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Ms. Hedges:

COMPLETION OF HANFORD FEDERAL FACILITY AGREEMENT AND CONSENT ORDER TARGET DATE M-045-91F-T02, DUE MARCH 31, 2015

Reference: WRPS letter L.D. Olson to K.W. Smith, ORP, "Washington River Protection Solutions LLC Submittal of Hanford Federal Facility Agreement and Consent Order Target M-045-91F-T02 Deliverable," WRPS-150006, dated January 13, 2015.

This letter documents the completion of the Hanford Federal Facility Agreement and Consent Order (HFFACO) Target Date M-045-91F-T02. This Target Date requires that the U.S. Department of Energy, Office of River Protection provide to the Washington State Department of Ecology (Ecology) a HFFACO secondary document, evaluating the common factors of liner failures for single-shell tanks (SST) that have leaked and will provide recommendations as appropriate, such as enhanced leak detection, monitoring, and mitigation. For purposes of this target, the SSTs that have leaked are identified through the RPP-32681, *Process to Assess Tank Farm Leaks in Support of Retrieval and Closure Planning*, Rev. 0.

The enclosed summary report (RPP-RPT-55804) satisfies the requirements of the subject Target Date. The report provides an analysis of the failure mechanisms for the SSTs identified as having leaked through RPP-32681. The results of the analysis have been discussed with members of the Ecology staff.

If you have questions, please contact Jeremy M. Johnson at 376-1866.

Kevin W. Smith
Manager

TPD:JMJ

Attachment 1229140, 1229141

Distribution: Page 2

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ATTACHMENT

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RPP-RPT-55804

Common Factors Relating to Liner Failures in Single-Shell Tanks

Rev. 1

DOCUMENT RELEASE AND CHANGE FORM

Prepared For the U.S. Department of Energy,
Assistant Secretary for Environmental Management
By Washington River Protection Solutions, LLC., PO Box 850, Richland, WA 99352
Contractor For U.S. Department of Energy, Office of River Protection, under Contract DE-AC27-08RV14800

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Common Factors Relating to Liner Failures in Single-Shell Tanks

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Abstract: This report fulfills the requirement for target T04 for Hanford Federal Facility Agreement and Consent Order milestone M-045-91F. The goal of this report is to identify the common factors that may have contributed to liner failures in single-shell tanks. The tanks with probable liner failures are identified through the process identified in RPP-32681, Rev. 0, "Process to Assess Tank Farm Leaks in Support of Retrieval and Closure Planning."

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Common Factors Relating to Liner Failures in Single-Shell Tanks

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Washington River Protection Solutions

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EXECUTIVE SUMMARY

Hanford Federal Facility Agreement and Consent Order (HFFACO) Tri-Party Agreement (TPA) interim milestones and target dates regarding single-shell tank (SST) integrity assurance were established via TPA change package M-45-10-01, in January 2011. The change package addressed recommendations from nationally recognized experts convened as the Single-Shell Tank Integrity Expert Panel (Panel). The TPA interim milestone M-045-91F was established as part of that change package to address the recommendations associated with liner degradation (LD). The TPA target M-045-91F-T02 was established specifically to address the Panel's recommendation LD-6.

> *DOE shall provide to Ecology as a HFFACO secondary document a report, evaluating the common factors of liner failures for SSTs that have leaked and will provide recommendations as appropriate, such as enhanced Leak Detection, Monitoring, and Mitigation. For purposes of this milestone, the SSTs that have leaked are identified through the RPP-32681, Rev 0, Process to Assess Tank Farm Leaks in Support of Retrieval and Closure Planning.*

This report has been prepared to meet the requirements of TPA target date M-045-91F-T02 which provides a tank liner common failure analysis of the SSTs with probable liner failures compared to tanks without probable liner failures. The SSTs were identified as having a probable liner failure (25 tanks), as being sound (76 tanks), or indeterminate (48 tanks). Tanks with probable liner failures were identified in assessments conducted using RPP-32681, *Process to Assess Tank Farm Leaks in Support of Retrieval and Closure Planning*. Inconclusive tanks are recommended for more detailed assessment according to TFC-ENG-CHEM-D-42, *Tank Leak Assessment Process*.

The method used to perform the analysis consists of first identifying the broadest set of mechanisms that could reasonably cause or play a supportive role in causing liner failure. Each mechanism was evaluated to determine if the factors necessary for the mechanism to occur might be present in SSTs and if so, the mechanism was considered possible. Out of the extensive list of mechanisms evaluated, a total of 28 mechanisms were identified as possibly contributing to tank liner failures. Available historical information about the tanks and their operation were reviewed in detail to identify if the underlying factors are indeed present and standard statistical techniques were employed to analyze the mechanisms. For convenience, the mechanisms were categorized into design and design modification flaws, procured materials, tank construction defects, operational service related failure mechanisms, and external environment failure mechanisms.

Adequate historical information was not available related to 14 of the 28 possible failure mechanisms, and therefore, it was not possible to make a determination on whether factors associated with these 14 mechanisms were likely common factors contributing to liner failure. For the remaining 14 mechanisms with historical information, it is important to recognize that small sample sets of tanks with and without a particular factor present can limit confidence in the results. Additionally, because the evaluations were based on field data rather than carefully controlled "experiments", confounding factors (variables not controlled in the data set that correlate with the variables of interest) may be present that mask the real common factors contributing to liner failure. Of the 14 mechanisms with historical information, factors

associated with six of them were evaluated as likely common factors contributing to tank liner failure. The 28 failure mechanisms are presented in Table ES-1 including identification of whether each factor is considered likely, unlikely or indeterminate as a common factor.

Table ES-1. Analysis Results of Possible Failure Mechanisms

Liner Failure Mechanisms	Indeterminate	Unlikely	Likely
Design and Design Modification Flaws			
Lack of Post-Weld Stress Relieving			X
Liner Bottom to Wall Transition Design			X
Exterior Finish of Tank Liner	X		
Lack of Vent Path for Gases Formed Below Tank Liner		X	
Procured Material Defects			
Properties of Liner Materials			
Carbon Equivalent		X	
Yield Strength			X
Material Standard and Grade	X		
Liner Plate Thickness	X		
Steel Liner Plate Defects	X		
Weld Material Defects	X		
Tank Fabrication Defects			
Brittle Fracture or Crack Propagation During Fabrication		X	
Cold Working and Strain Aging (shop fabricated knuckles		X	
Weld Joint Discontinuities and Defects	X		
Operational Service Related Failure Mechanisms			
Low-Cycle Fatigue		X	
Temperature Induced Failure			
Rate of Rise	X		
High Temperature			X
Corrosion			
General or Uniform Corrosion		X	
Pitting Corrosion	X		
Crevice Corrosion	X		
Stress-Corrosion Cracking			
Nitrate-Induced[1]			X[1]
Caustic Cracking		X	
Carbonate-Induced	X		
Concentration Cell Corrosion			
Liquid-Air Interface	X		
Solid-Liquid Interface	X		
Solid-Solid Interface		X	
Vapor Space Corrosion	X		
Differential Temperature Cell Corrosion	X		
External Environmental Failure Mechanisms			
Pressurization External to Tank Liner			X

[1] Nitrate-induced stress-corrosion cracking is likely for three waste types: TBP waste if it is the first waste in a tank; REDOX concentrated and neutralized salt waste; and, in-farm nitrate leaching. Nitrate-induced SCC is unlikely for other waste types considered, except for PUREX 1970 Thoria Campaign waste for which the analysis was indeterminate.

Likely common factors for a significant number of tank liner failures are the lack of post-weld stress relieving, tank liner bottom to wall transition design, high operational temperatures, and

storage of waste types conducive to nitrate-induced stress corrosion cracking. Nitrate-induced stress corrosion cracking involved waste storage from the tri-butyl phosphate (TBP) process, REDOX process, and in-farm nitrate leaching. Some or all of the factors may be acting individually or together to result in tank liner failure. The precise identification of the cause of each of the 25 SSTs with probable liner failures is not possible with the available information.

The M-045-91F-T02 target date states that recommendations such as leak detection, monitoring or mitigation (LDMM) activities would be provided as appropriate. There were no conclusions from this analysis to question current LDMM activities or to recommend changes to LDMM activities. As such, no bases for specific recommendations have been identified in the areas of LDMM associated with the SSTs.

Observations are given in three additional areas for future application.

1. Any tank forensics effort would be improved by providing for documentation of an entire project from procurement, through construction, into operations, and beyond with complete, accurate, and retrievable records. This should also include archiving construction material specimens to aid in future investigations.
2. Undesirable factors from past design and construction activities are unchangeable in the SSTs but should be eliminated in new construction. These include reduction of residual stresses by better design, post-weld stress relief, and proper material selection.
3. Transient operational factors that can change with time including temperature, aggressive chemical environments, or conditions allowing external pressurization resulting in a bulged liner should be considered when they may affect future storage of waste in the SSTs. For instance, waste temperatures are declining which generally results in a lower rate or likelihood of corrosion.

The identification of stress corrosion cracking (SCC) as a common factor is in some conflict with historical corrosion testing. Historical tests, especially those related to SCC were limited and lack the sensitivity of modern corrosion testing. Therefore, testing of select waste types using modern testing methods is planned to gauge their propensity for SCC. The testing will use simulants based on compositions provided in this document and be conducted at temperatures representative of historical storage conditions. This testing is integrated with ongoing DST corrosion testing. The waste types selected for testing include Uranium Recovery TBP waste, REDOX concentrated and neutralized waste, and nitrate leaching waste.

The assessment results of tanks recommended for future SST leak assessments per the TFC-ENG-CHEM-D-42 process could affect the results of this document. If a large number of tanks that go through the TFC-ENG-CHEM-D-42 process are identified as having liner leaks, it may be desirable to assess any benefit that would be derived from revisiting this failure analysis. In the event that most tanks are found to be considered sound, it would not make sense to revisit the failure analysis.

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LIST OF TERMS

Terms

Assumed Leaker. The 'Assumed Leaker' term refers to the list of 61 single-shell tanks that are listed in HNF-EP-0182, Rev. 321, *Waste Tank Summary Report for Month Ending September 30, 2014*. These tanks were assumed to have leaked in the past or the integrity of the tanks has been questioned based on liquid level decreases in the tank and/or increased gamma radioactivity discovered in soil near the tanks.

Confirmed Leaker. The 'Confirmed Leaker' term refers to the list of 25 single-shell tanks that were identified as having probable liner leaks via the reports prepared via the RPP-32681, Rev 0, *Process to Assess Tank Farm Leaks in Support of Retrieval and Closure Planning* process. This term does not include tanks for which liquid level decreases in the tanks and/or gamma activity discovered in the soil near the tanks may be attributed to sources other than a tank liner leak; such as overfills, line breaks, surface leaks, etc.

Abbreviations and Acronyms

IAW	REDOX stream 1A column waste
1C	First cycle decontamination
2C	Second cycle decontamination
AFAN	ammonium fluoride and ammonium nitrate
Al_2O_3	aluminum oxide
ALC	air-lift circulator
ANN	aluminum nitrate nonahydrate
ASME	American Society of Mechanical Engineers
ASTM	American Society for Testing Materials
B&PV	Boiler and Pressure Vessel
$BiPO_4$	Bismuth Phosphate
BMZ	base metal zone
BNW	Battelle-Northwest waste
CAW	current acid waste
CE	Carbon Equivalent
CW	coating removal waste
DBTT	ductile-to-brittle transition temperature
DOE	U.S. Department of Energy
dpa	displacements per atom
DST	double-shell tank
DTPA	diethylenetriaminepentaacetate
EB	evaporator bottoms
Ecology	State of Washington, Department of Ecology
EDTA	ethylenediaminetetraacetic acid
ft/sec	feet per second
FP	fission product
gpm	gallons per minute
HAZ	heat-affected zone

HEDTA	hydroxyethyl ethylenediamine triacetic acid
HFFACO	Hanford Federal Facility Agreement and Consent Order
HLO	Hanford Laboratories waste
HLW	high level waste
HNO_3	nitric acid
ITS	in-tank solidification
ITS-1	In-Tank Solidification Unit 1
ITS-2	In-Tank Solidification Unit 2
kgal	kilo-gallon
LAI	liquid-air interface
LD	liner degradation
LIP	leak identification and prevention
LW	222-S Laboratory Waste
M	Molar (moles/liter)
MCM	mitigation of contaminant migration
MIC	microbiologically-induced corrosion
mils	thousandth of an inch
mil/yr	mils per year
mpy	mils per year
Mrad	megarad
MW	Metal Waste
NACE	National Association of Corrosion Engineers
$NaNO_2$	sodium nitrite
$NaNO_3$	sodium nitrate
NRC	United States Nuclear Regulatory Commission
ORNL	Oak Ridge National Laboratories
ORP	U.S. Department of Energy, Office of River Protection
OWW	organic wash waste
Panel	Single-Shell Tank Integrity Project Expert Panel
PAS	PUREX acidified sludge
PAW	PUREX acid waste
PNNL	Pacific Northwest National Laboratory
PRTR	Plutonium Recycle Test Reactor
psi	pounds-force per square inch
psia	pounds-force per square inch absolute
PSN	PUREX supernatant
PSS	PUREX sludge supernatant
PTA	phosphotungstic acid
QI	questionable integrity
REDOX	Reduction and oxidation
RSN	REDOX supernatant
SCC	stress corrosion cracking
SCE	saturated calomel electrode
SI	structural integrity
SST	single-shell tank
SSTIP	Single-Shell Tank Integrity Project

TAD	total acid demand
TBP	tri-butyl phosphate
TPA	Tri-Party Agreement
UO_3	uranium trioxide
UPR	unplanned release
WI	weld interface
WMZ	weld metal zone
WRPS	Washington River Protections Solutions, LLC
ZAW	Zirflex acid waste

1.0 INTRODUCTION

The Hanford Federal Facility Agreement and Consent Order (Hanford Tri-Party Agreement [TPA]) milestone M-045-91, completed September 2010, required that the Department of Energy (DOE), Office of River Protection (ORP) establish a panel of nationally recognized, technical experts (Single-Shell Tank Integrity Expert Panel or Panel) to provide a report on single-shell tank (SST) integrity assurance review and submit to the State of Washington, Department of Ecology (Ecology) a TPA change package with interim milestones as necessary to implement the Panel's recommendations. The milestone required that the ORP establish the Panel:

> *...to review available data from retrieved single-shell tanks (SSTs) to (1) evaluate their existing known conditions, (2) evaluate proposed future uses, (3) recommend critical modifications and associated schedule to prevent or mitigate degradation, and (4) recommend additional evaluations and program elements that would improve understanding of SST integrity*

The Panel issued two reports: RPP-RPT-43116, *Expert Panel Report for Hanford Single-Shell Tank Integrity*, and RPP-RPT-45921, *Second Expert Panel Report for Hanford Site Single-Shell Tank Integrity Report*, thus completing the first part of milestone M-045-91 (i.e., provide a report on single-shell tank integrity assurance for review). The recommendations were focused on four key elements: (1) confirmation of tank structural integrity (SI); (2) assessment of the likelihood of future tank liner degradation (LD); (3) leak identification and prevention (LIP); and, mitigation of contaminant migration (MCM). For the key element LD, the Panel identified eleven recommendations. The LD-6 recommendation essentially suggests investigating whether the current waste composition could cause failure of the tank steel liner through the mode of corrosion. That recommendation is addressed by this report.

The second part of M-045-91 (i.e., submit TPA change package with interim milestones) was completed by transmittal of TPA change package M-45-10-01 (LET 10-ESQ-286, "Completion of Hanford Federal Facility Agreement and Consent Order (HFFACO) Interim Milestone M-045-91, Due September 30, 2010"). The TPA change package is discussed below.

1.1 TRI-PARTY AGREEMENT INTERIM MILESTONE M-045-91F AND ASSOCIATED TARGET DATES

The TPA interim milestones and target dates regarding SST integrity assurance were established, in January 2011, based on the Panel's recommendations and negotiations between ORP and Ecology. The eight interim milestones, established via TPA change package M-45-10-01, covered recommendations from the Panel under the key elements SI, LD, and LIP.

The TPA interim milestone M-045-91F originally contained four target dates, M-045-91F-T01 through -T04. Target date M-045-91F-T01 was eliminated via TPA change control form M-45-13-01 "...to de-emphasize the reference to Savannah River Site leak rate assessments." The scope was transferred to target date M-045-91F-T04, and refocused on leak rates for the 25 SSTs

identified as leaking by the RPP-32681, Rev 0, *Process to Assess Tank Farm Leaks in Support of Retrieval and Closure Planning*[1], process.

The M-045-91F-T02 target date requires that the DOE provide to Ecology a report on the SSTs which have been identified as having leaked in RPP-32681 leak assessment inventory reports. This report has been prepared to meet the requirements of target date M-045-91F-T02. The wording of the M-045-91F-T02 target date is repeated below:

> *DOE shall provide to Ecology as a HFFACO secondary document a report, evaluating the common factors of liner failures for SSTs that have leaked and will provide recommendations as appropriate, such as enhanced Leak Detection, Monitoring, and Mitigation. For purposes of this milestone, the SSTs that have leaked are identified through the RPP-32681, Rev 0, Process to Assess Tank Farm Leaks in Support of Retrieval and Closure Planning.*

Target date M-045-91F-T03 deals with assessing the feasibility of testing for ionic conductivity between the inside and outside of SSTs. That assessment is documented in RPP-ASMT-51526, *Tri-Party Agreement Target Milestone M45-91F-T-03 Ionic Conductivity Assessment*. The scope of M-045-91F-T03 does not directly apply to the work performed in this report.

Target date M-045-91F-T04 deals with leak causes, locations and rates for the 25, 100-Series SSTs documented in RPP-RPT-54909, *Hanford Single-Shell Tanks Leak Causes, Locations, and Rates: Summary Report*. That report includes assessments of the causes for failure of individual tanks. The scope of the work documented in this report is performed in conjunction with the work performed under M-045-91F-T04.

Figure 1-1 graphically depicts the relationships between the initial interim TPA milestone, M-045-91, and subsequent Panel work and M-045-91F interim milestones and target dates that relate to this report.

1.2 OBJECTIVE

The goal of this report is to identify the common factors that may have contributed to liner failure in SSTs that leaked. This analysis was conducted for the 149 Type I, Type II, Type III, and Type IV SSTs. The evaluation compares the conditions of tanks with probable liner failures to tanks not known to have liner failures to determine the commonality of possible causes for those probable failures. This report has been prepared to meet the requirements of target date M-045-91F-T02.

[1] Revision 1 to RPP-32681 was issued with a new section to address the identification and evaluation of tank liner leak locations and leak causes per TPA target date M-045-91F-T04. This revision did not change the process to assess tank farm leaks in revision 0 of RPP-32681.

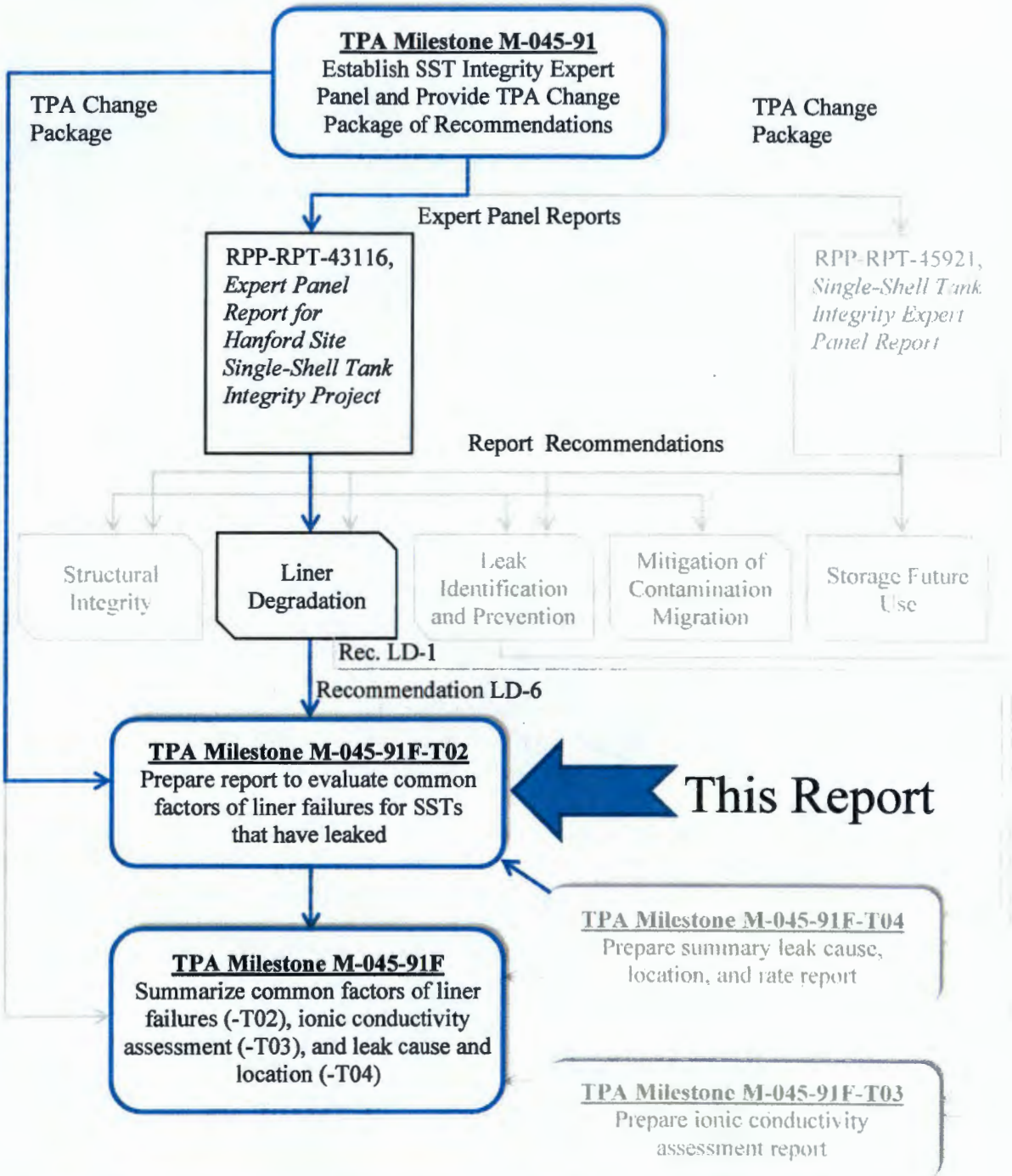


Figure 1-1. Tri-Party Agreement Target Date M-045-91-T02 Relational Diagram

2.0 SCOPE AND PROCESS

This report identifies the common factors that may have contributed to tank liner failure for the SSTs which have been identified as having leaked in leak assessment inventory reports developed via the process established in RPP-32681. A synopsis of the historical context of tank leak evaluations and results of the process outlined in RPP-32681 is provided in Appendix A. The report fulfills the requirements for target date M-045-91F-T02 which was reviewed with the ORP and Ecology personnel and documented in meeting minutes (see Appendix B).

2.1 PROCESS TO ASSESS TANK FARM LEAKS ACCORDING TO RPP-32681 AND INTEGRITY ASSESSMENTS ACCORDING TO TFC-ENG-CHEM-D-42

Ecology along with the Tank Farm Operations Contractor for the DOE developed a process to reassess selected tank leak estimates (volumes and inventories), and to update tank leak and unplanned release (UPR) volumes and inventory estimates as emergent field data are obtained (RPP-32681).

A team was assembled and a series of meetings were held with ORP and Ecology to present and discuss information reviewed pertaining to tank leak inventory estimates to be included in leak inventory assessment reports. The meeting process is described in RPP-32681 and each SST farm was assessed via the process laid out in RPP-32681. Each tank farm assessment was documented in a separate report with the exception of A and AX Farms which were documented in a single report. The most recent revisions of each of the reports are provided in Table 2-1. This meeting process was not a formal integrity assessment, but an assessment to estimate leak inventories in support of tank farm closure and risk assessments; formal integrity assessments are completed per TFC-ENG-CHEM-D-42, *Tank Leak Assessment Process*.

While estimating how much waste leaked from tanks and tank leak inventories, participants discovered that some of the tanks identified as "assumed leakers" may not have leaked and liquid level decreases in the tanks and/or gamma activity discovered in the vadose zone may be attributed to sources other than a tank liner leak. For example, some of the tanks were filled above spare inlet lines or cascade lines and releases previously reported to be attributed to liner leaks appear to be releases from these locations. Conversely, it was discovered that some tanks classified as "sound" tanks may have leaked.

Table 2-1. Leak Assessment Reports from the RPP-32681 Process

Tank Farm	Date Completed	Report Number & Revision
A AX	September 2014	RPP-ENV-37956, Rev 2, *Hanford A and AX Farm Leak Assessment Report*
B	September 2011	RPP-RPT-49089, Rev 0, *Hanford B-Farm Leak Inventory Assessments Report*
BX	February 2011	RPP-RPT-47562, Rev 0, *Hanford BX-Farm Leak Inventory Assessments Report*
BY	February 2011	RPP-RPT-43704, Rev 0A, *Hanford BY-Farm Leak Assessments Report*
C	January 2012	RPP-ENV-33418, Rev 2A[1], *Hanford C-Farm Leak Assessments Report*
S	May 2011	RPP-RPT-48589, Rev 0, *Hanford S-Farm Leak Assessment Report*
SX	February 2010	RPP-ENV-39658, Rev 0, *Hanford SX-Farm Leak Assessments Report*
T	August 2013	RPP-RPT-55084, Rev 0, *Hanford 241-T Farm Leak Inventory Assessment Report*
TX	August 2013	RPP-RPT-50870, Rev 0, *Hanford 241-TX Farm Leak Inventory Assessment Report*
TY	April 2010	RPP-RPT-42296, Rev 0, *Hanford TY-Farm Leak Assessments Report*
U	September 2011	RPP-RPT-50097, Rev 0, *Hanford 241-U Farm Leak Inventory Assessment Report*

[1]RPP-ENV-33418, Rev. 2A, is currently being updated

Formal tank integrity assessments (per TFC-ENG-CHEM-D-42) were recommended for tanks classified as "assumed leaker" in HNF-EP-0182 but for which sources other than a tank leak were identified that could explain liquid level decreases or gamma activity in the vadose zone. Similarly, formal tank integrity assessments were recommended for tanks classified as "sound" in HNF-EP-0182, but for which a tank liner leak appeared plausible.

The leak integrity status of all the SSTs is shown in Table 2-2. Of the 149 SSTs, there are 48 tanks that have been recommended for evaluation via TFC-ENG-CHEM-D-42. Of the 48 tanks to be further assessed via TFC-ENG-CHEM-D-42, 12 have previously been identified as "sound" in the HNF-EP-0182 waste tank summary report.

In accordance with TPA target date M-045-91F-T02, the common factors analyses were completed for those tanks where a liner leak appeared to be likely based on RPP-32681 process assessments. Table 2-3 lists those 25 SSTs that appeared to have a liner leak and their estimated failure dates.

For the purpose of common factors analysis, the interest lies in comparing tanks with confirmed liner leaks to all other tanks. The 48 tanks, or roughly 30% of the SSTs, that have been recommended for further evaluation of liner failure via TFC-ENG-CHEM-D-42 (which has not yet occurred) are assumed for the quantitative statistical analysis portion of this report to be "sound" tanks. Thus, the 25 tanks identified in Table 2-2 are the only tanks with probable liner failures for the purpose of this evaluation.

Table 2-2. Leak Integrity Status of the Single-Shell Tanks (4 Pages)

Tank	Leak Integrity Status (HNF-EP-0182, Rev. 321)	RPP-32681 Conclusions	TFC-ENG-CHEM-D-42 Results
241-A Farm			
A-101	Sound	Sound	N/A
A-102	Sound	Sound	N/A
A-103	Sound	D-42[1]	Sound (RPP-ASMT-42278[4])
A-104	Assumed Leaker	Confirmed Leaker	N/A
A-105	Assumed Leaker	Confirmed Leaker	N/A
A-106	Sound	Sound	N/A
6 Tanks Total	0 Tanks D-42	2 Tanks Confirmed Leakers	4 Tanks Sound
241-AX Farm			
AX-101	Sound	Sound	N/A
AX-102	Sound	D-42	Sound (RPP-ASMT-42628[4])
AX-103	Sound	Sound	N/A
AX-104	Sound	D-42	Sound (RPP-ASMT-57574[4])
4 Tanks Total	0 Tanks D-42	0 Tanks Confirmed Leakers	4 Tanks Sound
241-B Farm			
B-101	Assumed Leaker	D-42	Not yet performed
B-102	Sound	Sound	N/A
B-103	Assumed Leaker	D-42	Not yet performed
B-104	Sound	Sound	N/A
B-105	Assumed Leaker	D-42	Not yet performed
B-106	Sound	D-42	Not yet performed
B-107	Assumed Leaker	Confirmed Leaker	N/A
B-108	Sound	Sound	N/A
B-109	Sound	Sound	N/A
B-110	Assumed Leaker	D-42	Not yet performed
B-111	Assumed Leaker	D-42	Not yet performed
B-112	Assumed Leaker	D-42	Not yet performed
B-201	Assumed Leaker	D-42	Not yet performed
B-202	Sound	Sound	N/A
B-203	Assumed Leaker	D-42	Not yet performed
B-204	Assumed Leaker	D-42	Not yet performed
16 Tanks Total	10 Tanks D-42	1 Tank Confirmed Leaker	5 Tanks Sound
241-BX Farm			
BX-101	Assumed Leaker	D-42	Not yet performed
BX-102	Assumed Leaker	D-42	Not yet performed
BX-103	Sound	Sound	N/A
BX-104	Sound	Sound	N/A
BX-105	Sound	Sound	N/A
BX-106	Sound	Sound	N/A
BX-107	Sound	D-42	Not yet performed
BX-108	Assumed Leaker	D-42	Not yet performed
BX-109	Sound	Sound	N/A
BX-110	Assumed Leaker	D-42	Not yet performed
BX-111	Assumed Leaker	D-42	Not yet performed
BX-112	Sound	Sound	N/A
12 Tanks Total	6 Tanks D-42	0 Tanks Confirmed Leaker	6 Tanks Sound

Table 2-2. Leak Integrity Status of the Single-Shell Tanks (4 Pages)

Tank	Leak Integrity Status (HNF-EP-0182, Rev. 321)	RPP-32681 Conclusions	TFC-ENG-CHEM-D-42 Results
241-BY Farm			
BY-101	Sound	D-42	Not yet performed
BY-102	Sound	D-42	Not yet performed
BY-103	Assumed Leaker	Confirmed Leaker	N/A
BY-104	Sound	D-42	Not yet performed
BY-105	Assumed Leaker	D-42	Not yet performed
BY-106	Assumed Leaker	D-42	Not yet performed
BY-107	Assumed Leaker	D-42	Not yet performed
BY-108	Assumed Leaker	D-42	Not yet performed
BY-109	Sound	D-42	Not yet performed
BY-110	Sound	D-42	Not yet performed
BY-111	Sound	D-42	Not yet performed
BY-112	Sound	D-42	Not yet performed
12 Tanks Total	11 Tanks D-42	1 Tank Confirmed Leaker	0 Tanks Sound
241-C Farm			
C-101	Assumed Leaker	Confirmed Leaker	N/A
C-102	Sound	Sound	N/A
C-103	Sound	Sound	N/A
C-104	Sound	Sound	N/A
C-105	Assumed Leaker	D-42	Confirmed Leaker (RPP-ASMT-46452[4])
C-106	Sound	Sound	N/A
C-107	Sound	Sound	N/A
C-108	Sound	Sound	N/A
C-109	Sound	Sound	N/A
C-110	Sound	D-42	Sound (RPP-ASMT-38219[4])
C-111	Sound	D-42	Sound (RPP-ASMT-39155[4])
C-112	Sound	Sound	N/A
C-201	Assumed Leaker	D-42	Not yet performed[2]
C-202	Assumed Leaker	D-42	Not yet performed[2]
C-203	Assumed Leaker	D-42	Not yet performed[2]
C-204	Assumed Leaker	D-42	Not yet performed[2]
16 Tanks Total	4 Tanks D-42	2 Tanks Confirmed Leakers	10 Tanks Sound
241-S Farm			
S-101	Sound	Sound	N/A
S-102	Sound	Sound	N/A
S-103	Sound	Sound	N/A
S-104	Assumed Leaker	D-42	Not yet performed
S-105	Sound	Sound	N/A
S-106	Sound	Sound	N/A
S-107	Sound	Sound	N/A
S-108	Sound	Sound	N/A
S-109	Sound	Sound	N/A
S-110	Sound	Sound	N/A
S-111	Sound	Sound	N/A
S-112	Sound	Sound	N/A
12 Tanks Total	1 Tank D-42	0 Tanks Confirmed Leakers	11 Tanks Sound

Table 2-2. Leak Integrity Status of the Single-Shell Tanks (4 Pages)

Tank	Leak Integrity Status (HNF-EP-0182, Rev. 321)	RPP-32681 Conclusions	TFC-ENG-CHEM-D-42 Results
241-SX Farm			
SX-101	Sound	Sound	N/A
SX-102	Sound	Sound	N/A
SX-103	Sound	Sound	N/A
SX-104	Sound	D-42	Sound (RPP-ASMT-48143[4])
SX-105	Sound	Sound	N/A
SX-106	Sound	Sound	N/A
SX-107	Assumed Leaker	Confirmed Leaker	N/A
SX-108	Assumed Leaker	Confirmed Leaker	N/A
SX-109	Assumed Leaker	Confirmed Leaker	N/A
SX-110	Sound	D-42	Sound (RPP-ASMT-47140[4])
SX-111	Assumed Leaker	Confirmed Leaker	N/A
SX-112	Assumed Leaker	Confirmed Leaker	N/A
SX-113	Assumed Leaker	Confirmed Leaker	N/A
SX-114	Assumed Leaker	Confirmed Leaker	N/A
SX-115	Assumed Leaker	Confirmed Leaker	N/A
15 Tanks Total	0 Tanks D-42	8 Tanks Confirmed Leakers	7 Tanks Sound
241-T Farm			
T-101	Assumed Leaker	D-42	Not yet performed
T-102	Sound	D-42	In progress
T-103	Assumed Leaker	D-42	Not yet performed
T-104	Sound	Sound	N/A
T-105	Sound	D-42	In progress
T-106	Assumed Leaker	Confirmed Leaker	N/A
T-107	Assumed Leaker	D-42	Not yet performed
T-108	Assumed Leaker	D-42	Not yet performed
T-109	Assumed Leaker	D-42	Not yet performed
T-110	Sound	Sound	N/A
T-111	Assumed Leaker	Confirmed Leaker	N/A
T-112	Sound	Sound	N/A
T-201	Sound	Sound	N/A
T-202	Sound	Sound	N/A
T-203	Sound	Sound[3]	N/A
T-204	Sound	Sound[3]	N/A
16 Tanks Total	7 Tanks D-42	2 Tanks Confirmed Leakers	7 Tanks Sound
241-TX Farm			
TX-101	Sound	Sound	N/A
TX-102	Sound	Sound	N/A
TX-103	Sound	Sound	N/A
TX-104	Sound	D-42	Not yet performed
TX-105	Assumed Leaker	D-42	Not yet performed
TX-106	Sound	Sound	N/A
TX-107	Assumed Leaker	Confirmed Leaker	N/A
TX-108	Sound	Sound	N/A
TX-109	Sound	Sound	N/A
TX-110	Assumed Leaker	D-42	Not yet performed
TX-111	Sound	Sound	N/A

Table 2-2. Leak Integrity Status of the Single-Shell Tanks (4 Pages)

Tank	Leak Integrity Status (HNF-EP-0182, Rev. 321)	RPP-32681 Conclusions	TFC-ENG-CHEM-D-42 Results
TX-112	Sound	Sound	N/A
TX-113	Assumed Leaker	D-42	Not yet performed
TX-114	Assumed Leaker	Confirmed Leaker	N/A
TX-115	Assumed Leaker	D-42	Not yet performed
TX-116	Assumed Leaker	D-42	Not yet performed
TX-117	Assumed Leaker	D-42	Not yet performed
TX-118	Sound	Sound	N/A
18 Tanks Total	7 Tanks D-42	2 Tanks Confirmed Leakers	9 Tanks Sound
241-TY Farm			
TY-101	Assumed Leaker	D-42	Not yet performed
TY-102	Sound	Sound	N/A
TY-103	Assumed Leaker	Confirmed Leaker	N/A
TY-104	Assumed Leaker	Confirmed Leaker	N/A
TY-105	Assumed Leaker	Confirmed Leaker	N/A
TY-106	Assumed Leaker	Confirmed Leaker	N/A
6 Tanks Total	1 Tank D-42	4 Tanks Confirmed Leakers	1 Tank Sound
241-U Farm			
U-101	Assumed Leaker	D-42	Not yet performed
U-102	Sound	Sound	N/A
U-103	Sound	Sound	N/A
U-104	Assumed Leaker	Confirmed Leaker	N/A
U-105	Sound	Sound	N/A
U-106	Sound	Sound	N/A
U-107	Sound	Sound	N/A
U-108	Sound	Sound	N/A
U-109	Sound	Sound	N/A
U-110	Assumed Leaker	Confirmed Leaker	N/A
U-111	Sound	Sound	N/A
U-112	Assumed Leaker	Confirmed Leaker	N/A
U-201	Sound	Sound	N/A
U-202	Sound	Sound	N/A
U-203	Sound	Sound	N/A
U-204	Sound	Sound	N/A
16 Tanks Total	1 Tank D-42	3 Tanks Confirmed Leakers	12 Tanks Sound

[1] D-42 refers to the recommendation from the RPP-32681 process to further assess the tank per TFC-ENG-CHEM-D-42.

[2] Tanks C-201, C-202, C-203, and C-204 have been retrieved to date; however these tanks still have been recommended to be further assessed via TFC-ENG-CHEM-D-42.

[3] Tanks T-203 and T-204 were further assessed and concluded to be "Sound" in RPP-RPT-55264, Rev. 0, *Evaluation of Tanks 241-T-203 and 241-T-204 Level Data and In-Tank Video Inspections*, and RPP-RPT-57960, Rev. 0, *Results of June 2013 and June 2014 Breather Filter Inlet Valve Closure Test for Tanks 241-T-203 and 241-T-204.*

[4] References: RPP-ASMT-42278, *Tank 241-A-103 Leak Assessment Report.*
RPP-ASMT-42628, *Tank 241-AX-102 Integrity Assessment Report.*
RPP-ASMT-57574, *Tank 241-AX-104 Integrity Assessment Report.*
RPP-ASMT-46452, *Tank 241-C-105 Leak Assessment Completion Report.*
RPP-ASMT-38219, *Tank 241-C-110 Leak Assessment Report.*
RPP-ASMT-39155, *Tank 241-C-111 Leak Assessment Report.*
RPP-ASMT-48143, *Tank 241-SX-104 Leak Assessment Completion Report.*
RPP-ASMT-47140, *Tank 241-SX-110 Leak Assessment Report.*

Table 2-3. Listing of Twenty-Five Single-Shell Tanks with Probable Liner Failures as Determined by RPP-32681 Process

Tank	Earliest Assumed Failure
A-104	1975(1)
A-105	1963(1)
B-107	1969(2)
BY-103*	1969 or 1973(3)
C-101	1965(4)
C-105	1974(5)
SX-107	1964(6)
SX-108	1962(6)
SX-109	1965(6)
SX-111	1974(6)
SX-112	1969(6)
SX-113	1958(6)
SX-114	1972(6)
SX-115	1965(6)
T-106	1973(7)
T-111	1974(7)
TX-107	c. 1975(8)
TX-114	1974(8)
TY-103	1973(9)
TY-104	1974(9)
TY-105	1960(9)
TY-106	1959(9)
U-104	1953(10)
U-110	1975(10)
U-112	1969(10)

* High radiation readings found in drywell near BY-103 in 1969 and classified as borderline leaker in 1970. Tank was classified as a confirmed leaker in 1973.

(1) RPP-ENV-37956, Rev 1.
(2) RPP-RPT-49089, Rev 0.
(3) RPP-RPT-43704, Rev 0.
(4) RPP-ENV-33418, Rev 2A.
(5) RPP-ASMT-46452, Rev 0.
(6) RPP-ENV-39658, Rev 0.
(7) RPP-RPT-55084, Rev 0.
(8) RPP-RPT-50870, Rev 0.
(9) RPP-RPT-42296, Rev 0.
(10) RPP-RPT-50097, Rev 0.

2.2 SINGLE-SHELL TANK LEAK CAUSES, LOCATIONS, AND RATES EVALUATIONS

In accordance with TPA target date M-045-91F-T04, tank leak causes, locations, and rates evaluations were completed for those tanks where a liner leak was identified as likely based on RPP-32681 process assessments. The 25 tanks identified as confirmed leakers (see Table 2-3) were evaluated in a series of eight leak causes and locations reports and those results summarized in a single report, RPP-RPT-54909, Rev. 0. That report finds that the main causes for the liner leaks were:

- high tank operating temperatures that exceeded design parameters,
- high rates of temperature increases that exceeded design parameters,
- tank construction design factors limiting thermal expansion of liners, and
- storage of waste types with chemistry conducive to corrosion of the tank liner.

The predominant corrosive waste types are identified as tri-butyl phosphate waste (TBP), REDOX waste, and nitrate leached REDOX waste. These waste types fail to meet current double-shell tank (DST) chemistry specifications. The role of these causes in each of the 25 tank liner failures is summarized in Table 2-4 as excerpted from RPP-RPT-54909. Information and results from the leak cause and location reports are considered as part of this analysis. Report RPP-RPT-54909 lists additional information on the leak locations and leak rates which were not considered in part of the common factors analysis.

Table 2-4. Single-Shell Tank Liner Leak Causes Identified in Leak Cause and Location Reports (2 Pages)

Farm	Tank	Primary Leak Cause(s)
241-A	A-104	- High operating temperature and high temperature rate of rise - Tank design
	A-105	- Tank bulge - High temperature rate of rise - Tank design
241-B	B-107	- Waste chemistry conducive to corrosion, stress corrosion cracking (SCC) and pitting due to storage of possible low pH 1C/CW and TBP waste
241-BY	BY-103	- Waste chemistry conducive to corrosion, SCC and pitting due to storage of TBP waste
241-C	C-101	- Waste chemistry conducive to corrosion, SCC and pitting due to storage of TBP waste
	C-105	- Waste chemistry conducive to corrosion, SCC and pitting due to storage of TBP waste - Operating temperatures near boiling conditions
241-SX	SX-107	- High operating temperature and high temperature rate of rise
	SX-108	- Tank design - Waste chemistry conducive to corrosion, SCC and/or pitting - Ductile-to-brittle transition temperature
	SX-109	- High temperature rate of rise - Tank design - Waste chemistry conducive to corrosion, SCC and/or pitting - Ductile-to-brittle transition temperature
	SX-111	- High operating temperature and high temperature rate of rise

Table 2-4. Single-Shell Tank Liner Leak Causes Identified in Leak Cause and Location Reports (2 Pages)

Farm	Tank	Primary Leak Cause(s)
	SX-112	- Tank design - Waste chemistry conducive to corrosion, SCC and/or pitting - Ductile-to-brittle transition temperature
	SX-113	- High temperature rate of rise - Tank design - Ductile-to-brittle transition temperature
	SX-114	- High operating temperature and high temperature rate of rise
	SX-115	- Tank design - Chemistry-corrosion, SCC and/or pitting - Ductile-to-brittle transition temperature
241-T	T-106	- No apparent cause
	T-111	- Possible liner defects as a result of rapid 241-T tank farm liner replacements and liner quality
241-TX	TX-107	- Waste chemistry conducive to corrosion, SCC and/or pitting due to REDOX and EB waste storage
	TX-114	- Waste chemistry conducive to corrosion, SCC and/or pitting due to EB waste storage - Operating temperature
241-TY	TY-103	- Waste chemistry conducive to corrosion, SCC and/or pitting due to storage of TBP waste
	TY-104	
	TY-105	
	TY-106	
241-U	U-104	- Tank bulge - Possible high temperature rate of rise
	U-110	- Waste chemistry conducive to corrosion, SCC and pitting due to REDOX waste storage
	U-112	

Note: See Abbreviations and Acronyms for the waste types listed.

3.0 METHODOLOGY

This section describes the method used in attempting to identify the common factors contributing to liner failure in SSTs that are known to have leaked. A block diagram showing the process is provided in Figure 3-1.

The first step in the methodology consists of identifying the broadest set of mechanisms (i.e., a series of events or processes) that could reasonably cause or play a supportive role in causing liner failure (see Section 4.0). Each mechanism is evaluated against historical information regarding the design, procurement, construction and operation of the SSTs to determine whether the factors necessary for the mechanism to occur might be present. If it is known those factors are not present or are not significant, then those mechanisms are eliminated as not being likely. All other remaining mechanisms are considered potentially likely. They are potentially likely because they have not been evaluated in detail to determine whether or not the mechanism is likely. These potentially likely mechanisms are summarized in Section 4.0.

For the mechanisms deemed potentially likely, the presence of the factors causing the mechanism is evaluated in greater detail. This involves reviewing available detailed information to see if the underlying factors are indeed present. The level of confidence in determining the likelihood of a particular mechanism and its underlying factors in contributing to liner failure is dependent upon the availability and accuracy of information associated with each SST. This is true for both tanks that are known to have liner failures and those not known to have liner failures. Available SST background information associated with the various underlying factors is presented in Section 5.0.

The information from the detailed review of background information related to the various underlying factors associated with potentially likely mechanisms and the identified individual tank leak cause analyses (see Section 2.2) is used in concert to analyze whether a particular factor is a common factor in tank liner failures. The analysis, where possible, will rely on statistical tests for dichotomous categorical data. Dichotomous categorical data can only have two possible outcomes as opposed to continuous numerical data. The dichotomous categories of interest for this report are "probable liner failure" and "liner failure not known". The use of statistical tests must be based on judgment and understanding of the data. There is significant complexity in evaluating the data properly due to the relatively large number of variables that cannot be eliminated from consideration and the relatively small data set available that can account for the seemingly large variability between the tanks. The details of this analysis are presented in Section 6.0.

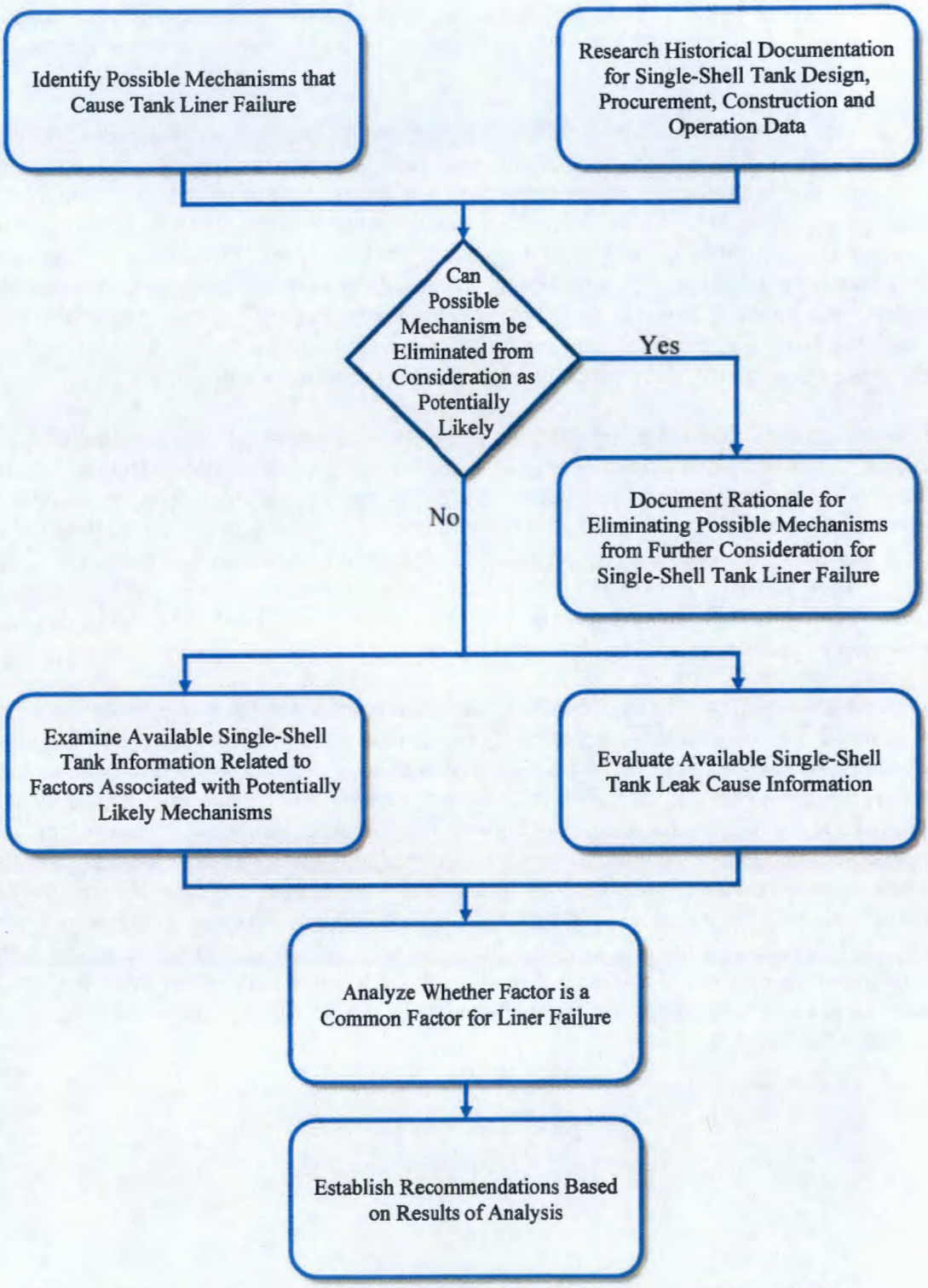


Figure 3-1. Methodology for Identifying Common Factors Contributing to Liner Failures

4.0 CONSIDERATION OF LINER FAILURE MECHANISMS

In the context of this report, the term liner failure mechanism will be used to describe the sequence of events or process by which a SST liner may fail. Failure is considered a through-wall penetration of the tank liner resulting in a release of waste from the tank. Historically, during active operation of the SSTs, either an otherwise inexplicable change in liquid level measurement of 0.5 to 2 in. (depending on waste type) or a significant increase in gamma activity in a drywell, lateral or leak detection pit was generally sufficient to list a tank as either "questionable integrity" or "assumed leaker". In some, but certainly not all, cases the "questionable integrity" listing was followed by further investigation to determine whether the leak was caused by a loss of integrity of the tank or because of some other reason (e.g., overflow, line leak, etc.). Generally, investigations were focused on whether or not it was possible to return a tank to service.

Historical evaluations of liner failures have generally focused on corrosion failure mechanisms (e.g., WHC-EP-0722, *Characterization of the Corrosion Behavior of the Carbon Steel Liner in Hanford Site Single-Shell Tanks*, WHC-SD-WM-ER-414, *Hanford Waste Tank System Degradation Mechanisms*). In a limited number of cases, bulges of the tank liner bottom have also been explored for the relation of bulging to liner failure (e.g., ARH-78, *PUREX Tk-105-A Waste Storage Tank Liner Instability and its Implications on Waste Containment and Control*). However, tank liners may fail due to any of a number of mechanisms (see BNL-52527, *Guidelines for Development of Structural Integrity Programs for DOE High-Level Waste Storage Tanks*, for examples). This section considers the broadest set of mechanisms that could reasonably cause or play a supportive role in causing liner failure. Where appropriate, an explanation is given why a particular mechanism is not considered a significant factor contributing to liner failure. Those mechanisms which are potentially significant are subsequently examined in Section 6.0 and form the basis for the detailed evaluation of factors contributing to liner failure.

The American Society of Mechanical Engineers (ASME) Boiler and Pressure Vessel (B&PV) Code provides, as part of a nonmandatory appendix, an extensive listing of potential issues to be considered as part of good engineering judgment during design of any ASME B&PV Code component. The listing of issues identifies items that could result in potential change in the material's properties or performance related to fabrication, installation or service. It is important to note that the SSTs were not built to the ASME B&PV Code nor is there any intention to infer that the tanks should have considered the list of issues associated with materials of construction as identified in the ASME B&PV Code. A number of the issues were not known or understood at the time of construction of the various SSTs. Rather, the listing provides a convenient extensive list of potential issues that may have contributed to SST liner failure. This list of issues was used as a cross-check of the potential SST liner failure mechanism considered in this report. The cross-check of potential issues associated with materials used in ASME Code construction to potential SST liner failure mechanisms is provided in Appendix C.

In the following subsections a broad set of failure mechanisms that could reasonably cause or play a supportive role in causing liner failure will be examined in detail for applicability to SST liner failure. Each of those mechanisms examined was categorized as either improbable or possible in terms of causing or aiding in liner failure. Table 4-1 tabulates the results of the

examination of each failure mechanism. For those failure mechanisms that are determined to be possible, additional specific information related to the design, procurement, construction, operation, and environment of the SST liners is provided in Section 5.0.

Table 4-1. Categorization of Examined Failure Mechanisms as Improbable or Possible (2 Pages)

Liner Failure Mechanisms	Improbable	Possible
4.1 Design and Design Modification Flaws		
4.1.1. Lack of Post-Weld Stress Relieving		X
4.1.2. Liner Bottom to Wall Transition Design		X
4.1.3. Lack of Asphaltic Coating on Liner Exterior Shell		X
4.1.4. Lack of Vent Path for Gases Formed Below Tank Liner		X
4.2. Procured Materials		
4.2.1. Properties of Liner Material		X
4.2.2. Steel Liner Plate Defects		X
4.2.3. Weld Material Defects		X
4.3. Tank Construction Defects		
4.3.1. Brittle Fracture or Crack Propagation During Construction		X
4.3.2. Cold Working and Strain Aging During Construction		X
4.3.3. Weld Joint Discontinuities and Defects		X
4.4. Operational Service Related Failure Mechanisms		
4.4.1. High-Cycle Fatigue	X	
4.4.2. Low-Cycle Fatigue		X
4.4.3. High Temperature-Induced Failure		X
4.4.4. Creep	X	
4.4.5. Stress Relaxation	X	
4.4.6. Wear	X	
4.4.7. Erosion	X	
4.4.8. Hydrogen Damage		
4.4.8.1. Hydrogen Embrittlement or Hydrogen-Induced Cracking	X	
4.4.8.2. Hydrogen-Induced Blistering	X	
4.4.8.3. Cracking from Internal Hydrogen Precipitation	X	
4.4.9. Corrosion		
4.4.9.1 General or Uniform Corrosion		X
4.4.9.2 Pitting Corrosion		X
4.4.9.3 Crevice Corrosion		X
4.4.9.4 Stress Corrosion Cracking		X
4.1.9.4.1. Nitrate-Induced Stress Corrosion Cracking		X
4.1.9.4.2. Caustic Stress Corrosion Cracking		X
4.1.9.4.3. Carbonate/Bicarbonate-Induced Stress Corrosion Cracking		X
4.4.9.5 Microbiologically-Induced Corrosion	X	
4.4.9.6 Corrosion Fatigue	X	
4.4.9.7 Erosion Corrosion	X	
4.4.9.8 Concentration Cell Corrosion		X
4.1.9.8.1. Liquid-Air Interface		X
4.1.9.8.2. Solid-Liquid Interface		X
4.1.9.8.3. Solid-Solid Interface		X

Table 4-1. Categorization of Examined Failure Mechanisms as Improbable or Possible (2 Pages)

Liner Failure Mechanisms		Improbable	Possible
4.4.9.9	Vapor Space Corrosion		X
4.4.9.10	Differential-Temperature Cell Corrosion		X
4.4.9.11	Corrosion of Tank Liner External Surface	X	
4.4.10	Radiation-Induced Defects	X	
4.4.11	Vacuum Internal to Tank	X	
4.4.12	Pressurization Internal to Tank	X	
4.4.13	Operational Errors or Accidents	X	
4.4.14	Improper or Inadequate Operational Procedures or Processes	X	
4.5	External Environmental Failure Mechanisms		
4.5.1	Soil Settlement and External Loads on a Tank	X	
4.5.2	External Water or Soil-Induced Corrosion	X	
4.5.3	Pressurization External to Tank Liner		X

It is convenient to organize failure mechanisms, however, such organization can be somewhat arbitrary. Organization of the failure mechanisms simply allows a means to bin mechanisms according to common features. The important point is to ensure that all reasonable mechanisms are addressed rather than how those mechanisms are ordered. For convenience, the failure mechanisms have been organized according to the major periods of a facility's life, namely design, procurement, construction, and operation.

