSURE

## 5.1 Introduction to the Safety Impacts

This chapter was written to document the following:

1) The development of a limited material balance across the treatment and pH restoration tanks, based on the dissolution of Hypothetical Worst Case Sludge (HWCS).

2) The evaluation of the safety impacts (*i.e.,* corrosion rates, heating, gas generation, and pressure on the treatment and pH restoration tanks from oxalic acid sludge heel removal in SRS HLW Tanks 1 through 15).

Based on measured SRNL testing, the recommended cleaning solution was determined to consist of three strikes of 8 wt% oxalic acid solution, in a volume ratio of 20:1 oxalic acid solution to sludge (Adu-Wusu, *et al*, 2003:71). As part of this chapter, a Hypothetical Worst Case Sludge is first defined, a material balance developed, and the safety impacts evaluated.

## 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 such an approach, single representative species are used to account primarily for all 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, as well as account for the interactions between the constituents. Although the characterization database must be used carefully, it is extremely beneficial since it enables initial forecasts on effectiveness, safety, flammability, and downstream processing impacts to be made, such that resources (*e.g.*, new sampling) can be allocated to only those activities where refinement is required.

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 the following (HLW, 2005):

Radionuclides:

Th-238 (thorium); U-232 (uranium); U-233, U-234; U-235; U-236; U-238; Np-236 (neptunium); Np-237; Pu-238 (plutonium); Pu-239; Pu-240; Pu-241; Pu-242; Pu-244; H-3 (tritium); Cs-135 (cesium); Cs-137, C-14 (carbon); Co-60 (cobalt); Se-79 (selenium); Y-90 (yttrium); Nb-94 (niobium); Tc-99 (technetium); Ru-106 (ruthenium); Rh-106 (rhodium); Sb-125 (antimony); Sn-126 (tin); I-129 (iodine); Ba-137m (barium); Ce-144 (cerium); Pr-144 (praseodymium); Pm-147 (promethium); Eu-154 (europium); Am-241 (americium); Am-242m; Am-244; Cm-245 (curium).

Chemical Compounds:

$Al(OH)_3$ (aluminum hydroxide); $BaSO_4$ (barium sulfate); $Ca_3(PO)_4$ (calcium phosphate); $CaC_2O_4$ (calcium oxalate); $CaF_2$ (calcium fluoride); $CaSO_4$ (calcium sulfate); $Ce(OH)_3$ (cerium hydroxide); $Co(OH)_3$ (cobalt hydroxide); $Cr(OH)_3$ (chromium hydroxide); $Cu(OH)_2$ (copper hydroxide); $Fe(OH)_3$ (iron hydroxide); HgO (mercury oxide); $KNO_3$ (potassium nitrate); $La(OH)_3$ (lanthanum hydroxide); $Mg(OH)_2$ (magnesium hydroxide); $MnO_2$ (manganese oxide); $Na_2SO_4$, (sodium sulfate); $Na_3PO_4$ (sodium phosphate); NaCl (sodium chloride); NaF (sodium fluoride); NaI (sodium iodide); $NaNO_3$ (sodium nitrate); NaOH (sodium hydroxide); $Ni(OH)_2$ (nickel hydroxide); $PbCO_3$ (lead carbonate); $PbSO_4$ (lead sulfate); $Pr(OH)_3$ (praseodymium hydroxide); $Pu(OH)_4$ (plutonium hydroxide); $RuO_2$ (ruthenium oxide); $SiO_2$ (silicon dioxide); $SrCO_3$ (strontium carbonate); $ThO_2$ (thorium oxide); $TiO_2$ (tin oxide); $UO_2(OH)_2$ (uranium hydroxide); $Zn(OH)_2$ (zinc hydroxide); $Zr(OH)_2$ (zirconium hydroxide).

The process database, however, is not a complete database, as its uncertainty exceeds the tolerance needed to quantify the effects of energetic compounds and organics. To ensure data is appropriately applied, energetic compounds and organics are generally not recorded in the database. On a mass basis, the quantity of energetic compounds and organics required to have a significant impact on flammability are very small. Generally, sample results have shown that energetic compounds and organics within the tanks are near or less than the lower levels of detectability (Swingle, *et al*, 1999; Britt, 2003; Hobbs, 1999). Energetic compounds and organics were not quantified using the process database, but were addressed separately as part of Chapter 6.

Initially when attempting to characterize the sludge, all of the transfers to Tanks 1-15 were listed, and a worst-case transfer for each constituent was defined. Since approximately 65 vol% must be water for OLI$^{©}$ to work (Badheka & Ketusky, 2003:117), the solids were too concentrated for the OLI$^{©}$ program to work, resulting in the software "timing out." The strategy eventually implemented was to consider all of the metal constituents in the transfers such that approximately 90% of the mass would be accounted for (Badheka & Ketusky, 2003:91). Additionally, those constituents that could contribute to safety impacts (*i.e.,* corrosion rate, heating, gas generation, including hydrogen generation from corrosion, and pressure) were considered when determining the sludge constituents.

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 modeling**

| 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 and hydroxides included in the Chapter 4, as well as various other constituents.

The range of constituents for sludge transfers to Tanks 1-15 are shown in Table 5-2.

**Table 5-2 Range of transfer constituent sludge mass for Tanks 1-15**

| Tank constituent | Tank 1-15 range (kg) | | |
|---|---|---|---|
| AgOH | 0 | to | 3.73E-3 |
| $Al(OH)_3$ | 9.66E-2 | to | 1.18E-1 |
| $CaC_2O_4$ | 0 | to | 2.46E-2 |
| $CaCO_3$ | 5.41E-3 | to | 6.46E-2 |
| $Fe(OH)_3$ | 2.73E-2 | to | 6.54E-1 |
| HgO | 6.72E-4 | to | 4.03E-2 |
| $KNO_3$ | 9.70E-4 | to | 9.06E-3 |
| $Mn(OH)_2$ | 3.04E-2 | to | 3.47E-1 |
| NaCl | 8.06E-4 | to | 2.15E2 |
| $NaNO_3$ | 5.25E-3 | to | 3.83E-2 |
| NaOH | 1.91E-2 | to | 4.86E-2 |
| $Ni(OH)_2$ | 1.63E-4 | to | 1.35E-1 |
| $PbCO_3$ | 1.02E-4 | to | 2.28E-3 |
| $SiO_2$ | 3.76E-3 | to | 1.24E-1 |
| $UO_2(OH)_2$ | 3.15E-4 | to | 1.78E-1 |
| $SrCO_3$ | 7.24E-4 | to | 1.37E-3 |
| $Pu(OH)_4$ | 0 | to | 3.73E-3 |
| Total Solids | 7.13E-1 | to | 9.26E-1 |

Since transfers vary in size, the values contained in Table 5-2 needed to be normalized for comparative purposes. To normalize data for comparative purposes, each constituent mass was divided by the total mass in the considered tank. Refer to Table 5-3.

**Table 5-3 Normalized maximum sludge mass**

| Constituent | *Maximum Mass* ($kg/kg_{total}$) |
|---|---|
| AgOH | 4.28E-3 |
| $Al(OH)_3$ | 5.74E-1 |
| $CaC_2O_4$ | 2.70E-2 |
| $CaCO_3$ | 7.42E-2 |
| $Fe(OH)_3$ | 7.51E-1 |
| HgO | 4.42E-2 |
| $KNO_3$ | 1.04E-2 |
| $Mn(OH)_2$ | 3.93E-1 |
| NaCl | 2.47E-2 |
| $NaNO_3$ | 4.20E-2 |
| NaOH | 5.58E-2 |
| $Ni(OH)_2$ | 1.89E-1 |
| $PbCO_3$ | 3.03E-3 |
| $SiO_2$ | 1.36E-1 |
| $UO_2(OH)_2$ | 2.50E-1 |
| $SrCO_3$ | 1.78E-3 |
| $Pu(OH)_4$ | 3.72E-4 |
| Total Solids | 1.0 |

The "*Max Mass* $kg/kg_{total}$" column in Table 5-3 was multiplied by the concentration of dry solids in a liter of sludge. For conservatism, 2.96E-1 $kg_{total}/l$ was used, except for plutonium, in which 3.49E-1 $kg_{total}/l$ was used for conservatism. Additionally, to convert to a "per sludge heel," the concentration per liter was multiplied by the assumed 19,000 liter heel size, as shown in Equation 5-1.

$$Mass = Max\ mass \times Solids\ concentration \times volume \qquad \text{(Equation 5-1)}$$

Where:

*Mass* = mass of constituent in sludge heel (kg)

*Max mass* = kg of constituent solids per 19,000 liter of sludge ($kg/kg_{total}$)

= value from Table 5-3

*Solids concentration* = concentration of dry solids in one liter of heel

= conservatively assumed to be 2.96E-1 $kg_{total}/l$, except for plutonium which is assumed to be 3.49E-1 $kg_{total}/l$.

*volume* = sludge heel volume = 19,000 liter

Table 5-4 shows the mass of each constituent in the 19,000 l of HWCS.

**Table 5-4 HWCS heel**

| Constituent | Mass (kg/19,000 l of HWCS) |
|---|---|
| AgOH | 2.4E+0 |
| $Al(OH)_3$ | 3.2E+3 |
| $CaC_2O_4$ | 1.5E+1 |
| $CaCO_3$ | 4.2E+2 |
| $Fe(OH)_3$ | 4.2E+3 |
| HgO | 2.5E+2 |
| $KNO_3$ | 5.9E+1 |
| $Mn(OH)_2$ | 2.3E+3 |
| NaCl | 1.4E+2 |
| $NaNO_3$ | 2.4E+2 |
| NaOH | 3.2E+2 |
| $Ni(OH)_2$ | 1.1E+3 |
| $PbCO_3$ | 1.7E+1 |
| $SiO_2$ | 6.9E+2 |
| $UO_2(OH)_2$ | 1.4E+3 |
| $SrCO_3$ | 1.8E-3 |
| $Pu(OH)_4$ | 2.5E+0 |

## 5.3 Supernate in pH Restoration Tank

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

The supernate characterization is shown in Table 5-5.

**Table 5-5 Supernate characterization**

| Constituent | Tank 8 | Tank 13 | Tank 33 | Max |
|---|---|---|---|---|
| | (kg) | | | |
| Ag | 1.14E-5 | 1.51E-7 | 1.51E-7 | 1.51E-7 |
| Al | 2.59E-1 | 3.81E-1 | 1.08E-1 | 3.81E-1 |
| $CO_3$ | 3.18E-2 | 3.41E-2 | 4.54E-2 | 4.54E-2 |
| $C_2O_4$ | 2.60E-3 | 2.27E-3 | 2.27E-3 | 2.60E-3 |
| Fe | 1.06E-4 | 6.76E-5 | 6.76E-5 | 6.76E-5 |
| Hg | 1.14E-4 | 7.57E-5 | 7.57E-5 | 7.57E-5 |
| Mn | 3.19E-6 | 2.61E-6 | 3.22E-6 | 3.22E-6 |
| Ni | 1.14E-5 | 9.48E-6 | 1.15E-5 | 1.15E-5 |
| $NO_2$ | 4.79E-1 | 5.29E-1 | 4.70E-1 | 5.29E-1 |
| $NO_3$ | 4.69E-1 | 5.28E-1 | 3.76E-1 | 5.28E-1 |
| NaOH | 0.65 used | 0.65 used | 0.65 used | 0.65 used |

The values were converted to the simplest compounds of OH, except for NaOH that was based on maintaining the corrosion control program.

For the 19,000 liter heel, the characterization input was developed and is shown in Table 5-6.

**Table 5-6 Model input for 19,000 l of HWCS**

| Constituent | Mass (kg/19,000 l of HWCS) |
|---|---|
| AgOH | 1.74E+0 |
| $Al(OH)_3$ | 5.50E+3 |
| $Na_2CO_3$ | 5.23E+2 |
| $HgC_2O_4$ | 1.87E+1 |
| $Fe(OH)_3$ | 1.01E+0 |
| HgO | 7.7E+0 |
| $Mn(OH)_2$ | 2.61E-2 |
| $Ni(OH)_2$ | 9.06E-2 |
| $HNO_2$ | 2.70E+3 |
| $NaNO_3$ | 9.76E+3 |
| NaOH | 3.25E+3 |

## 5.4 Material /Energy Balance and Safety Impacts

The purpose of the material balance was to estimate the contents in the treatment tank and pH restoration tank throughout each evolution of the treatment.

### 5.4.1 Hypothetical Worst Case Sludge material balance

A material balance diagram for the three acid strikes was developed and is shown in Figure 5-1.

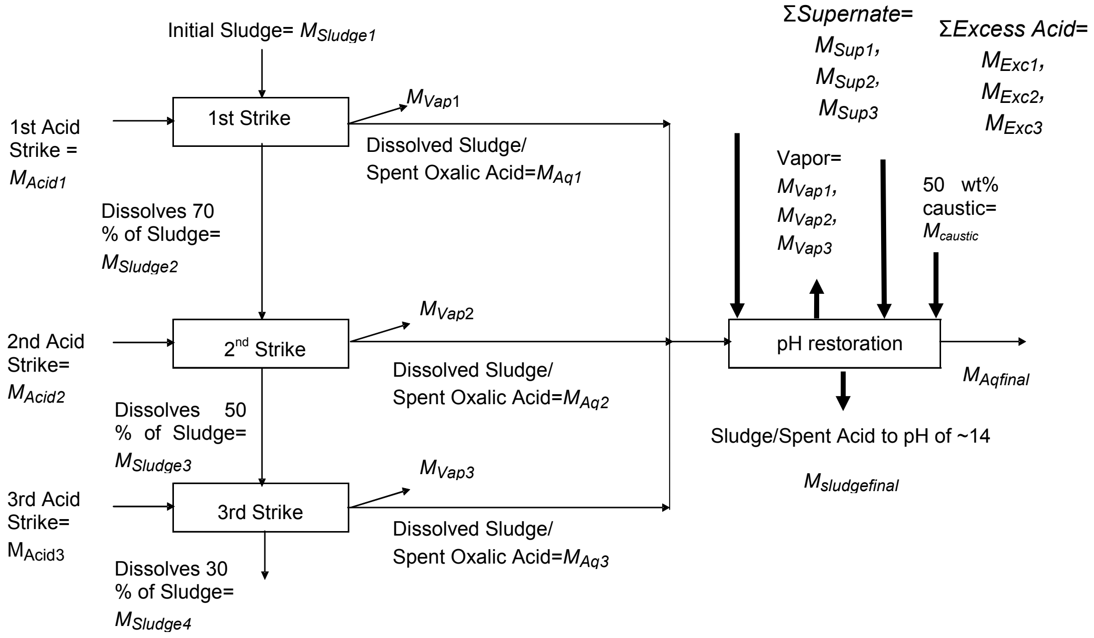


**Figure 5-1 Treatment and pH restoration tank material balance diagram**

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

$$M_{AcidN} + M_{SludgeN} =$$

$$M_{SludgeN} + M_{AqN} + M_{VapN} \qquad \text{(Equation 5-2)}$$

Where:

$N$ = Acid strike number (*i.e.,* first strike, second strike, or third 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 would be made from dissolved sludge/reacted acid and would be transferred to the pH restoration tank

$M_{VapN}$ = Vapor that would be released from the treatment tank after strike “N”

$M_{AcidN}$ = Acid needed for desired dissolution in Strike “N”

The equation did not include unreacted acid, $M_{ExcN}$; therefore, to show unreacted acid in the system, the acid was added to both sides of the equation as shown in Equation 5-3.

$$\begin{aligned} &M_{ExcN} + M_{AcidN} + M_{SludgeN} = \\ &M_{SludgeN} + M_{AqN} + M_{VapN} + MExcN \end{aligned} \qquad \text{(Equation 5-3)}$$

Where:

$M_{ExcN}$ = Excess acid that did not react in the treatment tank, but passed through the system until reacting in the pH restoration tank

For the three strikes in the treatment tank, this can be expressed as Equation 5-4.

$$\begin{aligned} &M_{Sludge1} + \Sigma_N M_{Acid} + \Sigma_N M_{Excess} = \\ &M_{Sludge4} + \Sigma_N M_{Aq} + \Sigma_N M_{Vap} + \Sigma_N MExc \end{aligned} \qquad \text{(Equation 5-4)}$$

$M_{Vap1}$, $M_{Vap2}$, and $M_{Vap3}$ would be released to the atmosphere from the treatment tank. $M_{Sludge4}$ would be the remaining sludge heel, while $M_{Aq1}$, $M_{Aq2}$, $M_{Ag3}$, $M_{Exc1}$, $M_{Exc2}$, and $M_{Exc3}$ would be added to the pH restoration tank. The pH restoration tank was assumed initially to have a heel of 37,854 l 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 and were evaluated to be acceptable because they are a normal part of maintaining the corrosion control program.

The material balance for the pH restoration tank is shown as Equation 5-5.

$$M_{Snate1} + M_{Caustic} + \sum_N M_{Aq} + \sum_N M_{Exc} = \\ \sum M_{\Pr ec} + \sum M_{Gas} + M_{SnateEnd} \qquad \text{(Equation 5-5)}$$

Where:

$M_{Snate1}$ = Initial supernate in pH restoration tank

$M_{Caustic}$ = Estimated caustic pre-added to the pH restoration tank to ensure pH remained 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 pH restoration tank

$\sum M_{Exc}$ = $M_{Exc1}+M_{Exc2}+M_{Exc3}$ = Unspent acid which was added during the acid strikes, but did not react in system until reaching the pH restoration tank. Each excess is transferred with the corresponding aqueous (*i.e.,* $M_{Ag1}+M_{Exc1}$ was transferred from treatment tank, $M_{Acid2}$ was added to treatment tank and mixed, and then $M_{Ag2}+M_{Exc2}$ transferred out of treatment tank to the pH restoration tank)

$\sum M_{Prec}$ = $M_{Prec1}+M_{Prec2}+M_{Prec3}$ = Precipitate that would form in the pH restoration tank after transfers from the treatment tank

$\sum M_{Gas}$ = $M_{Gas1}+M_{Gas2}+M_{Gas3}$ = pH restoration vapor produced from aqueous and excess acid of strike transferred into the pH restoration tank

$M_{SnateEnd}$ = End Aqueous in the pH restoration tank after $\sum M_{Aq}$ and $\sum M_{Exc}$ additions to the pH restoration tank and reactions were complete

### 5.4.2 Modeling input and assumptions

For speciation, the amount of oxalic acid added was based on obtaining 70 vol%, 50 vol% and 30 vol%, as determined by using OLI Stream Analyzer©. Adu-Wusu, *et al*, (2003:71) recommended that 3 strikes of 8 wt% oxalic acid solutions in volume ratios of 20:1 acid to sludge be used to dissolve the sludge. The excess acid was not assumed to react, but to pass through the system with the aqueous until finally reacting within the pH restoration tank. No corrosion inhibitors were required to be added to the treatment tank during acid cleaning or post acid cleaning. Since the treatment tank was scheduled to be closed, without significant process changes/requirements, no additional NaOH was added to the treatment tank.

Salt/supernate was removed prior to acid heel dissolution, based on space availability and ease of separation. The minimum pump down level was assumed 19,000 l. At the minimum pump down level, the tank contained the 19,000 l of HWCS and 70 vol% of which was assumed to be interstitial liquid, which had been rinsed down to mostly water.

The rheology, morphology and geometry of the sludge was assumed not to hinder the acid from chemically interacting with the sludge. Additionally, adequate time was allowed for the reactions to come to equilibrium. Oxalic acid vapors were minimized for the material balance. Bounding calculations based on an energy balance were used to calculate input for pressurization concerns.

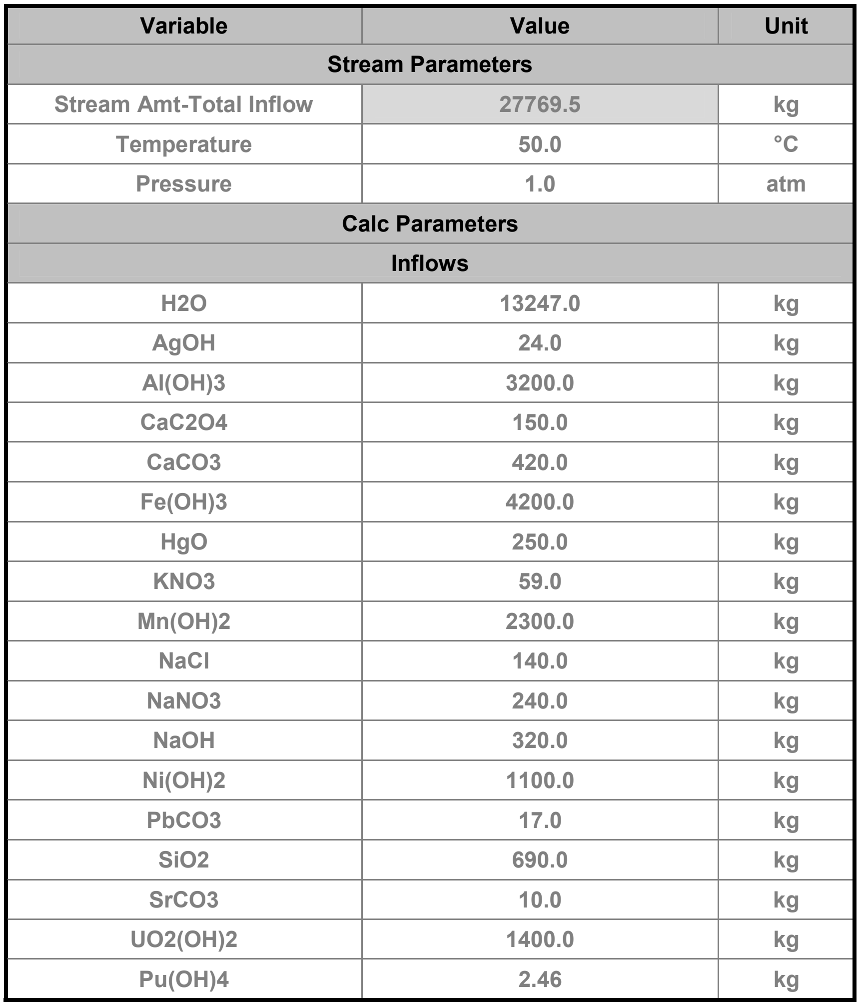
Small additions, round offs, and speciation simplification based on perceived process, risk importance, and over-all concentration were assumed acceptable based on the likelihood that they were within the uncertainty. This included the interstitial liquid, since the volume was very small compared to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

Solids carryover was considered negligible for the speciation and was not factored into the model (*i.e.,* without knowing the pumping capabilities of the system, only dissolved solids were considered to be transferred in the mass balance. Furthermore, this was considered to be outside the scope of the material balance). Enthalpy, temperature, gas generation, and dissolution were independently maximized. Such an approach was conservative. The HWCS volume, when acid heel dissolution begins, was assumed to be limited to about 19,000 l.

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

### 5.4.3 Material balance modeling

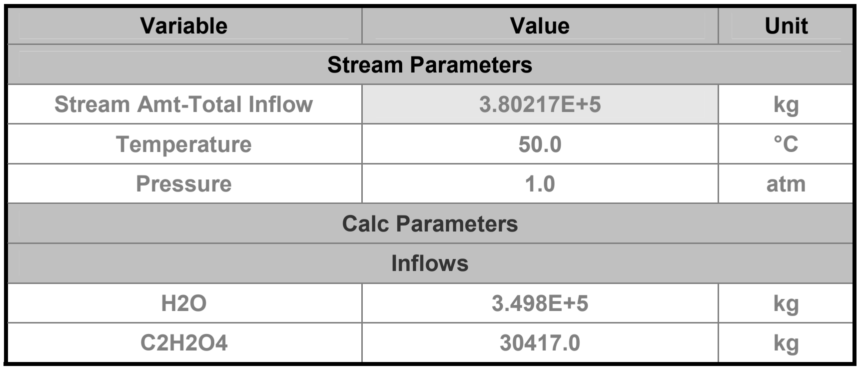
The input screen for the initial 19,000 l of $M_{Sludge1}$ uses Table 5-4 and is shown in Figure 5-2. In addition to HWCS, the interstitial liquid was assumed to be water, occupying 70 vol% of the sludge.



| 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 Input screen for Hypothetical Worst Case Sludge**

The white background cells under "inflows" were manually entered, whereas, the shaded, "Stream Amt-Total Inflow" were automatically calculated by OLI Stream Analyzer©. The "Output" (not shown) estimated the mass of the solids as about 14,500 kg and having a volume of 5,700 l. Adu-Wusu, *et al*, (2003:70) recommends that first strike of 8 wt% of a 20:1 volume ratio be added to result in 70 vol% of the sludge heel dissolved. The input screen used for acid is shown in Figure 5-3.



| Variable | Value | Unit |
|---|---|---|
| **Stream Parameters** | | |
| Stream Amt-Total Inflow | 3.80217E+5 | kg |
| Temperature | 50.0 | °C |
| Pressure | 1.0 | atm |
| **Calc Parameters** | | |
| **Inflows** | | |
| H2O | 3.498E+5 | kg |
| C2H2O4 | 30417.0 | kg |

**Figure 5-3  Input screen for recommended amount of acid for first strike**

Through trial and error, enough 8 wt% oxalic acid solution was added to dissolve 70 vol% of the solid heel volume (only 5,700 l) and result in approximately 1,700 l.  This value, $M_{Acid1}$ equals 0.418 multiplied by the literature-recommended amount of acid.

In Figure 5-4, the literature-recommended amount of acid was 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 input screen used for the first strike is 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 1 | 27769.5 | 3.80217E+5 | 1.867E+5 | kg |
| Temperature | 50.0 | 25.0 | 50.0 | °C |
| Presure | 1.0 | 1.0 | 1.0 | atm |
| **Inflows** | | | | |
| H2O | 13247.0 | 3.48E+5 | 1.59463E+5 | 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 screen for first acid strike**

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

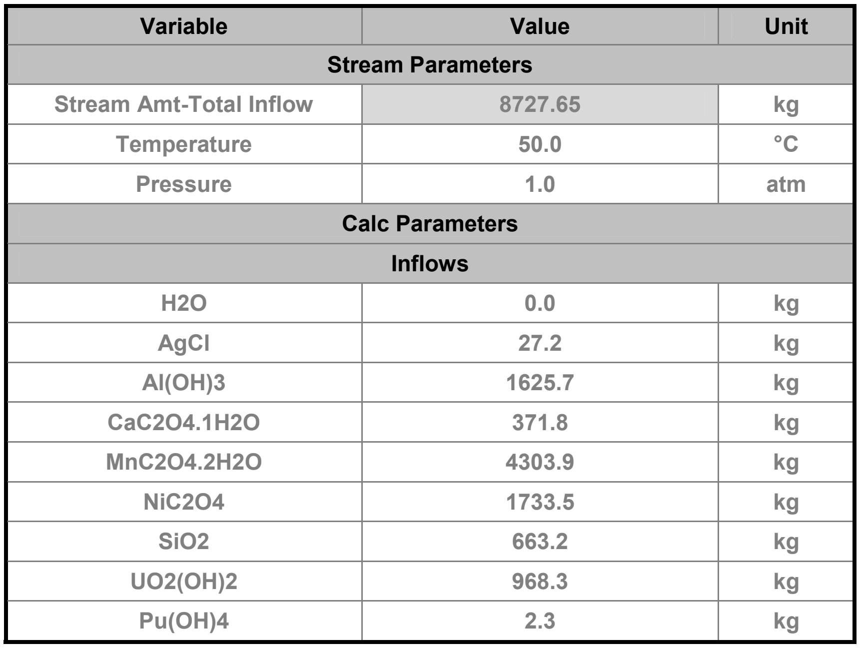
**Table 5-7 Output from the first acid strike**

| Constituent | Aqueous ($M_{Aq1}$) | Excess acid ($M_{Exc1}$) | Vapor ($M_{Vap1}$) | Solid ($M_{Sludge2}$) |
|---|---|---|---|---|
| | (kg) | | | |
| $H_2O$ | 1.63E+5 | = 0.582 x 3.5E+5 | 4.47E+0 | 0.00E+0 |
| $Al(OH)_3$ | 0.00E+0 | | 0.00E+0 | 1.63E+4 |
| $CaC_2O_4$ | 3.62E+2 | | 0.00E+0 | 0.00E+0 |
| $SiO_2$ | 2.68E+1 | | 0.00E+0 | 6.63E+2 |
| $Pu(OH)_4$ | 0.00E+0 | | 0.00E+0 | 2.33E+0 |
| $C_2H_2O_4$ | 2.48E+3 | = 0.582 x 3.04E+5 | 0.00E+0 | 0.00E+0 |
| $Ag_2C_2O_4$ | 3.61E-1 | | 0.00E+0 | 0.00E+0 |
| $AgCl$ | 0.00E+0 | | 0.00E+0 | 2.72E+1 |
| $Al(NO_3)_3$ | 2.42E+2 | | 0.00E+0 | 0.00E+0 |
| $AlCl_3$ | 9.8E+1 | | 0.00E+0 | 0.00E+0 |
| $CaC_2O_4.1H_2O$ | 1.10E+3 | | 0.00E+0 | 0.00E+0 |
| $CO_2$ | 0.00E+0 | | 0.00E+0 | 3.72E+2 |
| $Fe_2(C_2O_4)_3$ | 1.13E+2 | | 7.79E+1 | 0.00E+0 |
| $HCl$ | 7.38E+3 | | 0.00E+0 | 0.00E+0 |
| $HgC_2O_4$ | 0.00E+0 | | 9.81E-11 | 0.00E+0 |
| $HgCl_2$ | 3.33E+2 | | 00.0E+0 | 0.00E+0 |
| $HNO_3$ | 0.00E+0 | | 7.45E-5 | 0.00E+0 |
| $K_2C_2O_4$ | 0.00E+0 | | 8.19E-9 | 0.00E+0 |
| $MnC_2O_4$ | 4.85E+1 | | 0.00E+0 | 0.00E+0 |
| $MnC_2O_4.2H_2O$ | 2.59E+2 | | 0.00E+0 | 0.00E+0 |
| $Na_2C_2O_4$ | 0.00E+0 | | 0.00E+0 | 4.30E+3 |
| $NaAlO_2$ | 8.86E+2 | | 0.00E+0 | 0.00E+0 |
| $NiC_2O_4$ | 7.44E+0 | | 0.00E+0 | 1.73E+3 |
| $PbC_2O_4$ | 1.88E+1 | | 0.00E+0 | 0.00E+0 |
| $Pu(C_2O_4)_2$ | 1.76E-1 | | 0.00E+0 | 0.00E+0 |
| $SiCl_4$ | 0.00E+0 | | 0.00E+0 | 0.00E+0 |
| $SrC_2O_4$ | 1.19E+1 | | 0.00E+0 | 0.00E+0 |
| $UO_2C_2O_4$ | 1.65E+3 | | 0.00E+0 | 0.00E+0 |

$M_{Exc1}$ was 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 were transferred to the pH restoration tank, while the vapor, $M_{Vap1}$ was released to the atmosphere. The sludge solids, $M_{Sludge2}$ remained in the treatment tank.

After dissolution, the remaining sludge was assumed to be flushed. Flushing will lower the ionic strength of the remaining interstitial solution within the treatment tank. The interstitial liquid, however, was not considered significant within the model, since the volume was very small compared to the amount of acid solution added. Solids were assumed not to carry over. Spent acid/dissolved sludge and unspent acid, $M_{Aq1}$, $M_{Exc1}$ were transferred to the pH restoration tank, with the remaining solids.

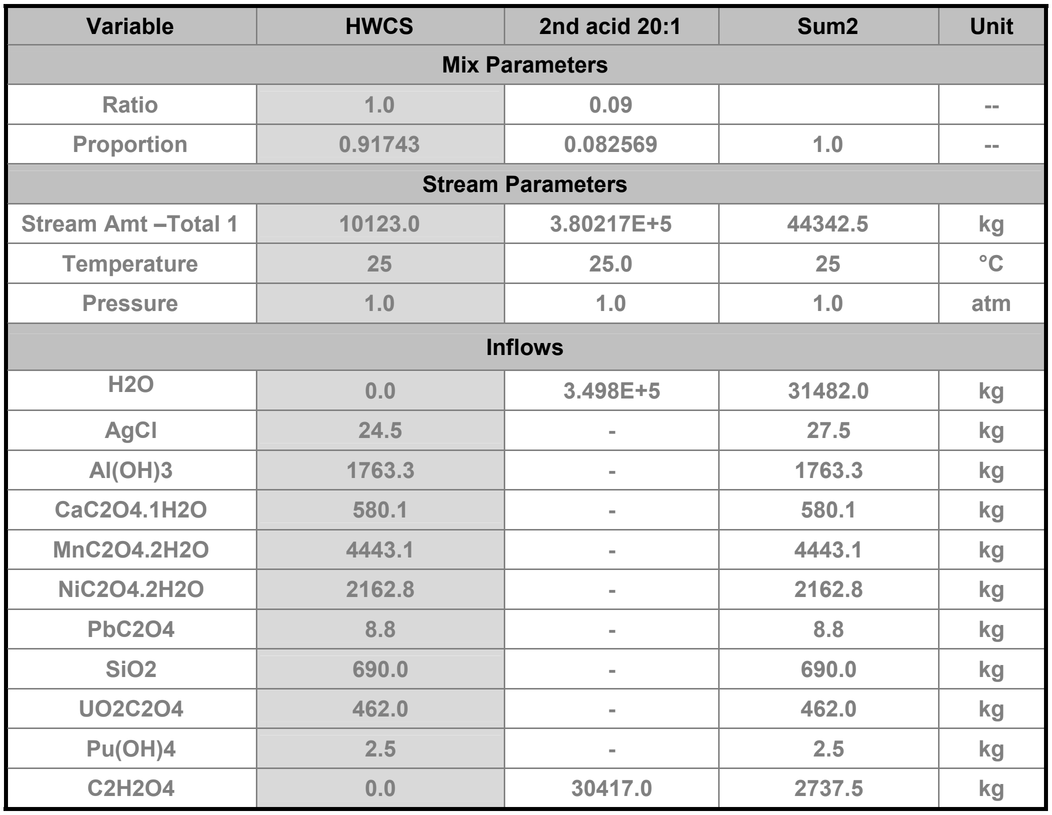
The software's capability to separate each phase was used to separate the liquid fraction from the solids, and the solids were used as input into the second strike. Refer to Figure 5-5.



| Variable | Value | Unit |
|---|---|---|
| **Stream Parameters** | | |
| Stream Amt-Total Inflow | 8727.65 | kg |
| Temperature | 50.0 | °C |
| Pressure | 1.0 | atm |
| **Calc Parameters** | | |
| **Inflows** | | |
| H2O | 0.0 | kg |
| AgCl | 27.2 | kg |
| Al(OH)3 | 1625.7 | kg |
| CaC2O4.1H2O | 371.8 | kg |
| MnC2O4.2H2O | 4303.9 | kg |
| NiC2O4 | 1733.5 | kg |
| SiO2 | 663.2 | kg |
| UO2(OH)2 | 968.3 | kg |
| Pu(OH)4 | 2.3 | kg |

**Figure 5-5 Input screen for solids after first acid strike**

The literature-recommended amount of 8 wt% oxalic acid solution, to result in a 50 vol% dissolution for the second strike, was a 0.3 fraction of the initial acid. Using trial and error, it was determined that only 0.09 from the initial quantity was required for the model to dissolve 50 vol% of the remaining sludge; therefore, $M_{Acid2}$ = 0.09 x $M_{Acid1}$. Refer to Figure 5-6.



| Variable | HWCS | 2nd acid 20:1 | Sum2 | Unit |
|---|---|---|---|---|
| **Mix Parameters** | | | | |
| Ratio | 1.0 | 0.09 | | -- |
| Proportion | 0.91743 | 0.082569 | 1.0 | -- |
| **Stream Parameters** | | | | |
| Stream Amt –Total 1 | 10123.0 | 3.80217E+5 | 44342.5 | kg |
| Temperature | 25 | 25.0 | 25 | °C |
| Pressure | 1.0 | 1.0 | 1.0 | atm |
| **Inflows** | | | | |
| H2O | 0.0 | 3.498E+5 | 31482.0 | kg |
| AgCl | 24.5 | - | 27.5 | kg |
| Al(OH)3 | 1763.3 | - | 1763.3 | kg |
| CaC2O4.1H2O | 580.1 | - | 580.1 | kg |
| MnC2O4.2H2O | 4443.1 | - | 4443.1 | kg |
| NiC2O4.2H2O | 2162.8 | - | 2162.8 | kg |
| PbC2O4 | 8.8 | - | 8.8 | kg |
| SiO2 | 690.0 | - | 690.0 | kg |
| UO2C2O4 | 462.0 | - | 462.0 | kg |
| Pu(OH)4 | 2.5 | - | 2.5 | kg |
| C2H2O4 | 0.0 | 30417.0 | 2737.5 | kg |

**Figure 5-6 Input screen for second acid strike**

$M_{Exc2}$ was based on 10.3 multiplied by the initial acid required (Badheka & Ketusky, 2003:121).

