S

ENGINEERING CHANGE NOTICE

Page 1 of 2

1. ECN 669247

Proj. ECN

2. ECN Category (mark one)	3. Originator's Name, Organization, MSIN, and Telephone No.	4. USQ Required?	5. Date
Supplemental ☐ Direct Revision ☒ Change ECN ☐ Temporary ☐ Standby ☐ Supersedure ☐ Cancel/Void ☐	L.A. Fort, Process Control, R2-11, 376-0178	☐ Yes ☒ No	09/18/01
	6. Project Title/No./Work Order No.: Technical Basis for Chemistry Control Program	7. Bldg./Sys./Fac. No.: N/A	8. Approval Designator: N/A
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13a. Description of Change

Complete revision.

13b. Design Baseline Document? ☐ Yes ☒ No

14a. Justification (mark one)	14b. Justification Details
Criteria Change ☒ Design Improvement ☐ Environmental ☐ Facility Deactivation ☐ As-Found ☐ Facilitate Const. ☐ Const. Error/Omission ☐ Design Error/Omission ☐	Document was completely revised.

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1. ECN (use no. from pg. 1): ECN-669247

16. Design Verification Required	17. Cost Impact				18. Schedule Impact (days)	
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☐ Yes	Additional ☐	$	Additional ☐	$	Improvement ☐	
☒ No	Savings ☐	$	Savings ☐	$	Delay ☐	

19. Change Impact Review: Indicate the related documents (other than the engineering documents identified on Side 1) that will be affected by the change described in Block 13. Enter the affected document number in Block 20.

SDD/DD	☐	Seismic/Stress Analysis	☐	Tank Calibration Manual	☐
Functional Design Criteria	☐	Stress/Design Report	☐	Health Physics Procedure	☐
Operating Specification	☒	Interface Control Drawing	☐	Spares Multiple Unit Listing	☐
Criticality Specification	☒	Calibration Procedure	☐	Test Procedures/Specification	☐
Conceptual Design Report	☐	Installation Procedure	☐	Component Index	☐
Equipment Spec.	☒	Maintenance Procedure	☒	ASME Coded Item	☒
Const. Spec.	☒	Engineering Procedure	☐	Human Factor Consideration	☐
Procurement Spec.	☐	Operating Instruction	☐	Computer Software	☐
Vendor Information	☐	Operating Procedure	☒	Electric Circuit Schedule	☒
OM Manual	☒	Operational Safety Requirement	☐	ICRS Procedure	☐
FSAR/SAR	☒	IEFD Drawing	☐	Process Control Manual/Plan	☐
Safety Equipment List	☒	Cell Arrangement Drawing	☐	Process Flow Chart	☐
Radiation Work Permit	☐	Essential Material Specification	☐	Purchase Requisition	☐
Environmental Impact Statement	☐	Fac. Proc. Samp. Schedule	☐	Tickler File	☐
Environmental Report	☐	Inspection Plan	☐		☐
Environmental Permit	☐	Inventory Adjustment Request	☐		☒

20. *Other Affected Documents: (NOTE: Documents listed below will not be revised by this ECN.) Signatures below indicate that the signing* organization has been notified of other affected documents listed below.

Document Number/Revision	Document Number/Revision	Document Number/Revision
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Cog. Mgr. M.A. Knight	MAKnight	9/18/01	QA		
QA			Safety		
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Environ.			Environ.		
Other			Other		
J.W. Lentsch	JW Lentsch	9/20/01			

DEPARTMENT OF ENERGY

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DOE Reading Room	H2-53	H			
Pacific Northwest National Laboratory					
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C. W. Stewart	K7-15	X			

Technical Basis for Chemistry Control Program

L. A. Fort
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Technical Basis for Chemistry Control Program

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EXECUTIVE SUMMARY

This report establishes the sampling and analysis requirements for the Double-Shell Tank (DST) and Aging Waste Facility (AWF) tank waste in accordance with the Tank Farms Technical Safety Requirements (TSR) Administrative Control (AC) 5.15, Chemistry Control Program (CHG 2001). The sampling and analysis requirements are based on evaluation of the chemical composition of the waste, mechanisms for chemistry change, and operations and waste transfers in the tanks.

The waste in DSTs and AWF tanks is sampled in accordance with field working schedules that are derived from the Technical Sampling Basis – Waste Information Requirements Document (TSB-WIRD) (Adams et al. 2001). The sampling schedule established in this document will be incorporated in the next revision of the TSB-WIRD to meet the specific needs of the Chemistry Control Program. Requirements for analysis of waste samples have been established in a Data Quality Objective (DQO) for the Chemistry Control Program (Banning 2001) and incorporated in Tank Sampling and Analysis Plans (TSAPs).

The DST waste composition data for nitrite, nitrate, and hydroxide ions used in this evaluation were extracted from the Caustic Limits Report (CLR) produced from the Best-Basis Inventory (BBI) within the Tank Waste Information Network System (TWINS) published in April 2001 with an effective date of January 1, 2001.

Maintaining a minimum specified free hydroxide ion concentration within the DST waste is central to the chemistry control program. However, chemical reactions can occur in the waste that consume free hydroxide and can cause the waste to move outside of the chemistry control limits. The important chemical reactions for free hydroxide ion consumption are absorption of carbon dioxide from ventilation air, oxidation of sodium salts of organic species, and reaction with hydrated aluminum oxide. Two empirical equations were used to estimate the rate of depletion of free hydroxide ions within the tank waste and to predict the future tank liquid hydroxide ion concentration over the next five-year period based on historical sample results or

on engineering estimates of tank composition where actual sample data were not available. One of the equations is based on work undertaken by Hobbs at the Savannah River Site and estimates the rate of hydroxide depletion due to absorption of carbon dioxide from ventilation air in the tanks. This equation was applied to all waste types in the DST and AWF tanks. The other equation used in this evaluation was based on work by Carothers, who developed an empirical equation for the rate of hydroxide depletion with time in concentrated complexant (CC) waste stored in tank 241-AN-102 and subsequently tank 241-AN-107. This equation was applied only to CC and dilute complexant (DC) wastes. Although the Carothers equation was developed for CC waste, containing both organic complexants and aluminum, insufficient sample data were available to directly correlate the rate of depletion of hydroxide to the concentration of these species.

Although uncertainty exists in the absolute accuracy of the equations for predicting changes in tank chemistry with time, evaluations have been performed of the equation predictions against available tank sampling data. However, the number of tank samples available with which to validate the equations predictions is limited. These evaluations indicate that for measured hydroxide concentrations above 0.1M, the concentrations predicted by the equations are within twenty percent of the measured free hydroxide ion concentration from sample analysis. The evaluations also illustrate considerable variability in the predicted concentrations compared to the measured concentrations for very low hydroxide ion concentrations. This variability reflects both analytical accuracy and the accuracy of the equations in this very low concentration region. Uncertainty will continue to exist in the accuracy of the equations until additional sample data are obtained over time to either validate the current empirical equations or enable alternates to be developed. Despite the noted uncertainty in the absolute accuracy of the predictions, by restricting the timeframe of prediction to a five-year period together with the application of a limit on the elapsed time between tank sampling events as discussed below, the equations are considered to provide an adequate basis for establishment of a sampling schedule and for identifying those tanks most susceptible to hydroxide depletion.

The Hobbs equation illustrates that the rate of hydroxide depletion due to carbon dioxide absorption is sensitive to the volume of waste in a tank, ventilation rate, and hydroxide

concentration of the waste. Small waste heels remaining in tanks after inter-tank transfers are shown to be particularly susceptible to depletion of free hydroxide from the waste. Particular attention needs to be paid to these conditions during waste transfer analysis to prevent a tank from exceeding the established concentration limits.

The future waste concentrations predicted by these equations were used as input to establish a prioritized sampling and analysis schedule to allow for early detection of a tank approaching the established limits, and to identify preventive actions to avoid tanks going outside the limits. This sampling schedule will be incorporated in the next revision of the TSB-WIRD and provide the sampling requirements for the Chemistry Control Program. Sampling dates have been established one fiscal year prior to the predicted date of a tank reaching the established concentration limit. In addition, it is recommended that all DST and AWF tanks be sampled at no greater than a five-year periodicity in order to check waste chemistry changes, verify compliance with AC 5.15, and develop the database for prediction of hydroxide ion depletion. For those tanks not predicted to reach the concentration limit within the five-year window of prediction considered in this report, a recommended sampling date has been established based on a five-year interval from the previous sampling event. For those tank wastes that do not have analytical data obtained within the last five years, sampling and/or analysis is recommended within the next fiscal year in order to establish a concentration baseline. Where tanks are predicted to reach the established concentration limits within the next two years, preventive actions have been identified to avoid exceeding the limits. The preventive actions include waste transfer and/or chemical addition and sampling. For preventive actions, sampling should generally be performed after completion of a waste transfer or chemical addition to confirm that the tank waste is within specification and may also be performed prior to waste transfer and/or chemical addition if required to confirm the initial tank conditions or caustic demand of the waste.

Because of the uncertainties in the absolute predictions previously discussed, the empirical equations are not used as the basis to declare a DST or AWF tank out of specification, but rather to identify those tanks most susceptible to hydroxide depletion. Actual waste sample analysis is the only basis for declaring a tank out of specification.

The following are the specific findings of the evaluation. Recommendations are provided for each finding:

- *The evaluation confirmed a previous finding that tanks 241-AN-102, 241-AN-107, 241-AY-101, and 241-AY-102 should be currently under corrosion control surveillance and corrective actions. Sampling of the waste in these tanks is recommended for Fiscal Years 2002, 2003, and 2004 as part of the recovery plan and preventative actions.*
- *It is predicted that tank 241-AN-106 could already be caustic deficient. It is recommended that this tank be sampled in Fiscal Year (FY) 2001 followed by chemical addition and verification sampling in FY 2002 to ensure compliance with chemistry limits.*
- *It is predicted that tank 241-AW-105 could already be caustic deficient. It is recommended that this tank be sampled in FY 2001, followed by chemical addition and verification sampling in FY 2002 to ensure continued compliance with the chemistry limits.*
- *Tank 241-AW-102 is the 242-A Evaporator feed tank and is subject to frequent filling and emptying with dilute wastes processed through the evaporator. The small waste heels that are left in this tank after evaporator operations are particularly susceptible to hydroxide depletion because of their initially low concentration. Based on the Caustic Limits Report with an effective date of January 2001, the waste heel in tank 241-AW-102 could already be caustic deficient. This evaluation did not account for the waste transferred from tank 241-AW-104 in January 2001 and processed through the evaporator between January and March 2001. However, the waste transferred from tank 241-AW-104 was more dilute than the waste originally contained in tank 241-AW-102, and the waste heel now remaining in the tank is subject to rapid depletion. It is recommended that the next batch of waste scheduled to be processed through the evaporator (tank 241-AP-107) be transferred to this tank at the earliest opportunity and that an engineering calculation be undertaken based on sample analysis of the sending tank to confirm that both the sending and receiving tanks remain within specification. Additional evaporator campaigns are planned in FY 2002 and FY 2003. The need for further evaluations will be evaluated in subsequent revisions to this document.*

- *It is predicted that tank 241-AP-108 could become hydroxide deficient within one year. It is recommended that waste be transferred into this tank in FY 2001 to adjust the free hydroxide ion concentration, followed by a verification sample in FY 2001.*
- *It is predicted that tanks 241-AW-104 and 241-AZ-102 could become caustic deficient within one year. It is recommended that tank 241-AW-104 be sampled in FY 2001, followed by chemical addition and verification sampling in FY 2002 to ensure continued compliance with the chemistry limits. It is recommended that tank 241-AZ-102 be sampled in FY 2001 or FY 2002, followed by chemical addition and verification sampling in FY 2002.*
- *It is predicted that tanks 241-AP-103 and 241-AY-101 (based on December 2000 caustic addition) could become hydroxide deficient in three years. Sampling of tank 241-AY-101 is covered by a mitigation plan and preventative action through FY 2004. It is recommended to sample tank 241-AP-103 in FY 2003.*
- *The historical sampling schedule shows that it has been five years or longer since tanks 241-AN-105, 241-AP-102, and 241-AP-105 were sampled. It is recommended to sample waste in these tanks in FY 2002 to check waste chemistry changes, verify compliance with AC 5.15, and develop the database for prediction of hydroxide ion depletion.*
- *Tanks 241-AN-103 and 241-AN-104 were sampled in 2000 for the Waste Treatment Plant, Interface Control Document (ICD)-23, and the samples archived. It is recommended to gain agreement to undertake analysis of a fraction of these archived samples to check the waste chemistry, verify compliance with AC 5.15, and develop the database for prediction of hydroxide ion depletion. Both tanks were previously sampled in 1996.*
- *Tank 241-SY-103 was sampled in 2000, and tank 241-AP-104 was sampled in 2001. However, analytical data from these events are not yet available. Analytical data from these sampling events are needed to check the waste chemistry, verify compliance with AC 5.15, and develop the database for prediction of hydroxide ion depletion. Tank 241-SY-103 was previously sampled in 1994.*

- *The analysis of archive samples must be completed as soon as possible because historical results have shown that both physical and chemical properties of archive samples change during prolonged storage. Should the archived samples noted above for analysis not be usable by the Chemistry Control Program, sampling of the identified tanks will be required before the time indicated in the schedule.*

Table ES-1 lists the proposed DST and AWF tank sampling and analysis schedule through FY 2006 to satisfy the needs of AC 5.15, Chemistry Control Program. The table also identifies the preventive actions required to avoid going outside the established concentration limits. The table shows chemical addition to tanks that are susceptible to depletion. The need for chemical addition to these tanks will be based on sample results. The sampling requirements shall be incorporated into the next annual revision of the TSB-WIRD. Actions for this fiscal year have been coordinated with the Characterization Program Office.

This technical basis report will be updated at least annually and the identified requirements incorporated in the TSB-WIRD to meet the needs of the Chemistry Control Program.

Table ES-1. Integrated Sampling Schedule and Preventative Action Requirements for the Chemistry Control Program

Fiscal Year	2001					2002					2003					2004					2005					2006					Comments (FY 2001) ♦ (Grab Sample) Θ (Core Sample)
Tank	Action Required					Action Required					Action Required					Action Required					Action Required					Action Required					
	Chemical Addition		Transfer Waste	Sample	Analysis	Chemical Addition		Transfer Waste	Sample	Analysis	Chemical Addition		Transfer Waste	Sample	Analysis	Chemical Addition		Transfer Waste	Sample	Analysis	Chemical Addition		Transfer Waste	Sample	Analysis	Chemical Addition		Transfer Waste	Sample	Analysis	
	OH^-	NO_2^-				OH^-	NO_2^-				OH^-	NO_2^-				OH^-	NO_2^-				OH^-	NO_2^-				OH^-	NO_2^-				
241-AN-101														♦	•																
241-AN-102				♦	•	•			♦ ♦	•				Θ	•				Θ	•											Recovery Plan in place
241-AN-103										•														Θ	•						Results from 2000 Sample
241-AN-104										•														Θ	•						Results from 2000 Sample
241-AN-105									Θ	•																					
241-AN-106				♦		•			♦	•																			♦	•	Sample After Transfer
241-AN-107				♦	•	•			♦ ♦	•				Θ	•				Θ	•											Recovery Plan in place
241-AP-101																								♦	•						
241-AP-102									♦	•																					
241-AP-103														♦	•	•			♦	•											
241-AP-104										•																			♦	•	Results from 2001 Sample
241-AP-105									Θ	•																					
241-AP-106														♦	•																
241-AP-107										•														♦	•						Results from 2000 Sample
241-AP-108			•	♦						•																			♦	•	Sample after Transfer
241-AW-101										•														Θ	•						Results from 2000 Sample
241-AW-102				♦*				•		•*			•	•*	•*														♦	•	Evaporator Feed Tank. *Sample and analyze sending tank waste. Calculate to confirm final conditions.
241-AW-103									Θ						•																
241-AW-104				Θ		•			♦	•																					
241-AW-105				Θ		•			♦	•																					Sample before and after
241-AW-106																															Sample before and after
241-AY-101				♦	•				Θ	•				Θ	•	•			♦	•				Θ	•						Evaporator Receipt Tank
241-AY-102				♦	•		•		♦ Θ	•				Θ	•					•											Recovery Plan in place
241-AZ-101										•														Θ	•						Recovery Plan in place
241-AZ-102						•			♦	•				Θ	•																Results from 2000 Sample
241-SY-101																								Θ	•						Sample before and after
241-SY-102																								Θ	•						
241-SY-103					•																			Θ	•						Results from 2000 Sample

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LIST OF ACRONYMS

AC	Administrative Control
AWF	Aging Waste Facility
BBI	Best-Basis Inventory
CC	Complexant Concentrate Waste
CP	Concentrated Phosphate Waste
DC	Dilute Complexed Waste
DN	Dilute Non-Complexed Waste
DOE	U.S. Department of Energy
DQO	Data Quality Objective
DSS	Double-shell slurry
DSSF	Double-shell slurry feed
DST	Double-shell tank
ft^3/min	cubic feet per minute
FY	Fiscal Year
g mol	gram moles
g mol/L	gram moles per liter
kgal	kilogallons
L	liters
L/ft^3	liters per cubic feet
LAW	low-activity waste
M	molarity (moles per liter)
min/day	minutes per day
%	Percent
SRL	Savannah River Laboratory
SST	single-shell tank
TSB-WIRD	Technical Sampling Basis - Waste Information Requirements Document
TSR	Technical Safety Requirements
TWINS	Tank Waste Information Network System

LIST OF ACRONYMS, Continued

WTP	Waste Treatment Plant
°C	degrees Celsius
°F	degrees Fahrenheit

1.0 INTRODUCTION

Administrative Control (AC) 5.15, "Chemistry Control Program," of the *Tank Farm Technical Safety Requirements* (TSR), HNF-SD-WM-TSR-006 (CHG 2001), implements a program to maintain and control double-shell tank (DST) waste chemistry to minimize corrosion of the primary tank. One element of this program is to verify that the waste remains in compliance with the waste corrosion concentration limits to ensure the waste containment integrity of the DSTs. This verification requires that waste sampling occur at a frequency dictated by the changes occurring in the waste. For this document, the term DST includes the Aging Waste Facility (AWF) tanks. Waste chemistry limits for corrosion control apply to all DSTs.

As part of the DST Chemistry Control Program, periodic assessments of the nitrite, nitrate, and hydroxide ion concentrations are necessary to ensure that the waste within the DSTs stays within the established chemistry control limits of AC 5.15. This assessment includes predicting the caustic consumption rate of the wastes. When predictions indicate that waste compositions are approaching the chemistry control limits, administrative actions are necessary to ensure continued compliance. Planning of sampling frequencies for each DST is one method of monitoring waste chemistry.

The original corrosion control and the associated waste composition specifications for DSTs were based on Savannah River Laboratory (SRL) stress corrosion cracking investigations (RHO 1982). The SRL studies determined that the corrosion of low carbon steels was dependent on the maintenance of minimum levels of the inhibitor species hydroxide and nitrite relative to nitrate, the primary aggressive ion present in tank waste. The addition of other potentially aggressive minor constituents in tank wastes, such as phosphate, sulfate, silicate, fluoride, or chloride in low concentrations, was found to have little effect on corrosion potential. Carbonate, although a significant constituent in tank wastes, was also found to have a minor effect on corrosion due to the known formation of a pH buffer. The dominant species (hydroxide, nitrite, and nitrate ions) control the corrosion rate of the primary tank.

Findings in 1980 showed that the available corrosion data did not adequately portray all wastes proposed for storage in the DSTs. At that time, an experimental data development task was undertaken to provide the necessary corrosion data to define safe and acceptable operating specifications for the DSTs. This experimental data development task consisted of several thousand corrosion coupon tests performed by Pacific Northwest Laboratory (now Pacific Northwest National Laboratory). All the coupon tests were performed in simulated waste compositions consistent with the waste chemistry specifications. The results of these coupon tests (RHO 1984, PNL 1985) showed that for temperatures within the normal DST operating range (at or below 100 °C), no corrosion rates were observed above the design limits, and there was no stress corrosion cracking observed. In general, corrosion outside the design limits was observed in very dilute nitrite and hydroxide solutions, and in concentrated hydroxide solutions at high temperatures. Stress corrosion cracking was observed only on highly stressed U-bend coupons in solutions with high nitrate and low hydroxide concentrations and in solutions that were high in hydroxide concentrations at elevated temperatures. Supplemental work in 1994 identified that even at low nitrate concentrations, some presence of nitrite was important to

protect against pitting and stress corrosion cracking (PNL 1994). The results of these tests and tests performed at the Savannah River Laboratory (Ondrejcin 1978) form the technical basis for the DST corrosion control requirements. In 1994, a corrosivity factor, within the compositional limits indicated by the corrosion specifications, was developed (Anantatmula et al. 1994) to verify if a given DST waste is benign or aggressive toward the carbon steel containment. This factor was subsequently included in the corrosion specifications.

In 1992, Savannah River Laboratory developed correlations (Zapp and Hobbs 1992), based on experimental studies, between nitrate and nitrite concentrations to inhibit pitting corrosion in carbon steel exposed to dilute radioactive waste slurries. The 1994 report by Anantatmula et al. on single-shell tank corrosion concluded that Microbiologically Induced Corrosion is not a viable mechanism for the Hanford Site waste tanks.

The possible degradation mechanisms that are involved in the corrosion of the inner wall of the primary tank by the waste and water vapor contained in the tank are discussed in Edgemon and Anantatmula (1995). The principal corrosion mechanisms, which could play an active role in the corrosion of the primary wall contacting the waste, are uniform corrosion, pitting/crevice corrosion, and stress corrosion cracking.

The DST waste chemistry specifications were developed to protect against general corrosion, pitting corrosion, and stress corrosion cracking of the primary tank. In addition, these specifications are consistent with the guidance for protection against pitting/crevice corrosion provided by BNL (1997).

2.0 PURPOSE

The purpose of this evaluation is to establish sampling and analysis requirements for DST waste to ensure continued adherence to the waste chemistry limits provided in the AC 5.15, "Chemistry Control Program" (CHG 2001) and included in Table 2-1. Limit values for hydroxide ion and nitrite ion are dependent on the concentration range of nitrate ion and temperature of the waste. The sampling requirements are based on a review of chemical composition, mechanisms for chemistry changes, and operations in the tanks. The document also identifies preventive actions required to avoid going outside the established concentration limits.

Table 2-1. Double-Shell Tank Chemistry Limits

For $[NO_3^-]$ Range	Variable	For Temperature (T) Range		
		$T<167\ ^oF$	$167\ ^oF \leq T \leq 212\ ^oF$	$T > 212\ ^oF$
$[NO_3^-] \leq 1.0\ \underline{M}$	$[OH^-]$	$0.010\underline{M} \leq [OH^-] \leq 8.0\underline{M}$	$0.010\underline{M} \leq [OH^-] \leq 5.0\underline{M}$	$0.010\underline{M} \leq [OH^-] < 4.0\underline{M}$
	$[NO_2^-]$	$0.011\underline{M} \leq [NO_2^-] \leq 5.5\underline{M}$	$0.011\underline{M} \leq [NO_2^-] \leq 5.5\underline{M}$	$0.011\underline{M} \leq [NO_2^-] \leq 5.5\underline{M}$
	$[NO_3^-]/([OH^-] + [NO_2^-])$	< 2.5	< 2.5	< 2.5
$1.0\underline{M} < [NO_3^-] \leq 3.0\underline{M}$	$[OH^-]$	$0.1\ ([NO_3^-]) \leq [OH^-] < 10\underline{M}$	$0.1\ ([NO_3^-]) \leq [OH^-] < 10\underline{M}$	$0.1\ ([NO_3^-]) \leq [OH^-] < 4.0\underline{M}$
	$[OH^-] + [NO_2^-]$	$\geq 0.4\ ([NO_3^-])$	$\geq 0.4\ ([NO_3^-])$	$\geq 0.4\ ([NO_3^-])$
$[NO_3^-] > 3.0\ \underline{M}$	$[OH^-]$	$0.3\underline{M} \leq [OH^-] < 10\underline{M}$	$0.3\underline{M} \leq [OH^-] < 10\underline{M}$	$0.3\underline{M} \leq [OH^-] < 4\underline{M}$
	$[OH^-] + [NO_2^-]$	$\geq 1.2\ \underline{M}$	$\geq 1.2\ \underline{M}$	$\geq 1.2\ \underline{M}$
	$[NO_3^-]$	$\leq 5.5\ \underline{M}$	$\leq 5.5\ \underline{M}$	$\leq 5.5\ \underline{M}$

3.0 APPROACH

The approach undertaken to determine the DST sampling schedule needed to ensure compliance with AC 5.15 is comprised of three steps. Tank characterization data from sample analysis for nitrite, nitrate, and hydroxide liquid phase concentrations is entered into the Tank Characterization Database (TCD) within the Tank Waste Information Network System (TWINS). From the sample data contained within the TCD, or engineering calculations if sample analysis is unavailable, a Best-Basis Inventory (BBI) for the DSTs is compiled. The BBI has the capability of generating a Caustic Limits Report, summarizing the liquid phase concentrations of nitrite, nitrate, and hydroxide in the DSTs. The first step is to review the data in the Caustic Limits Report to ensure that all current sample information has been incorporated in the respective BBI. The second step is to input this analytical data and process knowledge information into a spreadsheet that baselines the sample data and chemical constituents to the sample date and forecasts the projected hydroxide concentration based on predicting empirical equations. The third step is to assess the information summarized in the spreadsheet against sampling criteria and develop a chemistry control-based DST sampling schedule from applying the free hydroxide ion consumption prediction equations and time since the tank was last sampled. From this assessment, sampling recommendations were formulated based on ranking criteria.