4.1 DESIGN AND DESIGN MODIFICATION FLAWS

The SST liners were designed as absolutely liquid tight liners within concrete shells. The design of the tanks changed over the years as newer tank farms were constructed. Most notably the transition between the cylindrical wall and the tank bottom changed as the tank design changed. Additional design features such as the asphaltic membrane on the exterior of the liner wall were eliminated in later designs and liquid collection channels were added under the last SST Farm designed. A later design feature, post-weld stress relieving, was used on the DSTs but not on any of the SSTs. These mechanisms are discussed below and a determination is made whether each mechanism is a potentially likely contributor to liner failure.

4.1.1 Lack of Post-Weld Stress Relieving

Welding causes rapid thermal expansion and contraction along a localized area of the steel liner. The area of welding is rapidly heated causing expansion as it becomes molten. As the molten pool solidifies there is resistance to shrinkage by the already solidified surrounding weld metal and the metal adjacent to the point of welding. This resistance can create tensile strains that may result in distortion, buckling, stress corrosion cracking (SCC) or shortened fatigue life. Heat input, base metal thickness, cooling rate, restraint of the weldment, and the welding process can all factor into the level of residual stress present.

To relieve the residual stress from welding, thermal and mechanical methods are available. However, post-welding stress relieving of the SST liners was not performed. Stress corrosion cracking in waste storage tanks came under greater scrutiny in 1962 when four tanks at the Savannah River Site were discovered to have cracks (SRNL-STI-2012-00745, *Corrosion Control Measures for Liquid Radioactive Waste Storage Tanks at the Savannah River Site*). Subsequently, tanks constructed at the Savannah River Site underwent thermal stress relief on the tank walls to prevent cracking. All SSTs at Hanford were constructed before the benefits of stress relieving tanks in order to stop SCC were understood. Post-weld stress relieving was not specified for any of Hanford's SSTs.

Based on the above description, lack of post-weld stress relieving is considered a potentially likely factor in causing liner failure.

4.1.2 Liner Bottom to Wall Transition Design

The 200-Series, Type I tanks were designed with a 3-ft radius, rounded knuckle, bottom to sidewall transition. The 100-Series, Type II and Type III tanks were designed with a 4-ft radius, rounded knuckle, bottom to sidewall transition. These knuckles for Type I, II and III tanks were joined to the dished bottom and the vertical wall via full penetration butt welds. When designing SX Farm (Type IV tanks), the knuckle design was eliminated in favor of a nearly orthogonal joint between the dished bottom and vertical sidewall of the tanks. The bottom and wall were joined via a double fillet weld. For A Farm (Type IV tanks) the flat, rather than dished, liner bottom to wall transition was orthogonal and the weld type was a double-beveled double fillet weld. A small bottom knuckle design, 4 to 8-in. radius, was applied in the design of AX Farm (Type IV tanks). This small radius knuckle was joined to the flat bottom and the vertical wall via full penetration butt welds.

Thus there are four different types of bottom to wall transition designs: large radius knuckle with full penetration butt weld; orthogonal joint with partial penetration double fillet weld; orthogonal joint with full penetration double fillet weld; and, small radius knuckle with full penetration butt weld. These different designs and weld methods affect how loads are transferred from the bottom to the wall. It is possible that these differences in design could result in different liner failure rates. Based on these differences, the liner bottom to wall transition design could be a potentially likely factor in causing liner failure.

4.1.3 Exterior Finish of Tank Liner

With the exception of A, AX, and SX Farms, the exterior of the tank liner walls and bottoms of the remaining 100-Series SSTs are completely surrounded by an asphaltic coating. The liner bottom and bottom asphaltic coating are separated by a layer of grout used to protect the asphalt during placement of the liner. However, the bottom and side asphaltic coatings are contiguous.

The tanks in A and SX Farm only have the bottom asphaltic coating below the grout layer where the bottom liner is placed but no asphalt coating on the sidewalls. The tanks in AX Farm do not

have any asphaltic coating applied on any portion of the exterior of the steel liner. Similarly, the 200-Series SSTs do not have any asphaltic coating applied to the exterior of the steel liner.

The application of an asphaltic coating provides several benefits: it is a waterproofing layer on the exterior of the tank that protects the exterior liner from external corrosion; it allows for some thermal expansion of the liner due to the flexibility of the asphalt in comparison to the rigidity of the concrete; and, impedes the flow of waste from inside the tank in the case of a liner failure. It is plausible to consider that the continuous asphaltic coating on the exterior of the tank liner may limit mechanisms that could cause liner failure (e.g., external corrosion, and mechanical failure from thermal stresses).

Based on the above description, the exterior finish of the tank liner cannot be eliminated from consideration as a potentially likely contributor to a liner failure mechanism.

4.1.4 Lack of Vent Path for Gases Formed Below Tank Liner

In the most basic sense, the SSTs are all designed with a steel liner within a concrete shell. Depending on the type (I, II, III, IV) and series (100, 200), the steel tank liner wall is either in contact with the concrete shell (Type IV) or separated from the concrete shell by some combination of cement mortar, gunite, an asphaltic membrane, or a wire mesh blanket. In all instances the bottom steel liner of the tank is either in direct contact with a 2-in. grout layer or the concrete slab.

Of all the SSTs, only those in AX Farm were designed with nominally 5-in. wide drain slots spaced 13 ft 9 in. apart (square array). Although the intention of the drain slots was to direct and collect any liquid that may be present underneath the tank to a sump, the drain slots also provided an engineered vent path for any gases that may be present or form underneath the tank bottom liner.

All SST liners were filled with water during pouring of the concrete shell surrounding each liner. The liners were filled to counteract the hydrostatic load of the concrete. The temperature of this water dictates the amount of thermal expansion the steel would undergo during pouring of the concrete. Waste temperatures during operational service less than the water temperature during concrete pouring could result in contraction of the liner away from the concrete shell offering a vent path for gases from under the liner up along the shell. Conversely, waste temperatures greater than the water temperature during concrete pouring could result in expansion of the steel liner. Increases in temperature inside the tank would also result in thermal expansion of the concrete which has a slightly lower linear thermal expansion coefficient. The concrete would not be expected to expand as much as the steel liner due to its lower temperature via the thermal gradient through the concrete to the surrounding. With the exception of AX Farm, the liner systems do not include an engineered system that allows for gases formed under the liner to be vented.

It should be noted that this factor is very closely related to the factor considered in Section 4.5.3 which considers pressurization external to the tank liner. The distinction between these two factors is whether the lack of an engineered vent path contributed to liner failure without

considering whether or not external pressurization occurred. In the case of considering external pressurization as a common factor, the focus is on whether the subset of tanks which experienced external pressurization resulted in liner failure because of the pressurization.

Uplift, or bulging, of the tank bottom has been seen on a number of occasions in the SSTs. It is hypothesized this bulging is caused by trapped gasses underneath the bottom liner. The lack of a vent path for trapped gases could be a potentially likely factor in causing liner failure.

4.2 PROCURED MATERIALS

The SST liner consists of welded plates with angle stiffener rings stitch welded to the interior walls of the liner. The procured materials that could contribute to liner failure are either the steel plates making up the liner or the weld material used to join the steel plates together. Details of each are discussed in the following subsections.

4.2.1 Properties of Liner Material

Because this study is evaluating common factors associated with liner failures it is obvious to consider whether the grade of steel used to construct the liner may have played a role in contributing to the failures. The chemical composition and mechanical properties of the carbon steels used to construct the tanks changed with time as new specifications for carbon steel were developed over the twenty year period during which SSTs were constructed. Based on this, the properties of the liner material are considered a potentially likely factor in causing liner failure.

4.2.2 Steel Liner Plate Defects

Several defects are possible during the fabrication of a steel plate. Defects introduced during fabrication of the plate may go undetected and be carried forward to construction and service where the defect may cause problems or failures. Inappropriate application of the manufacturing process or lack of proper process control can introduce defects and associated residual stresses.

Defects may be introduced when the material is in the molten state or after solidification and while being further processed. Defects generated during molten processing include:

- Segregation (heterogeneous distribution of chemical elements or material phases due to non-uniform rejection of elements from solidifying metal)
- Porosity (entrapped gas ejected from cooling metal that is unable to escape prior to solidification of the metal, subsequent rolling can reduce the porosity)
- Shrinkage (contraction cavities can form at the surface and in the core upon cooling)
- Inclusions (small intermetallic particles such as oxides and sulfides which do not cause significant problem unless concentrated, or large foreign particles such as refractory or slag that physically gets incorporated into the material)

Defects generated during the forming process include:

- Lap (surface defect when the oxidized surface of the material is rolled into the material or a section of metal is folded over without welding into the surrounding material causing crevices)
- Seam (longitudinal crevice tight or closed at the surface caused by inclusions, cracks, tears, porosity which lengthen during rolling)
- Delamination (crack defect parallel to the rolling plane from inclusions or defects elongating during the rolling process resulting in a splitting of the plate at the defect)

Segregation can result in non-uniform properties, local differences in composition leading to corrosion problems, embrittlement, and sections of material being out of specification. Quench-age embrittlement, which can occur in low carbon steels due to precipitation of carbides during rapid cooling, can decrease material ductility resulting in embrittlement of the material. Porosity, core shrinkage and inclusions can cause voids which can induce cracks or cause delamination in more extreme cases. Lap and seam can produce crevices which can become sites for corrosion. None of these defects by themselves are expected to result in a failure of the tank liner, but instead could contribute to or accelerate another mechanism (e.g., crevice corrosion).

Earlier standards specified for steel plate used in construction of SSTs required the material shall be free from injurious defects. Injurious defects are those which affect the full utility of the piece. However, certain defects would not be visible and specifications did not require additional inspections, beyond those in the standards specified for steel plate.

Based on the above description, steel plate defects cannot be eliminated from consideration as a potentially likely contributor to a liner failure mechanism.

4.2.3 Weld Material Defects

Weld material defects are possible that could lead to poor welds ultimately resulting in liner failure. Defects introduced during fabrication of the weld rod or electrodes or production of the shielding gas may go undetected and carried forward to construction and service where the defect may cause problems or failures. Weld rod or electrode defects could include inadequate mechanical properties or improper chemical composition of the weld rod, flux, or electrode. A shielding gas defect would be the improper chemical composition of the gas. It is expected that weld material with defects would be more likely to result in defective welds that would be identified during weld inspection as part of fabrication. However, weld joint defects during fabrication of the tank liner are discussed separately below.

Based on the above description, weld material defects cannot be eliminated from consideration as a potentially likely contributor to a liner failure mechanism.

4.3 TANK CONSTRUCTION DEFECTS

The SST liner construction consisted of welding plates outside in ambient conditions throughout the year. Welding could occur during any season including winter. Identified tank construction defects that could contribute to liner failure are cold weather brittle fracture cracks, cold working, and welding discontinuities and defects while joining the steel plates together.

4.3.1 Brittle Fracture or Crack Propagation during Construction

At adequately low temperatures carbon steel can undergo brittle fracture. Brittle fracture is associated with little plastic deformation of the material and low energy absorption before fracture. A low energy impact can be enough to produce brittle fracture. If the elastic strain energy released by the crack exceeds the energy required to extend the crack, then the crack will extend to the end of the material. The crack will stop growing if it enters an area of the material under reduced stress or compressive stress.

Although minimum design metal temperature was not specified for the steels used on SSTs, similar thickness and similar steel types used for current-day pressure vessels (see ASME Boiler and Pressure Vessel Code, Section VIII, Part UC-66) have a minimum design metal temperature of 18°F without impact testing.

It is important to note that current-day standards for minimum design metal temperature are not necessarily conservative with regard to protection against brittle fracture for older steels. The work of Hamel in 1958 (Hamel, "An Investigation of the Impact Properties of Vessel Steels (A Progress Report)") identified that then current steels, including A 283, A 285 and A 201, may be subject to brittle fracture at ambient temperatures and a temperature of 100°F or higher was required before danger of brittle failure became negligible. The range of temperature showing impact resistance was very wide. Based on testing of site specific materials and general literature data, the Savannah River Site has instituted a minimum tank wall temperature technical standard of 70°F to avoid conditions conducive to brittle fracture (WSRC-TR-94-038, *Fracture Characterization and Toughness of ASTM A285 Carbon Steel for Types I and II Waste Tanks*).

Tank liners fabricated on site were subjected to local environmental conditions including ambient temperature. Winter time temperatures could be quite low at the Hanford Site, certainly below 18°F which could be low enough to induce brittle fracture or crack propagation from a low energy impact. It is considered that brittle fracture resulting in a through-crack of the steel plate would be highly unlikely because of inspection and subsequent construction activities. Except for the Type I tanks (B, C, T, U, and BX Farms), each tank was filled with water prior to any exterior work on the liner (e.g., asphalt membrane application, gunite application, concrete placement). It would be expected that a through-crack of the steel plate would have resulted in a noticeable water leak requiring repair. For those farms where the tanks were not filled with water, a cracked liner would have resulted in leakage upon first use which was never indicated.

Work at the Savannah River Site identified that brittle fracture in a ductile mode requires a flaw 1 to 2 ft long with stresses equal to the yield stress of the steel and such a crack would leak at a rate greater than 2.5 gallons per minute (gpm) or 3600 gal per day (DP-1476, *Materials Aspects*

of SRP Waste Storage – Corrosion and Mechanical Failure). However, brittle fracture resulting in an arrested crack could have occurred leaving the tank intact but with a crack or cracks present (RPP-RPT-54910, *Hanford Single-Shell Tank Leak Causes and Locations – 241-SX Farm*).

Based on the above description, cracks from brittle fracture cannot be eliminated from consideration as a potentially likely contributor to a liner failure mechanism.

4.3.2 Cold Working and Strain Aging during Construction

Cold working is the plastic deformation of a metal below its recrystallization temperature in which the material is hardened by the strain but the ductility of the material decreases (ASME B&PVC, Section II, Part D, Nonmandatory Appendix A). Cold working raises the ductile-to-brittle transition temperature of steel making it susceptible to brittle fracture at higher temperatures than would be expected for non-cold worked material.

Cold working of steel include bending, hole-punching, rolling, and shearing among other fabrication techniques. The rolling of the steel plates making up the cylindrical vertical wall of the SST liners is one form of cold working that was performed during construction.

When steel has been cold worked (plastically deformed) and then allowed to age, the steel has been subjected to what is known as strain aging. Strain aging is an age-hardening phenomenon in which the tensile strength and hardness of a cold-worked material are increased and the ductility reduced when that material is exposed to moderately elevated temperatures, normally as a result of service, although it can also occur during fabrication (ASME B&PVC, Section II, Part D, Nonmandatory Appendix A). The most common mechanism for strain aging is precipitation of nitrides at dislocations and crystalline defects created during cold working. Strain age damage is far more prevalent in older versions of carbon steels where control of the nitrogen content was less effective. The effects of strain aging can be minimized or eliminated by a stress-relieving heat treatment following the cold working, where the temperature of the stress relief is sufficiently high to substantially reduce the number of available initiation sites for the nitride precipitation.

Based on the above description, cold working and strain aging during construction cannot be eliminated from consideration as potentially likely contributors to a liner failure mechanism.

4.3.3 Weld Joint Discontinuities and Defects

Welding gained its current position in the United States as the principal method of joining steel during World War II when greater attention was given to the development of steels specifically for welded construction rather than the previously customary methods of riveting and bolting (Weldability of Constructional Steels – USA Viewpoint [Doty 1971]). Along with the use of welding came the need to nondestructively qualify the welds to confirm the welded systems were safe to use. Several types of discontinuities may exist due to welding. A discontinuity is an interruption of the typical structure of a material, such as a lack of homogeneity in its mechanical or metallurgical, or physical characteristics, but not necessarily a defect (AWS

D1.1/D1.1M.2010, *Structural Welding Code – Steel*, p. 335). Depending on the severity or frequency of these discontinuities, cumulatively they can result in a weld defect. A defect is a discontinuity or discontinuities that by nature or accumulated effect render a part or product unable to meet minimum applicable acceptance standards or specifications, thus designating rejectability (AWS D1.1/D1.1M.2010, p. 334).

The most common types of weld discontinuities are listed in Table 4-2. The list indicates where the discontinuity is generally located in the weld. Weld and base metal discontinuities of specific types are more common when certain welding processes and joint details are used. Discontinuities commonly encountered with some common arc welding processes are listed in Table 4-3.

Table 4-2. Common Types of Weld Discontinuities

Type of Discontinuity[1]	Location[1]	Remarks[1]
(1) Porosity		Porosity could also be found in the base metal and heat-affected zone if the base metal is a casting
(a) Scattered	weld metal zone (WMZ)	
(b) Cluster	WMZ	
(c) Piping	WMZ	
(d) Aligned	WMZ	
(e) Elongated	WMZ	
(2) Inclusion		
(a) Slag	WMZ, weld interface (WI)	
(b) Tungsten	WMZ, WI	
(3) Incomplete Fusion	WMZ/WI	Fusion face or between adjoining weld beads
(4) Incomplete joint penetration	base metal zone (BMZ)	Weld root in a groove weld
(5) Undercut	WI/heat-affected zone (HAZ)	Adjacent to weld toe or weld root in base metal
(6) Underfill	WMZ	Weld face or root surface of a groove weld
(7) Overlap	WMZ	Weld toe or root surface
(8) Lamination	BMZ	Base metal, generally near midthickness of section
(9) Delamination	BMZ	Base metal, generally near midthickness of section
(10) Seam and lap	BMZ	Base metal, generally aligned with rolling direction
(11) Lamellar tear	BMZ	Base metal near heat affected zone
(12) Crack (hot and cold)		
(a) Longitudinal	WMZ, HAZ, BMZ	Weld metal or base metal adjacent to WI
(b) Transverse	WMZ, HAZ, BMZ	Weld metal (may propagate to HAZ or BMZ)
(c) Crater	WMZ	Weld metal at point where arc is terminated
(d) Throat	WMZ	Parallel to weld axis. Through the throat of a fillet weld.
(e) Toe	WI, HAZ	
(f) Root	WMZ	Root surface or weld root
(g) Underbead and heat affected zone	HAZ	
(13) Concavity	WMZ	Weld face of a fillet weld
(14) Convexity	WMZ	Weld face of a fillet weld
(15) Weld reinforcement	WMZ	Weld face or root surface of a groove weld
(16) Spatter	WMZ, BMZ	Weld face or base metal surface
(17) Arc strike	WMZ, BMZ	Weld face or base metal surface

[1]Information taken from Table 1, AWS B1.10M/B1.10:2009, *Guide for the Nondestructive Examination of Welds*, American Welding Society.

Table 4-3. Discontinuities Commonly Encountered with Arc Welding Processes

Welding Process[1]	Porosity	Slag	Incomplete Fusion	Incomplete Joint Penetration	Undercut	Overlap	Cracks
Submerged Arc Welding	X	X	X	X	X	X	X
Gas Tungsten Arc Welding	X		X	X	X		X
Gas Metal Arc Welding	X		X	X	X	X	X
Fluxed Core Arc Welding	X	X	X	X	X	X	X
Shielded Metal Arc Welding	X	X	X	X	X	X	X

[1] Information taken from Table 2, AWS B1.10M/B1.10:2009.

The earliest specifications for welding inspection required correction of all flaws in the welds (HW-1946, *Specification for Composite Storage Tanks – Building Number 241*). Later specifications were more specific. However, not all discontinuities or defects would necessarily be detected via inspection. Due to location or orientation, some discontinuities or defects could have gone undetected.

Based on the above description, weld joint defects cannot be eliminated from consideration as a potentially likely contributor to a liner failure mechanism.

4.4 OPERATIONAL SERVICE RELATED FAILURE MECHANISMS

The SST liners were designed and fabricated to be absolutely liquid tight, a condition of their acceptance for operation. Operational service of the tanks included filling, storage, emptying of a variety of precipitated solids and basic solutions of dissolved solids with a range of heat producing radioactive isotopes resulting in elevated temperatures. Mechanical, chemical, and nuclear mechanisms could potentially contribute to liner failure. These mechanisms are discussed below and a determination is made whether each mechanism is a potentially likely contributor to liner failure.

4.4.1 High-Cycle Fatigue

Fatigue is the gradual deterioration of a material subjected to repeated or fluctuating loads above the fatigue limit of the material. The fatigue limit is the stress value which will not produce failure, regardless of the number of applied cycles (*Marks' Standard Handbook for Mechanical Engineers* [Avallone and Baumeister 1996]). The fatigue limit for most steels is between 2 and 10 million cycles. The SST liners are static with the exception of addition and removal of equipment, and filling and emptying the tanks of their contents which were warmer than the tank surroundings. The equipment or live loads and the hydrostatic loads have only negligible effects on the tanks' strength (SD-RE-TI-012, *Single-Shell Waste Tank Load Sensitivity Study*, p. 14). The mechanical stress associated with the live loads from addition and removal of equipment, and change in hydrostatic loads from filling and emptying of the tanks is small and the frequency

not extremely large such that fatigue from these mechanical forces would be considered not significant.

Based on the above description, high-cycle fatigue is not considered a potentially likely liner failure mechanism.

4.4.2 Low-Cycle Fatigue

Thermal cycling from tank fill and empty cycles during which the liners are subject to contraction and expansion resulting in thermal fatigue could be an area of concern (BNL-52527). Surface defects, such as roughness or scratches, and notches or shoulders all reduce the fatigue strength of a material (Avallone and Baumeister 1996). Also, corrosion and galling can cause great reduction of fatigue strength for a material, sometimes amounting to as much as 90 percent of the original endurance limit (Avallone and Baumeister 1996). Overstressing materials above the fatigue limit for periods shorter than necessary to produce failure at that stress which reduces the fatigue limit in a subsequent test. Cyclically stressing the liner into the plastic range, such as by cyclic thermal stresses, can result in failure referred to as low-cycle fatigue. Early stages of cyclic stressing into the plastic range results in the initiation of a crack (this crack may also be present from other sources such as welding). Following initiation, the crack grows during crack propagation. Eventually, the crack becomes large enough for some terminal mode of failure to take over (e.g., ductile rupture, brittle fracture).

It is reasonable to consider that significant residual stress was present in the tank liners following welding. It is possible that some allowable plastic deformation of the liner occurred from welding. After the initial tank construction, specifications provided for limits on liner deformation, likely in response to excessive deformation in T Farm tank liners leading to replacement of the liner bottoms. As an example, for TY Farm, allowable deformation between a crest and trough was limited in the specification to 1 ½ percent of the distance between crests when the tank was loaded with two feet of water or equivalent (HW-3061, *Paragraph D. "Steel Tank Lining" of Part IX of Specifications for TX-Construction of Composite Storage Tanks*). Subsequent temperature cycling within the tanks during filling operation could induce additional stress in the liner and depending on the conditions could possibly lead to low-cycle fatigue.

The smaller, 55,000 gal Type I tanks have never been subjected to elevated temperatures or large temperature changes, thus the effects of cyclic thermal loads for these tanks have not been considered because they are not significant. Low-cycle fatigue is not considered a potentially likely liner failure mechanism in the Type I tanks.

For the 75-ft diameter tank types, the soil overburden is the largest load on the tank and the greatest contributor to static demands. Thermal loads are also significant when temperatures are the highest (RPP-RPT-49989, *Single-Shell Tank Integrity Project Analysis of Record Hanford Type II Single-Shell Tank Thermal and Operating Loads and Seismic Analysis*, RPP-RPT-49990, *Single-Shell Tank Integrity Project Analysis of Record Hanford Type III Single-Shell Tank Thermal and Operating Loads and Seismic Analysis*, RPT-RPT-49992, *Single-Shell Tank Integrity Project Analysis of Record Hanford Type IV Single-Shell Tank Thermal and Operating Loads and Seismic Analysis*, Section 13 in each). For the 75-ft diameter tanks, the steel liner is

restrained by the concrete foundation and sidewalls. With the exception of A, AX, and SX Farms, the liner wall is surrounded by a 3/8-in. thick external asphaltic coating between the concrete and steel liner. As the waste temperature warmed, this asphaltic coating would soften providing some give during expansion of the liner thus reducing the effects of cyclic thermal loads. AX Farm has no asphaltic coating on the exterior of the steel liner. A and SX Farms only have the asphaltic coating below a 2-in. thick grout layer below the bottom plate of the steel liner but not along the sidewalls. These last three tank farms also were subjected to the highest temperatures.

Low-cycle fatigue cannot be eliminated from consideration as a potentially likely contributor to liner failure.

4.4.3 High Temperature-Induced Failure

The decay of radionuclides results in heating of atoms as the radiative energy (e.g., alpha, beta, gamma radiation) is absorbed by the surrounding medium. Within the SSTs this radioactive decay heat is dissipated into the waste solution, tank structure and surrounding soil. The decay heat within a particular tank is dependent upon the concentration of the fission products in the waste and the "age" of the waste. Later processes, such as REDOX and PUREX, would process nuclear fuels that had greater exposure in the reactor resulting in higher concentrations of fission products in the fuel. These later processes were also more efficient in terms of creating smaller volumes of waste containing the fission products which also increased the concentration of fission products in the waste. Beginning with waste generated by the REDOX process, the waste contained fission products in high enough concentration that the waste would self-boil. As the waste ages the radioactive decay heat from the fission products lessens resulting in a lowering of the waste temperatures.

High temperatures or high temperature gradients (temporal and spatial) within SSTs potentially can create conditions under which a mechanical or chemical tank liner failure mechanism is more likely to occur. A higher temperature may initiate a mechanism that would not occur at a lower temperature or accelerate a mechanism resulting in it occurring more quickly. Potential chemical and mechanical liner failure mechanisms described elsewhere that may be affected by temperature (e.g., corrosion) are not repeated here, rather temperature dependence of those mechanisms will be considered as part of the evaluation of that specific mechanism.

Three high-temperature related conditions are considered as potential mechanisms that could contribute to tank liner failure. The conditions considered are high temperature, spatial temperature gradient within the liner, and temporal gradient within the waste and tank structure. Each of these will be discussed below.

High Temperature

As operating temperature increases within the tanks, thermal stresses can increase within the tank liner and the mechanical properties of the tank liner material may start to diminish. Each of these potential effects from high temperature operation will be considered as potential contributing factors to liner failure.

Tank A-104 had the highest recorded waste temperature within any SST with a probable liner failure. The peak temperature reported for this tank is 437°F (RPP-RPT-54912, Rev 0, *Hanford Single-Shell Tank Leak Causes and Locations- 241-A Farm*, p 4-5). It is worth noting that "sound" tank A-106 had the highest recorded temperature found in available records for SSTs at 312°C (594°F) on May 15, 1963 (RHO-CD-1172, *Survey of the Single-Shell Tank Thermal Histories*). Other tanks with probable liner failures were subjected to lower operational temperatures with tanks containing boiling waste seeing the highest operating temperatures. The tanks that contained boiling waste with probable liner failures had the following maximum recorded operating temperatures (see Table 4-4).

Table 4-4. Maximum Recorded Operating Temperature for Boiling Waste Single-Shell Tanks with Liner Leaks

Tank	Maximum Recorded Operating Temperature
241-SX-107	390°F
241-SX-108	320°F
241-SX-109	290°F
241-SX-111	320°F
241-SX-112	316°F
241-SX-113	254°F
241-SX-114	357°F
241-SX-115	266°F
241-A-104	437°F
241-A-105	285°F

The specified steel of construction for tanks in A Farm was ASTM A-283-52T, Grades B, C (HWS-5614, *Specification HWS-5614 Specifications for PUREX Waste Disposal Facility Project CA-513-A*). The specified steel of construction for tanks in SX Farm was ASTM A-283-52T, Grades A, B (HW-49574, *Examination of Corrosion Test Coupons in PUREX 101 Waste Storage Tanks – Rm-147*). ASME Boiler & Pressure Vessel Code (ASME B&PVC, 2013 Edition, July 1, 2013), Section II, Materials, Part D, Properties, includes tabulation of allowable stresses for ferrous materials used in ASME B&PVC Section I; Section III, Division 1, Classes 2 and 3; Section VIII, Division 1; and, Section XII Construction. Although the SSTs were not constructed to the ASME B&PVC, the tabulated allowable stresses can be used for comparison to actual conditions experienced in the SSTs. According to the tabulated allowable stresses, the maximum temperature limit for construction under Section VIII, Division 1 for steel of current (i.e., not 1952 as specified in HWS-5614) specification SA-283, Grades A and B, is 650°F (ASME B&PVC, Section II, Part D, Table 1A). Additionally, there is no reduction in the maximum allowable stress in SA-283, Grade A and B plate for metal temperature not exceeding 500°F (ASME B&PVC, Section II, Part D, Table 1A). In general, it is expected that the applicability of maximum allowable stress and maximum temperature limit would apply to earlier versions of the same specification and grade of steel although such an extrapolation between versions is absolutely guaranteed. Based on the maximum operating temperatures in comparison to maximum allowable stress and maximum temperature limit for the steel used in these two tank farms, a high-temperature failure mechanism related to reduction in liner mechanical properties is not a potentially likely contributor to liner failure.

Although increased temperature experienced by the SST liners that are known to fail did not alter mechanical properties, the increased temperature could result in added stress being placed on the tank liner. A structural evaluation of the SSTs in 1955 (HW-37519, *Structural Evaluation Underground Waste Storage Tanks*) recognized this possibility:

> *Still another factor to be considered is the elevated temperatures which are associated with the waste material to be stored in the tank...Not only is the steel liner at a higher temperature than the concrete, but it also has a somewhat higher thermal expansion coefficient. The overall temperature in the tank is trying to expand the steel but since it is retained by the concrete shell the result is to increases the tensile forces already imposed on the concrete...Therefore, the tank is restrained in effect at these points, causing the wall and the tank bottom centers to bulge.*

A subsequent report regarding self-concentration of REDOX waste (HW-50216, *Current Status of REDOX Waste Self-Concentration*) described potential concerns regarding operability of air-lift circulators (ALC) and buckling of the tank bottom:

> *Recent experience at both REDOX and PUREX has increased concern about the temperature of the sludge in tanks holding self-concentrating waste...Distortion of the welded steel tank bottom, as a result of thermal stresses, might conceivably cause a circulator to tilt far enough to break the air supply line...The possibility, however, that excessive thermal stresses might cause buckling and resultant failure of the tank liner indicates a need for further evaluation of the control of sludge temperatures.*

Tank A-105 bottom plate was evaluated for thermal buckling from restraint and showed for that particular tank that uplift of the tank bottom was possible (ARH-78). The analysis showed that tank liner instability could come about through the restraint exerted by differential thermal expansion between the concrete cylinder and bottom plate of the steel tank liner.

Based on this evaluation, the tank bottom liner being subjected to a high temperature is considered a potentially likely factor contributing to liner failure.

High Spatial Temperature Gradient

The waste solution may contain either or both a liquid phase with dissolved and/or suspended solids and a semi-solid (or settled solid) phase generally with interstitial liquid between solid particles. Heat transfer within the liquid phase is dominated by convective heat transfer and within the settled-solid phase is dominated by conductive heat transfer. Convective heat transfer generally allows greater heat transfer resulting in lower temperatures in the liquid portion of the waste than the semi-solid phase. As waste from fuel reprocessing became more concentrated, higher temperatures were encountered in the tanks, especially at elevations just above the tank bottom where a conductive sludge layer would accumulate resulting in a vertical temperature variation along the cylindrical wall of the tank liner.

This situation was considered in HW-56821, *Temperature Transients in Underground Tanks Storing Nuclear Process Residues*, which found:

> *Some measurements have indicated that the sludge temperature varies by about 100°F per foot depth, neglecting transient local hot spots. The temperatures along the vertical steel liner will be nearly those of the contained fluid, and the effect of conductivity vertically along the steel side walls will be very small.*
>
> *If the steel temperature drops by 100°F in a vertical height of 1 ft., the corresponding contraction tends to be about 0.6" on a 75 ft. diameter, and this would tend to pull the steel liner inward and away from the concrete shell. Counteracting this tendency is liquid pressure on the liner. A liquid depth of 15 ft. at 1.6 specific gravity would stretch the liner by about 0.36" on the diameter, leaving only a small actual contraction. Bending stress in the vertical liner would be correspondingly small.*

Based on this evaluation of vertical temperature gradient in the cylindrical wall of the tank liner, a high spatial temperature gradient in the liner is not considered a potentially likely factor in causing liner failure.

High Temporal Temperature Gradient

As process waste became more concentrated, higher waste storage temperatures were encountered within the SSTs resulting in a more rapid temperature rise within the tank structure. This situation raised questions regarding possible temperature stresses in the tank materials and the possible effects on the integrity of the tank liners and structures (HW-56821). The analysis of sudden temperature rise in a tank from introducing hot waste found:

> *In the calculations, a sudden temperature rise in the liquid waste is assumed, such as could occur if hot fluid were admitted to an empty tank...As might be expected, the steel rises almost immediately to very nearly the liquid temperature...If the filling is slow enough to permit steel and concrete to warm up at nearly the same rate, there should be little differential expansion between steel and concrete; the concrete base can undoubtedly push outward through the back fill for the very short distances required by thermal expansion.*
>
> *As a benchmark, if the bottom steel in a 75 ft. dia. tank were <u>suddenly</u> heated through a 175°F range, the total linear expansion of the steel would be about one inch, and the concrete would not immediately expand at all. If the steel were rigidly confined and remained flat, the compression stress would be about 33,000 psi. Since concrete and steel have almost equal coefficients of thermal expansion, this stress is reduced practically to zero if the steel and concrete are heated slowly and are at nearly the same temperature at any time.*

The analysis shows that tank liner instability could come about through the restraint exerted by differential thermal expansion between the concrete cylinder and bottom plate of the steel tank liner when the tank is subjected to rapid temperature rises.

Based on this evaluation of a rapid temporal temperature gradient in the tank liner, a rapid temperature rise resulting in a high temporal temperature gradient is considered a potentially likely factor contributing to liner failure.

4.4.4 Creep

The following is excerpted from BNL-52527. Creep is the time-dependent inelastic deformation of a material subjected to a stress that is typically below the elastic limit. It is not a concern for steels below a temperature of 800°F. Therefore, this phenomenon should not occur in waste storage tanks during operation.

Based on the above description, creep is not considered a potentially likely liner failure mechanism.

4.4.5 Stress Relaxation

A material initially stressed may after a time period have a remaining stress lower than the initial stress. This time-dependent stress reduction is called stress relaxation (ASTM DS 60, *Compilation of Stress-Relaxation Data for Engineering Alloys*). As examples, this initial stress may result from fabrication or operational service thermal gradients. The stress relaxation at temperatures below about 0.4 of the melting temperature (roughly 1000°F) are a result of inelastic strains which after a time period reach a limit that is a function of the initial stress and the temperature.

Residual tensile stresses present in non-stress-relieved welds of the SSTs may diminish with time as the material is exposed to moderately elevated operating temperatures. Diminished tensile stresses could lead to a reduction in the risk of SCC. Conversely, continued high residual tensile stresses could result in a continued risk of SCC.

Limited data is available regarding stress relaxation of carbon steel at temperatures comparable to waste storage temperatures in SSTs. ASTM data series publication DS 60, "Compilation of Stress-Relaxation Data for Engineering Alloys," provides a compilation of reported stress-relaxation data for carbon steel among other materials. Almost all reported data are at higher temperatures than the SSTs were operated. The small amount of data for lower temperature stress relaxation testing includes weld metal, stress-relieved rolled plate, steel strip, and wire of various diameters and compositions are shown in Table 4-5.

Table 4-5. Stress Relaxation Data at Low to Moderate Temperatures for Various Carbon Steel Materials

Material Type	Composition	Test Temperature	Test Duration	Percent Reduction in Initial Stress[1]
Weld metal built up on mild steel strip	0.075% C 0.41% Mn 0.12% Si	68°F	1 hour	0.4%
			10 hours	1.7%
			100 hours	3.9%
Rolled plate, stress-relieved	0.17% C 0.56% Mn 0.028% Si 0.064% Cr 0.11% Ni	68°F	1 hour	0-12%
			10 hours	0-14%
			100 hours	1.8-15%
		212°F	100 hours	2%
		392°F	100 hours	16-36%
Strip steel, water quenched	0.75-0.84% C 0.15-0.30% Mn 0.15-0.30% Si 0.15% Cr maximum 0.20% Ni maximum	140°F	2 hours	3%
		176°F	2 hours	10%
		212°F	2 hours	22%
		257°F	2 hours	29%
		302°F	2 hours	43%
		347°F	2 hours	55%
		392°F	2 hours	68%
Strip steel, water quenched and tempered in a lead bath	0.95-1.04% C 0.15-0.20% Mn 0.15-0.30% Si 0.15% Cr maximum 0.20% Ni maximum	Room temperature	1,000 hours	6%
			10,000 hours	8%
			46,500 hours	9%

[1]Values based on data reported in ASTM DS 60.

The weld metal at room temperature saw a 4% reduction from the initial stress over a 100 hour test. The stress-relieved rolled plate at room temperature, 212°F and 392°F saw a 2-15%, 2% and 16-36% reduction from the initial stress, respectively, over a 100 hour test. The testing of strip steel at various temperatures for a two hour period showed an increase in the amount of stress relaxation with an increase in temperature. The longer term testing of strip steel at room temperature showed a flattening out of the stress relaxation with time, with only a 9% reduction in final stress from initial stress.

The Single-Shell Tank Integrity Panel has previously identified the tensile stresses necessary for driving SCC result primarily from residual stresses around non-stress-relieved welds and hoop stresses caused by the sludge and saltcake (RPP-RPT-43116). The panel recommended analysis or study of stress relaxation in the steel liners to determine whether SCC is a risk in the future. During M-045-91 TPA negotiations, work on this recommendation was deferred until the second phase of tank integrity work (LET 10-ESQ-286).

Based on the above description, stress relaxation is not considered a potentially likely liner failure mechanism. However, lack of information on stress relaxation could result in continued uncertainty regarding risk for future SCC.

4.4.6 Wear

Wear is degradation resulting from relative motion between two materials. The tanks are large and have large static loads and are not normally prone to motion, other than from changes to static or thermal loads. During filling or emptying of the tank there could be movement of the liner due to changes in static loads and changes in temperature that would affect expansion/contraction of the liner. The number of loading and unloading cycles is considered small. The asphaltic coating adhered to the exterior surface of the walls of the liner exterior (except for A, AX and SX Farms) would reduce any wear-related motion on the sidewalls of the liner.

Based on the above description, wear is not considered a potentially likely liner failure mechanism.

4.4.7 Erosion

Erosion is a degradation mechanism where flowing waste slurries impinge on the steel surface of the tank liner. The steel is mechanically eroded away by the solid particles impacting the metal surface. This process can lead to localized or general thinning and potentially penetration of the steel tank liner.

In most SSTs, the contents are essentially stagnant for much or all of the time. The primary exceptions are sluicing operations during metal waste recovery and strontium recovery campaigns. Metal waste recovery operations performed between 1952 and 1957 included sluicing in 43 tanks in seven tank farms (HNF-3018, *Single-Shell Tank Sluicing History and Failure Frequency*,). Strontium recovery operations were performed between 1962 and 1978 in the 10 tanks in A and AX Farms.

Metal waste sluicing was performed in the 75-ft diameter tanks using two, 1 3/8-in. nozzles at a flow rate of 250 to 300 gpm per nozzle (SD-WM-TI-302, *Hanford Waste Tank Sluicing History*). This resulted in a jet velocity of 65 ft/sec. In the 20-ft diameter tanks a single 5/8-in. nozzle was used at a flow rate of 100 gpm (SD-WM-TI-302). This resulted in a jet velocity of 100 ft/sec. Based on chemical/physical properties determined for tank U-101 metal waste sludge, the solids consisted of 60% by weight of a soft material, primarily needle-like crystals of sodium uranyl phosphate, and 40% by weight of a harder material, primarily a hard dense agglomerate of crystalline carbonate. The consistency of the harder material was described as blackboard chalk (SD-WM-TI-302) and had penetrometer values comparable to chalk (HW-19140, *Uranium Recovery Technical Manual*). Studies of erosion behavior of metal waste slurry in steel pipe found the erosion rate to be less than 30 mil/yr (measured at an elbow) for a linear slurry velocity of 15 ft/sec (HW-19544, *Erosion of Carbon Steel Pipe in the Waste Metal Recovery Process (Project C-362)*). Translating this result for pipes to the tank surface is not straightforward and is not attempted here. However, the above information indicates that erosion of the piping during the metal waste recovery campaign was evaluated and determined it was not a significant concern.

A total of forty-three SSTs underwent metal waste removal operations to provide feed to the TBP Plant (WHC-MR-0132, *A History of the 200 Area Tank Farms*). Of those forty-three tanks, it has been determined that four tanks leaked waste through liner failures. In addition, eighteen tanks underwent multiple metal waste removal operations, while only one tank in that population has been classified as having a liner leak. The tanks that had metal waste sluiced for feed to the TBP Plant are shown in Table 4-6 below, where tanks with liner failures are displayed in red.

Table 4-6. Compilation of Tanks Which Underwent Metal Waste Removal Operations[1]

Tank	Metal Waste Removal Start Date
B-101	Mar. 1953
B-102	June 1953
B-103	July 1953[2]
BX-101	June 1953
BX-102	June 1953
BX-103	June 1953
BX-104	July 1954
BX-105	Dec. 1954
BX-106	May 1955
BY-101	Jan. 1954[2]
BY-102	Mar. 1954[2]
BY-103	May 1954[2]
BY-104	June 1954[2]
BY-105	Aug. 1954[2]
BY-109	May 1955
BY-111	Feb. 1955
BY-112	Feb. 1955
C-101	Oct. 1952
C-102	Nov. 1952
C-103	Nov. 1952
C-104	Sep. 1953
C-105	Dec. 1953
C-106	Dec. 1953[2]

Tank	First Metal Waste Removal Start Date	Second Metal Waste Removal Start Date	Third Metal Waste Removal Start Date
T-101	June 1953	May 1956	-
T-102	Oct. 1953	June 1956	-
T-103	Oct. 1953	Jan. 1957	-
TX-101	Jan. 1954	Nov. 1955	-
TX-102	June 1954	Sep. 1956	-
TX-103	July 1954	-	-
TX-104	Feb. 1954	Sep. 1956	-
TX-105	Apr. 1955	Nov. 1956	-
TX-106	May 1955	-	-
TX-107	Aug. 1954	July 1956	-
TX-108	Mar. 1955	Oct. 1956	-
U-101	Feb. 1952	Apr. 1955	Sep. 1956
U-102	Jan. 1953	Sep. 1955	Oct. 1956
U-103	Dec. 1952	Nov. 1955	Nov. 1956
U-104	Jan. 1953	July 1956	-
U-105	June 1953	Sep. 1956	-
U-106	Jan. 1953	Dec. 1956	-
U-107	Oct. 1953	Oct. 1955	Jan. 1957
U-108	Nov. 1953	Feb. 1956	-
U-109	Dec. 1953	Apr. 1956[2]	-

[1] Dates taken from SD-WM-TI-302, p. 63-95, which used monthly reports from a variety of sources.
[2] Exact month of sluicing is estimated based on surrounding cascade tanks.
Tanks with liner failures are highlighted in red.

When comparing the estimated failure date for the four tanks in red from Table 4-6 with the dates they were sluiced, it is found tanks BY-103, C-101, and C-105 did not leak earlier than at least 13-21 years after sluicing. However, tank U-104 was found to be leaking during the second metal waste removal operation in 1956 (HW-44024-RD, *TBP Plant and Tank Farm Weekly Summary – Process Unit – 6-29-56 thru 8-31-56*). Tank U-104 was first filled with metal waste in July 1947. As indicated in Table 4-6, the first sluicing took place in January 1953. Sluicing operations continued on and off through the first half of 1953 and water was used as the sluicing medium during the final cleanout in June 1953 (SD-WM-TI-302, p. 79). The tank was re-filled with metal waste between September and November of 1954 and roughly a year and a half later

began its second sluicing in July 1956. During the sluicing operations, a light assembly was installed in tank U-104 to enhance visibility, which revealed a bulge in the center of the tank (HW-44024-RD, p. 39). Pictures of the tank were taken, which indicated that the bottom of the tank was bulged in several places. Based on leak testing between 1957 and 1961, it was determined that tank U-104 had, in fact, leaked. While tank U-104 was found to have leaked during metal waste removal operations, it is not believed that the operations of metal waste removal were the cause of the leak. Based on the sluicing method used, the removal of metal waste should not have put the tanks at a higher risk for failure of the steel liner, nor would it introduce issues observed in high waste temperature scenarios, such as liner bulging. For those reasons, in addition to the fact that only four of the metal waste removal tanks leaked and three of those tanks leaked after a significant amount of time had passed since sluicing, metal waste retrieval operations likely did not put the tanks at higher risk for liner failure and is not considered a likely failure mechanism.

Strontium recovery was performed in A and AX Farms using two, 1-in. nozzles at a flow rate of 300 to 350 gpm per nozzle (SD-WM-TI-302). This resulted in a jet velocity of 140 ft/sec. Based on analysis of the sludges in A and AX Farms, the solids contained iron and silicon, with most tanks also containing aluminum, sodium, and lesser amounts of magnesium and manganese. Physical description of the sludge varied tank by tank but commonly consisted of softer red solids along with crystalline solids or hard clumps or chunks of solids (SD-WM-TI-302). Sluicing was performed with both a short sluicer and primarily in AX Farm a long sluicer which extended just below the ALCs.

Of the 10 tanks in A and AX Farms only tanks A-104 and A-105 are confirmed leakers, and tank A-105 was a confirmed leaker prior to sluicing. Tank A-104 was sluiced in 1969 and again in 1974-1975, with radiation detected under the tank during sluicing in 1975. While tank A-104 was found to have leaked during strontium recovery operations, it is not believed that the operation of sluicing for strontium recovery was the cause of the leak. Based on the sluicing method used, the removal of sludge should not have put the tanks at a higher risk for failure of the steel liner as discussed in the subsequent paragraphs.

A report, RPP-31938, *Basis for Minimum Height of the High Pressure Mixer above the Tank Floor*, was issued in 2007 to assess the minimum height of a high pressure (23,000 pounds-force per square inch [psi]) mixer above the floor of tank S-102 to limit erosion. That report identifies a number of erosion rates for various solids against different base materials. The most similar system consisted of 150 micron alumina (Al_2O_3) at 30 wt%. For mild steel subjected to this alumina, the wear rates approached zero below 2 m/s (6.6 ft/s). The report also identifies that a jet centerline velocity, U_c, can be defined as

$$U_c = K\left(\frac{U_o d_o}{x}\right)$$

where U_o = nozzle discharge velocity
d_o = nozzle diameter
K = diffusion coefficient for the jet, what has been determined from experimental data to range from 5.7 to 6.8 for air and water jets over a range of Reynolds Numbers
x = distance from nozzle exit

In examining the nozzle discharge velocity and nozzle diameter for metal sluicing in 75-ft diameter and 20-ft diameter tanks and strontium recovery in 75-ft diameter tanks, the greatest product of $U_o d_o$, and therefore jet centerline velocity, exists for the sluicing nozzles used for strontium recovery. For the sluicing performed for strontium recovery the centerline jet velocity of 140 ft/sec would drop to around 2 m/s at a distance of 12 ft from the nozzle. However, for the long sluicer the distance from the nozzle to the tank bottom would be less than 12 ft in an area around the nozzle. The minimum distance would probably be on the order of 1-2 ft between the sluice nozzle and tank bottom. At a distance of 1.5 ft from the nozzle the centerline velocity of the jet would be about 50 ft/sec. Document RPP-50817 examined erosion-corrosion from retrieval mixer pump operation in DST AY-102 and identified a maximum erosion rate on Type A515 Grade 60 carbon steel of 2730 mil/yr when subjected to a jet velocity of 50 ft/sec and an impingement angle of 90 degrees. Some smaller erosion rate would be expected at distances up to about 12 ft from the nozzle, and the wear rate would be expected to be negligible beyond this distance from the nozzle.

During sluicing operations, the solids in the tank were covered with some level of liquid so the sluice nozzle jet velocity would dissipate in the liquid before contacting the solids. During the majority of the sluicing operation the sludge that was being mobilized was not contacting the tank liner because only a portion of the depth of solids would be sluiced at any time and only when the liner was exposed would it be susceptible to erosion. Not until the end of sluicing operations at the cleanout campaign would the tank liner directly below the sluicer be exposed allowing for particles to impact the metal surface. So the period of time that any portion of the liner bottom or wall would be exposed to conditions causing erosion would be limited. Document RHO-ST-30, *Hanford Radioactive Tank Cleanout and Sludge Processing*, discusses final cleanout explaining one to two days of sluicing was followed by removal of liquid and photographing the tank bottom to determine progress. Durations were tank specific and, "In some tanks, repeated sluicing campaigns were required, with the whole operation consuming weeks of effort. In other tanks, several days of actual sluicing cleared most of the tank bottom down to bare metal." Actual sluicing operation would have only been a portion of the time during the cleanout campaigns, and during sluicing operation only a portion of the time would have been directed to one specific area of the tank. If one simply considers that the dispersion angle of the jet is equal to the fraction of time in that dispersion angle, then on average any portion of the tank would be exposed to the sluice jet for a fraction of time equal to the fraction of the dispersion angle to the entire tank. Document RPP-31938 reports a jet half-angle of 7.2 degrees for water at 77°F. Assuming a horizontal jet with a dispersion angle of 15 degrees, the jet would cover up to about 0.04 of the tank bottom at any time. If sluicing operations were ongoing during half of the cleanout period and the cleanout period lasted six weeks the expected erosion that would occur from a 50 ft/sec jet at a 90 degree impingement angle would be about 6-7 mils. Lower erosion rates would be expected at lesser impingement angles. This amount of erosion is not considered appreciable relative to the tank liner thicknesses.

Based on the above description, erosion is not considered a likely liner failure mechanism.

4.4.8 Hydrogen Damage

Hydrogen damage is a general term used to cover several types of possible material degradation caused by hydrogen. Carbon steel can be susceptible to a number of different types of hydrogen damage. Hydrogen damage can develop in a wide variety of environments under a range of conditions. Common hydrogen damage mechanisms that may be applicable to the SSTs are discussed below.

4.4.8.1. Hydrogen Embrittlement or Hydrogen-Induced Cracking

Hydrogen embrittlement is caused by diffusion of hydrogen atoms through metal and then recombining to molecular hydrogen within the metal matrix creating pressure within the metal. This pressure can increase, reducing the ductility and tensile strength of the material and at even higher levels can crack the metal via hydrogen-induced cracking. The problem of hydrogen embrittlement is more likely to occur in hardened, high-carbon steels. Decreasing the carbon content and hardness decreases the likelihood of hydrogen embrittlement but does not completely eliminate the possibility of hydrogen embrittlement.

The DOE commissioned testing and evaluation of hydrogen effects of fracture behavior of radioactive waste storage tanks (DOE/ER/75784-TI, *A Study of Hydrogen Effects on Fracture Behavior of Radioactive Waste Storage Tanks*). The project was performed to evaluate hydrogen uptake and changes to mechanical properties of low-carbon steels immersed in water and subjected to high gamma radiation fields. Three different steels were tested: ASTM A516, Grade 70; AISI 1020; and, ASTM A354. Only the ASTM A516, Grade 70 steel was used to measure the hydrogen uptake and hydrogen diffusion coefficient. Steel specimens of all three steels were tested for changes to tensile strength.

The ASTM A516, Grade 70 steel specimens tested for hydrogen uptake were subjected to 40,000 rad/hr gamma radiation exposure (^{60}Co source) in water (with tritium tracer) at 80°C. The total radiation exposure that specimens were subjected to ranged from 13 megarad (Mrad) to 27 Mrad. The reported diffusion coefficient from these tests was 2.7×10^{-11} cm^2/sec. It was reported that this diffusion coefficient was very small compared to the published data of hydrogen diffusion in steels. As an example, WSRC-STI-2007-00211, *Tensile Testing of Carbon Steel in High Pressure Hydrogen*, reports a diffusion coefficient for hydrogen in body-centered cubic iron at room temperature of 9.2×10^{-5} cm^2/sec.

The steel specimens tested for effect of gamma radiation on mechanical properties were exposed to up to 20 Mrad (^{60}Co source) in water at 80°C. No discernible effect from gamma radiation and associated radiolysis of the water on strength or ductility was found. Changes to mechanical property values, in the range of radiation exposure examined, were considered negligible, with results in many cases being within the experimental scatter of unirradiated specimens.

The United States Nuclear Regulatory Commission (NRC) publication NUREG/CR-6706, *Capacity of Steel and Concrete Containment Vessels with Corrosion Damage*, states that low-carbon steel is not sensitive to hydrogen embrittlement at temperatures reactor containments are maintained. Tests on ASTM A516 pressure vessels subjected to 10,000 psi internal pressure

of hydrogen during long term storage tests did not suffer degradation of material ductility or strength. None of the SSTs were fabricated using ASTM A516 carbon steel. ASTM A516, Grade 70 plates have a tensile strength of 70-90 ksi and for plates ½-in. thick or less have a maximum carbon content of 0.27%. These values are slightly higher strength and carbon content than for the various materials specified for SST construction but the results are generally illustrative of high pressure hydrogen on low-carbon steel.

Relatively small amounts of hydrogen are generated in the tanks (below the lower flammability limit). The tanks are operated at low pressure (e.g., atmospheric or slight vacuum). The tanks are fabricated from low-carbon steel plate which is not impacted by hydrogen embrittlement under these conditions.

Based on these reports, hydrogen embrittlement or hydrogen-induced cracking of the steel liner plate during operational service life are not considered viable failure mechanisms for SSTs.

4.4.8.2. Hydrogen-Induced Blistering

Hydrogen-induced blistering is a condition that involves formation of blisters on or below a metal surface due to excessive internal hydrogen pressure (ASME BPV Code, Section II, Part D, Nonmandatory Appendix A). This pressure may be generated by corrosion. Hydrogen is absorbed into the metal and diffuses inward where it can precipitate as molecular hydrogen at internal voids, laminations or inclusions. As hydrogen molecules accumulate and concentrate at a particular location, pressure can increase to levels where internal cracks form. If these cracks are just below the surface, the gas pressure in the cracked area can cause the metal at the surface to become raised and bulge out, creating a blister-like protuberance on the surface.