Table 5-8 shows the output of the second acid strike, where $M_{Exc2}$ was excess and had to be hand entered, so as not to react until reaching the pH restoration tank.

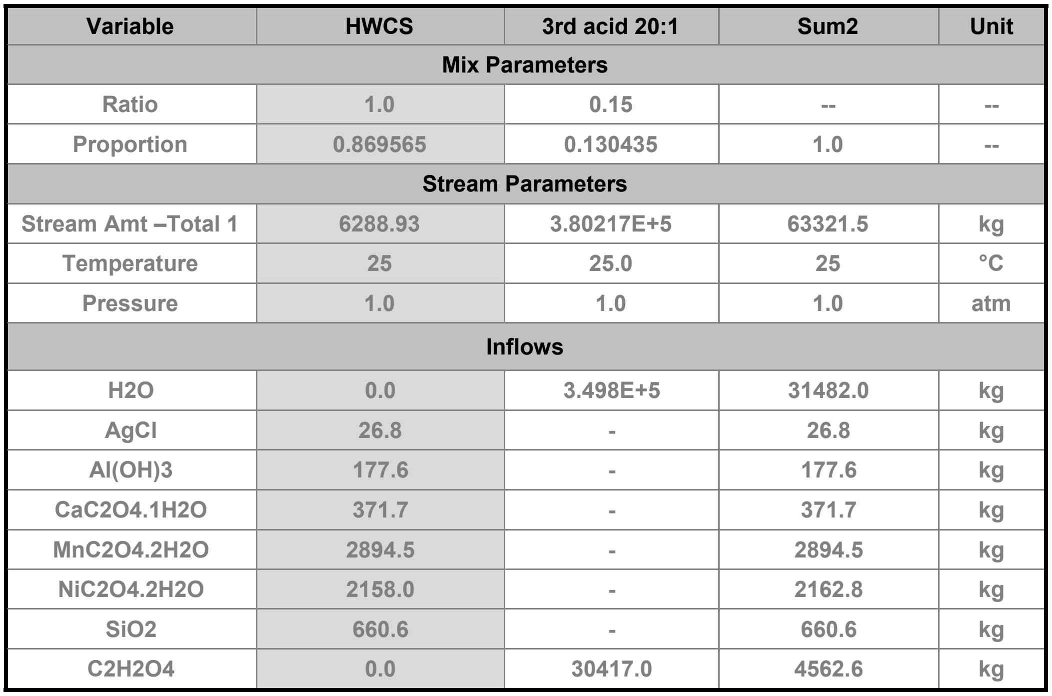
**Table 5-8 Output from second acid strike**

| Constituent | Aqueous ($M_{Aq2}$) | Excess Acid ($M_{Exc2}$) | Vapor ($M_{Vap2}$) | Solid ($M_{Sludge3}$) |
|---|---|---|---|---|
| | (kg) | | | |
| $H_2O$ | 3.17E+4 | =0.7X1.05E+5 | 0.00E+0 | 0.00E+0 |
| AgCl | 4.24E-1 | | 0.00E+0 | 2.68E+1 |
| $Al(OH)_3$ | 0.00E+0 | | 0.00E+0 | 1.78E+2 |
| $CaC_2O_4.1H_2O$ | 0.00E+0 | | 0.00E+0 | 3.72E+2 |
| $MnC_2O_4.2H_2O$ | 0.00E+0 | | 0.00E+0 | 2.89E+3 |
| $NiC_2O_{4.}2H2O$ | 1.19E+0 | | 0.00E+0 | 2.16E+3 |
| $SiO_2$ | 2.66E+0 | | 0.00E+0 | 6.61E+2 |
| $C_2H_2O_4$ | 2.74E+3 | =0.7 x 9125.1 | 0.00E+0 | 0.00E+0 |
| AlO(OH) | 1.11E+3 | | 0.00E+0 | 0.00E+0 |
| $CaC_2O_4$ | 3.44E-2 | | 0.00E+0 | 0.00E+0 |
| $MnC_2O_4$ | 1.13E+0 | | 0.00E+0 | 0.00E+0 |
| $Pu(C_2O_4)_2$ | 0.00E+0 | | 0.00E+0 | 2.16E+3 |

After the second acid strike, the aqueous and excess acid solutions were transferred to the pH restoration tank, and the vapor was released into the atmosphere. The solids remained within the treatment tank. The interstitial liquid, although 70 vol% of the sludge, was considered to be negligible compared to $M_{Acid2}$. The sludge was again treated with oxalic acid.

The third strike of oxalic acid was estimated to dissolve 30 vol% of the sludge. This time, the Adu-Wusu, *et al*, (2003:70) recommended amount of 8 wt% oxalic acid is equal to that required, based on the dissolution trials. $M_{Acid3}$ was expressed in terms of $M_{Acid1}$ for convenience.

The input for the third strike is shown in Figure 5-7.



| Variable | HWCS | 3rd acid 20:1 | Sum2 | Unit |
|---|---|---|---|---|
| **Mix Parameters** | | | | |
| Ratio | 1.0 | 0.15 | -- | -- |
| Proportion | 0.869565 | 0.130435 | 1.0 | -- |
| **Stream Parameters** | | | | |
| Stream Amt –Total 1 | 6288.93 | 3.80217E+5 | 63321.5 | kg |
| Temperature | 25 | 25.0 | 25 | °C |
| Pressure | 1.0 | 1.0 | 1.0 | atm |
| **Inflows** | | | | |
| H2O | 0.0 | 3.498E+5 | 31482.0 | kg |
| AgCl | 26.8 | - | 26.8 | kg |
| Al(OH)3 | 177.6 | - | 177.6 | kg |
| CaC2O4.1H2O | 371.7 | - | 371.7 | kg |
| MnC2O4.2H2O | 2894.5 | - | 2894.5 | kg |
| NiC2O4.2H2O | 2158.0 | - | 2162.8 | kg |
| SiO2 | 660.6 | - | 660.6 | kg |
| C2H2O4 | 0.0 | 30417.0 | 4562.6 | kg |

**Figure 5-7 Input screen for third acid strike**

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

**Table 5-9 Output from the third acid strike**

| Constituent | Aqueous | Excess Acid | Vapor | Solid |
|---|---|---|---|---|
| | $M_{Aq3}$ | $M_{Exc3}$ | $M_{Vap3}$ | $M_{Sludge4}$ |
| | (kg) | | | |
| $H_2O$ | 5.25E+4 | =0.15 x 3.8E+5 | 0.00E+0 | 0.00E+0 |
| AgCl | 1.75E-1 | | 0.00E+0 | 2.66E+1 |
| $CaC_2O_4.1H_2O$ | 0.00E+0 | | 0.00E+0 | 3.65E+2 |
| $MnC_2O_4.2H_2O$ | 0.00E+0 | | 0.00E+0 | 2.87E+3 |
| $NiC_2O_4.2H_2O$ | 0.00E+0 | | 0.00E+0 | 2.16E+3 |
| $SiO_2$ | 5.97E+0 | | 0.00E+0 | 6.55E+2 |
| $C_2H_2O_4$ | 4.56E+3 | =0.15 x 3.0E+4 | 0.00E+0 | 0.00E+0 |
| AlO(OH) | 1.37E+2 | | 0.00E+0 | 0.00E+0 |
| $CaC_2O_4$ | 6.31E+0 | | 0.00E+0 | 0.00E+0 |
| $MnC_2O_4$ | 1.69E+1 | | 0.00E+0 | 0.00E+0 |
| $NiC_2O_4$ | 1.48E+0 | | 0.00E+0 | 0.00E+0 |

Again, the aqueous and excess acid was transferred out, the vapor was released to the atmosphere, and a total of about 6,100 kg of solids, $\Sigma M_{Sludge4}$ remained. Since 70-50-30 vol% was assumed to be dissolved, the sludge heel in the treatment tank decreased from a volume of about 19,000 l to a volume of about 2,000 l. The pH restoration tank was assumed to initially contain about 378,500 l of supernate and was pre-charged with caustic to ensure that the pH would remain within the corrosion control program.

The input used for the pH restoration tank is shown in Figure 5-8.

| Variable | Supernate | Caustic | Sum2 | Unit |
|---|---|---|---|---|
| **Mix Parameters** | | | | |
| Ratio | 2.0 | 5.8 | -- | -- |
| Proportion | 0.25641 | 0.74359 | 1.0 | -- |
| **Stream Parameters** | | | | |
| Stream Amt –Total 1 | 40985.3 | 22712.4 | 2.13702E+5 | kg |
| Temperature | 25 | 25.0 | 25 | °C |
| Pressure | 1.0 | 1.0 | 1.0 | atm |
| **Inflows** | | | | |
| H2O | 18927.9 | 11356.2 | 1.0372E+5 | kg |
| HgC2O4 | 18.7 | - | 37.4 | kg |
| HNO2 | 2700.0 | - | 5400.0 | kg |
| AgOH | 1.7 | - | 3.5 | kg |
| Al(OH)3 | 5500.0 | - | 11000.0 | kg |
| Na2CO3 | 819.0 | - | 1638.0 | kg |
| Fe(OH)3 | 1.0 | - | 2.0 | kg |
| HgO | 7.7 | - | 15.4 | kg |
| Mn(OH)2 | 2.6E-2 | - | 5.2E-2 | kg |
| Ni(OH)2 | 9.1E-2 | - | 1.8E-1 | kg |
| SiO2 | 9760.0 | - | 19520.0 | kg |
| NaOH | 3250.0 | 11356.2 | 72366.0 | kg |

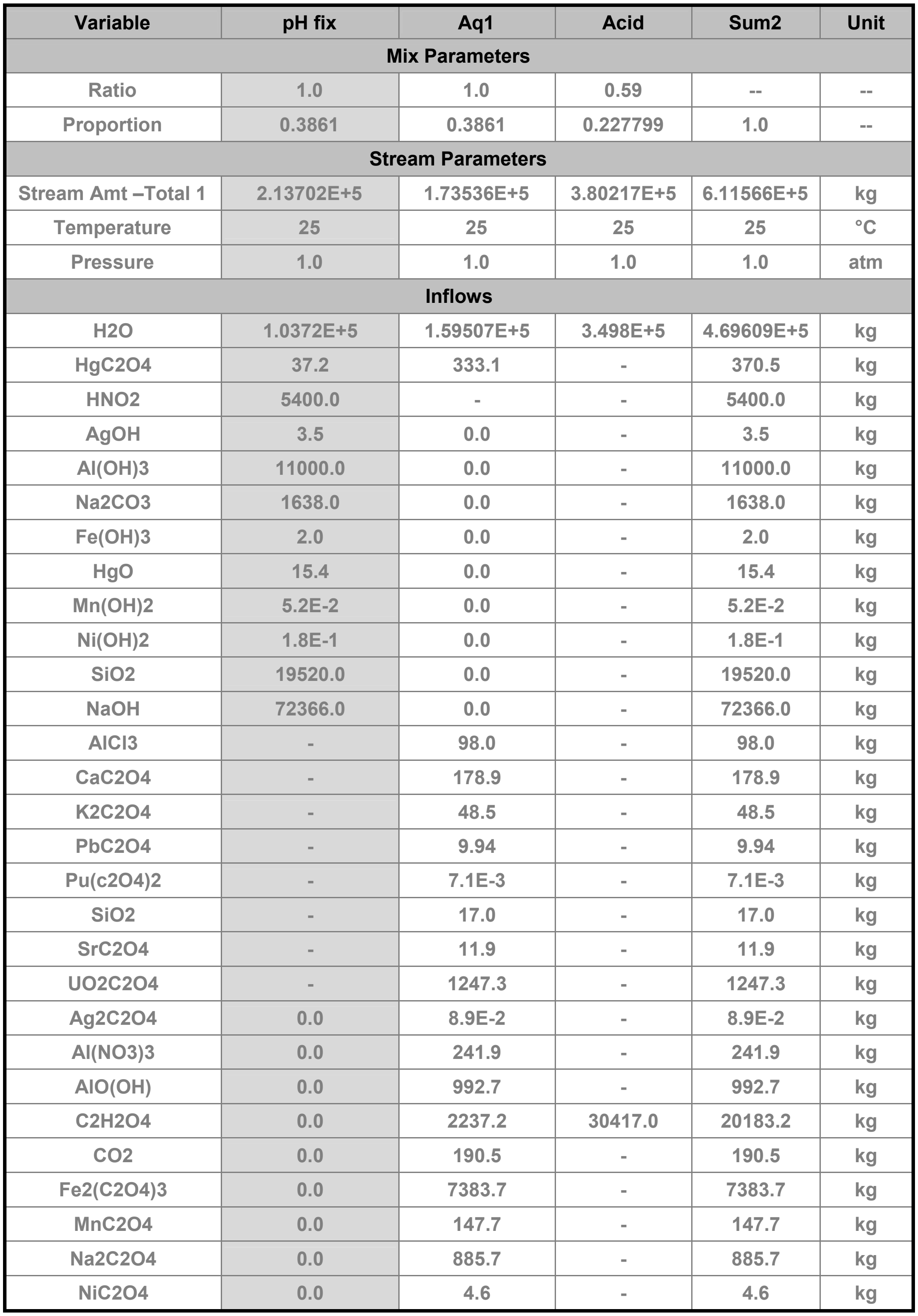
**Figure 5-8 Input screen to pH restoration**

The output from the addition of caustic to spent/excess acid is shown in Table 5-10.

**Table 5-10 pH restoration with supernate and spent/excess acid**

| Constituent | Aqueous | Vapor | Solid |
|---|---|---|---|
| | (kg) | | |
| $H_2O$ | 1.11E+5 | 0.00E+0 | 0.00E+0 |
| AgOH | 3.48E+0 | 0.00E+0 | 0.00E+0 |
| $Na_2CO_3$ | 1.64E+3 | 0.00E+0 | 0.00E+0 |
| $Fe(OH)_3$ | 2.02E+0 | 0.00E+0 | 0.00E+0 |
| HgO | 4.35E+1 | 0.00E+0 | 0.00E+0 |
| $Mn(OH)_2$ | 5.22E-2 | 0.00E+0 | 0.00E+0 |
| $Ni(OH)_2$ | 1.81E-1 | 0.00E+0 | 0.00E+0 |
| $NaNO_3$ | 1.86E+4 | 0.00E+0 | 8.73E+2 |
| NaOH | 6.21E+4 | 0.00E+0 | 0.00E+0 |
| $Na_2C_2O_4$ | 8.18E-1 | 0.00E+0 | 1.65E+1 |
| $NaAlO_2$ | 1.16E+4 | 0.00E+0 | 0.00E+0 |
| $NaNO_2$ | 7.92E+3 | 0.00E+0 | 0.00E+0 |

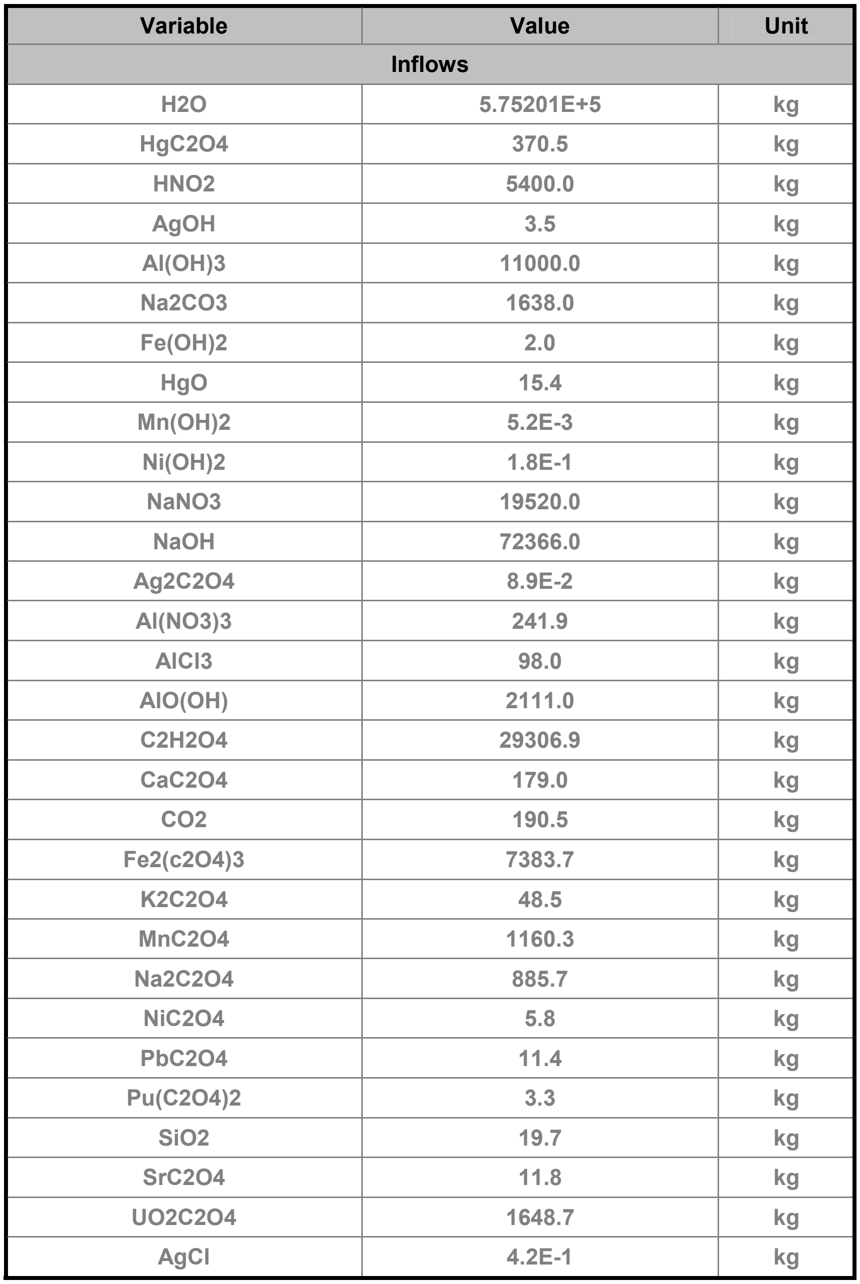
$M_{Aq1}$ and $M_{Exc1}$ were added to the pH restoration tank as shown in Figure 5-9. $M_{Exc1}$ was calculated based on $M_{Acid1}$+$M_{Exc1}$ equaling the recommended amount of acid to be added, based on literature (Adu-Wusu, *et al*, 2003:70).



| Variable | pH fix | 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 –Total 1 | 2.13702E+5 | 1.73536E+5 | 3.80217E+5 | 6.11566E+5 | kg |
| Temperature | 25 | 25 | 25 | 25 | °C |
| Pressure | 1.0 | 1.0 | 1.0 | 1.0 | atm |
| **Inflows** | | | | | |
| H2O | 1.0372E+5 | 1.59507E+5 | 3.498E+5 | 4.69609E+5 | kg |
| HgC2O4 | 37.2 | 333.1 | - | 370.5 | kg |
| HNO2 | 5400.0 | - | - | 5400.0 | kg |
| AgOH | 3.5 | 0.0 | - | 3.5 | kg |
| Al(OH)3 | 11000.0 | 0.0 | - | 11000.0 | kg |
| Na2CO3 | 1638.0 | 0.0 | - | 1638.0 | kg |
| Fe(OH)3 | 2.0 | 0.0 | - | 2.0 | kg |
| HgO | 15.4 | 0.0 | - | 15.4 | kg |
| Mn(OH)2 | 5.2E-2 | 0.0 | - | 5.2E-2 | kg |
| Ni(OH)2 | 1.8E-1 | 0.0 | - | 1.8E-1 | kg |
| SiO2 | 19520.0 | 0.0 | - | 19520.0 | kg |
| NaOH | 72366.0 | 0.0 | - | 72366.0 | kg |
| AlCl3 | - | 98.0 | - | 98.0 | kg |
| CaC2O4 | - | 178.9 | - | 178.9 | kg |
| K2C2O4 | - | 48.5 | - | 48.5 | kg |
| PbC2O4 | - | 9.94 | - | 9.94 | kg |
| Pu(c2O4)2 | - | 7.1E-3 | - | 7.1E-3 | kg |
| SiO2 | - | 17.0 | - | 17.0 | kg |
| SrC2O4 | - | 11.9 | - | 11.9 | kg |
| UO2C2O4 | - | 1247.3 | - | 1247.3 | kg |
| Ag2C2O4 | 0.0 | 8.9E-2 | - | 8.9E-2 | kg |
| Al(NO3)3 | 0.0 | 241.9 | - | 241.9 | kg |
| AlO(OH) | 0.0 | 992.7 | - | 992.7 | kg |
| C2H2O4 | 0.0 | 2237.2 | 30417.0 | 20183.2 | kg |
| CO2 | 0.0 | 190.5 | - | 190.5 | kg |
| Fe2(C2O4)3 | 0.0 | 7383.7 | - | 7383.7 | kg |
| MnC2O4 | 0.0 | 147.7 | - | 147.7 | kg |
| Na2C2O4 | 0.0 | 885.7 | - | 885.7 | kg |
| NiC2O4 | 0.0 | 4.6 | - | 4.6 | kg |

**Figure 5-9 Input screen of first spent acid transfer to pH restoration tank**

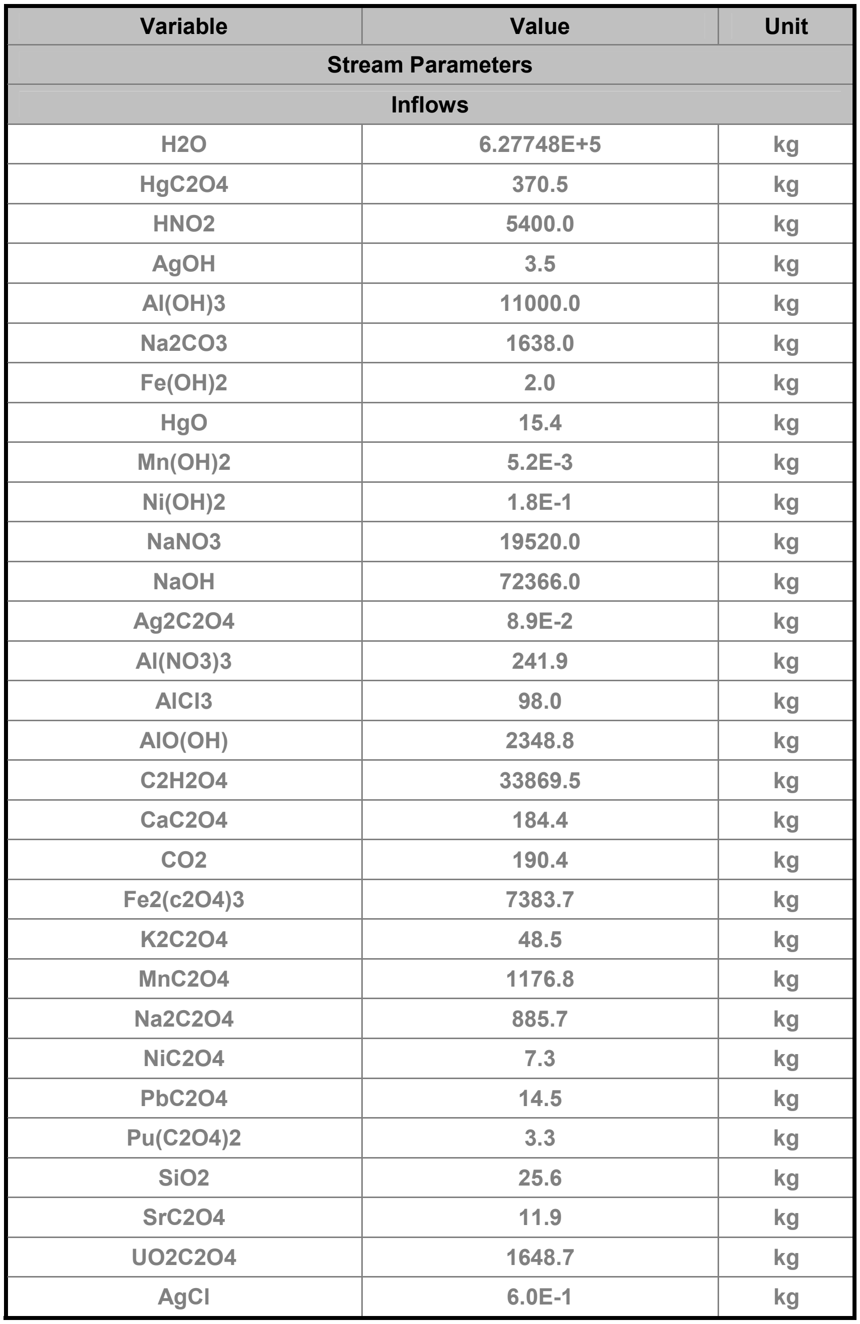
$M_{Aq2}$ and $M_{Exc2}$ were added to the pH restoration tank as shown in Figure 5-10.



| Variable | Value | Unit |
|---|---|---|
| **Inflows** | | |
| H2O | 5.75201E+5 | kg |
| HgC2O4 | 370.5 | kg |
| HNO2 | 5400.0 | kg |
| AgOH | 3.5 | kg |
| Al(OH)3 | 11000.0 | kg |
| Na2CO3 | 1638.0 | kg |
| Fe(OH)2 | 2.0 | kg |
| HgO | 15.4 | kg |
| Mn(OH)2 | 5.2E-3 | kg |
| Ni(OH)2 | 1.8E-1 | kg |
| NaNO3 | 19520.0 | kg |
| NaOH | 72366.0 | kg |
| Ag2C2O4 | 8.9E-2 | kg |
| Al(NO3)3 | 241.9 | kg |
| AlCl3 | 98.0 | kg |
| AlO(OH) | 2111.0 | kg |
| C2H2O4 | 29306.9 | kg |
| CaC2O4 | 179.0 | kg |
| CO2 | 190.5 | kg |
| Fe2(c2O4)3 | 7383.7 | kg |
| K2C2O4 | 48.5 | kg |
| MnC2O4 | 1160.3 | kg |
| Na2C2O4 | 885.7 | kg |
| NiC2O4 | 5.8 | kg |
| PbC2O4 | 11.4 | kg |
| Pu(C2O4)2 | 3.3 | kg |
| SiO2 | 19.7 | kg |
| SrC2O4 | 11.8 | kg |
| UO2C2O4 | 1648.7 | kg |
| AgCl | 4.2E-1 | kg |

**Figure 5-10 Input screen of second spent acid transfer to pH restoration tank**

$M_{Aq3}$ and $M_{Exc3}$ were added to the pH restoration tank as shown in Figure 5-11.



| Variable | Value | Unit |
|---|---|---|
| **Stream Parameters** | | |
| **Inflows** | | |
| H2O | 6.27748E+5 | kg |
| HgC2O4 | 370.5 | kg |
| HNO2 | 5400.0 | kg |
| AgOH | 3.5 | kg |
| Al(OH)3 | 11000.0 | kg |
| Na2CO3 | 1638.0 | kg |
| Fe(OH)2 | 2.0 | kg |
| HgO | 15.4 | kg |
| Mn(OH)2 | 5.2E-3 | kg |
| Ni(OH)2 | 1.8E-1 | kg |
| NaNO3 | 19520.0 | kg |
| NaOH | 72366.0 | kg |
| Ag2C2O4 | 8.9E-2 | kg |
| Al(NO3)3 | 241.9 | kg |
| AlCl3 | 98.0 | kg |
| AlO(OH) | 2348.8 | kg |
| C2H2O4 | 33869.5 | kg |
| CaC2O4 | 184.4 | kg |
| CO2 | 190.4 | kg |
| Fe2(c2O4)3 | 7383.7 | kg |
| K2C2O4 | 48.5 | kg |
| MnC2O4 | 1176.8 | kg |
| Na2C2O4 | 885.7 | kg |
| NiC2O4 | 7.3 | kg |
| PbC2O4 | 14.5 | kg |
| Pu(C2O4)2 | 3.3 | kg |
| SiO2 | 25.6 | kg |
| SrC2O4 | 11.9 | kg |
| UO2C2O4 | 1648.7 | kg |
| AgCl | 6.0E-1 | kg |

**Figure 5-11 Input screen of third spent acid transfer to pH restoration tank**

Table 5-11 shows the combined output that was added to the pH restoration tank.

**Table 5-11 Combined output in the pH restoration tank**

| Constituent | Aqueous | Vapor | Solid |
|---|---|---|---|
| | $M_{Snate2}$ | $\sum M_{gas}$ | $\sum M_{Prec}$ |
| | | (kg) | |
| $H_2O$ | 6.45E+5 | 0.00E+0 | 0.00E+0 |
| $K_2C_2O_4$ | 4.85E+1 | 0.00E+0 | 0.00E+0 |
| $Na_2C_2O_4$ | 2.20E+3 | 0.00E+0 | 5.91E+4 |
| $Al(OH)_3$ | 0.00E+0 | 0.00E+0 | 9.25E+3 |
| $Na_2CO_3$ | 1.90E+3 | 0.00E+0 | 0.00E+0 |
| $Fe(OH)_3$ | 9.62E+1 | 0.00E+0 | 4.11E+3 |
| HgO | 2.14E+1 | 0.00E+0 | 2.72E+2 |
| $Mn(OH)_2$ | 5.81E+0 | 0.00E+0 | 8.66E+2 |
| $Ni(OH)_2$ | 7.17E-1 | 0.00E+0 | 5.85E+0 |
| $NaNO_3$ | 1.98E+4 | 0.00E+0 | 0.00E+0 |
| NaOH | 2.88E+4 | 0.00E+0 | 0.00E+0 |
| $Ag_2CO_3$ | 0.00E+0 | 0.00E+0 | 4.46E+0 |
| $Ag_2O$ | 2.41E-1 | 0.00E+0 | 0.00E+0 |
| $CaC_2O_4.1H_2O$ | 0.00E+0 | 0.00E+0 | 4.15E+2 |
| $CaCl_2.CaO$ | 2.67E+0 | 0.00E+0 | 0.00E+0 |
| $Na_2SiO_3$ | 7.19E+1 | 0.00E+0 | 0.00E+0 |
| $NaAlO_2$ | 5.20E+3 | 0.00E+0 | 0.00E+0 |
| NaCl | 1.27E+2 | 0.00E+0 | 0.00E+0 |
| $NaNO_2$ | 7.92E+3 | 0.00E+0 | 0.00E+0 |
| PbO | 1.42E+1 | 0.00E+0 | 0.00E+0 |
| $Pu(OH)_4$ | 0.00E+0 | 0.00E+0 | 2.46E+0 |
| $SrCl_2$ | 6.74E-1 | 0.00E+0 | 0.00E+0 |
| $SrCO_3$ | 0.00E+0 | 0.00E+0 | 9.37E+0 |
| $UO_2(OH)_2$ | 0.00E+0 | 0.00E+0 | 1.40E+3 |
| $UO_2Cl_2$ | 6.56E-1 | 0.00E+0 | 0.00E+0 |

The resultant aqueous and solids were assumed to remain in the tank, while the gas was released to the atmosphere. 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, the mass increased by a factor of 5; therefore, although oxalic acid helped remove sludge heels from tanks destined to be closed, it significantly increased the solids within the system.

### 5.4.4 Energy balance

Energy balances were used to calculate the bounding temperature changes associated with heel removal in the treatment tank and the caustic adjustments in the pH restoration tank. Since three strikes were used, only the maximum resulting case was analyzed.

In order to calculate the maximum amount of heat gained by adding 8 wt% oxalic acid in a 20:1 volume ratio with 19,000 l of sludge, an energy balance was developed using Equation 5-6.