3.1 SOURCE OF DATA

Data used as the basis for the evaluation were obtained from the Tank Characterization Database and the BBI within TWINS.

A Caustic Limits Report is generated from the BBI for the liquid waste contained in each DST (comprised mostly of supernatant constituent values, but in some cases includes the statistical mean of the drainable liquids). The Caustic Limits Report lists the nitrite, nitrate, hydroxide, total organic carbon, aluminum, specific gravity, liquid volume, sample date, the hydroxide limit (upper and lower limits), nitrite limit (upper and lower limits), nitrate/(hydroxide + nitrite) ratio, and sum of hydroxide and nitrite for all of the DSTs (See Appendix E). All updated BBI data were reviewed to ensure that the concentrations of the analytes of concern were representative of current tank conditions and that the hydroxide concentration data were based directly or indirectly on sample analysis and not calculated from a charge balance. For this evaluation, the sample date reported on the Caustic Limits Report was used to start the hydroxide depletion calculation. Appendix A contains the summary table that includes this information.

At low hydroxide ion concentrations, insufficient free hydroxide ion exists to enable its reliable measurement by titration because of the presence of interfering ions. Therefore, for those tanks with a pH of less than 12.5 and/or a direct hydroxide ion concentration less than 0.03 M as reported in the Tank Characterization Database, the BBI calculates the free hydroxide concentration from the reported pH value. At higher hydroxide concentrations, sodium affects the measurement of pH. Therefore, for tanks with pH greater than 12.5, the BBI uses the direct hydroxide measurement reported in the Tank Characterization Database.

Because very limited data exist in the current Caustic Limits Report for interstitial liquid contained within the saltcake and/or sludge DST phases, this evaluation focuses on the liquid, supernatant phase. As additional data becomes available for interstitial liquid as a result of future waste sampling, it will be evaluated in future revisions of this document.

The mean nitrite and nitrate ion concentrations were used in all of the lower limit hydroxide determinations. The limit values are presented in the Appendix A table. The lowest limit is 0.01 M hydroxide. If no value is applicable or available, then NA appears.

All calculations were independently verified.

3.2 MECHANISMS FOR DEPLETION OF INHIBITOR CHEMICALS

The DST waste chemistry specifications were developed to protect against general corrosion, pitting corrosion, and stress-corrosion cracking of the primary tank. The specifications are based on the maintenance of minimum levels of the inhibitor species hydroxide and nitrite relative to nitrate, the primary aggressive ion present in tank waste. The primary inhibitor species is the free hydroxide ion. The presence of a minimum concentration of nitrite is also important in dilute waste solutions. Chemical reactions are known to occur in tank wastes that consume these inhibitor species over time. Free hydroxide is the species that is most susceptible to depletion. Mechanisms are also known to exist for consumption of nitrite in tank waste and are discussed below.

The important chemical reactions for free hydroxide ion consumption are absorption of carbon dioxide from air ventilation of the tanks, oxidation of sodium salts of organic species, and reaction with hydrated aluminum oxide. These reactions are listed as follows:

$$OH^- + CO_2 \rightarrow HCO_3^- \quad (1)$$

$$HCO_3^- + OH^- \rightarrow CO_3^{-2} + H_2O \quad (2)$$

$$HOCH_2CO_2Na + 2\ NaNO_3 + NaOH \rightarrow NaO_2CCO_2Na + 2\ NaNO_2 + 2\ H_2O \quad (3)$$

$$Al(OH)_3 + OH^- \rightarrow Al(OH)_4^- \quad (4)$$

Equations 1 and 2 show the direct absorption of CO_2 from air and subsequent reaction to form bicarbonate and carbonate ions. The rate of absorption is dependent on the hydroxide concentration of the waste and the ventilation rate of air through the headspace of the DST, i.e., the CO_2 available for reaction. These reactions continue until steady-state conditions are reached as established by hydroxide, bicarbonate, and carbonate equilibria in solutions, and the CO_2 concentrations in air. This steady state occurs at a pH of 10.34 in a water-carbon dioxide-hydroxide system (Pourbaix 1974).

Equation 3 shows consumption of hydroxide ion by oxidation of a sodium salt organic anion. The glycolate ion is oxidized to oxalate ion, and the nitrate ion is reduced to nitrite ion. The sodium salts of organic complexants and solvents are oxidized through long sequences of chemical reactions to form volatile compounds as the inorganic oxidants are reduced to form nitrogen-containing gases and hydrogen. Organic oxidation reactions are much slower than the CO_2 absorption reaction because of the low temperatures of the waste.

Aluminum is present in significant quantities in certain tank wastes. At high pH, the aluminum is soluble in the form of the aluminate ion, $Al(OH)_4^-$, as indicated in Equation 4, which shows the dissolution of hydrated aluminum oxide (Gibbsite) sludge by hydroxide ion to form aluminate ion. The aluminum concentration in solution is a function of the hydroxide ion concentration: at low hydroxide ion concentrations gibbsite, $Al(OH)_3$, precipitates, and at high hydroxide ion concentrations sodium aluminate, $NaAlO_2$ precipitates. Equation 5 shows the reaction between aluminate ion and CO_2 to form insoluble Dawsonite sludge.

$$Na^+ + Al(OH)_4^- + CO_2 \rightarrow NaAlCO_3(OH)_2 + H_2O \qquad (5)$$

Other reactions also have the potential for lowering (or raising) the free hydroxide ion concentration of the liquid phase. These reactions include tank corrosion, water radiolysis, air radiolysis, and radiolysis of organics (Wodrich et al. 1992).

Tank waste solutions contain high concentrations of nitrates and nitrites. Radiolysis of the nitrate anion results in the production of nitrite ion and nitrogenous gases. The nitrite anion is an active oxidant in the tank wastes and reacts to produce nitrogenous gases and ammonia (Stock and Pederson 1997). The reaction sequences that are responsible for the conversion of nitrite ion into reduced nitrogenous gases occur both thermally and radiolytically, with the radiolytic pathway possessing much lower activation energy. The reaction proceeds through nitrogen dioxide and nitric oxide, through the many available oxidation states eventually leading to ammonia. In the absence of significant concentrations of organics, the rate of production of the nitrite anion from the nitrate anion exceeds the rate of destruction of nitrite to form nitrogenous gases. Hence, the concentration of nitrite tends to increase with time, whereas the concentration of nitrate decreases. However, work undertaken at the Savannah River Site (Walker et al. 1992) has shown that organic components serve an important role as reducing agents in this chemistry and greatly accelerate the consumption of both nitrate and nitrite, with the concentration of both species approaching zero at large accumulated radiation doses. This work notes that if nitrite is consumed by radiolysis in the presence of organic, then nitrite will have to be periodically replaced to continue to prevent tank corrosion. These mechanisms provide a potential explanation for the depletion of nitrite that has recently been reported in the solids layer of tank 241-AY-102.

Because nitrate and nitrite concentrations in DSTs are generally high, a lower limit for nitrite only exists for nitrate solutions < 1 M, and nitrite depletion from tank wastes had not, until recently, been reported or expected, this evaluation has focused on predicting the consumption of free hydroxide from tank wastes. Future revisions to this document will consider nitrite ion depletion.

3.3 EMPIRICAL EQUATIONS FOR EVALUATING TRENDS IN WASTE CHEMISTRY

The consumption of free hydroxide ion from the radioactive liquid waste stored in tanks at the U.S. Department of Energy (DOE) Savannah River Site and the Hanford Site prompted the development of empirical equations for calculating the time dependent concentration of free hydroxide ion in the waste.

3.3.1 Absorption of Carbon Dioxide in Waste Tanks

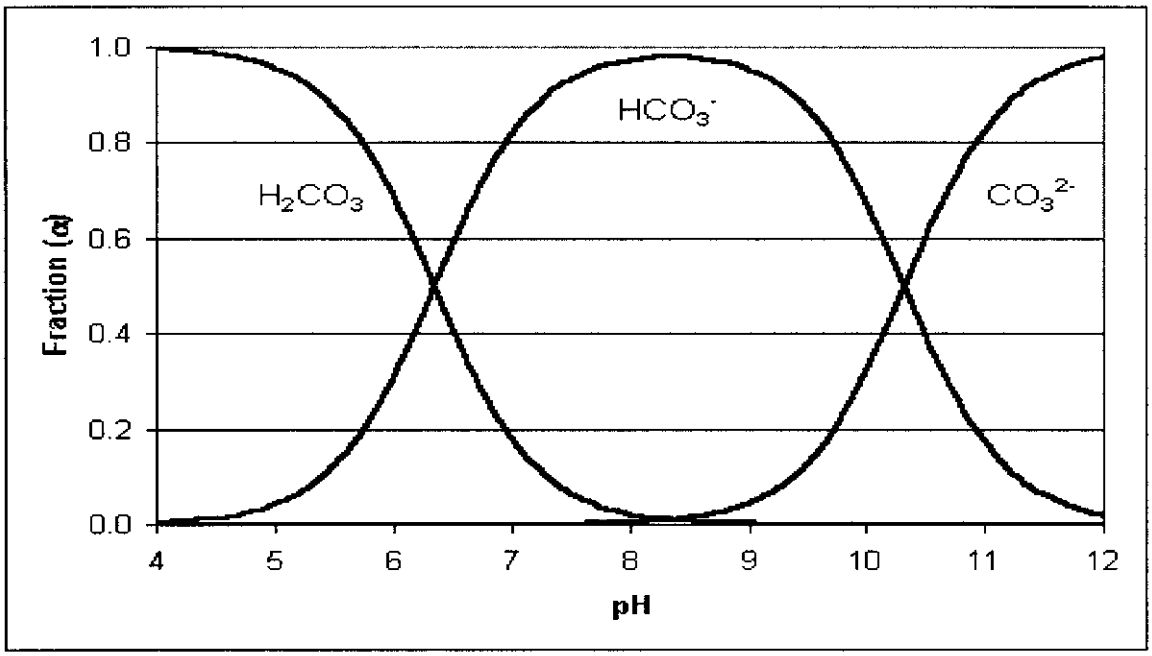
An empirical equation for hydroxide ion depletion due to carbon dioxide absorption was developed from data collected at the Savannah River Site. The equation was developed from data collected by Hobbs (1987) and based on washed sludge and washed precipitate that were stored in tanks. Regular measurements were taken of the flow rates of air through the waste tanks, levels of hydroxide and carbonate in the waste solutions, and the carbon dioxide concentrations in the air entering and exiting the waste tank. Measured carbon dioxide absorption in ventilation airflow through the tanks was 40 percent to 70 percent for pH 12 to pH 14, respectively. Because of significant excess hydroxide at pH 14, the tanks of concern were in the range of pH 12 to pH 13, where approximately 50 percent of the carbon dioxide was absorbed. The absorption of carbon dioxide by alkaline waste was shown to stop at a pH of about 9.5 because of the abundance of bicarbonate ion.

Figure 3-1 shows the fractional distribution of carbonate species as a function of pH. At pH 11 and above ($\geq$ 0.001 M OH), the predominant constituent is the $[CO_3^{-2}]$ ion. Therefore, at normal waste tank conditions, the $[CO_3^{-2}]$ ion will increase in concentration until the waste is saturated and a carbonate precipitate will form. This reaction would be essentially constant at these conditions. The rate of hydroxide ion depletion is dependent on the amount of hydroxide ion present in the supernatant and thereby further justifies the Hobbs equation. This evaluation uses an average fraction of carbon dioxide absorbed by the tank waste instead of a single hydroxide composition described by Hobbs and assumes a crust free liquid waste surface. As a result, the calculated amount of carbon dioxide absorbed by alkaline waste is conservative, particularly for those tank wastes known to possess a solid surface crust that would inhibit absorption.

The kinetics of reactions between hydroxide ion and carbon dioxide and bicarbonate are extremely fast. The rate-determining step for depleting hydroxide in the liquid phase is the transfer of carbon dioxide across the gas-liquid interface. The rate of carbon dioxide absorbed is calculated by multiplying the airflow rate through the tank by the concentration of carbon dioxide in air and by the fraction of carbon dioxide absorbed (Equation 6).

$$\text{Rate } CO_2 \text{ Absorbed} = \text{Air flow rate} \times [CO_2] \text{ in air} \times \text{Absorption fraction} \quad (6)$$

Figure 3-1. Fractional Distribution of Carbonate Species as a Function of pH[1]



The hydroxide depletion equation used for this evaluation is based on Equation 6 and derived as shown below:

$$[OH]_t = [OH]_i - [OH]_r \qquad (7)$$

where:

$[OH]_t$ is OH concentration (g mol/L) at time t,
$[OH]_i$ is OH concentration (g mol/L) at starting time, and
$[OH]_r$ is OH concentration (g mol/L) depleted by chemical reaction

The rate of hydroxide depletion is related to the rate of carbon dioxide absorption as follows:

From Equation 6, the rate of CO_2 absorption, R_{CO2}, is given by:

$$R_{CO2} = V \times A \times B \times D \times E \quad \text{g mol } CO_2\text{/day} \qquad (8)$$

where:

A = concentration CO_2 in outside air = 350 g mol CO_2 / 1E+06 g mol air,
B = fraction CO_2 absorbed by liquid waste = (0.165 (Log $[OH]_i$ + Log $[OH]_t$ + 28)-3.138)/2,

[1] Figure from http://www.chem.usu.edu/faculty/SBialkow/Classes/3650/Carbonate/Carbonic%20Acid.html

V = tank vent rate = ft^3/min,
D = ideal mol density air = 1 g mol air/ 22.4 L, and
E = conversion constant = 28.317 L/ft^3 x 1440 min/day.

Substituting gives:

$$R_{CO2} = 0.64 \times V \times B \quad \text{g mol } CO_2\text{/day} \tag{9}$$

From Equations 1 and 2, it can be seen that for each mole of CO_2 absorbed by the waste, two moles of hydroxide are consumed. Therefore, the rate of hydroxide depletion (R_{OH}) is twice the rate of CO_2 absorption:

$$R_{OH} = 2 \times R_{CO2} \tag{10}$$

$$= 1.27 \times V \times B \quad \text{g mol OH/day} \tag{11}$$

The concentration of hydroxide ion consumed in a given time period, $[OH]_r$, is given by:

$$[OH]_r = R_{OH} \times t / SV \quad \text{g mol OH/liter} \tag{12}$$

where:

t = reaction time = days, and
SV = Supernatant volume = liters.

Substituting from Equation 11 gives:

$$[OH]_r = 1.27(B)(V)(t)/(SV) \quad \text{g mol OH/liter} \tag{13}$$

Substituting Equation 13 into Equation 7 gives:

$$[OH]_t = [OH]_i - 1.27(B)(V)(t)/(SV) \quad \text{g mol OH/liter} \tag{14}$$

Equation 14 is the empirical equation used for estimating the rate of hydroxide consumption based on CO_2 absorption in the tank waste. This equation is subsequently referred to as the Hobbs equation.

3.3.2 Hydroxide Depletion in Complexed Waste Tanks

At the Hanford Site, the kinetics of hydroxide ion depletion was studied for complexed concentrate wastes stored in DSTs 241-AN-102 and 241-AN-107. These studies were based on observations, and there was no attempt to postulate a reaction mechanism. The studies included hydroxide consumption by CO_2 absorption, complexant oxidation, and hydrated aluminum oxide reactions (if any). Carothers (2001) developed the kinetic equation for hydroxide ion depletion in tank 241-AN-102 supernatant based on the first order kinetics and a nearly full waste tank. Equation 15 shows the Carothers equation.

The equation is applicable to both tank 241-AN-102 and tank 241-AN-107 based on recent information from Reynolds (See Appendix C).

$$[OH]_t = [OH]_i \, e^{-(0.0003t)} \tag{15}$$

where:

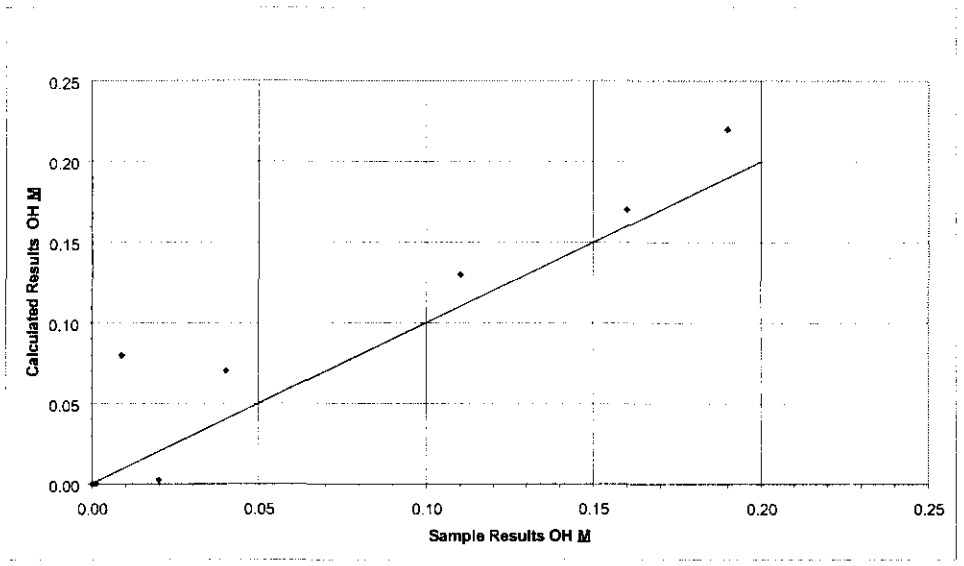
$[OH]_t$ is OH concentration (g mol/L) at time t,
$[OH]_i$ is OH concentration (g mol/L) at starting time, and
t is reaction time, days.

3.3.3 Evaluation of Hobbs and Carothers Equations for Estimating Hydroxide Depletion of Double-Shell Tank Supernatant

3.3.3.1. Comparison of Hobbs Equation Predictions to Available Sample Data

The estimate of free hydroxide ion depletion by the Hobbs equation was compared to sample results for ten data points resulting from seven DSTs. These tanks are 241-AN-102, 241-AN-107, 241-AP-104, 241-AW-104, 241-AY-101, 241-AY-102, and 241-AZ-102. Regression analysis of this data is shown in Appendix D and Figure 3-2. These evaluations indicate that for measured hydroxide concentrations above about 0.1M the concentrations predicted by the Hobbs equations are within twenty percent of the measured free hydroxide ion concentration from sample analysis. The evaluations also illustrate considerable variability in the predicted concentrations compared to the measured concentrations for very low hydroxide ion concentrations. This variability reflects both analytical accuracy and the accuracy of the equations in this very low concentration region. It is known that the Hobbs equation is not valid below about pH 9.5-10.5, because of the presence of bicarbonate. The data points illustrating the greatest variability are from tanks that have already been identified to have concentrations in this region and are already below the established chemistry limit. The application range of the equation has not been specifically determined but it appears to be usable from about 0.01 M to 0.2 M OH based on results shown in Figure 3-2. There is lack of data available to ensure that the equation has good accuracy for estimating hydroxide depletion over the range of hydroxide concentrations and waste types in the DST supernatant. The Hobbs equation will be used for estimating hydroxide ion depletion from all waste types until additional information becomes available to provide additional verification of the equation's applicability or to postulate alternate equations.

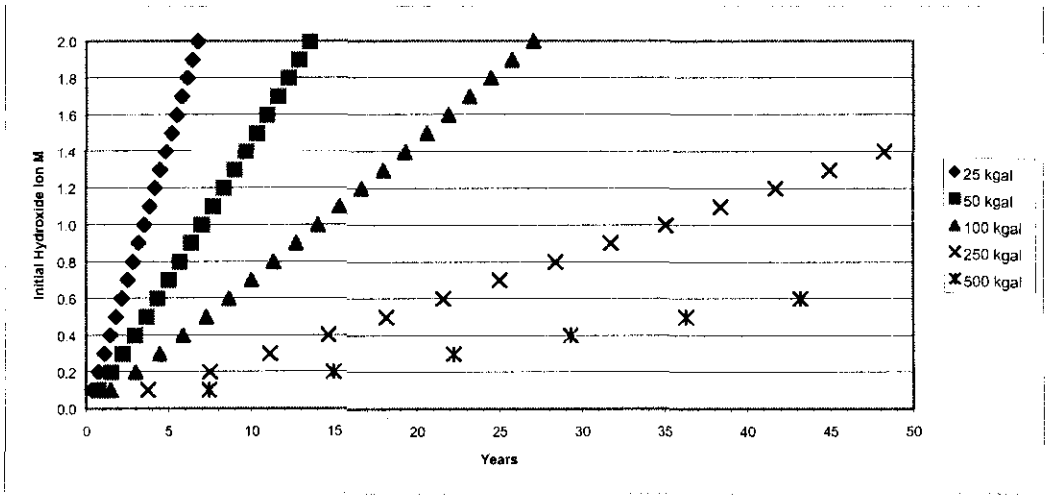
Figure 3-2. Comparison of Hobbs Equation Predicted Hydroxide Concentrations to Available Sample Data



3.3.3.2. Sensitivity of Hobbs Equation to Tank Waste Conditions

The Hobbs equation is affected by the ventilation rate, volume of liquid waste, and gas-liquid interface. Figures 3-3 illustrates the effect of reduced tank waste volumes on the time for a given initial hydroxide concentration in the waste to reduce to pH 12 (0.01 M OH). It can be clearly seen how the time to depletion is greatly reduced at waste volumes less than 100 kgal. Therefore, waste heels remaining after inter-tank transfers may be particularly susceptible to hydroxide depletion.

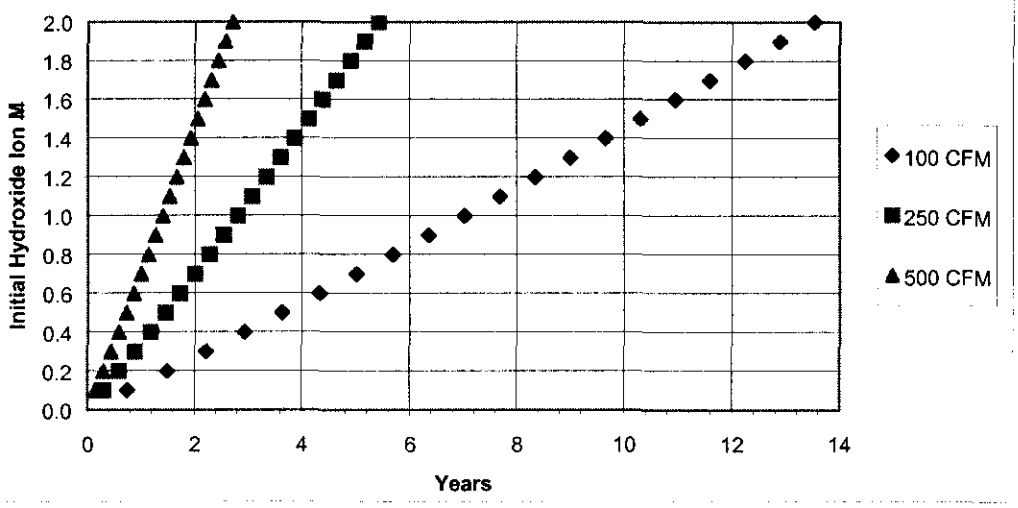
Figure 3-3. Sensitivity of Hobbs Equation to Tank Waste Volume*



*Based on a fixed ventilation rate of 100 cfm.

Figure 3-4 illustrates the effect of increasing ventilation rate on the time for a given initial hydroxide concentration to reduce to pH 12. It can be seen that high ventilation rates cause fast depletion of the hydroxide ion. Therefore, tanks containing higher heat wastes and requiring higher ventilation rates may exhibit increased rates of hydroxide depletion.

Figure 3-4. Sensitivity of Hobbs Equation to Ventilation Rate*



*Based on a tank waste volume of 50 kgal.