The conditions for hydrogen-induced blistering are similar to the conditions required for hydrogen-induced cracking. Because hydrogen-induced cracking is not considered a viable failure mechanism for SSTs neither is hydrogen-induced blistering.

4.4.8.3. Cracking from Internal Hydrogen Precipitation

Cracking from internal hydrogen precipitation during operational service would require hydrogen uptake in the metal. Section 4.4.8.1 showed that hydrogen uptake under waste storage conditions in SSTs would not result in any degradation. Based on this, cracking of the steel liner plate during the operational service life from internal hydrogen precipitation is not considered a viable failure mechanism for SSTs.

Cracking from internal hydrogen precipitation, when associated with welding, is called underbead cracking or hydrogen-delayed cracking or cold cracking (ASME BPV, Section II, Part D, Nonmandatory Appendix A). The cracking typically develops in the coarse-grained region of the heat-affected zone parallel to the fusion line. Welding discontinuities and defects, including cracking, are covered in Section 4.3.3.

4.4.9 Corrosion

Several types of corrosion can occur in various metals depending upon the environment and conditions to which the material is subjected. Textbooks and handbooks may identify somewhat different categorizations of corrosion but generally include: general (uniform) corrosion; pitting corrosion; crevice corrosion, stress corrosion cracking; galvanic corrosion; intergranular corrosion; selective leaching (dealloying); erosion corrosion; and, microbiologically-induced corrosion. See subsections below for additional details.

4.4.9.1. General or Uniform Corrosion

General or uniform corrosion can occur in carbon steel liners at a low rate when subject to a range of pH conditions. In alkaline wastes at pH of 11-14, carbon steel forms a protective oxide, and corrosion rates are expected to decrease with time. General corrosion in the carbon steel liners can occur at a uniform rate significantly less than 1 mil/yr. In this rate, general corrosion would penetrate less than half of the carbon steel liner thickness in 100 years (BNL-52527).

If the pH were to be above 14, the FeO_2-ion becomes stable, resulting in partial dissolution of the protective oxide layer, which would increase the corrosion rate. Literature suggests that the increase of the general corrosion rate at this high pH level would be up to 2 to 5 mil/yr at temperatures below 100°C. Due to the possible increase of corrosion rates, a pH of 14 is considered the upper limit for waste storage in the DSTs (BNL-52527).

The rate of general corrosion can also increase at pH values of less than 9, due to the increased solubility and the dissolution of the protective oxides. The rate of general corrosion could also be increased if the protective oxides were to be removed mechanically by the rubbing of the solid waste against the inside of the liner (BNL-52527).

Study of general corrosion of tank liners at Hanford has occurred over the years for specific waste types stored in the tanks. Tank chemistry and temperatures have existed at times in SSTs resulting in uniform corrosion rates greater than 1 mil/yr. For example, corrosion rates during a 1,000 hour test of mild steel samples in synthetic neutralized REDOX waste ranged from 0.02 to 6 mil/yr (HW-26201, *Corrosion Tests – SAE 1010 Mild Steel in Synthetic Neutralized REDOX Waste Solution*). At a general corrosion rate of 6 mil/yr, half the thickness of a $^3/_8$-in. steel liner would be removed in roughly 30 years.

Based on the above description, general corrosion is considered a possible liner failure mechanism.

4.4.9.2. Pitting Corrosion

Pitting corrosion is a type of localized corrosion that can occur in the carbon steel liners. In pitting corrosion, an electrochemical cell is formed consisting of a small anodic (corroding) area, surrounded by a larger cathodic (non-corroding) surface region that stimulates the localized dissolution at the anode. Pits may continue to grow autocatalytically at high rates once initiated.

As pitting proceeds, the pH and the concentration of oxygen inside the pit decrease and concentration of the aggressive anion increases, resulting in an increase in the rate of attack. The addition of inhibiting ions can be used to mitigate pitting corrosion. Laboratory testing has shown that pitting is most likely to occur in carbon steel at pH values of less than 10 (BNL-52527).

Pits can result in the perforation of a metal component while the rest of the metal piece remains unattacked. In the presence of an applied stress, pits can serve as sites to initiate SCC. Pits may be difficult to detect if they are covered with corrosion products (Introduction to Corrosion Science [McCafferty 2010]).

Pitting is caused by the presence of an aggressive anion in the electrolyte environment to which the metal is exposed. This ion is typically chloride but other anions, including bromine, iodine, sulfate, and nitrate, can also cause pitting. Chloride and halogen ions can cause localized breakdown of passivity on the surface of carbon steels at relatively low pH values. Nitrate and sulfate are also adverse for carbon steel, which results in the formation of a small anode, surrounded by a relatively large cathode, leading to pitting (BNL-52527).

The tendency of a metal to undergo pitting is characterized by a critical pitting potential as illustrated in Figure 4-1. The critical pitting potential is a characteristic property of a given metal, but can also depend on the concentration of the aggressive ion in the environment that causes pitting, the presence and concentration of inhibitors, and temperature. Although the critical pitting potential is important in determining whether pitting will occur, it does not indicate the rate of pit propagation or depth of pits formed.

Pitting corrosion propagates due to the small anodic site of the pit surrounded by the large cathodic region of the surrounding metal. This can set up a large current density resulting in attack on the metal within the pit (DOE-HDBK-1015/1-93, "DOE Fundamentals Handbook").

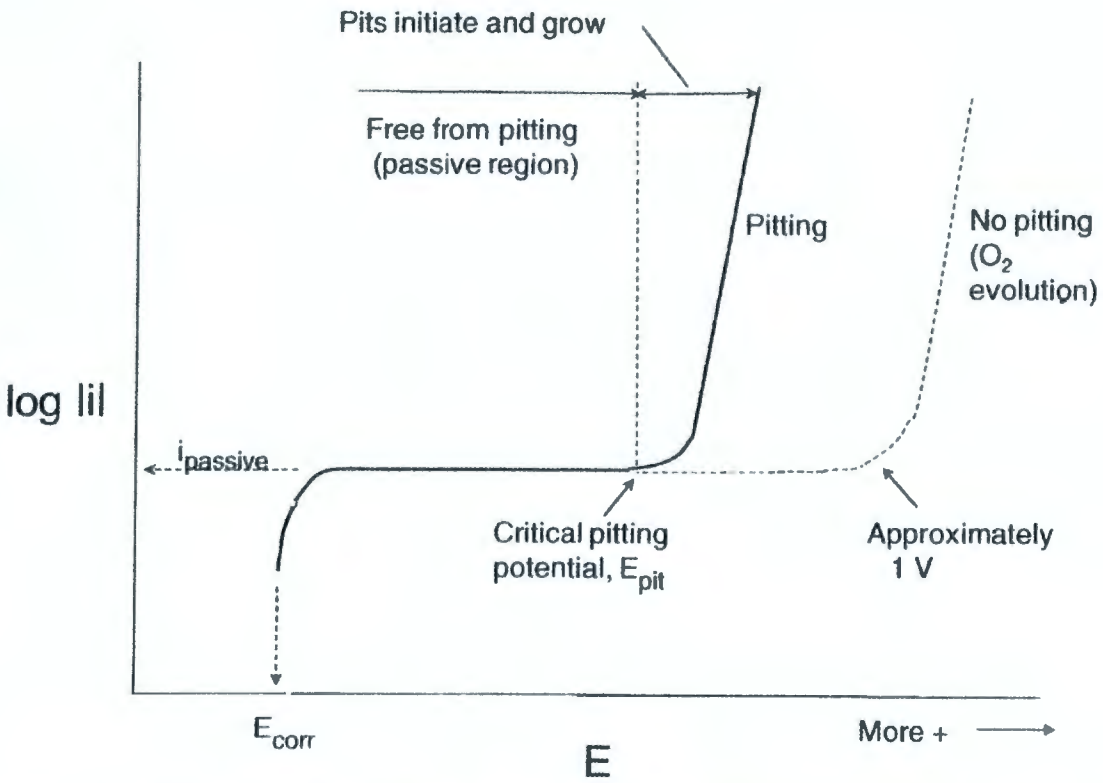


Figure 4-1. Schematic Illustration of Anodic Polarization Curve Showing Critical Pitting Potential
(McCafferty 2010)

Based on the above description, pitting corrosion is considered a possible liner failure mechanism.

4.4.9.3. Crevice Corrosion

The following discussion is derived primarily from McCafferty 2010. Crevice corrosion can occur in regions where a small volume of solution cannot readily mix with the bulk solution. These regions include:

- Under gaskets or seals
- Under bolt heads
- Between overlapping sheets
- Between metal flanges
- Within screw threads
- Under corrosion products
- Under sludge or other deposits during stagnant periods

Crevice corrosion often starts as a differential oxygen cell, where corrosion processes consume the dissolved oxygen in the solution within the crevice and the potential of the metal in that region becomes more active than the surfaces outside the crevice. Oxygen reduction occurs both on the metal surface which is exposed to the bulk electrolyte and also on the portion of the metal surface which is contained within the crevice. However, when oxygen is consumed within the narrow clearance of the crevice, it is not easily replaced due to the narrow diffusion path formed by the crevice. This results in oxygen becoming depleted in the crevice. The metal in the crevice with the lower oxygen concentration has a more negative potential than the bulk metal and the limiting current density for oxygen reduction, which is proportional to oxygen concentration, within the crevice is decreased relative to the bulk solution. Figure 4-2 schematically illustrates the initiation of crevice corrosion. Once initiated, crevice corrosion proceeds by the same mechanism as pitting corrosion (RPP-RPT-33306, *IQRPE Integrity Assessment Report for the 242-A Evaporator Tank System*).

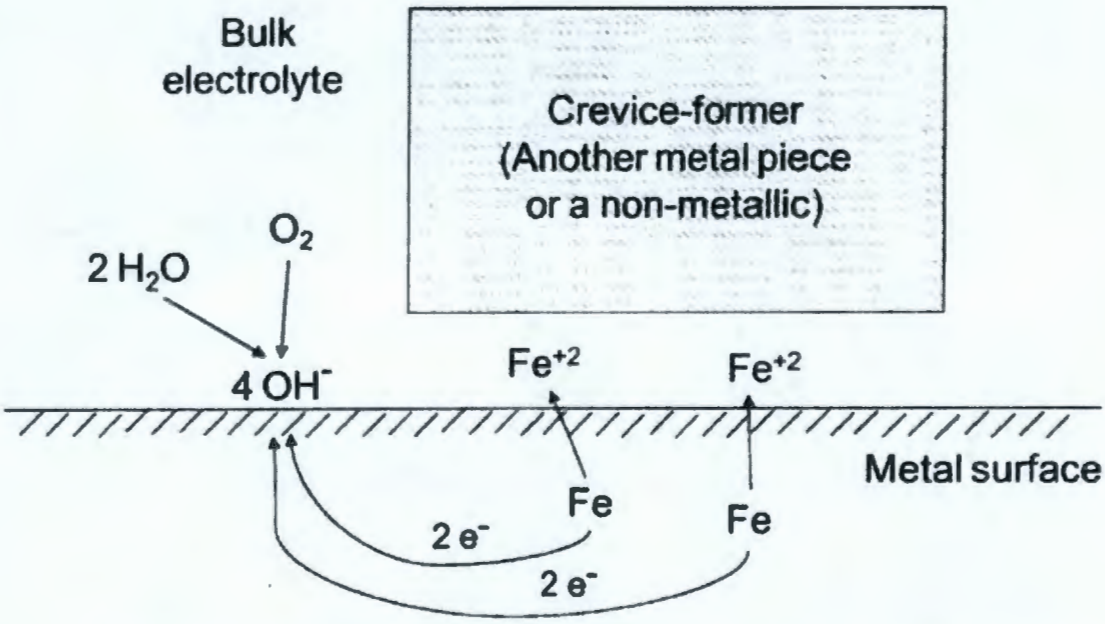


Figure 4-2. Schematic Illustration of Initiation of Crevice Corrosion (McCafferty 2010)

Crevice corrosion propagates by changes in the electrolyte composition within the crevice. The electrolyte in the crevice will become acidic relative to the bulk electrolyte and will contain concentrated amounts of cations discharged from the metal. This occurs because the narrow geometrical characteristic of the crevice restricts exchange between the crevice and bulk solutions. Cationic iron will react with water to produce iron hydroxide and hydrogen ions, thus acidifying the crevice solution.

One of the regions identified as a location for crevice corrosion is between overlapping sheets. The fabrication of SSTs with stiffener rings (described later in the report) on the interior wall is a candidate region for crevice corrosion. Also, corrosion products or undisturbed solids (sludges or saltcakes) are candidate regions for crevice corrosion.

Based on the above description, crevice corrosion is considered a possible liner failure mechanism.

4.4.9.4. Stress Corrosion Cracking (SCC)

Stress corrosion cracking (SCC) requires a susceptible material with the simultaneous presence of a sustained tensile stress and an aggressive environment (BNL-52527). Figure 4-3 portrays the process involved in SCC.

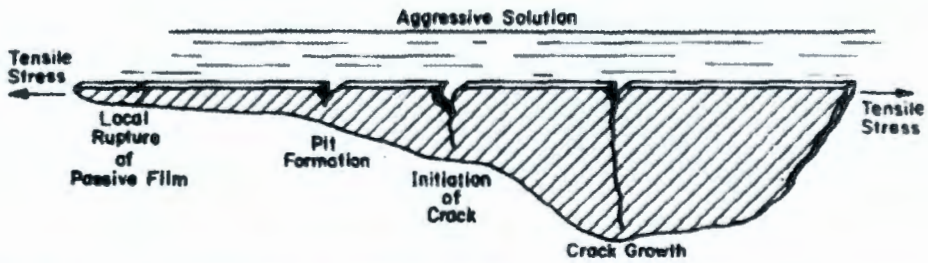


Figure 4-3. Progression of Process that Causes Stress Corrosion Cracking (Reference DP-1476)

Tensile stresses that cause SCC can come from applied stress during operation or residual stress from welding. Welding causes residual tensile stress (which is sustained unless a stress-relieving treatment is performed). Welding also causes changes in material adjacent to the weld making it susceptible to certain forms of SCC. Although tensile stresses may be present, they must be above a certain minimum stress intensity factor, K_{Iscc}, the critical stress intensity factor for SCC to occur. In general, stress intensity factor, K, is a measure of the ratio of localized stress, σ(local), to the average stress in the bulk of an otherwise uniform body, σ(average). Testing by various methods has shown that K_{Iscc} is considered to be a material property for a given environment (McCafferty 2010). The critical stress intensity factor for SCC, K_{Iscc}, is a function of the alloy type, alloy composition, strength level of the alloy, and the nature of the electrolyte. Stress corrosion cracking will not occur at a stress intensity factor less than K_{Iscc}. The value of the stress intensity factor which produces cracking in the dry specimen (i.e., in the absence of any electrolyte in contact with the specimen) is called the fracture toughness of the material and is given the symbol, K_{Ic}. At large applied loads in the presence of an environment causing SCC, the environment has little or no effect on the value of K_{Ic}. A generic graphical representation of cracking as a function of the stress intensity factor is presented in Figure 4-4. Stress corrosion cracking does not occur in Region I but does occur in Region II. Mechanical rupture occurs in Region III.

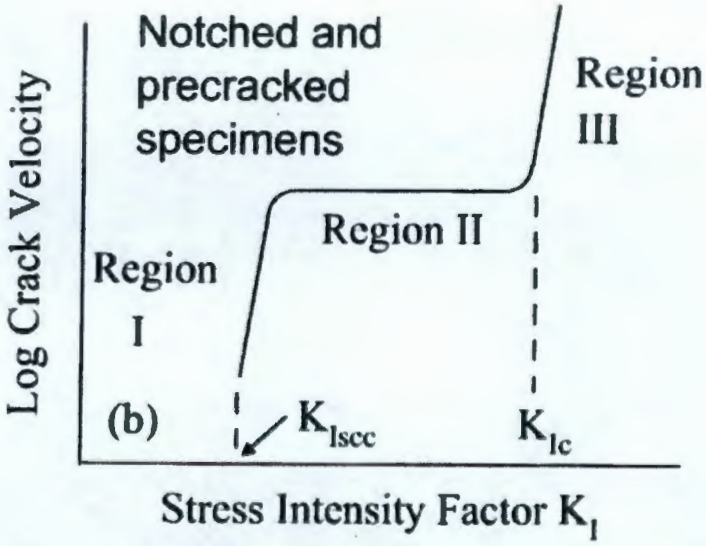


Figure 4-4. Stress Corrosion Cracking as a Function of Stress Intensity Factor (McCafferty 2010)

The discussion above assumes a flaw is present, greater than a critical size, which leads to SCC and failure if the stress intensity factor exceeds K_{Iscc}. However, for smooth specimens that do not contain intentional flaws, the measure of the resistance to SCC is the threshold stress, σ_{th}, below which SCC does not occur (McCafferty 2010). This holds true up to a particular flaw size, above which the propensity to crack is dependent upon K_{Iscc}. This is illustrated generically in Figure 4-5 based on adaptation of a figure from McCafferty 2010. The area below the hatched line is referred to the safe-zone or fracture-safe region. The elbow in the hatched line intersects at a particular flaw size. Inherent cracks or generated defects, say from pitting corrosion or crevice corrosion, greater than that size would lead to SCC if the stress intensity factor exceeds K_{Iscc}.

Low-strength steels (≤150 ksi yield strength) are quite susceptible to cracking in certain specific environments (Environmental Effects on Engineered Materials [Jones 2001]). The yield strength of the steel in this strength range is not particularly significant to the susceptibility to cracking, as it is for high-strength steels. Other factors such as applied stress, steel composition, pH, solution composition, potential, and temperature are more critical. Increasing applied or residual stresses, increasing temperature, and decreasing pH enhance the SCC of low-strength steels. Small concentrations of trace or impurity elements in the alloy can have an effect on SCC of steels.

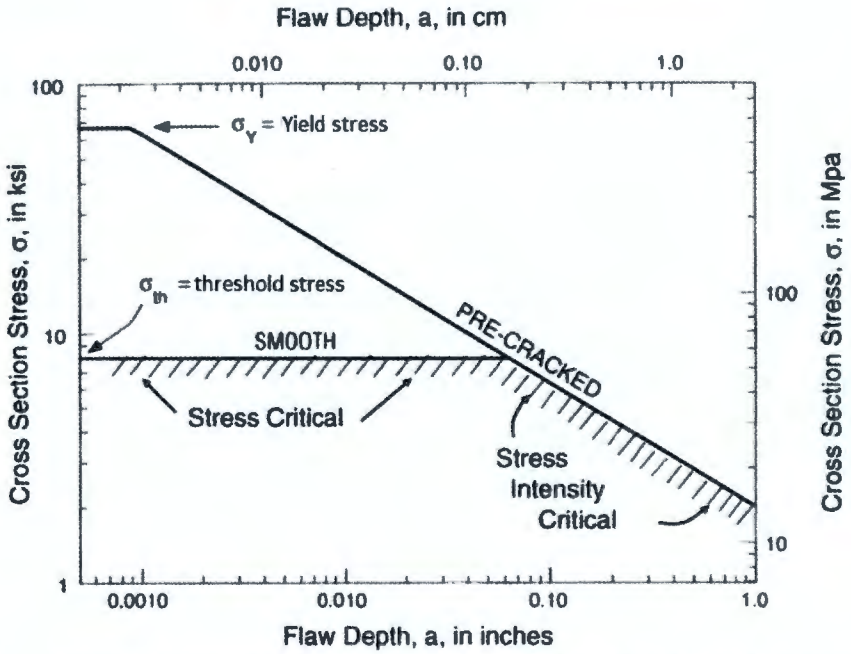


Figure 4-5. Stress Corrosion Cracking Zone for Smooth and Pre-Cracked Material (Adapted from McCafferty 2010)

Studies have shown that the propensity for SCC to occur in carbon steel tanks containing radioactive high-level waste may be reduced by the following operations (BNL-52527).

- Controlling the pH and hydroxide/nitrate ratios, and adding inhibitors to the high level wastes.
- Heat treating the inner tank at 590°C, followed by controlled slow cooling to relieve stresses in and adjacent to the welded joints.
- Reducing stress concentrations during construction.
- Using improved steel grade such as ASTM A 516 or A 570 Grade I for liners.

Only the first option is available for current and future prevention of SCC in the SSTs. The last three options were not implemented in the SSTs because SSC was not fully understood until the 1960's, after all of the SSTs were built. The effects of high nitrate concentrations and stresses in relation to SCC were not fully understood at the time of construction of the SSTs, and therefore were not of significant concern.

Some of the more common environments known to cause SCC of low-strength steels are liquid ammonia, carbon dioxide/monoxide, carbonate/bicarbonate, hydroxide, nitrate, and amine solutions. Generally, as the concentration of the solution increases, the susceptibility to SCC increases. Three environmental causes of SCC that are a potential concern in the carbon steel SSTs are nitrate, caustic and carbonate/bicarbonate solutions. Each of these three types of SCC, and their applicability to the SST liners, are discussed in more detail below.

4.4.9.4.1. Nitrate-Induced Stress Corrosion Cracking

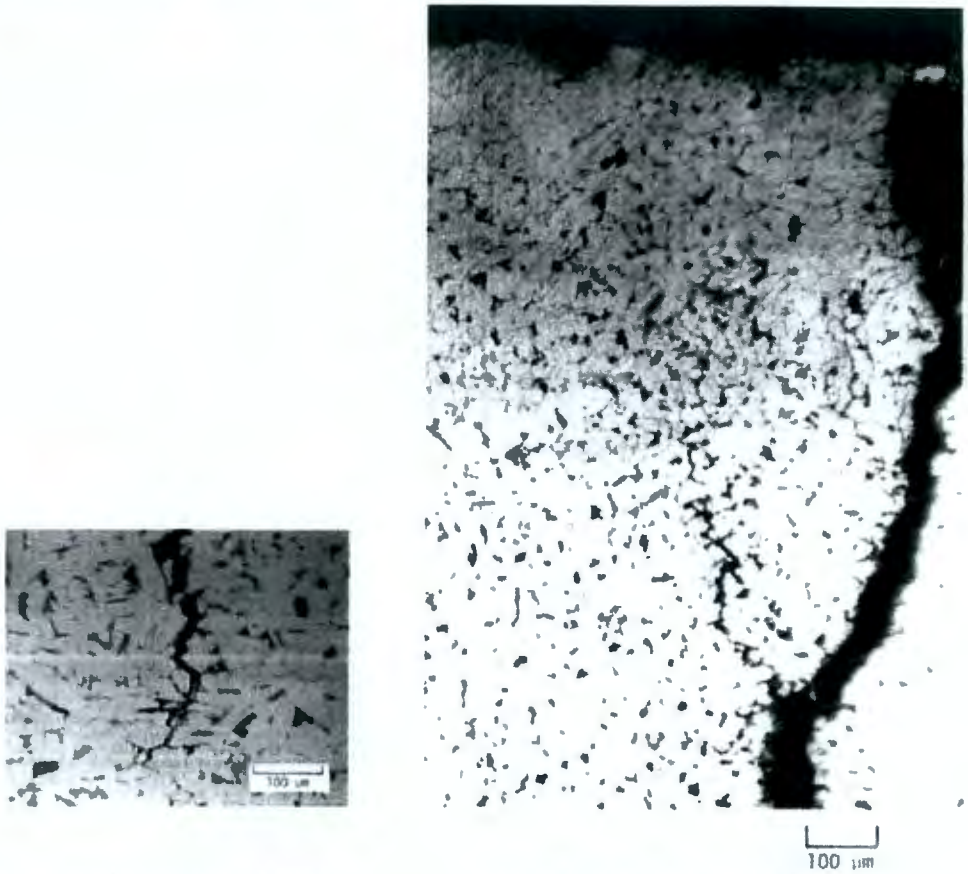
For solutions containing both nitrate and hydroxide, the ratio of nitrate and hydroxide ions determines whether SCC is likely to occur (BNL-52527). Nitrate and hydroxide are both inhibitors to SCC from high concentrations of the other. Nitrite ion has been found to inhibit nitrate-induced SCC. In service at the Savannah River Site, there has been extensive SCC in non-stress-relieved carbon steel tanks with nitrates providing the aggressive environment (BNL-52527). Of the first sixteen tanks constructed at the Savannah River Site between 1951 and 1956, none of which were stress-relieved, nine tanks have leaked detectable amounts of waste into the secondary (DP-1476). The first tank leaked in 1957 (DP-1476). Most of the observed leaks have been close to weld beads, oriented perpendicular to the weld, but seldom extending through it. The number of cracks in the tanks range from one to approximately 300. The time for cracks to develop ranged from a minimum of several months to many years after the tanks were placed in service. The type of cracking observed was intergranular. Figure 4-6 shows the path of a nitrate stress corrosion crack in A285-B steel compared to the crack found in the sample from the Savannah River Site's Tank 16. Both crack types are similar.

In response to the cracking of tanks, several test compositions were tested to determine when SCC would initiate (DP-1476). Based on this and other work, limits for maximum nitrate concentration (5.5 M), minimum hydroxide concentration (0.3 M), minimum combined hydroxide and nitrite concentration (1.2 M), and maximum temperature of fresh waste (70°C) and concentrated waste (boiling point) were developed (DP-1478, *Prediction of Stress Corrosion of Carbon Steel by Nuclear Process Liquid Wastes*). Higher nitrate concentrations, up to 8.5 M $NaNO_3$, have also been considered (WSRC-MS-2003-00882, *Review of Corrosion Inhibition in High Level Radioactive Waste Tanks in the DOE Complex*). At concentrations between 5.5 M and 8.5 M $NaNO_3$, minimum hydroxide concentration of 0.6 M and minimum combined nitrite and hydroxide concentration of 1.1 M will prevent SCC in the temperature range 35°C to 75°C. From DP-1476, the composite chemical composition of new (i.e., freshly generated, not aged within a tank) high-level liquid waste generated at the Savannah River Site consists of 3.3 M sodium nitrate, 1 M sodium hydroxide, <0.2 M sodium nitrite as well as sodium salts of aluminate, carbonate, sulfate and metal oxides and hydroxides. This composition, at elevated temperature, can initiate nitrate-induced SCC. Thus temperature limits were also implemented for fresh waste.

Specifications have been developed to minimize the threat of SCC in Hanford's DSTs (RPP-RPT-47337, *Specifications for the Minimization of the Stress Corrosion Cracking Threat in Double-Shell Tank Wastes*). These specifications considered data from pre-stressed as well as stress relieved steel specimens and at various chemical compositions and temperatures from 25°C to 140°C. For nitrate-rich waste these specifications are:

Maximum Temperature	50°C
Maximum Nitrate Ion	6.0 M
Maximum Hydroxide Ion	6.0 M
Minimum pH	11
Minimum Nitrite Ion	0.05 M
Minimum Nitrite/Nitrate Ion Ratio	0.15

Based on these experiences nitrate-induced SCC of the steel liner plate during operational service life is considered a viable failure mechanism for SSTs.



a. Intergranular Cracking in Constant-Current Tensile Test of A285-B Steel

b. Crack Extending through Wall of Savannah River Tank 16 (Exterior at Top)

Figure 4-6. Nitrate-Induced Intergranular Stress Corrosion Cracking (Reference from DP-1476)

4.4.9.4.2. Caustic Stress Corrosion Cracking

Carbon steels are known to be susceptible to caustic SCC. Caustic SCC of carbon steel occurs over a wide range of caustic concentrations. The lower limit of caustic cracking is a few weight percent of caustic. At higher caustic concentrations, carbon steel is susceptible to caustic SCC at lower temperatures. A caustic soda service chart of metallurgical requirements developed by the National Association of Corrosion Engineers (NACE) is provided in Figure 4-7.

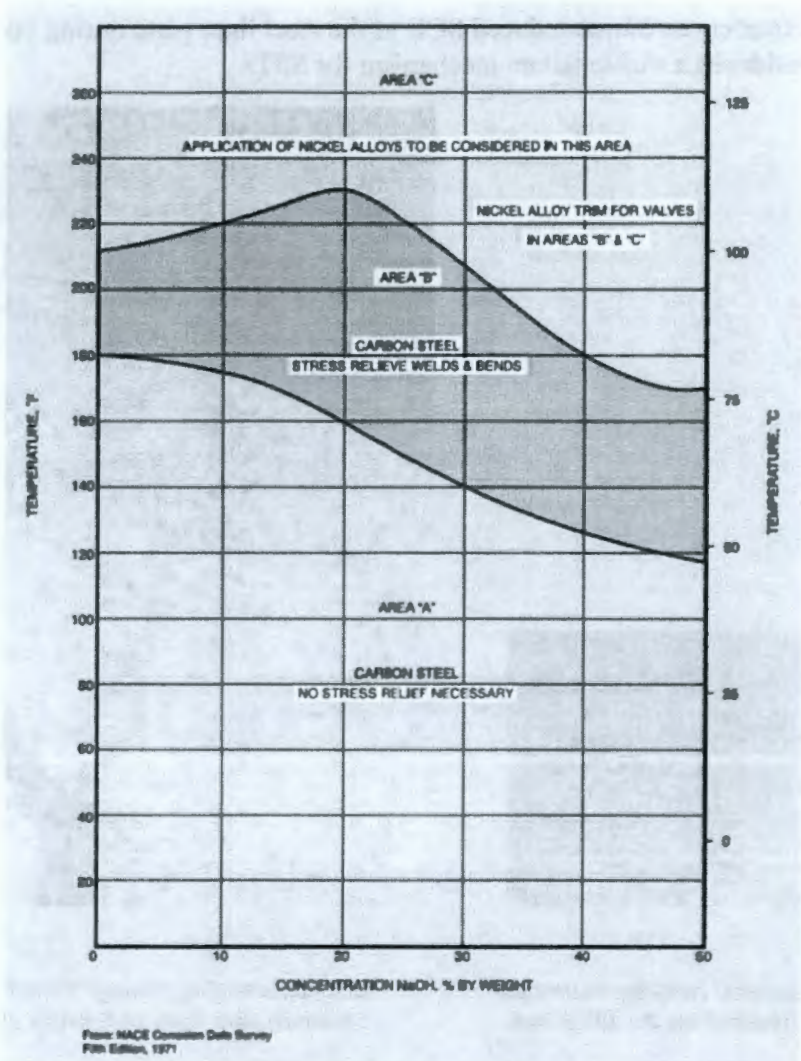


Figure 4-7. Caustic Soda Service Chart of Metallurgical Requirements

Under appropriate environmental conditions, caustic SCC is inhibited by the presence of nitrate (BNL-52527). However, at high enough caustic concentration and temperature caustic SCC can occur. Testing of 10 M hydroxide solutions with various concentrations of nitrate and nitrite showed cracking at 180°C, moderate nitrate concentration (1-5 M) and low nitrite concentration (0.2 M) (SD-WM-TI-161, *References for Technical Basis for Waste Tank Corrosion Specifications*, Section on Tank Corrosion Study High Temperature Tests Eight Month Evaluation).

Based on these experiences caustic-induced SCC of the steel liner plate during operational service life is considered a possible failure mechanism for SSTs.

4.4.9.4.3. Carbonate/Bicarbonate-Induced Stress Corrosion Cracking

Carbonate/bicarbonate-induced SCC is known to occur at two different pH ranges (MH-2-95, *Stress Corrosion Cracking on Canadian Oil and Gas Pipelines*). At a near neutral pH in the range of 5.5 to 7.5, SCC can occur in dilute bicarbonate solutions (bicarbonate is the dominant form of dissolved carbon dioxide in water at near neutral pH). At pH greater than 9.3, concentrated carbonate-bicarbonate solutions can induce SCC. Study of 2 N solution prepared by dissolving equivalent amounts of sodium carbonate and sodium bicarbonate have demonstrated SCC at temperatures from 90°C down to 22°C (Sutcliffe 1972, *Stress Corrosion Cracking of Carbon Steel in Carbonate Solutions*). Additional studies were performed with different ratios and amounts of bicarbonate and carbonate. These studies indicate SCC could be produced in more dilute solutions, down to 0.25 N mixtures. Cracking could not be produced in 2 N sodium carbonate but could be produced in 1 N sodium bicarbonate.

High pH carbonate/bicarbonate-induced SCC occurs in a narrow range of potentials. In a solution of 0.5 M sodium bicarbonate and 1 M sodium carbonate solution at 75°C, cracking occurs between approximately -0.7 V (vs. SCE) and -0.6 V (vs. SCE) (NWMO TR-2010-21, *Stress Corrosion Cracking of Carbon Steel Used Fuel Containers in a Canadian Deep Geological Repository in Sedimentary Rock*). The cracking is intergranular. The severity of high pH carbonate/bicarbonate-induced SCC increases with increasing temperature. Temperature increases the rate of dissolution at the crack tip following film rupture and widens the potential range for cracking.

As discussed later in this report, the bismuth phosphate-generated metal waste from extraction was neutralized with sodium hydroxide to near neutral conditions and then treated with soda ash to complete neutralization and to subsequently form a solid phase uranium phosphate carbonate complex while in storage in the SSTs. Analysis of a series of metal waste samples from the late 1940's showed the carbonate concentration of supernatant liquid in the tanks ranged from 0.30-0.912 M carbonate. These concentrations could potentially cause carbonate/bicarbonate-induced SCC.

Based on this description and the process knowledge of the bismuth phosphate process, carbonate/bicarbonate-induced SCC of the steel liner plate during operational service life is considered a possible failure mechanism for SSTs.

4.4.9.5. Microbiologically-Induced Corrosion

Microbiologically-induced corrosion (MIC) is corrosion brought about by the presence and/or activity of microorganisms in biofilms on the surface of a corroding metal (RPP-50821, *Corrosion Assessment of Effluent Treatment Facility (ETF) for Secondary Liquid Waste Treatment (SLWT) Project*). Microbiologically-induced corrosion can be an aggressive form of corrosion leading to through-wall failures in short periods of time. Once established, MIC can be difficult to eliminate, and can become a chronic problem. Failure to completely remove the bacteria associated with MIC in a system and subsequently preventing and controlling it typically results in reinfection by the same microorganisms within a short time period. Microbiologically-induced corrosion typically requires: 1) susceptible metal; 2) proper nutrients;

3) water; and, 4) oxygen. Under the appropriate environmental conditions microbial growth occurs, producing biofilms, biomass, and eventually tubercle formation and growth. The SSTs do contain all four requisite items for MIC. However, there are no known indications of biofilms or biomass accumulation within a SST that would need to be present for MIC to occur. Microorganisms and biofilms that could contribute to MIC has been found in spent fuel pools (DNFSB/Tech-22, *Savannah River Site Spent Nuclear Fuel, Technical Report*) demonstrating that in certain circumstances bacteria can survive and grow in radiation fields. Those microorganisms that cause MIC generally exist in a pH range of 4-9 but bacteria can live at a greater range of pH. Generally, waste present in SSTs is at a pH greater than 9 which would limit or eliminate growth of the microorganisms that cause MIC. In terms of corrosion problems for nuclear waste tank systems, MIC is more of a problem where the metal of the tank is in contact with groundwater or soil where the microorganisms are prevalent. Also, MIC has been found in nuclear waste piping systems from stagnant water remaining in piping after testing (BNL-52527).

Based on the above discussions MIC is not considered a viable failure mechanism for SSTs.

4.4.9.6. Corrosion Fatigue

Corrosion fatigue is the cracking of a metal due to the combined action of a repeated cyclic stress and a corrosive environment. Mechanical fatigue was discussed in Section 4.4.1 and shown to not be a likely failure mechanism. Because of the limited cyclic stresses the liners are subjected to, corrosion fatigue is not considered to be a likely failure mechanism.

4.4.9.7. Erosion Corrosion

Erosion corrosion is caused by mechanically assisted erosion of the protective layer from a metal surface exposing the metal to the corrosive environment. Mechanical erosion was discussed as a possible mechanism for liner failure in Section 4.4.7. Because of the limited amount of time that a limited set of tanks were subjected to an erosive environment, the amount of erosion experienced by any tank would be quite small and thus the potential for erosion corrosion would similarly by quite small.

Based on the limited amount of erosion occurring within the tanks, erosion corrosion is not considered a viable failure mechanism for SSTs.

4.4.9.8. Concentration Cell Corrosion

Localized attack on carbon steel can occur where concentration gradients can develop in the environment in contact with the steel. These concentration gradients can develop an electrolytic cell with discrete anodic and cathodic regions. If the potential difference is great enough the anodic region will corrode preferentially. A concentration cell may form anywhere a concentration difference exists in an electrolyte that will cause corrosion. In SSTs, these areas could include the liquid-air interface, solid-liquid interface, differential solid-solid interface with two different solid compositions, stagnant solids layer. Each of these will be discussed below.

4.4.9.8.1. Liquid-Air Interface (LAI)

Local differences in pH at a stagnant liquid-air interface (LAI) with lower pH values at the surface of the waste (e.g., from water evaporation and subsequent condensation at the surface or carbon dioxide absorption at the waste surface from the air space) can cause pitting.

An expert panel workshop on DST vapor space corrosion (RPP-RPT-31129, *Expert Panel Workshop on Double-Shell Tank Vapor Space Corrosion Testing*) identified that the primary corrosion concern at the LAI is pitting corrosion. In this case, the interfacial corrosion is considered to occur just above the liquid level. Reactions involving carbon dioxide in the air and hydroxide could have an effect on the corrosiveness of a thin liquid layer that migrates up the steel surface above the bulk solution. Therefore, as with vapor space corrosion mechanisms, it is possible that corrosion would be localized owing to a difference in local corrosiveness of the environment rather than because of a localized corrosion process involving passive film breakdown.

Document RPP-RPT-31129 goes on to state that nitrate, due to its relatively high concentrations in radioactive waste, has typically been considered the controlling anion for pitting at the LAI. However, other species such as chloride, sulfate and fluoride, also present in waste solutions have been shown to be aggressive above critical concentration levels. At pH 10 conditions such as those that exist at the LAI, nitrite has been found to be an effective inhibitor against pit initiation. A critical concentration of nitrite required to prevent pitting is observed. Localized corrosion occurred at nitrite concentrations below this critical level regardless of the nitrate concentration. An increase in temperature also results in an increase in the minimum nitrite concentration necessary to prevent pitting. A least squares fit of a multiple variable regression analysis of results from testing of waste simulant solutions for pitting yielded an equation expressing the minimum nitrite concentration to inhibit pitting as a function of nitrate concentration (M) and temperature, T, in degrees Celsius:

$$[NO_2^-] = 0.025 * [NO_3^-] * 10^{0.041T}$$

Based on the above discussions LAI is considered a viable failure mechanism for SSTs.

4.4.9.8.2. Solid-Liquid Interface

Similar to the LAI, local differences in composition could possibly occur between interstitial liquid in equilibrium with solids and the liquid above at a solid-liquid interface. Based on the comparison to LAI corrosion, solid-liquid interface corrosion could be a possible failure mechanism.

4.4.9.8.3. Solid-Solid Interface

Different waste types, containing solids or from which solids precipitate, were transferred into and out of SSTs at different times. This could result in layering of heterogeneous solids within a SST. These layers of solids will have different chemical compositions and differing equilibrium

concentrations of electrolytes in the interstitial liquid. Depending on the concentration of certain electrolytes, a concentration cell could occur between the interstitial liquid of two adjacent layers of solids within the tank. This concentration difference could result in corrosion (e.g., general, pitting, SCC) within the anodic layer. Based on this discussion, solid-solid interface corrosion could be considered as a potentially likely failure mechanism.

4.4.9.9. Vapor Space Corrosion

Localized forms of vapor space corrosion in carbon steel, such as pitting or SCC, can develop in the presence of an electrolyte that contains aggressive anions such as chloride, nitrate, or sulfate that are found in the aqueous phase of liquid waste (SRNL-STI-2009-00649, *Vapor Space and Liquid/Air Interface Corrosion Tests*). Pitting has been detected in carbon steel specimens in the vapor space above a number of Hanford-specific waste types (HW-24136, *Corrosion Tests-SAE 1010 Mild Steel in Synthetic Metal Waste Solution*, HW-30641, *Field Corrosion Tests-SAE 1020 Steel in Bismuth Phosphate Process Waste Solution Tanks*, HW-31884, *Project CA 539 241-SX Tank Farm Description and Use of Facilities*).

An expert panel workshop on DST vapor space corrosion (RPP-RPT-31129) identified that corrosion in a tank vapor space can corrode by atmospheric corrosion processes. Although similar, vapor space corrosion of the metal surface occurs under an aqueous layer in equilibrium with humid gaseous environments. The gaseous environment allows ready access to oxygen from the environment. Corrosion products or precipitates on the surface can affect the corrosion process.

Based on the above discussion, most notably the detection of vapor space pitting in carbon steel specimens exposed to Hanford wastes, vapor space corrosion is considered a possible failure mechanism for SSTs.

4.4.9.10. Differential-Temperature Cell Corrosion

Differential-temperature cell corrosion is a relatively obscure corrosion process that causes metal loss when different parts of the same metal are immersed in an electrolyte that varies in temperature from one location to another (ASME BPV, Section II, Part D, Nonmandatory Appendix A). If the anode and cathode are areas located on a single piece of metal (or on two electrically connected pieces of the same metal) immersed in the same electrolyte, corrosion will proceed as in any short-circuit galvanic cell. Differential-temperature cell corrosion occurs most frequently in heat transfer equipment and piping, where substantial temperature differences exist between the inlet and the outlet portions exposed to the same electrolyte.

Single-shell tanks store wastes that contain both precipitated and dissolved solids. The waste contains radionuclides that generate heat via radioactive decay. The precipitated solids form a settled layer on the bottom of the tank. Heat transfer through this settled layer is via conduction resulting in a temperature gradient through the layer between the tank bottom and the liquid layer above where heat transfer is through convection. Temperatures throughout the liquid are relatively more uniform but a temperature differential exists between the settled solids and the

liquid containing the dissolved solids. Depending on the temperature differential, the electrolyte, and the proximity of the high and low temperature areas, a differential-temperature cell can form resulting in corrosion at the anodic site.

Based on the above discussion differential-temperature cell corrosion is considered a possible failure mechanism for SSTs.

4.4.9.11. Corrosion of Tank Liner Exterior Surface

Corrosion of the exterior surface of the tank liner would require the presence of water, oxygen and/or organic material. The exterior of the bottom portion of the liner of all SSTs is in contact with a cement or grout layer. With the exception of A, AX and SX Farms, the 100-Series tank liner wall is surrounded by a 3/8-in. thick external asphaltic coating between the concrete and steel liner. The exterior of the wall liner for A, AX and SX Farms are in direct contact with the concrete walls of the tanks. The exterior of the 200-Series tank liner wall is in direct contact with a metal mesh blanket material.

Asphaltic coating is a typical protective coating for all types of direct buried steel storage tanks. The coating is applied to prevent external corrosion of the tank which may be in contact with moist soil or groundwater. For the areas of those tanks with asphaltic coatings on the wall liner, it is not expected that corrosion of the tank liner exterior surface is a likely contributor to tank liner failure. The presence of the asphaltic coating should eliminate contact of the liner with water.

A steel liner within a concrete shell is a typical construction technique for buried tanks and nuclear reactor containment buildings. The steel liners act as a leak tight barrier within a thicker load-bearing concrete shell. The relatively high pH of the concrete pore water protects the carbon steel from general corrosion. The mechanisms for steel corrosion in contact with concrete are more likely to be through chloride ingress via water intrusion or reduction in pH through carbonation of the concrete from reaction with atmospheric carbon dioxide. The expected air diffusion through concrete or cracks, if present, and the soil cover are expected to be very low such that carbonation and associate reduction in pore water pH would not be a significant concern. Considering water intrusion, the groundwater table is well below the bottom of the SSTs and the climate is relatively dry. Except for A and AX Farms, there is no driving force to pull air from the soil into the tank interior through the concrete shell (potentially exposing the exterior of the liner to moisture in the air) because the tanks are passively ventilated. It isn't practical to consider groundwater infiltration would occur through the concrete shell of the tank to the exterior of the carbon steel liner for passively ventilated tanks. Although there are possible indications of water intrusion through penetrations in the dome of certain SSTs there are no known indications of water infiltration through the concrete shell or dome contacting the exterior of the steel liner. Water intrusion through the dome is deflected via lead flashing to the interior of the tank and would not contact the tank liner exterior. So corrosion of the exterior of the liner from water infiltration is not considered as a likely contributor to tank liner failure.

Organic material (wood forms, leather gloves, etc.) could have been left at the time of forming for pouring of the concrete shell surrounding the liner. The NRC has issued technical bulletins and reports regarding through-wall corrosion of three reactor containment liners initiating at the concrete interface. The reported through-wall corrosion had occurred primarily because of organic material embedded within the concrete in contact with the containment liner. Wood with an acidic pH can disrupt or prevent formation of a passive film on the steel allowing active dissolution of the low carbon steel. Although this phenomenon has been experienced, it is not common. Therefore, even though it is a possible mechanism to cause liner failure, the frequency of occurrence is low and therefore would not be considered as a potentially significant contributor to tank liner failure.

Although little is known about the metal mesh blanket material in contact with the exterior of the 200-Series SSTs, none of the 200-Series tanks are known to have liner failures after evaluation via the process outlined in RPP-32681. It is not possible to attribute the metal mesh blanket material as a factor causing liner failure when no failures exist.

Overall, the corrosion of the exterior surface of the tank liners is not considered a significant liner failure mechanism.

4.4.10 Radiation-Induced Defects

The following is excerpted from BNL-52527 and WSRC-TR-92-350 (WSRC-TR-92-350, *Potential Radiation Damage of Storage Tanks for Liquid Radioactive Waste (U)*). Radiation embrittlement of ferritic steels arises from displacement of atoms in the steel by gamma rays and neutron bombardment. Radiation embrittlement of carbon steels results in a reduction in ductility and/or a measurable increase in the ductile-to-brittle transition temperature of the steel. Thermal neutrons have a much smaller cross section for displacement damage (12 barns) than high energy neutrons (>0.1 MeV) (~500 barns) and therefore are less important in terms of overall damage. The only mechanism by which high levels of displacement of atoms from neutrons could develop would be if criticality were to occur for extended periods of time. No reported criticality has occurred in any SST (LA-13638, *A Review of Criticality Accidents*). Gamma irradiations normally have little effect since these primarily affect the electronic (or ionic) structure of solids, and free electrons are already present in metals including steels; however, very high energy gamma radiation can produce some atomic displacements.

In an attempt to estimate the combined effects of the spontaneous fission neutrons and high energy gamma radiation, WSRC-TR-92-350 calculated the possible displacements per atom (dpa) under a number of potential situations, specifically for the Savannah River Site tank wastes. The highest estimated damage level for a tank is less than 4×10^{-7} dpa, assuming 100 year exposure to newly generated high heat waste (i.e., 180 day-cooled fuel, no decay during exposure period). Almost all this damage is from high energy gamma irradiation and only a very small portion from neutron irradiation (less than 4×10^{-11} dpa or 0.01%). This total damage level is less than the limit of 1×10^{-5} dpa for measurement of radiation damage to the mechanical properties of carbon steels. The expected changes in mechanical properties are, therefore, negligible for the range of damage levels that have been estimated for high-level waste storage tanks.

Based on the above description, radiation-induced defects are not considered a significant liner failure mechanism.

4.4.11 Vacuum Internal to Tank

Active ventilation was operated on a number of the SSTs at different times during their operational life. The ventilation would remove gas, vapor and particulate via a fan that would produce a slight negative pressure within the tank. The vacuum internal to the tank could cause buckling of the tank liner sidewall or the tank bottom depending on the conditions.

Buckling of the tank sidewall was examined in SD-RE-TI-035, *Technical Bases for Single-Shell Tank Operating Specifications*, using an approximation of the classical critical buckling load for a cylindrical shell subjected to external pressure:

$$P_{cl-shell} = 0.807\frac{Et^2}{LR}\sqrt[4]{\left(\frac{1}{1-\nu^2}\right)^3\frac{t^2}{R^2}}$$

where:

$P_{cl\text{-}shell}$ = classical buckling load of a perfect cylindrical shell
E = Young's modulus
t = thickness of shell
L = length of shell
R = inside radius of shell
ν = Poisson's ratio

In practice, imperfections in shells and variations in geometry exist in thin cylindrical shells and the load carrying capacity of the shell is reduced. To account for this, a non-dimensional term can be used relating the actual critical buckling load to the classical buckling load of a perfect cylindrical shell.

Buckling of the ¼-in. thick tank steel liner bottom of the early 100-Series (B, C, T, U, and BX Farms) tanks was examined in RPP-8551, *Buckling Assessment of Hanford C Farm Tank Bottom Liner for Vacuum Loading*, using a classical critical buckling pressure correlation (and other means) for a complete spherical shell subjected to external pressure:

$$P_{cl-sphere} = \frac{2E}{\sqrt{3(1-\nu^2)}}\left(\frac{t_b}{R_b}\right)^2$$

where:

$P_{cl\text{-}sphere}$ = classical buckling load of a perfect spherical shell
E = Young's modulus
t_b = thickness of shell bottom
R_b = radius of shell bottom
ν = Poisson's ratio

In practice, variation in shell shapes, geometry, plate thickness, and residual loads reduce the effective buckling load of the spherical shell. Similar to cylindrical shells, a non-dimensional

term related to the shallowness of the spherical shell can be used to account for these variations that relate the actual critical buckling load to the classical buckling load of a perfect spherical shell.

For the 100-Series tanks, the vacuum level causing buckling/uplift of the tank bottom liner is less than the vacuum level causing sidewall buckling (RPP-11788, *Single-Shell Tank Waste Retrieval Allowable Vacuum Assessment*). The tanks with thinner bottom liners (i.e., B, C, T, and U Farms) will buckle/uplift at a lesser vacuum level than those tanks with thicker bottom liners. Because of the geometry, the sidewall liner of the 200-Series tanks would buckle before the bottom liner (RPP-11788).

Buckling analysis of C Farm tanks (RPP-8551) has shown that when one does not factor in hydrostatic head from the waste or when the tank bottom is uncovered, buckling of the bottom spherical shell will occur at a much lower internal vacuum level than the sidewall shell. Not accounting for corrosion, the nominal bottom liner (¼-in.) could begin to buckle at as little as 2 in. vacuum in the absence of any hydrostatic head. This analysis in general applies to Type II and Type III, 100-Series tanks, although the material thickness of the steel liner and the level of corrosion experienced by the liner are primary considerations affecting numerical results. The analysis in RPP-8551 points out that buckling of the bottom portion of the steel liner does not necessarily result in a liner breach. Calculations for nominal wall thickness (¼-in. tank bottom and $^{5}/_{16}$-in. knuckle with no corrosion) show that a net differential pressure of approximately 88 in. w.g. internal vacuum would yield the tank liner at its weak point, the circumferential weld where the bottom joins the knuckle. The cylindrical wall of the steel liner would also buckle at this level of vacuum.

After a large bulge and breach of tank A-105 was discovered, a model test of the tank was performed to determine the effect of differential pressure on the tank bottom and the required pressure to cause failure of the liner (RL-SEP-630, *105-A Waste Storage Tank Model Test*). The testing revealed that the test liner failed at 17.5 in. w.g. differential pressure across the bottom liner. Failure occurred adjacent to the weld at the bottom-to-side joint. Because of scaling of the model to the actual tank, the pressure causing failure in the model was equivalent to the required pressure to fail the actual tank.

Active ventilation systems with exhaust fans that could pull a negative pressure on a tank were not originally employed on the early non-boiling SSTs (tank farms prior to SX Farm construction). Originally, the early tanks were equipped with air-cooled condensers to condense water vapor from the air that was directly vented to the atmosphere. Subsequently, at different times over the course of operations active ventilation was supplied to various non-boiling waste storage tanks to provide cooling (e.g., ventilation of tanks C-105 and C-106 for cooling) (see OSD-T-151-00013, Rev D-1, *Operating Specifications for Single-Shell Waste Storage Tanks*, p. 10) or flow into the tank during planned openings of passively ventilated tanks (e.g., to take photos) or active ventilation system modifications (SD-WM-SAR-006, Rev 1, *Single-Shell Tank Isolation Safety Analysis Report*, p. 5-14).

Active ventilation was employed as part of the boiling waste tanks (SX, A, and AX Farms). An active ventilation system was connected to SX Farm to air cool some of the tanks. The K1-3-1

and K1-3-2 fans connected to the SX Farm tanks, ca. 1970, via vent headers were capable of 7 in. w.g. static pressure (H-2-35835, *Ventilation Plan & Details Tanks: 105-SX, 1C7-SX, 106-SX, 109-SX, 110-SX, 111-SX, 114-SX*). The earliest vacuum limit found for SX Farm was from 1954, identifying a vacuum limit in tanks of 6 in. w.g. (LET-121654, "Allowable Pressures and Vacuums in PUREX and 241-SX Tank Farms," O.H. Milkey). For A and AX Farms, tank vacuum was limited to 6 in. w.g. and tank pressure limited to 60 in. w.g. via a water-filled seal pot located in a 24-in. line between the vent header and stack (RL-SEP-269, *Specifications and Standards for Operational Control of the PUREX Self-Boiling Tank Farms*). The highest allowed operating specification limit found for vapor space vacuum in SSTs was 9 in. w.g. but this required a minimum of 10 in. w.g. equivalent waste height (OSD-T-151-00013, Rev C-3, *Operating Specifications for Single-Shell Waste Storage Tanks*, p. 11). In effect, this provided 1-in. w.g. of pressure on the bottom liner which would protect the bottom liner from uplift.

Because of the relatively large level of vacuum (i.e., 88 in. w.g.) required to breach an early 100-Series tank (B, C, T, and U Farms), it is not considered reasonable that any practical means are available to provide this level of vacuum within the tank vapor space of a SST. This large level of vacuum required to breach the liner would apply to all SSTs with large radius bottom knuckles, or all farms except SX, A and AX Farms. The model testing of tank A-105, a tank with an orthogonal bottom to wall joint, showed that only 17.5 in. w.g. vacuum was required to breach the tank liner. However, active ventilation used on these tanks were limited by design (6 in. w.g. for A and AX Farms) or equipment limitations (7 in. w.g. static pressure on fans) to levels of vacuum much less than that require to breach the liner. Although in certain circumstances, uplift of the tank bottom would be possible with the given ventilation systems, this would not necessarily result in failure of the liner.

Based on the above description, although vacuum internal to a tank could cause increased stress on the liner it could not breach the liner and therefore it is not considered a significant liner failure mechanism.

4.4.12 Pressurization Internal to Tank

A report, HW-37519, was issued in 1955 setting forth a basis for limiting values of internal vapor pressure and effective liquid specific gravity for SSTs to maximize use of the existing underground storage capacity. This report covered all farms with the exception of AX Farm which was not yet built. The report was prepared at a time when wastes were being generated with higher specific gravities and higher temperatures which related to higher vapor pressures. This imposed greater loads on early tank structures than was originally considered.

The report was based on allowing the reinforcing steel to approach a higher tensile stress under sustained hydrostatic pressure and transient vapor pressure. A maximum specific gravity and simultaneous vapor pressure was established for each of the 100-Series tank types. These values are presented in Table 4-7 below.