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

Where:

$E_{Sludge1}$ = Energy of the sludge going to equilibrium (kj)

$E_{Acid}$ = Energy of 8 wt% oxalic acid (kj)

$E_{HeatRxn}$ = Energy gained by the reaction of sludge to acid (kj)

$E_{Dissolved}$ = Energy required to dissolve 100% of the sludge (kj)

The initial temperature was assumed to be 25° C for the oxalic acid solution and 50° C for the sludge. To calculate the maximum heat gained by adding spent solution and excess acid to a pre-charged pH restoration tank of 50 wt%, an energy balance was again developed, this time using Equation 5-7. The initial temperature was assumed to be 25°C for the caustic and 50°C for the spent solution and excess acid. Conservatively, caustic was added to unspent oxalic acid. Refer to Equation 5-7.

$$E_{Acid} + E_{NaOH} + E_{HeatRxn} + E_{Dilution} = E_{pH,12} \qquad \text{(Equation 5-7)}$$

Where:

$E_{Acid}$ = Energy of 378,500 l of 8 wt% oxalic acid (kj)

$E_{NaOH}$ = Energy of 50 wt% NaOH required to restore the pH (kj)

$E_{pH,12}$ = Overall energy required to restore the pH (kj)

$E_{HeatRxn}$ = Energy gained by the reaction of oxalic acid to caustic (kj)

$E_{Dilution}$ = Energy change by the dilution of NaOH (kj)

By accounting for the energy, the maximum temperature changes were calculated. Refer to section 5.4.5.

### 5.4.5 Temperature

The maximum temperature associated with each evolution was calculated using OLI Stream Analyzer©.

The calculated temperatures are shown in Table 5-12.

**Table 5-12 Treatment tank and pH restoration tank temperature**

| Temperature of step in treatment process | Location | Temp (°C) | Change in Temp (°C) |
|---|---|---|---|
| $T_{Sludge1}$ = Initial sludge heel temperature | Treatment tank | 50 | NA |
| $T_{Acid}$ = Initial temp of oxalic acid when added to tank | Treatment tank | 25 | NA |
| $T_1$ = Resultant temp after first acid strike | Treatment tank | 39.9 | +14.9 |
| $T_2$ = Resultant temp after second acid strike | Treatment tank | 30.8 | -9.09 |
| $T_3$ = Resultant temp after third acid strike | Treatment tank | 25 | -5.8 |
| $T_{supernate}$ = Restoration supernate heel temp | supernate input | 25 | NA |
| $T_{caustic}$ = Temp of caustic | caustic input | 25 | NA |
| $T_{pre\text{-}charge}$ = Temp of pre-charged tank | pH restoration tank | 30.6 | +30.6 |
| $T_{Aq1\&excess}$ = Temp after Aqeous1 & excess added to pH restoration tank | pH restoration tank | 64.6 | +34.1 |
| $T_{Aq2\&excess}$ = Temp after Aqeous2 & excess added to pH restoration tank | pH restoration tank | 63.6 | -1.1 |
| $T_{Aq3\&excess}$ = Temp after Aqeous3 & excess added to pH restoration tank | pH restoration tank | 63.0 | -0.5 |

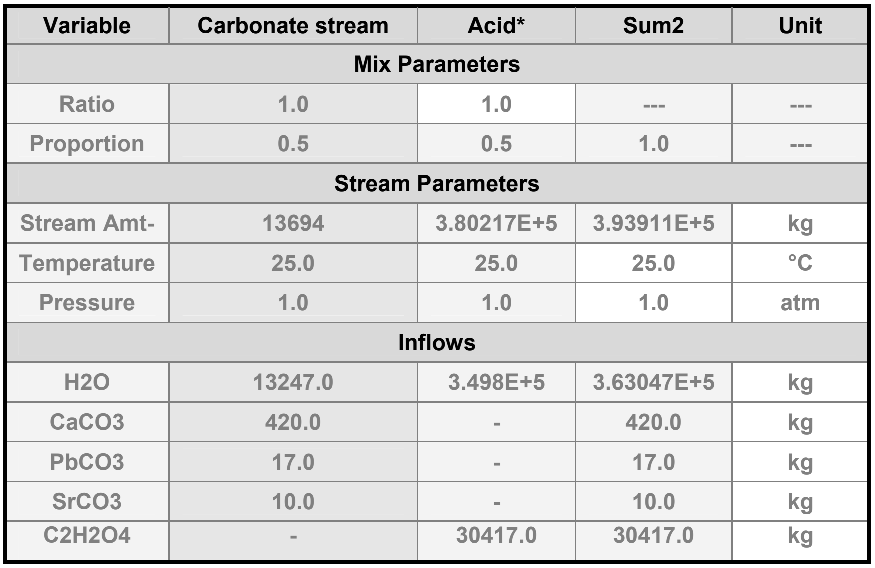
If approximately 378,500 l of 8 wt% oxalic acid were added to an approximate 19,000 l of HWCS, the Resultant temperature would be 32.7°C, slightly less than $T_1$. If none of the acid reacted, and the 378,500 l of 8 wt% oxalic acid were combined with the 66,000 l of 50 wt% NaOH, the resulting temperature would be 73.5°C. Although this value, 73.5°C, is larger than the maximum temperature shown in Table 5-12, it is considered unrealistic. That is, if dissolution were observed not to be occurring the acid additions would be stopped. Therefore, the possibility of the temperature reaching 73.5°C was discounted.

## 5.5 Maximum Vapor Generated

Based on the quantities of inflows and the kinetics of the reaction, although seven types of vapor could form, only two species of vapor were shown to be generated in sufficient quantities to potentially result in pressurizing the tanks. They are $CO_2$ and $H_2O$ vapor.

### 5.5.1 Maximum carbon dioxide

In order to maximize the amount of $CO_2$ and $H_2O$ released as vapor, approximately 378,500 l of oxalic acid were allowed to react with all of the carbonate that was present in the inflow. This is shown in Figure 5-12.



| Variable | Carbonate stream | Acid* | Sum2 | Unit |
|---|---|---|---|---|
| **Mix Parameters** | | | | |
| Ratio | 1.0 | 1.0 | --- | --- |
| Proportion | 0.5 | 0.5 | 1.0 | --- |
| **Stream Parameters** | | | | |
| Stream Amt- | 13694 | 3.80217E+5 | 3.93911E+5 | kg |
| Temperature | 25.0 | 25.0 | 25.0 | °C |
| Pressure | 1.0 | 1.0 | 1.0 | atm |
| **Inflows** | | | | |
| H2O | 13247.0 | 3.498E+5 | 3.63047E+5 | 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 screen to maximum carbon dioxide**

The maximum treatment tank or pH restoration tank temperature was calculated in Table 5-12 to be 64.6°C. The maximum gas generated was determined using the gas fraction function of OLI©.

The vapor output was determined to be 253 l at 1 atmosphere and 64.6°C. Although this was a conservative assumption, it also allows the $CO_2$ and $H_2O$ production to be maximized.

The reaction of acid and the carbonate in the sludge cannot be modeled because the $CO_2$ was not released as a gas, but instead reacted with the solid/aqueous and was not released as a vapor.

### 5.5.2 Maximum water vapor

The reaction of an acid plus a base results in a salt and water. Reacting an acid with a base, therefore, would result in the maximum amount of $H_2O$ vapor formed.

The change in temperature was first calculated with OLI©, setting the enthalpy change to zero. Using the resulting temperature, the volume of gas formed was calculated.

More specifically, the calculation added approximately 378,500 l of 8 wt% oxalic acid to an approximate 66,000 l of 50 wt% NaOH and calculated that less than 770 l of water vapor (at 73.5°C and at 1 atmosphere) would be released.

### 5.5.3 Corrosion induced hydrogen

If slurry pumps were utilized in the treatment tanks, they would ensure that the oxalic acid would be evenly distributed throughout the sludge, therefore, enhancing the dissolution process. The slurry pumps would erode away the sludge as the acid decreased the strength of the bonds binding the sludge particles. During the process, radiolysis of the acidic solution and corrosion of the carbon steel components in the treatment tanks, upon contact with the acidic solution, would 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, was evaluated. Figure 5-13 provided laboratory measured corrosion rates for representative carbon steel coupons in 4 wt% and 8 wt% oxalic acid solutions (Wiersma, 2004:43).

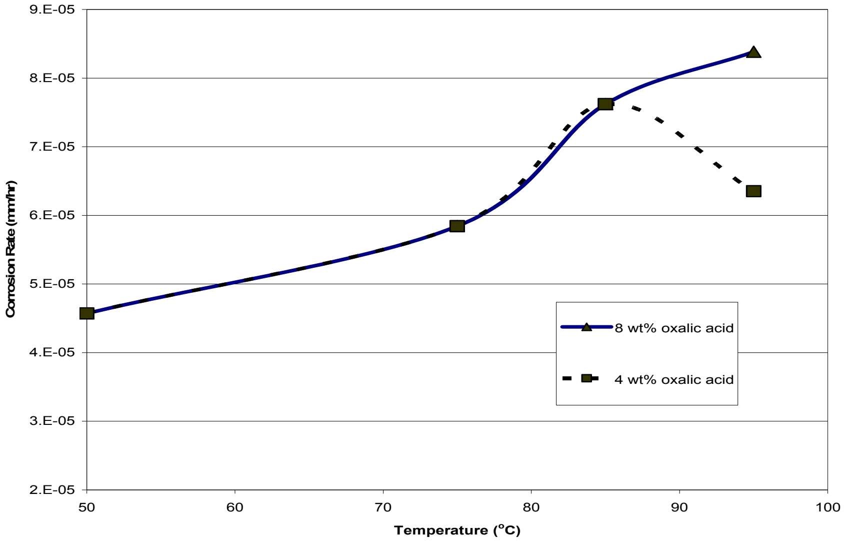


**Figure 5-13 Measured corrosion rates for oxalic acid exposed carbon steel**

Since the maximum temperature was calculated as 73.5°C, and the bounding corrosion rate from testing at 75°C was observed to be 5.84E-5 mm/hr, the volumetric flowrate of carbon steel consumed was calculated using Equation 5-8 (Lang, 2004:11).

$$V = Corrosion\ \ rate \times Surface\ \ area \qquad \text{(Equation 5-8)}$$

Where:

*V* = volumetric rate of carbon steel consumed per time ($m^3$/day)

*Corrosion rate* = corrosion rate of carbon steel in 8 wt% oxalic acid

= (5.84E-5 mm/hr) x (24hr/day) x (1 m/1,000 mm)

= 1.40E-6 m/day

*Surface area* = surface area of the carbon steel (including cooling coils)

= 1,370 $m^2$ (Phillips, 2004:1)

The amount of carbon steel consumed and hydrogen produced was determined by Reactions 5-1 and 5-2 that would occur from the corrosion of carbon steel.

$$2Fe \quad + 6H^{+} \rightarrow 2Fe^{+3} \quad + 3H_2$$ (Reaction 5-1)

$$Fe \quad + 2H^{+} \rightarrow Fe^{+2} + H_2$$ (Reaction 5-2)

The molar flow rate of the carbon steel consumed was calculated using Equations 5-9 and 5-10.

$$m = \frac{V}{MW} \times (p) \times \frac{1 \quad ml}{1E-6 \quad m^3}$$ (Equation 5-9)

$$m_{H2} = m \ \times \frac{n_{H2}}{n}$$ (Equation 5-10)

Where:

$V$ = volumetric rate of carbon steel consumed per time ($m^3$/day)
$P$ = density of carbon steel (g/ml) = 7.83 g/ml
$m$ = molar flow rate of carbon steel consumed (mole/day)
$MW$ = molecular weight of carbon steel (g/mole) = 55.82 g
$m_{H2}$ = molar flow rate of hydrogen produced (mole/day)
$n_{H2}$ = moles of hydrogen produced (mole)
= 1.5 mole (from Reaction 5-1) + 1 mole (from Reaction 5-2)
$n$ = moles of carbon steel consumed (mole)
= 1 mole (from Reaction 5-1 and Reaction 5-2)

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

$$V_{H2} = \frac{RT \times m_{H2}}{P} \times (1 day / 24 hr) = 10.25 m^3 / hr$$ (Equation 5-11)

Where:

$V_{H2}$ = Hydrogen generation rate due to corrosion ($m^3$/hr)

$m_{H2}$ = molar flow rate of hydrogen produced (mole/day)

$R$ = 8.2E-5 $m^3$-atm/K-mole

$T$ = 346.6 K

$P$ = 1 atm

The bounding hydrogen generation rate from corrosion was determined to be approximately 10.25 $m^3$/hr (or 10,250 l/hr). For certain tanks, this would likely overwhelm the tank purge exhaust.

## 5.6 Conclusion on Safety Impacts

Based on the modeling, acid aided heal removal should reduce the heel size by a factor of 10, while increasing the overall solids in the HLW system by a factor of 5. The modeling also showed that pressurizing the tanks and overheating should not be significant concerns. The maximum gas volume in the treatment tank from the sludge dissolution reactions was calculated to be less than 255 l (at 65°C and 1 atm.). The maximum calculated gas in the pH restoration tank was less than 770 l (at 74.5°C and 1 atm).

Corrosion induced hydrogen from the tank and cooling coil corrosion, however, was determined to be a potential concern with a generation rate of 10,250 l/hr (or 10.25 $m^3$/hr). Further evaluation and/or ventilation upgrades, therefore, would be required.

# 6 ENERGETIC COMPOUNDS

## 6.1 Introduction to Energetic Compounds

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 designed to characterize and/or quantify energetic compounds and organics. Instead, the behavior of each family of energetic compounds and organics must be individually evaluated. Since very small concentrations of energetic compounds and organics could impact flammability, some concentrations had to be "spiked" to understand behavior. The spiked material balance contained in Appendix 3 does not represent projected quantities of material (or all of the energetic compounds and organics), but instead significantly inflated quantities to clearly understand behavior and other characteristics of interest.

Hobbs (1999) showed that identified energetic compounds in the SRS HLW tanks can be grouped into 14 families. Other than hydrogen already considered a concern (as identified in Section 5.5.3), there are 13 families. They are as follows:

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.

Although 13 families have been identified in the SRS HLW, not all may be applicable or impacted when using oxalic acid and subsequent activities 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, had a low ionic strength, since the vast majority of the soluble constituents had been washed out during the previous bulk waste removal activities.

During the acid strikes, the sludge heel went dissolution, with solids, aqueous, and vapors possibly being formed. The treatment tank, at the time of each acid addition, was assumed to be well agitated and in contact with the sludge for a period of about two weeks. In all cases, the spent, dissolved sludge solution and any unspent acid was then transferred to the pH restoration tank.

Since the pH restoration tank continued to operate (*i.e.*, it is not being closed), it was be pre-charged with supernate or sodium hydroxide to ensure the overall pH did not enter the acidic regime (*i.e.,* pH will remain greater than 7) (Badheka & Ketusky, 2003:80). Solid precipitates formed and vapors were be generated.

High Level Waste (HLW) originated from separations, decontamination facilities, analytical laboratories, Research and Development laboratories, and the Defense Waste Processing Facility (DWPF). Tanks 1-15 had not received solids since the early 1980’s, and therefore the bulk of the solids were at least 25 yrs old (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, bulk liquids are tracked in Table 6-1, and solids are tracked under Table 6-2.

**Table 6-1 Tanks 2 through 7, 9, and 10 post 1979 supernate transfers**

| Yr | Tank | Source | Volume (3.8E+4 l) | 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 |
| 1985 | 3 | NA | 2 | Reel tape calibration/replacement |
| 1985 | 4 | NA | 4 | Reel tape calibration/replacement |
| 1995 | 4 | NA | 0.4 | Thermal expansion |
| 2000 | 5 | 22 | 30 | Supernate |
| 1992 | 6 | NA | 20 | Reel tape calibration/replacement |
| 2000 | 6 | 22 | 30 | Supernate |
| 1980 | 7 | 242-1F | 1 | Over specifications |
| 1980 | 7 | NA | 3 | Miscellaneous addition/transfer |
| 1980 | 7 | 10 | 10 | Concentrated supernate |
| 1980 | 7 | 18 | 100 | Dissolved salt |
| 1980 | 7 | 33 | 10 | Concentrated supernate |
| 1980 | 7 | 8 | 100 | Supernate |
| 1980 | 7 | 4 | 3 | Supernate |
| 1981 | 7 | 242-1F | 2 | Evaporator overheads |
| 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 | Evaporator overheads |
| 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 | Evaporator overheads |
| 1984 | 7 | 26 | 20 | Flush |
| 1984 | 7 | NA | 8 | Flush + catch tank |
| 1986 | 7 | NA | 12 | Unexplained increase/decrease |
| 1990 | 7 | NA | 6 | Thermal expansion |
| 1992 | 7 | NA | 1 | Reel tape error + thermal /transfer |
| 1994 | 7 | NA | 2 | Inter-area flush transfer |
| 1980 | 9 | NA | 0.3 | Flush water |
| 1981 | 9 | NA | 1 | Cooling coil water leak-chromate water |
| 1982 | 9 | NA | 1 | Reel tape calibration/replacement |
| 1980 | 10 | 23 | 30 | Miscellaneous addition/transfer |
| 1983 | 10 | NA | 10 | Reel tape calibration/replacement |
| 1985 | 10 | NA | 7 | Salt mining, reel tape, NaOH |
| 1986 | 10 | NA | 7 | Reel tape calibration/replacement |
| 1989 | 10 | NA | 2 | Reel tape calibration/replacement |

**Table 6-2 Tanks 12 through 13 post 1979 supernate transfers**

| Yr | Tank | Source | Volume (3.8E+4 l) | Description |
|---|---|---|---|---|
| 1983 | 11 | NA | 0.1 | 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 |
| 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 | Reel tape calibration/replacement or |
| 1992 | 12 | NA | 0.1 | Reel tape calibration/replacement or |
| 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 | Evaporator overheads |
| 1982 | 13 | 31,29 | 60 | Concentrated supernate |
| 1982 | 13 | 10 | 30 | Salt transfer |
| 1982 | 13 | 35 | 100 | Supernate |
| 1982 | 13 | 30 | 110 | Concentrated supernate |
| 1981 | 13 | 37, 36 | 1200 | 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 | Evaporator overheads |
| 1986 | 13 | 33 | 10 | Supernate |
| 1986 | 13 | 22 | 30 | Supernate |
| 1985 | 13 | NA | 3 | Flushes |
| 1986 | 13 | 32 | 80 | Supernate |
| 1987 | 13 | NA | 1 | Decontamination 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 |

Entries shown are for sources of supernate received into Tanks 1-15 since 1980. As shown in the last column of Table 6-1 and Table 6-2, Tanks 1-15 are recorded as not receiving DWPF recycle transfers. 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 6-3. (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 6-3 Post 1979 waste receipts into Tanks 1-15**

| Yr | Tank | Size (3.8E+4 l) | Campaign |
|---|---|---|---|
| 1980 | 4 | 2.5E+5 | Purex |
| 1980 | 8 | 1.1E+6 | Purex |
| 1981 | 11 | 2.6E+5 | HM |
| 1980 | 15 | 6.0E+3 | HM |

Table 6-3 shows the last Tank 1-15 sludge receipt was prior to 1982 (HLW, 2005). Since DWPF was not yet operational, Tanks 1-15 did not receive DWPF recycle, and therefore organics from DWPF were not a concern. The decomposition of organics, over this time period, ensures that volatile organics no longer represented a flammability concern (Britt, 2003:42). Table 6-4 summarizes the applicable organics and chemicals identified in Hobbs (1999) that are potentially present in Tanks 1-15.

**Table 6-4 Miscellaneous organics and chemicals**

| Parents | Constituents | Formula |
|---|---|---|
| ammonia | ammonia/ammonium ion | $NH_3/NH_4^+$ |
| ammonia | hydrazine | $N_2H_4$ |
| ammonia | hydroxylamine | $NH_2OH$ |
| dodecane | dodecane | $C_{12}H_{26}$ |
| TBP | tri-n-butyl phosphate | $(CH_3[CH_2]_3O)_3PO$ |
| TBP | di-n-butyl phosphate | $C_8H_{18}O_4P_1^-$ |
| TBP | mono-n-butyl phosphate | $C_4H_9O_4P_1^{-2}$ |
| TBP | n-butanol | $C_4H_{10}O$ |
| acid | gluconic acid | $C_6H_{12}O_7$ |
| acid | ascorbic acid | $C_6H_8O_7$ |
| resin | ion-exchange resins | $(C_8H_8)_n$ |
| resin | polydimethylsiloxane | $(C_2H_6OSi)_n$ |
| defoamers | hydrogenated tallow | NA |
| defoamers | thylene glycol | $C_2H_6O_2$ |
| defoamers | methylcellulose | $CH_4O_x$Unspecified |
| defoamers | myristoleic acid | $C_{14}H_{26}O_2$ |
| defoamers | siloxane | $SiO(C_xH_y)_n$ |

## 6.3 Acidic Chemistry Qualitative Assessment

During bulk waste removal, the solids in the tank become harder and harder to remove, and oxalic acid will be required to dissolve the solids. The oxalic acid additions to the tank will change the chemistry. Temperatures may slightly increase from exothermic reactions.

### 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 Reaction 6-1 (Hobbs, 1999, 18).

$$metal + 3OHNO_2 \rightarrow metalNO_3 + OHNO_2 + NO_2 \qquad \text{(Reaction 6-1)}$$

As shown in the material balance contained in Appendix 3, Table A3-1, the overall moles of $NO_3^-$ and $NO_2^-$ will decrease as part of the bulk waste and acid treatment activities. Table 6-5 summarizes the expected change to the overall quantities of $NO_3^-$ and $NO_2^-$.

**Table 6-5 Abundance of $NO_3^-$ and $NO_2^-$ during acid cleaning**

| Stage | Total | Aqueous | Vapor | Solid |
|---|---|---|---|---|
| | (% of initial mol) | | | |
| Pre-bulk waste | 5,000 | 5,000 | 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 | 5,000 | 5,000 | 0 | 0 |
| Caustic add | 5,000 | 5,000 | 0 | 0 |

The increase in $NO_3^-$ and $NO_2^-$ during the final two stages reflects the fact that normal tank farm supernate, to be added as part of restoring the pH, has elevated soluble $NO_3^-$ and $NO_2^-$ compared to the initial sludge heel dissolution starting point.

Besides nitrates, alcohols (*i.e.*, organics having–OH) are 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. This is shown in Reaction 6-2.

$$metalNO_3 + HNO_3 + C_2H_6O \rightarrow metal(ONC)_2 \qquad \text{(Reaction 6-2)}$$

Alcohols, however are restricted from the tank farms 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 similar organics. Methanol {*i.e.*, $CH_4O$} and isopropanol {*i.e.*, $C_3H_8O$} are two of the more likely alcohols. For example, monosodium titanate (MST) slurries, prepared and submitted by vendors, have been analyzed to contain <0.1 by volume alcohols (Hobbs, 1999:23).

Silver fulminate {*i.e.*, $Ag_2C_2N_2O_2$, Hf=+180 kj/mole} and mercury fulminate {*i.e.*, $HgC_2N_2O_2$, Hf=+200 kj/mole} are two energetics which potentially raise the most concern, as they are used in explosives and blasting caps.

Reports showed, however, that mercury fulminate decomposed because of the tank farm Cs-137 gamma radiation (Ketusky, 2005:31). Recent studies further detail the phenomena as the mercury fulminate decomposed into a less energetic state when subject to gamma radiation. In 1 M sodium hydroxide solution and a 1 rad/hr Cs-137 gamma field, the mercury fulminate would completely decompose. As such, any silver fulminate and mercury fulminate contained in the tank farm should also have already decomposed (Ketusky, 2005:31).

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 sludge 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 formations 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 (Hobbs, 1999:7).

Hydrazoic acid {*i.e.*, $HN_3$, Hf=+328 kj/mole} is reported to be dangerously explosive with a minimum explosive concentration of about 17 wt% in aqueous solutions. If within the HLW, the acid would easily react with the excess sodium to result in sodium azide {*i.e.*, $NaN_3$, Hf=+93 kj/mole}. Electropositive metal azides are not extremely 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 kj/mole} and mercury {*i.e.*, $Hg_3(N_2)_3$}, Hf=+590 kj/mole} are reported to be explosive and have been used in detonation assemblies (Hobbs, 1999:12).

As shown in Table 6-4, the initial sludge would be nitrogen depleted. Additionally $HN_3$ is extremely soluble and would be quickly removed 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 $NO_x$ compounds

Although NOx compounds are compounds that may include nitrites and nitrates, there are also many other different $N_xO_x$ anions. Some reported explosive $NO_x$ 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 kj/mole}, and nitrate salts {*e.g.*, $NaNO_3$}.

The only identified source of cellulose materials in the tank farm is from antifoam B emulsion (1 - 5% methylcellulose {*i.e.*, CH4O x unspecified}. It was used to minimize foaming in HLW evaporators. The quantity of methylcellulose added to the tank farm was very small. No incidents of uncontrolled reactions have been reported during evaporator operations and laboratory evaluations using this defoamer (Hobbs, 1999:15). The nitration of cellulose occurs only under strongly acidic conditions and elevated temperatures, greater than 160ºC. In the HLW tanks, any cellulose would decompose due to radiolysis and alkaline hydrolysis (Hobbs, 1999:21). Section 5.4.5 determined the maximum expected temperature to be less than 65°C; as such, the nitration of cellulose does not represent an issue.

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

As discussed in Table 6-5, since the solubility of $NO_2^-$ and $NO_3^-$ approach 90 gram/100 gram of water at 25°C, most should be removed as part of bulk waste removal (Britt, 2003:26). Since lead, silver, and mercury 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 additional energetic NOx compounds forming above routine HLW conditions is extremely low (Hobbs, 1999:14).

### 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 oxygen} have been reported to be explosive and exhibit moderate to strong shock sensitivity. 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. Based on the age of the waste, however, the ammonia should most likely no longer be present (Ketusky, 2004:42).

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, also shows the decrease in $NO_2^-$ and $NO_3^-$ during the oxalic acid aided heel removal. Table A3-1 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 kj/mole}, and mercury cyanide {*i.e.*, $Hg(CN)_2$, Hf=+264 kj/mole} explode when heated (Swingle, *et al*, 1999:4). Mercury cyanate {*i.e.*, $Hg(OCN)_2$} explodes when crushed. Endothermic compounds such as cadmium cyanide {*i.e.*, $Cd(CN)_2$, Hf=+267 kj/mole} and nickel cyanide {*i.e.,* $Ni(CN)_2$} can decompose explosively (Swingle, *et al*, 1999:4).

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, 2003:121). Appendix 3, TableA3-1 contains a spike of $Ni(CN)_2$ and $Hg(OCN)_2$ to show how cyanides and cyanate 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 indicated that the positive result for cyanide was an artifact of the experimental procedure (Ketusky, 2004:21). 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

Hobbs (1999:15) indicated 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 in water at 25°C, requiring an impact energy as low as 2E-9 kj to explode. Silver acetylide {AgCHO} is a more powerful detonator than Cu and explodes when heated to 120 - 140°C. Mercury acetylide {$Hg(CHO)_2$} is both shock and heat sensitive. Section 5.4.5 determined the maximum expected temperature to be less than 65°C.

Acetylene and terminal alkynes react with metal ions in solid/vapor 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 (Hobbs, 1999:15).

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 as shown in Appendix 3, Figure A3-1. The outcome of the model, Table A3-1, shows that the formation of metal acetylides is not preferred. Strict controls are placed on the precursors; thus, there is no identified mechanism for the formation and accumulation of metal acetylides. This class of explosive compounds is therefore 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. Hobbs (1999:4) stated that this mixture was extremely exothermic with the potential to generate large amounts of gas/heat if left uncontrolled.

Hobbs' (1999:4) 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. Section 5.4.5 determined the maximum expected temperature to be less than 65°C.

Table 6-5 summarizes the expected change to the overall quantities of $NO_3^-$ and $NO_2^-$ during oxalic acid heel removal based on OLI© modeling. Sodium nitrate has a solubility of about 90 g/100 g water at 25°C, while sodium oxalate has a solubility of about 3.5 g/100 g 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

Because of the oxalate solubility as further discussed in Sections 7.2 through 7.9, regardless of the disposition path chosen, adding oxalic acid to the strike tank would result in an increase in the overall quantity of oxalates in the HLW system. 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 (Ketusky, 2004:54).

Experimental testing by SRNL indicated that neither compound ignites by an electric arc when dispersed in air (Hobbs,1999:29). Explosions occur only when the materials are confined or dry and in pure form (Hobbs, 1999:29). Since the maximum expected temperatures is 65ºC, 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; 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 as follows (Hobbs, 1999:18).

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, 1999:6). As a gas, oxygen and hydrogen will quickly recombine with hydrogen peroxide to form water.

Sodium peroxide {*i.e.,* $Na_2O_2$, Hf=-450 kj/mole} is 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 (also shown in Appendix 3, TableA3-1), it is unlikely that appreciable quantities of sodium peroxide will 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. The concentration of organics in the waste, however, is very low. 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 kj/mole; CdO, Hf=-258 kj/mole; $Hg_2O$, Hf=-91 kj/mole; and $Zn_2O$, Hf=-351 kj/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 (>20ºC), potassium peroxide would decompose (Knovel, 2003). Refer to Table 6.6.

**Table 6-6 Properties of peroxides (based on 25°C in water or as indicated)**

| Constituent | Molecular Weight | Density (g/cm$^3$) | Melting Point (°C) | Boiling Point (°C) | Solubility (g/100 g) |
|---|---|---|---|---|---|
| $BaO_2$ | 169.3 | 4.96 | 450 | 800 | 1.5 |
| $CaO_2$ | 72.18 | 2.92 | 275 | | |
| $H_2O_2$ | 34.0 | 1.46 | -0.43 | 152 | |
| $Li_2O_2$ | 45.9 | 2.31 | > 195 | | |
| $MgO_2$ | 56.3 | 3.0 | 100 | | |
| $Na_2O_2$ | 78.0 | 2.8 | 675 | | |
| $SrO_2$ | 119.6 | 4.78 | 215 | | 0.018 |
| $UO_4$. $2H_2O$ | 338.1 | | 90-195 | >200 | |
| $ZnO_2$ | 97.4 | 1.57 | >150 | 212 | |

### 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 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 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. Using OLI© the solubility of $Cl^-$ throughout the dissolution process can be trended, as is shown in Table 6-7.

**Table 6-7 Estimated chloride abundance during acid cleaning**

| Stage | % Total | Aqueous | Vapor | Solid |
|---|---|---|---|---|
| | (% mole) | (% of initial mole) | | |
| Pre-bulk waste | 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 |

The increase in $Cl^-$ during the final two stages reflects the fact that normal tank farm supernate, to be added as part of restoring the pH, has elevated soluble $Cl^-$ compared to the initial sludge heel dissolution starting point.

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 with acid flushes. A small amount of the fission product iodine is reduced to iodide, 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 29 g/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. Using OLI©, the iodine behavior can be better understood by spiking the material balance and tracking its fate as summarized in Table 6-8.

**Table 6-8 Estimated iodine abundance during acid cleaning**

| Stage | % Total | Aqueous | Vapor | Solid |
|---|---|---|---|---|
| | (% of initial mole) | | | |
| Pre-bulk waste | 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 |

The increase in iodine during the final two stages reflects the fact that normal tank farm supernate, to be added as part of restoring the pH, has elevated soluble iodine compared to the initial sludge heel dissolution starting point.

Approximately 50 kg of silver was sent into Tank 13 between November 1969 and May 1970. From Tank 13, the waste was transferred into Tank 21, which was an Evaporator Feed Tank. A total of about 7.6 million l of waste transferred into Tank 21 from Tank 13 during this period. A total of about 11.4 million l of waste was processed through the Evaporator, producing slightly less than 3.8 million l of concentrate in Tank 10. After cooling, approximately 114,000 l of saltcake crystallized. After cooling, the concentrated supernate was transferred from Tank 10 into Tanks 11, 14, and 16 (Cavin & Crumm, 2003).

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, approximately 7.6 million l of waste, that contained only trace silver, was transferred into the evaporator system from other facilities and from Tank 12. In addition, 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 small burst type explosive noises have ever been reported with waste transferred into this tank or processed through the 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 (Cavin, 2003) . OLI$^©$ output, as shown in Table 6-9, forecasts that as dissolution begins, all of the insoluble (post first-strike) $Cl^-$ associated with the $Ag^+$ will form solids. Refer to Table 6-9.

**Table 6-9 Silver and chloride ion 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 kj/mole} and nitrogen trichloride {*i.e.*, $NCl_3$ =+230 kj/mole}, and halo-oxygen compounds such as chlorine dioxide {*i.e.,* $ClO_2$, Hf=+100 kj/mole} and dichloride heptaoxide {*i.e.*, $Cl_2O_7$, Hf =+270 kj/mole} are known to be potentially explosive (Hobbs, 1999:23). 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 $NO_x$, sulfates, and some low concentrations of acids. Since the halogen concentration is maintained very low, and the tank vapor 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 kj/mole} is normally produced by the dehydration of perchloric acid {*i.e.*, $HClO_4$, Hf=+8.36 kj/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 does not increase the risk of halo-nitrogen and halo-oxygen explosive events.

### 6.3.11 Metal nitrides

Metal nitrides of concern are 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. Using OLI©, the fate of nitride throughout the oxalic acid aided heel removal effort is detailed in Table 6-10.

**Table 6-10 Estimated nitride abundance during acid cleaning**

| Stage | Total | Aqueous | Vapor | Solid |
|---|---|---|---|---|
| | (% mole) | (% of initial mole) | | |
| pre-bulk waste | 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 | 5,000 | 5,000 | 0 | 0 |
| caustic add | 5,000 | 5,000 | 0 | 0 |

The increase in nitrides during the final two stages reflects the fact that normal tank farm supernate, to be added as part of restoring the pH, has elevated nitrides compared to the initial sludge heel dissolution starting point.

As seen in Table 6-10, any metal nitrides will quickly decrease during the oxalic acid aided heel removal effort, even potentially creating $NO_X$ emissions. The material balance, contained in Appendix 3, Table A3-1, is additionally spiked to confirm that because of solubility, nitrides will 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 (Britt, 2003:96). 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. The boiling point is -33°C (at 1 atm), while its melting point is -77.7°C. Its heat of vaporization is +23 kj/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. Knovel (2003) estimated the partial pressures of ammonia (with $Na^+$=6.2 M and $OH^-$=1.7 M; similar to routine non-evaporator system tank farm conditions) at various temperatures. Refer to Table 6-11.