3.3.3.3. *Limitations of Hobbs Equation*

The Hobbs equation only considers hydroxide depletion due to the effect of carbon dioxide absorption and does not account for other depletion mechanisms previously discussed such as organic degradation reactions or reactions with hydrated aluminum oxide. For waste tanks containing a high volume of waste and higher total hydroxide inventory, the depletion of hydroxide by carbon dioxide may be slow. If the waste also contains significant concentrations of other depleting species, such as organic carbon and aluminum, the Hobbs equation may under-predict the rate of depletion. However, Figure 3-2 indicates predictions within twenty percent of actual sample analysis. This comparison includes data points from tanks 241-AN-102 and 241-AN-107, which contain the highest concentration of organic species in the DSTs. The results would suggest that the contribution to hydroxide depletion from organic degradation is relatively small compared to carbon dioxide absorption. Carbon dioxide absorption from ventilation air is a surface effect in the DSTs, and conditions that reduce the surface area of the waste in contact with the ventilation stream will tend to reduce the rate of depletion. A floating crust has been observed on tanks 241-AN-103, 241-AN-104, 241-AN-105, 241-AW-101, 241-SY-101, and 241-SY-103. These crusts reduce the gas-liquid interface and the consumption rate of free hydroxide ion as predicted by the Hobbs equation. At low waste volumes and lower ventilation rates, there may be a tendency for the ventilation stream to have a low efficiency of contact with the waste surface, causing the Hobbs equation to over-predict the

rate of depletion. However, when all these factors are considered, on balance the Hobbs equation appears to provide a reasonable estimate of the rate of hydroxide depletion from a range of waste types as was illustrated in Figure 3-2. As additional analytical data are gathered over time, the application limits of the equation will continue to be reviewed. The DST ventilation rates are based on Hu (2001).

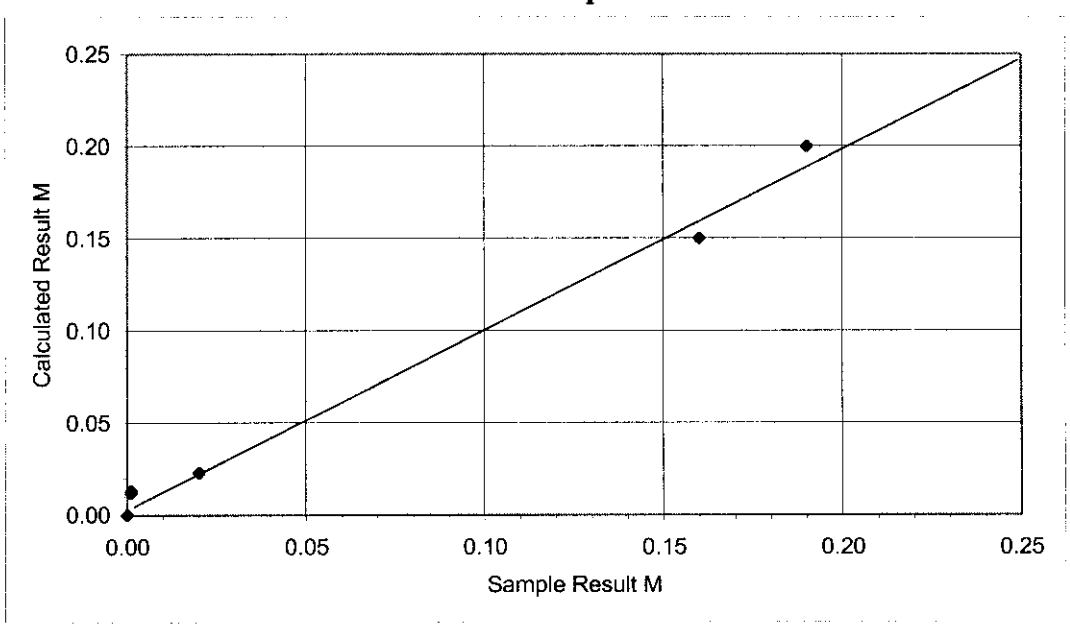
3.3.3.4. Comparison of Carothers Equation to Available Sample Data

The estimate of free hydroxide ion depletion by the Carothers equation was compared to sample results for six data points resulting from three DSTs. These tanks are 241-AN-102, 241-AN-107, and 241-AY-101. Regression analysis of this data is shown in Appendix D and Figure 3-5. For measured hydroxide concentrations above 0.02 M, the predicted concentrations provided by the Carothers equation appear to be within fifteen percent of the measured free hydroxide ion concentration for the complexant concentrate (CC) waste data available. Significant variability in the predicted and measured concentrations is noted at very low hydroxide concentrations, reflecting both limitations in analytical accuracy and equation predictions in this very low concentration region. The Carothers equation is used in this evaluation for hydroxide depletion prediction and historical trending of CC and dilute complexant (DC) wastes in addition to the Hobbs equation. Where both equations are used, the more conservative prediction resulting from the two equations is used as the basis for establishing a sampling schedule.

3.3.3.5. Sensitivity of Carothers Equation to Tank Waste Conditions

The Carothers equation is a simple fit of hydroxide concentration data over time to a first order kinetic relationship. Therefore, the equation is only sensitive to the initial hydroxide concentration of the waste. No correlation of the rate of depletion to the total organic carbon content of the waste was undertaken because of lack of comparative data from other tanks.

Figure 3-5. Comparison of Carothers Equation Predicted Hydroxide Concentrations to Available Sample Data



3.3.3.6. Limitations of Carothers Equation

The Carothers equation does not include the effect of temperature, waste volume, soluble total organic carbon, condition of the waste surface, ventilation rates, nor dominate buffering species. Because this equation was developed based on fairly full waste tanks, it may not fully reflect the increased effect of carbon dioxide absorption at lower waste volumes and may tend to under-predict the rate of depletion under these conditions. Tanks 241-AN-102 and 241-AN-107 contain the highest concentrations of total organic carbon in all the CC and DC wastes contained in the DSTs by a factor of approximately three to almost ten. The rates of depletion seen in these tanks may, therefore, be higher than those seen in tanks with lower organic concentrations and the equation may over-predict the rate of depletion under these conditions.

3.4 SAMPLING SCHEDULE

A DST waste sampling schedule is developed each year to accommodate several Hanford Site programmatic needs and requirements. A prioritized schedule for both core and grab sampling has been coordinated between the programs. The sampling requirements shall be reflected in the annual update of the *Technical Sampling Basis – Waste Information Requirements Document* (TSB-WIRD) (Adams et al. 2001). Previous revisions of the TSB-WIRD did not include specific sampling requirements to ensure compliance with chemistry control limits. Implementation of AC 5.15, "Chemistry Control Program" (CHG 2001), requires development of a DST sampling schedule based on chemical composition, mechanisms for chemistry changes, and operations in the tanks and incorporation of those sampling requirements into the next revision of the TSB-WIRD. The sampling and analysis schedules and priorities shall allow for early detection of a tank approaching the established limits, and for preventive action to avoid exceeding the limits.

3.4.1 Criteria for Development of the Chemistry Control Program Sample and Analysis Schedule

Development of a sampling and analysis schedule to satisfy the needs of the Chemistry Control Program is based on consideration of several factors including:

- The best estimate of the chemical composition of the waste, based on sample analysis and/or process knowledge. Actual sample analyses indicating that tank waste composition is outside the established chemistry control limits would lead to preparation of an occurrence report and recovery plan in accordance with AC 5.15.

- Changes in waste chemistry that occur over time and consume corrosion-inhibiting species present in the tank waste that lead to tank waste compositions approaching the established chemistry control limits.

- Waste transfers and operations in the tanks that result in conditions causing increased rate of chemistry change or compositions with a reduced margin above the established chemistry limits.

- The time period elapsed since a tank was previously sampled and the confidence in the waste composition data used as the basis for evaluation.

Data on tank waste composition are developed from sample analyses and collected in the Tank Characterization Database within TWINS. The data, together with information on tank waste transfers and operations, process knowledge, and engineering estimates where necessary, are used to compile a Best-Basis Inventory (BBI) for each tank that is updated quarterly. A Caustic Limits Report is generated from the BBI that lists the hydroxide, nitrate, and nitrite concentrations of tank waste supernatant and sludge and/or saltcake interstitial liquid, where available (See Appendix E). The BBI and Caustic Limits Report do not consider the effects of waste chemistry changes because the sampling event(s) are used as the basis of the waste inventory. In order to ensure continued compliance with the chemistry control limits over time, it is necessary to estimate the rate of change of tank waste chemicals and establish a sampling schedule that allows for early detection of waste compositions approaching the established limits.

The free hydroxide ion is the most rapidly changing waste chemical. The Hobbs and Carothers empirical equations described previously are used to estimate the change in free hydroxide concentration with time. Compositional data, the corresponding sample or engineering estimate base date, and waste volume information is extracted from the Caustic Limits Report. This information together with information on tank ventilation rates (Hu 2001) is used as input to these empirical equations.

Forward-looking estimates of tank waste compositions are restricted to a five-year window, in order to reduce the impact of uncertainties in the equation predictions. Estimates of tank waste composition are made for "now," set at March 2001, and for January 2006. As previously discussed, the Hobbs equation is applied to all tank waste types, and both the Hobbs and Carothers equations are applied to DC and CC wastes. Where both equations are applied, the more conservative prediction is used as the basis for further decisions.

Mean concentrations and liquid waste volumes provided in the Caustic Limits Report are used to predict the depleted concentration of free hydroxide ion over the next five years. The lower 95 percent limit or one standard deviation of the hydroxide sample mean determination is also included in the depletion calculation when possible (See Appendix A). For tanks predicted to reach the established chemistry control limit within the five-year window of prediction, predictions based on both the mean and the 95 percent confidence limit or one standard deviation will be reviewed, and the sampling or preventive action date will be based on the earlier predicted date.

Figure 3-6 displays the Chemistry Control Program Logic. The diagram illustrates the steps used to establish a sampling schedule to support the Chemistry Control Program and the actions to be taken for tanks requiring preventive actions to ensure compliance with the established chemistry control limits.

Predictions of tank waste composition are performed quarterly based on the Caustic Limits Report.

- Where tanks are predicted to reach the established concentration limits within the next two years, preventive actions are identified to avoid exceeding the limits. The preventive actions include waste transfer and/or chemical addition and sampling. For these tanks, sampling should generally be performed after completion of a waste transfer or chemical addition to confirm that the tank waste is within specification and may also be performed prior to waste transfer and/or chemical addition if required to confirm the initial tank conditions or caustic demand of the waste.

- Where tanks are predicted to reach the established chemistry control limits within the five-year window of prediction, sampling dates are scheduled one fiscal year prior to the predicted date of a tank reaching the established concentration limit, using the 95 percent confidence or one standard deviation based tank composition.

- Where tanks are not predicted to reach the established chemistry control limits within the five-year window of prediction, sampling dates are established based on a five-year interval from the previous sampling event.

- For those tank wastes that do not currently have analytical data available that have been obtained within the last five years, sampling and/or analysis is recommended within the next fiscal year in order to establish a concentration baseline.

Because of the uncertainties in the absolute predictions previously discussed, the empirical equations are not used as the basis to declare a DST or AWF tank out of specification, but rather to identify those tanks most susceptible to hydroxide depletion and to schedule preventive actions. Actual waste sample analysis is the only basis for declaring a tank out of specification.

The recommended sampling and analysis schedule and preventive actions identified as part of this evaluation are presented in Table 3-1. The table shows chemical addition to tanks susceptible to depletion. The need for chemical addition to these tanks will be based on sample results.

Analysis of samples recovered in accordance with this schedule will meet the requirements of the *Double-Shell Tanks Chemistry Control Data Quality Objectives* (Chemistry Control Program DQO)(Banning 2001). The final analytical results obtained will be entered in the Tank Characterization Database and will become part of the BBI and Caustic Limits Report. Tank waste compatibility assessments (CHG 2000) are performed prior to waste transfers to assess the final states of sending and receiving DSTs for compliance with the waste chemistry limits. The effects of waste transfers and new analytical data, where available, on tank waste volumes and compositions are included in the quarterly updates of the BBI and Caustic Limits Report and incorporated accordingly into the assessment process.

Figure 3-6. Chemistry Control Program Logic Diagram

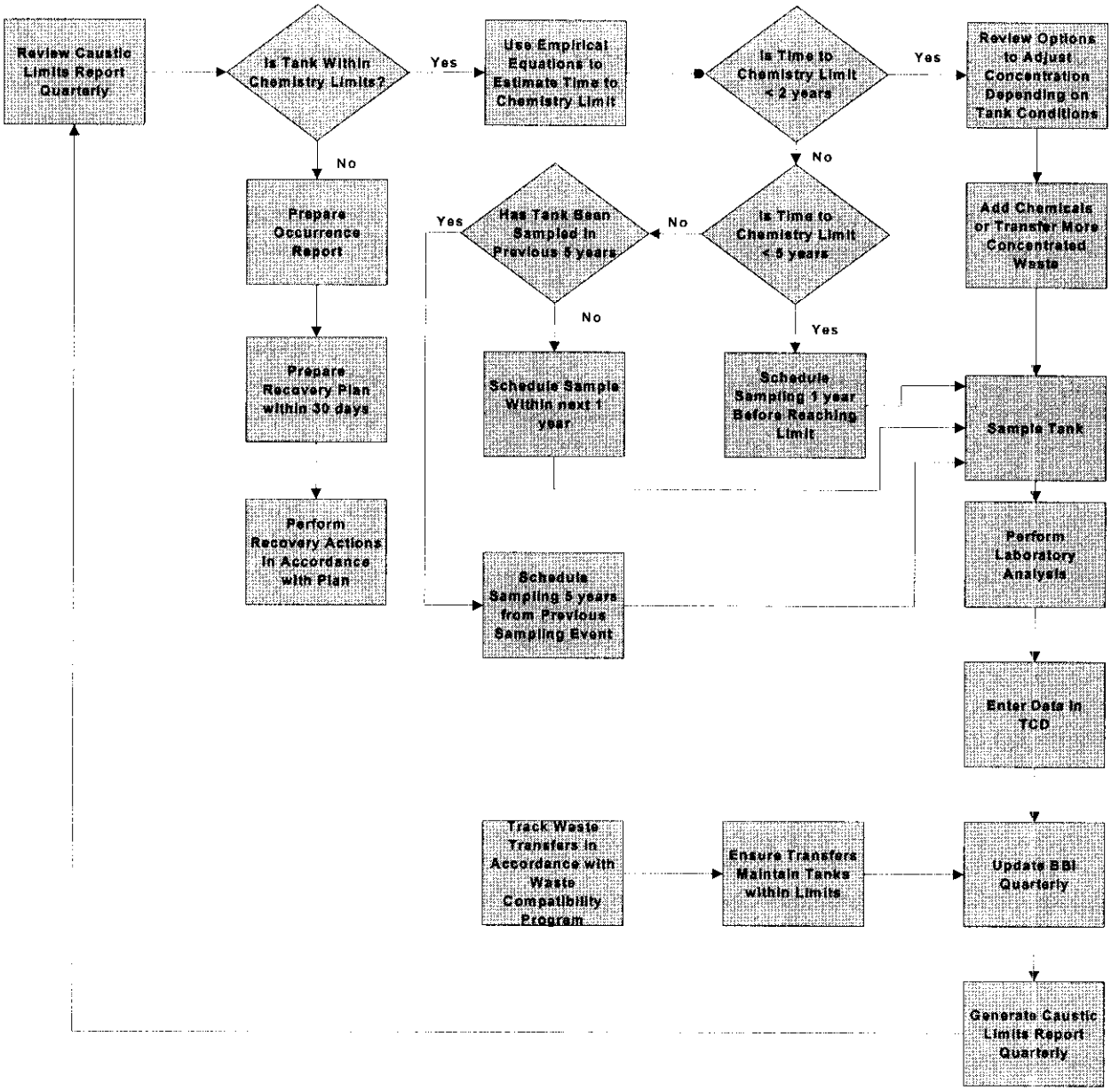


Table 3-1. Integrated Sampling Schedule and Preventative Action Requirements for the Chemistry Control Program

Fiscal Year	2001					2002					2003					2004					2005					2006					Comments (FY 2001) ♦ (Grab Sample) Θ (Core Sample)
Tank	Action Required					Action Required					Action Required					Action Required					Action Required					Action Required					
	Chemical Addition		Transfer Waste	Sample	Analysis	Chemical Addition		Transfer Waste	Sample	Analysis	Chemical Addition		Transfer Waste	Sample	Analysis	Chemical Addition		Transfer Waste	Sample	Analysis	Chemical Addition		Transfer Waste	Sample	Analysis	Chemical Addition		Transfer Waste	Sample	Analysis	
	OH^-	NO_2^-				OH^-	NO_2^-				OH^-	NO_2^-				OH^-	NO_2^-				OH^-	NO_2^-				OH^-	NO_2^-				
241-AN-101														♦	•																
241-AN-102				♦	•	•			♦ ♦	•				Θ	•				Θ	•											Recovery Plan in place
241-AN-103										•														Θ	•						Results from 2000 Sample
241-AN-104										•														Θ	•						Results from 2000 Sample
241-AN-105									Θ	•																					
241-AN-106				♦		•			♦	•																			♦	•	Sample After Transfer
241-AN-107				♦	•	•			♦ ♦	•				Θ	•				Θ	•											Recovery Plan in place
241-AP-101																								♦	•						
241-AP-102									♦	•																					
241-AP-103														♦	•	•			♦	•											
241-AP-104										•																			♦	•	Results from 2001 Sample
241-AP-105									Θ	•																					
241-AP-106														♦	•																
241-AP-107										•														♦	•						Results from 2000 Sample
241-AP-108			•	♦						•																			♦	•	Sample after Transfer
241-AW-101										•														Θ	•						Results from 2000 Sample
241-AW-102				* ♦				•		* •			•	* •	* •														♦	•	Evaporator Feed Tank *Sample and analyze sending tank. Calculate to confirm final conditions.
241-AW-103									Θ						•																
241-AW-104				Θ		•			♦	•																					Sample before and after
241-AW-105				Θ		•			♦	•																					Sample before and after
241-AW-106																								Θ	•						Evaporator Receipt Tank
241-AY-101				♦	•				Θ	•				Θ	•	•			♦	•											Recovery Plan in place
241-AY-102				♦	•		•		♦ Θ	•				Θ	•					•											Recovery Plan in place
241-AZ-101										•														Θ	•						Results from 2000 Sample
241-AZ-102						•			♦	•				Θ	•																Sample before and after
241-SY-101																								Θ	•						
241-SY-102																								Θ	•						
241-SY-103					•																			Θ	•						Results from 2000 Sample

3.4.2 Analysis and Sample Type Requirements

The analyses of samples to satisfy the requirements of the Chemistry Control Program are specified in the DQO for the Chemistry Control Program (Banning 2001).

The major analytical requirements specified in the DQO are summarized in this section. The waste chemistry limits are for the analytes OH^-, NO_2^-, and NO_3^- and can be found in the Technical Safety Requirements document (TSR) (CHG 2001). The DQO decision statements are listed below.

1. Determine whether or not the tank waste chemistry (supernatant and solids) meets the TSR waste chemistry limits and requires, or the application of the predictive empirical equations followed by the identification of future sampling or preventive actions.

2. Determine if additional waste chemistry criteria are needed.

3. Determine how certain waste components affect the TSR chemistry limit components (OH^-, NO_2^-, and NO_3^-).

To maintain the waste within the TSR limits and address the decision statements listed above, sampling and analyses will be required in two situations. The first situation is the sampling and analyses to determine if a tank meets the TSR limits (called initial sampling). The second is the sampling and analyses required after tank waste chemistry adjustments are made. Waste chemistry adjustments could be accomplished by adding chemicals to a tank, adding waste that is in compliance, mixing the waste (naturally or mechanically), or retrieving the waste.

Table 3-2 lists the information and data input needed to address the decision statements listed above. The data needs are listed along with the reason for inclusion (which decision statement is addressed), the type of waste analyzed, and any additional requirements or clarifications.

Analyses will be performed on three types of waste: supernatant, solids, and interstitial liquids from centrifuged solids. However, not all data inputs will be required for each waste type and not all waste types will be obtained in each sampling event. The information needed depends on the sampling situation (initial or after chemical adjustments) and the decision to be addressed by a specific analysis. Both initial sampling and sampling after waste chemistry adjustments are made will be conducted according to Table 3-3.

The supernatant will be sampled at the surface because the supernatant in a tank is expected to be fairly well mixed because of the thermal and density convection mechanisms. Solid samples will be obtained from the bottom of the solids layer. The bottom of the solids is the area with the least influence from the supernatant and will be the area most likely different from the supernatant. In addition, if the solids are greater than 60 inches deep, a sample will be taken just below the solids supernatant contact. This will provide an estimation of the range of waste compliance through the solids and provide better information to determine caustic consumption.

Table 3-2. Required Information and Reason for Inclusion. (2 Sheets)

Data Input	Reason for Inclusion (Number = Decision Statement Addressed)	Type of Material Analyzed and Comments
NO_3^-	1, 2, and 3	Supernatant and Interstitial (centrifuged) liquids. Each segment or grab.
NO_2^-	1, 2, and 3	Supernatant and Interstitial (centrifuged) liquids. Each segment or grab.
OH^-	1, 2, and 3	Supernatant and Interstitial (centrifuged) liquids. Each segment or grab.
pH	1, 2, and 3	Supernatant and Interstitial (centrifuged) liquids. Each segment or grab.
Na	See comment column.	Needed to evaluate pH data. Supernatant and Interstitial (centrifuged) liquids. Each segment or grab.
Cl^-	2	Supernatant and Interstitial (centrifuged) liquids. Each segment or grab.
F^-	2	Supernatant and Interstitial (centrifuged) liquids. Each segment or grab.
SO_4^{2-}	2	Supernatant and Interstitial (centrifuged) liquids. Each segment or grab.
PO_4^{3-}	2	Supernatant and Interstitial (centrifuged) liquids. Each segment or grab.
Al	3	Supernatant, Interstitial (centrifuged) liquids, and centrifuged solids. Each segment or grab.
TIC	3	Supernatant, Interstitial (centrifuged) liquids, and solids. Each segment or grab.
TOC	3	Supernatant, Interstitial (centrifuged) liquids, and solids. Each segment or grab.
$\%H_2O$	1 and 3	Supernatant and Interstitial (centrifuged) liquids. Each segment or grab.
Specific Gravity	1 and 3	Supernatant and Interstitial (centrifuged) liquids. Each segment.
Weight	1 and 3	Interstitial (centrifuged) liquids and centrifuged solids. Each segment.
Volume	1 and 3	Decanted (settled) solids, centrifuged solids, and centrifuged liquids. Each segment.
Caustic Demand Test	1	Supernatant and uncentrifuged solids (composite if two solid segments). Will only be conducted when waste analyses show it does not meet TSR chemistry limits.

Table 3-2. Required Information and Reason for Inclusion. (2 Sheets)

Data Input	Reason for Inclusion (Number = Decision Statement Addressed)	Type of Material Analyzed and Comments
Corrosion Potential	2	Interstitial (centrifuged) liquids or wet solids. A test plan will be prepared to control the tests.
Tank Supernatant and Solids Level (Volume)	1	From existing data.
Ventilation Rate	1	From existing data.

Notes:
TOC = Total organic carbon
TIC = Total inorganic carbon

When an initial sampling event is conducted, both the supernatant and solids will be sampled and analyzed. However, after adjustments are made to the waste chemistry in a tank, only the waste (supernatant or solids) that was out of compliance will be sampled and analyzed. Therefore, if only the supernatant samples were out of compliance, one grab sampling event will be conducted and only the surface of the supernatant sampled (first row of Table 3-3) regardless of the solids depth.

Table 3-3. Sampling Criteria

Solids Depth	Type of Sampling	Number and Location of Samples
< 25 inches	One grab sampling event from one riser.	One sample (consisting of two 125 ml bottles) at the surface of the supernatant is required. One bottle will be analyzed and the second archived.
25 to 60 inches	One core sampling event from one riser.	One sample (segment) as close to the supernatant surface as possible and one sample (segment) at the bottom of the solids.
> 60 inches	One core sampling event from one riser.	One sample (segment) as close to the supernatant surface as possible and two samples (segments) in the solids. One solids sample (segment) approximately three inches below the solids surface and one solids sample (segment) at the bottom of the solids.

The 25-inch minimum depth for a core is based on obtaining a full segment (19 inches) with a 3-inch safety margin at the bottom of the tank and a 3-inch contingency at the top of the segment to reduce the chance of commingling with the supernatant.

Sampling of the supernatant and solids will occur at different times after the chemistry of out-of-compliance waste is adjusted by adding chemicals, adding waste that is in compliance, mixing the waste (naturally or mechanically), or retrieving the waste. A supernatant sample will be taken (Table 3-3, row 1) 30 to 60 days after the chemistry adjustment, preferably, from a riser furthest from the riser used for the chemical adjustment. If the supernatant is still out of compliance, the existing recovery plan will be reviewed to determine if it covers planned recovery actions or should be revised to add additional recovery actions.