Table 4-7. Maximum Specific Gravity or Vapor Pressure by Tank Farm Design*

Tank Farm	Allowable Specific Gravity	Simultaneous Allowable Vapor Pressure (psig)
241-T, -U, -B, -C, -BX	1.9 – maximum	2.5
	1.0	5.5
241-S, -BY, -TX, -TY	1.2	1.8
	1.0	2.8
241-SX	1.5	4.8
	1.0	9.0
241-A	2.2	6.9
	1.85	10.0

Data taken from HW-37519 (Figure 2).

At lower specific gravity, a higher simultaneous vapor pressure is allowable. This is a linear relationship but is limited at a specific gravity of 1.0 (for aqueous waste solutions) or an upper pressure of 10 psig. The 10 psig limit was selected because the tank dome would be at jeopardy above that limit.

Document HW-37519 concludes that "...waste tanks subjected to the specific gravities and vapor pressures quoted will not present an undue structural hazard...The higher unit stresses change the degree of cracking that is permitted. However, the values are believed to be such that the structural stability of the tank in not endangered. As long as the integrity of the steel plate liner is not violated there need be but little concern about waste leakage to the sub-surface strata." This is interpreted to mean that although greater cracking of the concrete would be expected, the integrity of the steel plate liner is not violated under the conditions which result in these higher unit stresses.

Pressurizations internal to particular SSTs have occurred in the past due to steam bumps. The term "bumping" was first used to describe tanks in which the pressure variation were responsible for contamination spread from the tanks to the area surrounding the tanks (WHC-SD-WM-TA-021, *History of Tank Bumps in Aging Waste Tank*). Steam bumps occur when cooler supernatant mixes with hotter sludge under conditions which allow steam bubbles to form. If this heat transfer from sludge to supernatant is sudden and large enough, the steam bubbles escaping the surface of the waste can cause temporary pressurization of the tank and an increased condensate flow rate from the condensers on the tank. The then-available documented information on tank bumps was tabulated in a report issued in 1990. An abbreviated table showing information provided in that report, WHC-SD-WM-TA-021, is provided in Table 4-8.

Table 4-8. Tank Bumps in Aging Waste Tanks

Tank	S-104	S-101	SX-101	SX-104	SX-114	A-105	AX-101
Date	10/53-5/54	1/54-8/54	2/55-4/55	7/55	8/58	1/65	1968-69
Tank Pressure, psig	<1.6	<1.6	0.7-1.8	No information	2.6	1.8	No information
Duration, minutes	8-42	8-42	3-13	70	No information	30	20
Number of Events	Many	Many	>40	2	4	1	1

Data taken from WHC-SD-WM-TA-021 (Table 1).

In comparing the tank pressurization data in Table 4-8 to the allowable vapor pressures listed in Table 4-7, all listed tank pressurization events were less than the allowable vapor pressures at maximum specific gravity for the tank farms of interest. No significant impact to tank liner structural integrity would be expected from the tank pressurizations from steam bumps.

Based on the above description, pressurization internal to a tank is not considered a significant liner failure mechanism.

4.4.13 Operational Errors or Accidents

Operational errors or accidents consider those unintended activities (e.g., dropping equipment into a tank, unplanned contact with the liner, etc.) that could potentially compromise the integrity of the tank liner. In general, errors or accidents would only affect the particular tank involved in the error or accident unless there was some common activity that resulted in frequent errors or accidents.

Dropping or contacting equipment onto the bottom tank liner could cause scratches, partial cracks or through-liner cracks depending upon the severity of the impact. The tank liner is supported on its exterior by a grout or concrete layer which would also absorb the energy of impact. As part of this investigations performed for this study, no known immediate failures were discovered due to the dropping of equipment onto the tank liner.

If the equipment dropped into the tank is made of a dissimilar metal, then a galvanic corrosion cell could be set up resulting in galvanic corrosion. Two dissimilar metals with different electrode potentials in electrical contact in an electrolyte may result in increased corrosion of the anodic metal (more electronegative) due to galvanic corrosion. The possibility of galvanic corrosion is affected by a number of factors including: electrode potential; degree of polarization; electrolyte conditions (composition, temperature, electrical conductivity, pH); and, area ratio between anode and cathode. It is proposed the most common dissimilar metal that may be present in SSTs would be stainless steel. In general, stainless steel is more noble (cathodic) than mild steel (anodic) in the galvanic series of metals and alloys (Perry's Chemical Engineer's Handbook [Perry 1973], Table 23-1) which would result in the mild steel corroding. Any stainless steel present in SSTs (e.g., tapes, wires, pipe, etc.) would be relatively small in surface area relative to the area of the carbon steel tank. When the anode is a large surface area and the cathode relatively small, relatively little attack would occur over the much larger surface

area of the anode. So even if galvanic corrosion attack were to occur, the overall affect would be considered insignificant because of the relatively large surface area of the anode (carbon steel).

While core drilling for samples in tank BX-107, it was discovered an additional unrecorded section of drill rod had been attached to the drill string resulting in the drill bit coming in contact with the tank bottom. The period of time the drill bit was in contact with the tank bottom was approximately 10 seconds while in the rotary drill mode. Testing showed less than 0.05 in. of penetration into the tank liner could occur in this time frame.

As part of the investigations performed for this study, no known errors or accidents were uncovered resulting in the immediate failure of a tank. Based on the above description, operational errors or accidents are not considered a likely common liner failure mechanism.

4.4.14 Improper or Inadequate Operational Procedures or Processes

The topic of improper or inadequate operational processes or procedures is intended to consider accepted operational practices that unknowingly could contribute to a potential liner failure. An example would be inadequate chemistry control to limit nitrate-induced SCC. The seriousness of this issue was not fully understood until tank failures occurred at the Savannah River Site. After the issue was understood, modifications were made to chemistry control to protect against nitrate-induced SCC. This section explores changes and additions to operational limits to determine whether there are any potential liner failure mechanisms that otherwise have not been addressed.

Over the years of operation, process changes and improvements so changed the characteristics of the waste (higher specific gravity, higher temperature, increased vapor pressure) sent to the SSTs that it was recognized that structural reevaluation of the older SSTs was necessary in order to determine their continued suitability to contain the waste being generated (HW-37519, p 4). This early reevaluation, in 1955, of the acceptability of the existing tanks focused on setting forth limiting values of maximum specific gravity (hydrostatic load) and simultaneous internal vapor pressure without violating the structural integrity of the tanks.

With the advent of REDOX operations, more concentrated waste was generated that resulted in higher tank internal temperatures, particularly just above the tank bottom where high heat sludge would settle. This situation raised questions regarding possible temperature stresses in the tank materials, and the possible effects on the integrity of the tank liners and structures (HW-56821). A study was performed in 1958 and found that the greatest risk of buckling of the steel liner occurs during the initial filling, if the waste temperature is brought up too rapidly. Too rapid a temperature rise can result in unequal expansion of the steel liner and concrete wall. A rapid increase in temperature can also produce high temperature gradients and stresses within the thick concrete walls. This resulted in the recommendation to extend the rate of temperature increase from ambient (60°F) to boiling (235°F) over at least 1000 hours and preferably 1500 hours. Similarly, a recommendation was provided to extend the rate of temperature rise associated with settled sludge, which was estimated to rise to 400-500°F, over 1000 to 1500 hours.

In a 1959 report (HW-59919, *Limitations for Existing Storage Tanks for Radioactive Wastes from Separation Plants*), physical limitations for the existing storage tanks were defined to assure continued integrity of the existing SSTs. This included limits on specific gravity, temperature, temperature differential across the structure, liquid level, and allowable vapor pressure. This was partly in response to the instability (bulging) of the bottoms of the SX-113 and U-104 tanks which was postulated to have been caused by vaporization of moisture present in the grout between the asphaltic membrane and steel liner of the SSTs. When the vaporization pressure exceeds the hydrostatic load there is the possibility for the liner to become unstable and deform upward if the moisture vaporizes and remains trapped. Waste temperature limits and rate of rise temperature limits were also identified. Uniform temperature increases were limited to 2°F per day. Incremental temperature increase of up to 40°F was acceptable provided a minimum four week hold time occurred after the rise. These limits would keep the thermal gradient across the structural components to 23°F per ft, the value used to estimate thermal stresses in the components. Additionally, a maximum temperature for waste was identified.

The earliest specifications and standards for SSTs addressing both the structural integrity requirements described in the preceding paragraphs and chemical requirements including pH and composition instituted for corrosion control, to reduce the potential for tank pressurization, and temperature control are found in ARH-1601, *Specifications and Standards for the Operation of Radioactive Waste Tank Farms and Associated Facilities*. The specifications and standards for A and AX Farms (ARH-1601, Section B) associated with corrosion control include limits on pH and general requirements on waste chemical compatibility with the tank liner. The corrosion-related specifications and standards for SX Farm (ARH-1601, Section C) include limits on pH and general requirements on waste chemical compatibility with the tank liner. The specifications and standards associated with corrosion control for non-boiling waste storage tanks (ARH-1601, Section D) and tanks associated with evaporator operations (ARH-1601, Section F, H and J) include limits on pH, nitrite, nitrate, and hydroxide concentration.

Generally, these specifications and standards were established to protect against:

- damage to the tank dome via excessive vacuum or pressurization, including explosive atmosphere within the tank headspace,
- damage to the tank and/or its dome via dead and live loads,
- damage to the tank structure via thermal loads,
- liner corrosion, and
- criticality.

The potential impact of each of the bulleted areas above is already discussed as potential liner failure mechanisms in other subsections of Section 4.0. No other inadequacies in operational procedures or processes have been identified. Based on the above description, improper or inadequate operational processes or procedures, other than those already addressed elsewhere, are not considered a likely common liner failure mechanism.

4.5 EXTERNAL ENVIRONMENT FAILURE MECHANISMS

A set of external environmental factors are considered in the subsections below. For the purpose of this evaluation the external environment is considered to be the environment external to the tank liner. The tank liner consists of the cylindrical vertical steel wall and steel liner bottom. The external environment includes the remainder of the tank system which includes the concrete foundation, concrete walls and dome surrounding the tank liner as well as all risers, piping and other connections penetrating the tank liner or the remainder of the tank system.

4.5.1 Soil Settlement and External Loads on a Tank

A tank in contact with soil has the potential to settle due to compaction of the soil beneath the tank from the hydrostatic load of the filled tank in combination with loads on top of the tank. Uniform settlement of the soil beneath a tank would not result in differential stresses on the liner and is not considered a concern regarding tank liner failure. Excessive external loads on the tank dome in combination with the hydrostatic load in the tank could potentially result in demand/capacity ratios for the tank concrete slab, inside the wall footing, exceeding code allowable. A differential settlement between the tank wall footing and slab supporting the liner has been investigated.

Regarding hydrostatic and external loads, the analysis of record of Type II and Type III SSTs were reviewed. These analyses show that for the baseline cases, the demand/capacity ratios for peak temperatures and all load combinations are not greater than 1.0 (RPP-RPT-49989, RPP-RPT-49990) for shear, meridional and circumferential (hoop) directions. When concrete creep is not included in the Type II tank analysis, the demand/capacity ratio exceeds 1.0 for shear in a section of the slab near the inside of the tank wall footing. When concrete creep is not included and high concrete modulus is considered in the Type III tank analysis, the meridional demand/capacity ratio exceeds 1.0 in the center of the tank bottom slab. The impact of these potential situations where demand/capacity ratios exceed 1.0 is analyzed through isolating the slab from the tank wall footing (creating a gap) and determining the relative displacement across the gap. For the Type II and Type III tank slab element removal analysis, this relative displacement is 0.041 in. and 0.0379 in., respectively (RPP-RPT-49989, RPP-RPT-49990). This is a small displacement relative to the thickness of the steel liner and the asphalt membrane under the liner. It is stated in the analysis of this situation that it is likely that the liner would be able to bridge this small displacement offset without being damaged.

Regarding differential soil settlement, dome survey reports for Hanford SSTs (RPP-RPT-55202, *Dome Survey Report for Hanford Single-Shell Tanks*) were reviewed to determine the level of differential settlement that is occurring. Settlement of the tank can be determined by subtracting the most current elevation at the perimeter of the tank from the first, or oldest, survey elevation at the same location. Differential settlement of the tank requires at least two points at different locations along the perimeter. Roughly 30 SSTs have more than one survey location near the perimeter of the tank with recent measurements taken. Of these, the largest relative difference in measured height is less than ¼-in. between two points. This occurs at roughly 90 degrees apart on the perimeter of tank TX-107. Along the perimeter this is roughly 60 ft separating the two points. This is a very small differential settlement that would not result in damage to the liner.

Based on the above description, soil settlement or external loads on a tank are not considered a likely common liner failure mechanism.

4.5.2 External Water or Soil-Induced Corrosion

This topic was covered in Section 4.4.9.11 as part of the various corrosion mechanisms. External water or soil-induced corrosion is not considered a potential significant liner failure mechanism.

4.5.3 Pressurization External to Tank Liner

An external pressure source acting on the tank bottom liner could impart a significant force on the steel plate resulting in temporary or permanent deformation of the liner. Indications of bulging in the bottom of tank liners could be explained by pressurization via a gas or vapor external to the tank liner. This would require a high enough temperature in the waste and low enough hydrostatic load on the liner to allow the external vapor pressure to overcome the hydrostatic load acting downward on the bottom liner. A number of possible sources of gas or vapor exist including water vapor from residual water under the liner, water vapor liberated from the grout cap under the bottom tank liner, organic vapor from the asphaltic membrane, or leaked waste accumulating under the tank liner. External pressurization could occur if the vapor or gas was trapped such that it could not escape via a path underneath the tank or along the sidewalls out to the surroundings. Pressurization could also occur in the presence of a leak path if the rate of pressurization was greater than the rate the leak path could relieve the pressure.

It should be noted that this factor is very closely related to the factor considered in Section 4.1.4 which considers lack of a vent path underneath the tank liner. The distinction between these two factors is whether the lack of an engineered vent path contributed to liner failure without considering whether or not external pressurization occurred. In the case of considering external pressurization as a common factor, the focus is on whether the subset of tanks which experienced external pressurization resulted in liner failure because of the pressurization.

Based on the above description and the known evidence of bulged liners, pressurization external to the tank liner is considered a potential liner failure mechanism.

5.0 SINGLE-SHELL TANK HISTORY AND BACKGROUND INFORMATION

Section 4.0 of this report examined in general a wide range of liner failure mechanisms and whether each mechanism could potentially contribute to or cause tank liner failure. For those mechanisms that were shown to possibly contribute to or cause tank liner failure, specific details of the SST history and background information are necessary to evaluate whether or not certain factors were present in those tanks that failed. Available information has been reviewed and summarized in the following subsections.

5.1 GENERAL SINGLE-SHELL TANK BACKGROUND INFORMATION

Between 1943 and 1963, a total of 149 single-shell underground radioactive waste storage tanks were constructed for the retention of radioactive wastes at Hanford. These tanks are located in groups called farms, containing 4 to 18 tanks each. Each tank is constructed of a reinforced concrete shell with a mild steel liner covering the bottom and sidewalls. The carbon steel liner (1/4 to 3/8-in. thick) is the primary waste containment barrier and the reinforced concrete is the primary load support structure that resists internal hydrostatic loads, external soil loads and equipment loads. Table 5-1 identifies each tank farm, the years of construction, the number of tanks, and the size of the tanks. Most of the tanks are 75 ft in diameter and are constructed to hold from roughly 17 ft to 31 ft of liquid for a nominal capacity of 530,000 to 1,000,000 gal. The four original farms each included four smaller tanks, 20 ft in diameter, of the same basic design with a capacity of 55,000 gal each. Some later tanks were built with condensers and condensate disposal systems to permit the wastes to self-concentrate. These tanks are equipped with ALCs to avoid the fluctuating rate of boiling and resultant tank pressurization that could result from a stagnant self-heating system.

The original tank farms (241-B, 241-C, 241-T, and 241-U Farms) each featured 12 tanks each with a dished bottom, an operating depth of 17 ft, and a nominal 530,000 gal capacity (see Figure 5-1) and four smaller tanks each with a nominal 55,000 gal capacity (see Figure 5-2). The larger tanks had a 4-ft radius knuckle transition between the bottom and sidewall while the smaller tanks had a 3-ft radius knuckle. 241-BX Farm features 12 tanks identical to the larger tanks in the original tank farms but did not include any smaller tanks. The second generation tank farms (241-BY, 241-S, 241-TX, and 241-TY Farms) each feature tanks similar to the original tank farms except for increased capacity to nominally 750,000 gal (see Figure 5-3) via a taller sidewall and associated increased operating depth of nominally 23 ft. The third generation of tank farms, SX Farm, was the first tank farm where the tank bottom to wall transition eliminated the 4-ft radius knuckle. Instead the dished bottom transitioned directly to the wall section without any radius transition. This third generation of tank farms also had an increased nominal capacity of 1,000,000 gal (see Figure 5-4) via a taller sidewall and associated increased operating depth of nominally 31 ft. The fourth generation of tank farms, A Farm, was similar to the third generation with the exception that the tanks had flat rather than dished bottoms. The final generation of tank farms, AX Farm, was similar to the fourth generation with the addition of a grid of drain slots beneath the steel. This grid was included to collect potential tank leakage and divert that leakage to a leak detection well. The grids also served as an escape route if free water was formed from the concrete grout during initial heating of the tanks.

Table 5-1. Single-Shell Waste Storage Tanks at Hanford*

Tank Farm	Year Built	Number of Tanks	Tank Capacity (gal)	Tank Liner Diameter (ft)	Nominal Waste Depth
241-A	1954-55	6	1,000,000	75	30 ft - 3 $^{1}/_{8}$ in
241-AX	1963-64	4	1,000,000	75	31 ft - 5 $^{11}/_{16}$ in
241-B	1943-44	4 12	55,000 530,000	20 75	24 ft - 6 in 17 ft
241-BX	1946-47	12	530,000	75	17 ft
241-BY	1948-49	12	750,000	75	23 ft - 8 $^{5}/_{16}$ in
241-C	1943-44	4 12	55,000 530,000	20 75	24 ft - 6 in 17 ft
241-S	1950-51	12	750,000	75	23 ft - 8 $^{1}/_{16}$ in
241-SX	1953-54	15	1,000,000	75	30 ft - 10 $^{5}/_{16}$ in
241-T	1943-44	4 12	55,000 530,000	20 75	24 ft - 6 in 17 ft
241-TX	1947-48	18	750,000	75	23 ft - 8 $^{5}/_{16}$ in
241-TY	1951-52	6	750,000	75	23 ft - 8 $^{1}/_{16}$ in or 23 ft - 8 $^{9}/_{16}$ in
241-U	1943-44	4 12	55,000 530,000	20 75	24 ft - 6 in 17 ft

*Information taken from WHC-MR-0132, except operating depth which is depth from tank bottom center to liquid surface level (when available) or bottom of outlet nozzle as represented on tank drawings [liquid surface level for 241-B, 241-C, 241-T, 241-U from D-2 and D-20; liquid surface level for 241-BX from H-2-602; 241-TX assumed the same as 241-BY due to lack of drawing with nozzle detail; bottom of outlet nozzle for 241-BY from H-2-1313 and H-2-1318; bottom of outlet nozzle for 241-S from H-2-1783 and H-2-1789; bottom of outlet nozzle for 241-TY from H-2-2244 [shows height from top plate to outlet nozzle centerline as 14"] and H-2-2250 [shows height from top plate to outlet nozzle centerline as 14-½"]; liquid surface level for 241-SX from H-2-39511; liquid surface level for 241-A from H-2-55911; bottom of inlet nozzle for 241-AX from H-2-44562 and H-2-44635].

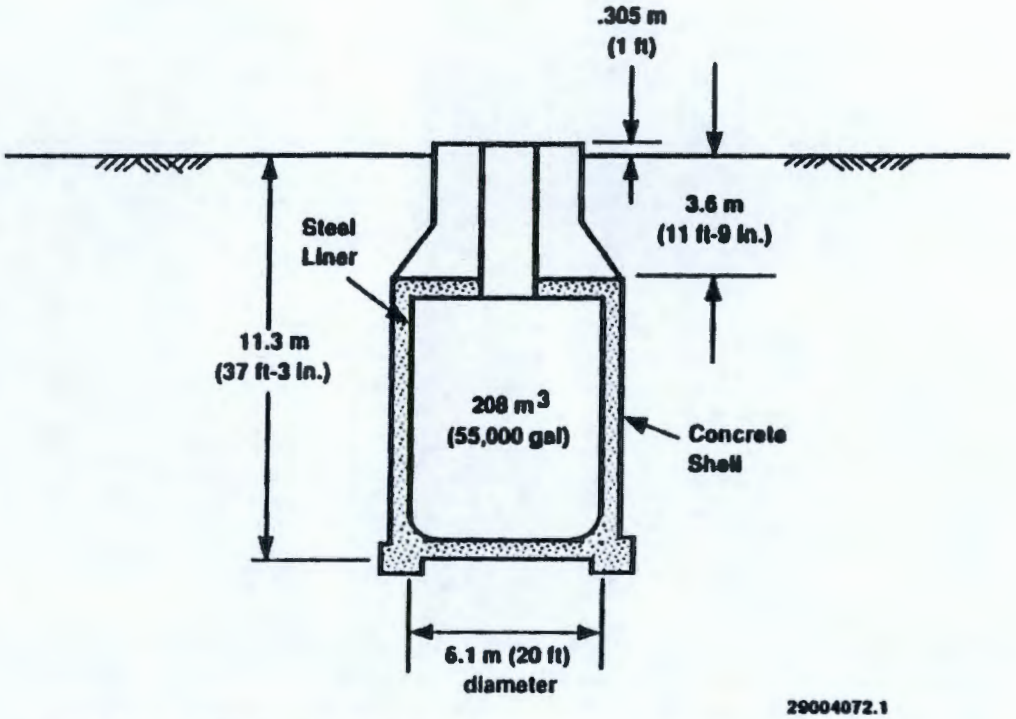


Figure 5-1. 200-Series, Type I, Twenty Feet Diameter, Single-Shell Tank

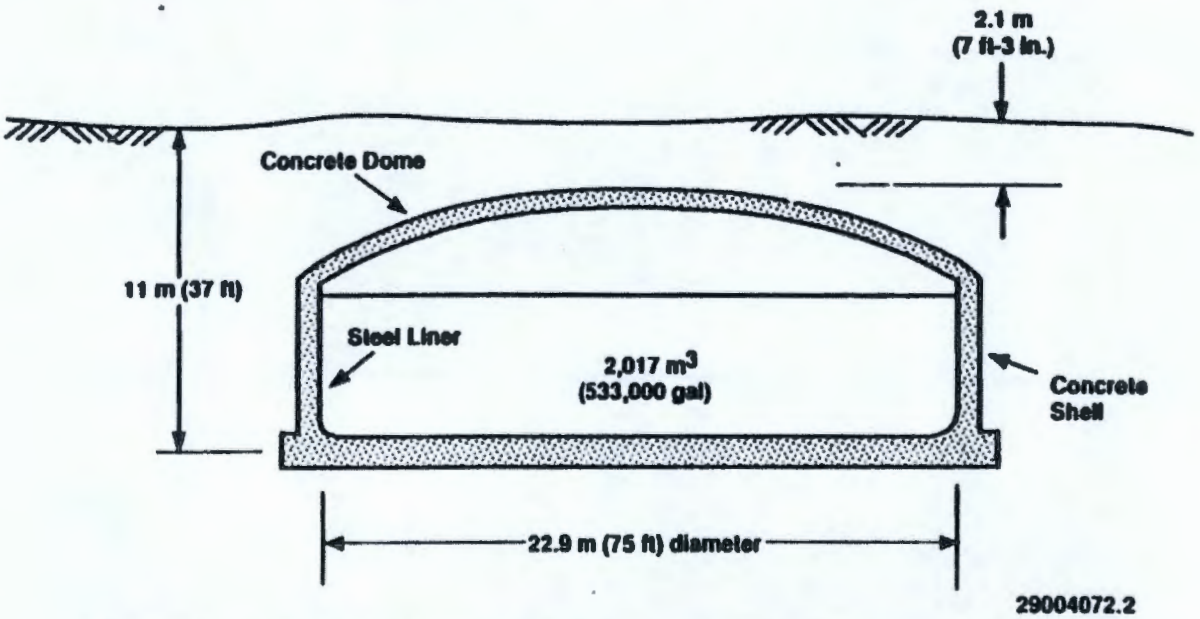


Figure 5-2. 100-Series, Type II, Seventy-Five Feet Diameter, Single-Shell Tank

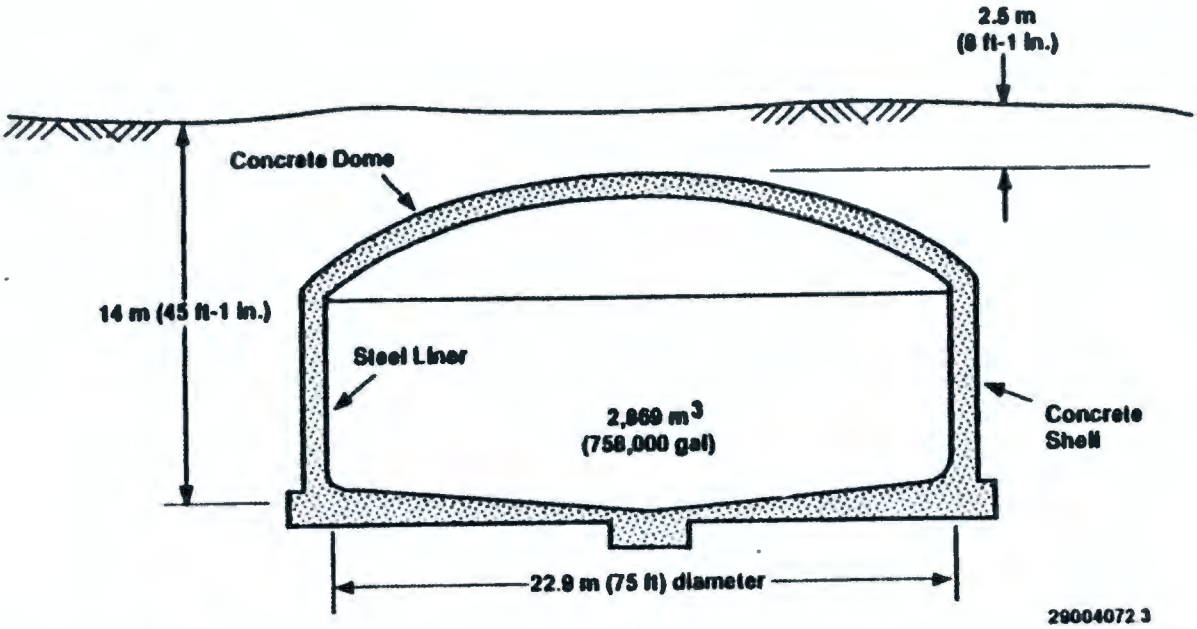


Figure 5-3. 100-Series, Type III, Seventy-Five Feet Diameter, Single-Shell Tank

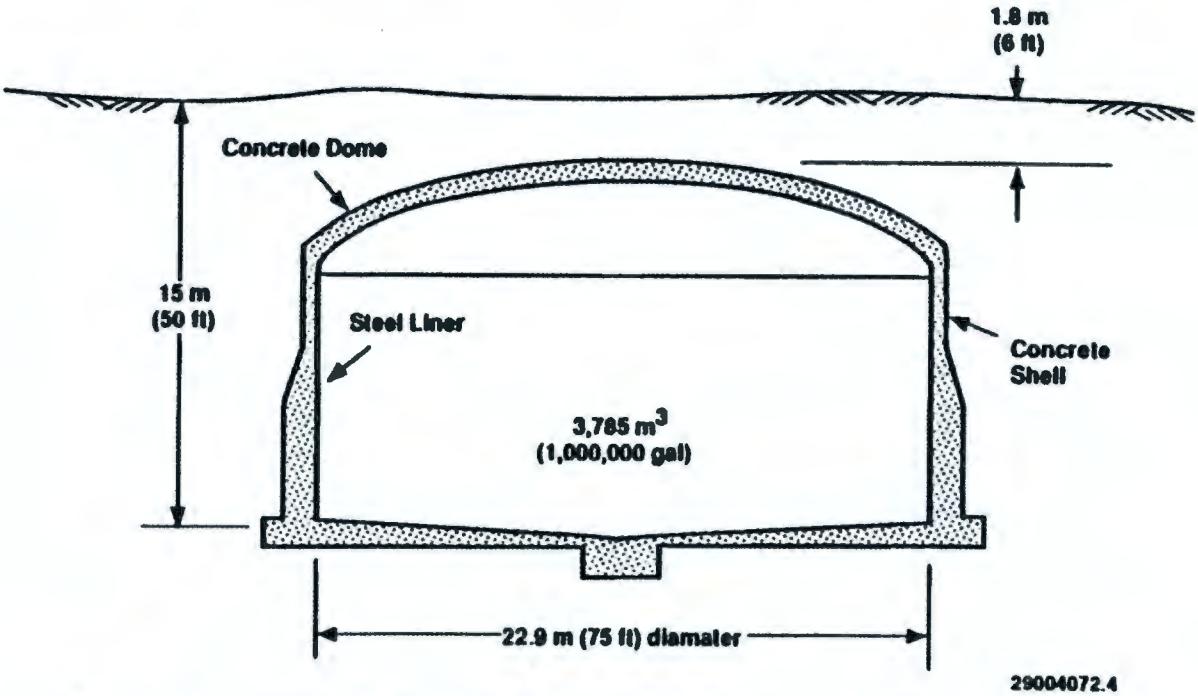


Figure 5-4. 100-Series, Type IV, Seventy-Five Feet Diameter, Single-Shell Tank

In the first nine tank farms, designed for non-boiling wastes, the 530,000 gal and 750,000 gal tanks were originally arranged in cascades of three, four or six tanks. The tanks were arranged in such a manner that when the first tank in a cascade was filled, it overflowed to the second tank, then to the third tank, etc. Through the years many of the overflows between tanks in the various

cascades have been removed, modified or blanked. Drywells located within the tank farms are used to monitor the soil for radioactivity, thus serving as a leak detection system. Generally, these drywells extend to a depth of approximately 75 ft, which is several feet below the bottom of the tanks. The storage tank waste levels have been monitored with various level detection instruments over the years.

The final three SST farms contained tanks equipped for boiling waste. SX Farm, used for storing REDOX salt wastes, was the first to be equipped for handling boiling waste solutions, although not all of the SX Farm tanks could accommodate self-boiling wastes. Of the 15 tanks in the farm, tanks SX-107 through SX-115 were equipped to handle self-boiling wastes. The A and AX Farms were built to store PUREX and B Plant aging wastes. Vapors from the boiling action (or self-concentration) were routed through headers to condensers which were vented to the atmosphere through filters. Condensate was either discarded to cribs or returned to the waste tank to maintain the desired liquid level.

5.2 TANK DESIGN

This section provides background information on the various design factors that may have contributed to liner failures. Aspects of tank design are important to investigate because they represent the possibility that some tanks may have been inherently at risk for failure before storing waste. This can also be important in determining whether certain conditions observed in the tanks were more detrimental because of distinguishing design features.

5.2.1 Post-Weld Stress Relieving

Welding causes rapid thermal expansion and contraction along a very localized area of the steel liner. The area of welding is rapidly heated causing expansion as it becomes molten. As the molten pool solidifies there is resistance to shrinkage by the already solidified surrounding weld metal and the metal adjacent to the point of welding. This resistance can create tensile strains that may result in distortion, buckling, SCC or shortened fatigue life.

Buckling, warping or distortion of the initially installed bottom liners of all 100-Series tanks within T Farm was so bad that they all had to be replaced (RPP-RPT-54916, *Hanford Single-Shell Tank Leak Causes and Locations – 241-T Farm*) during construction. No information has been found that indicates how this problem of excessive warping (indicative of residual stress) was resolved in the other SST farms. Post-welding stress relieving was not specified for any of the field-welded SST liners. All SSTs at Hanford were constructed before the benefit of stress relieving tanks in order to control SCC was understood.

As previously mentioned (see Section 4.1.1), SCC was recognized as a significant concern in nuclear waste storage tanks in 1962 when four tanks at the Savannah River Site were discovered to have cracks (SRNL-STI-2012-00745). The benefit of having the waste tanks undergo post-weld stress relief was identified subsequent to these failures.

A review of the construction specifications for the SSTs shows that no mention was made of stress relieving for construction of the first five tank farms (HW-1946). Construction history for TX Farm (HW-24800-35, *Design and Construction History, Project C-163, 241-TX Tank Farm*) and the specifications for BY Farm (HW-3783, *Additional Waste Storage Facilities, 200 East Area*), S Farm (HW-3937, *Waste Disposal Facility 241-S and 207-S*), and TY Farm (HW-4696, *Waste Disposal Facilities, 241-BZ and TY Tank Farms*) identify that the individual knuckle plates were stress relieved after forming and that shop-welded knuckle subassemblies, consisting of five individual plates, were low temperature stress relieved prior to shipment to the construction site. However, post-weld stress relieving of field welding is not mentioned. The specifications for SX Farm (HW-4957), A Farm (HWS-5614) and AX Farm (HWS-8237, *Specification for PUREX 241-AX Tank Farm, Project CAC-945*) do not specify any required stress relief of the tank liner.

A 1962 process design engineering basis document for AX Farm (HW-72780, *Process Design Engineering PUREX Essential Waste Routing System and 241-AX Tank Farm*) recommended that the tank liner be stress-relieved. The design of the tank farm evolved from the time of that design document, and no mention of stress relieving was found in subsequent design or construction media. The timing of HW-72780 coincides with the recognition of SCC at the Savannah River Site but no tie between these two items has been made.

The ASME Boiler & Pressure Vessel Code, Section VIII, Division 1, Part UCS-56, identifies requirements for post-weld heat treatment. Minimum holding temperatures and times are tabulated at nominal thickness ranges for various carbon and low-alloy steels. The minimum holding temperature tabulated for post-weld heat treatment in UCS-56 is 540°C (1000°F)[2]. For A/SA-283, all grades, and A/SA-285, all grades, carbon steel the minimum holding temperature for post-weld heat treatment is 595°C (1100°F) and the minimum holding time is 1 hr/in. material thickness with a 15 minute minimum. None of the SSTs were post-weld stress relieved and therefor none have been subjected to these temperatures for any period of time after welding.

5.2.2 Tank Liner Bottom to Wall Transition Design

The design of the tank liner bottom to wall transition design may be a liner failure common factor. A particular liner bottom to wall transition design can potentially be more susceptible to harsh conditions such as extreme temperature and chemistry in the tanks. Figures depicting the available drawing information for the various bottom to wall transition designs are provided below.

200-Series Type I Tanks

The 200-Series, Type I tanks in the first four tank farms (B, C, T, and U Farm) were designed with a 3-ft radius, rounded knuckle, bottom to sidewall transition (see Figure 5-5). The knuckle was joined to the dished bottom and the vertical wall via butt welds. Figure 5-5 includes details

[2] ASME Boiler and Pressure Vessel Code, Section VIII, Division 1, Section UCS-56 allows post-weld heat treatment at lower temperatures for longer periods of time when it is impractical to post-weld heat treat at the tabulated temperatures for the minimum holding times.

of the 3-pass, beveled, double welded, butt joint weld for the bottom and horizontal welds for the knuckle as well as the vertical wall weld.

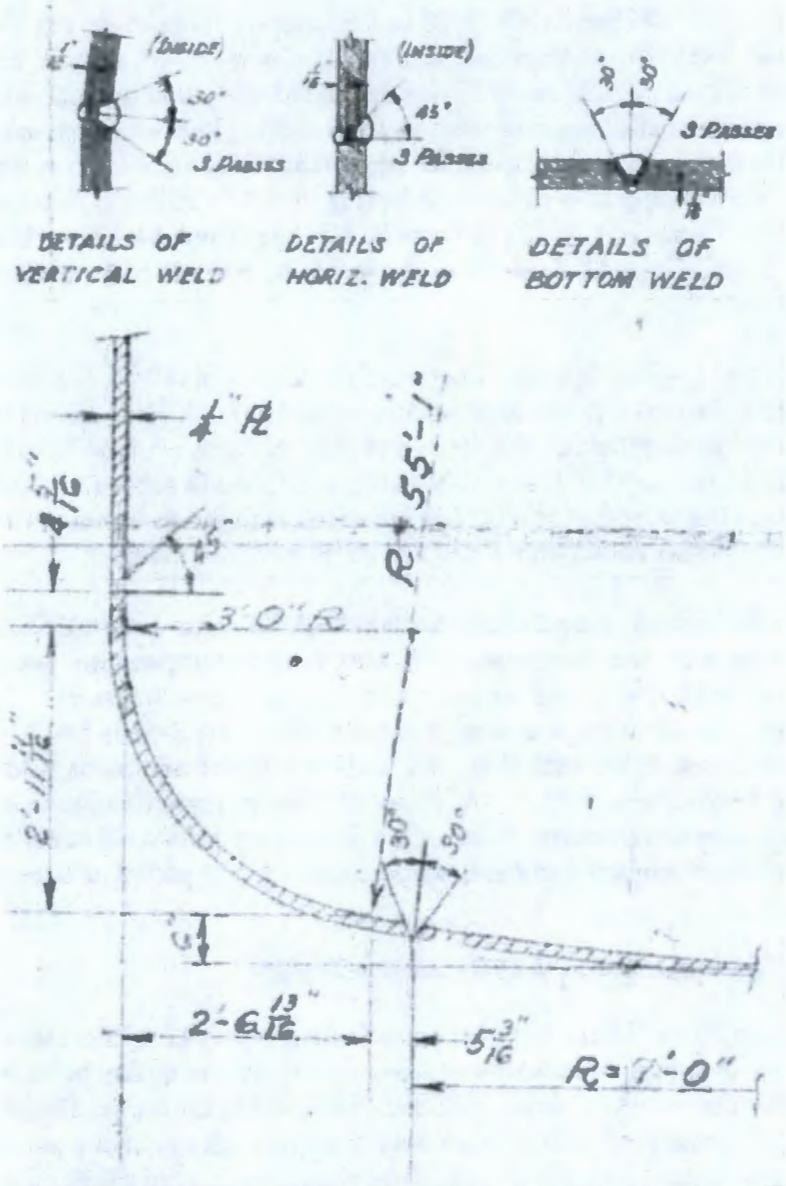


Figure 5-5. Construction Drawing for 241-B, -C, -T, and -U Farm, 200-Series Tanks Bottom Knuckle Weld (Drawing D-23)

100-Series Type II Tanks

The 100-Series, Type II tanks (B, C, T, U, and BX Farm) were designed with a 4-ft radius, rounded knuckle, bottom to wall transition as shown in Figure 5-6. The figure includes details of the 3-pass, beveled, double welded, butt joint weld for the bottom and horizontal welds for the

knuckle as well as the vertical wall weld. The 100-Series, Type II tanks are similar to the 200-Series, Type I tanks with the exception of the knuckle radius and material thickness.

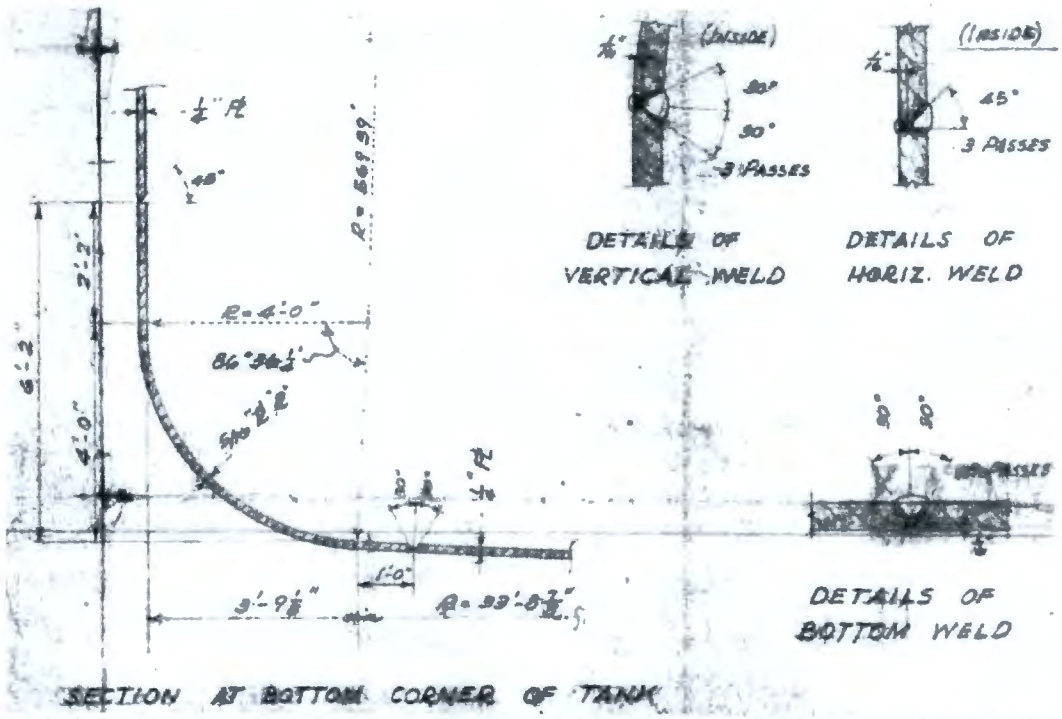


Figure 5-6. Construction Drawing for 241-B,-C,-T,-U, and -BX Farm, 100-Series, Type II Tanks Bottom Knuckle Weld (Drawing D-3)

100-Series Type III Tanks

The 100-Series Type III tanks (TX, BY, S, and TY Farm) were designed with a 4-ft radius, rounded knuckle, bottom to wall transition, similar to the 100-Series Type II tanks, which is shown in Figure 5-7 for TX Farm. Weld details for TX Farm are similar to the earlier 100-Series, Type II bottom to wall weld details with the exception of the addition of a 3-in. wide butt strap during welding (to be removed) for the bottom to knuckle transition and call out of the field gap for the sidewall to knuckle transition weld.

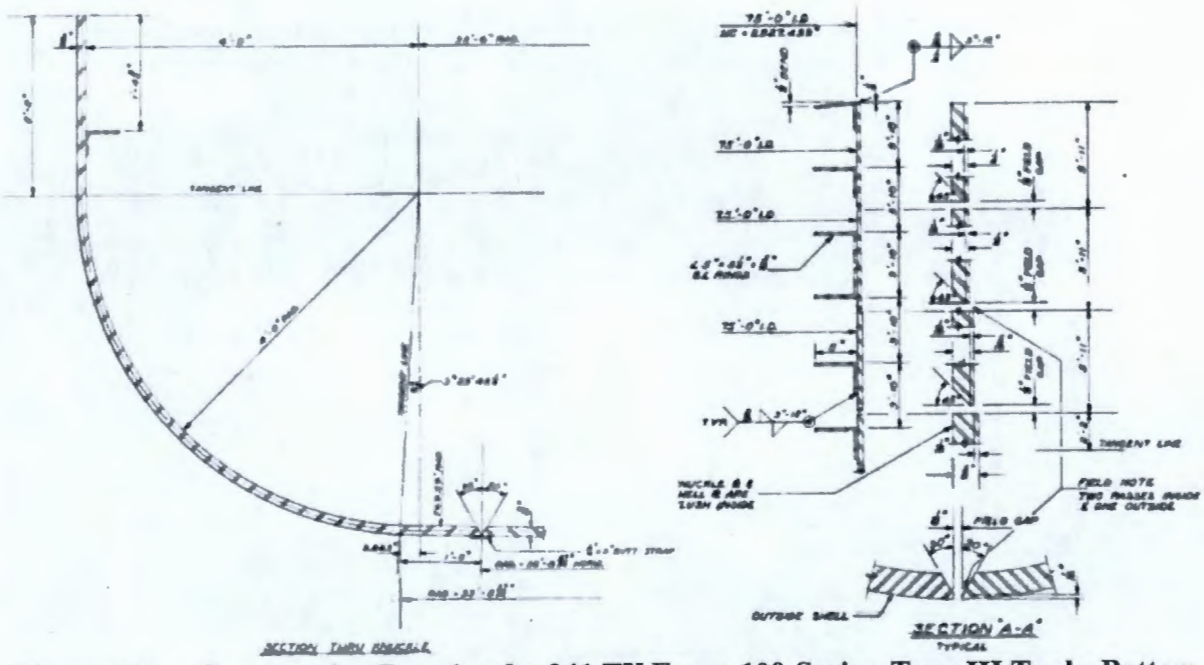


Figure 5-7. Construction Drawing for 241-TX Farm, 100-Series, Type III Tanks Bottom Knuckle Weld
(Drawing H-2-809, *75 Foot Tank Steel Plate Details, 241-TX*)

BY Farm was the next tank farm constructed with details of the bottom to wall transition weld design shown in Figure 5-8. The weld details are similar to those for TX Farm with the exception of an addition of a double bevel to the wall end of the knuckle to wall transition and change to the angle and depth of the bevel at the knuckle to bottom transition.

The drawings for the next 100-Series, Type III tank farms built, S and TY Farms, are not provided with a similar level of weld details. Specifications provided on the drawings for both tank farms identify that all joints in tank shell plating are to be double welded butt joints.

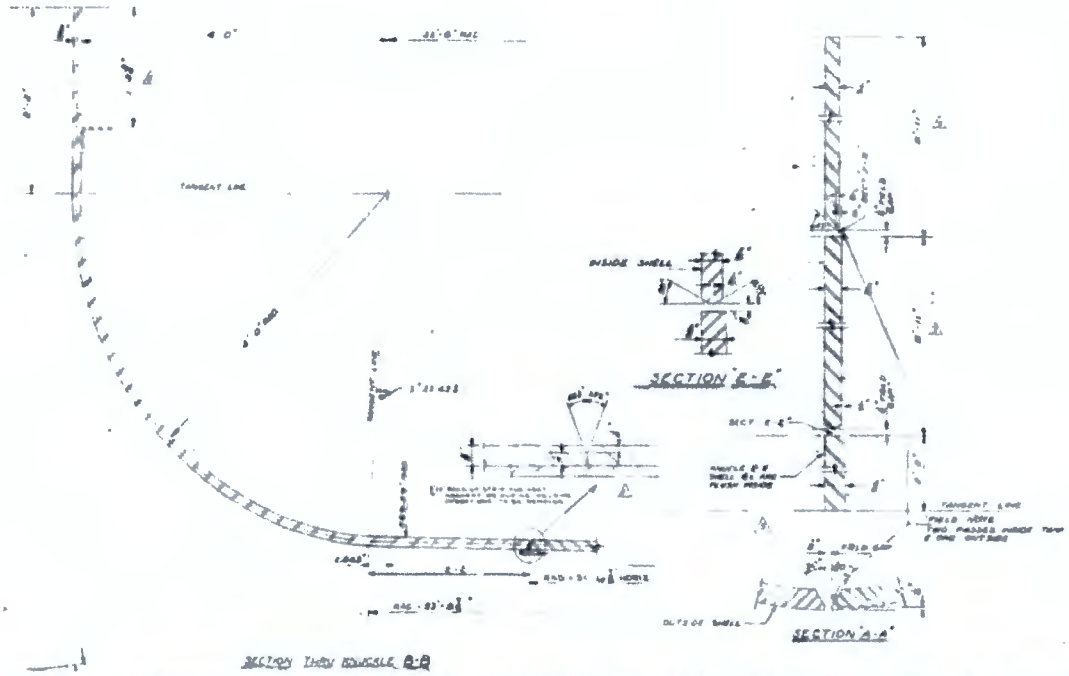


Figure 5-8. Construction Drawing for 241-BY Farm, 100-Series, Type III Tanks Bottom Knuckle Weld (Drawing H-2-1313, *75 Foot Tank Steel Plate Details*)

100-Series Type IV Tanks

The 100-Series, Type IV tanks (A, SX, and AX Farm) varied in transition design, with SX and A Farms being close to each other in design shown in Figure 5-9 and Figure 5-10 for SX and A Farm, respectively. Figure 5-9 shows the nearly orthogonal corner joint between the sidewall and bottom used in SX Farm. The joint consists of 5/16-in. fillet welds on both sides of the sidewall connection to the tank bottom. The joint is not orthogonal because the bottom liner is dished 1-ft 2 7/8 in. below the sidewall. The A Farm tanks also have a corner joint, but this joint is orthogonal because of the tank's flat bottom liner (see Figure 5-10). The welds at the tank bottom to wall transition for tanks in 241-A Farm are beveled fillet welds inside and out.

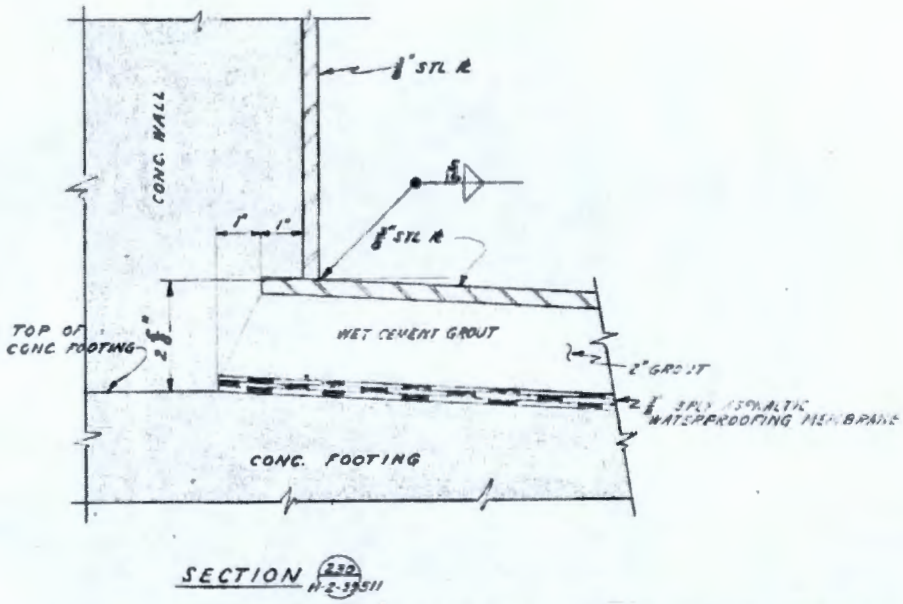


Figure 5-9. Construction Drawing for 241-SX Farm, 100-Series, Type IV Tanks Bottom to Wall Transition Weld
(H-2-39511, *75 Foot Storage Tanks Composite Section Waste Disposal Facility 241-SX*)

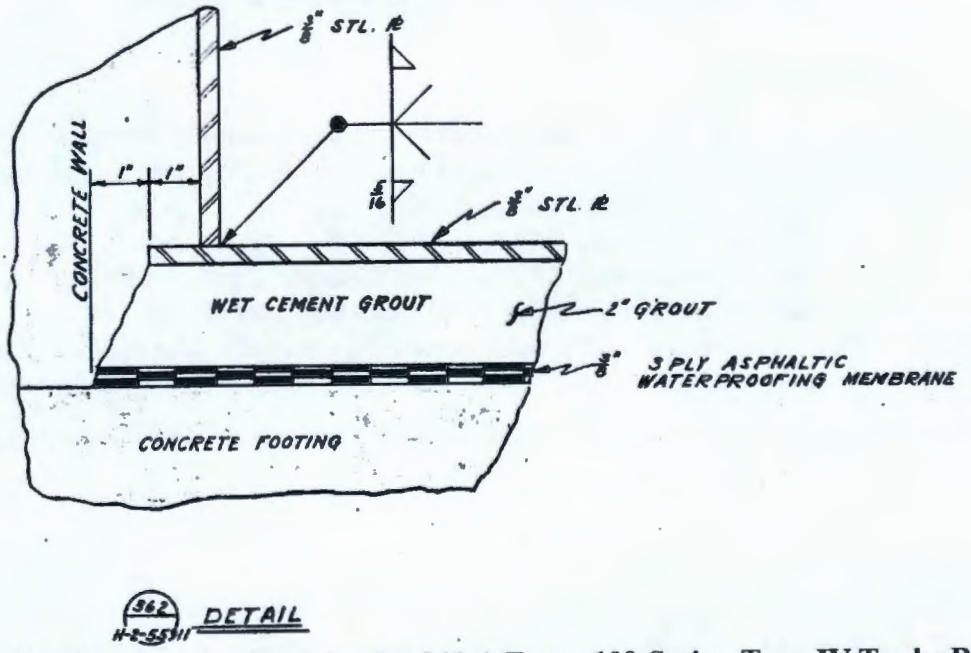


Figure 5-10. Construction Drawing for 241-A Farm, 100-Series, Type IV Tanks Bottom to Wall Transition Weld
(H-2-55911, *Waste Storage Tanks Composite Section, 241-A*)

The curved bottom knuckle design was reinstated for AX Farm as a 4 to 8-in. knuckle radius between the vertical wall and flat bottom as shown in Figure 5-11. Weld details are not provided on the drawing showing the knuckle. The construction specification for AX Farm states that

joints in the cylindrical section and subassemblies of the bottom shall be double welded butt joints with full penetration welds (HWS-8237).

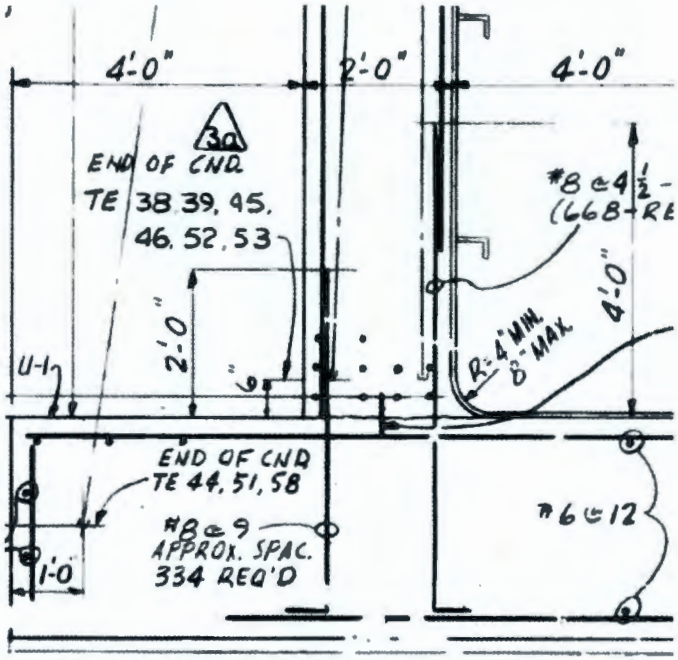


Figure 5-11. Construction Drawing for 241-AX Farm, 100-Series, Type IV Tanks Bottom to Wall Transition
(H-2-44562, *Structural Waste Storage Tanks Composite Section & Details*)

Tank Liner Bottom to Wall Transition Welding

Because SX and A Farm tank liners had corner joints instead of bottom knuckles, fillet welds were used in the liner joints. The construction specifications indicate a double fillet weld for the liner joint in the SX Farm design (H-2-39511) and a double bevel fillet weld for the liner joint in the A Farm tank liners (H-2-55911). The horizontal and vertical welds in the remainder bottom and wall plates were full penetration butt welds similar to previous tanks. All other tank designs included full penetration square butt weld at the bottom knuckle. As seen in Figure 5-5 through Figure 5-8, the bottom knuckle allows for the horizontal weld to be farther up the side of the tank liner, rather than at the corner. A weld at the corner of the tank liner adds more stress to the liner than if the joint is at the sidewall. Examples of the different types of weld used for the various SST bottom to wall transition designs are shown in Figure 5-12.