**Table 6-11 Partial pressures of ammonia (with 6.2 [$Na^+$], 1.7 [$OH^-$])**

| Ammonia | **Liquid phase ammonia concentrations** | | | | |
|---|---|---|---|---|---|
| | 3.85 | 1.27 | 0.834 | 0.0841 | 0.0417 |
| | 3.54 | 1.14 | 7.43E-1 | 7.43E-2 | 3.68E-2 |
| Temp. (°C) | **$K_h$** | **Partial pressure of $NH_4$ vapor (atm)** | | | |
| 25 | 23.91 | 1.48E-1 | 4.75E-2 | 3.11E-2 | 1.54E-3 |
| 30 | 19.68 | 1.80E-1 | 5.77E-2 | 3.78E-2 | 1.87E-3 |
| 40 | 13.56 | 2.61E-1 | 8.38E-2 | 5.48E-2 | 2.72E-3 |
| 50 | 9.55 | 3.70E-1 | 1.19E-1 | 7.78E-2 | 3.86E-3 |
| 57 | 7.68 | 4.61E-1 | 1.48E-1 | 9.68E-1 | 4.80E-3 |
| 70 | 5.02 | 7.05E-1 | 2.26E-1 | 1.48E-1 | 7.34E-3 |

Where $K_h$ represents Henry’s Law Constant.

It was estimated that up to 90 wt% of ammonia would be from the decomposition of the hydrazine {*i.e.,* $N_2H_4$, Hf=+149 kj/mole} and hydroxylamine {*i.e.*, $NH_3O$, Hf=-114 kj/mole} which entered the tank farms from the separations process (Britt, 2003:32). Besides ammonia, ammonium nitrate {*i.e.,* $NH_4NO_3$, Hf=-184 kj/mole}, ammonium nitrite {*i.e.*, $NH_4NO_2$, Hf=+116 kj/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 and hydroxylamine are considered soluble. The solubility for hydrazine and hydroxylamine, in water at 25°C, is shown in Table 6-12 (Knovel, 2003).

**Table 6-12 Properties of hydrazine and hydroxylamine (in water)**

| Formula | Specific gravity | Melting point | Boiling point | Solubility in 0ºC water | Solubility ( g/100 g ) |
|---|---|---|---|---|---|
| $N_2H_4$ | 1.01 | 1.4 | 113.5°C | soluble in all proportions | soluble in all proportions |
| $NH_2OH$ | 1.36 | 34 | 0.074 atm | $NH_2OH$ | 33 |

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

$$N_2H_4 + O_2 \rightarrow 2H_2O + N_2 \qquad \text{(Reaction 6-3)}$$

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

$$3N_2H_4 \rightarrow 4NH_3 + N_2 \qquad \text{(Reaction 6-4)}$$

$$2N_2H_4 \rightarrow H_2 + N_2 + 2NH_3 \qquad \text{(Reaction 6-5)}$$

Hydroxylamine possible reaction pathways are pH dependent. In an alkaline solution, the reaction pathway is shown in Reaction 6-6 (Hobbs, 1999:29).

$$3NH_3O \rightarrow NH_3 + N_2 + 3H_2O \qquad \text{(Reaction 6-6)}$$

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

$$4NH_3O \rightarrow N_2O + 2NH_3 + 3H_2O \qquad \text{(Reaction 6-7)}$$

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, $Ag(NH_3)_2$, most likely could not be created with the normal ammonia decay (Hobbs, 1999:31).

### 6.3.13 Organics

The possible miscellaneous organics and chemicals introduced into Tanks 1-15 have been previously shown in Table 6-4. Because of the age of both the supernate and sludge contained in Tanks 1-15, volatile organics would have long ago decomposed (Britt, 2003:5). A review of the SRNL analysis of samples demonstrated that the concentrations of volatile organics, along with hydrogen and NH3, did not pose a flammability hazard (Britt, 2003:5). 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 would 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 kj/mole, while sodium oxalate's heat of formation is -1318 kj/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 Tanks 1-15 organics are shown in Table 6-13.

**Table 6-13 Heat of combustion/formation for organics**

| Constituent | Formula | Heat of combustion (kj/ mole) | Heat of formation (kj/ mole) |
|---|---|---|---|
| oxalic acid | $(COOH)_2$ | 119 | -822 |
| dodecane | $C_{12}H_{26}$ | 7575 | -352.1 |
| tri-n-butyl phosphate | $(CH_3[CH_2]_3O)_3PO$ | 119 | -822 |
| di-n-butyl phosphate | $C_8H_{18}O_4P_1$(-1 charge) | 7514 | +28.1 |
| mono-n-butyl phosphate | $C_4H_9O_4P_1$(-2 charge) | 2456 | -2746 |
| n-butanol | $C_4H_{10}O$ | 2456 | -2746 |
| gluconic acid | $C_6H_{12}O_7$ | | -1587 |
| ascorbic acid | $C_6H_8O_7$ | | -731 |
| ion exchange resins | $(C_4H_8)_n$ | 4219 | +213 |
| polydimethylsiloxane | $(C_2H_6OSi)_n$ | | |
| hydrogenated tallow | NA | | |
| ethylene glycol | $C_2H_6O_2$ | 1058 | -304 |
| methylcellulose | $CH_4$Ox Unspecified | | |
| myristoleic acid | $C_{14}H_{26}O_2$ | | |

As seen in Table 6-13, dodecane has the largest heat of combustion/lowest-positive heat of formation. Dodecane, because of its very low vapor pressure {4.3E-4 atm at 20°C}, is removed by separation evaporators prior to its discharge to HLW. Based on the modeling of evaporation of organic liquids, any paraffin that reaches the tank farm will persist in the tank farms for less than a few months (Ketusky, 2004). Since Tanks 1-15 have not received fresh waste since the mid 1980's, any dodecane or volatile decomposition evaporated long ago.

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).

$$(C_4H_9O)_3PO^{+} + OH^{-} \rightarrow (C_4H_9O)_2PO_2^{-1} + C_4H_9OH \quad \text{(Reaction 6-8)}$$

$$(C_4H_9O)_2PO_2^{-} + OH^{-} \rightarrow (C_4H_9O)PO_3^{-2} + C_4H_9OH \quad \text{(Reaction 6-9)}$$

$$(C_4H_9O)_2PO3^{-2} + OH^{-} \rightarrow PO_4^{-3} + C_4H_9OH \quad \text{(Reaction 6-10)}$$

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 $CO_2$ 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 Tanks 1-15 (Britt, 2003).

Gluconic acid {*i.e.*, $C_6H_{12}O_7$, Hf=-1587 kj/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 kj/mole} is sometimes still used in the separation facilities for actinide valence adjustment. Gluconic and ascorbic acids hydrolyze rapidly in both acidic and basic solutions. Hydrolysis products include oxalic acid {*i.e.*, $(COOH)_2$, Hf=-822 kj/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, 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, 2003:32). 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, *et al*, 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 represents an explosive hazard.

As previously discussed, vapor and liquid samples were taken from H-Area Pump Tank 5 & F-Area Pump 3, as well as HLW Tanks 38, 43, 26, 33 and 46. Vapor samples, taken from the pump tanks, 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, *et al*, 1999:1). Vapor sampling revealed that for Tanks 1-15 organic explosives are not considered a potential flammability concern.

Red oil was produced when organics enter vessels containing uranyl nitrate solutions that are heated to relatively high temperatures (Robinson, *et al,* 2003:3). Based on industry locations where red oil has been found, the organic materials are generally TBP, diluents, and associated decomposition products. Since red oil was 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 was not considered to pose an explosive concern (Robinson, *et al*, 2003:3).

High Level Waste stored at SRS contains 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, 2003:6). The actual concentration, however, is much lower 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 more than 20 years of aging, will be significantly less (Britt, 2003:6).

### 6.3.14 Hydrogen

Hydrogen is generated either radiolytically or chemically. For the HLW tanks, radiolytic hydrogen generation rate, *X*, is calculated using Equation 6-1 (Davis, 2004:3).

$$X = R_{bg} H_{bg} + R_a H_a \qquad \text{(Equation 6-3)}$$

Where:

$X$ = *radiolytic* hydrogen generation rate (l/hr)

$R_{bg}$ = $H_2$ generated per heat added from beta and gamma decay (l/kj)

$H_{bg}$ = heat generated by beta and gamma decay (kj/hr)

$R_a$ = $H_2$ generated per heat added from alpha decay (l/kj)

$H_a$ = heat generated by alpha decay (kj/hr)

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

$$R_a = [134.7 - 82.3(NO_{eff})^{1/3} - 13.6(NO_{eff})^{2/3} + 11.8(NOeff)]/(9.45E-6) \quad \text{(Equation 6-4)}$$

$$R_{bg} = [48.36 - 52.78(NO_{eff})^{1/3} + 14.1(NO_{eff})^{2/3} + 0.572(NOeff)]/(9.45E-6) \quad \text{(Equation 6-5)}$$

Where:

$NO_{eff}$ = the nitrate concentration plus 1/2 the nitrite concentration (M)

Since nitrates and nitrites are very soluble and $NaNO_2$ has a solubility of about 85 g/100 g water at 25ºC, while $NaNO_3$ has a solubility of about 90 g/100 g of water at 25°C}, they will largely be washed out as part of bulk waste removal (prior to the actual oxalic acid additions). Refer to Section 6.3.1.

As discussed in Section 5.5.3, under acidic conditions, corrosion of the carbon steel tank was postulated to become the overwhelming source of hydrogen, masking the increase from the nitrate and nitrite reduction. Since the hydrogen from acid induced corrosion currently is not considered in the safety analyses, changes will be required to the basis to ensure that the risk does not increase.

## 6.4 Conclusion on Energetic Compounds

Hydrogen will effectively show an increased generation rate as part of the oxalic acid aided heel removal effort. Hydrogen is evaluated under the safety analyses (DSA, 2003:31). 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.

Although the quantity of oxalates will increase, as even dry sludge contains approximately 50 vol% liquid, they will remain wet, and will not represent an increase in risk.

No other increase in energetic compounds is expected.

# 7 DEVELOPING THE FLOWSHEET WHILE MINIMIZING IMPACTS

## 7.1 Introduction to Downstream Process Impacts

This chapter details the development of an integrated HLW process flowsheet that simulates the dissolution of a 19,000 liter heel of sludge, with the primary purpose of minimizing the resultant downstream process impacts. Chapter 5 used a Hypothetical Worst Case Sludge material balance across the treatment tank and pH restoration tank to understand the safety impacts. This chapter focuses on the development of an integrated flowsheet that uses representative sludge and minimizes the downstream impacts.

The integrated HLW process for chemical cleaning has four basic processing functions. The four functions are:

1) acid treatment/heel removal.
2) sludge washing and feed for DWPF.
3) evaporation of the supernate for volume reduction.
4) salt heel dissolution as feed to SWPF.

Schematically, each block is shown in Figure 7-1.

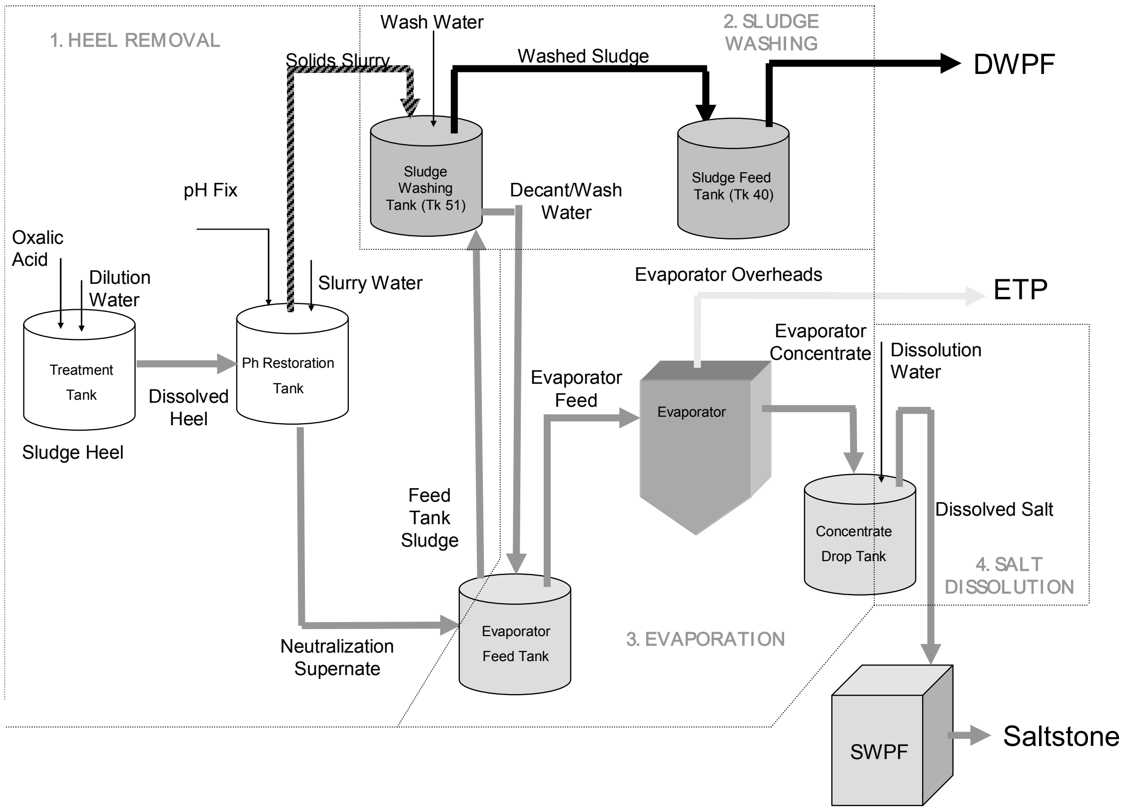


**Figure 7-1 Functions required as part of integrated flowsheet**

In this chapter, the preference for two different cases was also determined. The two cases were as follows:

1) Determine if effluent from heel dissolution process should be added to a washed sludge batch for DWPF feed (vitrification) instead of an unwashed sludge batch.
2) Determine if the dissolved sludge heel should be pH restored with existing waste supernate instead of fresh sodium hydroxide.

For the purposes of Chapter 7, the Tank 1-15 heel dissolution process has the following refinements:

1) Tank 8 and Tank 11 characterization data from the process database were used.
2) Water was added to establish necessary operating height.
3) pH restored spent acid/excess acid were decanted to the evaporator system.
4) The pH restoration tank was mixed to suspend the solids.
5) The Resultant sodium oxalate slurry was transferred to the DWPF feed tank

Existing evaporator process (Hang, 2002; Koffman, 2002) and sludge washing process simulations (Lillistan, 2004) combined with the use of OLI© were used to determine the respective downstream portions of the flowsheet. They are discussed in Sections 7.3 and 7.4, respectively.

## 7.2 Acid Treatment/Heel Removal

### 7.2.1 OLI© model

The unique portion of the sludge heel dissolution process, function 1, was modeled using OLI ESP©. Figure 7-2 is a schematic of the OLI ESP© model.

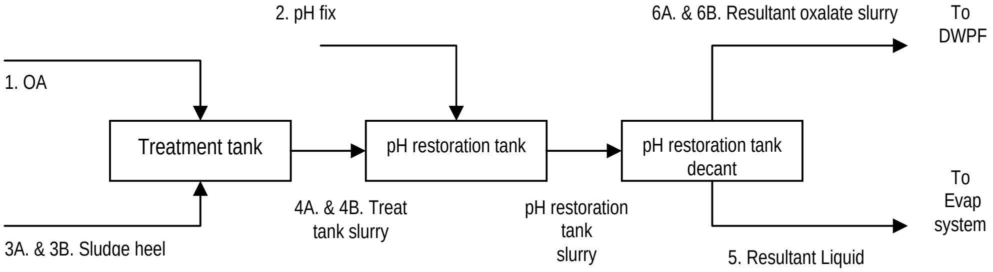


**Figure 7-2 Model of the sludge heel dissolution process**

Treatment tank

The Treat(ment) tank was designed as a mixer block. Two streams entered the mixer bock, oxalic acid (OA) and sludge heel. The oxalic acid stream had a starting temperature of 30°C, a pressure of 1 atm, and had a composition of 8 wt% oxalic acid.

The dissolution calculation was designed to be performed as an isothermal calculation with a final temperature of 30°C. The resultant stream was named Treat (ment) tank slurry. This stream is fed into the next mixer block, the pH restoration tank, where pH restoration was performed.

pH restoration tank

The pH restoration tank was also designed as a mixer block. Two streams enter into this block, Treat tank slurry and pH fix. The stream pH fix was represented by either 50 wt% caustic (50 wt% NaOH and 50 wt% $H_2O$) or average supernate. This calculation was performed as an isothermal calculation with a final temperature of 30°C. The resultant stream from the pH restoration tank was called the pH restoration tank slurry. This stream was fed into a separator block named pH restoration tank decanter. The separator block fractionalized the contents, to enable a 15 wt% solids slurry, pH restored oxalate slurry, and the available liquid - pH restored liquid to be transferred forward - to other unit operation.

pH restoration tank decanter

The pH restoration tank decant was a separator block. The resultant stream from the pH restoration tank mixer block was fed into this block so that the majority of the liquid could be separated from the solids. The stream of solids was called pH restoration solids, while the liquid stream was named the Resultant supernate. The calculation was performed as an entrainment calculation such that the stream named pH restoration solids contained 16.7 wt% solids.

At this point, the first function of the sludge heel dissolution model was complete. The associated forecasted inputs and results are detailed in Section 7.1.2.

### 7.2.2 Model inputs, calculations, and results

The sludge heel dissolution model assumed that the tank had completed bulk sludge removal, and as a result had already underwent significant washing. The remaining heel in the treatment tank had less than 19,000 ls of sludge slurry, which equates to a sludge slurry level of 5 cm. In addition, bulk sludge removal used inhibited water to establish the minimum operating level. This ensured that minimally soluble salts were present in the heel. Inhibited water in the process consisted of 0.01 to 1 M NaOH and 0.011 M $NaNO_3$, which resulted in about 0.02 M to 0.03 M total sodium salts. The heel, therefore, consisted 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 was taken from the process database (HLW, 2005). Since representative sludge was used in this chapter, only the composition is important, not the total amount of material in each tank. For this chapter, the relative percentage of each type of waste sent to the waste tank would 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 Tables 7-1 and 7-2. Note that the sludge composition included some soluble sodium salts.

The bulk waste removal effort includes substantial water contact with the heel that will reduce the soluble salts to much lower concentrations. These salts, however, are left in the estimated composition to conservatively estimate the consumption of acid required during dissolution.

**Table 7-1 Percent of waste stream to tanks**

| Tank | Purex Sludge | | | HM | | |
|---|---|---|---|---|---|---|
| | Low | Mixed | High | Low | Mixed | High |
| | (wt %) | | | | | |
| 1 | 15.2 | 47.1 | 37.7 | 0 | 0 | 0 |
| 2 | 0 | 100 | 0 | 0 | 0 | 0 |
| 3 | 3 | 0 | 100 | 0 | 0 | 0 |
| 4 | 4 | 0 | 6.1 | 93.9 | 0 | 0 |
| 5 | 5 | 0 | 67.2 | 32.8 | 0 | 0 |
| 6 | 6 | 0 | 0 | 100 | 0 | 0 |
| 7 | 7 | 79.4 | 16.3 | 4.2 | 0 | 0 |
| 8 | 70.6 | 14.6 | 14.8 | 0 | 0 | 0 |
| 9 | 0 | 100 | 0 | 0 | 0 | 0 |
| 10 | 0 | 98.3 | 0 | 0 | 1.7 | 0 |
| 11 | 6.3 | 0 | 0 | 25.9 | 2.7 | 65.2 |
| 12 | 0 | 16.9 | 0 | 0 | 0 | 83.1 |
| 13 | 12 | 13.1 | 3.3 | 57.4 | 2.1 | 12.1 |
| 14 | 0 | 0 | 58.7 | 24.9 | 0 | 16.4 |
| 15 | 0 | 0 | 0 | 8.7 | 33.1 | 58.1 |

**Table 7-2 Composition of sludge solids by waste type**

| Constituent | HM | | | Purex | | |
|---|---|---|---|---|---|---|
| | High | Low | Mixed | High | Low | Mixed |
| | (wt%) | | | | | |
| $Al(OH)_3$ | 67 | 20.6 | 62.0 | 6.50 | 13.9 | 11.4 |
| $CaC_2O_4$ | 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 |

Plutonium and strontium considered in HWCS were a very small fraction of the total waste and were not considered in evaluating the downstream process impacts.

**Table 7-3 Estimated composition of sludge solids in tank heels**

| **Const.** | **Tank** | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **9** | **10** | **11** | **12** | **13** | **14** | **15** |
| | **(wt%)** | | | | | | | | | | | | | | |
| $Al(OH)_3$ | 11 | 12 | 12 | 7 | 10 | 7 | 14 | 13 | 12 | 13 | 53 | 59 | 25 | 20 | 63 |
| $CaC_2O_4$ | 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 | 51 | 51 | 51 | 51 | 51 | 51 | 51 | 51 | 51 | 23 | 17 | 43 | 44 | 15 |
| 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 | 9.1 | 13 | 5.3 | 6.2 | 7.4 | 7.3 | 5.3 | 3.5 | 9.3 | 11 | 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 | 9.4 | 9.4 | 11 | 10 | 12 | 8.6 | 9.0 | 9.4 | 9.3 | 2.7 | 2.7 | 5.6 | 8.2 | 1.7 |
| Total | 100 | | | | | | | | | | | | | | |

**Table 7-4 Estimated composition of sludge slurry in tank heels**

| Const. | Tank | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 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 | 24 | 10 | 8.2 | 25 |
| $CaC_2O_4$ | 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 |
| $Fe(OH)_3$ | 21 | 21 | 21 | 21 | 21 | 21 | 21 | 21 | 21 | 20 | 9.1 | 6.9 | 17 | 17 | 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 |
| Total Solids | 40 (wt%) | | | | | | | | | | | | | | |
| $H_2O$ | 60 (wt%) | | | | | | | | | | | | | | |
| Total | 100 (wt%) | | | | | | | | | | | | | | |
| Slurry sp.g. | 1.2 | | | | | | | | | | | | | | |
| Solids/l Slurry | 0.48 (kg/l) | | | | | | | | | | | | | | |

As can be seen in Table 7-4, the heel composition for Tanks 1-8 were very similar. The heel compositions in Tanks 9-15, however, showed some variation. The heel compositions for Tanks 8 and 11 were picked to represent Purex and HM dissolution models. Table 7-5 shows the different sludge and pH restoration cases that were considered in the integrated flowsheet.

**Table 7-5 Integrated flowsheet pH restoration methods (Case 1 through 4)**

| Case | Sludge | pH restoration method |
|---|---|---|
| 1 | 8 | 50 wt% NaOH |
| 2 | 8 | supernate |
| 3 | 11 | 50 wt% NaOH |
| 4 | 11 | supernate |

Both pH restoration with 50wt% NaOH and existing supernate were considered because available free tank volume was in short supply, such that all additions to the tank farm were minimized. The use of 50 wt% NaOH was compared to the use of supernate, to ensure both tank space and downstream process impacts were considered. Table 7-6 shows the assumed supernate composition that was used to restore the pH of the spent/excess oxalic acid. The liquid was considered to be at the normal corrosion chemistry, $OH^- \geq 0.1$ M.

**Table 7-6 Average supernate composition**

| Component | Average (wt%) |
|---|---|
| $H_2O$ | 6.7E+2 |
| $NaNO_3$ | 1.6E+1 |
| NaOH | 7.6E+0 |
| $NaNO_2$ | 3.1E+0 |
| $NaAlO_2$ | 2.2E+0 |
| $Na_2SO_4$ | 1.8E+0 |
| $Na_2CO_3$ | 1.4E+0 |
| Other salts | 6.7E-1 |
| KOH | 7.4E-2 |
| $NH_4NO_3$ | 2.6E-3 |
| CsOH | 1.9E-3 |
| $Na_2U_2O_7$ | 6.2E-3 |
| Sludge | 4.8E-2 |
| HgO | 2.6E-3 |
| Total | 100 |
| Density | 1.27 (kg/l) |

Tables 7-7 and 7-9 show the model-generated material balance for heel dissolution using 50 wt% NaOH solution for the pH restoration. Table 7-8 and Table 7-10 show the same material balance using average supernate for the pH restoration.

**Table 7-7 Tank 8 Purex dissolution material balance, pH restored w/NaOH (Sheet 1 of 2)**

| **Stream** | **1** | **2** | **3A** | **3B** | **4A** | **4B** | **5** | **6A** | **6B** |
|---|---|---|---|---|---|---|---|---|---|
| | **OA** | **pH fix** | **Sludge heel** | | **Treatment tank slurry** | | **Resultant** | | |
| | | | | | | | **liquid** | **oxalate slurry** | |
| **Phase** | Aq | Aq | Aq | Solid | Aq | Solid | Aq | Aq | Solid |
| **Units** | **wtfrac** | | | | | | | | |
| $H_2O$ | 9.2E-1 | 5.0E-1 | 9.2E-1 | 0E+0 | 9.1E-1 | 0E+0 | 9.6E-1 | 9.6E-1 | 0E+0 |
| $H_2C_2O_4$ | 8.0E-2 | 0E+0 | 0.+0 | 0E+0 | 4.0E-2 | 0E+0 | 0E+0 | 0E+0 | 0E+0 |
| HCl | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 4.6E-4 | 0E+0 | 0E+0 | 0E+0 | 0E+0 |
| $HNO_3$ | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 4.8E-4 | 0E+0 | 0E+0 | 0E+0 | 0E+0 |
| $Na_2CO_3$ | 0E+0 | 0E+0 | 3.4E-4 | 0E+0 | 2.1E-3 | 0E+0 | 2.1E-3 | 2.1E-3 | 0E+0 |
| NaCl | 0E+0 | 0E+0 | 1.2E-2 | 0E+0 | 0E+0 | 0E+0 | 7.1E-4 | 7.1E-4 | 0E+0 |
| $NaNO_2$ | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 0E+0 |
| $NaNO_3$ | 0E+0 | 0E+0 | 1.1E-2 | 0E+0 | 0E+0 | 0E+0 | 6.2E-4 | 6.2E-4 | 0E+0 |
| NaOH | 0E+0 | 5.0E-1 | 3.4E-2 | 0E+0 | 0E+0 | 0E+0 | 4.6E-3 | 5.0E-3 | 0E+0 |
| $Na_2SO_4$ | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 0E+0 |
| $Na_2C_2O_4$ | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 4.4E-3 | 0E+0 | 2.9E-2 | 2.9E-2 | 7.0E-1 |
| $Al(OH)_3$ | 0E+0 | 0E+0 | 0E+0 | 1.5E-1 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 4.2E-2 |
| AlOOH | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 4.0E-3 | 0E+0 | 0E+0 | 0E+0 | 0E+0 |
| $NaAlO_2$ | 0E+0 | 0E+0 | 3.3E-3 | 0E+0 | 0E+0 | 0E+0 | 6.6E-4 | 6.6E-4 | 0E+0 |
| $CaC_2O_4$ | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 4.1E-4 | 2.8E-1 | 7.6E-7 | 7.6E-7 | 2.4E-2 |
| $CaCO_3$ | 0E+0 | 0E+0 | 0E+0 | 6.2E-2 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 0E+0 |

## Table 7-7 Tank 8 Purex dissolution material balance, pH restored w/NaOH (Sheet 2 of 2)

| **Stream** | **1** | **2** | **3A** | **3B** | **4A** | **4B** | **5** | **6A** | **6B** |
|---|---|---|---|---|---|---|---|---|---|
| | **OA** | **pH fix** | **Sludge heel** | | **Treatment tank slurry** | | **Resultant** | | |
| | | | | | | | **liquid** | **oxalate slurry** | |
| **Phase** | Aq | Aq | Aq | Solid | Aq | Solid | Aq | Aq | Solid |
| **Units** | **wtfrac** | | | | | | | | |
| $Ca(OH)_2$ | 0E+0 | 0E+0 | 2.4E-4 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 0E+0 |
| $Ce_2O_3$ | 0E+0 | 0E+0 | 1.3E-3 | 0E+0 | 0E+0 | 0E+0 | 7.6E-5 | 7.63E-5 | 0E+0 |
| $Ce_2(C_2O_4)$ | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 3.8E-5 | 9.1E-3 | 0E+0 | 0E+0 | 0E+0 |
| $Fe_2(C_2O_4)$ | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 3.3E-2 | 0E+0 | 2.6-5 | 2.5E-5 | 0E+0 |
| $Fe(OH)_3$ | 0E+0 | 0E+0 | 7.4E-5 | 5.8E-1 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 1.7E-1 |
| $K_2C_2O_4$ | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 0E+0 |
| KOH | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 0E+0 |
| $MnC_2O_4$ | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 4.5E-4 | 3.4E-1 | 2.8E-6 | 2.8E-6 | 0E+0 |
| $Mn(OH)_2$ | 0E+0 | 0E+0 | 8.8E-7 | 6.0E-2 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 1. 8E-2 |
| $NiC_2O_4$ | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 5.7E-5 | 2.9E-1 | 9.5E-8 | 9.5E-08 | 0E+0 |
| $Ni(OH)_2$ | 0E+0 | 0E+0 | 3.1E-7 | 4.5E-2 | 0E+0 | 0E+0 | 0E+0 | 0.E+0 | 1.4E-2 |
| $SiO_2$ | 0E+0 | 0E+0 | 1.2E-2 | 0E+0 | 3.8E-3 | 8.0E-2 | 7.1E-4 | 7.1E-4 | 0E+0 |
| $UO_2C_2O_4$ | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 3.8E-3 | 0E+0 | 1.1-4 | 1.07E-4 | 0E+0 |
| $UO_2OH_2$ | 0E+0 | 0E+0 | 2.7E-8 | 9.9E-2 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 2.9E-0 |
| Total (kg) | 2.6E+5 | 3.9E+4 | 1.7E+4 | 9.4E+3 | 2.9E+5 | 2.6E+3 | 1.5E+5 | 1.8E+5 | 3.2E+4 |
| Vol (l) | 2.5E+5 | 2.6E+4 | 1.6E+4 | 2.7E+3 | 2.6E+4 | 4.1E+2 | 1.4E+5 | 1.5E+5 | 2.8E+3 |
| $C_2O_4$(kg) | 2.1E+4 | 0E+0 | 0E+0 | 0E+0 | 1.9E+4 | 1.5E+3 | 2.7E+3 | 3.0E+3 | 1.5E+4 |

### Table 7-8 Tank 8 Purex dissolution material balance, pH restored w/supernate (Sheet 1 of 2)

| **Stream** | **1** | **2** | **3A** | **3B** | **4A** | **4B** | **5** | **6A** | **6B** |
|---|---|---|---|---|---|---|---|---|---|
|  | **OA** | **pH fix** | **Sludge heel** |  | **Treatment tank slurry** |  | **Resultant** |  |  |
|  |  |  |  |  |  |  | **liquid** | **oxalate slurry** |  |
| **Phase** | Aq | Aq | Aq | Solid | Aq | Solid | Aq | Aq | Solid |
| **Units** | **wtfrac** |  |  |  |  |  |  |  |  |
| $H_2O$ | 9.2E-1 | 6.8E-1 | 9.3E-1 | 0E+0 | 9.1E-1 | 0E+0 | 8.8E-1 | 8.7E-1 | 0E+0 |
| $H_2C_2O_4$ | 8.0E-2 | 0E+0 | 0E+0 | 0E+0 | 4.0E-2 | 0E+0 | 0E+0 | 0E+0 | 0E+0 |
| HCl | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 4.6E-4 | 0E+0 | 0E+0 | 0E+0 | 0E+0 |
| $HNO_3$ | 0.E+0 | 0E+0 | 0E+0 | 0E+0 | 4.8E-4 | 0E+0 | 0E+0 | 0E+0 | 0E+0 |
| $Na_2CO_3$ | 0.E+0 | 1.4E-2 | 3.4E-4 | 0E+0 | 2.1E-3 | 0E+0 | 8.1E-3 | 8.1E-3 | 0E+0 |
| NaCl | 0.E+0 | 0.E+0 | 1.2E-2 | 0E+0 | 0E+0 | 0E+0 | 4.4E-4 | 4.4E-4 | 0E+0 |
| $NaNO_2$ | 0E+0 | 3.1E-2 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 1.5E-2 | 1.6E-2 | 0E+0 |
| $NaNO_3$ | 0E+0 | 1.6E-1 | 1.1E-2 | 0E+0 | 0E+0 | 0E+0 | 7.7E-2 | 7.6E-2 | 0E+0 |
| NaOH | 0E+0 | 7.6E-2 | 3.4E-2 | 0E+0 | 0E+0 | 0E+0 | 4.2E-3 | 1.2E-2 | 0E+0 |
| $Na_2SO_4$ | 0E+0 | 1.8E-2 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 8.5E-3 | 8.5E-3 | 0E+0 |
| $Na_2C_2O_4$ | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 4.4E-3 | 0E+0 | 5.0E-3 | 4.9E-3 | 6.8E-1 |
| $Al(OH)_3$ | 0E+0 | 0E+0 | 0E+0 | 1.5E-1 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 1.5E-1 |
| AlOOH | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 4.0E-3 | 0E+0 | 0E+0 | 0E+0 | 0E+0 |
| $NaAlO_2$ | 0E+0 | 2.2E-2 | 3.3E-3 | 0E+0 | 0E+0 | 0E+0 | 7.7E-4 | 7.7E-4 | 0E+0 |