If the solids were initially out of compliance, samples of the solids will be obtained (Table 3-3, rows 2 or 3) between 12 and 18 months after adjustments to the waste are made. If these samples indicate the solids are still out of compliance, the waste will be sampled again (Table 3-3, rows 2 or 3). The timing for the second sampling event will be determined from the results of the first sampling and based on the planned recovery actions. This information will be specified in the recovery plan. The recovery plan describes all actions required to bring a tank back into compliance with the TSR chemistry limits.

4.0 TANK SPECIFIC FINDINGS

The following is a summary of the assessment of each DST against the sample priority attributes. Additional information on each tank is given in Appendix B on the sample history, estimated concentration of free hydroxide ion for depletion end dates of up to January 2006, and reprioritization of tank sampling. The schedule for sampling of the waste is based on Figure 3-6, Chemistry Control Program Logic Diagram. The schedule requires sampling the waste one-year before the estimated date for depletion of hydroxide ion to the lower limit or five years since the last sampling event. The sampling and laboratory analysis will follow the requirements in the Chemistry Control Program DQO (Banning 2001).

Tank 241-AN-101

The Hobbs equation was used to estimate depletion of free hydroxide ion of the dilute non-complexed (DN) waste in this tank. Results showed that the lower limit for free hydroxide ion should be maintained through January 2006. Tank 241-AN-101 was grab sampled in September 1995 and April 1998. Because the last sampling event was in 1998, a waste sample is needed by FY 2003.

Tank 241-AN-102

The Hobbs and Carothers equations were used for hydroxide ion depletion trending of the complexant concentrate (CC) waste in this tank. Depletion of October 1994 waste samples was compared to sample results from 1995 and 1998. The Carothers equation closely agreed with sample results while the Hobbs equation under-estimated depletion and gave slightly higher results. The Carothers equation was developed from data collected from tank 241-AN-102 and is expected to give good trending results.

Caustic addition to tank 241-AN-102 is scheduled for September 2001 in order to meet the free hydroxide ion requirement. Annual sampling of the waste is planned through FY 2004 to confirm that corrosion specification limits have been met. The mitigation sampling through September 2002 is satisfactory for the tank waste chemistry control program. Sampling of tank 241-AN-102 beyond mitigation will be based on preventative action requirements, Figure 3-6, and follow requirements in the Chemistry Control Program DQO (Banning 2001).

Tank 241-AN-103

The Hobbs equation was used to estimate the depletion of free hydroxide ion of the double-shell slurry (DSS) waste in this tank. Results showed that the lower limit for free hydroxide ion should be maintained through January 2006. Tank 241-AN-103 was core sampled in September 1996 and in February 2000 (WTP). Analytical data from the 2000 sampling event are needed for the chemistry control program. The next waste sample is needed by FY 2005.

Tank 241-AN-104

The Hobbs equation was used to estimate the depletion of free hydroxide ion of the double-shell slurry feed (DSSF) waste in this tank. Results showed that the lower limit for free hydroxide ion should be maintained through January 2006. Tank 241-AN-104 was core sampled in August 1996 and in August 2000 (WTP). Analytical data from the 2000 sampling event are needed for the chemistry control program. The next waste sample is needed by FY 2005.

Tank 241-AN-105

The Hobbs equation was used to estimate the depletion of free hydroxide ion of the DSSF waste in this tank. Results showed that the lower limit for free hydroxide ion should be maintained through January 2006. Tank 241-AN-105 was core sampled in June 1996. Because the last sampling event was in FY 1996, a waste sample is needed by FY 2001. Because of the number of chemistry control samples in FY 2001, it is recommended to defer waste sampling of tank 241-AN-105 to FY 2002.

Tank 241-AN-106

The Hobbs and Carothers equations were used to estimate depletion of free hydroxide ion of the CC waste. Results showed that the lower limit for free hydroxide ion was reached before March 2001 based on the Hobbs equation and should be maintained through January 2006 based on the Carothers equation. Tank 241-AN-106 was sampled in April 1989 and grab sampled in March 1995. Sampling of waste in this tank is needed in FY 2001 followed by chemical addition and verification sampling in FY 2002 in order to ensure compliance with tank waste chemistry requirements.

Tank 241-AN-107

The Hobbs and Carothers equations were used for hydroxide ion depletion trending of the CC waste in this tank. Hydroxide ion depletion of June 1985 and May 1993 waste samples was compared to sample results from 1993 and 1998. The hydroxide depletion of 1985 waste to 1993 waste closely followed the Carothers equation. Hydroxide depletion of 1985 waste to 1998 waste and 1993 waste to 1998 waste did not closely follow either equation.

Tank 241-AN-107 was grab sampled in February 2001. Plans are to add sodium hydroxide solution to tank 241-AN-107 in December 2001 and annually sample the waste through FY 2004. Mitigation sampling through June 2003 is satisfactory for the tank waste chemistry control program. Sampling of tank 241-AN-107 waste beyond mitigation will be based on preventative action requirements, Figure 3-6, and follow requirements in the Chemistry Control Program DQO (Banning 2001).

Tank 241-AP-101

The Hobbs equation was used to estimate the depletion of free hydroxide ion of the DSSF waste in this tank. Results showed that the lower limit for free hydroxide ion should be maintained through January 2006. Tank 241-AP-101 was grab sampled in February 2000. Because the last sampling event was in FY 2000, a waste sample is needed by FY 2005 depending on future plans for the tank.

Tank 241-AP-102

The Hobbs equation was used to estimate the depletion of free hydroxide ion of the concentrated phosphate (CP) waste in this tank. Results showed that the lower limit for free hydroxide ion should be maintained through January 2006. Because the last sampling event was in 1993, a waste sample is needed in FY 2001. Because of the number of chemistry control samples in FY 2001, it is recommended to defer sampling of tank 241-AP-102 waste until FY 2002.

Tank 241-AP-103

The Hobbs and Carothers equations were used to estimate the depletion of free hydroxide ion of the CC waste in this tank. Results showed that the lower limit for free hydroxide ion should be maintained through September 2004 based on the Hobbs equation and through January 2006 based on the Carothers equation. Sampling of this waste is needed by FY 2003. Tank 241-AP-103 waste was grab sampled in August 1999. This sampling date satisfies the one-year period before the estimated date of hydroxide ion depletion to the lower limit and the five-year period since the last sampling event.

Tank 241-AP-104

The Hobbs and Carothers equations were used to estimate the depletion of free hydroxide ion of the CC waste in this tank. Results showed that the lower limit for free hydroxide ion should be maintained through January 2006. Tank 241-AP-104 was grab sampled in October 1997 and January 2001 (analytical data not included in Caustic Limits Report for this evaluation). Most of the current waste added to tank 241-AP-104 was transferred from tank 241-SY-102 (grab sampled in January 2000). Analytical data from the 2001 sampling event are needed for the chemistry control program. The next waste sample is needed in FY 2006.

Tank 241-AP-105

The Hobbs equation was used to estimate the depletion of free hydroxide ion of the DSSF waste in this tank. Results showed that the lower limit for free hydroxide ion should be maintained through January 2006. Tank 241-AP-105 was grab sampled in September 1996 and core sampled in August 1997. Because the last sampling event was in FY 1997, a waste sample is needed in FY 2002.

Tank 241-AP-106

The Hobbs and Carothers equations were used to estimate the depletion of free hydroxide ion of the dilute complexed (DC) waste in this tank. Results showed that the lower limit for free hydroxide ion should be maintained through January 2006. Tank 241-AP-106 was grab sampled in November 1994, September 1996, August 1997, and in May 1998. Because the last sampling event was in FY 1998, a waste sample is needed in FY 2003.

Tank 241-AP-107

The Hobbs and Carothers equations were used to estimate the depletion of free hydroxide ion of the DC waste in this tank. Results showed that the lower limit for free hydroxide ion should be maintained through January 2006. Tank 241-AP-107 was grab sampled in August 1993, February 1995, May 1999, August 1999, and in December 2000 (analytical data not included in Caustic Limits Report for this evaluation). Analytical data from the 2000 sampling event are needed for the chemistry control program. The next waste sample is needed in FY 2005.

Tank 241-AP-108

The Hobbs equation was used to estimate the depletion of free hydroxide ion of the DN waste in this tank. Results showed that the lower limit for free hydroxide ion should be maintained through January 2002. Tank 241-AP-108 was grab sampled in January 1996, October 1997, September 1999, and in March 2000. Waste addition, followed by a verification sample of tank 241-AP-108 waste is needed by FY 2001 to ensure compliance with tank waste chemistry requirements.

Tank 241-AW-101

The Hobbs equation was used to estimate the depletion of free hydroxide ion of the DSSF waste in this tank. Results showed that the lower limit for free hydroxide ion should be maintained through January 2006. Tank 241-AW-101 was grab sampled in June 1990, May 1998, and in July 2000 (WTP). Analytical data from the FY 2000 sampling event are needed for the chemistry control program. The next waste sample is needed by FY 2005.

Tank 241-AW-102

The Hobbs equation was used to estimate the depletion of free hydroxide ion of the DN waste in this tank. Results showed that the lower limit for free hydroxide ion has been reached. Tank 241-AW-102 was grab sampled in January 1998 and in January 1999. Tank 241-AW-102 is the evaporator feed tank. It receives dilute waste from other DSTs, and end of campaign residual bottoms and water flushes of the evaporator. Actions are needed in FY 2001 to ensure continued compliance with tank waste chemistry requirements.

The waste in tank 241-AP-107 is the next batch scheduled for addition to tank 241-AW-102. The 241-AW-102 waste batch will be transferred to the evaporator by March 2002. It is recommended to transfer the waste from tank 241-AP-107 to tank 241-AW-102 in FY 2002. Engineering calculations are used to confirm final conditions and ensure that waste in both the sending and receiving tanks comply with tank waste chemistry requirements. Frequent filling and emptying of tank 241-AW-102 requires paying close attention to hydroxide ion depletion of stored waste and tank heel liquid.

Tank 241-AW-103

The Hobbs equation was used to estimate the depletion of free hydroxide ion of the DN waste in this tank. Results showed that the lower limit for free hydroxide ion should be maintained through January 2006. Tank 241-AW-103 was sampled in September 1994 and in August 1999. Because the last sampling event was in FY 1999, a sample is needed by FY 2004. Current plans are to sample the tank in FY 2002.

Tank 241-AW-104

The Hobbs equation was used to estimate the depletion of free hydroxide ion of the DN waste in this tank. Results showed that the lower limit for free hydroxide ion should be maintained through July 2001. Tank 241-AW-104 was grab sampled in July 1999 and in August 2000. It is recommended that this tank be sampled in FY 2001, followed by chemical addition and verification sampling in FY 2002 to ensure continued compliance with the chemistry limits.

Tank 241-AW-105

The Hobbs equation was used to estimate the depletion of free hydroxide ion of the DN waste in this tank. Results showed that the lower limit for free hydroxide ion has been reached. Tank 241-AW-105 was grab sampled in August 1995 and August 1996, and core sampled in May 1997. It is recommended that this tank be sampled in FY 2001, followed by chemical addition and verification sampling in FY 2002 to ensure continued compliance with the chemistry limits.

Tank 241-AW-106

The Hobbs equation was used to estimate the depletion of free hydroxide ion of the DSSF waste in this tank. Results showed that the lower limit for free hydroxide ion should be maintained through January 2006. Tank 241-AW-106 is currently the receiver tank for the 242-A Evaporator bottoms. It was grab sampled in August 1991, August 1995, January 1998, and May 2000. Because the last sampling event was in FY 2000, a waste sample is needed in FY 2005. Frequent filling and emptying of the tank require paying close attention to hydroxide ion depletion of stored waste and tank heel liquid.

Tank 241-AY-101

The Hobbs and Carothers equations were used for estimating the depletion of free hydroxide ion of the DC waste. Results showed that the after partial caustic addition in December 2000, the lower limit for free hydroxide ion should be maintained through May 2004 based on the Hobbs equation and January 2006 based on the Carothers equation. Mitigation added additional caustic to the tank in January 2001 and grab sampled the waste in February 2001. Annual waste sampling is planned through FY 2004. Mitigation sampling through February 2002 is satisfactory for the tank waste chemistry control program. Sampling of tank 241-AY-101 beyond mitigation will be based on preventative action requirements, Figure 3-6, and follow requirements in the Chemistry Control Program DQO (Banning 2001).

Tank 241-AY-102

The Hobbs equation was used to estimate the depletion of free hydroxide ion of the DN waste in this tank. Results showed that the lower limit for free hydroxide has been reached. Caustic addition to the tank was started in February 2001. Tank 241-AY-102 was grab and core sampled in March 2001. Mitigation will add sodium nitrite solution in November 2001 and annually sample the waste through FY 2002. Preventative action sampling extends the sampling of tank 241-AY-102 through FY 2003. Sampling of tank 241-AY-102 beyond mitigation will be based on preventative action requirements, Figure 3-6, and follow requirements in the Chemistry Control Program DQO (Banning 2001).

Tank 241-AZ-101

The Hobbs equation was used to estimate the depletion of free hydroxide ion of the DN/AW waste in this tank. Results showed that the lower limit for free hydroxide ion should be maintained through January 2006. Tank 241-AZ-101 was grab sampled in March 1995, core sampled in November 1999, grab sampled in March to May 2000 (for the mixer pump test), and core sampled in August 2000 (WTP). Analytical data from the FY 2000 sampling event are needed for the chemistry control program. The next waste sample is needed by FY 2005.

Tank 241-AZ-102

The Hobbs equation was used to estimate the depletion of free hydroxide ion of the DN/AW waste in this tank. Results showed that the lower limit for free hydroxide ion should be maintained through September 2001. Sampling of this waste is needed in FY 2002 followed by chemical addition and verification sampling in FY 2002 to ensure continued compliance with the chemistry limits. A core sample is planned in FY 2003.

Tank 241-SY-101

The Hobbs and Carothers equations were used to estimate the depletion of free hydroxide ion of the CC waste in this tank. Results showed that the lower limit for free hydroxide ion should be maintained through January 2006. Tank 241-SY-101 was grab sampled in March 1999 and in April 2000. Because the last sampling event was in FY 2000, a waste sample is needed in FY 2005.

Tank 241-SY-102

The Hobbs and Carothers equations were used to estimate the depletion of free hydroxide ion of the DC waste in this tank. Results showed that the lower limit for free hydroxide ion should be maintained through January 2006 based on October 2000 sample results. Tank 241-SY-102 was grab sampled in October 1995, January 1997, March 1998, September 1998, September 1999, January 2000, October 2000, and in December 2000 (analytical data not included in Caustic Limits Report for this evaluation). Tank 241-SY-102 is the cross-site transfer tank from 200 West Area to 200 East Area. Because the last sampling event was FY 2001, a sample of the current waste is needed by FY 2006. The current schedule is to sample the waste in FY 2005. Frequent filling and emptying of the tank require paying close attention to hydroxide ion depletion of stored waste and tank heel liquid and the chemistry control logic of Figure 3-6.

Tank 241-SY-103

The Hobbs and Carothers equations were used to estimate the depletion of free hydroxide ion of the CC waste in this tank. Results showed that the lower limit for free hydroxide ion should be maintained through January 2006 based on the August 1994 sample results. Tank 241-SY-103 was grab sampled in September 1994 and core sampled in March 2000. Analytical data from the FY 2000 sampling event are needed for the chemistry control program. The next waste sample is needed in FY 2005.

5.0 RECOMMENDATIONS

The waste chemistry evaluation confirmed previous findings that tank 241-AN-102, 241-AN-107, 241-AY-101, and 241-AY-102 should be currently under corrosion control surveillance and corrective actions. Sampling of the waste in these tanks is recommended in FYs 2002, 2003, and 2004 as part of the recovery plan and preventative actions.

It is predicted that tank 241-AN-106 could already be caustic deficient, and it is recommended that waste be sampled in FY 2001, followed by caustic addition and verification sampling in FY 2002 to ensure compliance with the chemistry limits.

It is predicted that tank 241-AW-105 could already be caustic deficient. It is recommended that this tank be sampled in FY 2001, followed by chemical addition and verification sampling in FY 2002 to ensure continued compliance with the chemistry limits.

Tank 241-AW-102 is the 242-A Evaporator feed tank, and it is subject to frequent filling and emptying with dilute wastes processed through the evaporator. The small waste heels that are left in this tank after waste is transferred to the evaporator and addition of end of campaign water flushes of the evaporator are particularly susceptible to hydroxide depletion because of their initially low concentration. Based on the Caustic Limits Report with an effective date of January 2001, the waste heel in tank 241-AW-102 could already be caustic deficient. This evaluation did not account for the waste transferred from tank 241-AW-104 in January 2001 and processed through the evaporator between January and March 2001. However, the waste transferred from tank 241-AW-104 was more dilute than the waste originally contained in tank 241-AW-102, and the waste heel now remaining in the tank is subject to rapid depletion. It is recommended that the next batch of waste (tank 241-AP-107) scheduled to be processed through the evaporator be transferred to this tank at the earliest opportunity and that an engineering calculation be undertaken based on sample analysis of the sending tank to confirm that both the sending and receiving tanks remain within specification. Additional evaporator operations are planned in FY 2002 and FY 2003. The need for further evaluations will be evaluated in subsequent revisions to this document.

It is predicted that tank 241-AP-108 could become hydroxide deficient within one year. It is recommended that waste be transferred into this tank in FY 2001 to adjust the free hydroxide ion concentration, followed by a verification sample in FY 2002.

It is projected that tanks 241-AW-104 and 241-AZ-102 could become caustic deficient within one year. It is recommended that tank 241-AW-104 be sampled in FY 2001, followed by chemical addition and verification sampling in FY 2002 to ensure continued compliance with the chemistry limits. It is recommended that tank 241-AZ-102 be sampled in FY 2002, followed by chemical addition and verification sampling in FY 2002.

It is projected that tanks 241-AP-103 and 241-AY-101 (after December 2000 caustic addition) could become hydroxide deficient in three years. Sampling of tank 241-AY-101 is covered by a

mitigation plan and preventative action sample schedule through FY 2004. It is recommended to sample tank 241-AP-103 in FY 2003.

The historical sampling schedule shows that it has been more than five years since tanks 241-AN-105, 241-AP-102, and 241-AP-105 were sampled. It is recommended to sample waste in these tanks in FY 2002 to check waste chemistry changes, verify compliance with AC 5.15, and develop the database for prediction of hydroxide ion depletion.

Tanks 241-AN-103 and 241-AN-104 were sampled in FY 2000 for the Waste Treatment Plant, ICD-23, and the samples archived. It is recommended to gain agreement to undertake analysis of a fraction of these archived samples to check the waste chemistry, verify compliance with AC 5.15, and develop the database for prediction of hydroxide ion depletion. Both tanks were previously sampled in FY 1996.

Tank 241-SY-103 was sampled in FY 2000, and tank 241-AP-104 was sampled in FY 2001. However, analytical data from these events are not yet available. Analytical data from these sampling events are needed to check the waste chemistry, verify compliance with AC 5.15, and develop the database for prediction of hydroxide ion depletion. Tank 241-SY-103 was previously sampled in FY 1994. Tank 241-AP-104 was previously sampled in FY 1998.

The analysis of archive must be completed as soon as possible because historical results have shown that both physical and chemical properties of archive samples change during prolonged storage. Should the archived samples noted above for analysis not be usable by the Chemistry Control Program, sampling of the identified tanks will be required before the times indicated in the schedule.

Table 3-1 lists the proposed DST and AWF tank sampling and analysis schedule through FY 2006 to satisfy the needs of AC 5.15, Chemistry Control Program. The table also identifies the preventive actions required to avoid going outside the established concentration limits. The need for chemical additions to tanks that are susceptible to depletion will be based on sample results. The sampling requirements shall be incorporated into the next annual revision of the TSB-WIRD. Actions for this fiscal year have been coordinated with the Characterization Program Office.

This technical basis report will be updated at least annually and the identified requirements incorporated in the TSB-WIRD to meet the needs of the Chemistry Control Program.

6.0 REFERENCES

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APPENDIX A

WASTE CHEMISTRY LIMITS EVALUATION

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ASSUMPTIONS

The following assumptions were used in the development of the spreadsheet, Table A-1.

- Convection and other natural forces mix the DST supernatant in the tank. Supernatant mixing maintains a near uniform concentration of waste constituents (as measured by the mean, lower 95 % confidence limit, and standard deviation values).
- The free hydroxide ion concentration is determined from the analytical laboratory titration method when the pH is > 12.5.
- The free hydroxide ion concentration is determined from the analytical laboratory pH measurement when the pH of the waste is < 12.5.
- The tank corrosion control limits are based on a waste temperature of less than 167 °F and the appropriate concentration range of nitrate ion.
- The sampling date of the tank waste is used as start date for depletion the free hydroxide ion.
- The limiting hydroxide ion concentration for hydroxide ion depletion calculation is based on the corrosion control limitations and the mean concentration of nitrate and nitrite ions.
- Two empirical equations are used to predict or model the depletion of free hydroxide ion.
    - The Hobbs equation is based on adsorption of carbon dioxide from air ventilation of the waste tank and uses an average value for fraction of carbon dioxide absorbed by the supernatant. The equation is used for depletion prediction and historical trending (when applicable) of all waste types and end dates of up to January 2006.
    - The Carothers equation is based on observations of actual phenomena for complexed concentrate waste stored in tank 241-AN-102. The equation is applicable to tank 241-AN-107 based on recent information from Reynolds (See Appendix C). There was no attempt to postulate a reaction mechanism. The equation included any hydroxide consumption by CO_2 absorption, complexant oxidation, and hydrated aluminum oxide reactions (if any). The equation is used for hydroxide depletion prediction and historical trending (when applicable) of CC and DC wastes and end dates of up to January 2006. It complements the predictions by Hobbs.
- There is no correction for floating crusts.
- The average fraction of CO_2 adsorbed by the tank waste was used in place of a single hydroxide composition as described in the Hobbs equation.
- The DST ventilation rates are based on information by Hu (2001).