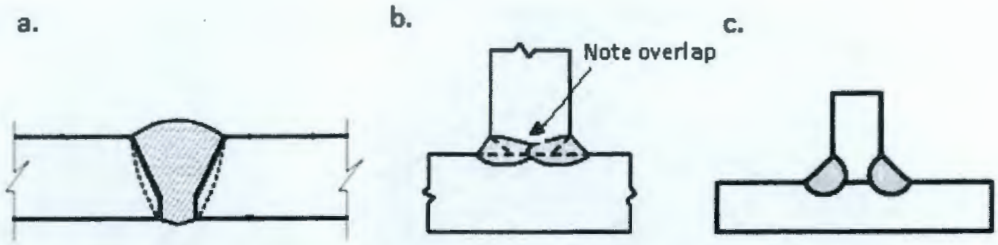


Figure 5-12. Weld Types used in Tank Liners (a) 3-pass full penetration square butt weld, (b) double bevel fillet weld, (c) double fillet weld (AWS B1. 10M)

The full penetration square butt weld (Figure 5-12a) is the strongest and most resistant to stresses due to the full penetration between the two sections of steel liner. The double-bevel fillet weld (Figure 5-12b) used in A Farm tanks shows an overlap between the two welds, which strengthens the weld overall, but is not as effective as full penetration. The double fillet weld (Figure 5-12c) used in SX Farm tanks has the least resistance to stress and a higher potential for crack propagation.

Table 5-2 summarizes the basic differences between the fillet welds and butt welds used in the tanks.

Table 5-2. Basic Fillet Weld and Butt Weld Differences*

Attribute	Fillet weld	Butt weld
Preparation Costs	Inexpensive	Expensive
Welding Speed (Progress)	Fast	Slow
Load Bearing	Good for static loads (structures)	Good for dynamic loads (pressure vessels)
Quality	Inferior resistance to fatigue High potential for crack propagation More distortion and stress buildup	Greater resistance to fatigue Weld is stronger than base metal Minimal change in stress
Inspection	Difficult to perform high quality inspection (unable to radiograph)	Easier to perform high quality inspection (radiograph)

Table taken from RPP-RPT-54910, Rev 0, *Hanford Single-Shell Tank Leak Causes and Locations – 241-SX Farm* (Table 3-1).

A review of literature to compare historical failure rates for fillet welds and butt welds did not identify any relevant information that could be related to the tank farm waste tanks. There was recognition that the base of the SX Farm tanks was considered fixed and excessive steel stresses could be expected during pressure surges and elevated temperatures (HW-51730, *Commentary Report on Final Report on Study of Waste Storage Facilities by Ammann and Whitney (GEH-23501)*).

The possible consequences of the corner joint design of SX and A Farm tanks are best described by L.E. Brownell in the following excerpt from HW-57274, *Instability of Steel Bottoms in Waste Storage Tanks*.

"A steel liner which fits tightly inside a concrete shell provides no means for differential thermal expansion. Such expansion can result in high compressive stresses in the steel which may produce elastic instability. Instability is particularly likely to occur in the flat bottom of the liner resulting in rippling of the bottom. This is more apt to occur in designs in which the junction at the lower corner is 90 degrees as in the SX Tanks than in designs in which a radius is used as in the BX and TX Tanks of earlier design. Empty tanks in the SX farm have been observed to have rippled bottom liners before filling.

A hydraulic head would tend to flatten the ripples but filling with hot waste would tend to increase the degree of rippling because of the restraint of the concrete shell. Under certain conditions this might cause rupture of a joint. The severity of the rippling is believed to have been demonstrated by the instability of the bottom of tank 113-SX after it was emptied. It is suggested that the restraint offered by the concrete shell be reduced by a return to the use of an asphalt expansion joint between the steel shell and the concrete shell."

Weld Examination Methods

Weld inspections for the fillet welds were not as rigorous as for butt welds. Because the angle of exposure influences the radiograph, fillet welds are difficult or impossible to examine via a radiographic method. No indication was found in the available specifications or drawings that radiographic inspection was performed on the fillet welds of A and SX Farms. Additionally, only spot (as opposed to full) radiographic examination was performed on A and SX Farm tanks, and instead the vacuum soap test at 10 in. of mercury was used. Vacuum soap testing only determines leaks in the tanks and the soundness of welds rather than identifying discontinuities. Radiographic inspection has the advantage of being able to detect both surface and subsurface discontinuities of the weld; however, this method is more expensive and time consuming (p. 23 AWS B1.10M).

Table 5-3 provides a listing of the applicability of the weld examination methods used in inspection of the various SSTs to detecting common discontinuities encountered in welds. This table demonstrates that no single examination method is applicable for detecting all types of discontinuities. Also, some types of discontinuities (i.e., incomplete fusion and overlap) may not have been detected because of the marginal applicability or inapplicability of an examination method to detect the particular discontinuity. Although radiographic and visual examination methods are identified as applicable examination methods for a number of discontinuities, radiographic examination is superior to visual examination because of its ability to detect subsurface discontinuities.

Table 5-4 provides a listing of the applicability of a particular method for examining specific weld joint types. The table demonstrates that radiography of T-joints and leak testing in general are only marginal as weld examination methods for the joint types employed on the SSTs.

In looking at these two tables it is demonstrated that leak testing is only marginal at best in detecting leak discontinuities and most likely shouldn't be relied upon as a primary weld

examination method. Also visual and radiographic examination methods share applicability to identifying certain discontinuities, but only radiographic examination can detect subsurface discontinuities. Full radiographic examination must be considered superior, although much more expensive, to spot radiographic examination.

Table 5-3. Applicability of Common Weld Examination Methods to Detect Discontinuities

Discontinuity	Examination Method[1]		
	Radiographic	Visual	Leak Testing
Porosity	Applicable Method	Applicable Method	Marginal Applicability[2]
Slag Inclusions	Applicable Method	Applicable Method	Usually Not Used
Incomplete Fusion	Marginal Applicability	Marginal Applicability	Marginal Applicability
Incomplete Joint Penetration	Applicable Method	Marginal Applicability	Usually Not Used
Undercut	Applicable Method	Applicable Method	Usually Not Used
Overlap	Usually Not Used	Marginal Applicability	Usually Not Used
Cracks	Marginal Applicability	Applicable Method	Marginal Applicability
Laminations	Usually Not Used	Applicable Method	Usually Not Used

1 Information taken from AWS B1.10M/B1.10:2009, Guide for the Nondestructive Examination of Welds, American Welding Society.

2 Applicability depends on other factors such as material thickness, discontinuity size, orientation, and location.

Table 5-4. Applicability of Common Weld Examination Methods for Weld Joint Types Used in Single-Shell Tank Construction

Weld Joint	Examination Method[1]		
	Radiographic	Visual	Leak Testing
Butt Joint	Applicable Method	Applicable Method	Marginal Applicability[2]
T-Joint	Marginal Applicability[2]	Applicable Method	Marginal Applicability[2]

1 Information taken from AWS B1.10M/B1.10:2009, Guide for the Nondestructive Examination of Welds, American Welding Society.

2 Applicability depends on other factors such as material thickness, discontinuity size, orientation, and location.

Tank Liner Bottom to Wall Transition Design Summary

The 100-Series, Type II and Type III tanks in the first nine tank farms were designed with a 4-ft radius, rounded knuckle, bottom to sidewall transition. The knuckle was joined to the dished bottom and the vertical wall via butt welds. A construction photo of T Farm (see Figure 5-13) shows the construction of the 3-ft radius typical of Type I, 200-Series tanks (foreground) and the 4-ft radius knuckle typical of Type II and Type III, 100-Series tanks (background).

When designing SX Farm (Type IV tanks), the knuckle design was eliminated in favor of a nearly orthogonal joint between the dished bottom and vertical sidewall of the tanks. The bottom and wall were joined via a double fillet weld. For A Farm (Type IV tanks) the flat, rather than dished, liner bottom to wall transition was orthogonal and the weld type was similar to the SX Farm design. A smaller bottom knuckle design, 4 to 8-in. radius, was applied in the design of AX Farm (Type IV tanks). The knuckle was joined to the flat bottom and the vertical wall via butt welds. Details of each of these five bottom to wall transition designs are shown in Table 5-5 below.

The bottom of Figure 5-14 shows the nearly orthogonal joint between the tank bottom and sidewall for SX Farm Type IV, 100-Series tanks. The background of Figure 5-15 shows the orthogonal joint between the tank bottom and sidewall for A Farm Type IV, 100-Series tanks. Figure 5-16 shows the tank bottom to sidewall transition for AX Farm Type IV, 100-Series tanks. Unfortunately, no better photos during or after construction could be located showing more detail of the bottom to wall transition for the Type IV, 100-Series tanks. However, the available photos show a much different transition than in the earlier Type I-III tanks.

In summary, there are significant differences in the tank liner bottom to wall transition design including inspection of the joint. Section 6.2.2 contains the analysis of whether or not these differences may be considered as a potential common factor contributing to liner failure.

Table 5-5. Summary of Tank Design and Welding

Tank Farm	Tank Size	Design Feature	Type of Weld	Weld Inspection	Source
B,C,T,U	50,000 gal (Type I, 200 Series)	3 ft. bottom knuckle, 6 in. dish in bottom	3-pass, continuous, double welded, beveled butt weld	Full radiographic inspection	Drawing D-20, HW-1946
B,C,T,U,BX	533,000 gal (Type II, 100 Series)	4 ft. bottom knuckle, 1 ft. dish in bottom	3-pass, continuous, double welded, beveled butt joint weld	Full radiographic inspection	Drawing D-3, HW-1946
TX	758,000 gal (Type III, 100 Series)	4 ft. bottom knuckle, 1 ft. dish in bottom	3-pass, continuous except tank bottom. 2-pass machine or hand welding on tank bottom with backing strips. 2-pass machine or 3-pass hand welding on tank bottom without backing strips.	Full radiographic inspection	H-2-809, HW-3061
BY			Continuous, double welded butt joint weld	Full radiographic inspection	H-2-1313, HW-3783
S					H-2-1784[1], HW-3937
TY					H-2-2245[2], HW-4696
SX	1 million gal (Type IV, 100 Series)	Corner joint, 1 ft. 2 7/8 in. dish in bottom	Continuous, double fillet weld (inside and outside vertical wall)	Vacuum soap test at 10 in. of mercury and spot radiographic testing	H-2-39511, HW-4957
A	1 million gal (Type IV, 100 Series)	Corner joint, flat bottom	Continuous, double bevel fillet weld (inside and outside vertical wall)	Vacuum soap test at 10 in. of mercury and spot radiographic testing	H-2-55911, HWS-5614
AX	1 million gal (Type IV, 100 Series)	4-8 in. bottom knuckle, flat bottom	3-pass, full penetration square butt weld	Vacuum soap test at 10 in. of mercury and full radiographic inspection except for closure welds between sub-assemblies of tank bottom sections made against a backing strip	H-2-44562, HWS-8237

References: [1]H-2-1784, *75-Foot Tank Steel Tank Liner Details 241-S.*
[2]H-2-2245, *75-Foot Tank Steel Tank Liner Details 241-TY.*

Figure 5-13. 241-T Farm Construction Showing the Bottom Knuckle Transition in 200-Series (Front) and 100-Series (Back), Photo P2569, May 3, 1944

Figure 5-14. 241-SX Farm Construction Showing Welding of Vertical Wall and the Bottom to Wall Transition, Photo 2367, November 9, 1953

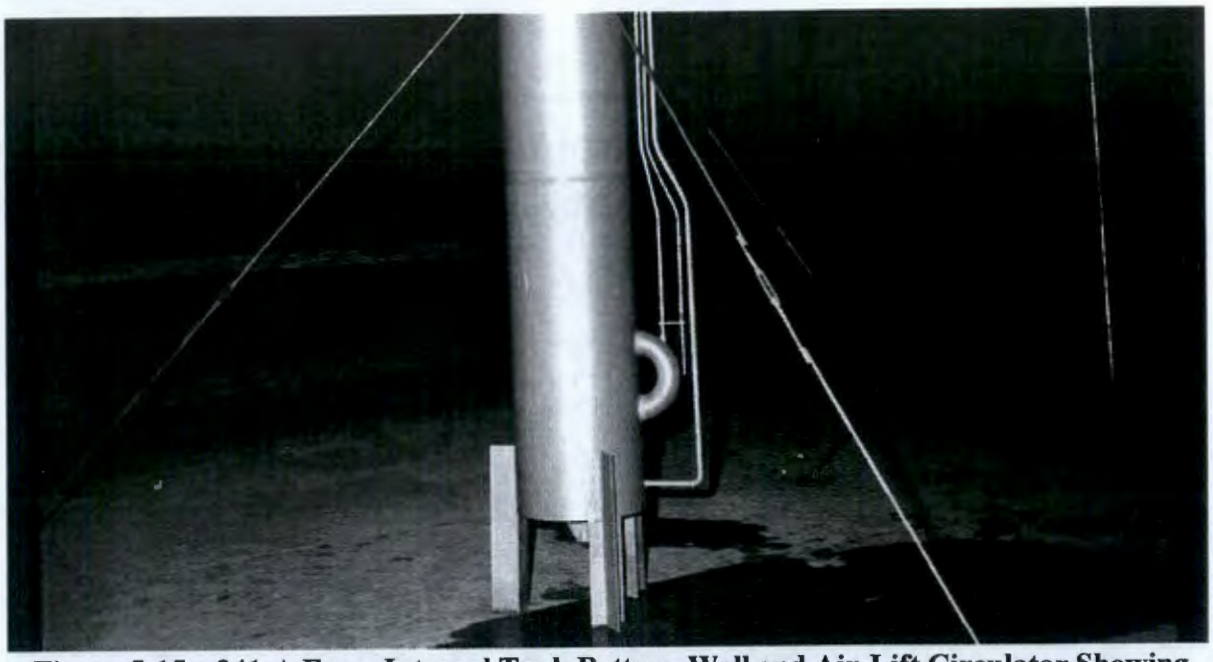


Figure 5-15. 241-A Farm Internal Tank Bottom, Wall and Air-Lift Circulator Showing the Corner Joint between the Sidewall and Bottom Liner

Figure 5-16. 241-AX Farm Internal Tank Bottom, Wall and Air-Lift Circulators Showing the Bottom to Wall Transition, Photo 37937-2, October 26, 1964

5.2.3 Exterior Finish Material Design of Tank Liner

100-Series Type II and Type III Tanks

Prior to construction of the Type IV tanks, a 3-ply asphaltic waterproofing membrane was applied to both the exterior of the 100-Series tank liner sidewall and between a 2-in. grout layer (directly underneath the bottom liner) and the basemat concrete. This asphaltic coating consisted of three layers of alternating waterproofing asphalt and lapped asphalt impregnated waterproofing fabric. Over the last layer of fabric a final layer of asphalt was placed. This asphalt membrane was nominally $^3/_8$ in. thick. This asphalt membrane was protected from damage during pouring of the concrete walls by either cement mortar or gunite (Type II, 100-Series) or gunite (Type III, 100-Series) applied to the outside of the asphaltic membrane.

Drawings for TX, BY, TY, and S Farms show the asphaltic membrane for the bottom liner and sidewall liner overlapping. Figure 5-17 shows this typical design feature. The drawings for the first five tank farms (B, C, T, U, and BX Farms) do not show details of the joining of the bottom and sidewall asphaltic membranes. However, the construction specification does mention that these features are overlapped (HW-1946):

> *At the time the waterproofing is placed on the foundation slab, provision shall be made to provide a circumferential lap with the tank waterproofing of not less than 1-foot and so lapped layer for layer as to provide an absolutely liquid tight connection.*

The above description for the 100-Series, Type II tanks is similar to what is shown in Figure 5-17 which is representative of 100-Series, Type III tanks constructed later.

100-Series Type IV Tanks

For SX, A, and AX Farms the asphaltic membrane on the sidewall was eliminated from the design. The concrete of the tank wall was poured directly in contact with the exterior of the tank liner. For AX Farm the asphaltic membrane was also eliminated below the bottom liner. Instead, the AX Farm design includes drain slots in the concrete basemat, which lead to a pipe emptying into a leak detection pit.

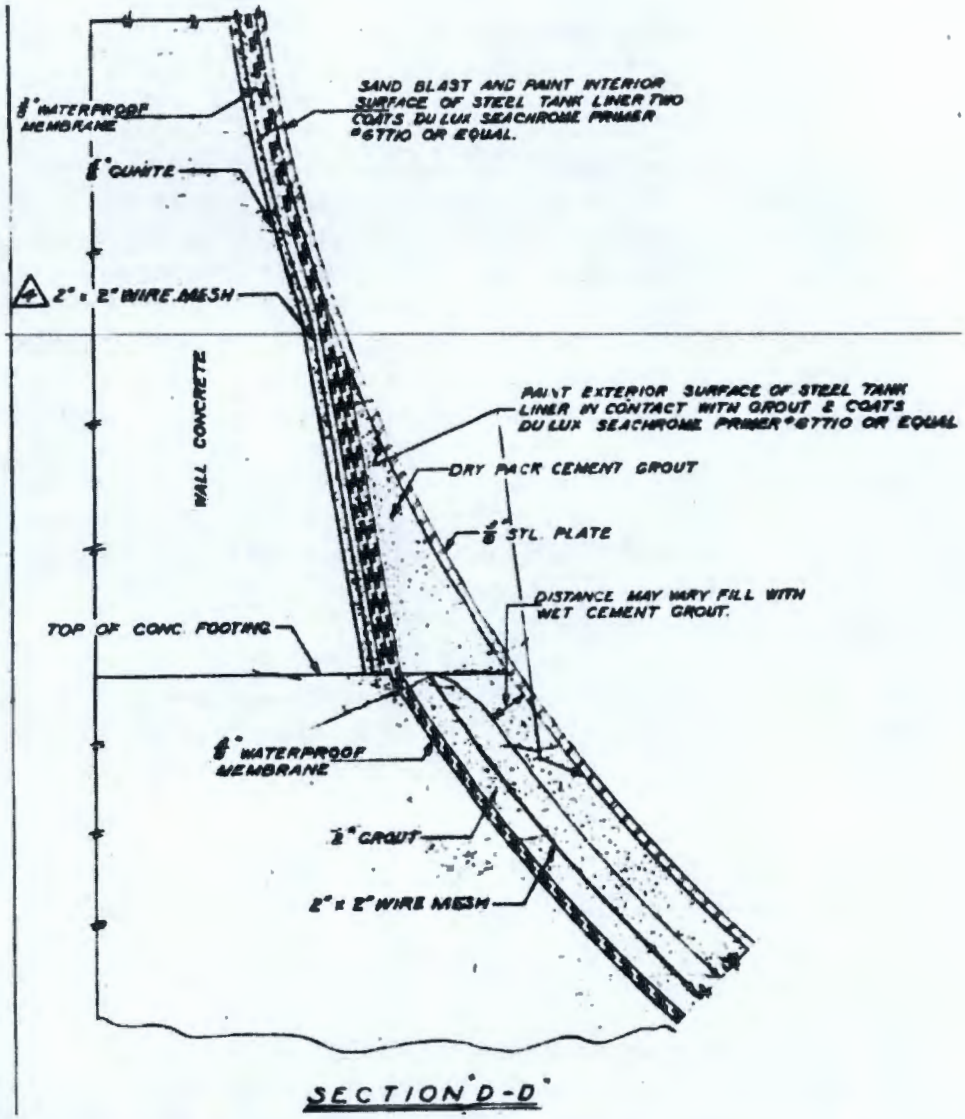


Figure 5-17. 241-TX Farm Asphalt Membrane, Typical of External Tank Liner for 100-Series Tanks Constructed Prior to 241-SX Tank Farm

200-Series Type I Tanks

The 200-Series tanks constructed in B, C, T, and U Farms also did not have an asphaltic membrane. The exterior steel tank sidewalls of the 200-Series tanks were covered with, "…1-in. thickness Banrock Wire Mesh Blanket, Style #102" (Drawing D-20). The Banrock blanket is not described but it is most likely an insulating blanket material made from mineral wool. The Banrock blanket only extends downward to the point of the foundation and sidewall concrete joint at the tank linker but not below. No mention is made on the drawing of this blanket material providing any level of waterproofing nor does the description of its installation and tying together of joints between sections of the blanket lead to an expectation that it would provide waterproofing. The blanket material was then covered with ½-in. of cement mortar or

gunite prior to placement of the concrete wall. There is no indication from the available information whether the blanket material is yielding or rigid. The extent of the wire mesh blanket material is shown in Figure 5-18.

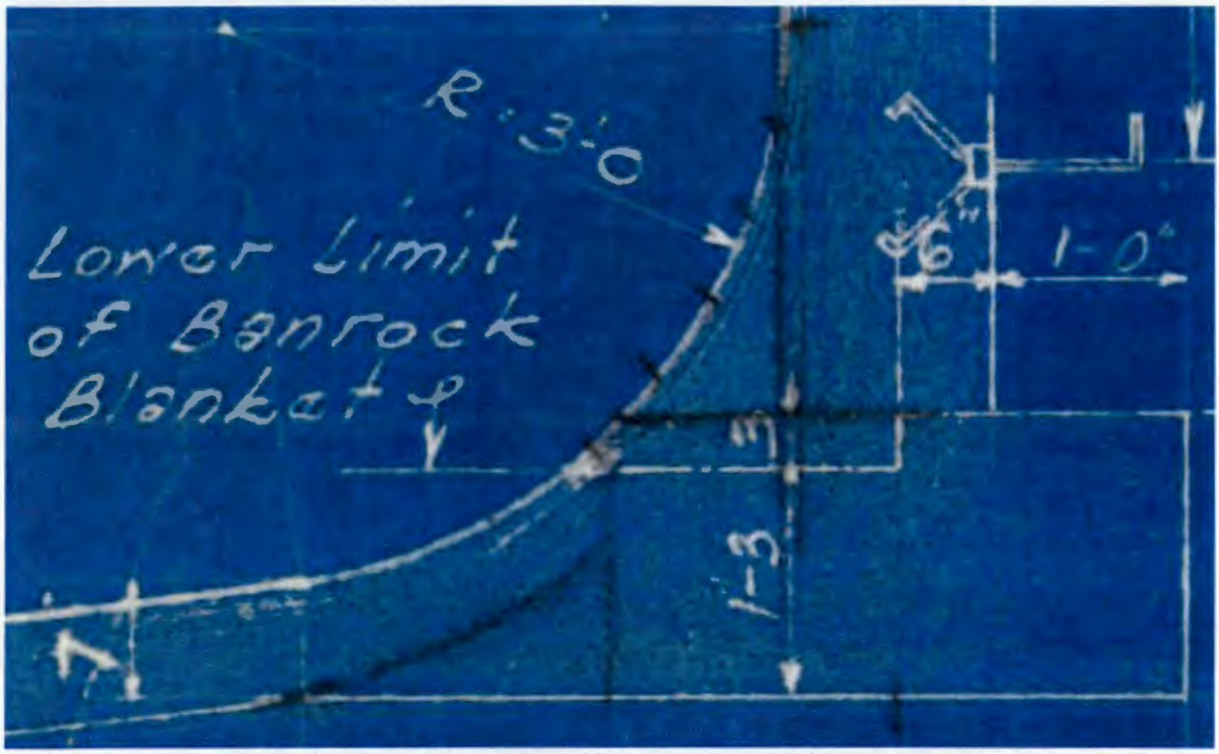


Figure 5-18. 200-Series Tank Wire Mesh Blanket Lining Material on the External Tank Liner for 200-Series Tanks

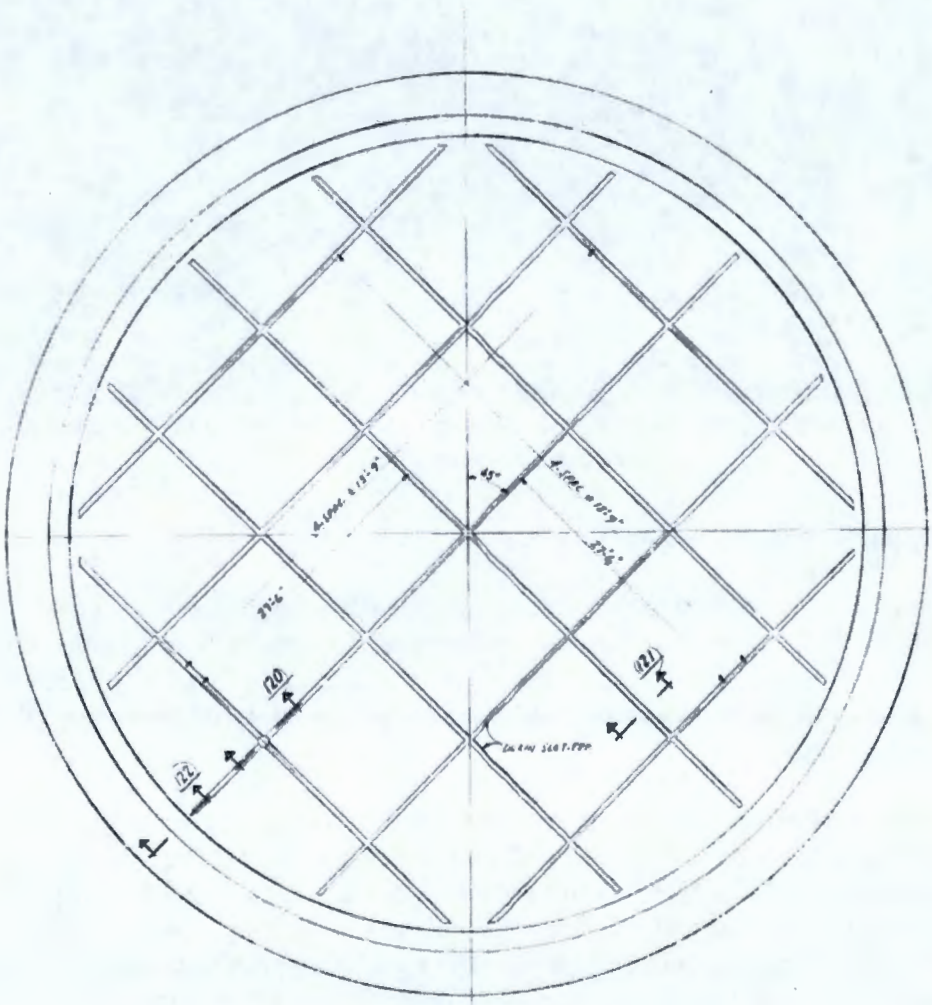
Benefits of Asphaltic Waterproofing Membrane

The application of a $^3/_8$-in. thick asphaltic membrane provides several benefits: it is a waterproofing layer on the exterior of the tank that protects the exterior liner from external corrosion; it allows for some thermal expansion of the liner due to the flexibility of the asphalt in comparison to the rigidity of the concrete; and, impedes the flow of waste from inside the tank in the case of a liner failure.

Regarding expansion under heating, the thermal coefficient of expansion for iron is 6.5×10^{-6} in/in-°F (Avallone and Baumeister 1996, Table 6.4.1, p. 6-50). For simple comparison, a 75-ft long plate subjected to a 125°F temperature rise would expand approximately 0.73 in. This level of expansion is roughly equivalent to the gap on both sides ($^3/_8$-in. times 2) of the liner. The previous sentences should be considered illustrative of the general extent of expansion of an iron-based metal rather than an estimate of the expansion of a 100-Series steel liner with a complex geometry.

5.2.4 Vent Path for Gases Formed Below Tank Liner

One design aspect that differentiates AX Farm from the other SST farms is the presence of drain slots underneath the tank bottom liner. These drain slots are 5 in. wide, 2 ½ in. wide, and spaced 13-ft 9 in. apart (square array). Although the intention of the drain slots was to direct and collect any liquid that may be present underneath the tank to a detection sump, the drain slots also provide an engineered vent path for any gases that may be present or form underneath the tank bottom liner. Figure 5-19 shows a plan view of the base mat with the drain slot arrangement (H-2-44563, *Structural Waste Storage Tanks Drain Arrangement and Details 241-AX*). These slots connect, via a 12-in. pipe that travels under the foundation, to a 24-in. diameter leak detection well. This well extends up to grade where it is enclosed within a leak detection pit. Vapor or gas formed under the bottom liner could eventually make its way through the drain collection pipe and to the leak detection well.



PLAN - DRAIN SLOT ARRANGEMENT

Figure 5-19. 241-AX Farm Tank Basemat Drain Slot Arrangement

In summary there are significant differences in the availability of a vent path for gases and vapors that may form underneath the tank liner bottom. Section 6.2.4 contains the analysis of whether or not this difference is considered a potential common factor contributing to liner failure.

5.3 PROCURED TANK MATERIALS

This section provides background information on features of the tank materials that may have contributed to liner failures. Aspects of tank materials are important to investigate because they represent the possibility that some tanks may have been inherently at risk for failure without consideration of the stored waste. This can also be important in determining whether certain conditions observed in the tanks were more detrimental because of distinguishing material features.

5.3.1 Properties of Liner Materials

Since the primary feature of the twenty-five confirmed leakers from Table 2-3 is leakage through failure of the steel liner, it is considered that the steel used to construct the liner may have played a role in contributing to the failures. Table 5-6 shows the available chemical composition and physical and mechanical properties of the steel plate used in fabrication of the various tank liners by tank farm as well as the number of confirmed tanks with liner failures. Chemical composition values shown are generally from Hanford-defined specifications or national standards in use at the time of construction. In addition, some early reports on corrosion testing of steels from the first several tank farms (B, C, T, U, BX, and TX Farms) reported carbon content from plate material used in construction of the liners to range from 0.10% to 0.12% (HW-13620, *Waste Storage Tank Corrosion Tests*, HW-14946, *A Survey of Corrosion Data and Construction Details, 200 Area Waste Storage Tanks*). This is significantly lower than the specified maximum carbon content for the steels specified for construction of the liners. No original analyses or reports could be located for the various steel liners.

The minor elements present in the steel can have a significant effect on the properties of the steel. It is difficult to isolate the influence of one compositional variable with respect to all others, since in testing the variables cannot be isolated from each other. However, the general influence of any one compositional variable can be examined.

Table 5-6. Design and ASTM Chemical and Physical Specifications for Steel Liners[1]

Tank Farm	Grade Type	Specification	S max. %	P max. %	Mn max. %	C max. %	Carbon Equivalent[2]	Composition Parameter[3]	Liner Thickness	Min. Tensile Strength, ksi	Min. Yield Strength, ksi	Failed Tanks
B, C, T, U, BX	A7-39	HW-1946	0.05	0.04	-	0.35[4] [0.12][5]	0.35 [0.12][5]	0.35 [0.12][5]	¼" (bottom & wall), 5/16" (knuckle)	60	33	8/76
TX	A285-46, Grade A, B, C	HW-24800-35, H-2-809	0.04	0.04	**0.10**	**0.30** [0.12][5]	0.32 [0.14][5]	0.31 [0.13][5]	3/8" (bottom & knuckle), 5/16" (mid wall), ¼" (top wall)	45	24	2/18
BY		HW-3783			**1.00**	**0.25** [0.12][5]	0.42 [0.29][5]	0.30 [0.17][5]	same as above			1/12
S	A283-46T, Grade B	HW-3937	**0.05**	**0.04**	**0.50**	**0.14**	0.22	0.17	same as above	50	27	0/12
TY	A283-49T, Grade B	HW-4696	**0.05**	**0.04**	**0.50**	**0.16**	0.24	0.19	same as above	50	27	4/6
SX	A283-52T, Grade A, B	HW-4957	0.05	0.04	**0.60**	**0.26**	0.36	0.29	3/8" (all)	45	24	8/15
A	A283-52T, Grade B, C	HWS-5614	**0.05**	**0.04**	**0.60**	**0.26**	0.36	0.29	3/8" (all)	50	27	2/6
AX	A201-61T, Grade A	HW-72780, HWS-8237	0.04	0.04	0.80	**0.22**	0.35	0.26	3/8" (all)	55	30	0/4

1 Values in bold represent chemical composition requirements, verified with ladle analyses, directly outlined in the specification for a given tank farm. Non-bolded values are those outlined by the ASTM standard.

2 Carbon Equivalent (CE) was calculated using the AWS D1.1/D1.1M.2010, *Structural Welding Code – Steel*, equation for carbon equivalent from Annex I, Guideline on Alternative Methods for Determining Preheat: CE = C + (Mn + Si)/6 + (Cr+Mo+V)/5 + (Ni+Cu)/15. Because Si values are not available for the chemical specifications of the steels listed, the values for CE are based on Si=0 and the CE values are the same as those calculated using the Deardon-O'Neill form of carbon equivalent (CE = C + Mn/6 + (Cr+Mo+V)/5 + (Ni+Cu)/15).

3 Composition Parameter was calculated using the AWS D1.1/D1.1M.2010, *Structural Welding Code – Steel*, equation for composition parameter, P_{cm}, from Annex I, Guideline on Alternative Methods for Determining Preheat: P_{cm} = C + Si/30 + Mn/20 + Cu/20 + Ni/60 + Cr/20 + Mo/15 + V/10 + 5B.

4 Carbon maximum value for A7-39 is the maximum allowable percent carbon for rolled base plates over 2 in. in thickness. Plates used for tank liners were thinner than this, but no carbon composition maximum is specified in A7-39, *Standard Specifications for Steel for Bridges and Buildings*, in general or for thinner plates. Avallone and Baumeister 1996, Some Typical Application of Carbon Steels, p. 6-22, that steel with 0.20-0.35 weight percent carbon is used for structural steel and plate.

5 HW-13620 and HW-14946 identify that steel plate from the originally constructed tanks through 241-TX tank farm were analyzed for carbon content and found to contain 0.10 to 0.12% carbon. No original records for carbon analysis of steel plates for the tanks were located. The analyzed quantity of carbon is significantly below the specification limit for the steel grades specified and result in significantly lower carbon equivalent and composition parameter values.

Sulfur and Phosphorous Equivalent

Both sulfur and phosphorous are residual impurities in steel at the levels presented in Table 5-6. However, sulfur is sometimes added for improved machinability and phosphorous is sometimes added to improve strength and atmospheric corrosion resistance. Sulfur is removed from steel

because it can reduce weldability, impact toughness and ductility. Phosphorous is removed from steel because it can make the steel less tough and less ductile while increasing brittleness. There are minor to no differences in maximum phosphorous and sulfur content among the various grades of steel specified for the SST liners. Because all steels used for fabrication of SST liners have the same or nearly the same maximum allowable sulfur and phosphorous, their content cannot be considered as a contributing common factor to liner failure. If measured sulfur and phosphorous content of the actual steels used in each tank were available, then that information could be evaluated to identify whether the sulfur and phosphorous contents were a contributing common factor to liner failure. No such information has been located in the searched records.

Carbon Equivalent

Carbon is the principle hardening element in steel responsible for increasing tensile strength, hardness, and resistance to wear and abrasion. When carbon is present in high quantities it can affect ductility, toughness and machinability of steel. Manganese contributes to the strength and hardness of steel, but to a lesser extent than carbon and in a manner dependent upon carbon content. Manganese also ties up sulfur. Manganese improves tensile strength, hardness, and resistance to wear and abrasion.

The presence of carbon and to a lesser extent other elements such as manganese effect the weldability of the steel. A well-recognized compositional indicator of carbon steel weldability is the carbon equivalent (CE). In 1940, a CE formula to characterize hardness was introduced by Dearden and O'Neill (Dearden and O'Neill 1940, *A Guide to the Selection and Welding of Low Allow Structural Steels*, p. 203-214) where the relative influence on hardness of the different important elements in steel were weighted against the influence of carbon. That formula was simplified by the International Institute of Welding twenty-seven years later into the generally accepted form:

$$CE = C + \frac{Mn}{6} + \frac{(Cr + Mo + V)}{5} + \frac{(Ni + Cu)}{15}$$

Where CE = carbon equivalent, C = carbon, Mn = manganese, Cr = chromium, Mo = molybdenum, Ni = nickel, and Cu = copper (Bailey 1994, *Weldability of Ferritic Steels*).

The current formula for carbon equivalent in AWS D1.1/D1.1M, Annex I, includes silicon in the formula:

$$CE = C + \frac{(Mn+Si)}{6} + \frac{(Cr+Mo+V)}{5} + \frac{(Ni+Cu)}{15}.$$

Where CE = carbon equivalent, C = carbon, Mn = manganese, Si = silicon, Cr = chromium, Mo = molybdenum, Ni = nickel, V = vanadium, and Cu = copper.

Higher concentration of carbon tends to increase hardness and decrease ductility, which decreases weldability and increases the tendency of the steel toward cold cracking. Although originally developed as a hardenability formula, the formula has come to be used as a formula for avoiding hydrogen cracking.

An early waste storage tank corrosion test program at the Hanford Site was performed for simulated waste from the REDOX process (HW-12701, *Corrosion Program*). The program included testing of welded, stressed and unstressed, metal samples of SAE 1010 and SAE 1020 steel for three different waste simulants. This work recognized the potential for weld cracking under stress as the level of carbon present in the steel plate increased. Reported discussion of cracking of welded SAE 1020 material (HW-13620) as part of specimen preparation is repeated below:

> *Low carbon steel plates in the SAE 1010 and SAE 1020 composition ranges were obtained and welded under identical conditions with a Lincoln automatic welding machine.*
>
> *Transverse specimens were cut from these welded plates and stressed by bending in a standard, guided-bend test jig. The SAE 1010 welded plate was successfully bent without machining the weld bead flush with the plate. The SAE 1020 welded plate, however, cracked along the weld-metal interface when bent in a similar fashion.*
>
> *This failure has been attributed to the higher carbon content of the SAE 1020 (C 0.18-0.23%) as compared to that of the SAE 1010 (C 0.08-0.13%). According to A. B. Kinzel, "Ductility of Steels for Welded Structures," Trans. ASM, Vol. 40, 1948, p. 33, difficulties in welding structural low-alloy steels are not to be expected if the carbon content is 0.14% or lower. Slightly higher carbon content introduces other factors, such as alloy content and the specific nature and mass of the steel which affect its weldability.*
>
> *The SAE 1020 welded plate was then exposed to another bend test in which the weld bead was ground flush to the plate prior to bending. This test, less severe in nature, was successfully withstood by the SAE 1020 plate, and it was decided to corrosion test stressed specimens of this material which had been bent in this fashion.*
>
> *These tests indicate that superior weldments in waste storage tank construction can be assured through use of low carbon steel with a 0.14% maximum carbon content.*
>
> *The results of the chemical analyses of some 12-odd low carbon steel plates employed in former and current (Project C-271 241 BY) waste tank construction show their carbon content to range from 0.10 to 0.12%.*

Note that HW-13620 refers to carbon content rather than carbon equivalent but does point to the link between carbon content and weldability. SAE 1010 steel contains 0.08%-0.13% carbon and 0.30-0.50% manganese while SAE 1020 steel contains 0.18%-0.23% carbon and 0.30-0.60% manganese (Avallone and Baumeister 1996, Table 6.2.8, p. 6-28). Both SAE 1010 and SAE 1020 contain a maximum of 0.04% phosphorous and 0.05% sulfur. With the compositional ranges given, the carbon equivalent of SAE 1010 is 0.13-0.21 and SAE 1020 is 0.23-0.33.

Carbon can be associated with the potential formation of martensite, a hard and brittle form of steel susceptible to cracking. Martensite can form during the cooling of the weld and heat-affected zone. By limiting the amount of carbon present in the steel and/or controlling the cool down rate of the weld area, the amount of martensite that can form can be limited to levels that do not significantly increase the likelihood of cracking. By preheating the area to be welded, the cool down period for the weld is extended because of the larger heated mass. This in turn limits the formation of martensite and the possibility of cracking.

The lower the carbon equivalent, the more weldable the steel becomes. Conversely, at higher carbon equivalent values the steel is more susceptible to cracking and requires elevated preheat and interpass temperatures to eliminate cracking. Table 5-6 shows the changes to the maximum allowable manganese and carbon contents and the effect on carbon equivalent as the grades of steel changed with construction. Because of this relationship between carbon equivalent and weldability, carbon equivalent will be analyzed as a potential common factor.

Yield Strength

The discussion above focuses on chemical differences between the different grades of steel used to construct the SST liners. The different grades of steel could also have differing propensities to fail by a particular mechanism based on the mechanical properties. One such relationship is based on the relationship between grain size and SCC. A fine grain size has been shown to increase the resistance to SCC of carbon steels in solutions containing nitrates (McCafferty 2010, p. 336). Based on the Hall and Petch effect, there is an inverse relationship between grain size and yield strength. Thus carbon steels with higher yield strengths would have smaller grain size and a lesser propensity to failure via SCC. Therefore, material yield strength will be analyzed as a potential common factor. Because yield strength and tensile strength follow one another in the grades of steel used to construct the liners, there is no need to analyze tensile strength separately.

Steel Grade and Liner Thickness

Other possible ways to examine whether there are differences in failure rates based on the liner material properties are to examine differences in the steel grade and the liner thickness. These approaches make no consideration of the underlying properties but simply rely on differences in specified materials among the various tank farms. If differences do exist based on specified grade of material or liner thickness, then further investigation of the causes for differences could be warranted. Based on this consideration, the specification of steel grade and the liner thickness will be analyzed as potential common factors.

Properties of Liner Materials Summary

In summary, four properties of the liner material are considered as potential common factors of liner failure: carbon equivalent; yield strength; steel grade; and, liner thickness. Section 6.3 contains the analysis of these four factors as potential common factors contributing to liner failure.

5.3.2 Steel Liner Plate Defects

Steel liner plate defects could not be eliminated from consideration as a potentially likely factor contributing to liner failure (see Section 4.2.2). However, no relevant information was found regarding the types and severity of defects present in the steel used to construct the SSTs in the various tank farms. In general, one may expect an improvement in the quality of steel plate with time and an associated reduction in the frequency and severity of defects. However, making specific qualifications regarding the steel used in SST construction based on generalities related to the U.S. steel industry as a whole is not appropriate. Due to the lack of specific information regarding defect severity and frequency, steel liner plate defects cannot be analyzed as a mechanism and the presence of common factors associated with plate defects cannot be determined. This does not mean that a particular liner plate defect did or did not play a role as a common factor contributing to liner failure, rather that no information is available to make such a claim.

5.3.3 Weld Material Defects

Weld material defects could not be eliminated from consideration as a potentially likely factor contributing to liner failure (see Section 4.2.3). However, no relevant information was found regarding the types and severity of defects present in the weld materials used to construct the SSTs in the various tank farms. Due to the lack of specific information regarding defect severity and frequency, weld material defects cannot be analyzed as a mechanism and the presence of common factors associated with weld material defects cannot be determined. This does not mean that a particular weld material defect did or did not play a role as a common factor contributing to liner failure, rather that no information is available to make such a claim.

5.4 TANK CONSTRUCTION

This section provides background information on the construction factors that may have contributed to liner failures. Aspects of tank construction are important to investigate because they represent the possibility that some tanks may have been inherently at risk for failure before storing waste. This can also be important in determining whether certain conditions observed in the tanks were more detrimental because of distinguishing construction features.

5.4.1 Brittle Fracture or Crack Propagation during Construction

Tank farm construction during extreme cold weather temperatures is of particular interest due to the ductile-to-brittle transition temperature (DBTT) behavior of the steel liner material. Based on construction dates, a number of the tank farms would have been subjected to temperatures below their DBTT. The DBTT represents a critical temperature at which the fracture toughness, or ductility, drops significantly. The DBTT represents a point where a metal has a greater tendency to crack when impacted, rather than bend.

For mild steels of the thicknesses used in the construction of the steel liner in SSTs, the DBTT has been reported as approximately 50°F (RPP-RPT-43116). Below this temperature, the steel begins to lose its ability to absorb induced loads or impacts without fracturing. At temperatures significantly below 50°F, it could be possible to form micro-fissures or hairline cracks from impacts to the steel and later, when the liner is subjected to high stresses from operational conditions such as high heat waste storage, the cracks could propagate through the steel or subject the weakened portions to increased susceptibility of corrosion.

Current standards for construction of pressure vessels, ASME Boiler & Pressure Vessel Code (B&PVC), Section VIII, *Rules for Construction of Pressure Vessels*, provide requirements for vessels constructed of carbon and low alloy steels with respect to minimum design metal temperatures. Because of the old age of the standards identified for the various steels used for liner construction and changes to the standards, the current standard does not necessarily apply directly to those steels. However, general carbon and low alloy steels are listed when a specific standard is not identified. Current B&PVC Section VIII requirements specify, for non-specific carbon and low alloy steel up to 0.394-in.in thickness, a minimum design metal temperature of 18°F. This represents the highest minimum design metal temperature (i.e., most conservative) specified for carbon and low alloy steels. For the purposes of this report, it will be assumed that the 18°F design temperature is applicable to the fabrication of all the steel liners for the various SSTs.

Construction of the various tank farms took at least ten months from beginning to end, but for the purposes of looking at liner failure, much of that construction time (i.e. excavation, activities after the dome is poured, etc.) is not significant. Therefore, the primary timeframe to investigate for cold weather issues is from the beginning of liner construction until after the concrete had been poured for the walls and dome, since after dome construction it is not likely that other construction activities in the farm would result in impact to the liner. Based on photographic evidence, as well as construction timelines (when available), the status of liner construction was determined for all the tank farms and Table 5-7 below shows the approximate dates of construction using the beginning of liner construction as the start time and the end of dome construction as the end time. The minimum reported temperature during the time frame is also identified. The grey rows represent tank farms built during a period when the minimum temperature was less than 18°F. It should be noted that the actual DBTT for a material would need to be determined by testing. No evidence of such testing has been found and it is not likely such testing was done on the materials used for the SST liners.

Table 5-7. Approximate Construction Period for Steel Liners of Single-Shell Tanks and Associated Minimum Environmental Temperatures

Tank Farm	Steel Liner Material	Approximate Liner Construction Start[1]	Approximate Dome Construction End[1]	Minimum Temperature During Period	Reference
A	A283-52T, Grade B,C	April 1954	October 1954	14°F	RPP-RPT-54912
AX	A-201-61T, Grade A	November 1963	June 1964	7°F	PNNL-15160[2]
B	A7-39	July 1944	October 1944	12°F	RPP-RPT-54913, *Hanford Single-Shell Tank Leak Causes and Locations – 241-B Farm*
BX	A7-39	April 1947	September 1947	32°F	PNNL-15160
BY	A285-46, Grade A,B,C	December 1949	May 1949	-2°F	RPP-RPT-54911
C	A7-39	August 1944	November 1944	>18°F	RPP-RPT-54914, *Hanford Single-Shell Tank Leak Causes and Locations – 241-C Farm*
S	A238-46T, Grade B	December 1950	May 1951	6°F	PNNL-15160
SX	A283-52T, Grade A,B	October 1953	March 1954	-6°F	RPP-RPT-54910
T	A7-39	May 1944	August 1944	12°F	RPP-RPT-54916
TX	A285-46	March 1948	July 1948	13°F	RPP-RPT-54917, *Hanford Single-Shell Tank Leak Causes and Locations – 241-TX Farm*
TY	A283-49T, Grade B	July 1951	October 1951	4°F	RPP-RPT-54911
U	A7-39	March 1944	August 1944	>18°F	RPP-RPT-54915, *Hanford Single-Shell Tank Leak Causes and Locations – 241-U Farm*

[1] Dates were estimated using construction photographs.
[2] PNNL-15160, *Hanford Site Climatological Summary 2004 with Historical Data.*

Nine of the 12 tank farms were constructed at a time when the minimum temperature was less than 18°F. While the steel in many tanks were certainly at temperatures below the minimum design metal temperature for the plate steel used in the liner, this fact alone would not result in liner failure. There are inherent risks to having the exposed steel at these low temperatures, but the danger is not permanent and would subside once the steel temperature rose above the minimum design metal temperature. However, if the steel liner were to be impacted at temperatures below the minimum design metal temperature, it is possible the resulting deformation of the liner could pose a significant risk of failure even after the steel temperature rose above the minimum design metal temperature. If significant impact (e.g., tools dropped in the tank, a truck backing up into the liner, contact from the crane use, etc.) was made to the tank during these construction activities at low temperature, then it is entirely possible that a crack could form in the liner and result in failure and leakage from stresses applied during waste storage operations. It should be noted that if an impact did occur and a crack formed, leak testing would only have indicated if a crack substantial enough to allow leakage existed. If a

crack was formed during the cold weather period, the ensuing storage of waste could cause larger stress-induced fractures stemming from the original crack and provide a leak path for the waste. Relying on leak testing to indicate cracks also does not preclude tanks from forming cracks due to impacts to the liner after leak testing was completed.

One of the most severe examples of the potential risk from brittle fracture was found in SX Farm. Figure 5-20 below is a picture taken of SX Farm during construction (IDMS Photograph 2471-PHOTO). The photograph was taken on January 20, 1954 on a day when the high temperature was 11°F and the low was -6°F. The winter of 1953-1954, during which this picture was taken, was one of the coldest and harshest recorded at the Hanford Site. Specifically, during the two week period surrounding this photograph (1/16/1954 to 1/29/1954) the temperature rarely reached above freezing with an average daily high temperature of 24°F and dipped into single digits throughout the period with an average daily low temperature of 9°F.

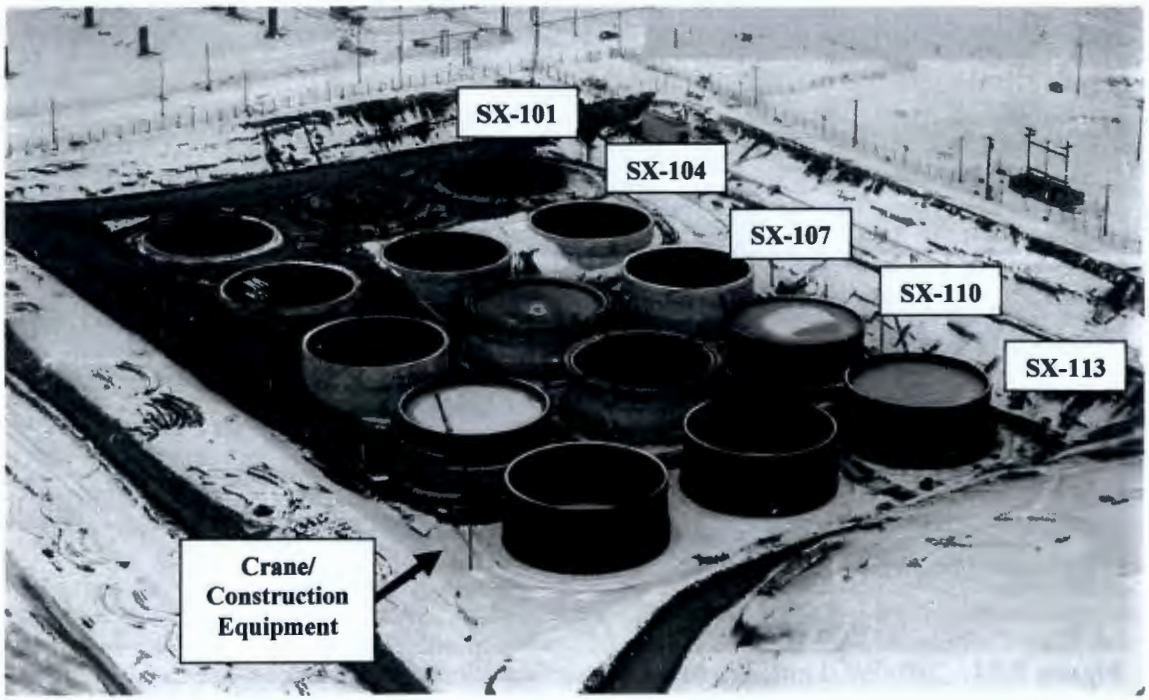


Figure 5-20. 241-SX Tank Farm Construction Photograph Taken January 20, 1954

As can be seen from Figure 5-20, leak testing operations of tanks SX-108, SX-110, SX-112, and SX-113 were underway when the cold weather hit. It appears these tanks may have frozen over. There are also ongoing construction activities in the farm, as noted by the crane equipment and vehicles seen around a number of the tanks, which would increase the likelihood of impact to the tanks. It is of interest to note that eight of the nine tanks that had not been backfilled at the time of the picture were found to have leaked (SX-107 through SX-115; excluding SX-110).

Another extreme example of cold weather construction was found in BY Farm. Whereas the extreme cold weather hit SX Farm during the concrete wall pouring portion of the construction, the cold weather hit BY Farm construction through ongoing liner fabrication. Figure 5-21 and Figure 5-22 show that significant construction activities, including welding of the steel plates, were taking place through January and February 1949. Similar to the conditions found in SX Farm, during the time period between January 19, 1949 and February 9, 1949, the daily high temperature was rarely above freezing with an average of 26°F and the daily average low temperature of 7°F, at one point dropping to -11°F. The extremely cold temperatures coupled with the clear evidence of ongoing construction activities suggest a significant opportunity to develop cracks with impacts to the steel.

Figure 5-21. 241-BY Tank Farm Construction Photograph Taken January 19, 1949

Figure 5-22. 241-BY Tank Farm Construction Photograph Taken February 9, 1949

While BY and SX Farms represent the most extreme construction conditions, as mentioned previously, a large number of the tank liners were at temperatures below 18°F at some point during construction of the steel liner through completion of the dome.

5.4.2 Cold Working and Strain Aging

Cold Working

Cold working of steel includes bending, hole-punching, rolling, and shearing among other fabrication techniques. The rolling of the steel plates making up the cylindrical vertical wall of the SST liners and the large radius knuckle of the Type I, II and III tanks is one form of cold working that was performed during construction. Cold working makes steel susceptible to brittle fracture at higher temperatures than non-cold worked material.

One notable piece of information regarding corrosion and cold working can be found in a report on laboratory corrosion testing of SAE 1010 subjected to simulated neutralized PUREX process waste solution (HW-32734, *A Laboratory Study of the Extent of Pitting and General Corrosion of SAE-1010 Steel in Simulated Neutralized Purex Process Waste Solution*). The report discusses both general and pitting corrosion. Regarding pitting corrosion, the report states:

> *In examining the specimens it was noted that many of the pits occurred around the support holes and in the region of the identification numbers. These are the*

> *regions in which the metal was cold worked, and which had probably assumed an anodic potential with respect to other areas.*

No specific details have been found regarding the actual amount of cold working done for each tank or tank farm. Some indication of the cold working that may have been performed is available through examination of the construction specifications for the various tank farms.

Document HW-1946, *Specification for Composite Storage Tanks Building Number 241*, applicable to the first five tank farms (B, C, T, U, and BX Farms), does not make any mention of cold working or relieving the stress induced by cold working. Similarly, HW-3061, applicable to TX Farm, does not make any mention of cold working or relieving the stress induced by cold working.