### Table 7-8 Tank 8 Purex dissolution material balance, pH restored w/supernate (Sheet 2 of 2)

| Stream | 1 | 2 | 3A | 3B | 4A | 4B | 5 | 6A | 6B |
|---|---|---|---|---|---|---|---|---|---|
| | OA | pH fix | Sludge heel | | Treat tank slurry | | Resultant | | |
| | | | | | | | liquid | oxalate slurry | |
| **Phase** | Aq | Aq | Aq | Solid | Aq | Solid | Aq | Aq | Solid |
| **Units** | **wtfrac** | | | | | | | | |
| $CaC_2O_4$ | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 4.1E-4 | 2.8E-1 | 2.2E-6 | 2.1E-6 | 1.8E-3 |
| $CaCO_3$ | 0E+0 | 0E+0 | 0E+0 | 6.2E-2 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 0E+0 |
| $Ca(OH)_2$ | 0E+0 | 0E+0 | 2.4E-4 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 0E+0 |
| $Ce_2O_3$ | 0E+0 | 0E+0 | 1.3E-3 | 0E+0 | 0E+0 | 0E+0 | 4.7E-5 | 4.7E-5 | 0E+0 |
| $Ce_2(C_2O_4)_3$ | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 3.7E-5 | 9.1E-3 | 0E+0 | 0E+0 | 0E+0 |
| $Fe_2(C_2O_4)_3$ | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 3.3E-2 | 0E+0 | 3.2E-5 | 3.2E-5 | 0E+0 |
| $Fe(OH)_3$ | 0E+0 | 0E+0 | 7.4E-5 | 5.8E-1 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 1.3E-1 |
| $K_2C_2O_4$ | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 5.3E-4 | 5.3E-4 | 0E+0 |
| KOH | 0E+0 | 7.5E-4 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 0E+0 |
| $MnC_2O_4$ | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 4.6E-4 | 3.4E-1 | 2.0E-7 | 2.0E-7 | 0E+0 |
| $Mn(OH)_2$ | 0E+0 | 0E+0 | 8.8E-7 | 6.0E-2 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 1.4E-2 |
| $NiC_2O_4$ | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 5.7E-5 | 2.9E-1 | 0E+0 | 1.2E-7 | 0E+0 |
| $Ni(OH)_2$ | 0E+0 | 0E+0 | 3.1E-7 | 4.5E-2 | 0E+0 | 0E+0 | 1.2E-7 | 0E+0 | 0E+0 |
| $SiO_2$ | 0E+0 | 0E+0 | 1.2E-2 | 0E+0 | 1.1E-4 | 8.0E-2 | 4.4E-4 | 4.4E-4 | 1.0E-2 |
| $UO_2C_2O_4$ | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 3. 8E-3 | 0E+0 | 2.3E-3 | 2.3E-3 | 0E+0 |
| $UO_2OH_2$ | 0E+0 | 0E+0 | 2.7E-8 | 9.9E-2 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 0E+0 |
| Total (kg) | 2.6E+5 | 2.3E+5 | 1.7E+4 | 9.4+3 | 2.9E+5 | 2.6E+3 | 0E+0 | 0E+0 | 0E+0 |
| Vol (l) | 2.5E+5 | 1.9E+5 | 1.6E+4 | 2.7E+3 | 2.7E+5 | 4.1E+2 | 0E+0 | 0E+0 | 0E+0 |
| $C_2O_4$ (kg) | 2.1E+4 | 0E+0 | 0E+0 | 0E+0 | 1.9E+4 | 1.5E+3 | 2.8E+5 | 2.0E+5 | 4.1E+4 |

**Table 7-9 Tank 11 HM dissolution material balance, pH restored w/NaOH (Sheet 1 of 2)**

| **Stream** | **1** | **2** | **3A** | **3B** | **4A** | **4B** | **5** | **6A** | **6B** |
|---|---|---|---|---|---|---|---|---|---|
| | **OA** | **pH fix** | **Sludge heel** | | **Treat tank slurry** | | **Resultant** | | |
| | | | | | | | **liquid** | **oxalate slurry** | |
| **Phase** | Aq | Aq | Aq | Solid | Aq | Solid | Aq | Aq | Solid |
| **Units** | **wtfrac** | | | | | | | | |
| $H_2O$ | 9.2E-1 | 5.0E-1 | 9.4E-1 | 0E+0 | 9.1E-1 | 0E+0 | 9.6E-1 | 9.6E-1 | 0E+0 |
| $H_2C_2O_4$ | 8.0E-2 | 0E+0 | 0E+0 | 0E+0 | 6.3E-2 | 0E+0 | 0E+0 | 0E+0 | 0E+0 |
| HCl | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 8.7E-5 | 0E+0 | 0E+0 | 0E+0 | 0E+0 |
| $HNO_3$ | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 5.1E-4 | 0E+0 | 0E+0 | 0E+0 | 0E+0 |
| $Na_2CO_3$ | 0E+0 | 0E+0 | 6.2E-5 | 0E+0 | 4.4E-4 | 0E+0 | 4.3E-4 | 4.3E-4 | 0E+0 |
| NaCl | 0E+0 | 0E+0 | 3.1E-3 | 0E+0 | 0E+0 | 0E+0 | 1.3E-4 | 1.3E-4 | 0E+0 |
| $NaNO_2$ | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 0E+0 |
| $NaNO_3$ | 0E+0 | 0E+0 | 1.6E-2 | 0E+0 | 0E+0 | 0E+0 | 6.7E-4 | 6.7E-4 | 0E+0 |
| NaOH | 0E+0 | 5.0E-1 | 1.8E-2 | 0E+0 | 0E+0 | 0E+0 | 4.4E-3 | 4.6E-3 | 0E+0 |
| $Na_2SO_4$ | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 0E+0 |
| $Na_2C_2O_4$ | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 1.8E-3 | 0E+0 | 3.1E-2 | 3.1E-2 | 7.7E-1 |
| $Al(OH)_3$ | 0E+0 | 0E+0 | 0E+0 | 5.9E-1 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 1.4E-1 |
| AlOOH | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 1.1E-2 | 0E+0 | 0E+0 | 0E+0 | 0E+0 |
| $NaAlO_2$ | 0E+0 | 0E+0 | 4.4E-5 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 6.1E-4 | 0E+0 |
| $CaC_2O_4$ | 0E+0 | 0E+0 | 4.8E-5 | 0E+0 | 4.0E-5 | 0E+0 | 7.4E-7 | 7.4E-7 | 0E+0 |
| $CaCO_3$ | 0E+0 | 0E+0 | 0E+0 | 1.7E-2 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 0E+0 |
| $Ca(OH)_2$ | 0E+0 | 0E+0 | 4.3E-5 | 0E+0 | 0E+0 | 0E+0 | 9.6E-1 | 9.6E-1 | 0E+0 |

### Table 7-9 Tank 11 HM dissolution material balance, pH restored w/NaOH (Sheet 2 of 2)

| Stream | 1 | 2 | 3A | 3B | 4A | 4B | 5 | 6A | 6B |
|---|---|---|---|---|---|---|---|---|---|
| | OA | pH fix | Sludge heel | | Treat tank slurry | | Resultant | | |
| | | | | | | | liquid | oxalate slurry | |
| **Phase** | Aq | Aq | Aq | Solid | Aq | Solid | Aq | Aq | Solid |
| **Units** | **wtfrac** | | | | | | | | |
| $Ce_2O_3$ | 0E+0 | 0E+0 | 2.7E-3 | 0E+0 | 0E+0 | 0E+0 | 1.2E-4 | 1.2E-4 | 0E+0 |
| $Ce_2(C_2O_4)_3$ | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 6.1E-5 | 0E+0 | 0E+0 | 0E+0 | 0E+0 |
| $Fe_2(C_2O4)_3$ | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 1.1E-2 | 0E+0 | 2.4E-5 | 2.4E-5 | 0E+0 |
| $Fe(OH)_3$ | 0E+0 | 0E+0 | 9.6E-7 | 2.5E-1 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 6.2E-2 |
| $K_2C_2O_4$ | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 0E+0 |
| KOH | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 0E+0 |
| $MnC_2O_4$ | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 2.8E-4 | 0E+0 | 3.6E-6 | 3.6E-6 | 0E+0 |
| $Mn(OH)_2$ | 0E+0 | 0E+0 | 1.0E-7 | 5.9E-2 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 1.4E-2 |
| $NiC_2O_4$ | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 5.1E-5 | 3.3E-1 | 8.9E-8 | 8.9E-8 | 0E+0 |
| $Ni(OH)_2$ | 0E+0 | 0E+0 | 4.5E-9 | 1.1E-2 | 0E+0 | 0.E+0 | 0E+0 | 0E+0 | 2.7E-3 |
| $SiO_2$ | 0E+0 | 0E+0 | 2.0E-2 | 0E+0 | 1.0E-4 | 6.7E-1 | 8.7E-4 | 8.7E-4 | 0E+0 |
| $UO_2C_2O_4$ | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 9.0E-4 | 0E+0 | 1.2E-6 | 1.2E-6 | 0E+0 |
| $UO_2OH_2$ | 0E+0 | 0E+0 | 2.7E-7 | 3.1E-2 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 7.5E-3 |
| $ThO_2$ | 0E+0 | 0E+0 | 5E-14 | 1.1E-2 | 0E+0 | 0E+0 | 4.8E-5 | 5E-14 | 2.7E-3 |
| HgO | 0E+0 | 0E+0 | 3.9E-5 | 3.1E-2 | 7.6E-4 | 0E+0 | 3.8E-5 | 3.8E-5 | 7.1E-3 |
| $Th(C_2O_4)_2$ | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 4.3E-4 | 0E+0 | 0E+0 | 0E+0 | 0E+0 |
| Total (kg) | 3.2E+5 | 5.2E+4 | 1.6E+4 | 9.4E+3 | 3.7E+8 | 1.8E+6 | 1.9E+5 | 1.9E+5 | 3.8E+4 |
| Vol (l) | 3.5E+4 | 3.4E+4 | 1.6E+4 | 3.3E+3 | 3.4E+5 | 3.1E+2 | 1.9E+5 | 1.9E+5 | 3.2E+3 |
| $C_2O_4$ (kg) | 2.7E+4 | 0E+0 | 5.5E-1 | 0E+0 | 2.6E+4 | 3.6E+2 | 3.8E+3 | 3.9E+3 | 1.9E+4 |

### Table 7-10 Tank 11 HM dissolution material balance, pH restored w/supernate (Sheet 1 of 2)

| **Stream** | **1** | **2** | **3A** | **3B** | **4A** | **4B** | **5** | **6A** | **6B** |
|---|---|---|---|---|---|---|---|---|---|
|  | **OA** | **pH fix** | **Sludge heel** |  | **Treat tank slurry** |  | **Resultant** |  |  |
|  |  |  |  |  |  |  | **liquid** | **oxalate slurry** |  |
| **Phase** | Aq | Aq | Aq | Solid | Aq | Solid | Aq | Aq | Solid |
| **Units** | **wtfrac** |  |  |  |  |  |  |  |  |
| $H_2O$ | 9.2E-1 | 6.8E-1 | 9.4E-1 | 0E+0 | 9.1E-1 | 0E+0 | 8.8E-1 | 8.7E-1 | 0E+0 |
| $H_2C_2O_4$ | 8.0E-2 | 0E+0 | 0E+0 | 0E+0 | 6.3E-2 | 0E+0 | 0E+0 | 0E+0 | 0E+0 |
| HCl | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 8.7E-5 | 0E+0 | 0E+0 | 0E+0 | 0E+0 |
| $HNO_3$ | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 5.1E-4 | 0E+0 | 0E+0 | 0E+0 | 0E+0 |
| $Na_2CO_3$ | 0E+0 | 1.4E-2 | 6.2E-5 | 0E+0 | 4.4E-4 | 0E+0 | 7.3E-3 | 7.2E-3 | 0E+0 |
| NaCl | 0E+0 | 0E+0 | 3.1E-3 | 0E+0 | 0E+0 | 0E+0 | 8.2E-5 | 8.2E-5 | 0E+0 |
| $NaNO_2$ | 0E+0 | 3.1E-02 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 1.5E-2 | 1.5E-2 | 0E+0 |
| $NaNO_3$ | 0E+0 | 1.6E-1 | 1.6E-2 | 0E+0 | 0E+0 | 0E+0 | 7.9E-2 | 7.9E-2 | 0E+0 |
| NaOH | 0E+0 | 7.6E-2 | 1.7E-2 | 0E+0 | 0E+0 | 0E+0 | 4.1E-3 | 1.2E-2 | 0E+0 |
| $Na_2SO_4$ | 0E+0 | 1.8E-2 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 8.7E-3 | 8.7E-3 | 0E+0 |
| $Na_2C_2O_4$ | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 1.7E-3 | 0E+0 | 5.4E-3 | 5.4E-3 | 7.1E-1 |
| $Al(OH)_3$ | 0E+0 | 0E+0 | 0E+0 | 5.8E-1 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 2.2E-1 |
| AlOOH | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 1.1E-2 | 0E+0 | 0E+0 | 0E+0 | 0E+0 |
| $NaAlO_2$ | 0E+0 | 2.2E-2 | 4.4E-5 | 0E+0 | 0E+0 | 0E+0 | 7.5E-4 | 7.5E-4 | 0E+0 |
| $CaC_2O_4$ | 0E+0 | 0E+0 | 4.4E-5 | 1.6E-2 | 4.0E-5 | 2.1E-1 | 2.2E-6 | 2.2E-6 | 6.7E-3 |
| $CaCO_3$ | 0E+0 | 0E+0 | 0E+0 | 1.6E-2 | 0E+0 | 0+0 | 0E+0 | 0E+0 | 0E+0 |

**Table 7-10 Tank 11 HM dissolution material balance, pH restored w/supernate (Sheet 2 of 2)**

| Stream | 1 | 2 | 3A | 3B | 4A | 4B | 5 | 6A | 6B |
|---|---|---|---|---|---|---|---|---|---|
| | OA | pH fix | Sludge heel | | Treat tank slurry | | Resultant | | |
| | | | | | | | liquid | oxalate slurry | |
| **Phase** | Aq | Aq | Aq | Solid | Aq | Solid | Aq | Aq | Solid |
| **Units** | wtfrac | | | | | | | | |
| $Ca(OH)_2$ | 0E+0 | 0E+0 | 4.3E-5 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 0E+0 |
| $Ce_2O_3$ | 0E+0 | 0E+0 | 2.7E-3 | 0E+0 | 0E+0 | 0E+0 | 7.0E-5 | 7.0E-5 | 0E+0 |
| $Ce_2(C_2O_4)_3$ | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 6.1E-5 | 2.4E-2 | 0E+0 | 0E+0 | 0E+0 |
| $Fe_2(C_2O_4)_3$ | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 1.1E-2 | 0E+0 | 3.1E-5 | 3.1E-5 | 0E+0 |
| $Fe(OH)_3$ | 0E+0 | 0E+0 | 9.6E-7 | 2.49E-1 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 4.5E-2 |
| $K_2C_2O_4$ | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 5.4E-4 | 5.4E-4 | 0E+0 |
| KOH | 0E+0 | 7.5E-4 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 0E+0 |
| $MnC_2O_4$ | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 2.8E-4 | 4.8E-1 | 1.9E-7 | 1.9E-7 | 0E+0 |
| $MnOH_2$ | 0E+0 | 0E+0 | 1.0E-7 | 5.8E-2 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 1.0E-2 |
| $NiC_2O_4$ | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 5.1E-5 | 9.1E-2 | 1.2E-7 | 1.2E-7 | 0E+0 |
| $Ni(OH)_2$ | 0E+0 | 0E+0 | 4.5E-9 | 1.1E-2 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 2.0E-3 |
| $SiO_2$ | 0E+0 | 0E+0 | 2.0E-2 | 0E+0 | 1.0E-4 | 1.9E-1 | 5.3E-4 | 5.3E-4 | 0E+0 |
| $UO_2C_2O_4$ | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 9.0-4 | 0E+0 | 5.3E-4 | 5.3E-4 | 0E+0 |
| $UO_2OH_2$ | 0E+0 | 0E+0 | 2.7E-7 | 3.0E-2 | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 0E+0 |
| $ThO_2$ | 0E+0 | 0E+0 | 5E-14 | 1.1E-2 | 0E+0 | 0E+0 | 4E-14 | 4E-14 | 2.0E-3 |
| HgO | 0E+0 | 0E+0 | 3.9E-5 | 3.0E-2 | 7.6E-4 | 0E+0 | 3.1E-5 | 3.1E-5 | 5.1E-3 |
| $Th(C_2O_4)_2$ | 0E+0 | 0E+0 | 0E+0 | 0E+0 | 4.3E-4 | 0E+0 | 0E+0 | 0E+0 | 0E+0 |
| Total (kg) | 3.5E+5 | 3.1E+2 | 1.7E+1 | 9.4E+0 | 3.7E+2 | 1.8E+0 | 3.7E+5 | 2.6E+5 | 5.2E+4 |
| Vol (l) | 3.2E+5 | 2.5E+5 | 1.7E+4 | 3.3E+3 | 3.4E+5 | 3.1E+2 | 3.4E+5 | 2.4E+5 | 5.8E+3 |
| $C_2O_4$ (kg) | 2.7E+4 | 0E+0 | 5.8E-1 | 1.1E+02 | 2.6E+4 | 9.4E+2 | 1.5E+3 | 1.0E+3 | 2.5E+4 |

As demonstrated in Tables 7-6 through 7-10, the fate oxalates will either be in the Resultant liquid or the Resultant oxalate slurry. The downstream process flowsheet, therefore, is largely dependent on how the two streams are processed, as well as OLI's© ability to predict oxalate solubility. To ensure the model accurately forecasted the oxalate fate, the OLI© oxalate solubility as a function of sodium concentration was compared to measured solubility results. Refer to Section 7.2.1.

### 7.2.3 Model's sodium oxalate solubility acceptability

The primary solid materials formed using oxalic acid to clean the waste tanks were metal oxalates and sodium oxalates. Figure 7-3 shows the measured and forecasted solubility of sodium oxalate. Measured results were based on oxalate in NaOH,

$NaNO_3$ and supernate simulant (Fowler, 1980; Wiley, 1978). Forecasted results were based on oxalate solubility in average supernate (provided in Section 7.1.2 Table 7-6) being diluted/concentrated to achieve applicable sodium concentration.

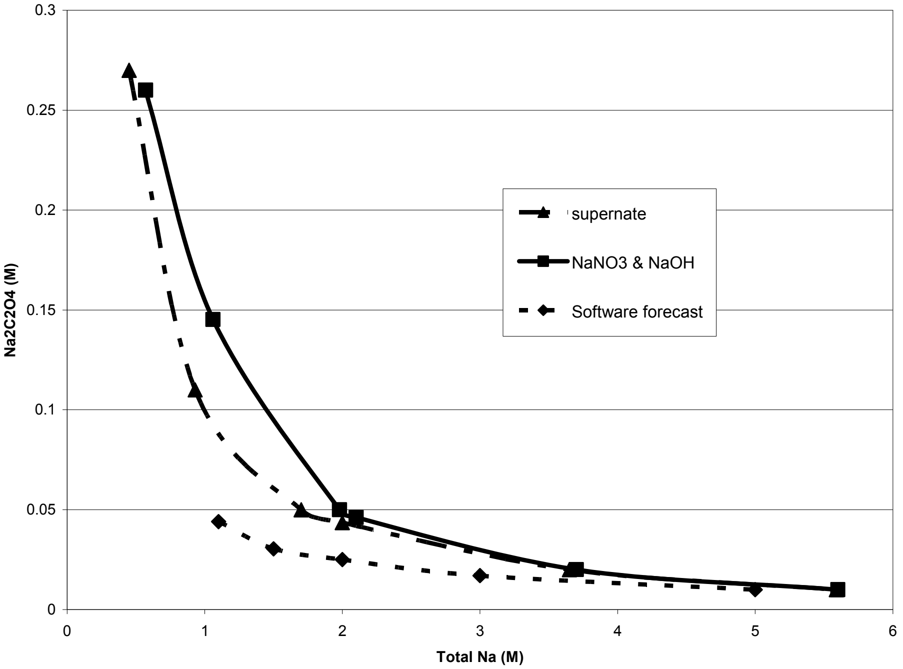


**Figure 7-3 Oxalate solubility curve**

In Figure 7-3, the measured results, containing only sodium nitrate and sodium hydroxide, used by Fowler and Wiley, are presented by squares. The triangles represent the solubility in simulated average supernate. The diamonds represent the OLI© forecasts.

The figure shows that dilution and concentration as part of Functions 2, 3, and 4 in Figure 7-1, will largely determine the fate of the oxalates.

## 7.3 Sludge Washing

### 7.3.1 Sludge washing model

Assuming the oxalates were added to an unwashed Sludge Batch 3, the effect of 5 washes was determined using a combined mathematical estimate of the sludge washing process model (Lillistan, 2004) with the solubility of the oxalates estimated by OLI©. The model is graphically shown in Figure 7.4.

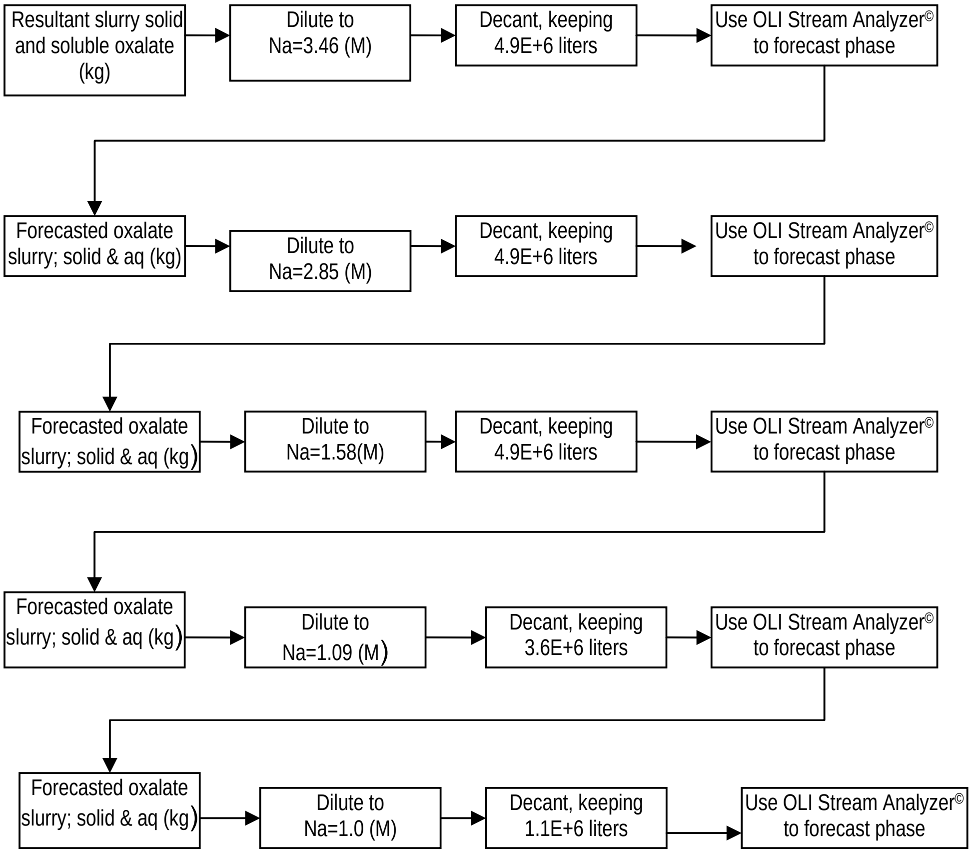


**Figure 7-4 Effect of sludge washing on the oxalate model**

### 7.3.2 Model inputs, calculations, and results

Assuming that the slurry from heel removal was added to the sludge washing tank at the beginning of the sludge batch, the decanted liquid from sludge transfers and washing will remove oxalate from the sludge batch. The sludge washing targeted a total sodium concentration of less than 1.0 M. Assuming the same target was acceptable, the effect on sludge washing is shown in Table 7-11. Most of the added sodium oxalate from one dissolved heel would be washed out of the sludge batch ending up being transferred to the evaporator system.

**Table 7-11 Sodium oxalate balance for sludge washing**

| Case | | Initial | Wash 1 | Wash 2 | Wash 3 | Wash 4 | Wash 5 | Total to evap sys |
|---|---|---|---|---|---|---|---|---|
| | | | After Decant | | | | | |
| **Tank 8 with pH restoration using NaOH (Case 1)** | | | | | | | | |
| $Na^+$ (M) | | | 3.46 | 2.85 | 1.58 | 1.09 | 1.0 | |
| Volume (l) | | | 1.3E+6 | 1.3E+6 | 1.3E+6 | 9.5E+5 | 2.9E+5 | |
| Sodium Oxalate (kg) | Solids | 2.2E+4 | 2.0E+4 | 1.3+4 | - | - | - | |
| | Soluble | 4.6E+3 | 3.5E+3 | 5.1E+3 | 9.5E+3 | 5.7E+3 | 4.7E+3 | |
| | Total | 2.7E+4 | 2.3E+4 | 1.8E+4 | 9.5E+3 | 5.7E+3 | 4.7E+3 | 2.2E+4 |
| **Tank 8 with pH restoration using supernate (Case 2)** | | | | | | | | |
| $Na^+$ (M) | | | 3.46 | 2.85 | 1.58 | 1.09 | 1.0 | |
| Volume (l) | | | 1.3E+6 | 1.3E+6 | 1.3E+6 | 9.5E+5 | 2.9E+5 | |
| Sodium Oxalate (kg) | Solids | 2.2E+4 | 1.6E+4 | 9.5E+3 | - | - | - | |
| | Soluble | 1.0E+3 | 3.5E+3 | 5.1E+3 | 7.6E+3 | 4.6E+3 | 3.8E+3 | |
| | Total | 2.3E+4 | 1.9E+4 | 1.5E+4 | 7.6E+3 | 4.6E+3 | 3.8E+3 | 1.9E+4 |
| **Tank 11 with pH restoration using NaOH (Case 3)** | | | | | | | | |
| $Na^+$ (M) | | | 3.5 | 2.9 | 1.6 | 1.1 | 1.0 | |
| Volume (l) | | | 1.3E+6 | 1.3E+6 | 1.3E+6 | 9.5E+5 | 2.9E+5 | |
| Sodium Oxalate (kg) | Solids | 2.9E+4 | 2.8E+4 | 2.1E+4 | 3.4E+3 | - | - | |
| | Soluble | 5.9E+3 | 3.5E+3 | 5.1+3 | 1.2E+4 | 9.3E+3 | 7.7E+3 | |
| | Total | 3.5E+4 | 3.1E+4 | 2.7E+4 | 1.5E+4 | 9.3E+3 | 7.7E+3 | 2.3E+4 |
| **Tank 11 with pH restoration using supernate (Case 4)** | | | | | | | | |
| $Na^+$ (M) | | | 3.5 | 2.9 | 1.6 | 1.1 | 1 | |
| Volume (l) | | | 1.3E+6 | 1.3E+6 | 1.3E+6 | 9.5E+5 | 2.9E+5 | |
| Sodium Oxalate (kg) | Solids | 3.7E+4 | 3.1E+4 | 2.5E+4 | 6.9E+3 | - | - | |
| | Soluble | 1.4E+3 | 3.5E+3 | 5.1E+3 | 1.2E+4 | 1.1E+4 | 9.5E+3 | |
| | Total | 3.8E+4 | 3.5E+4 | 3.0E+4 | 1.9E+4 | 1.1E+4 | 9.5E+3 | 2.9E+4 |

With no changes to the washed sludge 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 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, two to three dissolved heels were 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 consisted of other metal oxalates formed from dissolution of the heel. The final sodium oxalate from one heel dissolution from Case 4 (Tank 11 with pH restored using supernate) equated to 7.3 wt%. The sodium concentration in solution was about 1 M, but the total sodium in the slurry would increase substantially, by about 13,200 kg.

Thermodynamically, the formation of iron, manganese, and aluminum oxalates are favored; 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 would 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 sodium that is more soluble 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.

## 7.4 Evaporation

### 7.4.1 Evaporation model

A simple model was constructed to determine the effect of adding the Resultant liquid directly to the evaporator feed tank. Refer to Figure 7-5.

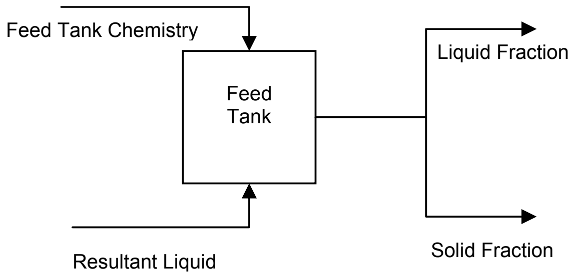


Figure 7-5 Solubility model for evaporator feed tank

Since there are strict controls placed on feeding solids to the evaporator, the transfer pump out of the tank is well above the solids level. The amount of oxalate that remains in the feed tank, therefore, is a function of the oxalates solubility and the feed rate to the evaporator.

The oxalate solubility was determined using OLI©, while the depletion rate was determined using the feed rate of the evaporator.

### 7.4.2 Model inputs, calculations, and results

Table 7-12 shows the initial feed tank composition.

**Table 7-12 Evaporator feed tank initial composition**

| Chemical compound | Concentration (M) |
|---|---|
| $NaNO_3$ | 1.82E+0 |
| $Na_2CO_3 \cdot H_2O$ | 8.76E-2 |
| $NaNO_2$ | 1.69E+0 |
| $NaAlO_2 \cdot 2H_2O$ | 1.14E-1 |
| $Na_2C_2O_4$ | 6.19E-2 |
| $Na_2SO_4$ | 2.39E-2 |
| NaCl | 3.48E-2 |
| NaF | 5.79E-2 |
| NaOH | 4.71E+0 |
| $Na_3PO_4$ | 6.51E+3 |
| $Na_2SiO_3$ | 7.84E-2 |

Table 7-13 shows the results for transferring one liquid decant from heel dissolution to the evaporator feed tank for each case.

**Table 7-13 Sodium oxalate balance for the evaporator**

| Tank | Case 1- Tank 8 NaOH | | Case 2- Tank 8 supernate | | Case 3- Tank 11 NaOH | | Case 4- Tank 11 supernate | |
|---|---|---|---|---|---|---|---|---|
| | $Na_2C_2O_4$ (kg) | % Add | $Na_2C_2O_4$ (kg) | % Add | $Na_2C_2O_4$ (kg) | % Add | $Na_2C_2O_4$ (kg) | % Add |
| 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 |
| Transfer to drop tank | 1150 | - | 1250 | - | 1230 | - | 990 | - |

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. The amount of sodium oxalate in the evaporator feed decreased to the point that the remaining sodium oxalate in the feed tank practically remained constant.

The concentration in the aqueous phase decreases due to the increase in total sodium concentration or ionic strength. Additionally, more sodium oxalate would transfer to the drop tank with each large transfer of fresh, relatively dilute waste into the feed tank. If no additional sodium oxalate was added to the tank, the remaining oxalate eventually be deposited into the drop tank. The bottom of the feed tank, however, contained 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 Resultant liquid 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. The addition of the Resultant liquid to the evaporator drop tank and evaporator feed tank are contrasted in Figures 7-6 and 7-7. Figure 7-6 shows that if the Resultant liquid is transferred to the feed tank, it will be slowly transferred through the evaporator. In fact, at approximately 3,000 hrs, only 15% of the oxalate remains in the feed tank. Alternately, if the material is transferred to the drop tank 91 wt% (2,400 kg) will remain in the drop tank as a precipitate.

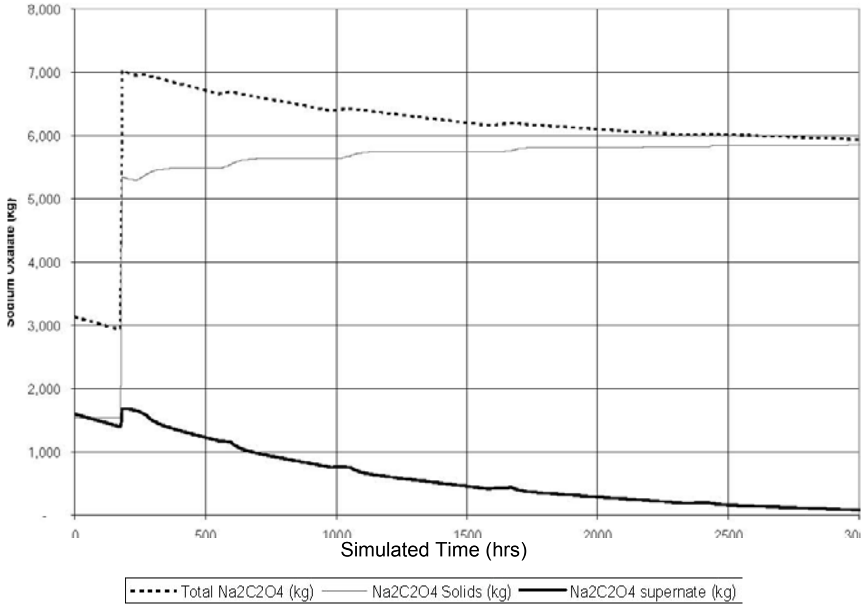


**Figure 7-6 Oxalate from Resultant liquid added to feed tank (Tank 8 with pH fix via supernate)**

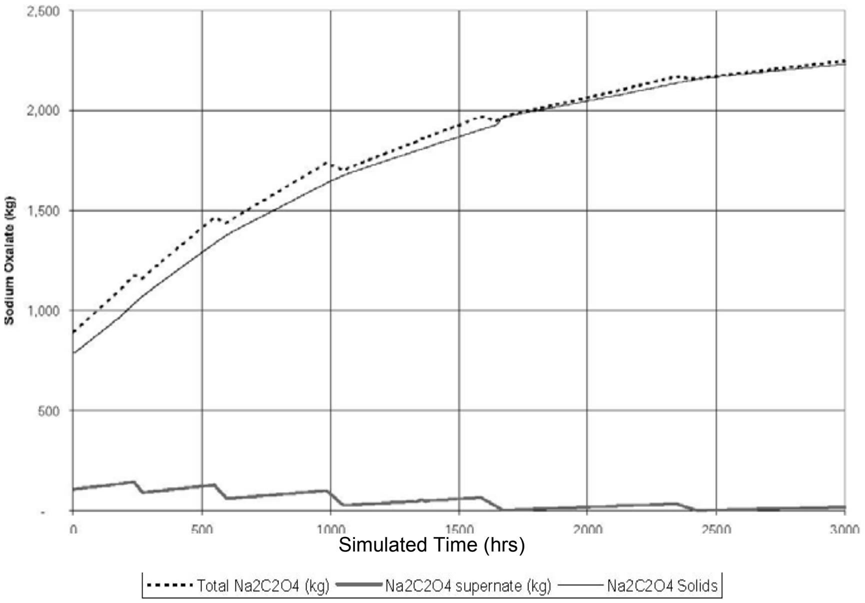


**Figure 7-7 Oxalate from Resultant liquid added to drop tank (Tank 8 with pH fix via supernate)**

The decant wash water, will simply add additional sodium oxalate directly to the solids layer in the evaporator 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.

If more than two or three heel dissolutions accumulated in the evaporator feed tank, *(i.e.*, about 60,000 kg of sodium oxalate), because of the suction pump height, all of the additional sodium oxalate would be transferred through the evaporator. A quantity less than 60,000 kg will tend to remain in the feed tank until eventual heel removal.