Table A-1 Summary of Waste Tank Chemistry Conditions For Chemistry Control Program

Tank	Waste	Waste Analysis Basis		OH mol/l			Mean mol/l				Mean Based [NO2] Limits: [NO2]≤1.0 mol/l, [NO2]/([OH]+[NO2])	1.0<[NO2]≤3.0, [NO2] mol/l	[NO2]>3.0, [OH] + [NO2] mol/l	Lower [OH] Limit	Lower [OH] Limit Based [NO2] Limits: [NO2]≤1.0 mol/l, [NO2]/([OH]+[NO2])	1.0<[NO2]≤3.0, [NO2] mol/l	[NO2]>3.0, [OH] + [NO2] mol/l	Vent Rate	Waste Vol	Date and Estimated OH Concentrations (mol/l)											
																			Based on Mean OH								Based on 95% or S Deviation LL OH					
																			Hobbs				Carothers				Hobbs				Carothers	
241-	Type	Date	Sample/Calc.	Mean	Confidence Level Lower 95% Limit	S Deviation Lower Limit	[NO3]	[NO2]	[Al]	[TOC]	<2.5 Limit	≥0.011 to ≤5.5	≥0.4([NO2])	≥ 1.2 mol/l	mol/l	<2.5 Limit	≥0.011 to ≤5.5	≥0.4([NO2])	≥ 1.2 mol/l	CFM	K Gal											
AN-101	DN	9/1/95	Sup Sample	1.85	1.65	1.60	1.56	1.05			NA	NA	TRUE	NA	0.16	NA	NA	TRUE	NA	113	1010	NA		NA		NA		NA		NA		NA	
	DN	4/8/98	Sup Sample	1.17	NA	NA	1.1	0.83	0.37	0.09	NA	NA	TRUE	NA	0.11	NA	NA	TRUE	NA	113	224	Mar-01	1.04	Jan-06	0.82	NA		NA		NA		NA	
AN-102	CC	10/21/94	Sup Sample	0.23	NA	NA	3.63	1.80			NA	NA	NA	TRUE	0.30	NA	NA	NA	TRUE	119	995					Caustic to be added during FY 2001							
	CC	11/30/95	Sup Sample	0.192	NA	NA	NA	NA												119	995	10/94-11/95	0.22			10/94-11/95	0.26						
	CC	2/1/98	SupSample	0.156	0.14	NA	3.82	2.05	0.60	2.15	NA	NA	NA	TRUE	0.30	NA	NA	NA	TRUE	119	965	11/95-2/98	0.17			11/95-2/98	0.15						
	CC	2/1/98	SupSample	0.156	0.14	NA	3.82	2.05	0.60	2.15	NA	NA	NA	TRUE	0.30	NA	NA	NA	TRUE	119	965	Mar-01	0.10	NA		Mar-01	0.08	NA		Mar-01	0.09	NA		Mar-01	0.07	NA
AN-103	DSS	9/1/96	Sup Sample	4.92	3.97	NA	2.69	3.56	1.11	0.22	NA	NA	TRUE	NA	0.27	NA	NA	TRUE	NA	100	497	Mar-01	4.83	Jan-06	4.72	NA		NA		Mar-01	3.88	Jan-06	3.78	NA		NA	
AN-104	DSSF	8/1/96	Sup Sample	4.21	3.83	NA	2.77	2.44	1.44	0.26	NA	NA	TRUE	NA	0.28	NA	NA	TRUE	NA	100	550	Mar-01	4.12	Jan-06	4.03	NA		NA		Mar-01	3.74	Jan-06	3.65	NA		NA	
AN-105	DSSF	6/10/96	Sup Sample	3.40	3.29	NA	2.6	2.63	1.52	0.30	NA	NA	TRUE	NA	0.26	NA	NA	TRUE	NA	100	636	Mar-01	3.33	Jan-06	3.25	NA		NA		Mar-01	3.21	Jan-06	3.14	NA		NA	
AN-106	CP	4/12/89	Sup Sample	0.47	NA	NA	1.01	0.64			NA	NA	TRUE	NA	0.10	NA	NA	TRUE	NA	117	1030									NA		NA		NA		NA
	CC	4/1/95	Sup Sample	0.85	NA	NA	1.14	0.41	0.13	0.39	NA	NA	TRUE	NA	0.11	NA	NA	TRUE	NA	117	403/21	Mar-01	0.00001	NA	NA	Mar-01	0.45	Jan-06	0.27	NA		NA		NA		NA
AN-107	CC	2/28/85	Sample	0.05	NA	NA	NA	NA			NA	NA	NA	NA		NA	NA	NA	NA																	
	CC	6/29/85	Sample	0.06	NA	NA	NA	NA			NA	NA	NA	NA		NA	NA	NA	NA	129	1106					Caustic to be added during FY 2001							
	CC	5/13/93	Sample	0.02	NA	NA	NA	NA			NA	NA	NA	NA	0.30	NA	NA	NA	NA	129	933	6/85-5/93	0.00256			6/85-5/93	0.023			NA		NA		NA		NA
	CC	4/17/98	Sup Sample (pH)	0.00105	NA	NA	3.86	1.44			NA	NA	NA	TRUE	0.30	NA	NA	NA	TRUE	129	794	6/85-4/98	4.11E-05			6/85-4/98	0.013			NA		NA		NA		NA
	CC	4/17/98	Sup Sample (pH)	0.00105	NA	NA	3.86	1.44	0.01	3.45	NA	NA	NA	TRUE	0.30	NA	NA	NA	TRUE	129	794	5/93-4/98	2.44E-05			5/93-4/98	0.012			NA		NA		NA		NA
	CC	4/17/98	Sup Sample (pH)	0.00105	NA	NA	3.86	1.44	0.01	3.45	NA	NA	NA	TRUE	0.30	NA	NA	NA	TRUE	129	794	Mar-01	0.000002	NA		Mar-01	0.001	NA		NA		NA		NA		NA
AP-101	DSSF	11/13/95	Sup Sample	2.91	2.68	NA	2.48	0.91			NA	NA	TRUE	NA	0.25	NA	NA	TRUE	NA		737															
	DSSF	2/8/00	Sup Sample	2.43	2.30	NA	2.13	0.91	0.26	0.16	NA	NA	TRUE	NA	0.21	NA	NA	TRUE	NA	108	1114	Mar-01	2.42	Jan-06	2.37	NA		NA		Mar-01	2.29	Jan-06	2.24	NA		NA	
AP-102	CP	4/30/93	Sup Sample	0.54	0.46	NA	1.27	0.83	0.43	0.28	NA	NA	TRUE	NA	0.13	NA	NA	TRUE	NA	135	1089	Mar-01	0.46	Jan-06	0.41	NA		NA		Mar-01	0.38	Jan-06	0.33	NA		NA	
AP-103	DN	9/24/91	Sample	0.08	NA	NA															1033															
	DN	8/21/97	Sup Sample	0.000929	0.000621	NA	0.059	0.04			TRUE	TRUE	NA	NA	0.01	TRUE	TRUE	NA	NA		27															
	DN	4/1/98	Sup Sample	0.000147	0.0000991	NA	0.063	0.04			TRUE	TRUE	NA	NA	0.01	TRUE	TRUE	NA	NA		25															
	CC	8/12/99	Sup Sample	0.67	0.51	NA	2.21	2.34	0.32	0.32	NA	NA	TRUE	NA	0.22	NA	NA	TRUE	NA	200	282	Mar-01	0.47	Aug-05	0.22	Mar-01	0.48	Jan-06	0.28	Mar-01	0.42	Sep-04	0.22	Mar-01	0.43	Jan-06	0.26
AP-104	DN	1/24/96	Sup Sample	0.03	0.03	NA	0.047	0.02			TRUE	TRUE	NA	NA	0.01	TRUE	TRUE	NA	NA		1126															
	DN	10/6/97	Sup Sample	0.000141	0.0000450	NA	0.094	0.03			FALSE	NA	NA	NA	0.01	TRUE	TRUE	NA	NA		26	1/96-10/97	6.90E-07			NA	NA								
	CC	1/10/00	Sup Sample (SY-102)	0.75	NA	NA	1.68	1.29	0.64	0.43	NA	NA	TRUE	NA	0.17	NA	NA	TRUE	NA	71	1109	Mar-01	0.74	Jan-06	0.71	Mar-01	0.66	Jan-06	0.39	NA		NA		NA		NA	
AP-105	DN	9/3/96	Sup Sample	1.97	NA	NA	1.6	1.02			NA	NA	TRUE	NA	0.16	NA	NA	TRUE	NA		970															
	DN	7/14/97	Core Sample	2.46	NA	NA	2.96	1.29			NA	NA	TRUE	NA	0.30	NA	NA	TRUE	NA		617															
	DSSF	5/24/00	Sup Sample (AW-106)	0.70	NA	NA	3.85	2.22	0.78	0.24	NA	NA	NA	TRUE	0.30	NA	NA	NA	TRUE	176	1045	Mar-01	0.69	Jan-06	0.67	NA		NA		NA		NA		NA		NA	
AP-106	DN	11/18/94	Sample	0.31	NA	NA															819															
	DN	9/12/96	Sup Sample	0.72	NA	NA	0.87	0.29			TRUE	TRUE	NA	NA	0.06	TRUE	TRUE	NA	NA		246															
	DN	8/27/97	Sup Sample	0.36	NA	NA	0.26	0.43			TRUE	TRUE	NA	NA	0.01	TRUE	TRUE	NA	NA		340															
	DN	5/28/98	Sup Sample	0.66	NA	NA	0.68	0.31			TRUE	TRUE	NA	NA	0.01	TRUE	TRUE	NA	NA		373															
	DC	2/25/00	Sup Sample (SY-102)	0.76	NA	NA	1.47	1.28	0.56	0.46	NA	NA	TRUE	NA	0.15	NA	NA	TRUE	NA	111	623	Mar-01	0.74	Jan-06	0.67	Mar-01	0.68	Jan-06	0.40	NA		NA		NA		NA	
AP-107	DN	8/13/93	Sample	0.01		NA															1114															
	DN	2/1/95	Sample	0.32		NA															996															
	DN	5/18/99	Sup Sample	0.36	0.12	NA	1.18	0.41			NA	NA	TRUE	NA	0.12	NA	NA	TRUE	NA		705															
	DN	8/31/99	Sup Sample	0.57	0.55	NA	1.54	0.61			TRUE	TRUE	NA	NA	0.15	TRUE	TRUE	NA	NA		977															
	DC	10/2/00	Sup Sample (SY-102)	0.81	NA	NA	1.59	1.31	0.56	0.34	NA	NA	TRUE	NA	0.16	NA	NA	TRUE	NA	342	986	Mar-01	0.80	Jan-06	0.65	Mar-01	0.78	Jan-06	0.46	NA		NA		NA		NA
AP-108	DN	1/4/96	Sup Sample	0.16																																
	DC	10/10/97	Sup Sample	0.56			0.81	0.29			TRUE	TRUE	NA	NA	0.04	TRUE	TRUE	NA	NA																	
	DN	9/22/99	Sup Sample	0.72	0.44	NA	1.44	0.70			NA	NA	TRUE	NA	0.14	NA	NA	TRUE	NA																	
	DN	3/1/00	Sup Sample	0.73	0.68	NA	1.29	0.62	0.35	0.08	NA	NA	TRUE	NA	0.13	NA	NA	TRUE	NA	129	32	Mar-01	0.39	Mar-02	0.13	NA		NA		Mar-01	0.34	Jan-02	0.13	NA		NA	

Table A-1 Summary of Waste Tank Chemistry Conditions For Chemistry Control Program

Tank	Waste	Waste Analysis Basis			OH mol/l			Mean mol/l				Mean Based [NO2] Limits					Lower [OH] Limit	Lower [OH] Limit Based [NO2] Limits					Vent Rate	Waste Vol	Date and Estimated OH Concentrations (mol/l)											
												[NO2]≤1.0 mol/l		1.0<[NO2]≤3.0		[NO2]>3.0		[NO2]≤1.0 mol/l		1.0<[NO2]≤3.0		[NO2]>3.0			Based on Mean OH						Based on 95% or S Deviation LL OH					
												[NO2]/([OH]+[NO2])	[NO2] mol/l	[OH] + [NO2] mol/l				[NO2]/([OH]+[NO2])	[NO2] mol/l	[OH] + [NO2] mol/l					Hobbs				Carothers		Hobbs				Carothers	
241-	Type	Date	Sample/Calc.	Mean	Confidence Level Lower 95% Limit	S Deviation Lower Limit	[NO2]	[NO2]	[Al]	[TOC]	<2.5 Limit	≥0.011 to ≤5.5	≥0.4([NO2])	> 1.2 mol/l	mol/l	<2.5 Limit	≥0.011 to ≤5.5	≥0.4([NO2])	> 1.2 mol/l	CFM	K Gal													
AW-101	DSSF	6/28/90	Sup Sample	5.07	4.96	NA	3.46	2.20			NA	NA	NA	TRUE	0.30	NA	NA	NA	TRUE		1122														
	DSSF	4/22/98	Sup Sample	5.64	5.53	NA	2.74	2.61	1.22	0.33	NA	NA	TRUE	NA	0.27	NA	NA	TRUE	NA	100	739	Mar-01	5.60	Jan-06	5.53	NA	NA	Mar-01	5.49	Jan-06	5.42	NA	NA
AW-102	DN	6/5/91	Sample	0.18	0.15	NA	0.23	0.06			TRUE	TRUE	NA	NA	0.04	TRUE	TRUE	NA	NA															
	DN	8/25/95	Sup Sample	0.60																														
	DC	1/14/98	Sup Sample	0.29	NA	NA	0.54	0.51			TRUE	TRUE	NA	NA	0.01	TRUE	TRUE	NA	NA															
	DN	1/29/99	Sup Sample	0.44	0.41	NA	0.28	0.15			TRUE	TRUE	NA	NA	0.01	TRUE	TRUE	NA	NA	292	976/34	Mar-01	0.000963	NA		NA	NA	NA		NA		NA	NA
	DN	8/30/99	Sup Sample (AP-107)	0.41	NA	NA	0.99	0.41	0.22	0.06	TRUE	TRUE	NA	NA	0.01	TRUE	TRUE	NA	NA															
AW-103	DN	9/24/94	Sup Sample	0.19	NA	NA	0.06	0.03			TRUE	TRUE	NA	NA	0.01	TRUE	TRUE	NA	NA															
	DN	8/25/99	Sup Sample	0.57	NA	NA	0.07	0.04	0.002	0.06	TRUE	TRUE	NA	NA	0.01	TRUE	TRUE	NA	NA	134	196	Mar-01	0.48	Jan-06	0.21	NA	NA	NA		NA		NA	NA
AW-104	DN	9/28/94	Sup Sample	0.20											0.01																			
	DN	7/15/99	Sup Sample	0.21	NA	0.09	0.27	0.12			TRUE	TRUE	NA	NA	0.01	TRUE	TRUE	NA	NA	141	882	9/94-8/00	0.13											
	DN	8/23/00	Sup Sample	0.11	0.02	0.08	0.14	0.04	0.004	0.05	TRUE	TRUE	NA	NA	0.03	TRUE	TRUE	NA	NA	141	895/94	Mar-01	0.09	Oct-01	0.03	NA	NA	Mar-01	0.07	Jul-01	0.03	NA	NA
AW-105	DN	8/29/95	Sup Sample	0.23	NA	NA	0.27	0.02			TRUE	TRUE	NA	NA	0.09	TRUE	TRUE	NA	NA															
	DN	8/27/96	Sup Sample	0.21	NA	0.19	0.42	0.03			TRUE	TRUE	NA	NA	0.14	TRUE	TRUE	NA	NA	194	172													
	DN	5/9/97	Sup Core Sample	0.40	NA	0.37	0.55	0.06	0.01	0.08	TRUE	TRUE	NA	NA	0.17	TRUE	TRUE	NA	NA	194	172	Mar-01	0.87	NA		NA	NA	Mar-01	0.06	NA		NA	NA
AW-106	DN	8/21/91	Sample	0.58																														
	DSSF	8/24/95	Sup Sample	1.63																														
	DSSF	5/1/97	Sup Sample	0.58	0.51	NA	1.94	2.14			NA	NA	TRUE	NA	0.19	NA	NA	TRUE	NA															
	CC	1/12/98	SupSample	0.58	0.50	NA	1.94	2.13			NA	NA	TRUE	NA	0.19	NA	NA	TRUE	NA															
	DSSF	5/5/00	Sup Sample	0.56	NA	NA	1.37	3.16			NA	NA	TRUE	NA	0.14	NA	NA	TRUE	NA															
	DSSF	5/24/00	Sup Sample	0.70	NA	NA	3.09	1.38	0.74	0.18	NA	NA	NA	TRUE	0.30	NA	NA	NA	TRUE	158	500	Mar-01	0.68	Jan-06	0.54	NA	NA	NA		NA		NA	NA
AY-101	DC	2/28/85	Sample	0.30	NA	NA															687													
	DC	3/14/85	Sample	0.88	NA	NA															714													
	DC	6/23/87	Sample	0.13	NA	NA														250	839													
	DC	7/20/88	Sample	0.47	NA	NA														250	941													
	DC	2/28/96	Sample Sup (pH)	0.0000602	0.0000562	NA	0.42	0.77			TRUE	TRUE	NA	NA	0.01	TRUE	TRUE	NA	NA	250	849													
	DC	3/19/97	Sample Sup (pH)	0.0000302	0.0000105	NA	0.19	1.17			TRUE	TRUE	NA	NA	0.01	TRUE	TRUE	NA	NA	250	808	2/96-5/97	0.00002			2/96-5/97	0.000053								
	DC	12/19/00	Sample Sup	1.69	NA	NA	0.19	1.17	0.001	0.25	TRUE	TRUE	NA	NA	0.01	TRUE	TRUE	NA	NA	250	37	Mar-01	1.56	May-04	0.81	Mar-01	1.65	Jan-06	0.97	NA		NA	NA		NA
	DC	1/1/00	Liq Sludge (pH)	0.0000525	NA	NA	0.11	1.42	0.02	0.25	TRUE	TRUE	NA	NA	0.01	TRUE	TRUE	NA	NA		16	NA		NA		Mar-01	0.000046	Jan-06	0.000027	NA		NA	NA		NA
AY-102	DN	10/5/96	Sup Sample	0.15	NA	NA	0.007	0.02			TRUE	TRUE	NA	NA	0.01	TRUE	TRUE	NA	NA	250														
	DN	1/16/98	Sup Sample	0.07	NA	NA	0.106	0.05			TRUE	TRUE	NA	NA	0.01	TRUE	TRUE	NA	NA	250														
	DN	7/7/98	Sup Sample	0.58	NA	NA	0.008	0.03			TRUE	TRUE	NA	NA	0.01	TRUE	TRUE	NA	NA	250								Caustic added during June - July 1998							
	DN	8/26/99	Sup Sample	0.11	NA	NA	0.01	0.15			TRUE	TRUE	NA	NA	0.01	TRUE	TRUE	NA	NA	250								Caustic added during July 1998							
	DN	10/14/99	Sup Sample	0.09	0.02	NA	0.007	0.16			TRUE	TRUE	NA	NA	0.01	TRUE	TRUE	NA	NA	250	403	10/99-1/00	0.08	NA		NA		NA		10/99-1/00	0.013				
	DN	1/5/00	Sup Sample (pH)	0.00856	0.0079	NA	0.0056	0.17	0.05	0.17	TRUE	TRUE	NA	NA	0.01	TRUE	TRUE	NA	NA	250	395	Feb-01	0.000002					Caustic added during February 2001							
AZ-101	AW	3/3/95	Sup Sample	0.67	0.61	NA	1.06	1.23			NA	NA	TRUE	NA	0.11	NA	NA	TRUE	NA															
	DN/AW	11/10/99	Core Comp Sample	0.62	NA	NA	1.06	1.45	0.29	0.03	NA	NA	TRUE	NA	0.11	NA	NA	TRUE	NA	150	865	Mar-01	0.60	Jan-06	0.53	NA		NA		NA		NA		NA
AZ-102	AW	2/23/95	Sup Sample	0.11	0.08	NA	0.38	0.60			TRUE	TRUE	NA	NA	0.01	TRUE	TRUE	NA	NA	112	853/820	2/95-5/99	0.07												
	DN/AW	8/1/99	Sample Core Comp (pH)	0.04	0.02	NA	0.28	0.72	0.02	0.09	TRUE	TRUE	NA	NA	0.01	TRUE	TRUE	NA	NA	112	892	Mar-01	0.03	Jan-04	0.01	NA		NA		Mar-01	0.013	Sep-01	0.01	NA		NA
SY-101	CC	3/30/99	Push Sample	3.25	NA	NA																												
	CC	4/1/00	Sup Sample	1.55	1.35	NA	2.27	1.91	0.60	0.51	NA	NA	TRUE	NA	0.23	NA	NA	TRUE	NA	461	694	Mar-01	1.49	Jan-06	1.19	Mar-01	1.40	Jan-06	0.82	Mar-01	1.29	Jan-06	1.00	Mar-01	1.22	Jan-06	0.72
SY-102	DN	10/20/95	Sup Sample	0.25		NA																												
	DN	1/14/97	Sup Sample	0.35		NA																												
	DN	3/10/98	Sup Sample	0.07		NA																												
	DN	9/23/98	Sup Sample	0.18	0.09	NA	0.84	0.29			TRUE	TRUE	NA	NA	0.05	TRUE	TRUE	NA	NA															
	DN	9/9/99	Sup Sample	1.03	0.97	NA	2.05	1.02			NA	NA	TRUE	NA	0.21	NA	NA	TRUE	NA															
	DN	1/10/00	Sup Sample	0.96	0.25	NA	1.96	1.26			NA	NA	TRUE	NA	0.20	NA	NA	TRUE	NA															
	DC	10/2/00	Sup Sample	0.81	NA	NA	1.49	1.39	0.69	0.25	NA	NA	TRUE	NA	0.15	NA	NA	TRUE	NA	363	759	Mar-01	0.79	Jan-06	0.59	Mar-01	0.78	Jan-06	0.45	NA		NA		NA		NA
SY-103	CC	8/1/94	Sup Sample	1.7	1.42	NA	2.84	3.06	1.28	0.82	NA	NA	TRUE	NA	0.28	NA	NA	TRUE	NA	115	359	Mar-01	1.50	Jan-06	1.36	Mar-01	0.83	Jan-06	0.49	Mar-01	1.23	Jan-06	1.09	Mar-01	0.69	Jan-06	0.41

Liq = Liquid
Comp = Composite
Sup = Supernatant
(Tank) = Based on sample from identified tank
(pH) = OH concentration calculated from pH measurement of <12.5
NA = Not Available or Not Applicable
TOC = Total organic carbon

AW = Aging Waste
CC = Concentrated Complexed
CP = Concentrated Phosphate
DC = Dilute Complexed
DN = Dilute Supernatant
DSS = Double Shell Slurry
DSSF = Double Shell Slurry Feed

APPENDIX B

TANK SPECIFIC ASSESSMENTS

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APPENDIX B

TANK SPECIFIC ASSESSMENTS

This appendix summarizes the tank specific depletion of free hydroxide ion in the DSTs. The hydroxide depletion was based on DST sampling information and the best-basis liquid waste concentration information for free hydroxide, nitrite, and nitrate ions extracted from the TWINS database and listed in the baseline Caustic Limits Report. The free hydroxide ion concentration at the mean (average) and lower limit at the 95 percent confidence level or lower limit at one standard deviation (SD) were used for starting values. The concentration of free hydroxide was determined from the pH measurement for pHs of less than 12.5. The mean concentrations were used for the nitrate and nitrite ions. The Hobbs and Carothers equations for free hydroxide depletion were used to predict the future free hydroxide concentration over the next five-year period and trend historical sample results where possible. The Hobbs equation was used for all waste types and the Carothers equation was used for only the CC and DC waste types. The calculations were based on Equations 14 and 15 of Sections 3.2.1 and 3.2.2. The low limit hydroxide concentration was based on the corrosion control guidelines for waste temperature of less than 167 °F. The waste sampling date is based on a one-year period before the estimated depletion of hydroxide ion to the lower limit or a five-year period since the last sampling event.

B1.1 Tank 241-AN-101

Tank 241-AN-101 contains about 225 kgal of dilute non-complexed supernatant (DN) waste and was last grab sampled in April 1998. The tank was maintained near a surface level of approximately 50 inches from October 1996 to April 2000. Saltwell liquid from tanks 241-A-101 and 241-AX-101 and possibly a small volume of supernatant from tank 241-AN-102 will be added and fill tank 241-AN-101 to approximately 85 inches (231 kgal) by August 2003. Future plans call for transferring the combined wastes in tank 241-AN-101 to tank 241-AN-106. The tank will be cleaned out for use as an intermediate staging tank in fiscal year (FY) 2005 (Strode and Boyles 2000).

The Hobbs equation was used to predict free hydroxide ion concentration of the DN waste to end dates of March 2001 and January 2006. The results are listed in Table B-1 and show that the lower limit for free hydroxide ion (0.11 M) should be maintained through January 2006. Because the last sampling event was in 1998, a waste sample is needed in FY 2003. A sampling date of FY 2003 is at the end of waste addition from tanks 241-A-101 and 241-AX-101. The sampling and laboratory analysis will follow the requirements in the Chemistry Control Program DQO (Banning 2001).

Table B-1. Estimated Hydroxide Concentrations of Tank 241-AN-101 Supernatant Based on Current Static Waste Storage Conditions

Based on Average OH	
End Date Mar. 2001	End Date Jan. 2006
Hobbs Equation OH M	
1.04	0.82

B.1.1 Tank 241-AN-102

Tank 241-AN-102 contains approximately 965 kgal of complexant concentrate (CC) waste. The tank was grab sampled in August 2000 for the Waste Treatment Plant contract, and no analytical results have been entered into the TWINS database at this time. The tank was previously grab sampled in February 1998. The current plan for this tank is to transfer a small amount of waste to tank 241-AN-101, if necessary to test the pump transfer, add concentrated sodium hydroxide, grab sample the waste in August and September 2001, and then annually sample the waste through FY 2004. This sample schedule is based in mitigation and preventative action requirements. The tank surface level decreased from approximately 395 inches in October 1994 to 385 inches in early January 2001. This liquid loss was by evaporation. There is no plan through FY 2006 to transfer the tank 241-AN-102 waste to another tank (Strode and Boyles 2000).

Table B-2 lists the trended concentrations of free hydroxide ion based on the Hobbs and Carothers equations and sample results. Estimated hydroxide depletion for November 1995 was developed from the waste samples taken in October 1994. Estimated hydroxide depletion for February 1998 was developed from November 1995 sample results. Estimated hydroxide depletion for March 2001 was developed from February 1998 sample results.

The Hobbs equation under estimated hydroxide ion depletion gave slightly higher concentrations. The Carothers equation closely agrees with sample results because it was based on data collected from tank 241-AN-102. The corrosion control specification limit for the tank waste is 0.3 M free hydroxide ion. Mitigation sampling through September 2002 is satisfactory for the tank waste chemistry control program. After mitigation, sampling of tank 241-AN-102 will be based on preventative action requirements, Figure 3-6, and follow requirements in the Chemistry Control Program DQO (Banning 2001).