For BY Farm, knuckle plates were to be formed by hot or cold pressing (HW-3783). Stress-relieving shop fabricated knuckle plates was specified (HW-3783) as excerpted below:

> *Stress-relieving and code marking of tank plates are not required, except that knuckle plates or knuckle plate assemblies shop fabricated shall be stress-relieved in accordance with Paragraph U-76, Section VIII of the ASME Boiler Construction Code, 1946.*

Additionally, HW-3783 specified requirements for straightening of steel material during shop fabrication:

> *Any required straightening of material shall be done by methods which will not injure the steel. Straightening by hammering will not be permitted but shall be done by cold rolling or pressing.*

These requirements were also specified for the construction of S Farm (HW-3937) and TY Farm (HW-4696) with the exception that forming of knuckle plates was by cold pressing only for TY Farm (HW-4696).

For S Farm (HW-3937) and TY Farm (HW-4696), requirements were specified for peening of welds to relieve shrinkage stress.

> *Each layer of weld metal on manual multi-layer welds shall be peened to relieve shrinkage stresses, except that the final surface layer shall not be peened.*

Peening is a way to eliminate shrinkage forces from welding as the weld bead cools. While peening can relieve residual stresses from welding thus reducing distortion of the metal, peening can also increase the risk of concealing, covering or causing a crack. No mention is made in the specifications regarding temperature limitations for performing peening, so it is expected that some peening was performed below the steel recrystallization temperature, and therefore would be considered cold working. The level of care used in peening is critical to its success, and therefore peening can improve the situation by removing residual stress or can worsen the situation by cracking or hiding cracks in the material.

Strain Aging

Strain aging occurs when cold worked material is allowed to age. The material's tensile strength and hardness increase but ductility decreases when exposed to moderately elevated temperatures. The material can become brittle or have an increased nil ductility transition temperature in areas of high stress. The effect of strain aging can be reduced by a stress-relieving heat treatment following cold working. As discussed above, requirements for stress relieving the knuckles were established for BY, S and TY Farms which would limit the issue of strain aging of the shop fabricated portions of the knuckles for those tanks.

5.4.3 Weld Joint Discontinuities and Defects

As previously mentioned (see Section 4.3.3), several types of discontinuities may exist due to welding. Depending on the severity or frequency of these discontinuities, cumulatively they can result in a weld defect. The most common types of weld discontinuities were previously listed in Table 4-2. The earliest specifications for welding inspection required correction of all flaws in the welds (HW-1946). Later specifications were more specific; however, not all discontinuities or defects would necessarily be detected via inspection. Due to the method of inspection, location or orientation, some discontinuities or defects could have gone undetected.

Weld inspection results were only found for TX and AX Farms. A design and construction history report was issued for TX Farm (HW-24800-35). That report includes a summary table of radiographic inspection of each tank. The tabulated information includes the raw numbers of film and length (inches) of defective welding after each x-ray inspection performed as well as a summary total of defective welding. The information in that table is repeated here as Table 5-8. Construction history reports containing summary radiographic reports could not be located for any other tank farm. A records search uncovered original x-ray films and weld inspection reports for 241-AX tank farm that have subsequently been captured in a report (RPP-RPT-58370, *Tank Liner Radiographic Inspection Reports for Original Fabrication of 241-AX Tank Farm*). A summary of weld defect rate information from these radiographic inspection reports of AX Farm is tabulated in Table 5-9.

The total percentage of radiographic film that had defects for TX and AX Farms was 25.1% and 26.4%, respectively. These numbers are remarkably (perhaps coincidentally) similar, especially in light of the variability of percentage of films showing defects on a tank by tank basis within a farm. The TX Farm tank by tank range of films showing defects was 14.6% to 40.4% while for AX Farm it was 19.3% to 34.6%. Within TX Farm all but four of the eighteen tanks had at least one location which had to be welded four times before passing inspection and six tanks had at least one location which had to be welded five times before passing inspection. Within AX Farm all but one of the four tanks had at least one location which had to be welded four times before passing inspection and one tank had at least one location which had to be welded five times before passing inspection.

In TX Farm, tanks TX-107 and TX-114 are the only tanks with probable tank liner failures. Each of these tanks has film reject rates that are slightly less than the average film reject rate for TX Farm. The percentage of inches of rejected weld for tank TX-107 was slightly less than the

average rate while for tank TX-114 it was slightly greater in comparison to the range. Nothing in the available weld radiographic results report indicates a connection between the weld reject rate in TX Farm and tank liner failures of tanks TX-107 or TX-114.

Weld inspection reports for AX Farm also included remarks stating the type of defect(s) present. The percentage by weld defect types for each AX Farm tank and the total for the entire farm are tabulated in Table 5-10. The first three defects shown in Table 5-10 collectively can be considered gas defects. These gas defects account for 52% of all defects identified for AX Farm. The next most frequent type of defect is slag inclusion, accounting for 34% of all defects identified for AX Farm. Each of the other weld defects observed occurred at a frequency less than 5% over the entire farm and less than 10% on any particular tank. Gas defects can occur for several reasons: the lack of cover gas (i.e., presence of air – nitrogen and oxygen); the presence of organic contaminants; the presence of moisture; and, other factors can all result in porosity. The lack of cover gas could result from a number of issues including too little gas flow, too much gas flow (turbulence), no cover gas flow, or windy conditions. The presence of contaminants is an issue of cleanliness/preparation. The presence of moisture could occur in damp conditions, due to wet flux or wire, or inadequately heated base metal to drive off moisture or hydrogen during subsequent cooling of the weld. The presence of slag inclusions can occur when slag did not float to the top of the molten metal. This can be indicative of lack of cleanliness (residual slag) or too rapid cooling of the melt if the weld zone was not adequately heated to extend the cooling period to allow time for slag to be removed from the melt pool prior to resolidification.

Although a number of issues can result in weld discontinuities or defects, few of these issues can be accounted for during the construction because of the lack of information on the topic. For example, inadequate cleanliness could result in either porosity or slag inclusions but no such information regarding cleanliness is available from construction records. One potential issue that could result in porosity or slag inclusions is the cooling time of the melt. Shorter cooling times can allow gases or slag to be trapped in the weld. The way to eliminate this is to preheat the base metal prior to each welding pass. Preheating of the base metal was not specified for the first six tank farms (B, C, T, U, BX, and TX Farms) (HW-1946, HW-3061). For BY, S, and TY Farms qualitative temperature requirements were specified (HW-3783, HW-3937, and HW-4696):

> *Welding shall not be done when the temperature of the base metal is less than 0 deg. F.; when surfaces are wet from rain, snow or ice; when rain or snow is falling on the surfaces to be welded; nor during periods of high winds, unless the operator and the work are properly protected. At temperatures between 32 deg. and 0 deg. F., the surface within 3 inches of the point where the weld is to be started, shall be heated to a temperature warm to the hand before the welding is started.*

For SX, A, and AX Farms a quantitative temperature limit was specified in the referenced standard specification for welding carbon steel (HW-4926-S, *Standard Specifications for Welding Carbon Steels*):

Welding shall not be done when the temperature of the base metal is less than 40 F. Preheating may be used to raise the base metal to this temperature.

Whether welding was accomplished in a manner consistent with current preheating and interpass temperature requirements, these can be looked at as a surrogate potential indicator of weld defects. Preheat and interpass temperature requirements are established to limit hydrogen cracking but can also account for porosity or slag inclusion as described above.

Table 5-8. 241-TX Farm Radiographic Report Summary of Completed Tanks

Tank	Sequence of Erection	No. of 16" Radio-graphs	Total Inches of Weld	First X-Ray Defective Welding				Second X-Ray Defective Welding				Third X-Ray Defective Welding				Fourth X-Ray Defective Welding				Summary Defective Welding			
				Amount		Percentage		Amount		Percentage		Amount		Percentage		Amount		Percentage		Amount		Percentage	
				Film	Inches	Film	Inches	Film	Inches	Film	Inches	Film	Inches	Film	Inches	Film	Inches	Film	Inches	Film	Inches	Film	Inches
101	1	1562	24992	493	1584	31.6	6.34	86	207	17.4	13.07	27	44	31.4	21.26	2	2	7.4	4.55	608	1837	38.9	7.35
105	2	1670	26720	488	1877	29.2	7.02	159	338	32.6	18.01	26	45	16.4	13.31	1	1	3.8	2.22	674	2261	40.4	8.46
109	3	1624	25984	361	863	22.2	3.32	55	92	15.2	10.66	8	9	14.5	9.78	3	3	37.5	33.33	427	967	26.3	3.72
113	4	1574	25184	364	1181	23.1	4.69	41	82	11.3	6.94	4	7	9.8	8.54	--	--	--	--	409	1270	26.0	5.04
116	5	1581	25296	329	817	20.8	3.23	44	80	13.4	9.79	3	3	6.8	3.75	--	--	--	--	376	900	23.8	3.56
102	6	1553	24848	279	761	18.0	3.06	29	48	10.4	6.31	3	3	10.3	6.25	--	--	--	--	311	812	20.0	3.27
106	7	1563	25008	341	833	21.8	3.33	59	125	17.3	15.01	8	12	13.6	9.60	2	2	25.0	16.67	410	972	26.2	3.89
110	8	1564	25024	223	453	14.3	1.81	5	7	2.2	1.55	--	--	--	--	--	--	--	--	228	460	14.6	1.84
114	9	1514	24224	327	778	21.6	3.21	37	57	11.3	7.33	--	--	--	--	--	--	--	--	364	835	24.0	3.45
117	10	1574	25184	315	916	20.0	3.64	18	27	5.7	2.95	1	1	5.6	3.70	--	--	--	--	334	944	21.2	3.75
103	11	1547	24752	282	734	18.2	2.97	14	20	5.0	2.72	--	--	--	--	--	--	--	--	296	754	19.1	3.05
107	12	1514	24224	300	1024	19.8	4.23	40	74	13.3	7.23	2	5	5.0	6.76	--	--	--	--	342	1103	22.6	4.55
111	13	1501	24016	263	665	17.5	2.77	19	19	7.2	2.86	--	--	--	--	--	--	--	--	282	684	18.8	2.85
115	14	1516	24256	285	651	18.8	2.68	34	49	11.9	7.53	2	4	5.9	8.16	--	--	--	--	321	704	21.2	2.90
118	15	1514	24224	300	675	19.8	2.79	15	17	5.0	2.52	1	1	6.7	5.88	--	--	--	--	316	693	20.9	2.86
104	16	1501	24016	314	793	20.9	3.30	66	89	21.0	11.22	4	5	6.1	5.62	1	1	25.0	20.00	385	888	25.6	3.70
108	17	1505	24080	316	891	21.0	3.70	49	92	15.5	10.33	4	5	8.2	5.43	--	--	--	--	369	988	24.5	4.10
112	18	1505	24080	451	1470	30.0	6.10	89	135	19.7	9.18	9	11	10.1	8.15	--	--	--	--	549	1616	36.5	6.71
Total		27882	446112	6031	16966	21.6	3.80	859	1558	14.2	9.18	102	155	11.9	9.95	9	9	8.8	5.81	7001	18688	25.1	4.19

Tank with failed liner.

Table 5-9. 241-AX Farm Radiographic Report Summary of Completed Tanks

Tank	No. of 16" Radio-graphs	First X-Ray Defective Welding		Second X-Ray Defective Welding		Third X-Ray Defective Welding		Fourth X-Ray Defective Welding		Fifth X-Ray Defective Welding		Summary Defective Welding	
		Amount Film	Percent Film	Amount Film	Percent Film	Amount Film	Percent Film	Amount Film	Percent Film	Amount Film	Percent Film	Amount Film	Percent Film
101	951	192	20.2	64	33.3	12	18.8	4	33.3	1	25.0	273	28.7
102	845	131	15.5	28	21.4	4	14.3	--	--	--	--	163	19.3
103	1041	269	25.8	66	24.5	19	28.8	6	31.6	--	--	360	34.6
104	857	159	18.6	14	8.8	5	35.7	2	40.0	--	--	180	21.0
Total	3694	751	20.3	172	22.9	40	23.3	--	--	--	--	976	26.4

Table 5-10. 241-AX Farm Weld Defect Rate for Each Tank and Overall Farm

Tank	Defect Type										
	Porosity	Pinhole	Gas Hole	Slag Inclusion	Lack of Penetration	Lack of Fusion	Incomplete Weld	Undercut	Arc Strike	Crack	Burn Through
101	29.0%	5.8%	13.0%	40.6%	2.8%	5.2%	0.6%	1.7%	0.8%	0.6%	0.0%
102	24.2%	5.8%	12.1%	38.1%	4.5%	8.5%	2.2%	2.7%	0.0%	1.8%	0.0%
103	41.5%	10.5%	7.1%	26.9%	2.6%	3.0%	0.2%	8.1%	0.0%	0.2%	0.0%
104	29.0%	10.8%	12.0%	35.7%	4.1%	2.5%	0.4%	2.1%	0.4%	2.5%	0.4%
Total	32.7%	8.4%	10.5%	34.3%	3.2%	4.5%	0.7%	4.3%	0.3%	1.0%	0.1%

American Welding Society standard AWS D1.1/D1.1M.2010, *Structural Welding Code – Steel*, provides minimum preheat and interpass temperatures for listed steel specifications and qualified welding procedures methods. Such detailed requirements were not in place at the time the SST liners were fabricated. An alternative method to determining minimum preheat and interpass temperature is provided in Annex I to AWS D1.1/D1.1M.2010 based on the carbon equivalent and other parameters of the steel being welded. Annex I may be of value in identifying situations where the risk of cracking is increased due to composition, restraint, hydrogen level or lower welding heat input where higher preheat may be warranted. The calculation of the carbon equivalent and composition parameter of a steel grade relies on knowing the composition of some elements not specified for early steels, primarily silicon.[3] Based on the carbon equivalent, a method of welding control can be established to control cracking. Assuming use of the hydrogen control method, a susceptibility level is established based on the hydrogen level during welding and the steel's composition parameter (see Table 5-11). For the welding of the SST liners there was no demonstrable hydrogen control provided (e.g., low hydrogen electrodes from hermetically sealed containers used with moisture control methods). Lack of hydrogen control results in requiring greater minimum preheat and interpass temperatures. The minimum preheat and interpass temperature also depends on the level of restraint used during welding. The level of restraint for members already attached to structural work is considered medium restraint and for members where there is almost no freedom of movement, such as weld repairs, is considered high restraint. Table 5-11 provides the minimum preheat and interpass temperatures based on Annex I of AWS D1.1/1.1M.2010 for the various tank farm steels based on susceptibility index group, material thickness, and level of restraint.

[3] As an example maximum weight percent silicon in A36 steel is 0.4%. Assuming silicon present at 0.4% in the steels used in SST liners would increase the carbon equivalent values presented in Table 5-11 by 0.07 and the composition parameter values presented in Table 5-11 by 0.01. These differences would only increase the minimum required preheat values discussed in this paragraph for the steel liners used in 241-S tank farm.

Table 5-11. Minimum Preheat and Interpass Temperatures per AWS D1.1/D1.1M.2010 for Welding Single-Shell Tank Steel Liners[1]

Tank Farm	Carbon Equivalent[2]	Composition Parameter[3]	Susceptibility Index Group	Liner Thickness	Restraint Level	Minimum Preheat & Interpass Temperature, °F	Failed Tanks
B	0.35 [0.12][4]	0.35 [0.12][4]	G [C][4]	¼" (bottom & wall) 5/16" (knuckle)[5]	Medium	320 [<65][4]	8/64
C							
T					High	320 [<65][4]	
U							
BX	0.35 [0.12][4]	0.35 [0.12][4]	G [C][4]	¼" (wall) & 5/16" (knuckle)	Medium	320 [<65][4]	0/12
					High	320 [<65][4]	
				3/8" (bottom)	Medium	320 [65][4]	
					High	320 [150][4]	
TX	0.32 [0.14][4]	0.31 [0.13][4]	F [C][4]	5/16" (mid wall), ¼" (top wall)	Medium	280 [<65][4]	2/18
					High	300 [<65][4]	
				3/8" (bottom & knuckle)	Medium	290 [65][4]	
					High	320 [150][4]	
BY	0.42 [0.29][4]	0.30 [0.17][4]	F [C][4]	5/16" (mid wall), ¼" (top wall)	Medium	280 [<65][4]	1/12
					High	300 [<65][4]	
				3/8" (bottom & knuckle)	Medium	290 [65][4]	
					High	320 [65][4]	
S	0.22	0.17	C [or D][6]	5/16" (mid wall), ¼" (top wall)	Medium	<65 [<65][6]	0/12
					High	<65 [100][6]	
				3/8" (bottom & knuckle)	Medium	65 [175][6]	
					High	150 [220][6]	
TY	0.24	0.19	D	5/16" (mid wall), ¼" (top wall)	Medium	<65	4/6
					High	100	
				3/8" (bottom & knuckle)	Medium	175	
					High	220	
SX	0.36	0.29	F	3/8" (all)	Medium	290	8/15
					High	320	
A	0.36	0.29	F	3/8" (all)	Medium	290	2/6
					High	320	
AX	0.35	0.26	E	3/8" (all)	Medium	240	0/4
					High	280	

1 Values in table of minimum preheat and interpass temperatures assume no hydrogen control was performed during welding. Less than values (e.g. <65) indicate lower values may be acceptable but must be qualified by test.

2 Carbon Equivalent (CE) was calculated using the AWS D1.1/D1.1M.2010, *Structural Welding Code – Steel*, equation for carbon equivalent from Annex I, Guideline on Alternative Methods for Determining Preheat: CE = C + (Mn + Si)/6 + (Cr+Mo+V)/5 + (Ni+Cu)/15.

3 Composition Parameter, P_{cm}, was calculated using the AWS D1.1/D1.1M.2010, *Structural Welding Code – Steel*, equation for composition parameter, P_{cm}, from Annex I, Guideline on Alternative Methods for Determining Preheat: P_{cm} = C + Si/30 + Mn/20 + Cu/20 + Ni/60 + Cr/20 + Mo/15 + V/10 + 5B.

4 HW-13620 and HW-14946 identify that steel plate from the originally constructed tanks through TX Farm were analyzed for carbon content and found to contain 0.10 to 0.12% carbon. No original records for carbon analysis of steel plates for the tanks were located. The analyzed quantity of carbon is significantly below the specification limit for the steel grades specified and result in significantly lower carbon equivalent and composition parameter values. This in turn results in significantly lower minimum preheat and interpass temperatures.

5 The 100-Series, Type II tanks have a 5/16 in. knuckle but the 200-Series Type I tanks have a ¼ in. knuckle. This difference in thickness does not change the minimum preheat and interpass temperatures identified in the table.

6 Values in brackets assume the presence of 0.4 wt% silicon which would change the susceptibility index group of this particular steel. Assuming the presence of 0.4 wt% silicon in all other steels would not change the susceptibility index group for those grades of steel.

5.5 TANK OPERATIONAL SERVICE HISTORY

This section will discuss the major processes that produced the waste stored in the SSTs, in-farm processes that modified the physical and/or chemical characteristics of the stored waste in the tanks, and other minor processes contributing to the waste stored in the SSTs. The major chemical separation processes performed in the 200 Areas of the Hanford Site that generated waste sent to the SSTs are the Bismuth Phosphate ($BiPO_4$) process, Tri-Butyl Phosphate (TBP) or metal recovery process, the REDOX process, the PUREX process, fission product (FP) recovery processes, and waste evaporation processes. Each of the processes is described with an emphasis on identifying the waste streams generated by the process.

For each waste stream sent to the SSTs from a particular process, the available waste composition, waste temperature, and corrosion data are provided. Waste composition is based on available sample results and supplemented with flowsheet compositional information. The in-farm processes that resulted in physical or chemical changes to the waste being stored are in-farm scavenging, nitrate leaching, and sludge washing. A discussion of each process and available waste composition, waste temperature, and corrosion data are provided. Similar information is provided for other minor wastes generated. Finally, operational service in terms of total volume throughput on a tank by tank basis is presented.

5.5.1 Bismuth Phosphate Process Wastes Types (1944-1956)

The first full scale separations process to recover plutonium from irradiated uranium at Hanford was the $BiPO_4$ process. Two canyon facilities, T Plant and B Plant, were operated using this process generating five major waste streams that would be collected in various SSTs. The $BiPO_4$ process was operated at T Plant from 1944 until 1956 and at B Plant from 1945 until 1952. Information regarding the $BiPO_4$ process and stream information for the major waste streams is provided below.

A minor stream that was sent at times to SSTs was the neutralized, low-activity cell drainage waste (designated as 5-6 waste because of the collection tank designation in the canyon facility). For part of the operational period, this cell drainage waste was sent to the same tank cascade as the second decontamination cycle waste discussed below. This stream is not discussed as a separate stream for the purposes of this report.

5.5.1.1. Process Description

The $BiPO_4$ process separated the plutonium from the uranium metal in which it formed; removed the by-product fission products produced along with the plutonium in the nuclear reactors; and, isolated the plutonium from other constituents in a relatively pure state. The original nuclear fuel used for production of plutonium at Hanford is a uranium metal cylinder within an aluminum jacket. These fuel elements are irradiated within the nuclear reactors or piles and then cooled to allow decay of short-lived fission products. The following process description for the $BiPO_4$ process is taken from the Hanford Technical Manual (HW-10475 ABC, *Hanford Technical*

Manual, Section C) issued in May 1944. Figure 5-23 provides a simplified schematic identifying the major waste streams of the $BiPO_4$ process.

The first step in the $BiPO_4$ process is to remove the aluminum jacket surrounding the uranium by preferentially dissolving the aluminum in a dissolver vessel with a solution of sodium hydroxide and sodium nitrate. This solution dissolves the aluminum jacket without dissolving an appreciable amount of the uranium and associated plutonium and fission products. This dissolved aluminum within sodium hydroxide and sodium nitrate is removed from the dissolver and collected in a waste storage tank. The dissolver vessel containing the remaining uranium metal is then water washed and subsequently acid washed with a 5% nitric acid wash to remove residual material. The coating solution, water wash, and acid wash are combined for disposal to the tank farms. The combined solution is referred to as coating removal waste (CW).

After chemical removal of the aluminum jackets, the exposed uranium metal and accompanying plutonium and fission products are then dissolved in hot nitric acid. Some volatile fission products (e.g., xenon, krypton, iodine, etc.) are evolved during the dissolution process. The dissolver is operated with a condenser on the off gas to prevent acid and water vapor loss. Dissolver solution is digested to a specific gravity of nominally 1.8 at boiling and contains approximately 1% free nitric acid content. The metal solution is moved to storage tanks for further processing.

To separate the plutonium from the bulk uranium, the metal solution is diluted and sodium nitrite is added to ensure the proper valence state of the plutonium for precipitation. The precipitate is formed by first adding bismuth mononitrate/nitric acid solution to the metal solution followed by addition of phosphoric acid/nitric acid solution. The nitric acid does not enter the reaction but is used to keep bismuth mononitrate in solution and reduce the corrosivity of the phosphoric acid. The process creates a $BiPO_4$ precipitate that carries the plutonium and about 10% of the fission activity. The precipitate is centrifuged to isolate the precipitate from the solution. The precipitation and centrifugation vessels are water washed to remove residual solids. The water washes are combined with the solution remaining after precipitation and centrifugation. This combined solution consists of 21.5% uranyl nitrate hexahydrate, 3.6% sulfuric acid, 5.7% phosphoric acid, and 0.9% nitric acid as well as roughly 90% of the fission activity. This metal waste solution from extraction is neutralized and then sent to disposal in the tank farms. The separated precipitate bearing the plutonium is dissolved in nitric acid and staged for further decontamination of the plutonium from residual fission activity.

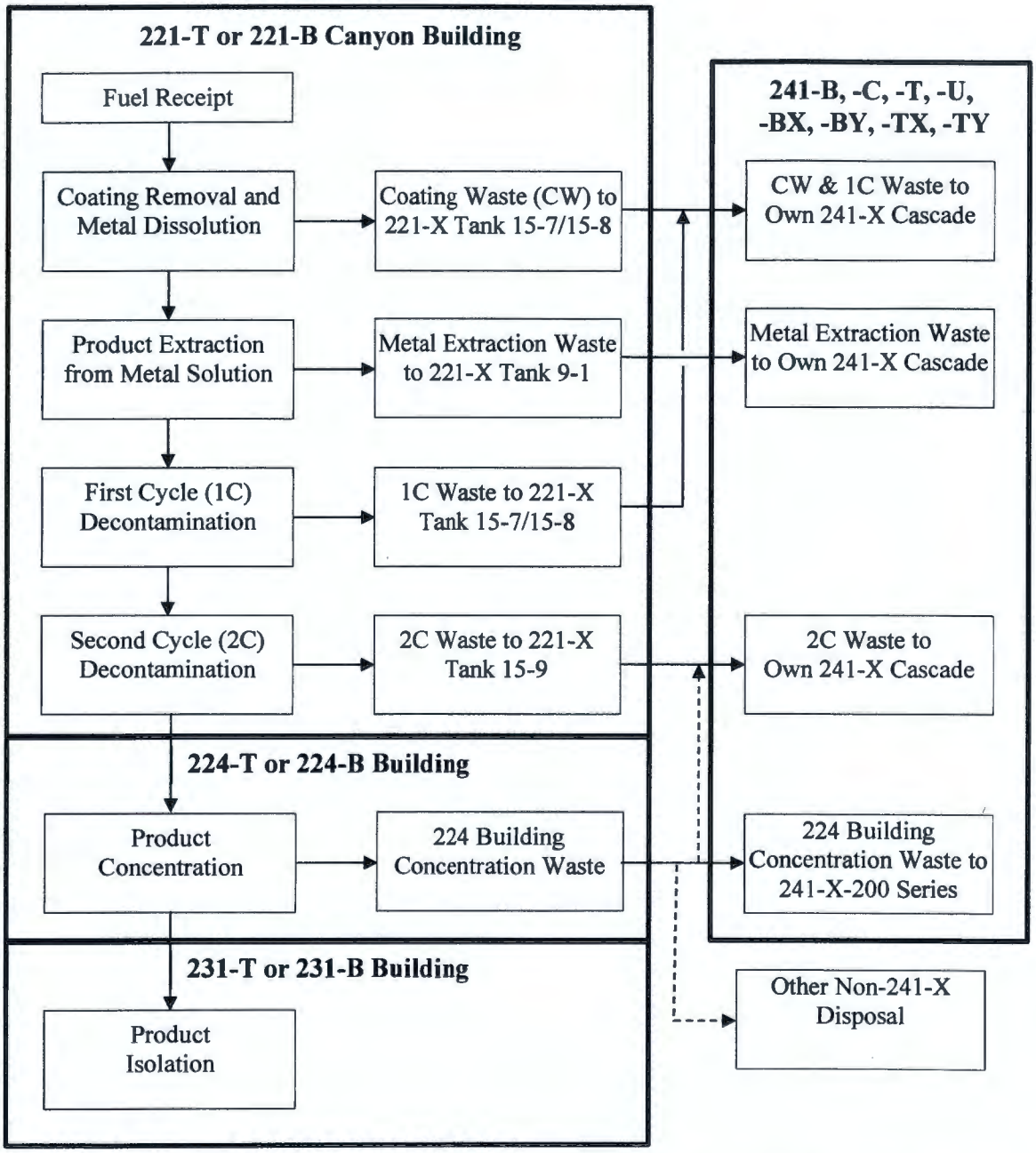


Figure 5-23. Bismuth Phosphate Simplified Schematic Showing Major Waste Streams Sent to Single-Shell Tanks

Two decontamination cycles are performed on the $BiPO_4$ solid carrying the plutonium in order to further remove the fission activity still associated with the plutonium. A decontamination cycle consists of precipitating phosphate-insoluble fission products away from the plutonium solution, then precipitating the plutonium from the solution away from the phosphate-soluble fission products, and finally the plutonium precipitate is redissolved and oxidized for subsequent processing.

In the first decontamination cycle, the dissolved $BiPO_4$ in nitric acid is first diluted to an intermediate nitric acid concentration. A sodium bismuthate slurry is added to the solution followed by addition of a sodium dichromate solution used as a holding oxidant to stabilize the oxidized plutonium. This solution is then diluted via addition of dilution water. A bismuth mononitrate solution is added partially forming the $BiPO_4$ precipitate. This precipitate carries a portion of the phosphate insoluble fission elements while leaving the plutonium in solution. Additional sodium dichromate is added to the solution to maintain the plutonium in solution. Ammonium ceric nitrate [$(NH_4)_2Ce(NO_3)_6$] and zirconium carbonate are added to scavenge cerium and zirconium fission products and phosphoric acid is added to complete precipitation. After centrifugation of the precipitate, it is water washed twice and the plutonium carrying solution and water washes are combined for subsequent plutonium separation. The cerium and zirconium phosphates created from the addition of the scavengers are difficult to remove from the centrifuge. Nitric acid and hydrogen peroxide are alternately added to the centrifuge to dissolve $BiPO_4$ and cerium phosphate, respectively. This leaves a thin slurry of zirconium phosphate which can be removed from the centrifuge. These waste materials are collected in a tank and agitated to complete dissolution of the soluble waste materials. These waste materials are collected in a waste storage tank within the canyon facility. The combination of segregated plutonium carrying solution and water wash solutions is treated with ammonium silicofluoride [$(NH_4)_2SiF_6$] to solubilize remaining phosphate-insoluble fission products which have carried through to this point in the process. Ferrous sulfate/ammonium sulfate [$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$] is added to reduce the plutonium valence state in solution in preparation for precipitation. Bismuth mononitrate in nitric acid is added to the solution followed by addition of phosphoric acid, resulting in $BiPO_4$ precipitate which carries the plutonium. The precipitate is then centrifuged and water washed twice to remove soluble fission products. This wash solution is combined with the other first decontamination cycle wastes. The separated precipitate bearing the plutonium is dissolved in nitric acid. Sodium bismuthate and sodium dichromate are then added to oxidize the plutonium in preparation for further decontamination of the plutonium from residual fission activity. After the first decontamination cycle, the plutonium bearing solution should have less than 1% of the initial fission product activity remaining. The waste streams from the first decontamination cycle are combined for neutralization and subsequent transfer to the tank farms for disposal. Scavenging of first cycle decontamination (1C) waste was initiated on October 20, 1954 (HW-33585-DEL, *Monthly Report Hanford Atomic Products Operation for October 1954*, p. Ed-8). Scavenging was conducted to determine if the supernatant liquid, after settling of precipitate, had low enough concentration long-lived fission products (e.g., cesium and strontium) to allow routine cribbing of the liquid. It was determined that CW and 1C waste had to be segregated to allow cribbing of the 1C waste supernatant. Equipment to separate the two wastes was installed, and routine scavenging of 1C waste was initiated on December 31, 1954 (HW-34631 DEL, *Monthly Report Hanford Atomic Products Operation for January 1955*, p. Ed-9).

The second decontamination cycle differs from the first cycle in that the scavenging chemicals, ammonium ceric nitrate and zirconium carbonate, are not used, the final oxidation of the plutonium in solution is not performed (sodium bismuthate and sodium dichromate are not added), and the volumes of chemicals used is lower. All the waste streams from the second decontamination cycle are combined for neutralization and subsequent transfer to the tank farms for disposal.

After the first and second decontamination cycles, concentration of the plutonium and additional decontamination is required. A mixture of sodium bismuthate and sodium dichromate is added to the plutonium-bearing solution to oxidize the plutonium. Phosphoric acid is added to precipitate $BiPO_4$ leaving the plutonium in solution. The precipitate is centrifuged and water washed. The plutonium-bearing solution and water wash liquid are collected for subsequent processing. The precipitate is dissolved in nitric acid and collected in a waste storage tank. The plutonium in the collected solution is oxidized via addition of potassium permanganate. Anhydrous hydrogen fluoride and subsequently a solution of lanthanum/ammonium nitrate [$La(NO_3)_3 \cdot (NH_4NO_3)_2 \cdot 4H_2O$] and nitric acid (to prevent hydrolysis) are added to the plutonium-bearing solution to precipitate lanthanum fluoride along with fluoride insoluble fission products including lanthanum and other rare earth elements. The lanthanum fluoride precipitate is centrifuged and acid washed with the plutonium-bearing solution and acid washes collected for subsequent processing. The lanthanum fluoride precipitate is slurried from the centrifuge via water additions and collected in the same waste neutralization tank used to store the dissolved $BiPO_4$. The plutonium in the remaining plutonium-bearing solution is reduced by the addition of oxalic acid to the solution. Again, anhydrous hydrogen fluoride and subsequently a solution of lanthanum nitrate and nitric acid are added to the plutonium-bearing solution. The reduced plutonium precipitates along with the lanthanum fluoride. The solid material is centrifuged and acid washed. The filtrate and washings are collected in the same waste neutralization tank as the other wastes from the plutonium concentration process. Water and potassium hydroxide are added to the plutonium-bearing solid to convert (metathesize) the lanthanum and plutonium to insoluble hydroxides. These hydroxides are then water washed to remove residual fluoride. The solution and water washes are collected in the same waste neutralization tank as the other wastes from the plutonium concentration process. The insoluble lanthanum and plutonium hydroxides are dissolved in nitric acid to produce soluble lanthanum and plutonium nitrates.

Following concentration of the plutonium, the plutonium is isolated from the carrier lanthanum and residual contaminants in the plutonium isolation process. The plutonium bearing stream is filtered to remove solids. Ammonium sulfate is added to the solution in preparation for precipitation of the plutonium. To this solution is then added ammonium sulfite to reduce the valence of the plutonium. The solution is then adjusted in nitric acid concentration by the addition of concentrated nitric acid. Hydrogen peroxide is added to form plutonium peroxide precipitate. The precipitate is allowed to settle and the liquid is decanted. The precipitate is washed three times with sulfuric acid. The supernatant liquid and wash liquid is collected in a catch tank. The precipitate is then dissolved in nitric acid and the resulting solution filtered to remove insoluble materials. A second precipitation cycle is employed to the dissolved plutonium solution to improve purity of the product. Water and a small amount of water are first added to the plutonium solution. No ammonium sulfate is used in the second precipitation, only hydrogen peroxide. The precipitate is allowed to settle and is decanted. The precipitate is then washed three times with dilute nitric acid. The supernatant liquid and wash liquid from this second precipitation is combined with the liquids collected from the first precipitation cycle. This collected liquid is treated with sodium nitrite to remove the residual hydrogen peroxide. Potassium permanganate is added to destroy excess nitrite. This stream is then returned to the concentration process to recover plutonium. The precipitate is dissolved in nitric acid. This final solution is concentrated via evaporation of water and nitric acid. Waste solutions from the

isolation process cells and laboratories containing trace plutonium are collected, sampled, neutralized with sodium hydroxide, and jetted to a reverse flow well or crib.

Each of the major waste streams sent to SSTs are discussed below. The available compositional information, temperature data during storage, and corrosion testing data are provided for each stream.

5.5.1.2. Coating Removal Waste (CW)

The coating removal waste (CW) composition is based on HW-10475-C DEL, Chapter IV, and DUH-1687, *Revised Hanford Separation Process Flowsheet*. The irradiated uranium slugs are charged to dissolvers in batches of nominally 6600 lbs (840 slugs at average weight of 7.85 lbs) containing roughly 210-220 lbs of aluminum coating material. The slugs are charged into 4000 lbs (405 gal or 1533 L) of 25% sodium nitrate ($NaNO_3$) (SpG = 1.19). Bring the dissolver solution to boiling, add 1000 lbs (79 gal or 299 liters) of 50% sodium hydroxide (NaOH) (SpG = 1.51). The combined solution consists of nominally 10% NaOH and 20% $NaNO_3$. The $NaNO_3$ suppresses the formation of hydrogen generated in the direct reaction between aluminum and NaOH in the absence of $NaNO_3$.

$$2Al + 2NaOH + 2H_2O \rightarrow 2NaAlO_2 + 3H_2$$

The reactions that proceed in the presence of nitrate are

$$8Al + 5NaOH + 3NaNO_3 + 2H_2O \rightarrow 8NaAlO_2 + 3NH_3$$

$$2Al + 2NaOH + 3NaNO_3 \rightarrow 2NaAlO_2 + 3NaNO_2 + H_2O$$

Several tests have shown that the reaction producing nitrite proceeds at 40-70%. The dissolved aluminum solution in the dissolver, assuming 6600 lbs uranium, 210 lbs aluminum, 50% of the aluminum reacting forming ammonia, and the other 50% forming sodium nitrite results in a solution with the following composition:

NaOH	282 lbs	5.5 %
$NaNO_3$	380 lbs	7.4 %
$NaAlO_2$	638 lbs	12.5 %
Na_2SiO_3	6 lbs	0.1 %
$NaNO_2$	402 lbs	7.9 %
H_2O	3402 lbs	66.5 %
Total	5110 lbs (532 gal)	

During coating removal, a portion of the aluminum-silicon bonding alloy between the aluminum and uranium is dissolved and partly forms scale which is flushed out of the dissolver with the CW.

The quantity of NaOH used suppresses precipitation of aluminum oxide (Al_2O_3) in the CW but is not great enough to cause dissolution of uranium. The $NaNO_3$ suppresses hydrogen at lower

concentration than used, but higher concentrations are more effective at removing solid residues from the dissolver.

After dissolution, 835 lbs (100 gal) of water is used to flush the dissolver. This flush water is sent to the same waste receiver tank as the dissolved aluminum solution.

After water flush, 4300 lbs (500 gal) of 5% nitric acid (HNO_3) is used to wash the dissolver. This acid wash is sent to the same waste receiver tank as the dissolved aluminum solution. The uranium does not appreciably dissolve in the dilute nitric acid wash.

The combined streams from aluminum dissolution, water flush, and acid wash are sufficiently alkaline for storage without any addition of sodium hydroxide. However, the nitric acid present in the dilute acid wash will react with sodium hydroxide from the dissolved aluminum solution when added to the waste receiver tank. The dissolved aluminum solution, water flush, and acid wash when combined in the waste receiver tank has the following composition:

NaOH	145 lbs	1.4 %	0.39 M
$NaNO_3$	670 lbs	6.5 %	0.83 M
$NaAlO_2$	638 lbs	6.2 %	0.82 M
Na_2SiO_3	6 lbs	0.1 %	0.01 M
$NaNO_2$	402 lbs	3.9 %	0.62 M
H_2O	8383 lbs	81.8 %	
Total	10245 lbs (1132 gal)		

A later flowsheet for the $BiPO_4$ process, HW-23043, *Flow Sheets and Flow Diagrams of Precipitation Separations Process*, shows the process in effect in October 1951. Caustic and sodium nitrate usage had not changed between the two flowsheets. Two water washes at a total volume of 300 gal were used in this later flowsheet instead of a water wash and dilute acid wash which was a combined 600 gal. This reduced the coating waste volume by about 300 gal and resulted in higher concentrations of constituents in the waste stream. From HW-23043, the dissolved aluminum solution and water flushes when combined in the waste receiver tank had the following composition:

NaOH	292 lbs	3.7 %	1.09 M
$NaNO_3$	414 lbs	5.2 %	0.73 M
$NaAlO_2$	638 lbs	8.1 %	1.16 M
Na_2SiO_3	27 lbs	0.3 %	0.04 M
$NaNO_2$	375 lbs	4.7 %	0.81 M
H_2O	6154 lbs	78.0 %	
Total	7900 lbs (795 gal)		

Up until 1955, the CW was routinely discharged in batches to the same tank used for collection of the 1C waste. Afterward, they were segregated as part of scavenging operations to allow cribbing of 1C waste supernatant liquid (HW-34631 DEL, p. Ed-9). Storage conditions, temperature data, and corrosion data of the combined CW and 1C waste are discussed in Section 5.5.1.5.

5.5.1.3. Metal Extraction Waste (MW)

The composition of metal waste from extraction (MW) is based on HW-10475-C DEL, Chapter V and IX. The dissolved uranium containing the plutonium as well as fission products is treated with bismuth mononitrate/nitric acid and subsequently phosphoric acid/nitric acid creating a $BiPO_4$ precipitate that carries the plutonium leaving behind the uranium in solution as well as about 90% of the fission product activity, nitric acid, sulfuric acid, phosphoric acid and sodium nitrate. Precipitation and centrifugation operations occur on batches that contain approximately half of the uranium from a dissolver charge. Upon centrifugation, the waste effluent solution is collected in a catch tank along with approximately 1000 lbs of water washes used to wash the precipitate. The combined stream of waste effluent and water washes has the following composition:

$UO_2(NO_3)_2 \cdot 6H_2O$	6950 lbs	21.5 %
HNO_3	290 lbs	0.9 %
H_2SO_4	1150 lbs	3.6 %
H_3PO_4	1823 lbs	5.7 %
$NaNO_3$	222 lbs	0.7 %
H_2O	21965 lbs	67.6 %
Total	32400 lbs (3200 gal)	

This solution is treated with sodium hydroxide and subsequently sodium carbonate. Sodium hydroxide is added in ratio to the amount of phosphoric acid, sulfuric acid, uranium metal. Sodium carbonate is added in ratio to the amount of sodium hydroxide and uranium metal. The ratios added are:

- For each 100 lbs of 73.5% phosphoric acid, add 84.0 lbs of 50% caustic
- For each 100 lbs of 93.0% sulfuric acid, add 136.6 lbs of 50% caustic
- For each 2200 lbs of uranium metal, add 1368.0 lbs of 50% caustic
- For each 100 lbs of 50% caustic required, add 49.2 lbs of 30% sodium carbonate
- For each 2200 lbs of uranium metal, add 12745. lbs of 30% sodium carbonate

The above ratios result in the addition of 5820 lbs of 50% caustic (460 gal). The amount of sodium hydroxide is 90% of that calculated to reach a pH of 7.0. Sodium carbonate addition is based on the formation of bicarbonate plus direct experimental determination of the amount of carbonate required to complex the uranium. The above ratios result in the addition of 19,375 lbs of 30% sodium carbonate (1750 gal). The uranium complex is a mixture of uranium, phosphate, and carbonate. The complex stays in solution at room temperature but precipitates upon elevation of temperature. At 75°C, about ½-¾ of the uranium precipitates in five days. Metal waste generation rate circa February 1946 was on the order of 4700 gal per run (HW-7-450, *Plant Assistance Report – 200 Areas – Weekly (2-27-46 thru 4-3-46)*).

A later flowsheet for the $BiPO_4$ process, HW-23043, shows the process in effect in October 1951. In the later flowsheet a small quantity of mercuric nitrate was added at the end of the dissolver cut. Slight variations exist in the quantity of chemical additions present in both flowsheets. The HW-23043 flowsheet contains a smaller batch size than from HW-10475-C

(roughly 19% of the uranium vs. ½ the uranium from a dissolver charge), but very similar weight percentage values of the main constituents with the exception of phosphoric acid. In January 1946, a one-third reduction in the amount of phosphoric acid used in the extraction process was made to the flowsheet (HW-19140, p. 205). From HW-23043, the MW had the following composition:

$UO_2(NO_3)_2 \cdot 6H_2O$	2615 lbs	18.4 %
HNO_3	110 lbs	0.8 %
H_2SO_4	492 lbs	3.5 %
H_3PO_4	514 lbs	3.6 %
$NaNO_3$	115 lbs	0.8 %
H_2O	10354 lbs	72.9 %
Total	14200 lbs (1443 gal)	

Analytical results from samples taken from 1946 through ca. 1949 of supernatant liquid and sludge in tanks storing MW were documented in a 1949 report in preparation for uranium recovery (HW-14157, *Compilation of Data on Composition of Bismuth Phosphate Process Metal Wastes*). These results along with some pH values documented in another report (HW-8697, *200 Area Waste Uranium Storage*) are presented in Table 5-12.

The MW contained roughly 90% of the fission product activity of the processed fuel and therefore the most significant heat load. The waste was cascaded through a number of tanks with solids precipitating preferentially in the first tank of a cascade. The solids which contained significant heat generating fission products would accumulate in the first tank of a cascade. These solids as they settled would heat up, relative to the supernatant liquid above the solids because heat loss in the solids is limited to conductive rather than convective and evaporative heat transfer. Available temperature data for the tanks containing neutralized MW have been collected in two graphs (HW-3-3369, *200 Area Report Technical Progress Letter Number 81*; HW-7-450; HW-8697; HW-17906 DEL, *Progress Report for April 1950, Process Section, Separations Technology Division*; HW-18812 DEL, *Progress Report for July 1950, Process Section, Separation Technology Division*; HW-19432 DEL, *Progress Report for September 1950, Process Section, Separation Technology Division*; HW-20201 DEL, *Progress Report for December 1950, Process Section, Separation Technology Division*). Records do not indicate the depth in the tank at which the temperature readings were taken. The first graph, Figure 5-24, lists those tanks used for storage of neutralized MW in the 200 West Area in support of T Plant operations. The second graph, Figure 5-25, lists those tanks used for storage of neutralized MW in the 200 East Area in support of B Plant operations.

For the most part, the temperature of MW stored in tanks was relatively low. First tanks in cascades had higher temperatures than subsequent tanks during active filling of the tanks. With the exception of three tanks (BX-101, BX-104 and TX-105), available data shows that no early tanks storing MW exceeded 200°F.

Table 5-12. Ionic Constituent and pH Results for Bismuth Phosphate Process Metal Waste from Extraction Supernatant and Sludge Stored at 241-T and 241-U Circa 1946-1949 (2 Pages)

Waste	Sample Date	Measured pH	Constituent Concentration, (g/L and [M])					
			U	Na^+	PO_4^{-3}	SO_4^{-2}	CO_3^{-2}	NO_3^{-2}
Supernatant								
T-101	12/12/46	10.1	--	--	--	--	--	--
T-101	7/1/47	10.0	6.7 [0.0282]	--	38.5 [0.405]	28.4 [0.296]	--	--
T-101	8/26/47	--	5.8 [0.0244]	--	35.1 [0.369]	--	--	--
T-101	ca. 1947	--	6.7 [0.0282]	70.3 [3.06]	31. [0.33]	23.8 [0.248]	27. [0.45]	35. [0.085]
T-102	7/1/47	9.9	24.0 [0.101]	--	31. [0.33]	27.1 [0.282]	--	--
T-102	8/26/47	--	21.8 [0.0916]	--	28.9 [0.304]	--	--	--
T-102	ca. 1947	--	21.5 [0.0903]	67.2 [2.92]	25.0 [0.263]	17.0 [0.177]	30.4 [0.507]	47.8 [0.771]
T-103	7/1/47	9.8	26.6 [0.112]	--	34.0 [0.358]	25.0 [0.260]	--	--
T-103	8/26/47	--	24.6 [0.103]	--	32.4 [0.341]	--	--	--
T-103	ca. 1947-48	--	26.4 [0.111]	76.1 [3.31]	25.4 [0.267]	21.6 [0.225]	54.7 [0.912]	37.4 [0.603]
T Composite	ca. 1948	--	19.0 [0.0800]	78.4 [3.41]	33.0 [0.347]	26.7 [0.278]	42.9 [0.715]	33.7 [0.543]
U-103	ca. 1948-49	--	20. [0.084]	34. [1.48]	10. [0.105]	11. [0.115]	20. [0.33]	23. [0.37]
U-103	ca. 1948-49	--	20. [0.084]	37. [1.61]	10. [0.105]	11. [0.115]	18. [0.30]	24. [0.39]
Sludge								
T-101	ca. 1947	--	112. [0.471]	116. [5.04]	111. [1.17]	24. [0.25]	3. [0.05]	51. [0.82]
T-101	ca. 1947	--	134. [0.563]	85. [3.70]	134. [1.41]	22. [0.23]	1. [0.02]	16. [0.26]
T-101	ca. 1948	--	162. [0.681]	104. [4.52]	128. [1.35]	19. [0.20]	15.8 [0.263]	--
T-101	ca. 1948	--	204. [0.857]	116. [5.04]	102. [1.07]	12. [0.125]	25.6 [0.427]	--
T-101	ca. 1948	--	363. [1.53]	137. [5.96]	48. [0.505]	8. [0.08]	115. [1.92]	--
T-101	ca. 1948	--	346. [1.45]	151. [6.57]	16. [0.17]	8. [0.08]	255. [4.25]	--
T-101	ca. 1948	--	365. [1.53]	146. [6.35]	15. [0.16]	6. [0.06]	263. [4.38]	--
U-101	ca. 1948-49	--	329. [1.38]	127. [5.52]	61. [0.64]	2.80 [0.0292]	181. [3.02]	2. [0.03]
U-101	ca. 1948-49	--	263. [1.11]	94. [4.09]	49. [0.52]	2.05 [0.0214]	166. [2.77]	3. [0.05]
U-101	ca. 1948-49	--	273. [1.15]	123. [5.35]	53. [0.56]	2.54 [0.0265]	162. [2.70]	3.5 [0.056]
U-101	ca. 1948-49	--	266. [1.12]	108. [4.70]	52. [0.55]	3.03 [0.0316]	41. [0.68]	2. [0.03]
U-102	ca. 1948-49	--	106. [0.445]	109. [4.74]	136. [1.43]	5.08 [0.0529]	69. [1.15]	3. [0.05]
U-102	ca. 1948-49	--	152. [0.639]	85. [3.70]	105. [1.11]	9.26 [0.0965]	90. [1.50]	2. [0.03]

Constituent concentrations taken from HW-14157. Reported pH values from HW-8697.

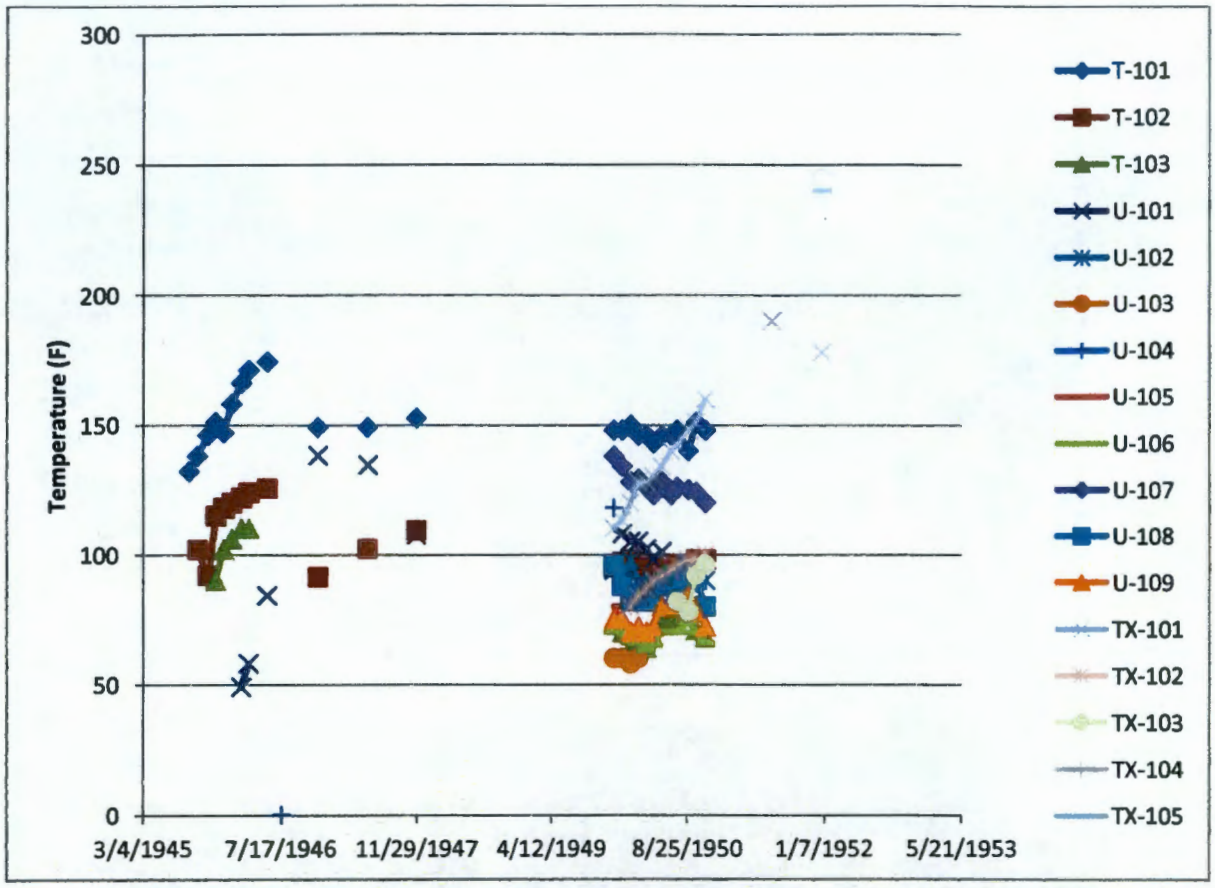


Figure 5-24. 200 West Area Metal Waste Tank Temperatures, 1945-1952

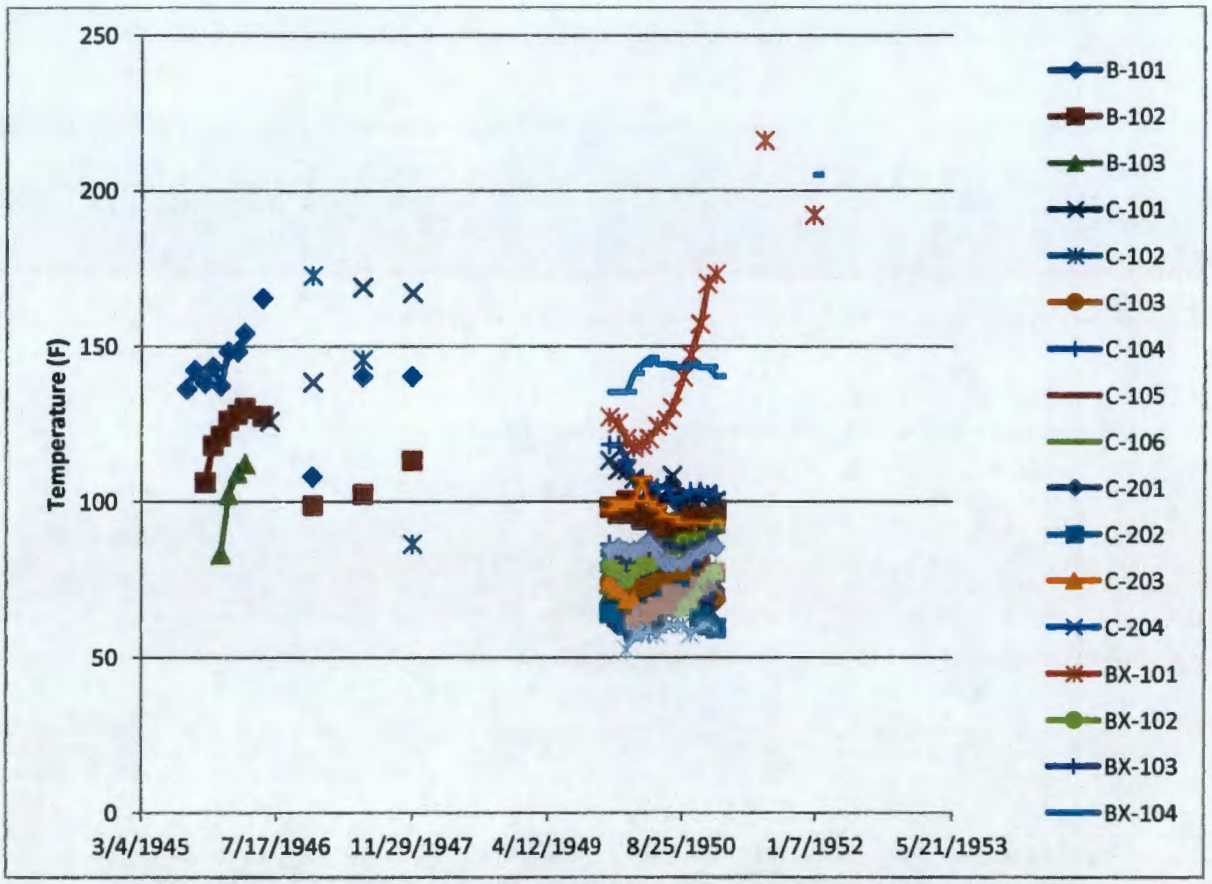


Figure 5-25. 200 East Area Metal Waste Tank Temperatures, 1945-1952

In 1949, a report was issued, HW-14946, to identify available corrosion data specific to waste solutions in the 200 Area SSTs. At that point in time, only one document (out of seventy surveyed) recorded the corrosive effect of synthetic $BiPO_4$ process waste solutions on mild steel. Additionally, one document discussed the effect of dissolving tank waste sludge in sulfuric acid on mild carbon steel, but that is beyond the scope of this report. The synthetic waste solutions tested include supernatant liquid from carbonate neutralized metal waste solution and alkaline 20% slurry of barium, zirconium, and carbonate precipitates from waste metal solution. Tests were performed at boiling temperatures using mild steel. No indication of the carbon content of the steel was provided. Four separate tests were performed for each solution and test durations ranged from 65 to 138 hours. The measured corrosion rate for the supernatant liquid ranged from none to 0.6 mil/yr. The measured corrosion rate for the precipitates from waste metal solution ranged from 0.04 to 0.4 mil/yr. These are quite low corrosion rates, measured at the material boiling point when generally, tanks containing MW are stored at appreciably lower temperatures. No indication of other corrosion mechanisms (e.g., SCC) was provided in the HW-14946 report.