## 7.5 Salt Dissolution

### 7.5.1 Salt dissolution equation

Salt dissolution is an ongoing effort within the tank farms. About 8.3 l of water is added to each 3.8 liter of saltcake to produce about 12.1 l of SWPF feed solution at a total sodium concentration of 6.4 M (Pike, 2002). In a salt tank with 3.8 million l of saltcake, about 12.1 million l 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 (Pike, 2002).

$$Max[Na_2C_2O_4] = \\ T \times (1.59E-3 \times I^{-1.44}) + (7.23E-2 \times I^{-1.42}) \qquad \text{(Equation 7-1)}$$

Where:

$Max[Na_2C_2O_4]$ = maximum soluble sodium oxalate (M)

$T$= temperature (°C)

$I$ = total sodium concentration (M)

Assuming 30°C, a typical temperature of a salt tank, and 6.4 M total sodium concentration, the saturation level of sodium oxalate is about 8.4E-3 M. At this saturation concentration, the total oxalate dissolved would be as much as 13,600 kg 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.

### 7.5.2 Model inputs, calculations, and results

Average saltcake solids contain about 0.45 wt% sodium oxalate. In 3.8 million l 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%) |
|---|---|
| $NaNO_3$ | 8.6E+1 |
| $Na_2CO_3 \cdot H_2O$ | 5.7E+0 |
| $NaNO_2$ | 8.2E-1 |
| $NaAlO_2 \cdot 2H_2O$ | 2.2E+0 |
| $Na_2C_2O_4$ | 4.5E-1 |
| $Na_2SO_4$ | 2.9E+0 |
| NaCl | 6.8E-3 |
| NaF | 1.7E-1 |
| NaOH | 7.3E-1 |
| $Na_3PO_4$ | 5.9E-1 |

All the dissolved sodium oxalate will pass through salt processing with the other soluble sodium salts being transferred to the Saltstone facility. About 13,600 kg of sodium oxalate is expected to be sent to salt processing per 3.8 million l of saltcake processed. There are no existing plans to remove solid heels after bulk salt removal. The planned salt processing 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.

## 7.6 Vitrification

SRNL studied the effect of substantial sodium oxalate in sludge batch 3 on the Defense 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

(Herman & Best, 2002; Peeler & Edwards, 2003). These studies showed the DWPF Sludge Receipt and Adjustment Tank (SRAT) was affected as follows.

1) Negligible amounts of iron and gadolinium became soluble with sodium oxalate at 5.74 wt% of total solids.
2) Iron became ten times more soluble when sodium oxalate increased to 8.37 wt% or 13.21 wt% of total solids.
3) Gadolinium became completely soluble at 13.21 wt% sodium oxalate.
4) Sodium oxalate mitigated the release of hydrogen.
5) More acid was 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 was kept below 6 wt%, solubility of iron and gadolinium was 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 showed that the process was highly influenced by the choice of the glass frit used to vitrify the waste.

Peeler and Edwards (2003) demonstrated a 5% increase in the number of canisters with moderate sodium oxalate content of about 3 wt% verses no sodium oxalate. The slightly higher waste loading offset the additional sodium in the sludge slurry. 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. An 8.37 wt% sodium oxalate represented 50% more oxalate than 5.74 wt% and resulted in 28% increase in canisters (Peeler & Edwards, 2003).

Using sludge batch 4 for an example, a 28% increase would change the net canisters predicted from 505 canisters to 646. This estimate, however, is only a guide to the magnitude of the change. A specific frit optimization study and batch qualification analysis would identify effects that are more precise. 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 on vitrification**

| Sodium oxalate (wt%) | Frit | Limitation | % Waste oxide loading | Canisters produced | Notes |
|---|---|---|---|---|---|
| 0 | 320 | Glass quality | 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 | Glass quality | 44.2 | 553 | |
| 8.37 | 202 | Durability | 37.0 | 714 | |
| 10.86 | 202 | Durability | | | No acceptable blend |

Residual transfers to the drop tank, including any sludge washing decants, resulted in large salt heels, that after bulk salt removal would consist of mostly of sodium oxalate.

Planned salt dissolution will send no more than 14,000 kg of dissolved sodium oxalate per 3.8 million l of saltcake to the salt waste processing and eventually to the Saltstone Facility.

## 7.7 Integrated Effect on Waste Processing

Sludge heel cleaning with oxalic acid essentially resulted in two waste streams. The first was the Resultant liquid, and the second was the sludge slurry with the precipitated sodium oxalate solids. This stream is called the Resultant oxalate slurry

### 7.7.1 Adjusted supernate

The Restored liquid would eventually be sent to the evaporator system. The liquid would be sent to either the evaporator feed or drop tank. If this liquid was sent to the evaporator feed tank, most of the sodium oxalate will precipitate and remain in the feed tank. Effectively, the sodium oxalate will build up in the sludge layer of the feed tank. This could become unmanageable for sludge blending. If the supernate is 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. About 6,000 kg of sodium oxalate per 19,000 liter sludge heel dissolved would be in this stream. The eventual dissolution would generate about 190,000 l of additional dilute Saltstone feed. Potentially, all the low solubility salts and sodium oxalate remaining could be dissolved and processed through the SWPF as additional Saltstone feed. The additional amount of sodium oxalate in the feed stream to the Saltstone Facility would have only a small impact on the volume of Saltstone produced.

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

### 7.7.2 Resultant solids slurry

The Resultant oxalate 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 was 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. 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.

The second option was to wash the sludge to a low enough sodium level first and then add the solids slurry to the batch. This resulted 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 (Peeler & Edwards, 2003). 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 sludge with a significantly larger sodium oxalate concentration at some future date.

### 7.7.3 Recommended process flowsheet

As previously shown in Tables 7-7 and 7-8, for a 19,000 liter Purex sludge heel, about 246,000 l of 8 wt% acid should be used. From Tables 7-9 and 7-10, for a similar HM sludge heel about 322,000 l of 8 wt% should be used.

Optimizing the overall functions required as part of the flowsheet (shown in Figure 7-1) to minimize downstream process impacts, can be summarized into two basic processing strategies. They are:

1) Maximize the precipitated solids processed out of the HLW system, by sending them directly to DWPF without rinsing.
2) Maximize the soluble oxalates sent directly to the evaporator drop tank, so as to minimize impacts to the evaporator and ensure their location.

Overall, incorporating these two basic process strategies into the flowsheet, results in the recommended process flowsheet as shown in Figure 7-8.

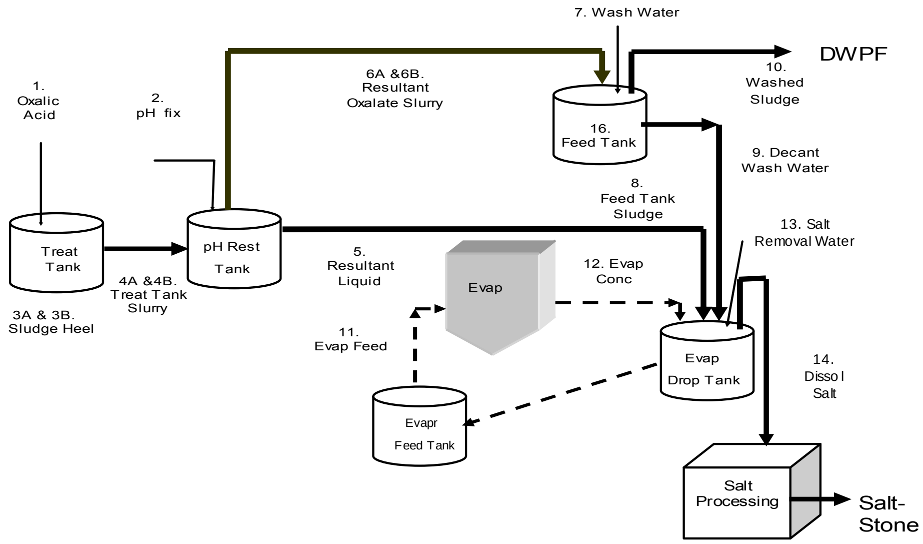


**Figure 7-8 Recommended heel removal flowsheet**

Specifically, the sludge heel is treated with oxalic acid. The dissolved heel is transferred to a pH restoration tank that has been pre-treated with pH fix. The Resultant oxalate slurry, as approximately 16 wt% solids, will be sent to an already qualified sludge batch. The Resultant liquid should be transferred to the evaporator drop tank. The oxalate will form a small amount of solids that will build up in the drop tank, until sometime in the future when the salt heel is removed.

## 7.8 Conclusion on Flowsheet and Process Impacts

Sludge heel cleaning with oxalic acid essentially results in two waste streams. The first is the pH adjusted supernate liquid stream, and the second is the sludge with the precipitated metal oxalate solids slurry stream. The preferred flowsheet 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 subsequently disposed with a sludge batch to the DWPF. The preferred flowsheets, Case 2 (Purex dissolution with pH restoration using supernate) and Case 4, (HM dissolution with pH restoration using supernate) include recommended amounts of oxalic acid based on sludge stream composition.

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

1) Sodium oxalate from the solids slurry can be added to a sludge batch without affecting the number of canisters produced.
2) The feed to the DWPF SRAT can tolerate up to 26 wt% sodium oxalate in total solids.
3) Increasing metal oxalate in the feed to the DWPF SRAT increases formic and nitric acid consumption, thus, increasing DWPF SRAT cycle time.
4) Glass quality limits the total amount of sodium in a batch without increasing the number of canisters produced.
5) 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.
6) 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.
7) 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 19,000 l of sludge heel cleaned from the treatment tank.
8) 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.

9) Solid slurries from tank heel cleaning should be bled into the DWPF feed stream at a relatively low rate.
10) 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.

1) Planned salt dissolution will send about 14,000 kg of dissolved sodium oxalate per 3.8 million l of saltcake, all of which currently exists in the saltcake, to the salt waste processing facilities and eventually to the Saltstone facility.
2) All sodium oxalate added to an evaporator drop tank will remain in the drop tank.
3) Planned bulk saltcake dissolution will remove none of the sodium oxalate added to an evaporator drop tank, thus, becoming part of the salt heel.

# 8 SENSITIVITY ANALYSIS

## 8.1 Introduction to Sensitivity

The purpose of the sensitivity analysis was to demonstrate the sensitivity of the model simulations to uncertainty and possible variations of input. Forecasts, based on an insensitive model, show similar outcomes regardless of variations in the input, and will have a predictable outcome. Alternately, sensitive models have a less predictable outcome.

A recommended flowsheet was determined in Chapter 7. For both Purex sludge heel dissolution and HM sludge heel dissolution, to maximize the available HLW tank space, readily available supernate will be used to restore the pH of the spent/excess oxalic acid. To help ensure sodium oxalate solids do not build up within the system, the precipitated solids will be added to a washed sludge batch, while the resultant pH restored liquid will be added to the evaporator drop tank.

The integrated flowsheet for the Tank 8 Purex sludge heel dissolution was mathematically presented in Table A5-2, while the defined processing plan for the Tank 11 HM case is presented in Table A5-4.

## 8.2 Sensitivity to Variations

As previously stated in Section 7.3, Tanks 1-9 have the same relative distributions, 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 8-1 shows modeled Purex sludge dissolution sensitivity to individual variations in sludge constituents.

Table 8-1 Sensitivity of dissolution to Purex sludge variations (per 19,000 l heel)

| Constituent | Mass (kg) | Change in Mass (kg)<br>Change in Remaining Total Solids (kg) | Approx. 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 |
| $UO_2(OH)_2$ | 929.5 | 100 / 1.5 | 700 -1,200 |
| $SiO_2$ | 211.6 | 100 / 94 | 150 -250 |
| $CaCO_3$ | 579 | 100 / 294 | 200 -700 |
| $Ce2O_3$ | 22.7 | 100 / 57 | 15 -30 |

Since the impact was expressed as a linear relationship, the observed forecast determined approximate linear graphic range. Outside this range for the modeling performed, the software results no longer showed a linear sensitivity/relationship. Because of limited measured results, however, no attempt was made to determine if it was actual or software related.

Based on Table 8-1, changes in carbonate mass have the biggest impact on Purex sludge dissolution, while dissolution was not as sensitive to small mass changes in $Al(OH)_3$ and $Fe(OH)_3$. Table 8-2 shows the variation in HM sludge dissolution based on changes to individual constituent mass.

**Table 8-2 Sensitivity of dissolution to HM sludge variations (per 19,000 l heel)**

| Constituent | Mass (kg) | Change in Mass (kg)<br>Change in Remaining total solids (kg) | Approx. 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 |
| ThO2 | 104.2 | 100 / 0.1 | NA |
| HgO | 287.3 | 100 / 0 | 200 -300 |

Based on Table 8-2, changes in carbonate mass also had the biggest impact on HM sludge dissolution, while $Al(OH)_3$ and $Fe(OH)_3$ appeared to be among the least sensitive. Using variations in quantities of oxalic acid and the 19,000 liter Purex sludge heel dissolution, the oxalic acid was varied and the precipitated mass of the treatment tank solids was determined as shown in Table 8-3.

**Table 8-3 Solids in Purex sludge treatment tank from excess oxalic acid**

| Oxalic acid (kg) | Precipitated treatment tank solids (kg) |
|---|---|
| 5,000 | 7.81E+3 |
| 10,000 | 3.74E+3 |
| 15,000 | 2.65E+3 |
| 20,000 | 2.75E+3 |
| 25,000 | 2.79E+3 |
| 30,000 | 2.80E+3 |
| 35,000 | 2.80E+3 |
| 40,000 | 5.41E+3 |
| 45,000 | 1.28E+4 |
| 50,000 | 2.01E+4 |
| 55,000 | 2.74E+4 |
| 60,000 | 3.48E+4 |
| 65,000 | 4.21E+4 |
| 70,000 | 4.95E+4 |

As can be seen in Table 8-3, adding excess oxalic acid for Purex sludge dissolution would cause precipitated oxalates to form in the treatment tank. Without adequate slurrying/mixing capability in the tank, these may remain in the treatment tank. For HM sludge dissolution, the similar effect was determined as shown in Table 8-4.

**Table 8-4 Solids in HM sludge treatment tank from excess oxalic acid**

| Oxalic acid (kg) | Precipitated treatment tank solids (kg) |
|---|---|
| 5,000 | 1.03E+4 |
| 10,000 | 4.84E+3 |
| 15,000 | 1.81E+3 |
| 20,000 | 1.94E+3 |
| 25,000 | 1.93E+3 |
| 30,000 | 1.91E+3 |
| 35,000 | 1.30E+4 |
| 40,000 | 2.91E+4 |
| 45,000 | 4.53E+4 |
| 50,000 | 1.03E+4 |
| 55,000 | 4.84E+4 |
| 60,000 | 1.81E+4 |
| 65,000 | 1.94E+4 |
| 70,000 | 1.93E+4 |

Based on the individual constituent variations in Tables 8-1 and 8-2, the forecasted change in the post pH restoration sludge mass was determined as shown in Tables 8-5 and 8-6.

**Table 8-5 Sensitivity of pH restored precipitate to Purex variations (per 19,000 l heel)**

| Constituent | Baseline mass (kg) | Mass variation (kg) | Precipitate 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 |
| $SiO_2$ | 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 |

Since most of the gas released was expected to be $CO_2$; and the model has been shown to treat $CO_2$ inappropriately as discussed in Section 5.5, the forecasted impacts from $CaCO_3$ variations in Purex sludge was likely over-predicted.

**Table 8-6 Sensitivity of pH restored precipitate to HM variations (per 19,000 l heel)**

| Constituent | Baseline mass (kg) | Mass variation (kg) | Precipitate 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 |

As evidenced in columns 3 and 4 of Tables 8-5 and 8-6, many of the metals were approximated by the same value (*i.e.,* 100 kg). This was indicative of the fact that the addition of oxalic acid and subsequent neutralization had the same net effect as the direct addition of sodium oxalate and water.

The additional supernate and oxalate solids added to the pH restoration tank from Purex sludge heel dissolution and HM sludge heel dissolution were determined as shown in Tables 8-7 and 8-8, respectively.

**Table 8-7 Liquid and solid increase from Purex sludge heel dissolution**

| Oxalic acid addition (kg) | Additional supernate (l) | Net pH restoration tank solids (kg) |
|---|---|---|
| 1.0E+4 | 2.37E+5 | 1.83E+4 |
| 1.5E+4 | 4.73E+5 | 2.58E+4 |
| 2.0E+4 | 7.11E+5 | 3.24E+4 |
| 2.5E+4 | 9.46E+5 | 3.41E+4 |
| 3.0E+4 | 1.18E+6 | 2.28E+4 |
| 3.5E+4 | 1.42E+6 | 2.46E+4 |
| 4.0E+4 | 1.66E+6 | 2.57E+4 |
| 4.5E+4 | 1.89E+6 | 2.57E+4 |
| 5.0E+4 | 2.13E+6 | 2.57E+4 |
| 5.5E+4 | 2.37E+6 | 2.57E+4 |
| 6.0E+4 | 2.60E+6 | 2.58E+4 |
| 6.5E+4 | 2.84E+6 | 2.58E+4 |
| 7.0E+4 | 3.08E+6 | 2.58E+4 |

**Table 8-8 Liquid and solid increase from HM sludge heel dissolution**

| Oxalic acid added (kg) | Additional supernate (l) | Net pH restoration tank solids (kg) |
|---|---|---|
| 1.0E+4 | 2.37E+4 | 1.76E+4 |
| 1.5E+4 | 4.73E+5 | 2.48E+4 |
| 2.0E+4 | 1.88E+5 | 3.12E+4 |
| 2.5E+4 | 2.50E+5 | 4.13E+4 |
| 3.0E+4 | 3.13E+5 | 4.35E+4 |
| 3.5E+4 | 3.75E+5 | 2.91E+4 |
| 4.0E+4 | 4.38E+5 | 2.91E+4 |
| 4.5E+4 | 5.00E+5 | 2.91E+4 |
| 5.0E+4 | 5.63E+5 | 2.91E+4 |
| 5.5E+4 | 6.25E+5 | 2.91E+4 |
| 6.0E+4 | 6.88E+5 | 2.92E+4 |
| 6.0E+4 | 7.50E+5 | 2.92E+4 |
| 7.0E+4 | 8.13E+5 | 2.92E+4 |

### 8.3 Conclusion on Sensitivity

Generally, variations in the quantity of metal oxides caused similar variations in the sludge feed to DWPF. Assuming adequate time was allowed for all of the acid to react, adding more acid did not necessarily result in an additional amount of sludge dissolved, but instead resulted in more oxalate solids. If significantly large quantities of excess acid were added, oxalate solids would begin to form in the strike tank.

Overall, it was concluded that both the Purex and HM models were rather insensitive to expected variations in constituent mass.

# 9 GENERAL CONCLUSION

The research design was originally based on extending the applicable acid dissolution sample data in terms of sensitivity analyses and variability analyses. Available OLI$^{©}$ software was used, as it allowed the effects on chemistry to be quickly estimated. The goal of the research was to determine if acid solutions could be used to effectively aid in sludge heel dissolution without the following:

1) Significantly increasing tank corrosion.
2) Creating gas/flammability/temperature hazards.
3) Creating undisposable process waste streams.

Early on, however, it was determined that both the use of nitric and citric acid could not currently be supported, and research would be limited to the use of oxalic acid. Additionally, there was a fundamental problem with the proposed original SVA approach. The evaluations that were originally proposed could only be accomplished, if the acceptability could be quantitatively based. Instead, almost all of the safety and processability evaluations proved to be qualitative. To meet the research need, instead of building SVAs into the evaluation, SVAs were limited to variations in acid quantities and slight variation in constituents. The following were evaluated/determined:

1) The model's ability to forecast dissolution effectiveness.
2) Possible pressurization, overheating, and flammability, and the effect of dissolution on organics and energetic materials.
3) A preferred and acceptable flowsheet.
4) The effects on downstream processing.

The results of the research showed that overall, sludge heel dissolution, using oxalic acid with subsequent pH restoration, could be effectively modeled.

For a 19,000 liter Purex sludge heel, somewhere between 246,000 liter to 511,000 liter of 8 wt% oxalic acid should be used. The 246,000 l was based on 100% excess of the equilibrium model, and the 511,000 l was based on observed laboratory testing, assuming three strikes of 20:1 volume ratio of 8 wt% acid dissolving 70-50-30% of the sludge heel volume.

For a 19,000 liter HM sludge heel, somewhere between 322,000 l to 511,000 l of 8 wt% oxalic acid should be used. The 322,000 l was based on 100% excess of the equilibrium model, and the 511,000 l was based on observed laboratory testing, assuming a 3-strike 20:1 volume ratio of 8 wt% acid dissolving 70-50-30% of the sludge heel volume.

The maximum expected temperature was bounded by 73.5°C, assuming 378,500 l of 8 wt% oxalic acid reacting with 66,000 l of 50 wt% NAOH. Operational controls, however, were credited with limiting the temperature to less than 64.6°C.

At 64.6°C, only 253 l of $CO_2$, and at 73.5°C only 770 l of water vapor was generated, and therefore pressurization was determined not to be a problem. The corrosion induced hydrogen was calculated at less than 10.25 $m^3$/hr (or 10,250 l/hr). At this rate, because of hydrogen's relatively low flammability, ventilation upgrades and/or additional studies were determined to be required (*i.e.,* only 4 percent is considered the lower flammability limit). Because of the aging of the Tank 1-15 sludge, and the washing effects of bulk waste removal, energetics and organics were determined not to represent a significant problem.

Because of the need to minimize glass canisters, the intentional formation of precipitated solids was minimized. Based on equilibrium modeling, it was determined that approximately three 19,000 liter sludge heel treatments could be processed in a DWPF sludge batch without a significant increase in the number of glass canisters produced. The actual number however, depended largely on the quantity of acid added and the initial volume of the sludge heel.

Based on the model excess determined in Chapter 7, about 56,800 l of oxalates could be added to a washed sludge batch with minimal impact on the number of additional glass canisters produced.

For each vitrification sludge batch, where one to three heel dissolutions were added, 60,000 kg of sodium oxalate entered the evaporator system, with most collected in the evaporator drop tank, until eventual salt heel removal. Assuming salt heel removal, for each 6,000 kg of sodium oxalate, about 189,000 l of additional dilute Saltstone feed would eventually be produced.

Overall, the model and testing showed that the amount of sodium oxalate and precipitated solids formed from Purex sludge heel dissolution and HM sludge heel dissolution were generally similar. Since the testing recommends equal quantities of acid for both Purex sludge dissolution and HM sludge dissolution, while equilibrium modeling also showed similar amounts of acid required (246,000 l for Purex and 322,000 l for HM), the processing of the sludge could be considered relatively insensitive to variations in constituents. Sludge heel dissolution, with oxalic acid and subsequent pH restoration, could best be considered sludge heel relocation with the net effect of five times more solids added to the system.

Assuming the treatment tank was ready for closure, the flammability issues associated with corrosion induced hydrogen could be overcome and hence did not represent significant process upsets. Ultimately, Tanks 1-15 sludge heel dissolution using oxalic acid seemed promising.

Overall, there were no significant process impacts which would forbid the use of oxalic acid in cleaning High Level Waste tanks.

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# APPENDICES

# Appendix 1 Proof-In-Principle

## A1.1 Comparisons with literature

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

To perform the proof-in-principle, the calculated OLI Stream Analyzer© equilibrium constants (ksp values) for manganese and iron were compared to referenced equilibrium constants found from literature (Badheka & Ketusky, 2003, 81). The first example considered was the dissolution of Mn(OH)2, which could be shown as Equation A1-1.

$$Mn(OH)_2 \leftrightarrow MN^{+2} + (OH)^{-1} \qquad \text{(Equation A1-1)}$$

OLI© predicted the pksp value as 1.4345E-13, where ksp = - log (pksp).

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

$$K_{sp,Mn(OH)2} = -\log(1.434E-13)$$

$$K_{sp,Mn(OH)2} = 12.8433$$

From Badheka and Ketusky (2003:81), $Mn(OH)_2$ has a ksp value of 12.72.

Another example considered was Iron (III) hydroxide, which from literature, had a ksp value of 38.55. According to OLI Stream Analyzer©, Iron (III) hydroxide had a ksp value of 37.5, which again was considered to be within reasonable limits.

For species that had several complexes that were soluble in water, Equation A1-2 was referred to.

$$pK_{sp} = pK_1 \times pK_2 \times pK_3 \times pK_n \qquad \text{(Equation A1-2)}$$

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 would be formed. An example was for $Al(OH)_3$. Refer to Equations A1-3 through A1-6.

$$Al(OH)_3 = Al^{+3} + 3(OH)^{-1} \qquad \text{(Equation A1-3)}$$

$$k_1 = 2.0962E-9$$

$$Al(OH)_3 = Al(OH)_2^{+1} + (OH)^{-1} \qquad \text{(Equation A1-4)}$$

$$k_2 = 2.4768E-9$$

$$Al(OH)_3 = Al(OH)^{+2} + (OH)_2^{-2} \qquad \text{(Equation A1-5)}$$

$$k_3 = 1.0382E-9$$

$$Al(OH)_3 = Al(OH)_2^{+1} + (OH)^{-1} \qquad \text{(Equation A1-6)}$$

$$k_4 = 7.2826E-8$$

Applying the equation to several species that are soluble to the complexes that Al(OH)3 produces in water yielded Equations A1-7 and A1-8.

$$k_{sp} = 2.0962E-9 \times 2.4768E-9 \times 1.0382E-9 \times 78.2826E-8 \qquad \text{(Equation A1-7)}$$

$$k_{sp=}3.9255E-34 \qquad \text{(Equation A1-8)}$$

From this, the $k_{sp}$ value of $Al(OH)_3$ was 33.406. Badheka and Ketusky (2003:81) found the solubility product constant to be 32.89, once again yielding close similarity in the values. It was therefore concluded that for the proof in principle tests, the software provided adequate approximations for $k_{sp}$.

## A1.2 Comparisons with other simulators

Barnes, *et al*, (2002:55) showed that a detailed comparison for the Aspen Plus$^{©}$ databank and the OLI$^{©}$ databank was performed for SRS HLW as part of modeling concerns associated with the SRS evaporators. The results of the detailed comparison showed that the forecasted behavior of the metal oxides using either Aspen Plus$^{©}$ or OLI$^{©}$ were similar.

## Appendix 2 Metal Dissolution Validation

As shown in Section 4.2, the iron oxides readily dissolved, while aluminum, manganese, and nickel did not. To demonstrate the behavior, using one strike of a 50:1 volume ratio of 4 wt% oxalic acid to Purex simulant, Table A2-1, shows the fate of the iron, aluminum, manganese and nickel oxides.

**Table A2-1 Dissolution outcome for metal oxides in Purex simulant**

| Initial compound | (% mole) | Final compound | Aqueous (% mole) | Solid (% mole) |
|---|---|---|---|---|
| $Fe(OH)_3$ | 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 |

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

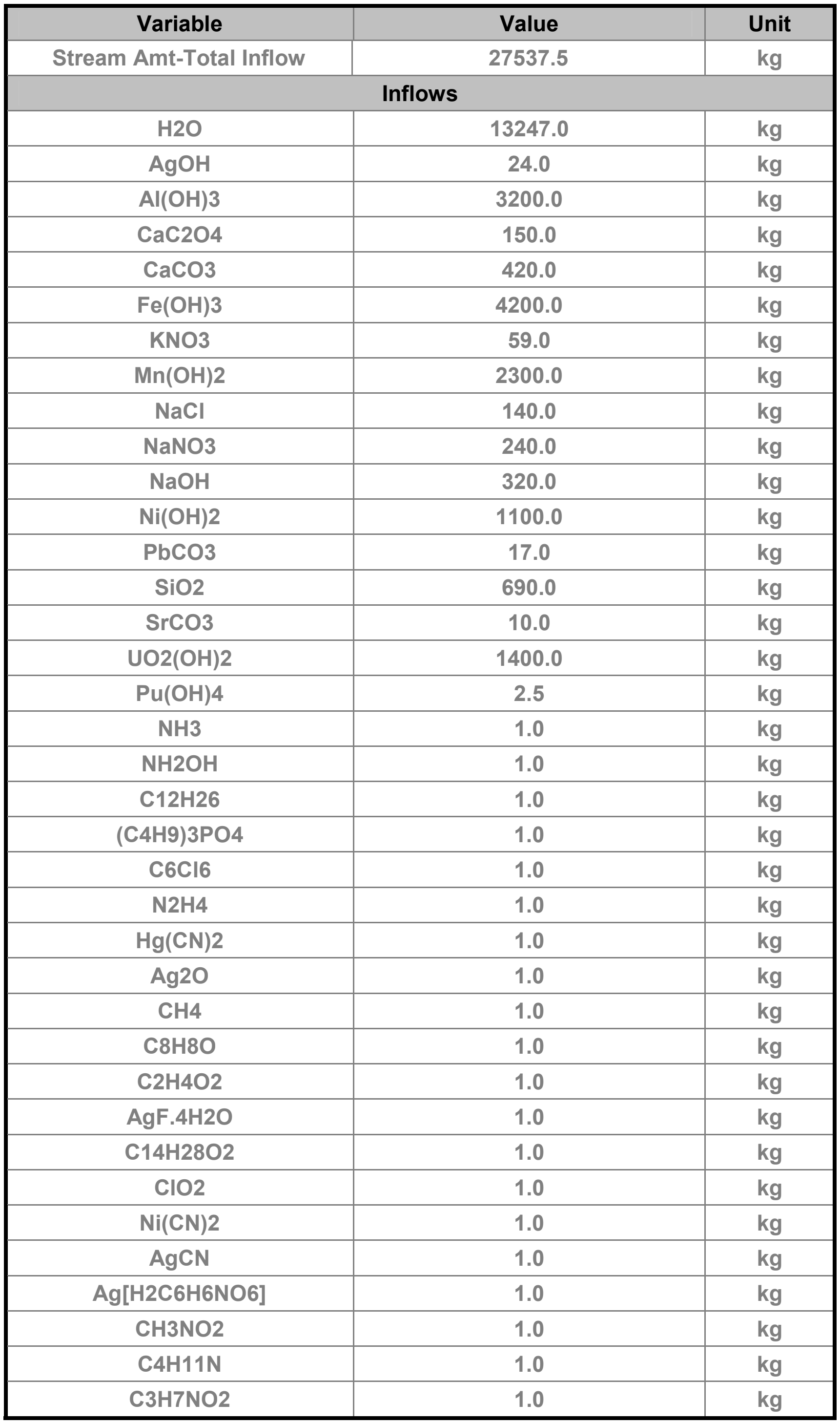
**Table A2-2 Dissolution outcome for metal oxides in HM simulant**

| Initial compound | (% mole) | Final compound | Aqueous (% mole) | Solid (% mole) |
|---|---|---|---|---|
| $Fe(OH)_3$ | 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 seen above, manganese and nickel formed mostly insoluble oxalate compounds.

## Appendix 3 Spiked Material Balance

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



| Variable | Value | Unit |
|---|---|---|
| Stream Amt-Total Inflow | 27537.5 | kg |
| **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 | 2.5 | 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 | 1.0 | kg |
| C4H11N | 1.0 | kg |
| C3H7NO2 | 1.0 | kg |

Figure A3-1 Input screen for spiked material balance

TableA3-1 shows the fate of the organics and other energetic chemicals added.