Table B-2. Comparisons of Depletion Estimated and Laboratory Results of Hydroxide Concentrations in Tank 241-AN-102 Supernatant

Oct. 1994 Average OH	Nov. 1995 Average OH			Feb. 1998 Average OH			Mar. 2001 Average OH	
Lab OH M	Hobbs OH M	Carothers OH M	Lab OH M	Hobbs OH M	Carothers OH M	Lab OH M	Hobbs OH M	Carothers OH M
0.23	0.22	0.20	0.19	0.17	0.15	0.16	0.1	0.08

B.1.3 Tank 241-AN-103

Tank 241-AN-103 contains approximately 500 kgal of double shell slurry (DSS) waste. The tank was core sampled in September 1996 and February 2000 (WTP). There are no waste transaction plans for this tank through FY 2006 (Strode and Boyles 2000).

The Hobbs equation was used to predict free hydroxide ion concentration of the DSS waste for end dates of March 2001 and January 2006 based on September 1996 sample results. The results

are listed in Table B-3 and show that the corrosion control lower limit for free hydroxide ion (0.27 M) should be maintained through January 2006. The last sampling event was in FY 2000 for WTP. The results will be made available to the chemistry control program. Therefore, the next waste sample is needed in FY 2005. The sampling and laboratory analysis will follow the requirements in the Chemistry Control Program DQO (Banning 2001).

Table B-3. Estimated Hydroxide Concentrations of Tank 241-AN-103 Supernatant Based on Current Static Waste Storage Conditions

95 % LL OH Sample Result		Average OH Sample Result	
End Date Mar. 2001	End Date Jan. 2006	End Date Mar. 2001	End Date Jan. 2006
Hobbs Equation OH M			
3.88	3.78	4.83	4.72

Note: LL = lower limit

B.1.4 Tank 241-AN-104

Tank 241-AN-104 contains approximately 550 kgal of double shell slurry feed (DSSF). The tank has maintained a surface level of approximately 385 inches since May 1985. The tank was core sampled in August 1996 and August 2000 (WTP). There are no waste transfer plans for the waste in this tank through FY 2006 (Strode and Boyles 2000).

The Hobbs equation was used to predict free hydroxide ion concentration of the DSSF waste for end dates of March 2001 and January 2006 based on August 1996 sample results. The results are listed in Table B-4 and show that the corrosion control lower limit for free hydroxide ion (0.28 M) should be maintained through January 2006. The last sampling event was in FY 2000 for the WTP. The results will be made available to the chemistry control program. Therefore, the next waste sample is needed in FY 2005. The sampling and laboratory analysis will follow the requirements in the Chemistry Control Program DQO (Banning 2001).

Table B-4. Estimated Hydroxide Concentrations of Tank 241-AN-104 Supernatant Based on Current Static Waste Storage Conditions

95 % LL OH Sample Result		Average OH Sample Result	
End Date Mar. 2001	End Date Jan. 2006	End Date Mar. 2001	End Date Jan. 2006
Hobbs Equation OH M			
3.74	3.65	4.12	4.03

B.1.5 Tank 241-AN-105

Tank 241-AN-105 contains about 640 kgal of DSSF waste and was core sampled in June 1996. The liquid level has remained at about 410 inches since June 1996. There are no waste transfer plans for this tank through FY 2006 (Strode and Boyles 2000).

The Hobbs equation was used to predict free hydroxide ion concentration of the DSSF waste for end dates of March 2001 and January 2006. The results are listed in Table B-5 and show that the lower limit for free hydroxide ion (0.26 M) should be maintained through January 2006. Because the last sampling event was in FY 1996, a waste sample is needed by FY 2001. Because of the number of chemistry control samples in FY 2001, it is recommended to defer sampling of tank 241-AN-105 waste until FY 2002. The sampling and laboratory analysis will follow the requirements in the Chemistry Control Program DQO (Banning 2001).

Table B-5. Estimated Hydroxide Concentrations of Tank 241-AN-105 Supernatant Based on Current Static Waste Storage Conditions

95 % LL OH Sample Result		Average OH Sample Result	
End Date Mar. 2001	End Date Jan. 2006	End Date Mar. 2001	End Date Jan. 2006
Hobbs Equation OH M			
3.21	3.14	3.33	3. 25

B.1.6 Tank 241-AN-106

Tank 241-AN-106 contains approximately 21 kgal of CC waste and was grab sampled in April 1989, April 1995, and November 1995. Hydroxide ion data is not available for November 1995.

Plans are to fill tank 241-AN-106 with saltwell liquid transferred from tank 241-AN-101 and then transfer the waste to the evaporator. The tank will be refilled with DSSF starting in 2005 based on Strode and Boyles (2000).

The Hobbs and Carothers equations were used to estimate the free hydroxide ion concentration of the CC waste for end dates of March 2001 and January 2006. The results are listed in Table B-6 and show that the lower limit for free hydroxide ion (0.11 M) was reached before March 2001 based on the Hobbs equation and should be maintained through January 2006 based on the Carothers equation. Sampling of tank 241-AN-106 waste is needed by FY 2001 followed by chemical addition and verification sampling in FY 2002 to ensure compliance with tank waste chemistry requirements. The samples and laboratory analysis will follow the requirements in the Chemistry Control Program DQO (Banning 2001).

Table B-6. Estimated Hydroxide Concentrations of Tank 241-AN-106 Supernatant Based on Current Static Waste Storage Conditions

Based on Average OH			
End Date Mar. 2001		End Date Jan. 2006	
Hobbs Equation OH M	Carothers Equation OH M	Hobbs Equation OH M	Carothers Equation OH
1E-05	0.45	<1E-05	0.27

B.1.7 Tank 241-AN-107

Tank 241-AN-107 contains approximately 794 kgal of CC waste and was last grab sampled in April 1998 and February 2001. Plans are to add sodium hydroxide solution to tank 241-AN-107 in December 2001, grab-sample the waste in December 2001, and then sample annually through FY 2004. The tank liquid level has dropped from about 400 inches in 1985 to 380 inches in January 2001. This liquid loss is believed to be a combination of solids settling and water evaporation. There is no waste transaction plan for this tank through FY 2006 (Strode and Boyles 2000).

Table B-7 lists the trended concentrations of hydroxide ion depletion based on the Hobbs and Carothers equations. The May 1993 and April 1998 estimates of depletion used the June 1985 and May 1993 sample results as start dates. The Carothers estimates of hydroxide concentration resulted in higher concentrations than the Hobbs equation. The Carothers equation was based on data collected from tank 241-AN-102. The corrosion control specification lower limit is 0.3 M free hydroxide ion.

Mitigation sampling through FY 2003 is satisfactory for the tank waste chemistry control program. After mitigation, sampling of tank 241-AN-107 will be based on preventative action requirements, Figure 3-6, and follow requirements in the Chemistry Control Program DQO (Banning 2001).

Table B-7. Comparisons of Estimated and Laboratory Results of Free Hydroxide Concentrations in Tank 241-AN-107

Start June 1985 Average OH	End Date May 1993 Average OH			End Date April 1998 Average OH		
Lab OH M	Hobbs OH M	Carothers OH M	Lab OH M	Hobbs OH M	Carothers OH M	Lab[1] OH M
0.06	2.6E-03	0.02	0.02	4E-05	0.01	1.5E-03

Start May 1993 Average OH	End Date April 1998 Average OH		
Lab OH M	Hobbs OH M	Carothers OH M	Lab[1] OH M
0.02	2E-05	0.01	1.5E-03

Note: [1]Hydroxide taken from Urie et al (1999) and based on pH measurement.

B.1.8 Tank 241-AP-101

Tank 241-AP-101 contains approximately 1,114 kgal of DSSF waste and was grab sampled in November 1999 and February 2000. The tank was maintained near a surface level of approximately 405 inches from January 1997 to the current time. No transfers into or from this

tank are planned prior to 2007 (Strode and Boyles 2000). During that year, the waste is to be transferred to the Waste Treatment Plant for processing.

The Hobbs equation was used to estimate the free hydroxide ion concentrations of the DSSF waste for end dates of March 2001 and January 2006. The results are listed in Table B-8 and show that the lower limit for free hydroxide ion (0.21 M) should be maintained through January 2006. Because the last sampling event was in FY 2000, a waste sample is needed by FY 2005. The sampling and laboratory analysis will follow the requirements in the Chemistry Control Program DQO (Banning 2001).

Table B-8. Estimated Hydroxide Concentrations of Tank 241-AP-101 Supernatant Based on Current Static Waste Storage Conditions

95 % LL OH Sample Result		Average OH Sample Result	
End Date Mar. 2001	End Date Jan. 2006	End Date Mar. 2001	End Date Jan. 2006
Hobbs Equation OH M			
2.29	2.24	2.42	2.37

B.1.9 Tank 241-AP-102

Tank 241-AP-102 contains approximately 1,089 kgal of concentrated phosphate (CP) waste. It was grab sampled in April 1993. The tank surface level has slowly decreased from approximately 402 inches to approximately 397 inches from January 1992 to the current time. The official baseline shows that no transfers into or from this tank are planned through 2006 (Strode and Boyles 2000). However, recent changes to the schedule show that tank 241-AP-102 waste may be moved to tank 241-AP-106 in approximately May 2001. This transfer did not happen. Then, tank 241-AP-102 will be used to receive saltwell liquid from BY-Farm, miscellaneous waste, and waste that has been transferred from the 200 West Area from June 2001 to December 2001.

The Hobbs equation was used to estimate the free hydroxide ion concentrations of the CP waste for end dates of March 2001 and January 2006. The results are listed in Table B-9 and show that the lower limit for free hydroxide ion (0.13 M) should be maintained through January 2006. Because the last sampling event was in 1993, a waste sample is needed in the next fiscal year. Because of the number of chemistry control samples in FY 2001, it is recommended to sample tank 241-AP-102 waste in FY 2002. The sampling and laboratory analysis will follow the requirements in the Chemistry Control Program DQO (Banning 2001).

Table B-9. Estimated Hydroxide Concentrations of Tank 241-AP-102 Supernatant Based on Current Static Waste Storage Conditions

95 % LL OH Sample Result		Average OH Sample Result	
End Date Mar. 2001	End Date Jan. 2006	End Date Mar. 2001	End Date Jan. 2006
Hobbs Equation OH M			
0.38	0.33	0.46	0.41

B.1.10 Tank 241-AP-103

Tank 241-AP-103 contains approximately 282 kgal of CC waste and was grab sampled in August 1999. The tank surface level has remained at approximately 103 inches from May 1999 to the current time. Tank 241-AP-103 is to be filled with CC waste by the end of FY 2002. No additional transfers into or from this tank are planned during 2003 - 2006 (Strode and Boyles 2000).

The Hobbs and Carothers equations were used to estimate the free hydroxide ion concentrations of the CC waste for end dates of March 2001, August 2005, and January 2006. The results are listed in Table B-10 and show that the lower limit for free hydroxide ion (0.22 M) should be maintained through September 2004 based on the Hobbs equation and January 2006 based on the Carothers equation. Therefore, sampling of this waste is needed by FY 2003. The last sampling event was in 1999. The FY 2003 sample date satisfies the one-year period before the estimated date to deplete hydroxide ion to the lower limit and the five-year period since the last sampling event. The sampling and laboratory analysis will follow the requirements in the Chemistry Control Program DQO (Banning 2001).

Table B-10. Estimated Hydroxide Concentrations of Tank 241-AP-103 Supernatant Based on Current Static Waste Storage Conditions

95 % LL OH Sample Result				Average OH Sample Result			
End Date Mar. 2001		End Date Sept. 2004	End Date Jan. 2006	End Date Mar. 2001		End Date Aug. 2005	End Date Jan. 2006
Hobbs OH M	Carothers OH M	Hobbs OH M	Carothers OH M	Hobbs OH M	Carothers OH M	Hobbs OH M	Carothers OH M
0.42	0.43	0.22	0.26	0.47	0.48	0.22	0.28

B.1.11 Tank 241-AP-104

Tank 241-AP-104 contains approximately 1,109 kgal of CC waste. It was grab sampled in January 1996, October 1997, and January 2001. An estimate of composition was made in January 2000 after waste from tank 241-SY-102 was sampled and transferred to tank 241-AP-104. The tank surface level has remained at approximately 403 inches from March 2000 to the current time. No additional transfers into or from this tank are planned through 2006 (Strode and Boyles 2000).

The Hobbs equation was used for historical trending the free hydroxide ion concentration of DN waste data between January 1996 and October 1997. The Hobbs equation over estimated the depletion of hydroxide ion as shown in Table B-11.

The Hobbs and Carothers equations were used to estimate the free hydroxide ion concentration of the CC waste beginning January 2000 to end dates of March 2001 and January 2006 based on January 2000 sample results. The results are listed in Table B-12 and show that the lower limit for free hydroxide ion (0.17 M) should be maintained through January 2006. Because the last sampling event was in FY 2001, a waste sample is needed by FY 2006. The sampling and laboratory analysis will follow the requirements in the Chemistry Control Program DQO (Banning 2001).

Table B-11. Comparison of Depletion Estimated and Laboratory Results of Hydroxide Concentrations of Tank 241-AP-104 Supernatant

Start Jan. 1996 Average OH	End Date Oct. 1997 Average OH	
Lab OH M	Hobbs Equation OH M	Lab OH M
0.03	7E-07	1.4E-04

Table B-12. Estimated Hydroxide Concentrations of Tank 241-AP-104 Supernatant Based on Current Static Waste Storage Conditions

Based on Average OH			
End Date Mar. 2001		End Date Jan. 2006	
Hobbs Equation OH M	Carothers Equation OH M	Hobbs Equation OH M	Carothers Equation OH M
0.74	0.66	0.71	0.39

B.1.12 Tank 241-AP-105

Tank 241-AP-105 contains approximately 1,045 kgal of DSSF waste. It was grab sampled in September 1996 and in August 1997, and an estimate was made in May 2000, when waste from tank 241-AW-106 was added to the tank. The tank surface level has remained at approximately 413 inches from June 2000 to the current time. No additional transfers into or from this tank are planned through 2006 (Strode and Boyles 2000).

The Hobbs equation was used to estimate the free hydroxide ion concentration of the DSSF waste for end dates of March 2001 and January 2006. The results are listed in Table B-13 and show that the lower limit for free hydroxide ion (0.30 M) should be maintained through January 2006. Because the last sampling event was in 1997, a waste sample is needed by

FY 2002. The sampling and laboratory analysis will follow the requirements in the Chemistry Control Program DQO (Banning 2001).

Table B-13. Estimated Hydroxide Concentrations of Tank 241-AP-105 Supernatant Based on Current Static Waste Storage Conditions

Based on Average OH	
End Date Mar. 2001	End Date Jan. 2006
Hobbs Equation OH M	
0.69	0.67

B.1.13 Tank 241-AP-106

Tank 241-AP-106 contains approximately 623 kgal of DC waste that was transferred from tanks 241-SY-101 and 241-SY-102. It was grab sampled in November 1994, September 1996, August 1997, and in May 1998, and an estimate was made in February 2000, when waste from tank 241-SY-102 was added to the tank. The tank surface level has remained at approximately 227 inches from March 2000 to the current time. The baseline schedule shows that the current waste is to be retrieved and evaporated during FY 2002. The tank will then be backfilled with DSSF waste (Strode and Boyles 2000). Recent planning changes show that the waste in tank 241-AP-106 is to be transferred to tank 241-AP-108 in April 2001. This transfer did not happen. The tank will then be used to receive waste from tank 241-AP-102 in May 2001.

The Hobbs and Carothers equations were used to estimate the free hydroxide ion concentrations of the DC waste for end dates of March 2001 and January 2006. The results are listed in Table B-14 and show that the lower limit for free hydroxide ion (0.15 M) should be maintained through January 2006. Because the last sampling event was in 1998, a waste sample is needed by FY 2003. The sampling and laboratory analysis will follow the requirements in the Chemistry Control Program DQO (Banning 2001).

Note that tank 241-AP-102 waste is to be transferred into this tank in approximately May 2001 and is expected to remain in operation for at least five years. This transfer did not happen.

Table B-14. Estimated Hydroxide Concentrations of Tank 241-AP-106 Supernatant Based on Static Waste Storage Conditions

Based on Average OH			
End Date Mar. 2001		End Date Jan. 2006	
Hobbs Equation OH M	Carothers Equation OH M	Hobbs Equation OH M	Carothers Equation OH M
0.74	0.68	0.67	0.40

B.1.14 Tank 241-AP-107

Tank 241-AP-107 contains approximately 986 kgal of DC waste. It was grab sampled in August 1993, February 1995, May 1999, August 1999, and in December 2000 (analytical data not included in Caustic Limits Report for this evaluation). A composition estimate was made in October 2000, when sampled waste from tank 241-SY-101 was added to the tank. The tank surface level has remained at approximately 357 inches from November 2000 to the current time. Tank 241-AP-107 is used to store dilute waste transferred from tank 241-SY-102, for use as evaporator feed. The level will fluctuate until June 2005, and then will remain stable through the end of 2006 (Strode and Boyles 2000).

The Hobbs and Carothers equations were used to estimate the free hydroxide ion concentrations of the DC waste for end dates of March 2001 and January 2006 based on the August 1999 sample results. The results are listed in Table B-15 and show that the lower limit for free hydroxide ion (0.16 M) should be maintained through January 2006. Because the last sampling event was in FY 2001, a waste sample is needed by FY 2006. The current plan is to sample the tank in FY 2005. The sampling and laboratory analysis will follow the requirements in the Chemistry Control Program DQO (Banning 2001).

Table B-15. Estimated Hydroxide Concentrations of Tank 241-AP-107 Supernatant Based on Current Static Waste Storage Conditions

Based on Average OH			
End Date Mar. 2001		End Date Jan .2006	
Hobbs Equation OH M	Carothers Equation OH M	Hobbs Equation OH M	Carothers Equation OH M
0.80	0.78	0.65	0.46

B.1.15 Tank 241-AP-108

Tank 241-AP-108 contains approximately 32 kgal of DN waste. It was grab sampled in January 1996, October 1997, September 1999, and in March 2000. The tank surface level has remained at approximately 14 inches since May 2000. The tank liquid level will vary because tank 241-AP-108 is a dilute waste receiver for the 200 East Area, and waste will be added and transferred out for evaporation (Strode and Boyles 2000). Recent planning shows that the saltwell liquid from tank 241-BY-106 (Fort 2001) and possibly waste from tank 241-AP-106 is to be transferred to tank 241-AP-108. The completion of tank 241-BY-106 saltwell pumping is scheduled for November 2002.

The Hobbs equation was used to estimate the free hydroxide ion concentration of the DN waste for end dates of March 2001 and March 2002. The results are listed in Table B-16 and show that the lower limit for free hydroxide ion (0.13 M) should be maintained through March 2002. Waste addition followed by verification sampling of tank 241-AP-108 waste are needed by FY 2001 to ensure compliance with tank waste chemistry requirements. The sampling and

laboratory analysis will follow the requirements in the Chemistry Control Program DQO (Banning 2001).

The transfer of tank 241-BY-106 waste to tank 241-AP-108 is a chemical adjustment step, which requires further evaluation to ensure compliance with tank waste chemistry requirements. The waste compatibility assessment estimates the free hydroxide concentration at 0.66 M (no hydroxide ion depletion) after addition of saltwell liquid from tank 241-BY-106 (Lechelt 2001).

Table B-16. Estimated Hydroxide Concentrations of Tank 241-AP-108 Supernatant Based on Static Waste Storage Conditions

95 % LL OH Sample Result		Average OH Sample Result	
End Date Mar. 2001	End Date Jan. 2002	End Date Mar. 2001	End Date Mar. 2002
Hobbs Equation OH M			
0.34	0.13	0.39	0.13

B.1.16 Tank 241-AW-101

Tank 241-AW-101 contains approximately 739 kgal DSSF waste. It was grab sampled in June 1990, April 1998, and July 2000 (WTP). The tank surface level has been maintained at approximately 409 inches from March 2000 to the current time. No transfers into or from the tank are planned through 2006 (Strode and Boyles 2000).

The Hobbs equation was used to estimate the free hydroxide ion concentrations of the DSSF waste for end dates of March 2001 and January 2006 based on April 1998 sample results. The results are listed in Table B-17 and show that the lower limit for free hydroxide ion (0.27 M) should be maintained through January 2006. Because the last sampling event was in FY 2000, a waste sample is needed by FY 2005. The sampling and laboratory analysis will follow the requirements in the Chemistry Control Program DQO (Banning 2001).

Table B-17. Estimated Hydroxide Concentrations of Tank 241-AW-101 Supernatant Based on Current Static Waste Storage Conditions

95 % LL OH Sample Result		Average OH Sample Result	
End Date Mar. 2001	End Date Jan 2006	End Date Mar. 2001	End Date Jan. 2006
Hobbs Equation OH M			
5.49	5.42	5.60	5.53

B.1.17 Tank 241-AW-102

Tank 241-AW-102 is the evaporator feed tank and contains approximately 34 kgal DN waste. It receives dilute waste from other DSTs and end of campaign residual bottoms and water flushes from the evaporator. It was grab sampled in January 1998 and in January 1999. Tank

241-AP-107 supernatant was sampled in August 1999 and then transferred to tank 241-AW-102 in December 1999. The tank 241-AW-102 supernatant was transferred to the waste evaporator in May 2000. The supernatant has remained at 34 kgal supernatant between May 2000 and January 2001. Tank 241-AW-104 waste was added to tank 241-AW-102 since the January 2001 Caustic Limits Report. No information on the current waste was available for evaluation. The waste in tank 241-AP-107 is the next batch scheduled for addition to tank 241-AW-102. The waste will be transferred to the evaporator by March 2002.

The Hobbs equation was used to estimate the free hydroxide ion concentrations of the DN waste. The results are listed in Table B-18 and show that the lower limit for free hydroxide ion (0.01 M) has been reached. It is recommended to transfer the waste in tank 241-AP-107 to tank 241-AW-102 in FY 2002. Engineering calculations will be used to confirm final conditions and ensure that the wastes in both tanks 241-AW-102 and 241-AP-107 comply with tank waste chemistry requirements. Additional evaporator operations are planned in FY 2002 and FY 2003. The need for further evaluations w ill be evaluated in subsequent revisions to this document.

Table B-18. Estimated Hydroxide Concentrations of Tank 241-AW-102 Supernatant Based on Current Static Waste Storage Conditions

Based on Average OH
End Date Mar. 2001
Hobbs Equation OH M
9E-04

B.1.18 Tank 241-AW-103

Tank 241-AW-103 contains approximately 196 kgal DN waste. It was grab sampled in September 1994 and in August 1999. The tank is to be filled with DSSF waste during 2001-2002 (Strode and Boyles 2000).

The Hobbs equation was used to estimate the free hydroxide ion concentrations of the DN waste for end dates of March 2001 and January 2006. The results are listed in Table B-19 and show that the lower limit for free hydroxide ion (0.01 M) should be maintained through January 2006. Because the last sampling event was in FY 1999, a waste sample is needed by FY 2004. Current plans are to sample the tank in FY 2002. The sampling and laboratory analysis will follow the requirements in the Chemistry Control Program DQO (Banning 2001).

Table B-19. Projected Hydroxide Concentrations of Tank 241-AW-103 Supernatant Based on Static Waste Storage Conditions Assessment

Based on Average OH	
End Date Mar. 2001	End Date Jan. 2006
Hobbs Equation OH M	
0.48	0.21

B.1.19 Tank 241-AW-104

Tank 241-AW-104 contains approximately 94 kgal DN waste as of January 31, 2001 (Caustic Limits Report shows 895 kgal at beginning of January 2001 and prior to transfer to the waste evaporator). The tank was grab sampled in August 1994 and July 1999, and core sampled in August 2000. It is to be filled with DSSF waste during 2000-2002 (Strode and Boyles 2000).

The Hobbs equation was used to trend the free hydroxide ion concentrations of DN waste between September 1994 and August 2000 and to predict future hydroxide depletion to end dates of March 2001 and October 2001. Future prediction was based on August 2000 sample results. The historical comparison results are shown in Table B-20. Future estimates are shown in Table B-21.

The historical results in Table B-20 closely agree with laboratory results. The hydroxide ion depletion of current waste (Table B-21) shows that the lower limit for free hydroxide ion (0.03 M) can be maintained through October 2001. It is recommended that this tank be sampled in FY 2001 to verify concentration and establish caustic demand. In FY 2002 caustic addition is needed to adjust the free hydroxide ion concentration and a verification sample taken following caustic addition. The sampling and laboratory analysis will follow the requirements in the Chemistry Control Program DQO (Banning 2001).