In 1950, a report was issued, HW-18595, *Corrosion of REDOX Waste Storage Tank Construction Materials*, primarily reporting the results of corrosion testing of REDOX waste on storage tank construction materials. The report also included some test results for carbon steel

subjected to "200A Waste (Synthetic) (UNH)" at pH 10 and 11. The given composition of the waste tested was similar to metal waste, as given below:

$UO_2(NO_3)_2 \cdot 6H_2O$	120-140 g/L	0.24-0.28 M
PO_4	24-28 g/L	0.25-0.29 M
SO_4	24-28 g/L	0.25-0.29 M
CO_3	42-45 g/L	0.70-0.75 M
Na	90-100 g/L	3.91-4.35 M

Specimens of SAE 1010 and 1020 were subjected to the waste composition above for up to 7.6 months. For each material type, a set of welded specimens and a set of welded and stressed specimens were prepared for both wastes at pH 10 and pH 11 for a total of eight sets of specimens. The as welded specimens were prepared from stock plates under field conditions by qualified welders using a Lincoln semi-automatic welding machine and Lincoln automatic rod type L-60. Standard procedures for welding this type material were followed. The final dimensions of these specimens were 2 in. x 4 in. x 3/8 in. The weld ran longitudinally through the center of the specimen. The welded and stressed specimens were welded in the same fashion as the as-welded specimens, however, their final dimensions were 1 in. x 6 in. x 3/8 in. and instead the weld ran transversely through the center of the specimen. The specimens were pre-stressed into the shape of a U, by bending around an arbor, through 180 degrees with the inside radius of the bend at ¾ in. The weld was at the bottom of the U. Travel rate of the stress die was 1-in. per minute. Final stressing was accomplished by means of stainless steel nuts and bolts which joined the legs of the U to maintain comparable stressing of each specimen. The stainless steel nuts and bolts were insulated from the mild steel by Lucite washers.

The weld beads of the SAE 1010 specimens were left as welded prior to stressing and no failures due to stressing were noted. In the case of the SAE 1020 steel specimens, cracks were noted at the toe of the welds after approximately a 160 degree bend so new test specimens were prepared by grinding the weld beads flush prior to stressing. This condition was less severe and no weld failures were noted. All samples were sandblasted to insure clean surfaces, duplicating field practices. The welded (non-stressed) specimens were partially immersed in the test solution and the welded and stressed specimens were fully immersed in the test solution. All tests were run at 70°C +/-1°C (158°F +/-2°F) without aeration, except what occurred from convective currents. Test solutions were air saturated at the start of the tests. Only two of the eight sets of test specimens showed cumulative weight loss during the test period. These two sets were the partial immersion tests of SAE 1010 and pH 10 and 11, with uniform corrosion rates of 0.14 and 0.09 mil/yr, respectively. Specimens were generally identified as being in good or fair condition and sound at the end of the test with varying amounts of superficial rust spots and discoloration on immersed portions and rust and scale on vapor portions. There was no mention of cracking or pitting in any of the specimens.

In 1952, corrosion tests of SAE 1010 mild steel specimens were performed with simulated MW at boiling (102°C) for 424 to 472 hours (HW-24136). The corrosion test specimens were fabricated from samples of the SAE 1010 grade mild steel plate used in the construction of BY Farm. The corrosion results for specimens immersed in liquid, at the liquid-vapor interface, and in the vapor space of boiling synthetic MW are provided in Table 5-13. The pH of the solution

was 10.5 at 25°C. The study found, "...pit-depth measurements and corrosion rates observed for a short exposure period do not fully show what may be occurring within the storage tanks...The pitting was severe...for the short time that the specimens were exposed."

The study concluded that extensive pitting occurred in the vapor phase and there was no evidence of accelerated attack at the solution-vapor interface. Immersed specimens were not pitted and very low general corrosion rates occurred.

Table 5-13. Corrosion Rates of Polished SAE 1010 Steel Coupons Exposed to Boiling Synthetic Metal Waste Solution

Condition Location	Specimen Number	Corrosion Data				
		Average Pit (mil)	Average Pit Pitting Rate (mil/yr)	Deepest Pit (mil)	Deepest Pit Pitting Rate (mil/yr)	Uniform Corrosion Rate (mil/yr)
Liquid	3F-76	--	--	--	--	0.09
	3F-79	--	--	--	--	0.08
Liquid Vapor Interface	3F-77	0.7	13	0.8	14	--
	3F-80	1.3	26	1.7	35	--
Vapor	3F-78	0.8	14	0.9	17	0.09
	3F-81	1.2	24	1.8	37	0.08

Data taken from HW-24136, Table 3. Values converted to mil and mil/yr from inches and inches/month in original table.

In 1953, results were reported for field corrosion testing of low carbon steel specimens in SSTs containing MW solution, 1C solution, and concentrated 1C solution (HW-28901, *Technical Activities Report, Corrosion and Welding, July 1953*). The SAE 1020 steel corrosion test coupons had been exposed in the $BiPO_4$ process waste storage tanks for 7-8 months between November 1952 and June 1953. The specimens were recovered and examined in the 111-B Building Radiometallurgy Facility to determine corrosion rates of the waste tank liners under actual service conditions. In this field test, two sets of specimens were placed in each of three tanks representative of the process waste solutions, one set in the vapor over the solution and one set in the solution supernatant. The data obtained from the specimens that were recovered indicate that at least one of the media investigated – the vapors over the MW solution – is corrosive to SAE 1020 steel. Specimens were exposed in tank TX-105 (MW solution). The vapor exposure specimens placed in tank TX-105 were recovered, but the supernatant exposure specimens were lost and could not be recovered. The set of specimens contained three polished and three sandblasted coupons, insulated from one another by Teflon and held together by steel plates. The sets of specimens were held in position by stainless steel wires during the exposure period. Two types of measurements were made: (1) weight loss measurements were obtained from specimen weights before and after exposure, and uniform corrosion rates were calculated from these weight losses; (2) pit depth measurements were made using a macroscope and microscope, and pitting corrosion rates were calculated from the pit depths.

The most corrosive of the media for which data were obtained was the vapor over the MW solution. Both the polished and sandblasted specimens were severely attacked in this media and very little of the original surface remained. Specimen weight measurements taken after exposure show that 0.27-0.33 g was lost during the seven month exposure period. The uniform corrosion rate for these specimens, calculated on the basis that the reaction rate was constant over the total

exposure period, is 0.2 x 10^{-3} in. penetration per month (2.4 mil/yr). Deep pits were observed on all parts of the specimen, except in that region covered by the Teflon strip during exposure. The deepest pit observed was 11.2 mils in depth while the average depth of the measured pits was 6 mils. The specimens were exposed in the MW solution (tank TX-105) during a period when the temperature of the solution had dropped off from an unknown maximum, and the corrosion rate of the tank wall may have been higher during the first part of the service period. No field information is available regarding the corrosion rate of the steel liner exposed to the MW solution itself. The service may be more corrosive due to the higher temperature of the solution and sludge, as compared to the vapor; on the other hand, the pH of these solutions is 10 or above, whereas the vapor over the MW solution may be less basic. No field information is available regarding the corrosion rate as a function of time. In laboratory corrosion tests of SAE 1010 steel exposed to vapors over boiling simulated MW solution, the maximum pit depth observed after 424 hours exposure was 1.8 mils (see above). In the field test the maximum pit depth observed after 5400 hours exposure was 11.2 mils. If it is assumed that the two media were equally corrosive, it appears that the pitting corrosion rate is decreasing slightly with time.

5.5.1.4. First Cycle Decontamination (1C) Waste

The composition of 1C waste from the original process flowsheet, HW-10475-C DEL, based on Chapters VI and IX, is based on half the uranium from a 6600-lb uranium dissolver charge. In the first decontamination cycle, the first precipitation step is performed to remove phosphate insoluble fission element while leaving the plutonium in solution. These solids are subsequently treated with nitric acid and hydrogen peroxide to dissolve $BiPO_4$ and cerium phosphate. These solutions and a slurry of zirconium phosphate are collected in a waste storage tank within the processing facility. This stream of waste effluent has the following composition:

$BiPO_4$	138 lbs	4.0 %
$CePO_4$	2 lbs	0.06 %
$Zr(PO_4)_4$	2.3 lbs	0.06 %
HNO_3	1823 lbs	43.7 %
H_2O_2	Nil	--
H_3PO_4	1 lbs	0.03 %
H_2O	1797 lbs	52.1 %
Total	3450 lbs (310 gal)	

A later flowsheet for the $BiPO_4$ process, HW-23043, shows the process in effect in October 1951. First cycle decontamination waste quantities from this flowsheet are based on smaller batches (about 19% of the uranium from a 6600-lb uranium dissolver charge). The process is very similar resulting in only minor variations in the relative composition of constituents in the waste slurry. Most notable is the doubling in volume from about 620 gal per 6600 lbs of uranium to 1220 gal per 6600 lbs of uranium processed. From HW-23043, the phosphate insoluble portion of 1C waste had the following composition:

$BiPO_4$	64.1 lbs	2.6 %
$CePO_4$	0.9 lbs	0.04 %
$Zr(PO_4)_4$	1.1 lbs	0.04 %
HNO_3	870 lbs	35.3 %
H_2O_2	Nil	--
H_3PO_4	Nil	--
H_2O	1529 lbs	62.0 %
Total	2465 lbs (232 gal)	

The second precipitation step is performed to precipitate plutonium away from phosphate soluble fission elements. The plutonium precipitate is separated from the soluble fission elements and water washed. The solution bearing phosphate soluble fission elements and the water wash are combined with the previous waste associated with removal of phosphate insoluble fission elements. The stream of waste effluent containing the soluble fission elements has the following composition:

HNO_3	1681 lbs	5.70 %
H_3PO_4	1595 lbs	5.38 %
$Fe_2(SO_4)_3$	199 lbs	0.67 %
$Cr(NO_3)_3$	15 lbs	0.05 %
$(NH_4)_2SO_4$	65 lbs	0.22 %
$(NH_4)_2SiF_6$	220 lbs	0.75 %
$NaNO_3$	5 lbs	0.02 %
NH_4NO_3	80 lbs	0.27 %
H_2O	25,770 lbs	86.94 %
Total	29,630 lbs (3290 gal)	

The later flowsheet, HW-23043, shows that the process in effect in October 1951 is very similar to the earlier flowsheet resulting in only minor variations in the relative composition of constituents in the insoluble fission element portion of the 1C waste. Most notable are the reduction in phosphoric acid and about 1000 gal increase in waste volume per 6600 lbs of uranium processed. From HW-23043, the phosphate insoluble portion of the 1C waste had the following composition:

HNO_3	692 lbs	5.5 %
H_3PO_4	441 lbs	3.5 %
$Fe_2(SO_4)_3$	84 lbs	0.7 %
$Cr(NO_3)_3$	13 lbs	0.1 %
$(NH_4)_2SO_4$	28 lbs	0.2 %
$(NH_4)_2SiF_6$	92 lbs	0.7 %
$NaNO_3$	9 lbs	0.07 %
NH_4NO_3	34 lbs	0.3 %
H_2O	11,308 lbs	89.0 %
Total	12,700 lbs (1430 gal)	

The combined waste streams from the first decontamination cycle are neutralized with sodium hydroxide. Initially (from HW-10475-C), the calculated basis for neutralization is based on 10% excess over the theoretical amounts to reach a pH of 7. The quantity of 50% sodium hydroxide required to neutralize each of the process solutions to a pH of 7, determined experimentally are:

- For each 100 lbs of 60% nitric acid, add 79.1 lbs of 50% caustic
- For each 100 lbs of 73.5% phosphoric acid/1.5% nitric acid, add 116.3 lbs of 50% caustic
- For each 100 lbs of 14% $(NH_4)_2SiF_6$ solution, add 29.2 lbs of 50% caustic
- For each 100 lbs of 24% $BiONO_3$ solution, add 27.4 lbs of 50% caustic
- For each 100 lbs of 20% Fe solution, add 0.7 lbs of 50% caustic

The neutralized wastes contain suspended solids, hydroxides and/or phosphates of bismuth, scavenger metals, chromium and iron and probably sodium silicofluoride. It was expected that these solids would carry 90% of the fission product activity.

In a report issued October 1945 (less than a year after first operation), it was found that neutralization of 1C and second decontamination cycle (2C) waste with 10% excess caustic resulted in a considerable amount of plutonium and fission product activity, along with appreciable amounts of dissolved bismuth, staying in solution because of the relatively high pH (9.5-10.2) rather than precipitating in the solid phase (HW-3-3220, *SE-PC #82, A Study of Decontamination Cycle Waste Solutions and Methods of Preparing them for Disposal*). One of the goals of the study was to reduce the amount of plutonium and fission products in the 2C waste stream sent to the tank farms so the supernatant liquid could be disposed to ground after passing through a cascade of SSTs. The lower pH would also reduce the demand for 50% caustic used in the processing plants. Studies showed that neutralizing the 1C and 2C wastes at pH's 5-7 resulted in wastes that were relatively non-corrosive for the steel-lined first and second cycle SST receivers. Recommendations were made to neutralize 1C and 2C waste to pH 6-7 in order to more completely precipitate the plutonium and fission product activity in the waste streams and to reduce the demand on caustic additions.

Samples from July 1945 showed the pH of 1C waste in 200 East Area (tank B-107) and 200 West Area (tank T-107) were both 10.2 (HW-3-3220). A titration curve was developed for the second half of the first cycle product waste solution obtained from the processing plant. Calculations were made to determine the amount of 50% caustic needed to neutralize 1C waste to various pH's. The practice at the time of the study was to add 397 gal of 50% caustic to the first half and 226 gal of 50% caustic to the second half of the 1C waste (0.17 gal 50% caustic/gal waste), resulting in a pH of ~10.2. To arrive at a pH of 7, these amounts of 50% caustic were reduced to 346 gal for the first half and 195 gal for the second half of the waste stream (0.15 gal 50% caustic/gal waste). HW-3-3220 states, "One of the recommendations of this report, namely the neutralization of decontamination wastes to pH 7, has already been adopted in the plant", at the time of the report, October 1945. The 1951 flowsheet, HW-23043, shows 0.13 gal 50% caustic/gal waste. This reduction in caustic addition could be explained by the reduction in both nitric acid and phosphoric acid used in the 1C process that ended up in the waste stream.

At the caustic additions required to neutralize to a pH 7, the total 1C waste (first half and second half combined) volume, simplistically assuming additive volumes, results in 8280 gal per 6600 lbs of uranium charged.

Samples of neutralized decontamination cycle wastes were obtained from the neutralization tanks within T Plant for the purpose of determining the final pH of the waste (HW-7-450). Results for three different runs were presented for the two halves of both the 1C and 2C waste streams. Results for the neutralized 1C waste are shown below:

	First Decontamination Cycle Waste	
Run	First Half	Second Half
T-6-02-B-18	5.9	8.0
T-6-02-B-19	7.9	7.9
T-6-02-B-20	7.0	6.5

From HW-23043, the 1951 $BiPO_4$ flowsheet, neutralized 1C waste has the following composition:

Bi^{+3}	0.24%	2.59 g/L	0.01	M
Ce^{+4}	0.0027%	0.030 g/L	0.0002	M
Zr^{+4}	0.0027%	0.030 g/L	0.0003	M
Fe^{+3}	0.13%	1.37 g/L	0.02	M
Cr^{+3}	0.015%	0.16 g/L	0.003	M
NH_4^+	0.18%	1.98 g/L	0.12	M
Na^+	4.3%	47.3 g/L	2.0	M
SiF_6^{-2}	0.40%	4.35 g/L	0.03	M
PO_4^{-3}	2.4%	26.2 g/L	0.28	M
NO_3^-	8.5%	93.1 g/L	1.5	M
SO_4^{-2}	0.43%	4.73 g/L	0.05	M
H_2O	83.3%	--		

Corrosion tests of SAE 1010 mild steel polished and sandblasted specimens were performed with simulated 1C wastes in the pH range 6-8 at 80°C for 3-6 months (HW-26202, *A Study of the Effect of pH of First Cycle Bismuth Phosphate Waste on the Corrosion of Mild Steel*). The corrosion test specimens were fabricated from samples of the SAE 1010 grade mild steel plate used in the construction of the BY Farm.

The corrosion results for specimens immersed in and at the liquid-vapor interface of 1C wastes are provided in Table 5-14. The study concluded, "...there is no basis for a correlation between the corrosion rate of mild steel and the pH of 1C waste in the pH range 6 to 8 for specimens exposed in the liquid or for specimens exposed at the liquid-vapor interface." The report goes on to state that several pits developed on one face of one of the polished specimens totally immersed in liquid at pH 6 and then speculated these pits may have come from inclusions in the steel.

Corrosion tests were also performed in the vapor phase over the liquid waste. The corrosion results for specimens in the vapor phase above simulated 1C wastes are provided in Table 5-15. The report, HW-26202, identifies significantly lower rate of corrosion of mild steel exposed to the vapors for pH 7 and above, compared to pH 6. Conjecture was given that the lower corrosion rates were due to the presence of ammonia in the vapor at higher pH which inhibited the corrosion rate. No details were given for the ammonia content of the vapor phase but it was considered the ammonia content varied widely during the execution of the testing. Finally, HW-26202 also reports the average depth of the deepest pits on polished specimens. These pitting results are provided in Table 5-16. The pit depth rate of increase was calculated in HW-26202 for the vapor phase over pH 6 solution. Between 2 and 3 months of exposure the calculated pit depth growth rate was 3.2 mil/yr. This is a relatively short period of time to extrapolate extended duration pit growth and may overestimate the pit depth growth rate.

Table 5-14. Corrosion Rates for Duplicate Specimens of SAE 1010 Mild Steel in Simulated Bismuth Phosphate Process First Cycle Waste at 80°C (+/- 2°C)

Specimen	Condition Location	Exposure Time	General Corrosion Rate (mil/yr)			
			pH 6	pH 7	pH 7	pH 8
Polished	Liquid-Vapor Interface	3 months	0.37 0.35	0.12 --	gain gain	0.25 gain
		6 months	0.1 0.06	0.02 0.06	0.01 0.02	0.01 nil
	Immersed	3 months	0.1 0.08	0.05 0.06	0.01 0.05	0.07 0.06
		6 months	0.04 0.04	0.01 gain	nil nil	Gain gain
Sandblasted	Liquid-Vapor Interface	3 months	0.20 0.26	gain nil	gain nil	gain 0.1
		6 months	0.17 0.12	0.01 0.06	nil 0.06	0.01 0.01
	Immersed	3 months	0.06 0.12	0.06 0.08	0.08 0.1	0.1 0.1
		6 months	0.05 0.07	gain gain	nil nil	gain gain

Data taken from HW-26202, Table 3. Values converted to mil/yr from 10^{-5} inches/month in original table.

Table 5-15. Corrosion Rates for Duplicate Polished Specimens of SAE 1010 Mild Steel Exposed to Vapors over Simulated Bismuth Phosphate Process First Cycle Waste at 80°C (+/- 2°C)

Specimen	Condition Location	Exposure Time	General Corrosion Rate (mil/yr)			
			pH 6	pH 7	pH 7	pH 8
Polished	Vapor Phase	1 month	5.0 6.7	4.2 3.1	-- --	2.5 3.1
		2 months	3.2 1.7	1.2 1.3	-- --	0.8 0.6
		3 months	2.9 2.0	0.5 0.4	0.2 0.8	1. 0.2

Data taken from HW-26202, Table 4. Values converted to mil/yr from 10^{-5} inches/month in original table.

Table 5-16. Average Depth of Eight Deepest Pits Noted on Duplicate Specimens of SAE 1010 Mild Steel in Simulated Bismuth Phosphate Process First Cycle Waste at 80°C (+/- 2°C)

Specimen	Condition Location	Exposure Time	Average Depth of Eight Deepest Pits (mil)			
			pH 6	pH 7	pH 7	pH 8
Polished	Liquid-Vapor Interface	3 months	0.91 1.18	1.38 1.38 (7)*	1.50 1.62 (4)	1.70 1.85 (6)
		6 months	1.06 1.38	1.38 1.70 (4)	1.30 1.22	0.87 (6) 1.06 (5)
	Vapor	1 months	1.46 1.42	2.20 1.97	-- --	1.62 1.62
		2 months	2.17 1.62	2.17 2.13	-- --	1.22 1.26
		3 months	2.24 2.09	2.17 1.85	0.67 0.83	1.02 0.51

Data taken from HW-26202, Table 5.

* Number in parentheses indicates the number of pits upon which the average measurement is based, when fewer than eight measurements were made.

Up until 1955, the 1C waste was discharged in batches to the same tank used for collection of CW. Storage conditions, temperature data, and corrosion data of the combined CW and 1C wastes are discussed in Section 5.5.1.5. After 1954, the 1C waste was segregated from CW as part of scavenging operations to improve cesium scavenging allowing cribbing of 1C waste supernatant liquid (HW-34631 DEL, p. Ed-9). From HW-33184, *$BiPO_4$ Plant Nickel Ferrocyanide Scavenging Flowsheet for First-Cycle Waste Containing No Coating-Removal Waste*, September 1954, the flowsheet for nickel ferrocyanide scavenging of $BiPO_4$ neutralized 1C waste (without CW) has the following composition:

	Scavenger Formation Waste	Supernatant Liquid for Cribbing	Stored Sludge[1]
$Ce_4(PO_4)_3$	0.0001 M		0.0005 M
$Zr_4(PO_4)_3$	0.0002 M		0.0010 M
Cr^{+3}	0.002 M	0.0024 M	
NH_4^+	0.137 M	0.164 M	
Na^+	2.31 M	2.77 M	
$Ni_2Fe(CN)_6$	0.0025 M		0.0125 M
$K_4Fe(CN)_6$	0.0025 M		
$FePO_4$	0.036 M		0.181 M
$BiPO_4$	0.018 M		0.09 M
SiF_6^{-2}	0.032 M	0.038 M	
PO_4^{-3}	0.254 M	0.30 M	
NO_3^-	1.83 M	2.20 M	
SO_4^{-2}	0.077 M	0.092 M	
K^+		0.024 M	
$Fe(CN)_6^{-4}$	0.0025 M		0.0125 M

[1] Sludge volume is 20% of the scavenged, neutralized waste volume.

The neutralized 1C, scavenger formation waste, and supernatant liquid have slightly higher concentrations of the major cations (ammonium, sodium) and anions (nitrate, phosphate, and sulfate) than neutralized 1C waste prior to scavenging of the waste. No corrosion data was found for the 1C waste from nickel ferrocyanide scavenging. It is expected data previously provided for 1C waste is fairly representative of the waste during scavenging operation.

5.5.1.5. Combined Coating Removal Waste (CW) and First Cycle Decontamination (1C) Waste

Circa March 1946, combined CW and 1C waste was generated at 4700 gal per run according to HW-7-450, without defining "run". In comparison, 1132 gal of CW per 6600 lbs of uranium charge is stated in the early flowsheet (HW-10475-C) as presented in Section 5.5.1.2, and 4141 gal of 1C waste per 3300 lbs of uranium processed through the first decontamination cycle (and subsequent process steps) as presented in Section 5.5.1.4. If a "run" consists of the processing of 3300 lbs of uranium through the process, then the HW-10475-C flowsheet would produce 4707 gal per run. The HW-10475-C flowsheet combined CW and 1C waste volume is the same value reported in HW-7-450. Nominally, the combined waste stream in the tank consists of 12% CW and 88% 1C waste, on an equivalent uranium basis.

Based on the 1951 flowsheet, HW-23043, 795 gal of CW and 10,900 gal neutralized 1C waste was generated per 6600 lbs of uranium charged to a dissolver. This is about a 25% volume increase in the volume of waste generated. Per HW-23043, processing of a 6600 lbs charge of uranium slugs resulted in the following CW and 1C waste shown in Table 5-17.

Table 5-17. Flowsheet-Based* Composition and Quantity of Combined Coating Removal Waste and Neutralized First Cycle Decontamination Waste from Bismuth Phosphate Process for Processing 6600 Pounds Uranium (2 Pages)

Constituent	Coating Removal Waste		Neutralized First Cycle Decontamination Waste		Combined Waste		
	Pounds	Wt%	Pounds	Wt%	Pounds	Wt%	M
Bi^{+3}	--	--	234	0.24%	234	0.22%	0.012
Ce^{+4}	--	--	2.7	0.0027%	2.7	0.0025%	0.00020
Zr^{+4}	--	--	2.7	0.0027%	2.7	0.0025%	0.00030
Fe^{+3}	--	--	124	0.13%	124	0.12%	0.023
Cr^{+3}	--	--	15	0.015%	15	0.014%	0.0029
NH_4^+	--	--	179	0.18%	179	0.17%	0.11
Na^+	590	7.5%	4271	4.3%	4862	4.6%	2.2
AlO_2^-	459	5.8%	--	--	459	0.43%	0.080
SiO_3^-	21	0.3%	--	--	21	0.019%	0.0028
SiF_6^{-2}	--	--	393	0.40%	393	0.37%	0.028
PO_4^{-3}	--	--	2374	2.4%	2374	2.2%	0.26
OH^-	124	1.6%	--	--	124	0.12%	0.075
NO_2^-	250	3.2%	--	--	250	0.24%	0.056
NO_3^-	302	3.8%	8407	8.5%	8709	8.2%	1.4
SO_4^{-2}	--	--	428	0.43%	428	0.40%	0.046

Table 5-17. Flowsheet-Based* Composition and Quantity of Combined Coating Removal Waste and Neutralized First Cycle Decontamination Waste from Bismuth Phosphate Process for Processing 6600 Pounds Uranium (2 Pages)

Constituent	Coating Removal Waste		Neutralized First Cycle Decontamination Waste		Combined Waste		
	Pounds	Wt%	Pounds	Wt%	Pounds	Wt%	M
H_2O	6154	77.9%	82037	83.3%	88191	82.9%	
Total	7900		98468		106368		
Volume (gal)	795		10858		11653		

* Constituents and values based on HW-23043.

Field corrosion tests of SAE 1020 steel polished and sandblasted specimens were performed with 1C waste (tank TX-109) and concentrated 1C waste (tank TX-117) for 7 months (HW-30641). Tests were performed to understand the corrosion rate and condition of the steel liners exposed to the vapor phase and liquid phase in each of the tanks. Unfortunately, it was not possible to recover the specimens in tank TX-117. The corrosion results for specimens immersed in the waste and in the vapor in tank TX-109 are provided in Table 5-18. The study concluded, "...the field data confirm earlier laboratory findings, namely, that neither the liquid nor the vapor is seriously corrosive to mild steel."

Table 5-18. Field Corrosion Rates of SAE 1020 Steel Coupons Exposed in First Cycle Waste Solution Tank 241-TX-109 for Seven Months (November 1952 - June 1953)

Condition Location	Specimen Type	Specimen Number	Corrosion Data		
			Deepest Pit (mil)	Deepest Pit Pitting Rate (mil/yr)	Uniform Corrosion Rate (mil/yr)
Vapor	Polished	4F-10	1.0	1.8	0.06
		4F-11	1.0	1.8	0.04
		4F-12	1.5	2.5	0.05
		Average	1.2	2.0	0.05
	Sandblasted	4F-28	2.0	3.4	0.05
		4F-29	1.9	3.2	0.1
		4F-30	1.1	1.8	0.16
		Average	1.7	2.8	0.1
Liquid	Polished	4F-1	2.0	3.4	0.18
		4F-2	1.9	4.1	0.14
		4F-3	1.1	2.3	0.1
		Average	1.7	2.8	0.14
	Sandblasted	4F-19	1.4	2.4	0.26
		4F-20	1.6	2.8	0.25
		4F-21	2.1	3.6	0.28
		Average	1.7	3.0	0.26

Data taken from HW-30641, Table 1. Values converted to mil and mil/yr from inches and inches/month in original table.

The combined CW and 1C waste contained roughly 10% of the fission product activity of the processed fuel and therefore substantially less heat load than the MW. The waste was cascaded through a number of tanks. The solids which contained the majority of heat generating fission products would accumulate in the first tank of a cascade. These solids as they settled would heat up, relative to the supernatant liquid above the solids because heat loss in the solids is limited to

conductive rather than convective and evaporative heat transfer. Available temperature data for the tanks containing CW and 1C waste have been collected in two graphs (HW-3-3369, HW-7-450, HW-8697, HW-17906 DEL, HW-18812 DEL, HW-19432 DEL, and HW-20201 DEL). Records do not indicate the depth in the tank at which the temperature readings were taken. The first graph, Figure 5-26, lists those tanks used for storage of CW and 1C waste in the 200 West Area in support of T Plant operations. The second graph, Figure 5-27, lists those tanks used for storage of CW and 1C waste in the 200 East Area in support of B Plant operations.

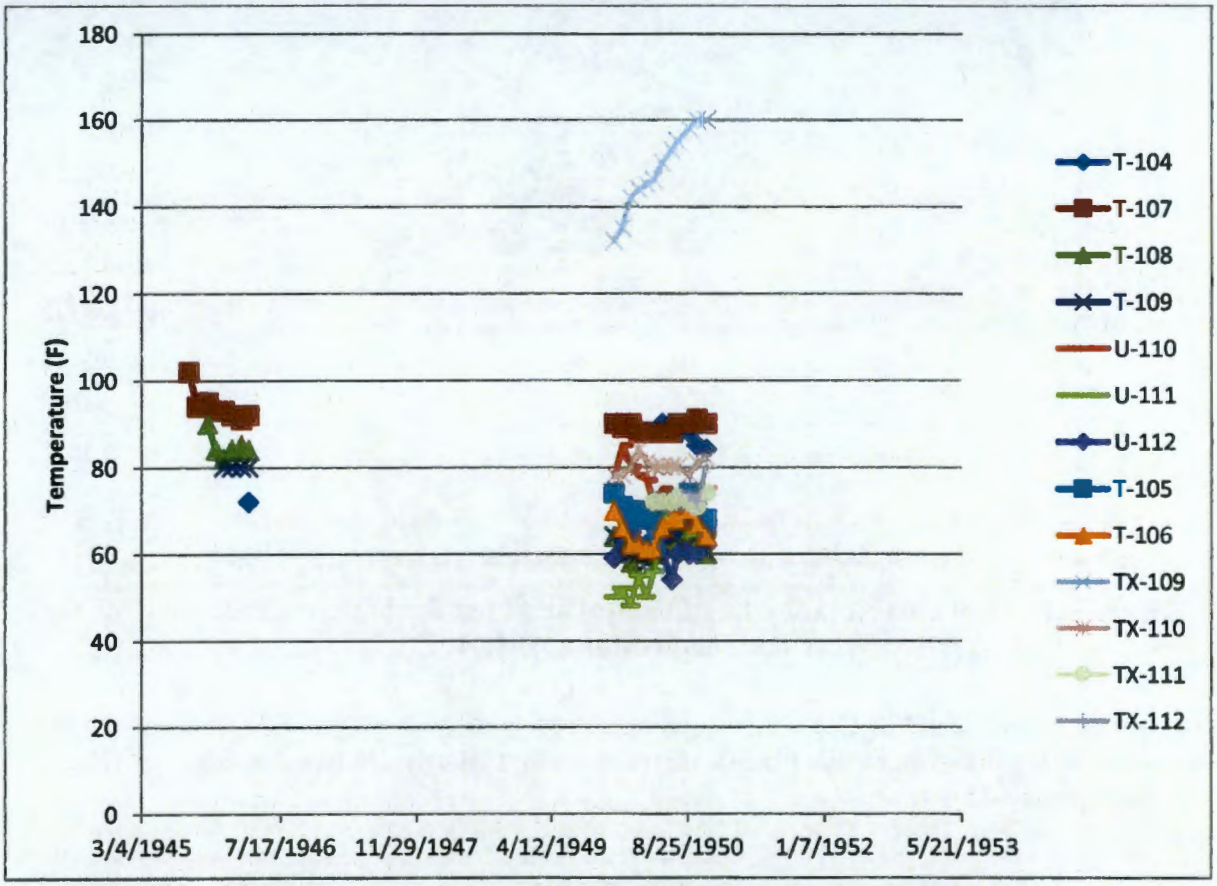


Figure 5-26. 200 West Area Coating Removal and First Cycle Decontamination Waste Tank Temperatures, 1945-1952

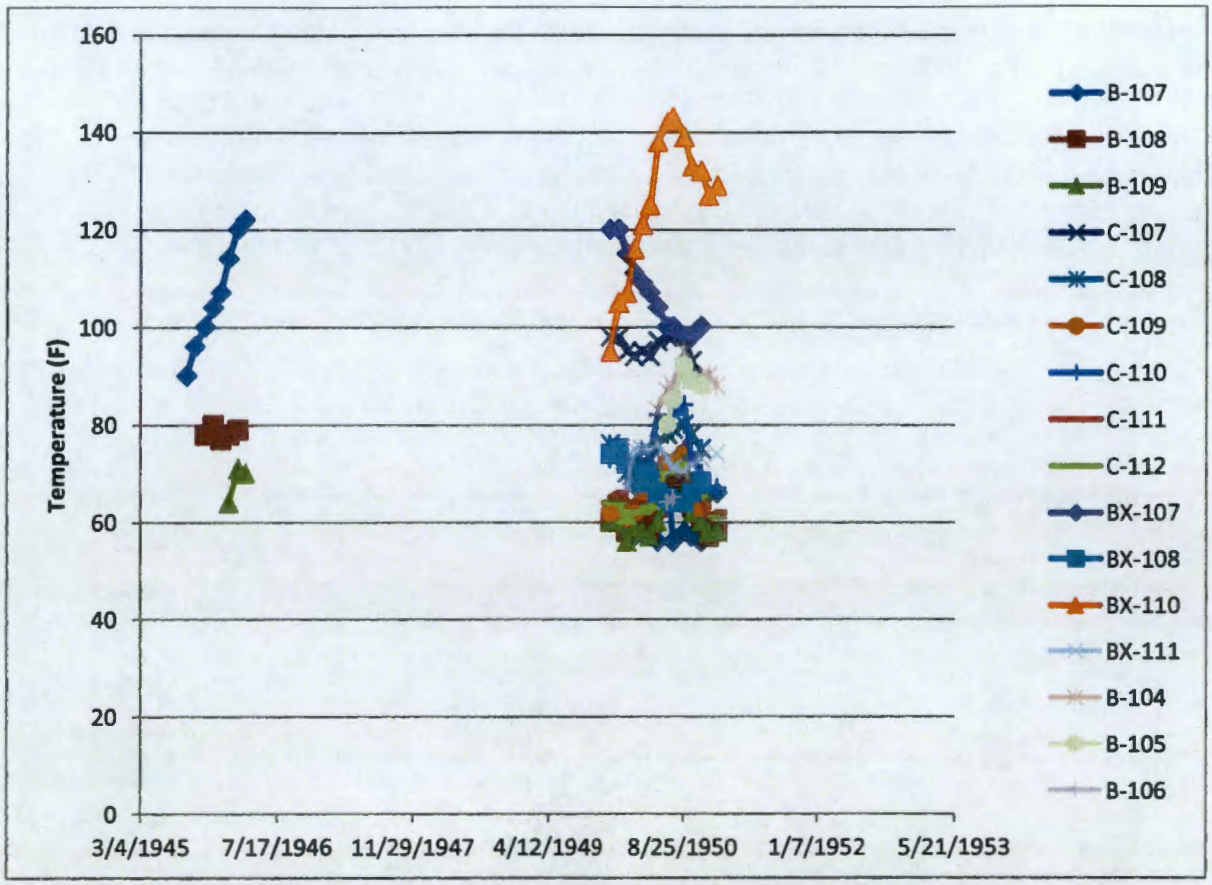


Figure 5-27. 200 East Area Coating Removal and First Cycle Decontamination Waste Tank Temperatures, 1945-1952

No specific reports could be found investigating corrosion of the combined CW and neutralized 1C waste. Corrosion data for the pH 6-8 1C waste was previously discussed in Section 5.5.1.4 and is not repeated here.

5.5.1.6. Second Cycle Decontamination (2C) Waste

The composition of 2C waste from the original process flowsheet, HW-10475-C DEL, based on Chapter VI and IX, is based on half the uranium from a 6600 lbs of uranium dissolver charge. The process steps from the second decontamination cycle are similar to the first decontamination cycle and result in similar waste streams but smaller volumes. The stream containing the phosphate insoluble fission elements has the following composition:

$BiPO_4$	69 lbs	3.9 %
HNO_3	660 lbs	36.9 %
H_2O	1061 lbs	59.2 %
Total	1790 lbs (170 gal)	

A later flowsheet for the $BiPO_4$ process, HW-23043, shows the process in effect in October 1951. Second cycle decontamination waste quantities from this flowsheet are based on smaller batches (about 19% of the uranium from a 6600 lbs uranium dissolver charge). From HW-23043, the phosphate insoluble portion of the 2C waste had the following composition:

$BiPO_4$	33.0 lbs	3.3 %
HNO_3	462 lbs	46.2 %
H_2O	505 lbs	50.5 %
Total	1000 lbs (90 gal)	

The second precipitation step is performed to precipitate plutonium away from phosphate soluble fission elements. The plutonium precipitate is separated from the soluble fission elements and water washed. The solution bearing phosphate soluble fission elements and the water wash is combined with the previous waste associated with removal of phosphate insoluble fission elements. The stream of waste effluent containing the soluble fission elements has the following composition:

HNO_3	1262 lbs	5.12 %
H_3PO_4	1311 lbs	5.33 %
$Fe_2(SO_4)_3$	161 lbs	0.65 %
$Cr(NO_3)_3$	15 lbs	0.06 %
$(NH_4)_2SO_4$	53 lbs	0.22 %
$(NH_4)_2SiF_6$	163 lbs	0.66 %
$NaNO_3$	5 lbs	0.02 %
NH_4NO_3	64 lbs	0.26 %
H_2O	21,616 lbs	87.68 %
Total	24,650 lbs (2800 gal)	

The later flowsheet, HW-23043, shows that the process in effect in October 1951 is very similar to the earlier flowsheet resulting in only minor variations in the relative composition of constituents in the insoluble fission element portion of the 2C waste. Most notable is the increase of over 2000 gal in waste volume per 6600 lbs of uranium processed. From HW-23043, the phosphate insoluble portion of the 1C waste had the following composition:

HNO_3	589.1 lbs	4.4 %
H_3PO_4	401.8 lbs	3.0 %
$Fe_2(SO_4)_3$	76 lbs	0.6 %
$Cr(NO_3)_3$	5.1 lbs	0.04 %
$(NH_4)_2SO_4$	25.1 lbs	0.2 %
$(NH_4)_2SiF_6$	79.8 lbs	0.6 %
$NaNO_3$	4.5 lbs	0.03 %
NH_4NO_3	30.4 lbs	0.2 %
H_2O	12,088 lbs	90.9 %
Total	13,300 lbs (1513 gal)	

The combined waste streams from the second decontamination cycle are neutralized with sodium hydroxide. Initially (from HW-10475-C), the calculated basis for neutralization is based on 10% excess over the theoretical amounts to reach a pH of 7. The quantity of 50% sodium hydroxide required is identical to that listed in Section 5.5.1.4. The study and recommendations discussing reduction in pH to 6-7 of 1C waste in Section 5.5.1.4 also applies to 2C waste.

A sample from July 1945 showed the pH of 2C waste in 200 West Area (tank T-110) was 9.8 (HW-3-3220). Similar to 1C waste, a titration curve was developed and calculations made to determine the amount of 50% caustic needed to neutralize 2C waste to various pHs. The practice at the time of the study was to add 250 gal of 50% caustic to the first half and 175 gal of 50% caustic to the second half of the 2C waste (0.14 gal 50% caustic/gal waste), resulting in a pH of ~10. To arrive at a pH of 7, these amounts of 50% caustic were reduced to 218 gal for the first half and 139 gal for the second half of the waste stream (0.12 gal 50% caustic/gal waste). Document HW-3-3220 states, "One of the recommendations of this report, namely the neutralization of decontamination wastes to pH 7, has already been adopted in the plant", at the time of the report, October 1945. The 1951 flowsheet, HW-23043, shows 0.11 gal 50% caustic/gal waste. In addition to the recommendation to neutralize 1C and 2C waste to pH 6-7, an additional recommendation was made in HW-3-3220 specifically for 2C waste. That recommendation was to neutralize current waste to a pH of 5-6 in order that they may carry some reserve acidity to the tanks but without causing corrosion of the tanks. The recommendation was to continue the practice until the pH measurement of the solution in the first tank in the cascade receiving 2C waste (tanks T-110 or B-110) attained the desired value of approximately 7. No record was found whether or not this recommendation was carried out. However, pH measurements reported on October 18, 1946 (HAN-45762, *200 Area Daily Logs from June 3 to December 31, 1946*) for tanks T-110, T-111 and T-112 show all three tanks had a pH of 6.3 at that time.

At the caustic additions required to neutralize to a pH 7, the total 2C waste (first half and second half combined) volume, simplistically assuming additive volumes, results in 6650 gal per 6600 lbs of uranium processed (based on HW-10475-C waste volumes).

Samples of neutralized decontamination cycle wastes were obtained from the neutralization tanks within T Plant for the purpose of determining the final pH of the waste (HW-7-450). Results for three different runs were presented for the two halves of both the 1C and 2C waste streams. Results for the neutralized 2C waste are shown below:

	Second Decontamination Cycle Waste pH	
Run	First Half	Second Half
T-6-02-B-18	6.4	6.6
T-6-02-B-19	6.1	6.1
T-6-02-B-20	6.2	6.3

From HW-23043, the 1951 $BiPO_4$ flowsheet, neutralized 2C waste has the following composition:

Bi^{+3}	0.12%	1.31 g/L	0.006	M
Fe^{+3}	0.173%	1.82 g/L	0.033	M
Cr^{+3}	0.006%	0.06 g/L	0.001	M
NH_4^+	0.16%	1.71 g/L	0.103	M
Na^+	3.5%	36.7 g/L	1.63	M
SiF_6^{-2}	0.35%	3.67 g/L	0.026	M
PO_4^{-3}	2.2%	23.0 g/L	0.247	M
NO_3^-	5.8%	61.3 g/L	1.01	M
SO_4^{-2}	0.34%	3.61 g/L	0.038	M
H_2O	83.3%	--		

Corrosion studies have not been located dealing specifically with 2C waste. Because of similarity in composition to 1C waste, results for those studies may be indicative of corrosion rates in 2C waste. Corrosion rate results for 1C waste were presented in Table 5-14 through Table 5-16.

Because of the lower fission product content of 2C waste in comparison to 1C waste, lower waste temperatures were associated with 2C waste storage in SSTs. The 2C waste contained roughly 1% of the fission product activity of the processed fuel. The waste was cascaded through a number of tanks. The solids, which contained the majority of heat generating fission products, would accumulate in the first tank of a cascade. These solids as they settled would heat up, relative to the supernatant liquid above the solids because heat loss in the solids is limited to conductive rather than convective and evaporative heat transfer. Available temperature data for the tanks containing 2C waste have been collected in two graphs (HW-3-3369, HW-7-450, HW-8697, HW-17906 DEL, HW-18812 DEL, HW-19432 DEL, and HW-20201 DEL). Records do not indicate the depth in the tank at which the temperature readings were taken. The first graph, Figure 5-28, lists those tanks used for storage of CW and 2C waste in the 200 West Area in support of T Plant operations. The second graph, Figure 5-29, lists those tanks used for storage of CW and 2C waste in the 200 East Area in support of B Plant operations.

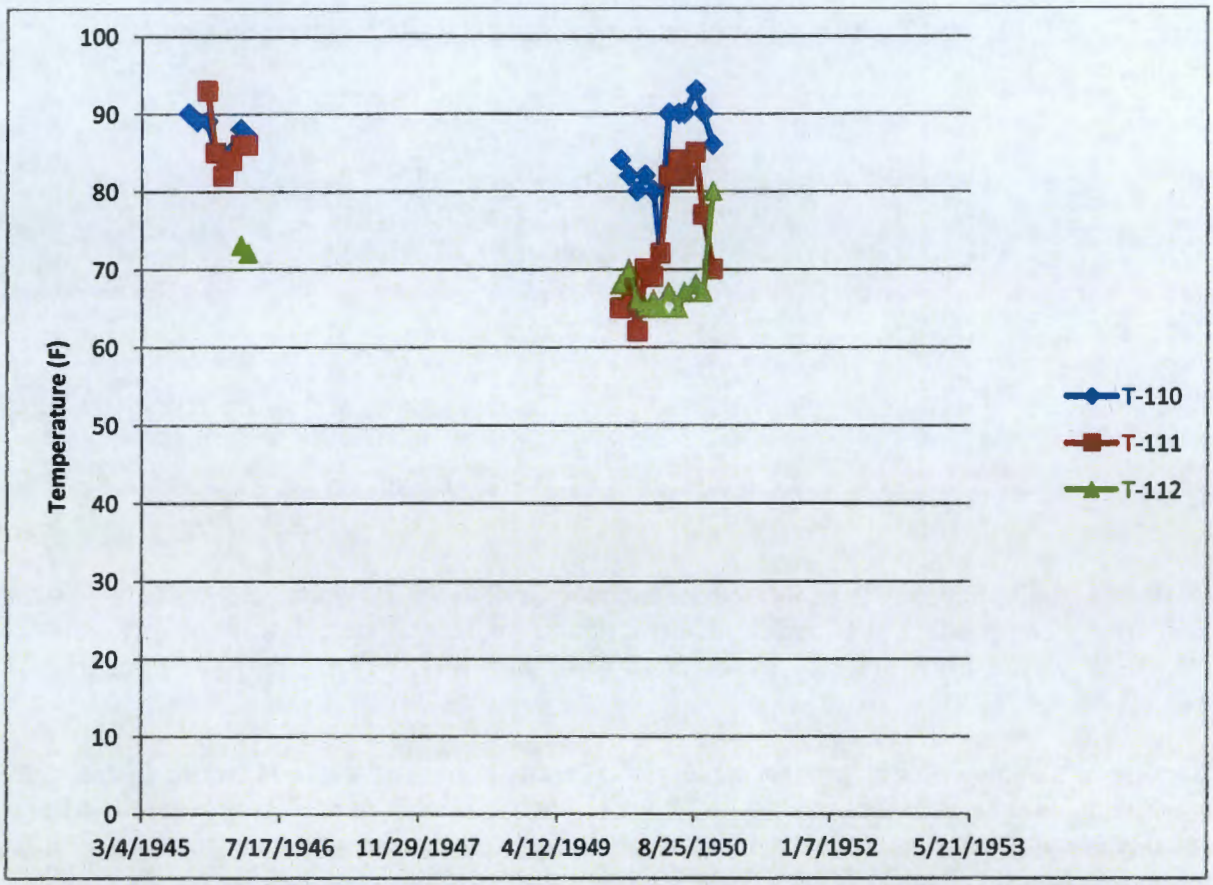


Figure 5-28. 200 West Area Second Decontamination Cycle Waste Tank Temperatures, 1945-1952

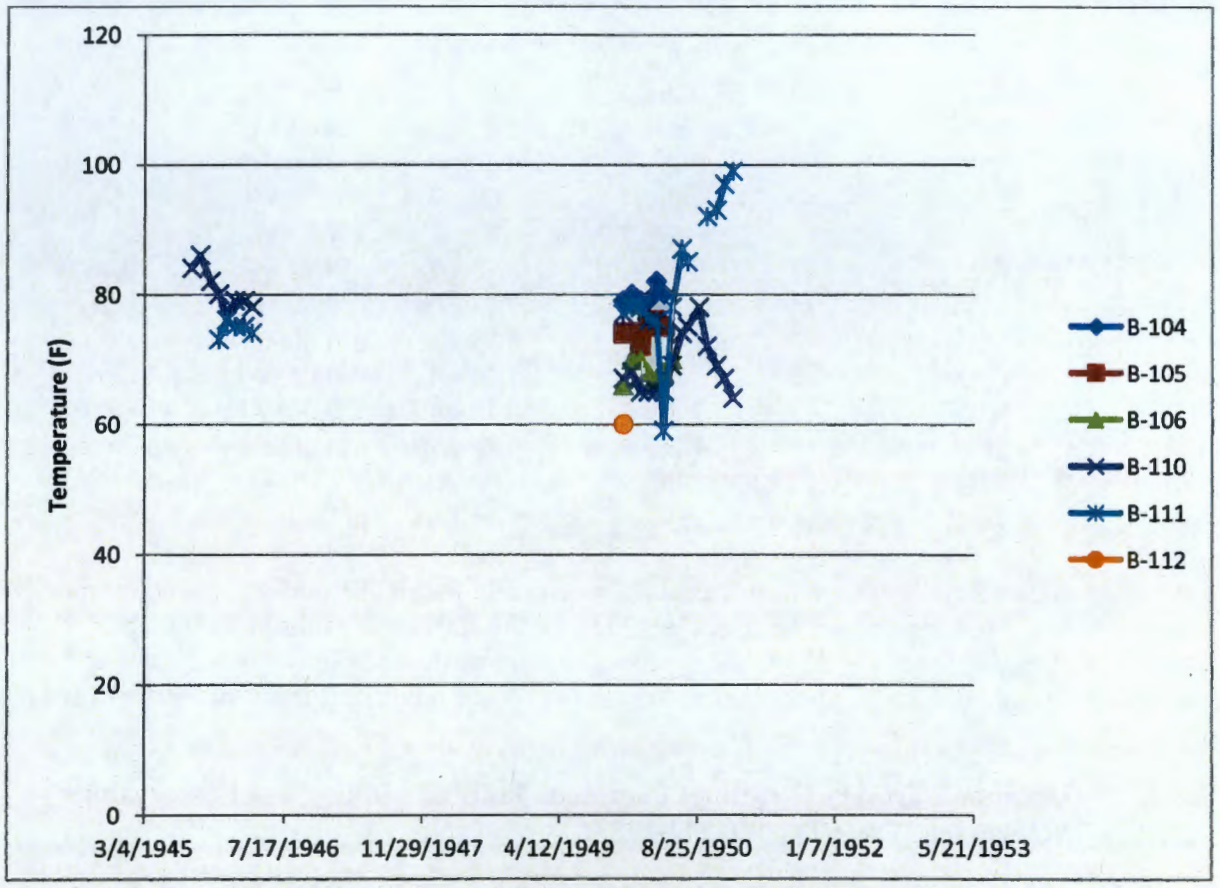


Figure 5-29. 200 East Area Second Decontamination Cycle Waste Tank Temperatures, 1945-1952

5.5.1.7. 224 Building Concentration Waste

The original process flowsheet, HW-10475-C DEL, does not provide a composition for 224 Building concentration waste. The flowsheet describes several different waste streams that are processed through the waste processing equipment and these streams may be processed individually or in combination. A later flowsheet in effect in October 1951 for the $BiPO_4$ process, HW-23043, provides a neutralized waste composition for 224 Building concentration waste. This neutralized waste is described as being buffered at a pH of approximately 10 and containing precipitates. From HW-23043, the 224 Building neutralized waste in the waste tank had the following composition:

Bi^{+3}	21.7 lbs	1.18 g/L	0.0056 M
PO_4^{-3}	55.9 lbs	3.05 g/L	0.032 M
NO_3^-	778 lbs	42.4 g/L	0.68 M
La^{+3}	9.0 lbs	0.49 g/L	0.0035 M
F^-	103 lbs	5.60 g/L	0.29 M
Na^+	675 lbs	36.8 g/L	1.6 M
K^+	157 lbs	8.53 g/L	0.22 M
Cr^{+3}	3.1 lbs	0.17 g/L	0.0033 M
Mn^{+2}	6.1 lbs	0.33 g/L	0.0060 M
$C_2O_4^{-2}$	23.7 lbs	1.29 g/L	0.015 M
NH_4^+	2.2 lbs	0.12 g/L	0.0067 M
SO_4^{-2}	6.4 lbs	0.35 g/L	0.0036 M
H_2O	18,059 lbs		
Total	19,900 lbs (2200 gal)	SpG = 1.08	pH ≈ 10

Corrosion studies have not been located dealing specifically with 224 Building concentration waste. Early waste temperatures were not recorded for the 200-Series tanks but would be expected to be quite low. The 224 Building concentration waste would have very little heat producing fission products or plutonium and thus not produce much heat from radioactive decay.

5.5.2 Uranium Recovery (Tri-Butyl Phosphate Process) and In-Plant Ferrocyanide Scavenging Waste Types (1952-1957)

The $BiPO_4$ separations plants were designed solely to perform the function of extracting and decontaminating plutonium from the uranium and fission products contained in irradiated uranium slugs. The uranium, together with fission products, small amounts of plutonium, and chemical wastes from the $BiPO_4$ process had been allowed to accumulate in the SSTs. Due to a shortage of high grade uranium ore ca. 1950, the recovery of the uranium stored in the SSTs was seen as critical to the continued success of the Atomic Energy Program (HW-19400, *An Introduction to the TBP and UO_3 Plants*, p. 19). Uranium recovery consisted of three component processes: removal of $BiPO_4$ process uranium waste (metal waste from extraction) from underground storage via sluicing; decontamination of the uranium from plutonium and fission products via the TBP process; and, conversion of decontaminated uranium to uranium trioxide (UO_3) powder via the UO_3 process. The TBP process operated for five years from the start of flowsheet shakedown runs with UNH starting June 13, 1952 (HW-24928, *Hanford Works Monthly Report for June 1952*, p. Ed-4) until final process flushing of 221-U canyon on April 12, 1957 (HW-50089, *Chemical Processing Department Monthly Report, April, 1957*, p. E-6). Sluicing of waste is not considered a potentially likely failure mechanism for tank liners (see Section 4.4.7). The UO_3 process at the UO_3 Plant did not produce any major streams sent to SSTs. The focus of this section will be on the TBP process and waste stream from the TBP process.