### Table A3-1 Outcome of organics and energetic materials (Sheet 1 of 3)

| First strike | | | | | | |
|---|---|---|---|---|---|---|
| Constituent | Spiked aqueous | Spiked vapor | Spiked solid | Actual aqueous | Actual vapor | Actual solid |
| | (% mole) | | | | | |
| $Ag^{+1}$ | 15.7 | 0.0 | 84.3 | 0.3 | 0.0 | 99.7 |
| $Al^{+3}$ | 46.6 | 0.0 | 53.4 | 44.9 | 0.0 | 55.1 |
| $C^{+4}$ | 71.4 | 28.6 | 0.0 | 100 | 0.0 | 0.0 |
| $C_{12}H_{26}$ | 1 | 99.0 | 0.0 | 0.0 | 0.0 | 0. |
| $Ca^{+2}$ | 43.0 | 0.0 | 57.0 | 26.0 | 0.0 | 74 |
| $CH_4$ | 11.0 | 89.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| $Cl^{-}$ | 92.4 | 0.0 | 7.6 | 92.0 | 0.0 | 8.0 |
| $Cl_6$BENZEN | 100.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| $CN^{-}$ | 100.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| $Cl^{+4}$ | 94.8 | 5.2 | 0.0 | 0.0 | 0.0 | 0.0 |
| $DLALANN^{-}$ | 100.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| $F^{-}$ | 100.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| $Fe^{+3}$ | 100.0 | 0.0 | 0.0 | 100.0 | 0.0 | 0.0 |
| $H^{+}$ | 99.1 | 0.0 | 1.0 | 98.7 | 0.0 | 1.3 |
| HDROXAMN | 100.0 | 0.0 | 0.0 | 0.00 | 0.0 | 0.0 |
| $Hg^{+2}$ | 100.0 | 0.0 | 0.0 | 100.0 | 0.0 | 0.0 |
| $K^{+}$ | 100.0 | 0.0 | 0.0 | 100.0 | 0.0 | 0.0 |
| MEFORMATE | 97.2 | 2.8 | 0.0 | 0.0 | 0.0 | 0.0 |
| $Mn^{+2}$ | 5.8 | 0.0 | 94.2 | 4.0 | 0.0 | 96.0 |
| $N^{+5}$ | 100.0 | 0.0 | 0.0 | 100.0 | 0.0 | 0.0 |
| $N^{-2}$ | 100.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| $N^{-3}$ | 100.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| $Na^{+}$ | 100.0 | 0.0 | 0.0 | 100.0 | 0.0 | 0.0 |
| $NI^{+2}$ | 0.51 | 0.0 | 99.5 | 0.3 | 0.0 | 99.7 |
| $NTA^{-3}$ | 100.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| $O^{-2}$ | 98.4 | 0.03 | 1.6 | 98.1 | 0.0 | 1.9 |
| $OXALAT^{-2}$ | 71.7 | 0.0 | 28.3 | 70.1 | 0.0 | 29.9 |
| $Pb^{+2}$ | 98.9 | 0.0 | 1.1 | 53.0 | 0.0 | 47.1 |
| $Pu^{+4}$ | 3.2 | 0.0 | 96.8 | 2.2 | 0.0 | 97.8 |
| $Si^{+4}$ | 3.2 | 0.0 | 96.8 | 2.5 | 0.0 | 97.5 |
| $Sr^{+2}$ | 100.0 | 0.0 | 0.0 | 100.0 | 0.0 | 0.0 |
| STYRENOX | 99.9 | 0.10 | 0.0 | 0.0 | 0.0 | 0.0 |
| TBP | 100.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| TEDEAC | 100.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| $U^{+6}$ | 94.3 | 0.0 | 5.7 | 75.7 | 0.0 | 24.4 |

### Table A3-1 Outcome of organics and energetic materials
(Sheet 2 of 3)

| Constituent | Spiked aqueous | Spiked vapor | Spiked solid | Actual aqueous | Actual vapor | Actual solid |
|---|---|---|---|---|---|---|
| (% mole) | | | | | | |
| **Second strike** | | | | | | |
| Ag$^{+}$ | 1.6 | 0.0 | 98.4 | 1.5 | 0.0 | 98.5 |
| Al$^{+3}$ | 85.2 | 0.0 | 14.8 | 82.5 | 0.0 | 17.5 |
| Ca$^{+2}$ | 0.0 | 0.0 | 100.0 | 0.01 | 0.0 | 100.0 |
| Cl$^{-}$ | 1.6 | 0.0 | 98.4 | 1.5 | 0.0 | 98.5 |
| CL$_6$BENZEN | 0.0 | 0.0 | 100.0 | 0.0 | 0.0 | 0.0 |
| H$^{+}$ | 96.4 | 0.0 | 3.6 | 28.5 | 0.0 | 71.5 |
| Mn$^{+2}$ | 28.6 | 0.0 | 71.4 | 0.1 | 0.0 | 99.9 |
| NI$^{+2}$ | 0.1 | 0.0 | 99.9 | 94.9 | 0.0 | 5.1 |
| O$^{-2}$ | 95.0 | 0.0 | 5.0 | 53.5 | 0.0 | 46.5 |
| OXALATE$^{-2}$ | 53.5 | 0.0 | 46.5 | 16.4 | 0.0 | 83.6 |
| Pb$^{+2}$ | 16.4 | 0.0 | 83.6 | 100.0 | 0.0 | 0.0 |
| Pu$^{+4}$ | 100.0 | 0.0 | 0.0 | 0.4 | 0.0 | 99.6 |
| Si$^{+4}$ | 0.4 | 0.0 | 99.6 | 100.0 | 0.0 | 0.0 |
| U$^{+6}$ | 100.0 | 0.0 | 0.0 | 100.0 | 0.0 | 0.0 |
| **Third strike** | | | | | | |
| Ag$^{+}$ | 0.66 | 0.0 | 99.3 | 0.7 | 0.0 | 99.3 |
| Al$^{+3}$ | 100.0 | 0.0 | 0.0 | 100.0 | 0.0 | 0.0 |
| Ca$^{+2}$ | 0.01 | 0.0 | 99.99 | 1.1 | 0.0 | 98.9 |
| Cl$^{-}$ | 0.5 | 0.0 | 99.5 | 0.7 | 0.0 | 99.3 |
| CL$_6$BENZEN | 0.7 | 0.0 | 99.3 | 0.0 | 0.0 | 0.0 |
| H$^{+}$ | 94.9 | 0.0 | 5.1 | 97.9 | 0.0 | 2.1 |
| Mn$^{+2}$ | 30.7 | 0.0 | 69.3 | 0.7 | 0.0 | 99.4 |
| NI$^{+2}$ | 0.03 | 0.0 | 99.97 | 0.1 | 0.0 | 99.9 |
| O$^{-2}$ | 94.0 | 0.0 | 6.0 | 97.2 | 0.0 | 2.8 |
| OXALATE$^{-2}$ | 42.7 | 0.0 | 57.3 | 60.4 | 0.0 | 39.6 |
| Pb$^{+2}$ | 24.4 | 0.0 | 75.6 | 42.4 | 0.0 | 57.6 |
| SI$^{+4}$ | 3.5 | 0.0 | 96.5 | 0.9 | 0.0 | 99.1 |

## Table A3-1 Outcome of organics and energetic materials
## (Sheet 3 of 3)

| pH restoration (% mole) | | | | | | |
|---|---|---|---|---|---|---|
| **Constituent** | **Spiked aqueous** | **Spiked vapor** | **Spiked solid** | **Actual aqueous** | **Actual vapor** | **Actual solid** |
| $Ag^{+}$ | 68.8 | 0.0 | 31.2 | 68.8 | 0.0 | 31.2 |
| $Al^{+3}$ | 26.5 | 0.0 | 73.5 | 0.0 | 0.0 | 100. |
| $C^{+4}$ | 99.3 | 0.0 | 0.7 | 99.3 | 0.0 | 0.68 |
| $C_{12}H_{26}$ | 100.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| $Ca^{+2}$ | 0.4 | 0.0 | 99.6 | 0.0 | 0.0 | 0.0 |
| $CH_4$ | 100.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| $Cl^{-}$ | 100.0 | 0.0 | 0.0 | 100.0 | 0.0 | 0.0 |
| $Cl_6$BENZEN | 0.1 | 0.0 | 99.9 | 0.0 | 0.0 | 0.0 |
| $CN^{-}$ | 100.0 | 0.0 | 0.0 | 100.0 | 0.0 | 0.0 |
| $Cl^{+4}$ | 100.0 | 0.0 | 0.0 | 100.0 | 0.0 | 0.0 |
| $DLALANN^{-}$ | 100.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| $F^{-}$ | 100.0 | 0.0 | 0.0 | 100.0 | 0.0 | 0.0 |
| $Fe_{+3}$ | 0.93 | 0.0 | 99.1 | 0.9 | 0.0 | 99.1 |
| $H^{+}$ | 99.2 | 0.0 | 0.9 | 99.2 | 0.0 | 0.9 |
| HDROXAMN | 100.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| $Hg^{+2}$ | 55.5 | 0.0 | 44.5 | 55.5 | 0.0 | 44.5 |
| $K^{+1}$ | 100.0 | 0.0 | 0.0 | 100.0 | 0.0 | 0.0 |
| $Mn^{+2}$ | 0.4 | 0.0 | 99.7 | 0.4 | 0.0 | 99.7 |
| $N^{+3}$ | 100.0 | 0.0 | 0.0 | 100.0 | 0.0 | 0.0 |
| $N^{+5}$ | 100.0 | 0.0 | 0.0 | 100.0 | 0.0 | 0.0 |
| $N^{-2}$ | 100.0 | 0.0 | 0.0 | 100.0 | 0.0 | 0.0 |
| $N^{-3}$ | 100.0 | 0.0 | 0.0 | 100.0 | 0.0 | 0.0 |
| $Na^{+}$ | 54.5 | 0.0 | 45.5 | 54.5 | 0.0 | 45.5 |
| $NI^{+2}$ | 4.8 | 0.0 | 95.2 | 4.8 | 0.0 | 95.2 |
| $NTA^{-3}$ | 100.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| $O^{-2}$ | 98.3 | 0.0 | 1.7 | 98.3 | 0.0 | 1.7 |
| OXALATE $^{-2}$ | 5.5 | 0.0 | 94.5 | 5.5 | 0.0 | 94.5 |
| $Pb^{+2}$ | 100.0 | 0.0 | 0.0 | 100.0 | 0.0 | 0.0 |
| $Pu^{+4}$ | 0.0 | 0.0 | 100.0 | 0.0 | 0.0 | 100.0 |
| $Si^{+4}$ | 100.0 | 0.0 | 0.0 | 100.0 | 0.0 | 0.0 |
| $Sr^{+2}$ | 2.6 | 0.0 | 97.5 | 0.0 | 0.0 | 100.0 |
| STYRENOX | 100.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| TBP | 100.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| $U^{+6}$ | 0.1 | 0.0 | 99.95 | 0.1 | 0.0 | 99.95 |

As seen in the first acid strike in Table A3-1, more vapors were given off if organics and miscellaneous vapors were present, as expected.  Notably, metals would also behaved somewhat differently with organics.

## Appendix 4 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.

**Table A4-1 Oxalic acid reactions with sludge components**

| Reaction | Reactants | Products |
|---|---|---|
| 1 | $2AlOOH + 3H_2C_2O_4$ | $Al_2(C_2O_4)_3 + 4H_2O$ ($Al^{+3}$ also appears in |
| 2 | $2Al(OH)_3 + 3H_2C2O4$ | $Al_2(C_2O_4)_3 + 6H_2O$ |
| 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 |
| 8 | $Fe_2O_3 + 2H_2C_2O_4$ | $2Fe(C_2O_4)_3 + H_2O + O_2$ (complexing) |
| 9 | $MnO + H_2C_2O_4$ | $Mn(C_2O_4)_3 + ½ O_2$ (complexing) |
| 10 | $Mn_2O_3 + 2H_2C_2O_4$ | $2Mn(C_2O_4) + 2H_2O + ½O_2$ |
| 11 | $Mn_3O_4 + 3H_2C_2O_4$ | $3Mn(C_2O_4) + 3H_2O + ½O_2$ |
| 12 | $H_2C_2O_4 + NaNO_2 + ½O_2$ | $NO + NaNO_3 + 2CO + H_2O$ |
| 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 of sludges, HM sludge, and Purex sludge. The HM sludge is higher in aluminum, 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 Tables A4-1 through A4-3. Table A4-4 shows the equivalent composition and ratios for Tank 16 sludge specifically. These data ranged 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 Oxalic acid needed to react with 1 kg of HM sludge**

| Constituent | Mass (g) | Oxalic acid needed (moles) |
|---|---|---|
| $Al(OH)_3$ | 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 Oxalic acid needed to react with 1 kg of Purex sludge**

| Constituent | Mass (g) | Oxalic acid needed (moles) |
|---|---|---|
| $Al(OH)_3$ | 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 Oxalic acid needed to react with 1 kg of Tank 16 sludge

| Constituent | Molecular weight (g/mole) | wt% | moles per 1 kg of sludge solids | Oxalic acid (moles) |
|---|---|---|---|---|
| $AlO_2^-$ | 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 |
| $SO4^{-2}$ | 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 of slurry | 0.48 kg |
| moles reactive sludge per kg slurry | 8.70 |
| moles OA reacted | 7.78 |

## Appendix 5 Downstream Processing Results

The OLI ESP$^{©}$ simulation of the entire HLW process was modeled using supernate and NaOH to restore the pH of the Resultant supernate the dissolved Tank 8 and Tank 11 sludge heel. Figure A5-1 shows the integrated process diagram.

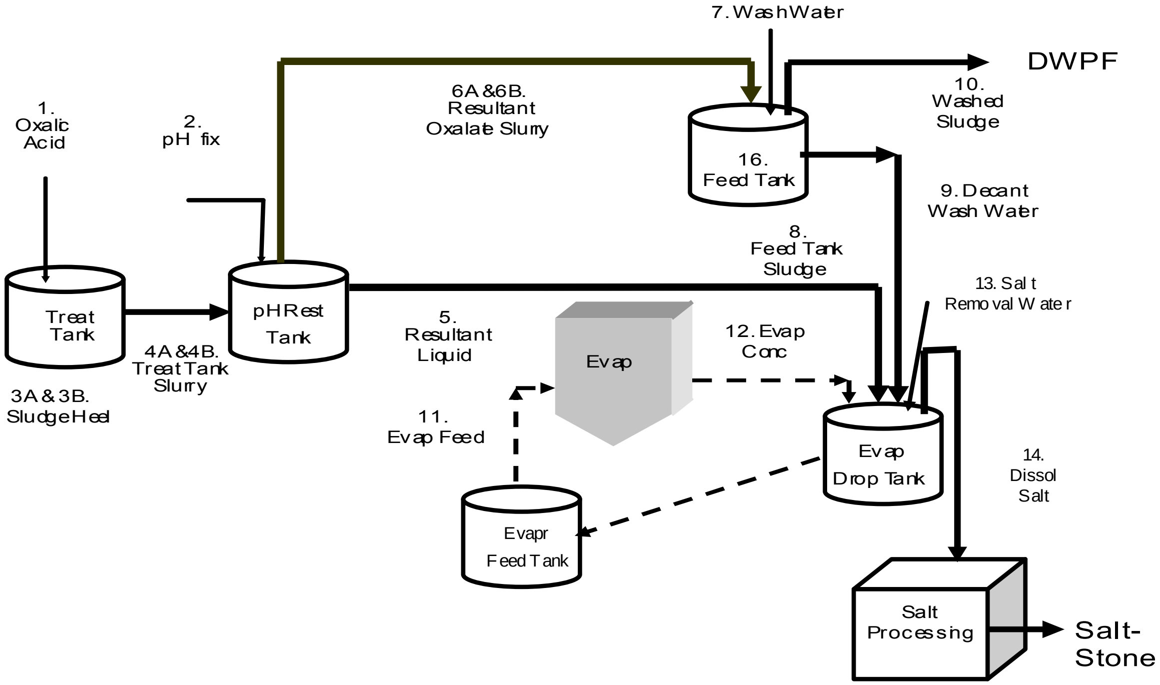


Figure A5-1 Sludge heel dissolution integrated flowsheet

Tables A5-1 and Table A5-3 show the material balance of the heel dissolution for these tanks using 50 wt% NaOH solution for pH restoration of the acid. Table A5-2 and Table A5-4 show the same material balance using an average supernate for pH restoration. Note that Tables A5-1 through A5-4 show the added materials, not necessarily existing tank farm material; thus, some streams show only a material balance for added sodium oxalate. Dissolved salt shows zero sodium oxalate transferred, because 100% remains in the heel.

**Table A5- 1 Tank 8 Purex integrated material balance, pH restored w/NaOH (Case 1 - Sheet 1 of 4)**

| **Stream** | **1** | **2** | **7** | **3a** | **3b** | **4a** | **4b** |
|---|---|---|---|---|---|---|---|
| | **Oxalic acid** | **pH fix** | **Wash water** | **Sludge heel** | | **Treat tank slurry** | |
| Phase | Aqueous | Aqueous | Aqueous | Aqueous | Solid | Aqueous | Solid |
| **Units** | **wtfrac** | | | | | | |
| $H_2O$ | 9.2E-1 | 5.0E-1 | 9.8E-1 | 9.2E-1 | 0.0E+0 | 9.1E-1 | 0.0E+0 |
| $H_2C_2O_4$ | 8.0E-2 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 4.0E-2 | 0.0E+0 |
| HCl | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 4.6E-4 | 0.0E+0 |
| $HNO_3$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 4.8E-4 | 0.0E+0 |
| $Na_2CO_3$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 3.4E-4 | 0.0E+0 | 2.1E-3 | 0.0E+0 |
| NaCl | 0.0E+0 | 0.0E+0 | 0.0E+0 | 1.2E-2 | 0.0E+0 | 0.0E+0 | 0.0E+0 |
| $NaNO_2$ | 0.0E+0 | 0.0E+0 | 2.4E-2 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 |
| $NaNO_3$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 1.1E-2 | 0.0E+0 | 0.0E+0 | 0.0E+0 |
| NaOH | 0.0E+0 | 5.0E-1 | 0.0E+0 | 3.4E-2 | 0.0E+0 | 0.0E+0 | 0.0E+0 |
| $Na_2SO_4$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 |
| $Na_2C_2O_4$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 4.4E-3 | 0.0E+0 |
| $Al(OH)_3$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 1.5E-1 | 0.0E+0 | 0.0E+0 |
| AlOOH | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 4.0E-3 | 0.0E+0 |
| $NaAlO_2$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 3.3E-3 | 0.0E+0 | 0.0E+0 | 0.0E+0 |
| $CaC_2O_4$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 4.1E-4 | 2.8E-1 |
| $CaCO_3$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 6.2E-2 | 0.0E+0 | 0.0E+0 |

**Table A5-1 Tank 8 Purex integrated material balance, pH restored w/NaOH (Case 1 - Sheet 2 of 4)**

| **Stream** | **1** | **2** | **7** | **3a** | **3b** | **4a** | **4b** |
|---|---|---|---|---|---|---|---|
| | **Oxalic acid** | **pH fix** | **Wash water** | **Sludge heel** | | **Treat tank slurry** | |
| Phase | Aqueous | Aqueous | Aqueous | Aqueous | Solid | Aqueous | Solid |
| **Units** | **wtfrac** | | | | | | |
| $Ca(OH)_2$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 2.4E-4 | 0.0E+0 | 0.0E+0 | 0.0E+0 |
| $Ce_2O_3$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 1.3E-3 | 0.0E+0 | 0.0E+0 | 0.0E+0 |
| $Ce_2(C_2O_4)_3$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 3.8E-5 | 9.1E-3 |
| $Fe_2(C_2O_4)_3$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 3.3E-2 | 0.0E+0 |
| $Fe(OH)_3$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 7.4E-5 | 5.8E-1 | 0.0E+0 | 0.0E+0 |
| $K_2C_2O_4$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 |
| KOH | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 |
| $MnC_2O_4$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 4.5E-4 | 3.4E-1 |
| $Mn(OH)_2$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 8.8E-7 | 6.0E-2 | 0.0E+0 | 0.0E+0 |
| $NiC_2O_4$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 5.7E-5 | 2.9E-1 |
| $Ni(OH)_2$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 3.1E-7 | 4.5E-2 | 0.0E+0 | 0.0E+0 |
| $SiO_2$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 1.2E-2 | 0.0E+0 | 3.8E-3 | 8.0E-2 |
| $UO_2C_2O_4$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 3.8E-3 | 0.0E+0 |
| $UO_2OH_2$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 2.7E-8 | 9.9E-2 | 0.0E+0 | 0.0E+0 |
| Total (kg) | 2.6E+5 | 3.9E+4 | 3.1E+6 | 1.7E+4 | 9.4E+3 | 2.9E+5 | 2.55E+3 |
| Vol (l) | 2.5E+5 | 1.4E+5 | 3.0E+6 | 1.6E+4 | 2.7E+3 | 2.6E+4 | 4.1E+2 |
| $C_2O_4$ (kg) | 2.1E+4 | 0.0E+0 | - | 0.0E+0 | 0.0E+0 | 1.93E+4 | 1.48E+3 |

**Table A5-1 Tank 8 Purex integrated material balance, pH restored w/NaOH (Case 1 - Sheet 3 of 4)**

| **Stream** | **5** | **11** | **12** | **13** | **14** | **6a** | **6b** | **10** | **9** | **8** |
|---|---|---|---|---|---|---|---|---|---|---|
| | **Resultant liquid** | **Evap feed** | **Evap conc** | **Salt removal water** | **Dissolved salt** | **Resultant oxalate slurry** | | **Washed sludge** | **Decant water** | **Feed tank sludge** |
| Phase | Aqueous | Aqueous | Aqueous | Aqueous | Aqueous | Aqueous | Solid | Slurry | Aqueous | Slurry |
| **Units** | **wtfrac** | | | | | | | | | |
| $H_2O$ | 9.61E-1 | - | - | 9.99E-1 | - | 9.61E-1 | 0.0E+0 | - | 8.09E-1 | - |
| $H_2C_2O_4$ | 0.0E+0 | - | - | 0.0E+0 | - | 0.00E+0 | 0.0E+0 | - | 0.0E+0 | - |
| HCl | 0.0E+0 | - | - | 0.0E+0 | - | 0.0E+0 | 0.0E+0 | - | 0.0E+0 | - |
| $HNO_3$ | 0.0E+0 | - | - | 0.0E+0 | - | 0.0E+0 | 0.0E+0 | - | 0.0E+0 | - |
| $Na_2CO_3$ | 2.07E-3 | - | - | 0.0E+0 | - | 2.07E-3 | 0.0E+0 | - | 1.01E-2 | - |
| NaCl | 7.12E-4 | - | - | 0.0E+0 | - | 7.11E-4 | 0.0E+0 | - | 2.40E-4 | - |
| $NaNO_2$ | 0.0E+0 | - | - | 7.50E-4 | - | 0.0E+0 | 0.0E+0 | - | 7.64E-2 | - |
| $NaNO_3$ | 6.23E-4 | - | - | 0.0E+0 | - | 6.22E-4 | 0.0E+0 | - | 6.98E-2 | - |
| NaOH | 4.55E-3 | - | - | 3.95E-4 | - | 4.99E-3 | 0.0E+0 | - | 1.76E-2 | - |
| $Na_2SO_4$ | 0.0E+0 | - | - | 0.0E+0 | - | 0.0E+0 | 0.0E+0 | - | 3.03E-3 | - |
| $Na_2C_2O_4$ | 2.90E-2 | 1.0E+0 | 1.0E+0 | 0.0E+0 | 0.0E+0 | 2.90E-2 | 7.01E-1 | 5.51E-2 | 5.79E-3 | 1.00E+0 |
| $Al(OH)_3$ | 0.0E+0 | - | - | 0.0E+0 | - | 0.0E+0 | 4.15E-2 | - | 0.0E+0 | - |
| AlOOH | 0.0E+0 | - | - | 0.0E+0 | - | 0.0E+0 | 0.0E+0 | - | 0.0E+0 | - |
| $NaAlO_2$ | 6.55E-4 | - | - | 0.0E+0 | - | 6.55E-4 | 0.0E+0 | - | 7.60E-3 | - |

**Table A5-1 Tank 8 Purex integrated material balance, pH restored w/NaOH (Case 1 - Sheet 4 of 4)**

| **Stream** | **5** | **11** | **12** | **13** | **14** | **6a** | **6b** | **10** | **9** | **8** |
|---|---|---|---|---|---|---|---|---|---|---|
| | **Resultant liquid** | **Evap feed** | **Evap conc** | **Salt removal water** | **Dissolved salt** | **Resultant oxalate slurry** | | **Washed sludge** | **Decant water** | **Feed tank sludge** |
| Phase | Aqueous | Aqueous | Aqueous | Aqueous | Aqueous | Aqueous | Solid | Slurry | Aqueous | Slurry |
| **Units** | **wtfrac** | | | | | | | | | |
| $CaC_2O_4$ | 7.62E-7 | - | - | 0.0E+0 | - | 7.61E-7 | 2.38E-2 | - | 0.0E+0 | - |
| $CaCO_3$ | 0.0E+0 | - | - | 0.0E+0 | - | 0.0E+0 | 0.0E+0 | - | 0.0E+0 | - |
| $Ca(OH)_2$ | 0.0E+0 | - | - | 0.0E+0 | - | 0.0E+0 | 0.0E+0 | - | 0.0E+0 | - |
| $Ce_2O_3$ | 7.64E-5 | - | - | 0.0E+0 | - | 7.63E-5 | 0.0E+0 | - | 0.0E+0 | - |
| $Ce_2(C_2O_4)_3$ | 0.0E+0 | - | - | 0.0E+0 | - | 0.0E+0 | 0.0E+0 | - | 0.0E+0 | - |
| $Fe2(C_2O_4)_3$ | 2.55E-5 | - | - | 0.0E+0 | - | 2.54E-5 | 0.0E+0 | - | 0.0E+0 | - |
| $Fe(OH)_3$ | 0.0E+0 | - | - | 0.0E+0 | - | 0.0E+0 | 1.74E-1 | - | 0.0E+0 | - |
| $K_2C_2O_4$ | 0.0E+0 | - | - | 0.0E+0 | - | 0.0E+0 | 0.0E+0 | - | 0.0E+0 | - |
| KOH | 0.00E+0 | - | - | 0.0E+0 | - | 0.0E+0 | 0.0E+0 | - | 0.0E+0 | - |
| $MnC_2O_4$ | 2.78E-6 | - | - | 0.0E+0 | - | 2.78E-6 | 0.0E+0 | - | 0.0E+0 | - |
| $Mn(OH)_2$ | 0.0E+0 | - | - | 0.0E+0 | - | 0.0E+0 | 1.78E-2 | - | 0.0E+0 | - |
| $NiC_2O_4$ | 9.54E-8 | - | - | 0.0E+0 | - | 9.53E-08 | 0.0E+0 | - | 0.0E+0 | - |
| $Ni(OH)_2$ | 0.0E+0 | - | - | 0.0E+0 | - | 0.0E+0 | 1.36E-2 | - | 0.0E+0 | - |
| $SiO_2$ | 7.12E-4 | - | - | 0.0E+0 | - | 7.11E-4 | 0.0E+0 | - | 0.0E+0 | - |
| $UO_2C_2O_4$ | 1.07E-4 | - | - | 0.0E+0 | - | 1.07E-4 | 0.0E+0 | - | 0.0E+0 | - |
| $UO_2OH_2$ | 0.0E+0 | - | - | 0.0E+0 | - | 0.0E+0 | 2.88E-0 | - | 0.0E+0 | - |
| Total (kg) | 1.41E+5 | 1.23E+3 | 1.23E+3 | 8.39E+6 | - | 1.57E+5 | 3.15E+4 | 4.01E+5 | 3.77E+5 | 5.06E+3 |
| Vol (l) | 1.4E+5 | - | - | 2.20E+6 | 8.3E+6 | 1.5E+5 | 2.8E+3 | 2.1E+6 | 5.2E+6 | - |
| $C_2O_4$ (kg) | 2.70E+3 | 8.08E+2 | 8.08E+2 | - | 0.0E+0 | 3.01E+3 | 1.50E+4 | 1.61E+4 | 1.44E+3 | 3.32E+3 |

**Table A5- 2 Tank 8 Purex integrated material balance, pH restored w/supernate (Case 2 - Sheet 1 of 4)**

| **Stream** | **1** | **2** | **7** | **3a** | **3b** | **4a** | **4b** |
|---|---|---|---|---|---|---|---|
| | **Oxalic acid** | **pH fix** | **Wash water** | **Sludge heel** | | **Treat tank slurry** | |
| Phase | Aqueous | Aqueous | Aqueous | Aqueous | Solid | Aqueous | Solid |
| **Units** | **wtfrac** | | | | | | |
| $H_2O$ | 9.20E-1 | 5.0E-1 | 6.79E-1 | 9.25E-1 | 0.0E+0 | 9.1E-1 | 0.0E+0 |
| $H_2C_2O_4$ | 8.00E-2 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 4.0E-2 | 0.0E+0 |
| HCl | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 4.6E-4 | 0.0E+0 |
| $HNO_3$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 4.8E-4 | 0.0E+0 |
| $Na_2CO_3$ | 0.0E+0 | 0.0E+0 | 1.42E-2 | 3.44E-4 | 0.0E+0 | 2.1E-3 | 0.0E+0 |
| NaCl | 0.0E+0 | 0.0E+0 | 0.0E+0 | 1.23E-2 | 0.0E+0 | 0.0E+0 | 0.0E+0 |
| $NaNO_2$ | 0.0E+0 | 0.0E+0 | 3.11E-2 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 |
| $NaNO_3$ | 0.0E+0 | 0.0E+0 | 1.59E-1 | 1.08E-2 | 0.0E+0 | 0.0E+0 | 0.0E+0 |
| NaOH | 0.0E+0 | 5.0E-1 | 7.62E-2 | 3.44E-2 | 0.0E+0 | 0.0E+0 | 0.0E+0 |
| $Na_2SO_4$ | 0.0E+0 | 0.0E+0 | 1.77E-2 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 |
| $Na_2C_2O_4$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 4.42E-3 | 0.0E+0 |
| $Al(OH)_3$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 1.53E-1 | 0.0E+0 | 0.0E+0 |
| AlOOH | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 3.95E-3 | 0.0E+0 |
| $NaAlO_2$ | 0.0E+0 | 0.0E+0 | 2.17E-2 | 3.29E-3 | 0.0E+0 | 0.0E+0 | 0.0E+0 |

**Table A5-2 Tank 8 Purex integrated material balance, pH restored w/supernate (Case 2 - Sheet 2 of 4)**

| Stream | 1 | 2 | 7 | 3a | 3b | 4a | 4b |
|---|---|---|---|---|---|---|---|
|  | **Oxalic acid** | **pH fix** | **Wash water** | **Sludge heel slurry** |  | **Treat tank slurry** |  |
| Phase | Aqueous | Aqueous | Aqueous | Aqueous | Solid | Aqueous | Solid |
| **Units** | **wtfrac** |  |  |  |  |  |  |
| $CaC_2O_4$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 4.08E-4 | 2.80E-1 |
| $CaCO_3$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 6.18E-2 | 0.0E+0 | 0.0E+0 |
| $Ca(OH)_2$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 2.40E-4 | 0.0E+0 | 0.0E+0 | 0.0E+0 |
| $Ce_2O_3$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 1.32E-3 | 0.0E+0 | 0.0E+0 | 0.0E+0 |
| $Ce_2(C_2O_4)_3$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 3.76E-5 | 9.07E-3 |
| $Fe_2(C_2O_4)_3$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 3.31E-2 | 0.0E+0 |
| $Fe(OH)_3$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 7.44E-5 | 5.81E-1 | 0.0E+0 | 0.0E+0 |
| $K_2C_2O_4$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 |
| KOH | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 |
| $MnC_2O_4$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 4.55E-4 | 3.40E-1 |
| $Mn(OH)_2$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 8.83E-7 | 5.95E-2 | 0.0E+0 | 0.0E+0 |
| $NiC_2O_4$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 5.71E-5 | 2.91E-1 |
| $Ni(OH)_2$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 3.07E-7 | 4.54E-2 | 0.0E+0 | 0.0E+0 |
| $SiO_2$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 1.23E-2 | 0.0E+0 | 1.12E-4 | 8.00E-2 |
| $UO_2C_2O_4$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 3.78E-3 | 0.0E+0 |
| $UO_2OH_2$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 2.66E-8 | 9.92E-2 | 0.0E+0 | 0.0E+0 |
| Total (kg) | 2.64E+5 | 2.31E+5 | 3.1E+6 | 1.72E+4 | 9.37E+3 | 2.88E+5 | 2.55E+3 |
| Vol (l) | 2.5E+5 | 2.6E+5 | 3.0E+6 | 1.6E+4 | 2.7E+3 | 2.7E+5 | 4.1E+2 |
| $C_2O_4$ (kg) | 2.07E+4 | 0.0E+0 | - | 0.0E+0 | 0.0E+0 | 1.93E+4 | 1.48E+3 |

**Table A5-2 Tank 8 Purex integrated material balance, pH restored w/supernate (Case 2 - Sheet 3 of 4)**

| Stream | 5 | 11 | 12 | 13 | 14 | 6a | 6b | 10 | 9 | 8 |
|---|---|---|---|---|---|---|---|---|---|---|
| | Resultant liquid | Evap feed | Evap conc | Salt removal water | Dissolved salt | Resultant oxalate slurry | | Washed sludge | Decant water | Feed tank sludge |
| Phase | Aqueous | Aqueous | Aqueous | Aqueous | Aqueous | Aqueous | Solid | Slurry | Aqueous | Slurry |
| **Flow Units** | **wtfrac** | | | | | | | | | |
| $H_2O$ | 8.78E-1 | - | - | 1.0E+0 | - | 8.71E-1 | 0.0E+0 | - | 8.08E-1 | - |
| $H_2C_2O_4$ | 0.0E+0 | - | - | 0.0E+0 | - | 0.0E+0 | 0.0E+0 | - | 0.0E+0 | - |
| HCl | 0.0E+0 | - | - | 0.0E+0 | - | 0.0E+0 | 0.0E+0 | - | 0.0E+0 | - |
| $HNO_3$ | 0.0E+0 | - | - | 0.0E+0 | - | 0.0E+0 | 0.0E+0 | - | 0.0E+0 | - |
| $Na_2CO_3$ | 8.11E-3 | - | - | 0.0E+0 | - | 8.07E-3 | 0.0E+0 | - | 1.00E-2 | - |
| NaCl | 4.42E-4 | - | - | 0.0E+0 | - | 4.39E-4 | 0.0E+0 | - | 2.40E-4 | - |
| $NaNO_2$ | 1.50E-2 | - | - | 7.50E-4 | - | 1.49E-2 | 0.0E+0 | - | 7.63E-2 | - |
| $NaNO_3$ | 7.69E-2 | - | - | 0.0E+0 | - | 7.65E-2 | 0.0E+0 | - | 6.97E-2 | - |
| NaOH | 4.18E-3 | - | - | 3.95E-4 | - | 1.16E-2 | 0.0E+0 | - | 1.76E-2 | - |
| $Na_2SO_4$ | 8.52E-3 | - | - | 0.0E+0 | - | 8.48E-3 | 0.0E+0 | - | 3.02E-3 | - |
| $Na_2C_2O_4$ | 4.95E-3 | 1.0E+0 | 1.0E+0 | 0.0E+0 | 0.0E+0 | 4.93E-3 | 6.79E-1 | 6.31E-2 | 7.66E-3 | 1.0E+0 |
| $Al(OH)_3$ | 0.0E+0 | - | - | 0.0E+0 | - | 0.0E+0 | 1.45E-1 | - | 0.0E+0 | - |
| AlOOH | 0.0E+0 | - | - | 0.0E+0 | - | 0.0E+0 | 0.0E+0 | - | 0.0E+0 | - |
| $NaAlO_2$ | 7.74E-4 | - | - | 0.0E+0 | - | 7.70E-4 | 0.0E+0 | - | 7.59E-3 | - |
| $CaC_2O_4$ | 2.15E-6 | - | - | 0.0E+0 | - | 2.14E-6 | 1.83E-2 | 1.83E-3 | 1.00E-6 | - |
| $CaCO_3$ | 0.0E+0 | - | - | 0.0E+0 | - | 0.0E+0 | 0.0E+0 | - | 0.0E+0 | - |