Table B-20. Comparison of Depletion Estimated and Laboratory Results of Hydroxide Concentrations of Tank 241-AW-104 Supernatant

Start Sept. 1994 Average OH	End Date Aug. 2000 Average OH	
Lab OH M	Hobbs OH M	Lab OH M
0.20	0.13	0.11

Table B-21. Estimated Hydroxide Concentrations of Tank 241-AW-104 Supernatant Based on Current Static Waste Storage Conditions

S Deviation OH Sample Result		Average OH Sample Result	
End Date Mar. 2001	End Date Jul. 2001	End Date Mar. 2001	End Date Oct. 2001
Hobbs Equation OH M			
0.07	0.03	0.09	0.03

B.1.20 Tank 241-AW-105

Tank 241-AW-105 contains approximately 172 kgal DN waste. It was grab sampled in August 1995 and August 1996, and core sampled in May 1997. The tank surface level is approximately 155 inches. The tank is to be filled with dilute waste from the 100 Area during 2002-2003 (Strode and Boyles 2000).

The corrosion control limit equation [$NO_3/(OH + NO_2) < 2.5$] was used to calculate the lower hydroxide limit at 0.55 M nitrate and 0.05 M nitrite for hydroxide depletion estimating. The result shows that lower hydroxide limit is 0.17 M because of the low nitrite concentration (0.05 M) in the May 1997 sample.

The Hobbs equation was used to estimate the free hydroxide ion concentrations of the DN waste for an end date of March 2001. The results are listed in Table B-22 and show that the estimated free hydroxide ion is below the 0.17 M lower limit. It is recommended that this tank be sampled in FY 2001 to verify concentration and establish caustic demand. In FY 2002 caustic addition is needed to adjust the free hydroxide ion concentration and a verification sample taken following caustic addition. The sampling and laboratory analysis will follow the requirements in the Chemistry Control Program DQO (Banning 2001).

Table B-22. Projected Hydroxide Concentrations of Tank 241-AW-105 Supernatant Based on Current Static Waste Storage Conditions

One S Deviation LL OH	Average OH Sample Result
End Date March 2001	
Hobbs Equation OH M	
0.06	0.07

B.1.21 Tank 241-AW-106

Tank 241-AW-106 contains approximately 500 kgal DSSF waste. It is a receiver tank for the evaporator bottoms. Tank waste was grab sampled in August 1991, August 1995, January 1998, and May 2000. Waste compatibility assessment and process knowledge estimates of hydroxide concentration were made in May 2000, and March 2001(Lechelt 2001). Because the tank is the

evaporator bottoms receiver, the tank will receive bottoms from the evaporator on a regular basis, and the waste will then be transferred to other tank (Strode and Boyles 2000).

The Hobbs equation was used to estimate the free hydroxide ion concentration of the DN waste for end dates of March 2001 and January 2006. The results are listed in Table B-23 and show that the lower limit for free hydroxide ion (0.30 M) can be maintained through January 2006. Because the last sampling event was in FY 2000, a waste sample is needed by FY 2005.

Because tank 241-AW-106 receives and transfers evaporator bottoms on a regular basis, regular sampling and paying close attention to hydroxide ion of stored waste and tank waste heels are required. Sampling of tank 241-AW-106 waste will be based on preventative action requirements, Figure 3-6, and follow requirements in the Chemistry Control Program DQO (Banning 2001).

Table B-23. Projected Hydroxide Concentrations of Tank 241-AW-106 Based on Current Static Waste Storage Conditions

Based on Average OH	
End Date Mar. 2001	**End Date Jan. 2006**
Hobbs Equation OH M	
0.68	0.54

B.1.22 Tank 241-AY-101

Tank 241-AY-101 contains approximately 37 kgal DC waste. It was grab sampled in February 1996 and in February 2001 (sample analysis is not completed). After caustic addition in January 2001, no further transfers into or from the tank are scheduled through 2006. The tank is reserved for emergency space through 2006. The tank is to receive waste from tank 241-C-104 single-shell tank (SST) retrieval starting in FY 2007 (Strode and Boyles 2000). Tank 241-AY-101 is scheduled to be sampled in FY 2001 through FY 2004 as part of the recovery plan and preventative action requirements. Some historical data on hydroxide is available but it could not be used for trending because of waste additions from C tank farm.

The Hobbs and Carothers equations were used to trend the free hydroxide ion concentration between February 1996 and May 1997 and develop future estimates of hydroxide depletion based on December 2000 caustic addition. The results are listed in Tables B-24 and B-25.

The historical results of Table B-24 show that the Hobbs equation over-predicts hydroxide depletion and the Carothers equation under-predicts hydroxide depletion for this tank. Estimates of hydroxide depletion based on December 2000 caustic addition show that the lower limit for free hydroxide ion (0.01 M) can be maintained through May 2004 (see Table B-25). Therefore, sampling of this waste is required by FY 2003. The mitigation-sampling through FY 2002 is satisfactory for the tank waste chemistry program. After mitigation, sampling of tank 241-AY-101 will be based on preventative action requirements, Figure 3-6, and follow requirements in the Chemistry Control Program DQO (Banning 2001).

Table B-24. Comparison of Depletion Estimated and Laboratory Results of Hydroxide Concentrations of Tank 241-AY-101 Supernatant

Start Feb. 1996 Average OH	End Date May 1997 Average OH		
Lab OH M	Hobbs OH M	Carothers OH M	Lab OH M
6.0E-05	1.8E-05	5.3E-05	3.0E-05

Table B-25. Estimated Hydroxide Concentrations of Tank 241-AY-101 Supernatant After December 2000 Caustic Addition and Static Storage Conditions

Average OH Sample Result			
End Date Mar. 2001		End Date May 2004	End Date Jan. 2006
Hobbs Equation OH M	Carothers Equation OH M	Hobbs Equation OH M	Carothers Equation OH M
1.56	1.65	0.01	0.97

B.1.23 Tank 241-AY-102

Tank 241-AY-102 contains approximately 395 kgal DN waste. It was grab sampled in October 1996; January, July, November, and December 1998; March, April, May, and June and October 1999; and November 2000 (all available as of February 2001). The tank surface level is approximately 208 inches. The tank is scheduled for caustic addition during FY 2001. After the caustic addition, no further transfers are planned into or from the tank through 2006 (Strode and Boyles 2000). Tank 241-AY-102 is scheduled to be sampled during FY 2001 through FY 2003 as part of the recovery plan and preventative action requirements.

The Hobbs equation was used for estimating the free hydroxide ion concentrations for January 2000 based on October 1999 sample results and for February 2001 based on January 2000 sample results. The results are shown in Table B-26. The mitigation sampling through FY 2002 is satisfactory for the tank waste chemistry program. After mitigation, sampling of tank 241-AY-102 will be based on preventative action requirements, Figure 3-6, and follow requirements in the Chemistry Control Program DQO (Banning 2001).

Earlier caustic additions limited use of historical data on trending of hydroxide depletion.

Table B-26. Comparison of Estimated and Laboratory Results of Hydroxide Concentrations of Tank 241-AY-102 Based on Static Waste Storage Conditions

Based on Oct. 1999 OH Sample Results			Based on Jan. 2000 Sample Result
Lab Result	End Date Jan. 2000		End Date Feb. 2001
(Start) OH M	Hobbs OH M	Lab Result[1]	Hobbs OH M
0.09	0.08	0.009	2E-06

Note: [1]Based on pH measurement

B.1.24 Tank 241-AZ-101

Tank 241-AZ-101 contains approximately 865 kgal DN/AW waste. It was core sampled in March 1995, November 1999, and in August 2000 (WTP) and grab sampled in March to May 2000. The tank surface level is approximately 336 inches. The tank is not scheduled to have any transfers into or out of it through 2005. The supernatant from tank 241-AZ-101 is scheduled for transferred to the Waste Treatment Plant as low-activity waste (LAW) feed as batch 2. However, the transfer may not occur until after 2006 (Strode and Boyles 2000).

The Hobbs equation was used for estimating the free hydroxide ion concentration in March 2001 and January 2006 based on November 1999 sample results. The results are listed in Table B-27 and show that the lower limit for free hydroxide ion (0.11 M) can be maintained through January 2006. Because the last sampling event was in FY 2000, a waste sample is needed by FY 2005. The sampling and laboratory analysis will follow the requirements in the Chemistry Control Program DQO (Banning 2001).

Table B-27. Projected Hydroxide Concentrations of Tank 241-AZ-101 Based on Current Static Waste Storage Conditions

Average OH Sample Result	
End Date Mar. 2001	End Date Jan. 2006
Hobbs Equation OH M	
0.60	0.53

B.1.25 Tank 241-AZ-102

Tank 241-AZ-102 contains approximately 892 kgal DN/AW waste. It was core sampled in February 1995 and core sampled in August 1999. The tank surface level is approximately 363 inches. The tank is not scheduled to have any transfers into or from the tank through 2006. The supernatant from tank 241-AZ-102 is scheduled for transfer to the Waste Treatment Plant as LAW as feed batch 3 (Strode and Boyles 2000).

The Hobbs equation was used to trend historical data and predicts estimates of hydroxide depletion from recent samples. Historical trending is between February 1995 and August 1999. Estimated results for March 2001and January 2004 were based on the August 1999 sample result. The results are listed in Tables B-28 and B-29.

The historical results of Table B-28 show that the Hobbs equation under predicted hydroxide depletion for this tank. The future predicted results are listed in Table B-29 and show that the lower limit for free hydroxide ion (0.01 M) can be maintained through January 2004. Therefore, grab sampling of the current waste is needed by FY 2003.

The under-prediction of hydroxide ion depletion by Hobbs and the low concentration of hydroxide ion (0.04 M mean) in the August 1999 sample suggest that the chemistry of tank 241-AZ-102 requires closer tracking. Therefore, it is recommended to sample the waste in tank 241-AZ-102 in FY 2002 followed by chemical addition and verification sampling in FY 2002 and FY 2003. The sampling and laboratory analysis will follow the requirements in the Chemistry Control Program DQO (Banning 2001).

Table B-28. Comparison of Depletion Estimated and Laboratory Results of Hydroxide Concentrations of Tank 241-AZ-102 Supernatant

Start Feb. 1995 Average OH	End Date Aug. 1999 Average OH	
Lab OH M	Hobbs OH M	Lab OH M
0.11	0.07	0.04

Table B-29. Estimated Hydroxide Concentrations of Tank 241-AZ-102 Supernatant Based on Current Static Waste Storage Conditions

Based on 95 % LL Sample OH		Based on Avg. Sample OH	
End Date Mar. 2001	End Date Sept. 2001	End Date Mar. 2001	End Date Jan. 2004
Hobbs Equation OH M			
0.013	0.01	0.03	0.01

B.1.26 Tank 241-SY-101

Tank 241-SY-101 contains approximately 694 kgal CC waste. It was grab sampled in March 1999 and in April 2000. The tank is not scheduled to have any transfers into or from the tank through 2006 (Strode and Boyles 2000).

The Hobbs and Carothers equations were used for estimating the free hydroxide ion concentration in March 2001 and January 2006. The results are listed in Table B-30 and show that the lower limit for free hydroxide ion (0.23 M) can be maintained through January 2006. Because the last sampling event was in FY 2000, a waste sample is needed by FY 2005. The

sampling and laboratory analysis will follow the requirements in the Chemistry Control Program DQO (Banning 2001).

Table B-30. Estimated Hydroxide Concentrations of Tank 241-SY-101 Supernatant Based on Current Static Waste Storage Conditions

95 % LL Sample OH				Avg. Sample OH			
End Date Mar. 2001		End Date Jan. 2006		End Date Mar. 2001		End Date Jan. 2006	
Hobbs OH M	Carothers OH M	Hobbs OH M	Carothers OH M	Hobbs OH M	Carothers OH M	Hobbs OH M	Carothers OH M
1.29	1.22	1.00	0.72	1.49	1.40	1.19	0.82

B.1.27 Tank 241-SY-102

Tank 241-SY-102 contains approximately 759 kgal DC waste. It was grab sampled several times, most recently in October 2000 and December 2000. The tank receives saltwell pumping waste, Plutonium Finishing Plant (PFP) waste, 222-S Laboratory waste, and will receive waste from SST retrieval (Strode and Boyles 2000). Although the current schedule does not show received SST waste entering tank 241-SY-102 prior to 2006, the tank will have to receive waste from two SSTs prior to that date to allow the *Hanford Federal Facility Agreement and Consent Order* (Tri-Party Agreement) (Ecology et al. 1996) milestones for retrieval of tanks 241-S-112 and 241-S-102 to be met.

The Hobbs and Carothers equations were used for estimating the free hydroxide ion concentration in March 2001 and January 2006 based on October 2000 sample results. The results are listed in Table B-31 and show that the lower limit for free hydroxide ion (0.15 M) can be maintained through January 2006. Because the last sampling event was in FY 2001, a sample of the current waste is needed by FY 2006. The current plan is to sample the tank waste in FY 2005.

Tank 241-SY-102 receives and transfers waste on a regular basis; therefore, regular sampling and paying close attention to hydroxide ion depletion of both stored waste and tank waste heels are required. The sampling and laboratory analysis will follow the requirements in the Chemistry Control Program DQO (Banning 2001).

Table B-31. Estimated Hydroxide Concentrations of Tank 241-SY-102 Based on Static Waste Storage Conditions

Based on Average OH Sample Results			
End Date Mar. 2001		End Date Jan. 2006	
Hobbs OH M	Carothers OH M	Hobbs OH M	Carothers OH M
0.79	0.78	0.59	0.46

B.1.28 Tank 241-SY-103

Tank 241-SY-103 contains approximately 369 kgal CC waste. It was grab sampled in August 1994 and core sampled in December 2000. The tank surface level is approximately 270 inches. The tank is not scheduled to have any transfers into or from the tank through 2006 (Strode and Boyles 2000).

The Hobbs and Carothers equations were used for estimating the free hydroxide ion concentration in March 2001 and January 2006 based on August 1994 sample results. The results are listed in Table B-32 and show that the lower limit for free hydroxide ion (0.28 M) can be maintained through January 2006. Because the last sampling event was in FY 2001, a sample of the current waste is needed by FY 2006. The current plan is to sample the tank waste in FY 2005. The sampling and laboratory analysis will follow the requirements in the Chemistry Control Program DQO (Banning 2001).

Table B-32. Estimated Hydroxide Concentrations of Tank 241-SY-103 Supernatant Based on 1994 Sampling and Static Waste Storage Conditions

95 % LL Sample OH				Average Sample OH			
End Date Mar. 2001		End Date Jan. 2006		End Date Mar. 2001		End Date Jan. 2006	
Hobbs OH M	Carothers OH M	Hobbs OH M	Carothers OH M	Hobbs OH M	Carothers OH M	Hobbs OH M	Carothers OH M
1.23	0.69	1.09	0.41	1.50	0.83	1.36	0.49

B2.0 REFERENCES

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APPENDIX C

DERIVATION OF REYNOLDS EQUATION FOR HYDROXIDE CONSUMPTION

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APPENDIX C

DERIVATION OF REYNOLDS EQUATION FOR HYDROXIDE CONSUMPTION

C1.0 INTRODUCTION

Evidence of hydroxide consumption has been observed in several Hanford Site double-shell tanks (DSTs). The DST chemistry controls are found in Administrative Control (AC) 5.15, "Chemistry Control Program," of the *Tank Farm Technical Safety Requirements*, HNF-SD-WM-TSR-006 (CHG 2001). Tanks 241-AN-102 and 241-AN-107 are both low in hydroxide when compared with limits.

C2.0 CHEMICAL KINETICS PRIMER

Changes in the concentration of the free hydroxide ion in a waste are considered either 1st order or 2nd order kinetics. Specific tests help to decide which order is appropriate to describe the disappearance of hydroxide.

C2.1 First Order Kinetics

First order kinetics is dependent to the 1st power of the concentration of a species of concern. This can be expressed by the following equation:

$$-\frac{dC}{dt} = k \times C \qquad \text{(C-1)}$$

This indicates that the change in concentration with time is proportional to the concentration. Equation C-1 can be integrated to give:

$$-\ln\left(\frac{C}{C_0}\right) = k \times t \qquad \text{(C-2)}$$

where:

the current concentration is C and the initial concentration is C_o;
t is time, and
the proportional or rate constant is k.

The concentration equation can be transformed to the C/C_o form and plotted on a semilog axis versus time. If the data plots a straight line, then the reaction rate is a 1st order equation. The data can then be regressed in the form:

$$Y = a \times x \qquad \text{(C-3)}$$

where:

a is the rate constant (k);
x is time (t), and
Y is $-\ln(C/C_o)$.

The regression is forced to have an intercept at 0. The rate constant is typically a function of temperature but this has not been factored in during the regression of tank data.

C2.1 Second Order Kinetics

Similar steps are taken for 2nd order kinetics. The starting concentration equation is raised to the square term; hence, 2nd order as shown in the following equation:

$$-\left(\frac{dC}{dt}\right) = k \times C^2 \qquad \text{(C-4)}$$

The equation can be integrated to give:

$$\frac{1}{C} - \frac{1}{C_o} = k \times t \qquad \text{(C-5)}$$

The test for this equation is to plot 1/C versus time. A straight line indicates a second order kinetics reaction. The equation can be rearranged to determine the current concentration as shown here:

$$\frac{1}{C} = k \times t + \frac{1}{C_o} \qquad \text{(C-6)}$$

This is in the form of a linear equation:

$$Y = a \times x + b \qquad \text{(C-7)}$$

where:

Y = 1/C and
b = $1/C_O$.

A linear regression would give k as the slope and $1/C_O$ as the intercept. This may be adequate for interpolation of the data or use with this particular data set. However, if the equation is to be used on other data sets, then the initial concentration, C_O, will be different and the equation will not be strictly applicable. Instead, the data will need to be transformed and regressed with the intercept set to 0 such as in the following equation:

$$Y = k \times t \qquad \text{(C-8)}$$

where:

$$Y = \frac{1}{C} - \frac{1}{C_o} \tag{C-9}$$

Regression in this form allows the slope, k, to be applied to other datasets with different initial concentrations.

C3.0 HYDROXIDE CONSUMPTION IN COMPLEXED CONCENTRATE

Complexed concentrate is waste that has high amounts of organic complexants. Experiments performed for the flammable gas program show that the organic complexants degrade and consume hydroxide in the process. The reaction is complicated, and there are many competing reactions. Radiation appears to enhance the chemical reactions.

Two tanks that have complexed concentrate in them have been declared out of corrosion specification and hydroxide needs to be added to them. These tanks are 241-AN-102 and 241-AN-107. The reaction kinetics of the consumption of hydroxide was studied for both tanks. A summary of these studies is given here.

C3.1 Hydroxide Consumption in Tank 241-AN-102

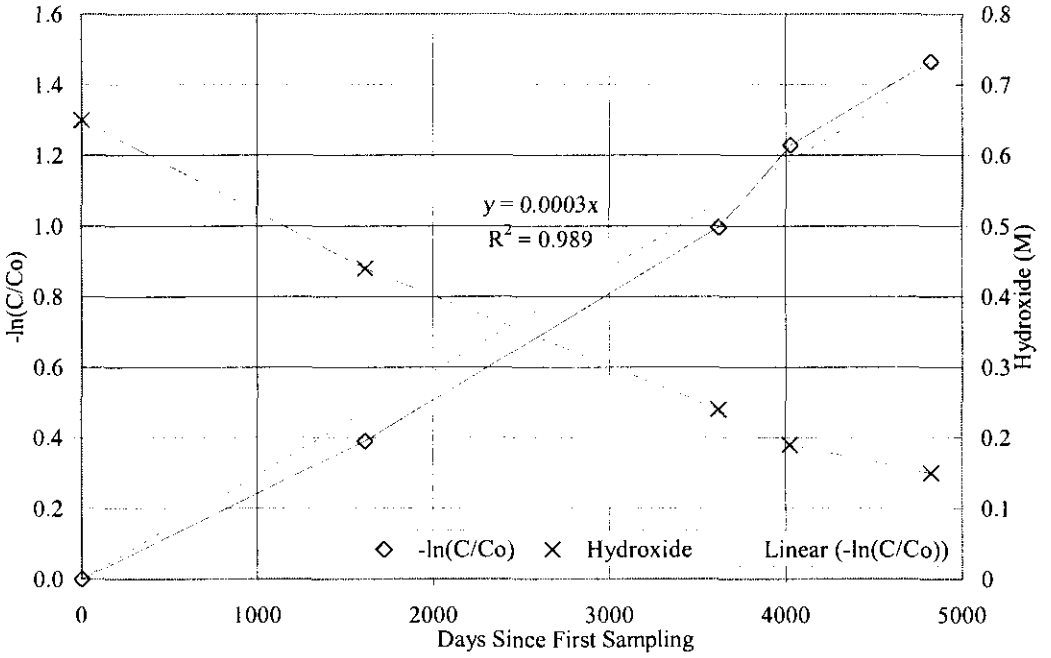
The decrease in hydroxide in tank 241-AN-102 was studied and reported in Carothers (2001) and is also shown here. Five samples were taken and analyzed over a 14-year timeframe. Table C-1 shows the date, hydroxide concentrations, the days since the first sample, and the value for $-\ln(C/C_O)$. The liquid waste volume was 1070 kgal to 1130 kgal during the sampling events.

Table C-1. Hydroxide Concentration in Tank 241-AN-102

Date of Sampling Event	Hydroxide Concentration (M)	Days Since First Sampling Event	$-\ln\left(\frac{C}{C_0}\right)$
11/20/84	0.65	0	0
04/20/89	0.44	1612	0.39
10/21/94	0.24	3622	0.996
11/20/95	0.19	4027	1.23
02/03/98	0.15	4823	1.47

Figure C-1 is a plot of the last three columns of Table C-1.

Figure C-1. Tank 241-AN-102 Hydroxide Concentration



The data falls on a nearly straight line, indicating that the hydroxide concentration follows a 1st order kinetics reaction. The trend line gives a k of 0.0003. A regression of the data gives the following equation that can be used to predict the current hydroxide concentration for first order kinetics, based on the initial concentration and the elapsed time:

$$C = C_o e^{-0.0003t} \tag{C-10}$$

C3.2 Hydroxide Consumption in Tank 241-AN-107

The complexed concentrate currently stored in tank 241-AN-107 was stored in tank 241-AZ-102 for a number of years before being transferred. Prior to the transfer, the waste in tank 241-AZ-102 was heated to a temperature that started an accelerated chemical reaction. A brown gas visible from the stack of the 241-A-702 ventilation building evidenced this reaction. The waste was transferred to tank 241-AN-107. The reaction stopped as the waste cooled during the transfer.

The data shown in Table C-2 were previously shown from Reynolds (1989). Five samples were taken and various analyses were performed. The table shows a comparison of the hydroxide, total organic carbon, and nitrate. The decrease in both total organic carbon (TOC) and nitrate follow second order kinetics, but the hydroxide does not. Table C-3 shows the hydroxide data and the calculated values for $-\ln(C/C_O)$ and $1/C$. The tank 241-AZ-102 liquid waste volume was approximately 920 kgal during the sampling events.

Table C-2. Decreasing Concentrations in Complexed Concentrate Waste Now Stored in Tank 241-AN-107

Tank Sampled	Date of Sampling Event	Hydroxide Concentration (M)	Total Organic Carbon (M)	Nitrate (M)
241-AZ-102	06/26/79	1.2*	121.8	4.26
241-AZ-102	08/27/81	1.1		4.08
241-AZ-102	09/20/82	0.998	76	
241-AZ-102	07/28/83	0.82	70	3.72
241-AN-107	11/26/84	<0.04	44.3	3.54

Note:

*Reynolds (1989) originally reported a hydroxide value of 1.03 M for the 1979 sample. Per Delegard (1979), each of four samples was analyzed twice, giving a total of 8 results in two sets. One set had 4 values that averaged 1.03 M, and this was the value used in Reynolds. The other set had 4 higher values averaging 1.2 M. This value was used here; it is more consistent with the observed decreases in hydroxide, total organic carbon, and nitrate.

Table C-3. Decrease in Hydroxide Concentration in Tanks 241-AZ-102 and 241-AN-107

Tank Sampled	Date of Sampling Event	Hydroxide Concentration (M)	Days Since First Sampling Event	$-\ln\left(\frac{C}{C_0}\right)$	$\frac{1}{C}$
241-AZ-102	06/26/79	1.2*	0	0	0.833
241-AZ-102	08/27/81	1.1	793	0.087	0.909
241-AZ-102	09/20/82	0.998	1182	0.184	1.002
241-AZ-102	07/28/83	0.82	1493	0.381	1.220
241-AN-107	11/26/84	<0.04#	1980	#	#

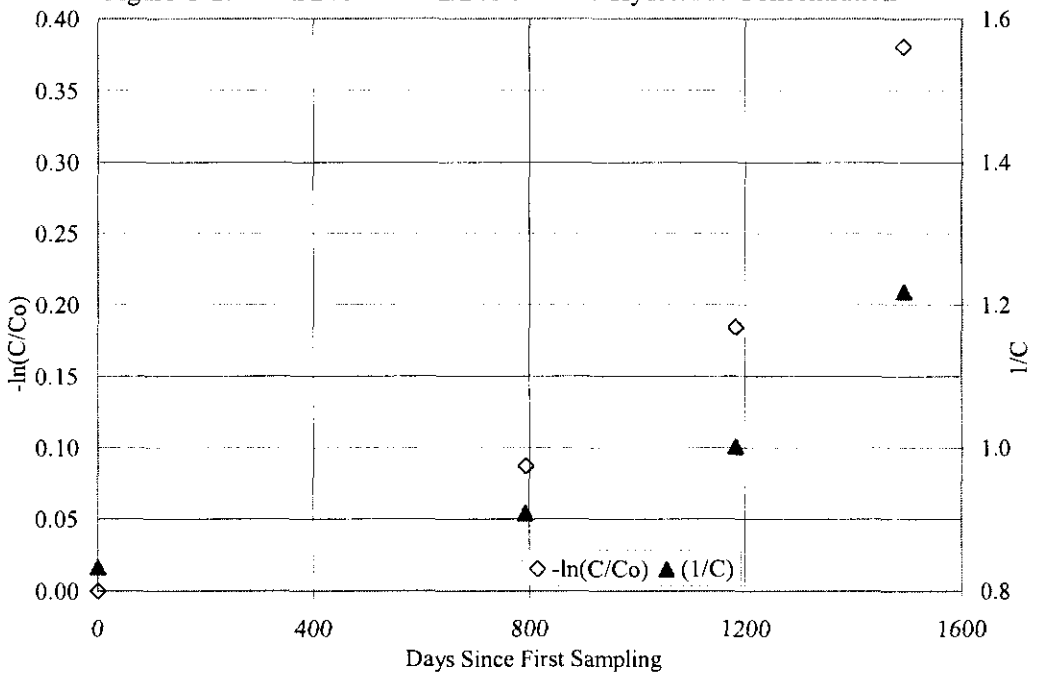
Note:

*See Note for Table C-2.

#The nondetected value for hydroxide is not used because of the reactions that happened in tank 241-AZ-102 prior to the waste transfer to tank 241-AN-107

Figure C-2 is a plot of the last three columns of Table C-3. The points do not fall on a straight line for either a 1st or 2nd order equation.

Figure C-2. Tank 241-AZ-102/241-AN-107 Hydroxide Concentration



Because the available data for the waste in tank 241-AN-107 does not fit the test for either 1st or 2nd order kinetics, the hydroxide consumption seen in this tank cannot be extrapolated to other tanks. Table C-4 shows several possible scenarios where the data was forced into either a 1st or 2nd order equation.

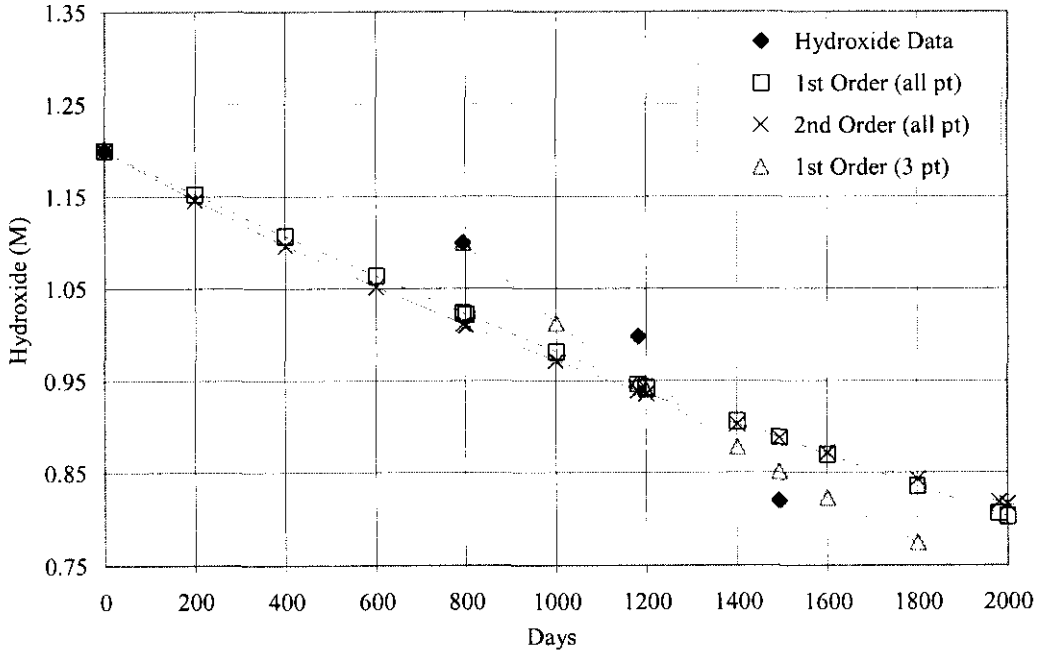
Table C-4. Forced Fit to Tank 241-AN-107 Data

	1st Order All point	**2nd Order All points**	**1st Order Three points, (excludes 1st point)**
k	0.000201	0.000196	0.00038
R^2	0.818	0.773	0.926
Equation Form	$C = C_o e^{-kt}$	$\frac{1}{C} - \frac{1}{C_o} = kt$	$C = C_o e^{-kt}$

Note that the 1st order equation for tank 241-AN-107 based on three data points is a better fit than the equation using all data points. This equation is also similar to the equation that was derived in Carothers (2001) using the data for tank 241-AN-102.

Figure C-3 shows the fit of these equations to the data that was used to derive the equations. Note that the y-axis has not been transformed, so the curves do not appear as straight lines.

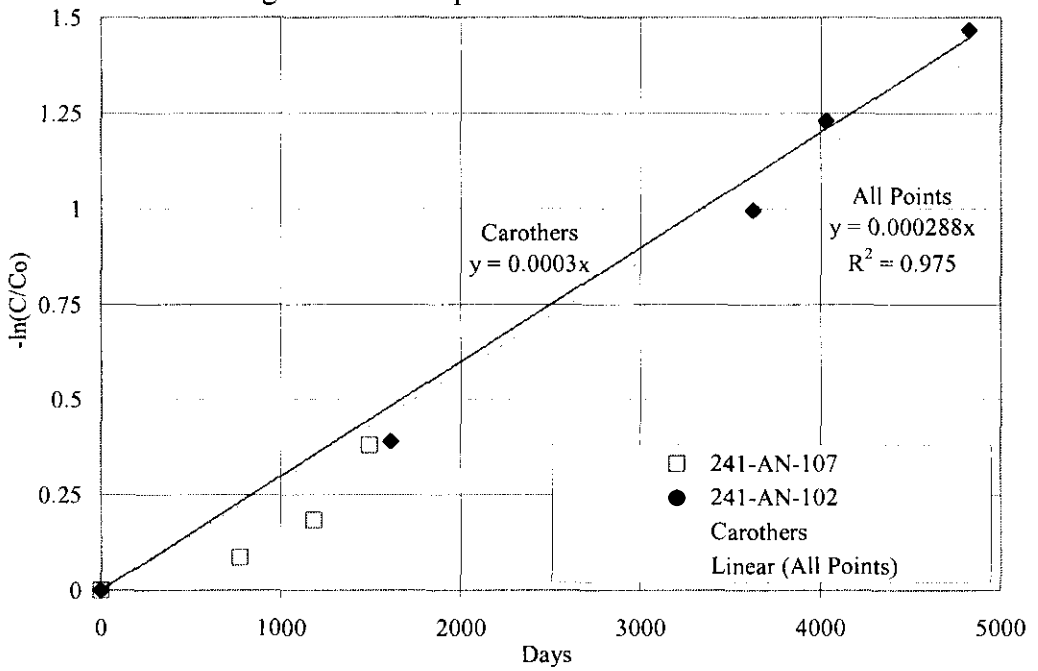
Figure C-3. Complexed Concentrate Now in Tank 241-AN-107



C3.3 Combined Data

Equations for both tanks 241-AN-102 and 241-AN-107 have coefficients, k, that are very close numerically. Both sets of data were combined and plotted on the same graph, Figure C-4. Data for both tanks are shown, along with plots of two equations. The derivation of the line labeled Carothers can be found in Carothers (2001) and in Section C3.1. The other line is the least square fit regression of data from both tanks. The use of the tank 241-AN-107 data with the tank 241-AN-102 data causes a slight drop in the regression line. The resultant coefficient is 0.000288. It can be rounded to 0.0003, which agrees with Carothers.

Figure C-4. Complexed Concentrate Kinetics



C4.0 CONCLUSIONS AND RECOMMENDATIONS

The plot of the data from both tanks 241-AN-102 and 241-AN-107 indicates that hydroxide consumption follows a 1st order kinetics reaction. The trend line for both tanks gives a k value of 0.000288. This can be rounded to 0.0003 and agrees with the k for tank 241-AN-102 alone. A regression of the data for both tanks gives the following equation that can be used to predict the current hydroxide concentration for first order kinetics, based on the initial concentration and the elapsed time:

$$C = C_o e^{-0.0003t} \qquad \text{(C-11)}$$

where:

t is the time in days.

The value for k is consistent with the rate constant for both tanks 241-AN-102 and 241-AN-107.

It is recommended that this equation only be applied to hydroxide consumption for complexed waste and only be used for interpolation up to 5,000 days.

C5.0 REFERENCES

Carothers, K. G., 2001 "Hydroxyl Ion Concentration Reaction Model for Tank 241-AN-102 Waste," (internal memorandum CL3120-01-034, March 29), CH2M HILL Hanford Group, Inc., Richland, Washington.

CHG, 2001, "Chemistry Control Program," *Tank Farms Technical Safety Requirements*, Section 5.15, HNF-SD-WM-TSR-006, Rev. 2B, CH2M HILL Hanford Group, Inc., Richland, Washington.

Delegard, C. H., 1979, "Analytical Data for Tanks 101-AZ, 102-AZ, 102-TX, and 102-AY Hot and Synthetic Liquors," (internal memorandum 65120-79-151 J, September 29).

Reynolds, D. A., 1989, "Reaction Kinetics in Complexed Concentrate," (internal memorandum 13314-89-050, June 6), Westinghouse Hanford Company, Richland, Washington.

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APPENDIX D

REGRESSION ANALYSIS

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Table D-1. Measured and Predicted Supernatant Hydroxide Concentrations

Tank	Waste Type	Measured	Hobbs		Carothers	
Tank 241-		OH M	OH M	% Error	OH M	% Error
AN-102	CC	1.60E-01	1.70E-01	6.25E+00	1.50E-01	-6.25E+00
AN-102	CC	1.90E-01	2.20E-01	1.58E+01	2.0E-01	5.26E+00
AN-107	CC	1.05E-03	2.44E-05	-9.77E+01	1.2E-02	1.04E+03
AN-107	CC	1.05E-03	4.11E-05	-9.61E+01	1.3E-02	1.14E+03
AN-107	CC	2.00E-02	2.60E-03	-8.70E+01	2.3E-02	1.50E+01
AP-104	DN	1.40E-04	6.90E-07	-9.95E+01	NA	NA
AW-104	DN	1.10E-01	1.30E-01	1.82E+01	NA	NA
AY-101	DC	3.00E-05	1.80E-05	-4.00+01	5.0E-05	6.67E+01
AY-102	DN	9.00E-03	8.00E-02	7.89E+02	NA	NA
AZ-102	DN/AW	4.00E-02	7.00E-02	7.50E+01	NA	NA

Table D-2. Regression Analysis Hobbs Equation with Intercept Not Equal to Zero.

SUMMARY OUTPUT)

Regression Statistics	
Multiple R	0.954204774
R Square	0.910506751
Adjusted R Square	0.899320094
Standard Error	0.025962804
Observations	10

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	0.054863823	0.054864	81.39222	1.8205E-05
Residual	8	0.005392538	0.000674		
Total	9	0.060256361			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	0.010266642	0.010359876	0.991	0.350709	-0.01362329	0.034156574
Measured	1.072934236	0.118927329	9.021764	1.82E-05	0.798687148	1.347181325

Table D-3. Regression Analysis Hobbs Equation with Intercept Equal to Zero.

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.948430566
R Square	0.899520538
Adjusted R Square	0.788409427
Standard Error	0.025936946
Observations	10

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	0.054201834	0.054202	80.57054	1.88968E-05
Residual	9	0.006054527	0.000673		
Total	10	0.060256361			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	0	#N/A	#N/A	#N/A	#N/A	#N/A
Measured	1.144812557	0.094155556	12.15874	6.88E-07	0.931817729	1.357807385

Table D-4. Regression Analysis Carothers Equation with intercept Not Equal to Zero.

Regression Statistics	
Multiple R	0.995640036
R Square	0.991299082
Adjusted R Square	0.989123852
Standard Error	0.008963339
Observations	6

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	0.036613336	0.036613	455.7216	2.84725E-05
Residual	4	0.000321366	8.03E-05		
Total	5	0.036934702			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	0.006264719	0.004616284	1.357091	0.246279	-0.006552166	0.019082
X Variable 1	0.968644524	0.045374789	21.34764	2.85E-05	0.842663651	1.094625

Table D-5. Regression Analysis Carothers Equation with Intercept Equal to Zero.

Regression Statistics	
Multiple R	0.993626171
R Square	0.987292968
Adjusted R Square	0.787292968
Standard Error	0.009688451
Observations	6

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	0.036465372	0.036465	388.4829	3.90833E-05
Residual	5	0.00046933	9.39E-05		
Total	6	0.036934702			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	0	#N/A	#N/A	#N/A	#N/A	#N/A
X Variable 1	1.00618409	0.038877725	25.88073	1.61E-06	0.90624588	1.106122

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APPENDIX E

CAUSTIC LIMITS REPORT BASED ON BEST-BASIS INVENTORY ISSUED APRIL 2001 WITH EFFECTIVE DATE JANUARY 1, 2001

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Table E-1. Caustic Limits Report Based on Best-Basis Inventory Issued April 2001 with Effective Date January 1, 2001

Tank Name	Waste Phase	NO_3 Molarity	OH Molarity	NO_2 Molarity	TOC Molarity	Al Molarity	Specific Gravity	Volume (kgal)	OH Sample or Calculation Date	OH Lower Limit	NO_2 Lower limit	$NO_3/(OH+NO_2)$	$OH+NO_2$
241-AN-101	Supernatant	1.10E+00	1.17E+00	8.30E-01	9.24E-02	3.74E-01	1.17E+00	2.24E+02	Apr 8 1998 (E)	1.10E-01	NA	5.51E-01	2.00E+00
241-AN-102	Salt Cake	NA	NA	NA	NA	NA	NA	8.90E+01	NA	NA	NA	NA	NA
241-AN-102	Supernatant	3.82E+00	1.56E-01	2.05E+00	2.15E+00	5.95E-01	1.43E+00	9.65E+02	Feb 1 1998 (S)	3.00E-01	NA	1.73E+00	2.21E+00
241-AN-103	Supernatant	2.69E+00	4.92E+00	3.56E+00	2.16E-01	1.11E+00	1.48E+00	4.97E+02	Sep 1 1996 (S)	2.70E-01	NA	3.17E-01	8.49E+00
241-AN-103	Salt Cake	NA	NA	NA	NA	NA	NA	4.05E+02	NA	NA	NA	NA	NA
241-AN-104	Supernatant	2.77E+00	4.21E+00	2.44E+00	2.62E-01	1.44E+00	1.41E+00	5.50E+02	Aug 1 1996 (S)	2.80E-01	NA	4.17E-01	6.65E+00
241-AN-104	Salt Cake	NA	NA	NA	NA	NA	NA	4.59E+02	NA	NA	NA	NA	NA
241-AN-105	Supernatant	2.60E+00	3.40E+00	2.63E+00	2.96E-01	1.52E+00	1.42E+00	6.36E+02	Jun 10 1996 (S)	2.60E-01	NA	4.32E-01	6.03E+00
241-AN-105	Salt Cake	NA	NA	NA	NA	NA	NA	4.68E+02	NA	NA	NA	NA	NA
241-AN-106	Salt Cake	NA	NA	NA	NA	NA	NA	1.69E+01	NA	NA	NA	NA	NA
241-AN-106	Supernatant	1.14E+00	8.54E-01	4.12E-01	3.89E-01	1.29E-01	1.18E+00	2.09E+01	Apr 1 1995 (E)	1.10E-01	NA	9.03E-01	1.27E+00
241-AN-107	Supernatant	3.86E+00	1.05E-03	1.44E+00	3.45E+00	1.09E-02	1.38E+00	7.94E+02	Apr 17 1998 (S)	3.00E-01	NA	2.68E+00	1.44E+00
241-AN-107	Salt Cake	NA	NA	NA	NA	NA	NA	2.47E+02	NA	NA	NA	NA	NA
241-AP-101	Supernatant	2.13E+00	2.43E+00	9.11E-01	1.63E-01	2.57E-01	1.31E+00	1.11E+03	Feb 8 2000 (S)	2.10E-01	NA	6.38E-01	3.34E+00
241-AP-102	Supernatant	1.27E+00	5.39E-01	8.29E-01	2.84E-01	4.28E-01	1.20E+00	1.09E+03	Apr 30 1993 (S)	1.30E-01	NA	9.25E-01	1.37E+00
241-AP-103	Supernatant	2.21E+00	5.67E-01	2.34E+00	3.23E-01	3.17E-01	1.31E+00	2.82E+02	Aug 12 1999 (S)	2.20E-01	NA	7.60E-01	2.90E+00
241-AP-104	Supernatant	1.68E+00	7.47E-01	1.29E+00	4.29E-01	6.41E-01	1.25E+00	1.11E+03	Jan 10 2000 (E)	1.70E-01	NA	8.25E-01	2.03E+00
241-AP-105	Supernatant	3.85E+00	7.00E-01	2.22E+00	2.40E-01	7.75E-01	1.35E+00	1.05E+03	May 24 2000 (E)	3.00E-01	NA	1.32E+00	2.92E+00
241-AP-105	Salt Cake	NA	NA	NA	NA	NA	NA	8.90E+01	NA	NA	NA	NA	NA
241-AP-106	Supernatant	1.47E+00	7.57E-01	1.28E+00	4.55E-01	5.60E-01	1.24E+00	6.23E+02	Feb 25 2000 (E)	1.50E-01	NA	7.20E-01	2.04E+00
241-AP-107	Supernatant	1.59E+00	8.11E-01	1.31E+00	3.36E-01	5.56E-01	1.23E+00	9.86E+02	Oct 2 2000 (E)	1.60E-01	NA	7.47E-01	2.12E+00
241-AP-108	Supernatant	1.29E+00	7.31E-01	6.23E-01	8.02E-02	3.54E-01	1.25E+00	3.20E+01	Mar 1 2000 (S)	1.30E-01	NA	9.50E-01	1.35E+00
241-AW-101	Supernatant	2.74E+00	5.64E+00	2.61E+00	3.34E-01	1.22E+00	1.47E+00	7.39E+02	Apr 22 1998 (S)	2.70E-01	NA	3.32E-01	8.25E+00
241-AW-101	Salt Cake	NA	NA	NA	NA	NA	NA	3.63E+02	NA	NA	NA	NA	NA
241-AW-102	Supernatant	9.87E-01	4.14E-01	4.13E-01	5.18E-02	2.23E-01	1.14E+00	3.41E+01	Aug 30 1999 (E)	1.00E-02	1.10E-02	1.19E+00	8.27E-01
241-AW-102	Sludge	NA	NA	NA	NA	NA	NA	3.01E+01	NA	NA	NA	NA	NA
241-AW-103	Supernatant	6.61E-02	5.66E-01	3.54E-02	6.41E-02	1.91E-03	1.06E+00	1.96E+02	Aug 29 1999 (S)	1.00E-02	1.10E-02	1.10E-01	6.01E-01
241-AW-103	Sludge	NA	NA	NA	NA	NA	NA	2.73E+02	NA	NA	NA	NA	NA
241-AW-103	Salt Cake	NA	NA	NA	NA	NA	NA	4.02E+01	NA	NA	NA	NA	NA
241-AW-104	Salt Cake (Liquids)	2.40E+00	NA	2.17E+00	3.15E-01	1.10E+00	1.44E+00	3.59E+01	NA	2.40E-01	NA	NA	NA
241-AW-104	Salt Cake (Solids)	NA	NA	NA	NA	NA	NA	1.21E+02	NA	NA	NA	NA	NA
241-AW-104	Supernatant	1.40E-01	1.09E-01	3.59E-02	4.74E-02	4.03E-03	1.07E+00	8.95E+02	Aug 23 2000 (S)	1.00E-02	1.10E-02	9.65E-01	1.45E-01
241-AW-104	Sludge (Solids)	NA	NA	NA	NA	NA	NA	4.99E+01	NA	NA	NA	NA	NA
241-AW-104	Sludge (Liquids)	1.89E+00	NA	1.51E+00	1.53E+00	6.08E-01	1.43E+00	1.61E+01	NA	1.90E-01	NA	NA	NA
241-AW-105	Sludge	NA	NA	NA	NA	NA	NA	2.55E+02	NA	NA	NA	NA	NA
241-AW-105	Supernatant	5.53E-01	3.96E-01	5.17E-02	7.81E-02	8.50E-03	1.06E+00	1.72E+02	May 9 1997 (S)	1.00E-02	1.10E-02	1.23E+00	4.48E-01
241-AW-106	Supernatant	3.09E+00	6.98E-01	1.38E+00	1.84E-01	7.36E-01	1.39E+00	5.00E+02	May 24 2000 (E)	3.00E-01	NA	1.49E+00	2.08E+00
241-AW-106	Salt Cake	NA	NA	NA	NA	NA	NA	2.39E+02	NA	NA	NA	NA	NA
241-AY-101	Supernatant	1.91E-01	1.69E+00	1.17E+00	2.50E-01	5.95E-04	1.00E+00	3.70E+01	Dec 19 2000 (E)	1.00E-02	1.10E-02	6.68E-02	2.86E+00
241-AY-101	Sludge (Solids)	NA	NA	NA	NA	NA	NA	9.19E+01	NA	NA	NA	NA	NA
241-AY-101	Sludge (Liquids)	1.09E-01	5.26E-05	1.42E+00	2.46E-01	1.96E-02	1.14E+00	1.61E+01	Jan 11 2000	1.00E-02	1.10E-02	7.68E-02	1.42E+00
241-AY-102	Sludge	NA	NA	NA	NA	NA	NA	1.84E+02	NA	NA	NA	NA	NA
241-AY-102	Supernatant	5.63E-03	8.56E-03	1.68E-01	1.69E-01	4.56E-02	1.13E+00	3.95E+02	Jan 6 2000 (S)	1.00E-02	1.10E-02	2.10E-02	1.77E-01
241-AZ-101	Supernatant	1.06E+00	6.23E-01	1.45E+00	2.78E-02	2.92E-01	1.22E+00	8.65E+02	Nov 10 1999 (S)	1.10E-01	NA	5.09E-01	2.08E+00
241-AZ-101	Sludge	NA	NA	NA	NA	NA	NA	5.20E+01	NA	NA	NA	NA	NA
241-AZ-102	Supernatant	2.77E-01	4.13E-02	7.16E-01	8.73E-02	2.30E-02	1.14E+00	8.92E+02	Aug 1 1999 (S)	1.00E-02	1.10E-02	3.66E-01	7.57E-01
241-AZ-102	Sludge	NA	NA	NA	NA	NA	NA	1.05E+02	NA	NA	NA	NA	NA
241-SY-101	Supernatant	2.27E+00	1.55E+00	1.91E+00	5.13E-01	4.97E-01	1.36E+00	6.94E+02	Apr 1 2000 (S)	2.30E-01	NA	6.58E-01	3.45E+00
241-SY-101	Salt Cake	NA	NA	NA	NA	NA	NA	2.60E+02	NA	NA	NA	NA	NA
241-SY-102	Sludge	NA	NA	NA	NA	NA	NA	7.11E+01	NA	NA	NA	NA	NA
241-SY-102	Supernatant	1.49E+00	8.11E-01	1.39E+00	2.46E-01	6.86E-01	1.23E+00	7.59E+02	Oct 2 2000 (E)	1.50E-01	NA	6.74E-01	2.20E+00
241-SY-103	Supernatant	2.84E+00	1.70E+00	3.06E+00	8.19E-01	1.28E+00	1.47E+00	3.69E+02	Aug 1 1994 (S)	2.80E-01	NA	5.96E-01	4.76E+00
241-SY-103	Salt Cake	NA	NA	NA	NA	NA	NA	3.51E+02	NA	NA	NA	NA	NA

* NA – not applicable

- Concentrations are not presented for solid waste phases as tank composition specifications for OH, NO_3 and NO_2 apply to liquid waste phases only.
- When NO_3 concentration is > 1.0 molar, NO_2 lower concentration limit is a function of OH or of both OH and NO_3.

* Separate interstitial liquid concentrations (Sludge (Liquids) and/or Salt Cake (Liquids)) are provided when these waste phases were included in the best-basis inventory.

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