Table A5-2 Tank 8 Purex integrated material balance, pH restored w/supernate (Case 2 - Sheet 4 of 4)

| **Stream** | **5** | **11** | **12** | **13** | **14** | **6a** | **6b** | **10** | **9** | **8** |
|---|---|---|---|---|---|---|---|---|---|---|
| | **Resultant liquid** | **Evap feed** | **Evap conc** | **Salt removal water** | **Dissolved salt** | **Resultant oxalate slurry** | | **Washed sludge** | **Decant water** | **Feed tank sludge** |
| Phase | Aqueous | Aqueous | Aqueous | Aqueous | Aqueous | Aqueous | | Solid | Slurry | Aqueous |
| **Units** | **wtfrac** | | | | | | | | | |
| $Ca(OH)_2$ | 0.0E+0 | - | - | 0.0E+0 | - | 0.0E+0 | 0.0E+0 | - | 0.0E+0 | - |
| $Ce_2O_3$ | 4.74E-5 | - | - | 0.0E+0 | - | 4.72E- | 0.0E+0 | 3.17E-6 | 2.21E-5 | - |
| $Ce_2(C_2O_4)_3$ | 0.0E+0 | - | - | 0.0E+0 | - | 0.0E+0 | 0.0E+0 | - | 0.0E+0 | - |
| $Fe_2(C_2O_4)_3$ | 3.17E-5 | - | - | 0.0E+0 | - | 3.16E- | 0.0E+0 | 2.12E-6 | 1.48E-5 | - |
| $Fe(OH)_3$ | 0.0E+0 | - | - | 0.0E+0 | - | 0.0E+0 | 1.34E-1 | - | 0.0E+0 | - |
| $K_2C_2O_4$ | 5.31E-4 | - | - | 0.0E+0 | - | 5.28E- | 0.0E+0 | 3.55E-5 | 2.47E-4 | - |
| KOH | 0.0E+0 | - | - | 0.0E+0 | - | 0.0E+0 | 0.0E+0 | - | 0.0E+0 | - |
| $MnC_2O_4$ | 1.98E-7 | - | - | 0.0E+0 | - | 1.97E- | 0.0E+0 | 1.32E-8 | 9.21E-8 | - |
| $Mn(OH)_2$ | 0.0E+0 | - | - | 0.0E+0 | - | 0.0E+0 | 1.37E-02 | - | 0.0E+0 | - |
| $NiC_2O_4$ | 0.0E+0 | - | - | 0.0E+0 | - | 1.18E- | 0.0E+0 | 7.92E-9 | 5.51E-8 | - |
| $Ni(OH)_2$ | 1.18E-7 | - | - | 0.0E+0 | - | 0.0E+0 | 0.0E+0 | - | 0.0E+0 | - |
| $SiO_2$ | 4.42E-4 | - | - | 0.0E+0 | - | 4.39E- | 1.04E-2 | - | 0.0E+0 | - |
| $UO_2C_2O_4$ | 2.28E-3 | - | - | 0.0E+0 | - | 2.26E- | 0.0E+0 | 1.52E-4 | 1.06E-3 | - |
| $UO_2(OH)_2$ | 0.0E+0 | - | - | 0.0E+0 | - | 0.0E+0 | 0.0E+0 | - | 0.0E+0 | - |
| $ThO_2$ | 0.0E+0 | - | - | 0.0E+0 | - | 0.0E+0 | 0.0E+0 | - | 0.0E+0 | - |
| HgO | 0.0E+0 | - | - | 0.0E+0 | - | 0.0E+0 | 0.0E+0 | - | 0.0E+0 | - |
| Total (kg) | 2.77E+5 | 1.25E+3 | 1.3E+3 | 8.39E+6 | - | 2.04E+ | 4.08E+4 | 4.10E+5 | 3.77E+5 | 3.01E+3 |
| Vol (l) | 2.6E+5 | - | - | 8.33E+6 | 4.54E+6 | 1.88E+ | 4.69E+3 | 2.08E+6 | 5.22E+6 | - |
| $C_2O_4$ (kg) | 1.14E+3 | 8.21E+2 | 8.2E+2 | - | 0.0E+0 | 8.37E+ | 1.87E+4 | 1.70E+4 | 2.05E+3 | 1.98E+3 |

**Table A5- 3 Tank 11 HM integrated material balance, pH restored w/NaOH (Case 3 - Sheet 1 of 4)**

| **Stream** | **1** | **2** | **7** | **3a** | **3b** | **4a** | **4b** |
|---|---|---|---|---|---|---|---|
| | **Oxalic acid** | **pH fix** | **Wash water** | **Sludge heel slurry** | | **Treat tank slurry** | |
| Phase | Aqueous | Aqueous | Aqueous | Aqueous | Solid | Aqueous | Solid |
| **Units** | **wtfrac** | | | | | | |
| $H_2O$ | 9.2E-1 | 5.0E-1 | 9.76E-1 | 9.40E-1 | 0.0E+0 | 9.10E-1 | 0.0E+0 |
| $H_2C_2O_4$ | 8.0E-2 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 6.27E-2 | 0.0E+0 |
| HCl | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 8.66E-5 | 0.0E+0 |
| $HNO_3$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 5.14E-4 | 0.0E+0 |
| $Na_2CO_3$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 6.20E-5 | 0.0E+0 | 4.41E-4 | 0.0E+0 |
| NaCl | 0.0E+0 | 0.0E+0 | 0.0E+0 | 3.14E-3 | 0.0E+0 | 0.0E+0 | 0.0E+0 |
| $NaNO_2$ | 0.0E+0 | 0.0E+0 | 2.41E-2 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 |
| $NaNO_3$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 1.57E-2 | 0.0E+0 | 0.0E+0 | 0.0E+0 |
| NaOH | 0.0E+0 | 5.0E-1 | 0.0E+0 | 1.75E-2 | 0.0E+0 | 0.0E+0 | 0.0E+0 |
| $Na_2SO_4$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 |
| $Na_2C_2O_4$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 1.75E-3 | 0.0E+0 |
| $Al(OH)_3$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 5.88E-1 | 0.0E+0 | 0.0E+0 |
| AlOOH | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 1.13E-2 | 0.0E+0 |
| $NaAlO_2$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 4.38E-5 | 0.0E+0 | 0.0E+0 | 0.0E+0 |
| $CaC_2O_4$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 4.87E-5 | 0.0E+0 | 3.96-5 | 0.0E+0 |
| $CaCO_3$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 1.66E-2 | 0.0E+0 | 0.0E+0 |
| $Ca(OH)_2$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 4.3E-5 | 0.0E+0 | 0.0E+0 | 0.0E+0 |

### Table A5-3 Tank 11 HM integrated material balance, pH restored w/NaOH (Case 3 - Sheet 2 of 4)

| **Stream** | **1** | **2** | **7** | **3a** | **3b** | **4a** | **4b** |
|---|---|---|---|---|---|---|---|
| | **Oxalic acid** | **pH fix** | **Wash water** | **Sludge heel slurry** | | **Treat tank slurry** | |
| | Phase | Aqueous | Aqueous | Aqueous | Aqueous | Solid | Aqueous |
| **Units** | **wtfrac** | | | | | | |
| $Ce_2O_3$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 2.69E-3 | 0.0E+0 | 0.0E+0 | 0.0E+0 |
| $Ce_2(C_2O_4)_3$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 6.07E-5 | 0.0E+0 |
| $Fe_2(C_2O4)_3$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 1.11E-2 | 0.0E+0 |
| $Fe(OH)_3$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 9.59E-7 | 2.54E-1 | 0.0E+0 | 0.0E+0 |
| $K_2C_2O_4$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 |
| KOH | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 |
| $MnC_2O_4$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 2.79E-4 | 0.0E+0 |
| $Mn(OH)_2$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 1.03E-7 | 5.85E-2 | 0.0E+0 | 0.0E+0 |
| $NiC_2O_4$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 5.11E-5 | 3.27E-1 |
| $Ni(OH)_2$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 4.53E-9 | 1.11E-2 | 0.0E+0 | 0.0E+0 |
| $SiO_2$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 2.04E-2 | 0.0E+0 | 1.02E-4 | 6.73E-1 |
| $UO_2C_2O_4$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 8.99E-4 | 0.0E+0 |
| $UO_2OH_2$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 2.69E-7 | 3.06E-2 | 0.0E+0 | 0.0E+0 |
| $ThO_2$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 4.92E-14 | 1.11E-2 | 0.0E+0 | 0.0E+0 |
| HgO | 0.0E+0 | 0.0E+0 | 0.0E+0 | 3.86E-5 | 3.06E-2 | 7.63E-4 | 0.0E+0 |
| $Th(C_2O_4)_2$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 4.29E-4 | 0.0E+0 |
| Total (kg) | 3.23E+5 | 5.21E+4 | 3.05E+6 | 1.63E+4 | 9.39E+3 | 3.68E+8 | 1.84E+6 |
| Vol (l) | 3.53E+4 | 1.9E+5 | 3.03E+6 | 1.56E+4 | 3.27E+3 | 3.38E+5 | 3.09E+2 |
| $C_2O_4$ (kg) | 2.69E+4 | 0.0E+0 | - | 5.47E-1 | 0.0E+0 | 2.61E+4 | 3.62E+2 |

**Table A5-3 Tank 11 HM integrated material balance, pH restored w/NaOH (Case 3 - Sheet 3 of 4)**

| | 5 | 11 | 12 | 13 | 14 | 6a | 6b | 10 | 9 | 8 |
|---|---|---|---|---|---|---|---|---|---|---|
| **Stream** | **Resultant liquid** | **Evap feed** | **Evap conc** | **Salt removal water** | **Dissolved salt** | **Resultant oxalate slurry** | | **Washed sludge** | **Decant water** | **Feed tank sludge** |
| Phase | Aqueous | Aqueous | Aqueous | Aqueous | Aqueous | Aqueous | Solid | Slurry | Aqueous | Slurry |
| **Units** | **wtfrac** | | | | | | | | | |
| $H_2O$ | 9.62E-1 | - | - | 9.99E-1 | - | 9.62E-1 | 0.0E+0 | - | 8.08E-1 | - |
| $H_2C_2O_4$ | 0.00E+0 | - | - | 0.0E+0 | - | 0.0E+0 | 0.0E+0 | - | 0.0E+0 | - |
| HCl | 0.00E+0 | - | - | 0.0E+0 | - | 0.0E+0 | 0.0E+0 | - | 0.0E+0 | - |
| $HNO_3$ | 0.00E+0 | - | - | 0.0E+0 | - | 0.0E+0 | 0.0E+0 | - | 0.0E+0 | - |
| $Na_2CO_3$ | 4.25E-4 | - | - | 0.0E+0 | - | 4.25E-4 | 0.0E+0 | - | 1.00E-2 | - |
| NaCl | 1.34E-4 | - | - | 0.0E+0 | - | 1.34E-4 | 0.0E+0 | - | 2.40E-4 | - |
| $NaNO_2$ | 0.0E+0 | - | - | 7.50E-4 | - | 0.0E+0 | 0.0E+0 | - | 7.63E-2 | - |
| $NaNO_3$ | 6.68E-4 | - | - | 0.0E+0 | - | 6.68E-4 | 0.0E+0 | - | 6.97E-2 | - |
| NaOH | 4.42E-3 | - | - | 3.95E-4 | - | 4.59E-3 | 0.0E+0 | - | 1.76E-2 | - |
| $Na_2SO_4$ | 0.0E+0 | - | - | 0.0E+0 | - | 0.0E+0 | 0.0E+0 | - | 3.03E-3 | - |
| $Na_2C_2O_4$ | 3.06E-2 | 1.0E+0 | 1.0E+0 | 0.0E+0 | 0.0E+0 | 3.06E-2 | 7.67E-1 | 8.76E-2 | 7.66E-3 | 1.0E+0 |
| $Al(OH)_3$ | 0.00E+0 | - | - | 0.0E+0 | - | 0.0E+0 | 1.37E-1 | - | 0.0E+0 | - |
| AlOOH | 0.00E+0 | - | - | 0.0E+0 | - | 0.0E+0 | 0.0E+0 | - | 0.0E+0 | - |
| $NaAlO_2$ | 0.0E+0 | - | - | 0.0E+0 | - | 6.11E-4 | 0.0E+0 | - | 7.59E-3 | - |
| $CaC_2O_4$ | 7.35E-07 | - | - | 0.0E+0 | - | 7.35E-7 | 0.0E+0 | 5.14E-8 | 3.22E-7 | - |
| $CaCO_3$ | 0.0E+0 | - | - | 0.0E+0 | - | 0.0E+0 | 0.0E+0 | - | 0.0E+0 | - |

Table A5-3 Tank 11 HM integrated material balance, pH restored w/NaOH (Case 3 - Sheet 4 of 4)

| **Stream** | **5** | **11** | **12** | **13** | **14** | **6a** | **6b** | **10** | **9** | **8** |
|---|---|---|---|---|---|---|---|---|---|---|
| | **Resultant liquid** | **Evap feed** | **Evap conc** | **Salt removal water** | **Dissolved salt** | **Resultant oxalate slurry** | | **Washed sludge** | **Decant water** | **Feed tank sludge** |
| | Aqueous | Aqueous | Aqueous | Aqueous | Aqueous | Aqueous | Solid | Slurry | Aqueous | Slurry |
| **Units** | **wtfrac** | | | | | | | | | |
| $Ce_2O_3$ | 1.15E-4 | - | - | 0.0E+0 | - | 1.15E-4 | 0.0E+0 | 8.03E-06 | 5.03E-5 | - |
| $Ce_2(C_2O_4)_3$ | 0.0E+0 | - | - | 0.0E+0 | - | 0.0E+0 | 0.0E+0 | - | 0.0E+0 | - |
| $Fe_2(C_2O_4)_3$ | 2.37E-5 | - | - | 0.0E+0 | - | 2.37E-5 | 0.0E+0 | 1.66E-6 | 1.04E-5 | - |
| $Fe(OH)_3$ | 0.0E+0 | - | - | 0.0E+0 | - | 0.0E+0 | 6.15E-2 | - | 0.0E+0 | - |
| $K_2C_2O_4$ | 0.0E+0 | - | - | 0.0E+0 | - | 0.0E+0 | 0.0E+0 | 0.00E+0 | 0.0E+0 | - |
| KOH | 0.0E+0 | - | - | 0.0E+0 | - | 0.0E+0 | 0.0E+0 | - | 0.0E+0 | - |
| $MnC_2O_4$ | 3.56E-6 | - | - | 0.0E+0 | - | 3.56E-6 | 0.0E+0 | 2.49E-7 | 1.56E-6 | - |
| $Mn(OH)_2$ | 0.0E+0 | - | - | 0.0E+0 | - | 0.0E+0 | 1.42E-2 | - | 0.0E+0 | - |
| $NiC_2O_4$ | 8.90E-08 | - | - | 0.0E+0 | - | 8.90E-8 | 0.0E+0 | 6.23E-9 | 3.91E-8 | - |
| $Ni(OH)_2$ | 0.0E+0 | - | - | 0.0E+0 | - | 0.0E+0 | 2.71E-3 | - | 0.0E+0 | - |
| $SiO_2$ | 8.69E-4 | - | - | 0.0E+0 | - | 8.69E-4 | 0.0E+0 | - | 0.0E+0 | - |
| $UO_2C_2O_4$ | 1.21E-6 | - | - | 0.0E+0 | - | 1.21E-6 | 0.0E+0 | 8.47E-8 | 5.31E-7 | - |
| $UO_2OH_2$ | 0.0E+0 | - | - | 0.0E+0 | - | 0.0E+0 | 7.45E-3 | - | 0.0E+0 | - |
| $ThO_2$ | 4.83E-5 | - | - | 0.0E+0 | - | 4.83E-14 | 2.71E-03 | - | 0.0E+0 | - |
| HgO | 3.83E-5 | - | - | 0.0E+0 | - | 3.83E-5 | 7.07E-03 | - | 0.0E+0 | - |
| $Th(C_2O_4)_2$ | 0.0E+0 | - | - | 0.0E+0 | - | 0.0E+0 | 0.0E+0 | - | 0.0E+0 | - |
| Total (kg) | 1.93E+5 | 1.23E+3 | 1.23E+3 | 8.39E+6 | - | 1.91E+5 | 3.83E+4 | 3.69E+5 | 3.77E+5 | 7.55E+3 |
| Vol (l) | 1.87E+5 | - | - | 8.33E+6 | 1.21E+7 | 1.85E+5 | 3.22E+3 | 2.09E+6 | 5.22E+6 | - |
| $C_2O_4$ (kg) | 3.87E+3 | 8.08E+2 | 8.08E+2 | | 0.0E+0 | 3.85E+3 | 1.93E+4 | 2.12E+4 | 1.90E+3 | 4.96E+3 |

**Table A5- 4 Tank 11 HM integrated material balance, pH restored w/supernate (Case 4 - Sheet 1 of 4)**

| Stream | 1 | 2 | 7 | 3a | 3b | 4a | 4b |
|---|---|---|---|---|---|---|---|
| | Oxalic acid | pH fix | Wash water | Sludge heel | | Treat tank slurry | |
| Phase | Aqueous | Aqueous | Aqueous | Aqueous | Solid | Aqueous | Solid |
| **Units** | **wtfrac** | | | | | | |
| $H_2O$ | 9.20E-1 | 6.79E-1 | 9.76E-1 | 9.40E-1 | 0.0E+0 | 9.10E-1 | 0.0E+0 |
| $H_2C_2O_4$ | 8.00E-2 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 6.27E-2 | 0.0E+0 |
| HCl | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 8.66E-5 | 0.0E+0 |
| $HNO_3$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 5.143E-4 | 0.0E+0 |
| $Na_2CO_3$ | 0.0E+0 | 1.42E-2 | 0.0E+0 | 6.20E-5 | 0.0E+0 | 4.41E-4 | 0.0E+0 |
| NaCl | 0.0E+0 | 0.0E+0 | 0.0E+0 | 3.14E-3 | 0.0E+0 | 0.0E+0 | 0.0E+0 |
| $NaNO_2$ | 0.0E+0 | 3.11E-02 | 2.41E-2 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 |
| $NaNO_3$ | 0.0E+0 | 1.59E-01 | 0.0E+0 | 1.57E-02 | 0.0E+0 | 0.0E+0 | 0.0E+0 |
| NaOH | 0.0E+0 | 7.62E-2 | 0.0E+0 | 1.74E-02 | 0.0E+0 | 0.0E+0 | 0.0E+0 |
| $Na_2SO_4$ | 0.0E+0 | 1.77E-2 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.00E+0 | 0.0E+0 |
| $Na_2C_2O_4$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 1.75E-3 | 0.0E+0 |
| $Al(OH)_3$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 5.78E-1 | 0.0E+0 | 0.0E+0 |
| AlOOH | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 1.13E-2 | 0.0E+0 |
| $NaAlO_2$ | 0.0E+0 | 2.17E-2 | 0.0E+0 | 4.38E-05 | 0.0E+0 | 0.0E+0 | 0.0E+0 |
| $CaC_2O_4$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 4.38E-05 | 1.64E-2 | 3.96E-5 | 2.13E-1 |
| $CaCO_3$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 1.63E-2 | 0.0E+0 | 0.0E+0 |

**Table A5–4 Tank 11 HM integrated material balance, pH restored w/supernate (Case 4 - Sheet 2 of 4)**

| **Stream** | **1** | **2** | **7** | **3a** | **3b** | **4a** | **4b** |
|---|---|---|---|---|---|---|---|
| | **Oxalic acid** | **pH fix** | **Wash water** | **Sludge heel** | | **Treat tank slurry** | |
| Phase | Aqueous | Aqueous | Aqueous | Aqueous | Solid | Aqueous | Solid |
| **Units** | **wtfrac** | | | | | | |
| $Ca(OH)_2$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 4.33E-5 | 0.0E+0 | 0.0E+0 | 0.0E+0 |
| $Ce_2O_3$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 2.69E-3 | 0.0E+0 | 0.0E+0 | 0.0E+0 |
| $Ce_2(C_2O_4)_3$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 6.07E-5 | 2.44E-2 |
| $Fe_2(C_2O_4)_3$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 1.11E-2 | 0.0E+0 |
| $Fe(OH)_3$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 9.59E-7 | 2.49E-1 | 0.0E+0 | 0.0E+0 |
| $K_2C_2O_4$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 |
| KOH | 0.0E+0 | 7.46E-4 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 |
| $MnC_2O_4$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 2.79E-4 | 4.84E-1 |
| $MnOH_2$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 1.03E-7 | 5.76E-2 | 0.0E+0 | 0.0E+0 |
| $NiC_2O_4$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 5.11E-5 | 9.10E-2 |
| $Ni(OH)_2$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 4.53E-9 | 1.10E-2 | 0.0E+0 | 0.0E+0 |
| $SiO_2$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 2.04E-2 | 0.0E+0 | 1.02E-4 | 1.88E-1 |
| $UO_2C_2O_4$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 8.99E-4 | 0.0E+0 |
| $UO_2OH_2$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 2.69E-7 | 3.01E-2 | 0.0E+0 | 0.0E+0 |
| $ThO_2$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 4.93E-14 | 1.1E-2 | 0.0E+0 | 0.0E+0 |
| HgO | 0.0E+0 | 0.0E+0 | 0.0E+0 | 3.86E-5 | 3.01E-2 | 7.63E-4 | 0.0E+0 |
| $Th(C_2O_4)_2$ | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 0.0E+0 | 4.29E-4 | 0.0E+0 |
| Total (kg) | 3.45E+5 | 3.09E+2 | 3.05E+3 | 1.72E+1 | 9.39E+0 | 3.68E+2 | 1.84E+0 |
| Vol (l) | 3.22E+5 | 3.4E+5 | 3.03E+6 | 1.57E+4 | 3.27E+3 | 3.38E+5 | 3.09E+2 |
| $C_2O_4$ (kg) | 2.69E+4 | 0.0E+0 | - | 5.75E-1 | 1.06E+02 | 2.61E+4 | 9.42E+2 |

**Table A5-4 Tank 11 HM integrated material balance, pH restored w/supernate (Case 4 - Sheet 3 of 4)**

| **Stream** | **5** | **11** | **12** | **13** | **14** | **6a** | **6b** | **10** | **9** | **8** |
|---|---|---|---|---|---|---|---|---|---|---|
| | **Resultant liquid** | **Evap feed** | **Evap conc** | **Salt removal water** | **Dissolved salt** | **Resultant oxalate slurry** | | **Washed sludge** | **Decant water** | **Feed tank sludge** |
| Phase | Aqueous | Aqueous | Aqueous | Aqueous | Aqueous | Aqueous | Solid | Slurry | Aqueous | Slurry |
| **Units** | **wtfrac** | | | | | | | | | |
| $H_2O$ | 8.78E-1 | - | - | 9.99E-1 | - | 8.71E-1 | 0.0E+0 | - | 7.63E-2 | - |
| $H_2C_2O_4$ | 0.0E+0 | - | - | 0.0E+0 | - | 0.0E+0 | 0.0E+0 | - | 0.0E+0 | - |
| HCl | 0.0E+0 | - | - | 0.0E+0 | - | 0.0E+0 | 0.0E+0 | - | 0.0E+0 | - |
| $HNO_3$ | 0.0E+0 | - | - | 0.0E+0 | - | 0.0E+0 | 0.0E+0 | - | 0.0E+0 | - |
| $Na_2CO_3$ | 7.26E-3 | - | - | 0.0E+0 | - | 7.23E-3 | 0.0E+0 | - | 1.00E-2 | - |
| NaCl | 8.18E-5 | - | - | 0.0E+0 | - | 8.15E-5 | 0.0E+0 | - | 2.40E-4 | - |
| $NaNO_2$ | 1.53E-2 | - | - | 7.5E-4 | - | 1.53E-2 | 0.0E+0 | - | 7.66E-2 | - |
| $NaNO_3$ | 7.89E-2 | - | - | 0.0E+0 | - | 7.85E-2 | 0.0E+0 | - | 6.790E-2 | - |
| NaOH | 4.13E-3 | - | - | 3.95E-4 | - | 1.16E-2 | 0.0E+0 | - | 1.76E-2 | - |
| $Na_2SO_4$ | 8.74E-3 | - | - | 0.0E+0 | - | 8.70E-3 | 0.0E+0 | - | 3.02E-3 | - |
| $Na_2C_2O_4$ | 5.44E-3 | 1.0E+0 | 1.0E+0 | 0.0E+0 | 0.0E+0 | 5.42E-3 | 7.11E-1 | 9.63E-2 | 7.66E-3 | 1.0E+0 |
| $Al(OH)_3$ | 0.0E+0 | - | - | 0.0E+0 | - | 0.0E+0 | 2.18E-1 | - | 0.0E+0 | - |
| AlOOH | 0.0E+0 | - | - | 0.0E+0 | - | 0.0E+0 | 0.0E+0 | - | 0.0E+0 | - |
| $NaAlO_2$ | 7.53E-4 | - | - | 0.0E+0 | - | 7.50E-4 | 0.0E+0 | - | 7.59E-3 | - |
| $CaC_2O_4$ | 2.24E-6 | - | - | 0.0E+0 | - | 2.23E-6 | 6.73E-3 | 9.49E-4 | 1.33E-6 | - |
| $CaCO_3$ | 0.0E+0 | - | - | 0.0E+0 | - | 0.0E+0 | 0.0E+0 | - | 0.0E+0 | - |

### Table A5-4 Tank 11 HM integrated material balance, pH restored w/supernate (Case 4 - Sheet 4 of 4)

| Stream | 5<br>Resultant liquid | 11<br>Evap feed | 12<br>Evap conc | 13<br>Salt removal water | 14<br>Dissolved salt | 6a<br>Resultant oxalate slurry | 6b | 10<br>Washed sludge | 9<br>Decant water | 8<br>Feed tank sludge |
|---|---|---|---|---|---|---|---|---|---|---|
| Phase | Aqueous | Aqueous | Aqueous | Aqueous | Aqueous | Aqueous | Solid | Slurry | Aqueous | Slurry |
| **Units** | **wtfrac** | | | | | | | | | |
| $Ca(OH)_2$ | 0.0E+0 | - | - | 0.0E+0 | - | 0.0E+0 | 0.0E+0 | - | 0.0E+0 | - |
| $Ce_2O_3$ | 7.03E-5 | - | - | 0.0E+0 | - | 6.99E-5 | 0.0E+0 | 6.66E-6 | 4.17E-5 | - |
| $Ce_2(C_2O_4)_3$ | 0.0E+0 | - | - | 0.0E+0 | - | 0.0E+0 | 0.0E+0 | - | 0.0E+0 | - |
| $Fe_2(C_2O_4)_3$ | 3.09E-5 | - | - | 0.0E+0 | - | 3.08E-5 | 0.0E+0 | 2.93E-6 | 1.84E-5 | - |
| $Fe(OH)_3$ | 0.0E+0 | - | - | 0.0E+0 | - | 0.0E+0 | 4.47E-2 | - | 0.0E+0 | - |
| $K_2C_2O_4$ | 5.44E-4 | - | - | 0.0E+0 | - | 5.42E-4 | 0.0E+0 | 5.16E-5 | 3.23E-4 | - |
| KOH | 0.0E+0 | - | - | 0.0E+0 | - | 0.0E+0 | 0.0E+0 | - | 0.0E+0 | - |
| $MnC_2O_4$ | 1.92E-7 | - | - | 0.0E+0 | - | 1.91E-7 | 0.0E+0 | 1.82E-8 | 1.14E-7 | - |
| $MnOH_2$ | 0.0E+0 | - | - | 0.0E+0 | - | 0.0E+0 | 1.04E-2 | - | 0.0E+0 | - |
| $NiC_2O_4$ | 1.15E-7 | - | - | 0.0E+0 | - | 1.15E-7 | 0.0E+0 | 1.09E-8 | 6.84E-8 | - |
| $Ni(OH)_2$ | 0.0E+0 | - | - | 0.0E+0 | - | 0.0E+0 | 1.97E-3 | - | 0.0E+0 | - |
| $SiO_2$ | 5.32E-4 | - | - | 0.0E+0 | - | 5.29E-4 | 0.0E+0 | - | 0.0E+0 | - |
| $UO_2C_2O_4$ | 5.30E-4 | - | - | 0.0E+0 | - | 5.28E-4 | 0.0E+0 | 5.02E-5 | 3.15E-4 | - |
| $UO_2OH_2$ | 0.0E+0 | - | - | 0.0E+0 | - | 0.0E+0 | 0.0E+0 | - | 0.0E+0 | - |
| $ThO_2$ | 3.71E-14 | - | - | 0.0E+0 | - | 3.7E-14 | 1.97E-3 | - | 0.0E+0 | - |
| HgO | 3.08E-5 | - | - | 0.0E+0 | - | 3.06E-5 | 5.06E-3 | - | 0.0E+0 | - |
| $Th(C_2O_4)_2$ | 0.0E+0 | - | - | 0.0E+0 | - | 0.0E+0 | 0.0E+0 | - | 0.0E+0 | - |
| Total (kg) | 3.67E+5 | 9.90E+2 | 9.90E+2 | 8.39E+6 | - | 2.60E+5 | 5.21E+4 | 3.69E+5 | 3.77E+8 | 3.90E+3 |
| Vol (l) | 3.38E+5 | - | - | 8.33E+6 | 1.21E+7 | 2.39E+5 | 5.75E+3 | 2.09E+6 | 5.22E+6 | - |
| $C_2O_4$ (kg) | 1.48E+3 | 6.5E+2 | 6.5E+2 | - | 0.0E+0 | 1.04E+3 | 2.46E+4 | 2.33E+4 | 2.00E+3 | 2.56E+3 |

## Appendix 6 Historical Experience of Cleaning Tank 16

In order to ensure flowsheet and model validation, historical data from oxalic acid cleaning of Tank 16 was compared to a model of the acid cleaning process. Table A6-1 shows the sequence of events with data needed to create the model inputs for the oxalic acid and water dilutions. The sludge heel is defined by the data shown in Table A6-2. Table A6-3 shows the output for after treating the tank in contrast with the sample data obtained in Tank 16 after each wash cycle. Sample data was not available to compare the results of Resultant oxalate slurry or the Resultant liquid.

Table A6-3 highlights one important aspect about using equilibrium models to forecast dissolution results; that is, the model forecasted 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 implied dissolution of iron in wash cycles after the first. The model showed the total concentration of all metals as decreasing by dilution effects only in each subsequent batch. The measured aluminum and manganese appeared to follow a similar trend, but the actual values and measured values differed considerably, perhaps because some solids were dissolving, or the analytical/sample variance in measured values was very high. The model very closely tracked the total soluble oxalate concentration. Although the information presented on solubility test solutions in Section 7.2 showed that OLI ESP$^{©}$ has a predilection to under-predict solubility, the forecasted concentrations were determined to be within the overall uncertainty, and hence deemed adequate when compared to field measured data. These determinations were considered to be consistent with the overall determinations of Chapter 4.

**Table A6- 1 Sequence of events for Tank 16 acid cleaning (Sheet 1 of 2)**

| Acid wash cycle 1 |
|---|
| 1) 13,000 l of heel to be treated with oxalic acid.<br>2) Sprayed about 140,000 l of water through Riser 1.<br>3) Added 48,000 l of 4 wt% oxalic acid directly to heel.<br>4) Flushed with 17,000 l of water 90ºC – 157,000 l total water added to tank.<br>5) Slurry pumps started when pump volutes became submerged.<br>6) Agitated for 2 days.<br>7) 87,000 l of seal water from pumps added to tanks – total water added.<br>8) Transferred to Tank 21 about 17,000 l of 50% wt% NaOH added to HPT-4 to achieve pH > 12.<br>9) 13,000 l of heel remained after transfer. |

**Table A6-1 Sequence of events for Tank 16 acid cleaning (Sheet 2 of 2)**

**Acid wash cycle 2**

1) Sprayed 155,000 l of water through Riser 1.
2) Sprayed 6,800-7,600 l of 4 wt% oxalic acid through each of 5 spray risers – 37,000 l total.
3) Flushed with 20,000 l of water – 176,000 l of total water added to tank.
4) Slurry pumps started when volutes became submerged.
5) Agitate for 40 hours.
6) 103,000 l of seal water from pumps added to tanks – total water added.
7) Transfer to Tank 21, 804,000 l of 50 wt% NaOH added to pump tank to achieve pH > 12.
8) 10,600 l of heel remained after transfer.

**Acid wash cycle 3**

1) Sprayed 34,000-45,000 l of 4 wt% oxalic acid at 90°C through each of 5 spray risers- 191,000 l total.
2) Flushed with 22,000 l of water.
3) Slurry pumps started when volutes became submerged.
4) Agitated for 48 hours.
5) 103,000 l of seal water from pumps added to tanks – total water added.
6) Transferred to Tank 22, 50 wt% NaOH added to pump tank to achieve pH >12.
7) 468,000 l heel remained after transfer.
8) Flushed with 22,000 l of water.
9) Slurry pumps started when volutes became submerged.
10) Agitated for 48 hours.
11) 103,038 l of seal water from pumps added to tanks – total water added.
12) Transferred to Tank 22, 50 wt% NaOH added to HPT-4 to achieve pH >12.
13) 468,000 l of heel remained after transfer.

**After wash cycle 3**

1) About 378 l of material remained in a pile.
2) 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 A6-2 Tank 16 sludge composition**

| **Constituent** | **wt%** |
|---|---|
| $AlO^{-2}$ | 16 |
| $Fe^{+3}$ | 40 |
| $MnO_2$ | 16 |
| $Na^{+}$ | 20 |
| $SO4^{-2}$ | 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 |

**Table A6-3 Comparison of Tank 16 forecast and measured dissolution**

| Step | density (kg/l) | Vol % solids | Concentration in Aqueous Phase | | | | | | | | Concentration in Slurry | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | $NO_3$ | $NO_2$ | OH | $C_2O_4$ | Fe | Mn | Al | H | Fe | Mn | Al |
| **Measured** | | | **(M)** | | | | | | | | | | |
| Sludge Heel | 1.0E+0 | 3.1E+0 | 5.5E-2 | 1.8E-3 | <1E-4 | NM | NM | NM | NM | NM | NM | NM | NM |
| Acid Wash 1 | 1.0E+0 | <0.5 | 2.5E-2 | NM | NM | 5.1E-2 | 4.0E-3 | NM | 2.1E-2 | 2.9E-2 | 1.7E-2 | 9.9E-3 | 4.0E-3 |
| Acid Wash 2 | 1.0E+0 | 6.0E-1 | 6.0E-3 | NM | NM | 4.8E-2 | 5.7E-3 | 4.4E-4 | 3.3E-3 | 5.4E-2 | 1.1E-2 | 6.5E-4 | 7.2E-3 |
| Acid Wash 3 | 1.0E+0 | <0.5 | 2.8E-3 | NM | NM | 3.1E-1 | 4.0E-2 | 7.4E-5 | 4.6E-3 | 4.9E-1 | 7.6E-2 | 7.0E-4 | 5.9E-3 |
| **Forecasted** | | | **(M)** | | | | | | | | | | |
| Acid Wash 1 | - | - | - | - | - | 7.0E-2 | 1.6E-2 | 4.0E-3 | 6.0E-3 | 7.4E-2 | 1.6E-2 | 4.0E-3 | 6.0E-3 |
| Acid Wash 2 | - | - | - | - | - | 5.8E-2 | 5.1E-4 | 1.3E-4 | 1.4E-3 | 1.1E-1 | 5.1E-4 | 1.3E-4 | 1.4E-3 |
| Acid Wash 3 | - | - | - | - | - | 2.9E-1 | 2.3E-5 | 6.0E-6 | 6.4E-5 | 5.7E-1 | 2.3E-5 | 6.0E-6 | 6.4E-5 |