5.5.2.1. Tri-Butyl Phosphate Process Description

The following process description is based on HW-19140 and HW-24301, *TBP Plant Operating Procedure*. The TBP process uses the preferential extractability of uranyl nitrate by TBP to separate uranium from the plutonium and fission products with which it is associated in the $BiPO_4$ process metal waste. Uranyl nitrate, the product of uranium dissolution in nitric acid, is very soluble in aqueous solutions and forms an organic-soluble complex with TBP. When an aqueous solution containing uranyl nitrate is contacted with an organic solution containing TBP, the uranium can be preferentially transferred into the organic phase by adding a salting agent (nitrate or nitric acid) to the aqueous phase. The fission elements and plutonium, if maintained trivalent, remain in the aqueous phase. This preferential distribution makes the separation of uranium from plutonium and fission products possible in the TBP process. Figure 5-30 provides a simplified schematic identifying the major waste stream of the $BiPO_4$ process.

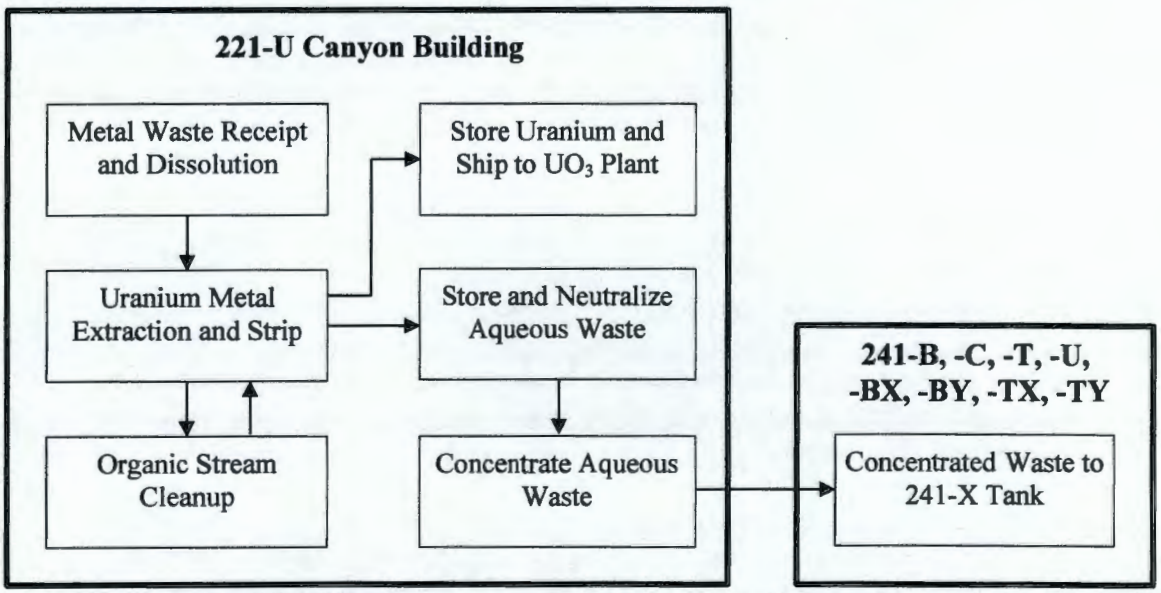


Figure 5-30. Metal Recovery or Tributyl Phosphate Process Simplified Schematic Showing Major Waste Stream Sent to Single-Shell Tanks

The first process step within the TBP plant is feed preparation. Blended metal waste sludge and supernatant liquid are fed to an agitated dissolver tank containing excess nitric acid. The excess nitric acid, beyond what is needed to dissolve the sludge, acts as a salting agent in the subsequent solvent extraction process. The dissolved and acidified feed solution is adjusted in acidity, as necessary. Depending upon the particular flowsheet used, this feed solution is or is not concentrated prior to processing through solvent extraction (HW-18169, *TBP (Tributyl Phosphate) Waste Metal Recovery Process Chemical Flowsheet TBP HW#4*; and, HW-18232, *BP (Tributyl Phosphate) Waste Metal Recovery Process Chemical Flowsheet, TBP HW #5*). No waste streams are generated from the feed preparation step that report to the SSTs.

The uranium-bearing solution from the feed preparation step is continuously pumped to an intermediate point between the top and bottom of the first solvent extraction column (RA column). An organic stream consisting of TBP dissolved in a hydrocarbon diluent is introduced

at the bottom of the column. As the feed stream and organic stream contact each other in the column, uranium transfers from the aqueous stream to the organic stream which is rising up through the column. At the top of the column an aqueous scrub stream is added containing nitric acid, sulfamic acid, and ferrous ammonium sulfate. The nitric acid is added in the scrub stream to extract residual fission products and plutonium from the rising organic stream. The ferrous ammonium sulfate and sulfamic acid are added to maintain plutonium in the trivalent state. The aqueous waste effluent that exits at the bottom of this first solvent extraction column is the RAW stream. The RAW stream contains the bulk of the fission products, plutonium, and other undesirable ions (e.g., SO_4^{-2}, PO_4^{-3}, etc.). The RAW stream is sent to waste treatment where it is treated along with the ROW stream (see below).

The uranium-bearing organic stream from the first solvent extraction column is sent to the bottom of a second column (RC column). Here the organic stream is contacted with an aqueous stream to strip the uranium out of the organic stream back into the aqueous stream. The organic stream is then put through a solvent treatment process (discussed later) to clean it of residual contaminants before being sent back to the first solvent extraction column. The aqueous stream contains a dilute concentration of uranium which is subsequently concentrated as part of the UO_3 plant operation.

The TBP-bearing, hydrocarbon diluent organic stream, after going through the solvent extraction process, contains traces of fission products and plutonium as well as solvent decomposition products formed as a result of contact of the solvent with the process solutions. The solvent is treated in a separate solvent extraction column (RO column). The contaminated solvent is introduced at the bottom of the column and contacted with an aqueous scrub solution that strips out the plutonium, fission products and degradation products from the organic stream. The aqueous effluent from the RO column, the ROW stream, is sent to waste treatment where it is treated along with the RAW stream.

The RAW and ROW waste streams are combined in a receiver tank. When the tank is filled it is sent to a sampling tank and sampled to determine the amount of 50% caustic to be added to neutralize the contents. The contents of the sample tank are transferred to the neutralization tank and 50% caustic is added at a rate controlled by the waste transfer rate into the tank. Waste is neutralized to a minimum pH of 9.5 per the flowsheet. When ready, the neutralized waste is transferred from the neutralization tank to the waste concentrator feed tank. Waste from the waste concentrator feed tank is fed to the waste concentrator where water is boiled off increasing the specific gravity of the waste. The concentrated waste from the evaporator is sent to a concentrated waste receiver tank. The concentrated waste is maintained above a minimum specific gravity of 1.32 at a temperature of 80°C. The concentrated waste is pumped to the 241-WR Diverter Station waste pump tank, TK-WR-001, where it is directed to a particular SST. The concentrated waste is maintained at 80°C in the concentrated waste receiver tank.

A later flowsheet, TBP HW-6 flowsheet (HW-29466, *TBP HW No. 6 Flowsheet*), was developed to provide adequate decontamination during processing of stored uranium-bearing wastes aged less than approximately four years. The two solvent extraction batteries which were operated in parallel under the original flowsheets were then operated in series instead. The TBP concentration is increased (30% instead of 12.5%) over the previous flowsheets. The waste from the second decontamination cycle is backcycled as a scrub solution in the first cycle. In support

of this the acidified metal waste feed is more dilute. In the first extraction column, the scrub solution at the top of the column is changed to demineralized water and the backcycle stream from the second decontamination cycle enters the midpoint of the scrub section. The second extraction column also employs demineralized water at the top of the scrub section and an intermediate scrub solution. For the second extraction column, the intermediate scrub solution is ferrous ammonium sulfate and sulfamic acid. No changes were identified to the aqueous waste collection, neutralization or concentration as part of the revised flowsheet.

A process was developed to scavenge the long-lived fission products from TBP Plant wastes, for the purpose of producing a large volume of supernatant liquid which could be cribbed and a small volume of sludge which required continued storage in the SSTs. On a test basis, approximately 500,000 gal of aqueous waste (produced October 10 to 18, 1953), were scavenged with $Ni_2Fe(CN)_6$, and stored in tank T-101. These tests confirmed cesium and strontium could be reduced through scavenging to low enough levels to allow discharge of the liquid waste to cribs (HW-29850, *Progress Report – Chemical Development Unit, Separations Technology Sub-Section Technical Section, Engineering Department, October, 1953*).

In April 1954, a study (HW-30041, *Corrosion Effects of Lowering the pH in TBP Waste Storage Tanks*) was conducted to determine the effect, if any, of lowering of the pH at which TBP waste is stored would have on the corrosion rate of SAE 1020 carbon steel, simulating the waste tank liner. Synthetic waste solution was made to flowsheet specifications from HW-19140. An additional solution was made for an alternate flowsheet with the same waste composition with the exception 0.05 M oxalic acid and 0.25 M sodium oxalate were substituted for 0.05 M ferrous ammonium sulfate and 0.10 M sulfamic acid. This study concluded, "...there is no significant difference in the corrosive effect on SAE-1020 carbon steel exposed to TBP waste at either pH 7, pH 8, or pH 9. Further, the data show that no significant difference exists between the corrosivity of waste produced with the ferrous ammonium sulfate flowsheet and the waste resulting from the oxalate flowsheet." Subsequent documentation (HW-38955-REV, *In-Farm Scavenging Operating Procedure and Control Data*) demonstrates that initially TBP waste was neutralized to a very high pH (greater than 11) while subsequent wastes were produced at lower pH in the range 8 to 10. Thus the amount of neutralization employed was lowered, although the exact date of this change is not known.

The TBP Plant waste scavenging process, implemented at the end of September 1954 (HW-35586, *Summary of TBP Waste Scavenging Performance, Economics and Recommended Program*), consists of removing the long-lived fission products (namely cesium and strontium) in the waste on the nickel ferrocyanide carrier precipitate (HW-31731, *TBP Waste Scavenging*). Each batch of process wastes collected in a sample tank has potassium ferrocyanide solution added to create a 0.005 M $K_4Fe(CN)_6$ solution in the neutralized waste. The waste is then pumped to the waste neutralization tank where caustic and nickel sulfate are added continuously. The caustic was added to maintain a pH near 9 with an acceptable range being between 8 and 10 and the nickel sulfate was added to create 0.005 M $NiSO_4$. Successful waste scavenging performance is dependent upon extremely careful pH control during the neutralization step. At a pH greater than 10, cesium decontamination falls off abruptly, and at pH values less than 8, strontium decontamination is similarly poor (HW-43066, *Metal Recovery Waste Scavenging Program*).

A number of changes were made to the TBP Plant scavenging process over the years (HW-43066), generally in response to inadequate decontamination of the waste. At various times the waste was concentrated before the addition of nickel sulfate. Potassium ferrocyanide was replaced by sodium ferrocyanide. Because of difficulty in meeting the strontium disposal criteria for cribbing waste, calcium nitrate and subsequently strontium nitrate were added to improve scavenging of strontium. The sodium ferrocyanide and nickel sulfate additions were reduced to 0.0025 M. Cobalt sulfate was added to provide cobalt scavenging.

The TBP process waste stream sent to SSTs is discussed below in two sections. Distinction is made to the changes associated with in-plant scavenging performed to allow cribbing of the waste. The available compositional information, temperature data during storage, and corrosion testing data are provided for each stream.

5.5.2.2. Tri-Butyl Phosphate Process Waste Prior to In-Plant Ferrocyanide Scavenging

The composition of TBP waste from the original process flowsheets (HW-18169, HW-18232, and HW-19140) are based on neutralizing the waste to pH greater than 9.5 and then concentrating. The degree of neutralization exerts a strong effect on temperature dependence of crystallization and pH 9.5 was selected as the lowest pH considered safe (i.e., avoid plugging of transfer lines) (HW-27482, *Metastability and Degree of Neutralization Effects on TBP Plant Waste Concentration*). Ammonium ion in the waste was converted to evolved ammonia gas as the pH of the waste was increased. In order to assure a minimum pH of 9.5 after concentration, additional caustic was added to carry the pH to at least 11.0 before concentration. The stream containing the concentrated neutralized waste has the following composition based on the two flowsheet conditions[4]:

	Flowsheet HW-4	Flowsheet HW-5
$UO_2(NO_3)_2 \cdot 6H_2O$	0.0026 M	0.0026 M
SO_4^{-2}	0.398 M	0.346 M
PO_4^{-3}	0.268 M	0.136 M
NO_3^-	6.19 M	6.19 M
Cl^-	0.022 M	0.022 M
OH^-	0.08 M	0.08 M
Na^+	7.83 M	7.96 M
Fe^{+3}	0.024 M	0.024 M

Nitrite is not reported in the TBP waste. The TBP technical manual, HW-19140 (p. 441), does point out that sulfamate ion ($NH_2SO_3^-$) reacts rapidly, smoothly and completely with nitrous acid to give nitrogen gas by the reaction:

$$HNO_2 + NH_2SO_3^- \rightarrow N_2 + SO_4^{-2} + H_2O + H^+$$

[4] Some values on the flowsheets are difficult to read and individual digits recorded here may not be correct but the values have been compared to other values in the flowsheet to make sure they are closely approximated.

Thus it is expected that any nitrite ion in the feed to the TBP process is destroyed by sulfamate within the first solvent extraction column (RA column).

A later flowsheet, flowsheet HW-6 for the TBP process (HW-29466), is illegible in the version available and the neutralized concentrated waste composition cannot be read. This later flowsheet was developed to operate the solvent extraction batteries in series rather than in parallel to provide greater decontamination of less aged (i.e., more fission products) uranium in storage. It is expected concentrations of the neutralized concentrated waste from that later flowsheet would be similar to that listed above.

Storage temperature data was not located for storage of TBP waste. However, it is known that the waste was maintained at 80°C (180°F) before being sent to a SST. The concentrated neutralized waste was pumped from the TBP Plant to the waste pump tank, 241-WR-001. Tank 241-WR-001 is a 50,000 gal stainless steel tank located in the 200 West Area, served as the routing tank to underground storage in the 200 East and West Areas. The tank was equipped with a steam sparger in order to maintain a waste temperature of 180°F and ensure the concentrated waste could be transferred to the 200 East Area tanks at temperatures above 110°F (H-2-40029, *Process Flow Diagram Auxiliary Tanks 241-WR Diversion Station Waste Metal Removal – Phase 1*, HW-19140, p. 1209). The inter-area pipe encasement for waste transfer piping was supplied with additional heat to compensate for losses to the ground when routing hot condensate to the 200 East Area. This maintained a high enough waste temperature to avoid solids formation in the transfer line.

Corrosion tests of two sets of polished SAE 1020 mild steel were performed with simulated TBP waste solutions in the pH range 7-9 at 30°C for 1-3 months (HW-30041). Samples were tested under two flowsheet conditions, one with ferrous ammonium sulfate and one with oxalate. The compositions of the synthetic waste streams are provided in HW-30041 and are repeated below as well as the compositions assuming neutralization to pH 7 and concentration to a specific gravity of 1.38:

	Ferrous Ammonium Sulfate Flowsheet		Oxalate Flowsheet	
	TBP Waste Stream	Neutralized to pH 7 and Concentrated*	TBP Waste Stream	Neutralized to pH 7 *
$UO_2(NO_3)_2\ 6H_2O$	0.0117 M	0.0143 M	0.011 M	0.0086 M
SO_4^{-2}	0.584 M	0.711 M	0.26 M	0.20 M
PO_4^{-3}	0.179 M	0.218 M	0.26 M	0.20 M
NO_3^-	4.45 M	5.42 M	7.71 M	6.05 M
Cl^-	0.016 M	0.019 M	0.023 M	0.018 M
$NH_2SO_3^-$	0.034 M	0.041 M	--	--
$C_2O_4^{-2}$	--	--	0.25 M	0.20 M
H^+	2.60 M	--	5.21 M	--
Na^+	3.54 M	7.48 M	4.32 M	7.48 M
Fe^{+2}/Fe^{+3}	0.017 M	0.021 M	--	--
NH_4^+	0.034 M	0.041 M	--	--

* Assume neutralization with 19 M NaOH. After neutralization, the solutions in the study were concentrated to a specific gravity of 1.38 (HW-30041). Assume ferrous ammonium sulfate flowsheet neutralized waste required concentration to 7.48 M and that the oxalate flowsheet neutralized waste did not require concentration to arrive at specific gravity of 1.38.

The general corrosion results for specimens immersed in the liquid and the vapor of the wastes are provided in Table 5-19. The pitting corrosion results for specimens immersed in the liquid and the vapor of the wastes are provided in Table 5-20. The study concluded, "…there is no significant difference in the corrosive effect on SAE-1020 carbon steel exposed to TBP waste at either pH7, pH8, or pH9. Further, the data show that no significant difference exists between the corrosivity of waste produced with the ferrous ammonium sulfate flowsheet and the waste resulting from the oxalate flowsheet. It must be pointed out, however, that these tests were of very limited duration for this type of study. Without sufficient exposure time to enable a determination of the change of corrosion rate with respect to long periods of time, extrapolation of these data must necessarily be done with extreme caution."

Table 5-19. General Corrosion Rates in Tri-Butyl Phosphate Waste Solutions

Flowsheet	Condition Location	Exposure Time	General Corrosion Rate (mil/yr)		
			pH 7	pH 8	pH 9
Ferrous Ammonium Sulfate	Liquid	1 month	0.12	0.17	0.18
		3 months	0.08	0.06	0.07
	Vapor	1 month	0.58	0.19	0.24
		3 months	0.06	0.24	0.36
Oxalate	Liquid	1 month	0.29	0.19	0.22
		3 months	--	0.14	0.12
	Vapor	1 month	--	0.14	0.19
		3 months	0.06	0.19	0.06

Data taken from HW-30041. Values converted to mil/yr from inches/month in original table.

Table 5-20. Maximum and Average Pitting Corrosion Rates in Tri-Butyl Phosphate Waste Solutions

Flowsheet	Condition Location	Exposure Time	Maximum and Average Pitting Corrosion Rate (mil/yr)		
			pH 7	pH 8	pH 9
Ferrous Ammonium Sulfate	Liquid	1 month	8.0 max 6.1 ave	12.2 max 8.8 ave	9.8 max 7.3 ave
		3 months	9.1 max 5.5 ave	5.2 max 4.6 ave	12.5 max 10. ave
	Vapor	1 month	11. max 9.6 ave	7.1 max 4.9 ave	12.2 max 8.9 ave
		3 months	13.3 max 9.1 ave	10. max 6.5 ave	11. max 9.2 ave
Oxalate	Liquid	1 month	17.9 max 12.2 ave	34.6 max 15.4 ave	14.2 max 11. ave
		3 months	6.6 max 5.5 ave	11. max 9.5 ave	7.1 max 5.4 ave
	Vapor	1 month	12.7 max 10. ave	14.0 max 12. ave	8.5 max 7.2 ave
		3 months	13.3 max 9.1 ave	9.5 max 8.9 ave	4.6 max 4.4 ave

Data taken from HW-30041. Values converted to mil/yr from inches/month in original table.

5.5.2.3. Tri-Butyl Phosphate Process Waste, Post In-Plant Ferrocyanide Scavenging

The TBP Plant waste was first scavenged in-plant to remove cesium from the aqueous phase on a test basis during October 1953 (HW-29850). Details of the tested process were not found. This tested waste (530,000 gal) was not concentrated before being sent to tank T-101 (HW-29905, *Separations Section, Waste – Status Summary*, HW-30250, *Separations Section, Waste – Status Summary*). Samples of scavenged supernatant were obtained from tank T-101 in October 1953 at 3, 8, and 13 ft depths, about 15 ft from the inlet (HW-29850). The pHs of the solutions, as received in the laboratory from the stated depths were 9.74, 9.73, and 10.88, respectively. Although the pH at the highest elevation was higher than the desired range of 9 to 10, no adjustments were made in-tank because the overall pH was satisfactory. No other analytical data were found for these samples. The test resulted in roughly half the tank volume, 256,000 gal, being discharged to a crib in December 1953 (HW-30498, *Separations Section, Waste – Status Summary*).

The TBP Plant waste scavenging process, implemented at the end of September 1954 (HW-35586), consisted of removing the long-lived fission products (namely cesium and strontium) in the waste on the nickel ferrocyanide carrier precipitate (HW-31731). Each batch of collected process waste in a sample tank had potassium ferrocyanide solution added after sampling of the waste to create 0.005 M $K_4Fe(CN)_6$ in the neutralized waste. The waste was then pumped to the waste neutralization tank where caustic and nickel sulfate were added continuously. The caustic was added to maintain a pH near 9 with an acceptable range being between 8 and 10 and the nickel sulfate was added to create 0.005 M $NiSO_4$. Successful waste scavenging performance was dependent upon extremely careful pH control during the neutralization step. At a pH greater than 10, cesium decontamination falls off abruptly, and at pH values less than 8, strontium decontamination is similarly poor (HW-43066).

The composition of TBP waste during in-plant ferrocyanide scavenging is based on neutralizing the waste to pH 8.5-9.0 with an acceptable range of 8.0 to 10.0 (HW-30399, *TBP Plant Nickel Ferrocyanide Scavenging Flowsheet,* and HW-43066). The dilute neutralized waste with added scavenger chemicals has the following composition based on the flowsheet conditions (HW-30399):

$Na_2UO_2O_7 \cdot 6H_2O$	0.0007 M
SO_4^{-2}	0.24 M
PO_4^{-3}	0.13 M
NO_3^-	3.30 M
Na^+	4.10 M
K^+	0.01 M
NH_4^+	0.06 M
$Na_4Fe(CN)_6$	0.0025 M
$K_4Fe(CN)_6$	0.0025 M
$Fe(OH)_3$	0.015 M

The constituent concentrations in the above neutralized dilute waste composition are about half the concentration in TBP Flowsheet HW#4 (HW-18169). In addition, ferrocyanide, potassium and ammonium are also present. Initially, this dilute neutralized waste was not concentrated prior to discharge to the SSTs. The waste was not concentrated because it was planned to discharge supernatant liquid to cribs after solids had settled out. After about five months of operation, the process was modified such that the neutralized waste was concentrated (HW-43066). Poor strontium scavenging results limited the discharge of supernatant liquid to cribs and concentration was performed to conserve tank space. The degree of concentration was not stated, however, the Uranium Recovery Technical Manual (HW-19140) discusses concentration of the waste to 75%-100% of the original uranium waste volume as a means to limit solids formation during transfers. This level of concentration would result in a corresponding specific gravity of 1.38-1.34. Summary discussion of flowsheet changes (HW-43066) show that subsequent process operations at times proceeded with concentration (when calcium nitrate was added for improved strontium scavenging) and at other times without concentration (when strontium nitrate was available for improved strontium scavenging).

Storage temperature data was not located for storage of TBP waste post in-plant scavenging. Disposal of concentrated waste would have continued with waste maintained at 80°C (180°F) before being sent to a SST. The dilute neutralized waste would not have required the same heating to protect against suspended solids formation during transport. Dilute neutralized waste had no suspended solids at 25°C (HW-19140).

No corrosion testing data was found for TBP waste after in-plant ferrocyanide scavenging was implemented. As mentioned above, concentrated waste was likely similar with the exception of the presence of ferrocyanide, potassium and ammonium.

5.5.3 REDOX Process Waste Types (1952-1966)

The first full scale solvent extraction separations process to recover plutonium and uranium from irradiated nuclear reactor fuel at the Hanford Site was the reduction and oxidation (REDOX) process. The canyon facility, S Plant, was operated using this process generating two major waste streams, CW, and concentrated and neutralized salt waste. This waste was collected in various SSTs although primarily in S and SX Farms. Initially the major waste streams and miscellaneous smaller streams were all discharged to a common SST but later discharge of the major waste streams was segregated. The REDOX process was operated for 15 years at S Plant from 1952 until 1966 (RHO-CD-505 RD, *Synopsis of REDOX Plant Operations*). Irradiated nuclear fuel processed via the REDOX process was primarily aluminum-clad metallic uranium elements from the single-pass reactors. Near the end of its life, the plant also processed a small amount of zircaloy-clad plutonium-aluminum alloy fuel from the Plutonium Recycle Test Reactor (during 1963-1966), zircaloy-clad metallic uranium fuel elements from the New Production Reactor (N Reactor) (during 1965-1966), Shippingport PWR Core 1 (1966), and other small amounts of miscellaneous fuels (during 1966) (RHO-CD-505 RD). Several modifications were made to the main process over the years of processing. These changes were captured in various flowsheets. Information regarding the REDOX process, including changes impacting waste streams sent to the SSTs, and stream information for the major waste streams are provided below.

5.5.3.1. REDOX Process Description

The following process description is based primarily on the REDOX technical manual (HW-18700-DEL, *REDOX Technical Manual*) and the facility flowsheets (HW-18700, HW-38684, *REDOX Chemical Flowsheet, HW No. 5*, HW-66203, *REDOX Chemical Flowsheet HW-No. 6,* RL-SEP-243, *REDOX Chemical Flowsheet HW No. 7 and HW No. 8*, and ISO-335, *REDOX Chemical Flowsheet – HW No. 9*). The focus of the description is initial operation with a subsequent explanation of significant operational changes. The fuel cladding removal and fuel dissolution processes used in the REDOX process are comparable to the processes performed as part of the $BiPO_4$ process. The subsequent portion of the REDOX process was designed to separate uranium and plutonium as product streams from the fission products with which they are associated in the irradiated nuclear fuel. The separation process used is solvent-extraction, in which the components (uranium, plutonium, and fission products) are separated from one another by controlling their relative distribution between aqueous solutions and the immiscible organic solvent, hexone. This is performed by adjusting the valence state of the uranium and plutonium at different stages of the process where the organic and aqueous phases are contacted thus allowing distribution of the constituents between phases. This preferential distribution makes the separation of uranium, plutonium, and fission products from each other possible in the REDOX process. Figure 5-31 provides a simplified schematic from the REDOX technical manual (HW-18700-DEL) identifying the major process steps and the one waste stream of the REDOX process that is discharged to the SSTs.

The first step within the REDOX process is feed preparation. The first part of feed preparation is to remove the aluminum jacket surrounding the uranium by preferentially dissolving the aluminum in a dissolver vessel with a solution of 10% sodium hydroxide and 20% sodium

nitrate. This process is similar to the process described in Section 5.5.1.1 as part of the $BiPO_4$ process. The resulting dissolved aluminum CW is collected along with water flushes. A dilute nitric acid flush may have been used initially but by the second major flowsheet (HW-38684 released in 1955) a dilute nitric acid flush is not shown. The combined aluminum CW and flushes are combined in a waste holdup tank. The combined waste and flushes, referred to as CW, are jetted from the waste holdup tank to an underground storage tank.

As part of feed preparation, additional waste streams are created that ultimately end up in underground storage tanks. Feed preparation requires oxidation of plutonium to the proper valence state to ensure it gets extracted along with the plutonium in the first solvent extraction column. Plutonium is oxidized via the addition of sodium dichromate. Along with this unit operation, ruthenium distillation is performed to reduce the amount of ruthenium sent to solvent extraction, thus improving decontamination of the uranium and plutonium. Ruthenium is converted to gaseous RuO_4 in the plutonium oxidizer by the addition of potassium permanganate. This ruthenium tetroxide is absorbed in a scrubber via a 25% caustic solution. Periodically, on the order of twice a week, the caustic solution is transferred to the waste neutralizer tank (see below). The humid air passing out of the scrubber is sent through a condenser to remove water. This condensed water is sent to a condensate evaporation system from which the bottoms are sent to the waste header receiver tank (see below).

Another operation in feed preparation is the elimination of solids in the feed solution. To reduce solids sent to the solvent extraction process, a clarification process using centrifuges is performed. The solids from centrifugation are washed with the wash liquid returned to the plutonium oxidation process. The solids are slurried out of the centrifuge and sent to the concentrated waste sample tank (see description below).

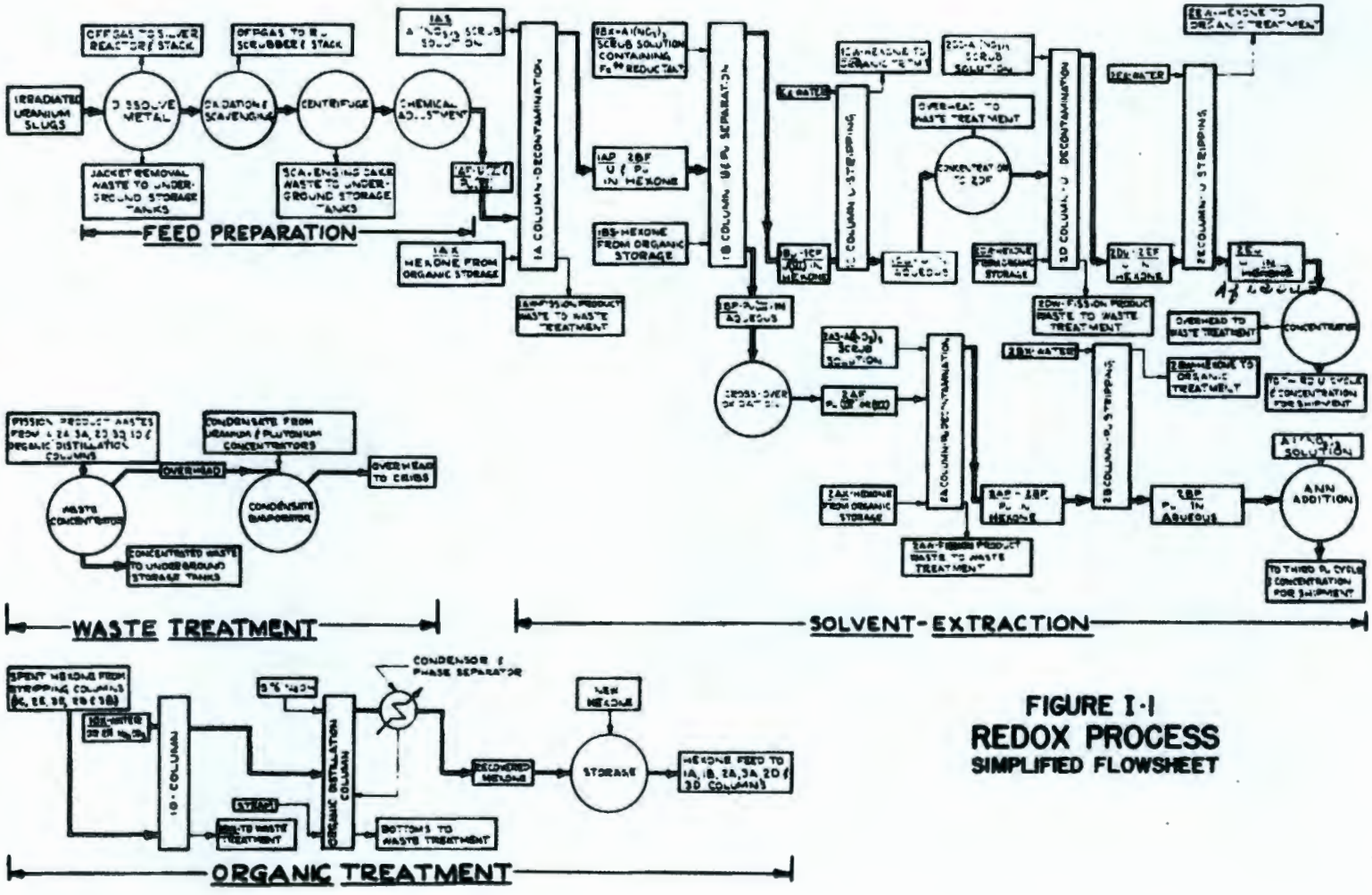


FIGURE I-1
REDOX PROCESS
SIMPLIFIED FLOWSHEET

Figure 5-31. REDOX Process Simplified Flowsheet, Circa 1951

After feed preparation, the feed solution is sent to solvent extraction that consists of a series of solvent extraction contacting columns used to separate the plutonium, uranium and fission products. Initially, the first solvent extraction cycle consisted of three columns IA, IB and IC. The feed is sent to the middle of the first column, IA, where the uranium and plutonium are extracted to the organic phase (acidified hexone) leaving the fission products in the aqueous stream. An aqueous stream containing aluminum nitrate, as a salting agent, is added at the top of the column. The aqueous waste stream coming out of the bottom of the IA column contains over 99% of the fission products. This stream is sent to the waste header where it collects in the waste receiver tank (see below). The organic stream bearing the uranium and plutonium is sent to the 1B column. The organic stream is contacted with a ferrous sulfamate and aluminum nitrate bearing aqueous stream causing the plutonium to strip back into the aqueous phase while leaving uranium in the organic phase. The plutonium leaves the column in the aqueous stream where it is directed to the second and third plutonium cycles for further decontamination. The uranium in the organic phase is sent to the IC column where it is contacted with an aqueous stream stripping the uranium into the aqueous phase. This aqueous stream is sent to a concentrator where the uranium is stripped of hexone, concentrated and adjusted to be acid-deficient. This concentrated uranium stream is sent to two additional uranium cycles for further decontamination.

The second uranium decontamination cycle removes residual plutonium and fission products from the uranium-bearing stream from the first solvent extraction cycle. The uranium-bearing aqueous stream is fed to the intermediate point of the 2D column and the uranium is extracted into the organic phase in the presence of an aluminum nitrate and ferrous sulfamate bearing aqueous strip solution. The aqueous waste stream from the 2D column is sent to the waste header where it is collected in the waste receiver tank. The uranium in the organic phase is sent to the 2E column where it is stripped back to the aqueous phase. The uranium bearing aqueous stream is stripped of hexone, concentrated, and adjusted to be acid deficient. Another uranium decontamination cycle similar to that described in this paragraph can also be used to further decontaminate the uranium. The aqueous waste stream from the 3D column is sent to the waste header and collected in the waste receiver tank.

The second plutonium decontamination cycle removes residual fission products from the plutonium-bearing stream from the first solvent extraction cycle. The plutonium-bearing aqueous stream from the first solvent extraction cycle is oxidized by the addition of nitric acid and sodium dichromate. The oxidized stream is fed to the intermediate point of the 2A column and the plutonium is extracted into the organic phase in the presence of an aluminum nitrate-bearing aqueous strip solution. The aqueous waste stream from the 2A column is sent to the waste header where it is collected in the waste receiver tank. The plutonium in the organic phase is sent to the 2B column where it is stripped back to the aqueous phase. This aqueous stream has aluminum nitrate added to it prior to feeding to an additional decontamination cycle. Another plutonium decontamination cycle similar to that described in this paragraph can also be used to further decontaminate the plutonium. The plutonium in this third plutonium decontamination cycle is concentrated for shipment to another facility for further processing. The aqueous waste stream from the 3A column is sent to the waste header and collected in the waste receiver tank.

The solvent extraction system uses hexone as the organic phase. The spent hexone streams from the 1C, 2E, 3E, 2B and 3B columns are treated to remove residual uranium, plutonium, fission products, and decomposition products. The first step in the treatment consists of a scrubber column where the organic is contacted with a water (or 2% sodium carbonate) stream to strip uranium, plutonium and fission products. The organic is then sent to a distillation column with an overhead water scrub for further removal of uranium, plutonium and fission products and separation of organic decomposition compounds. The bottoms stream from the distillation still is an aqueous stream. The still bottoms and the scrub solution from the scrubber column are directed to the waste receiver tank.

The aqueous waste streams from the solvent extraction and organic recovery systems and filter and stack drainage are collected for treatment in the waste treatment system within REDOX. In addition, bottoms from a condensate evaporator and cell drainage collection tank are sent batch wise to the aqueous waste receiver tank. The collected waste is stored in a waste receiver tank (tank D-13). The collected waste is sent to a hexone stripper column located on the top of the waste concentrator (D-12). The waste falls through a set of bubble cap plates to remove the residual hexone from the aqueous waste prior to concentration. The waste falls through the bubble cap trays to the pot of the waste concentrator where the waste is concentrated. Waste overflows from the concentrator into the waste concentrate receiver (D-10). Waste is jetted from the waste concentrate receiver to the waste concentrate sampler (D-9) where it is cooled and sampled. Prior to storage in the single-shell tanks, the waste solution is neutralized and adjusted to a pH of 13. This high pH is specified to maintain the aluminum salts present in the waste in a soluble form as aluminates rather than precipitated as oxides.

A number of process changes were made throughout the years to the original flowsheet (RHO-CD-505 RD). Several major flowsheet changes were made and documented throughout the plant's operational history (HW-38684, HW-66203, RL-SEP-243, and ISO-335). Larger equipment was put in place, chemical changes and concentration changes were made to improve decontamination efficiency and improve throughput. Waste streams from solvent extraction columns were used as the salting agents for prior cycles rather than directing the streams to the waste treatment system, reducing fresh chemical additions. Jumpers were installed to reroute streams to permit a precycle flowsheet to provide four decontamination cycles for plutonium and three for uranium. Additional treatment of the final uranium solution, including silica-gel treatment, is included to remove ruthenium, zirconium and niobium. Regeneration of the silica-gel uses oxalic acid. This oxalic acid regeneration waste is neutralized with sodium hydroxide resulting in a small volume of sodium oxalate and sodium hydroxide-bearing waste requiring disposal in the SSTs. A nitric acid recovery system was put in place to recover acid from the dissolving operation. A neptunium recovery flowsheet was put into place. Head-end oxidation for ruthenium removal was replaced by sodium dichromate oxidation in conjunction with ozonation. Along with this change, centrifuging of all solvent extraction feed was discontinued. Process modifications to feed preparation operations were required to process zircaloy-clad fuels. These zircaloy-clad fuels included Plutonium Recycle Test Reactor (PRTR) fuel consisting of zircaloy-clad, plutonium-aluminum alloy fuel; the NPR fuel consisting of zircaloy-clad, uranium metal fuel; and, Shippingport PWR Core 1 blanket fuel consisting of zircaloy-clad, uranium oxide fuel (ISO-642, *Chemical Processing Division Monthly Report for December, 1966*). The CW from processing zircaloy-clad fuel was very different than CW from processing aluminum

clad fuel. Aluminum nitrate was added to nitric acid to complex residual fluoride during nitric acid dissolution of the uranium metal. Compositional changes to the concentrated, neutralized salt waste with all of these changes above are discussed below in the context of the various major flowsheets.

Fuels processed at REDOX that had zircaloy cladding could not be decladded in the same manner as used for removing the aluminum jackets on Hanford's single pass reactor fuel elements. This resulted in a completely new cladding removal waste stream generated by the REDOX process. The zircaloy cladding removal process used a boiling aqueous solution of ammonium fluoride and ammonium nitrate (36 wt% [5.5 M] NH_4F – 7 wt% [0.5 M] NH_4NO_3) which produced ammonium hexafluorozirconate [$(NH_4)_2ZrF_6$], ammonia and hydrogen (HW-65979, *The ZIRFLEX Process Terminal Development Report,* ISO-417, *Operating Problems Associated with NPR Fuels Processing at the REDOX Plant*). The hydrogen and a large portion of the ammonia were liberated to the off gas. At the end of dissolution, the cladding solution was diluted with water prior to cooling to avoid precipitation. To alleviate line plugging problems the waste was neutralized via a reverse strike addition where the cladding waste was added to sodium hydroxide resulting in a more fluid precipitate.

The major waste streams sent to SSTs from the REDOX plant are the CW and the concentrated and neutralized salt waste. Although isolated from each other within the REDOX plant, during the first part of operation (until July 1953) these waste streams were separately sent to the same tank that was actively receiving waste at the time. After this time these wastes were sent to different tanks upon generation but some tanks may have received both waste types at different times. Because of the distinct chemistry of the concentrated and neutralized salt waste and the CW it is worth distinguishing between discharges of these wastes separately and as a combined stream.

From the first tank receiving REDOX waste, tank S-110, in January 1952 through July 1953, CW and concentrated and neutralized salt waste were sent to the same tank. Starting in July 1953, with then empty tank S-101, the concentrated and neutralized salt waste was sent to a separate cascade than the CW (sent to tank S-110 at that time). Coating waste was subsequently added to the tank S-101 through S-103 starting in January 1954. The concentrated and neutralized salt waste was first sent to a tank in SX Farm (tank SX-101) during June 1954. Waste in tank SX-101 was cascaded to the next two tanks (tanks SX-102 and SX-103). In January 1954, concentrated and neutralized salt waste was sent to tank U-110 and cascaded to tanks U-111 and U-112. Concentrated and neutralized waste was then sent to tank SX-104, starting in February 1955, and cascaded to tank SX-105. Waste directed to the last nine tanks of SX Farm was not cascaded but sent to individual tanks. This waste was later transferred among tanks within and outside SX Farm and condensate from tank SX-106 was also added to these tanks to replenish water evaporated through boiling and to dissolve sludge for nitrate leaching and recycle (see Section 5.5.7.2). The available compositional information, temperature data during storage, and corrosion testing data are discussed for each stream in the following sections.

5.5.3.2. REDOX Combined Waste

At the beginning of REDOX processing, all high-activity waste destined for SSTs was directed to a single tank. The waste consisted primarily of the concentrated neutralized salt waste from the solvent extraction process and CW, but also contained small amounts of other wastes including centrifuge cake waste, laboratory waste and condensates too hot to send to cribs. For the purposes of describing REDOX combined waste in this report, it is considered the concentrated and neutralized salt waste combined with CW. The discussion of waste transfers of REDOX combined waste is based on waste status summary reports issued during the time of REDOX operation. Tank S-110 began receiving REDOX combined waste in January 1952 and the cascade was filled by July 1952. The REDOX combined waste was then sent to the tank S-107 cascade which was filled by February 1953. Subsequently, centrifuge cake waste continued to be sent to the tank S-107 cascade while the REDOX combined waste was directed to the tank S-104 cascade. The tank S-104 cascade received REDOX combined waste from February 1953 until July 1953. After this time the concentrated and neutralized salt waste and the CW were sent to separate tanks within S Farm.

Corrosion testing was performed to evaluate corrosion of SAE 1010 mild steel in synthetic REDOX waste solutions, approximating the composition of the solution being stored in the first cascade containing REDOX waste at the elevated temperature (220°F) existing in the REDOX underground storage tanks (HW-24407, *Proposed Corrosion Program, Corrosion of SAE 1010 Mild Steel in REDOX Waste Storage Solutions*). The program was designed to provide information on corrosion resistance of mild steel exposed in the liquid, at the liquid vapor interface and in the vapor space. Waste pH values ranged from 11 to 13. The synthetic waste solution was developed based on the proposed process material balance in HW-22834, *REDOX Process Material Balance; ORNL June, 1949, Conditions*. The synthetic waste solution is based on combining CW, dissolver rinse, dissolver centrifuged solids, and concentrated neutralized salt waste. The solution composition is given below:

$NaNO_3$	23.4%	327.6 g/L	3.85 M
$NaNO_2$	0.43%	6.02 g/L	0.087 M
$NaAlO_2$	7.5%	105.0 g/L	1.28 M
NaOH	3.8%	53.2 g/L	1.33 M
Na_2SO_4	0.50%	7.0 g/L	0.049 M
Na_2SiO_3	0.01%	0.14 g/L	0.001 M
$Na_2U_2O_7$-$6H_2O$	0.06%	0.84 g/L	0.001 M
Na_2CrO_4	0.52%	7.28 g/L	0.045 M
K_2CrO_4	0.02%	0.28 g/L	0.001 M
NH_3	0.06%	0.84 g/L	0.049 M
Cr_2O_3-$2H_2O$	0.03%	0.42 g/L	0.002 M
$Fe(OH)_3$	0.19%	2.66 g/L	0.025 M
$Mn(OH)_2$	0.04%	0.56 g/L	0.006 M
NaCl	--	1.15 g/L	0.020 M
H_2O	63.45%		
Assumed Density	1400 g/L		

Results of a 1000-hour corrosion test of SAE 1010, low carbon steel in synthetic REDOX waste solutions are shown in Table 5-21. Tests were performed for waste solution temperature of 180°F, 200°F and 220°F in solutions neutralized to pH values of 11, 12, and 13. The duplicate steel specimens were located in the liquid, in the vapor and at the liquid-vapor interface. The steel specimens were cut from 3/8 in. SAE 1010 steel plate of the type used in the construction of the waste storage tanks. Specimens were sand-blasted to simulate field conditions. Considerable variation between duplicate specimens was observed under most of the conditions tested, and it was felt that the higher of the two rates was of greater significance than the average. Generally, attack was more severe for the steel exposed to the vapor than for the steel at the vapor-liquid interface or in the liquid-sludge at the same temperature. The testing of boiling solutions may not have accurately reflected the planned test temperature of 220°F. Temperature measurements in the flasks of boiling solutions indicated the sludge in the bottom of the pH 12 solution was at least 40°F above the nominal boiling point of 220°F. For specimens exposed to the vapor over the waste solutions, the corrosion rates are seen to increase with temperature. There also is a trend toward higher corrosion rates for specimens in lower pH solutions, however, not enough data was available to establish a definitive trend. Corrosion rates were typically low for specimens exposed in the liquid-sludge solutions and only slightly higher for specimens at the liquid-vapor interface. Corrosion was generally two to four times higher for the boiling solutions than the same solution at 180°F. The tests did not indicate whether or not pitting occurred at appreciable rates or if the general corrosion rates decreased with respect to time.

As mentioned previously, in February 1953, the small amount of centrifuge cake waste was sent to the tank S-107 cascade while the balance of waste was sent to the tank S-104 cascade. During 1953, four SAE 1020 steel coupons were lowered into tank S-104, which was storing REDOX combined waste solution (HW-29183, *Technical Activities Report, Corrosion and Welding, August 1953*). The purpose of this study was to obtain corrosion data for steel specimens exposed to REDOX process waste solution under actual operating conditions (HW-32755). Data was sought regarding the rates of general corrosion, pitting, and possibility of SCC. At the time the specimens were introduced into the tank, the waste was boiling and the sludge was known to have reached 250°F and may have exceeded 300°F. This was higher than the previously tested synthetic waste solution. This was the first field testing of REDOX waste solution. The testing consisted of three unstressed specimens to examine general and pitting corrosion and one stressed specimen to examine the possibility of SCC. Specimens were placed in holders in a bonnet with a spray chamber located above (HW-27097, *Technical Activities Report, Metallurgy – Applied Research Unit, January 1953*, HW-32755). The specimens in their holders were lowered on a wire to a location calculated to be two feet above the bottom of the tank in the sludge, where temperatures were expected to be highest.

Table 5-21. General Corrosion Rates of SAE 1010 Steel Coupons Exposed for 1000 Hours in Synthetic Neutralized REDOX Waste

Condition Location	Waste Solution pH	Specimen	Corrosion Rate Data, mil/yr		
			180°F	200°F	220°F
Vapor	11	A	3.14	3.58	1.37
		B	2.71	5.74	1.81
		Average	2.93	4.66	1.59
	12	A	3.73	3.29	4.08
		B	1.82	0.84	4.03
		Average	2.78	2.06	4.06
	13	A	0.92	1.80	3.35
		B	0.67	1.98	3.43
		Average	0.80	1.89	3.39
Vapor-Liquid Interface	11	A	0.07	0.18	0.34
		B	0.17	0.49	0.22
		Average	0.12	0.34	0.28
	12	A	0.32	0.43	1.54
		B	0.23	0.30	1.56
		Average	0.28	0.37	1.55
	13	A	0.11	0.08	1.92
		B	0.30	0.38	3.43
		Average	0.20	0.23	2.68
Liquid-Sludge	11	A	0.02	0.07	0.18
		B	0.04	0.11	0.19
		Average	0.03	0.09	0.19
	12	A	0.17	0.30	1.88
		B	0.16	0.56	4.37
		Average	0.16	0.43	3.13
	13	A	0.12	0.14	0.95
		B	0.08	0.23	1.01
		Average	0.10	0.19	0.98

Data taken from HW-26201, Table 1. Values converted to mil/yr from inches/month in original table.

No record was found of sample analysis characterizing the composition of the waste in tank S-104 during the time of the testing. The tank had been filled sometime around July 1953 with concentrated and neutralized salt waste, lab waste, CW, and hot condensate. Relative quantities of each were not listed in monthly waste status summary reports so it is not known how much dilution would have occurred from the addition of an unknown quantity of hot condensate. The corrosion specimens were introduced into the tank in August 1953 and retrieved from the tank in May 1954 (HW-32755). The tank was identified as self-evaporating in January 1954. The tank level decreased from full in July 1953 until February 1954 and started receiving concentrated and neutralized salt waste again in April 1954. From the end of July 1953 to the end of February 1954 the volume of waste in the tank went from 758,000 gal to 409,000 gal, a concentration factor of 1.85.

Originally the samples were to be exposed for six months but due to contamination surrounding the riser where the specimens were introduced to the tank, the specimens were in the waste for nine months (HW-32755). The corrosion rate of SAE 1020 steel within the self-concentrating liquid-sludge waste of tank S-104 was found to be relatively low and pits were comparable to

those found for $BiPO_4$ 1C waste. Table 5-22 lists the measured general corrosion rate and pitting data for these in-tank specimens.

Examination of the one stressed specimen from this testing, including visual and metallographic inspection, failed to reveal any evidence of SCC. Concern had existed about the possibility of caustic-induced SCC because of the SCC of carbon steel tanks experienced by the caustic industry.

The majority of fission products from REDOX combined waste would end up in the first tank of the cascade. Fuel processed early at REDOX had relatively low burnup and therefore did not contain as great a quantity of fission products as later higher burnup fuel that was processed through REDOX. Accordingly, tanks S-104, S-107, and S-110 were the first tanks in the cascades had the highest maximum temperature for each cascade (see Figure 5-32). Note that the figure also contains the temperatures for the tank S-101 cascade for convenience although this tank first received concentrated and neutralized salt waste rather than REDOX combined waste. One can see from the figure that tank S-104 attained the highest maximum temperature in S Farm. With the provision that the waste composition in tank S-104 was comparable to or more concentrated than waste in the other S Farm tanks, then the corrosion results for tank S-104 storing REDOX combined waste would be conservative relative to the remainder of the tanks in S Farm that also stored REDOX combined waste.

Table 5-22. General and Pitting Corrosion Data for SAE 1020 Steel Coupons Exposed for Nine Months in 241-S-104 REDOX Waste

Condition Location	Specimen	Corrosion Data			
		General Corrosion Rate, mil/yr	Average Depth of 3 Deepest Pits, mil	Depth of Deepest Pit, mil	Average Pitting Rate for Deepest Pit, mil/yr
Liquid-Sludge	4F-68	0.36	1.9	2.1	2.8
	4F-69	0.54	1.9	2.8	3.7
	4F-70	0.56	3.0	4.0	5.3

Data taken from HW-32755, Table II. Values converted to mil and mil/yr from inches and inches/month in original table.

Temperature rate of rise within the tanks was not controlled per se, and depended upon the rate of waste addition to the tank, incoming waste temperature, and decay heat of the waste. Because the concentrated and neutralized salt waste contained almost all the fission product activity, it had the highest decay heat density. Because the waste sent to the tanks S-110, S-107 and S-104 cascades originally contained both CW and concentrated and neutralized salt waste, the decay heat density of the waste sent to these cascades was lower than the waste sent to the tank S-101 cascade in which these streams were segregated. No initial rate of temperature rise data was found for the three S Farm tank cascades receiving REDOX combined waste.

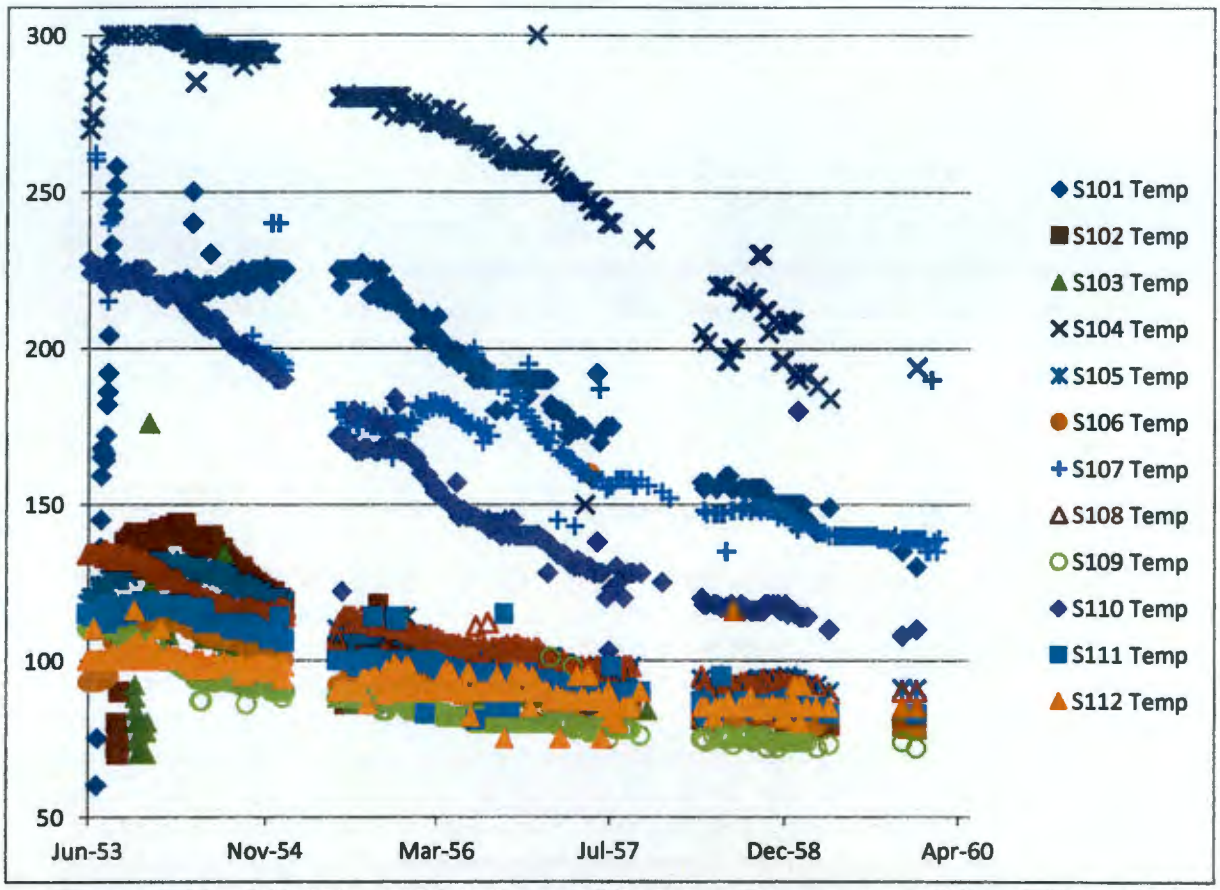


Figure 5-32. 241-S Farm Tank Content Maximum Temperatures When Filled with REDOX Waste, 1953-1960

5.5.3.3. Coating Removal Waste

The discussion of waste transfers is based on waste status summary reports issued during the time of REDOX operation. In July 1953, disposal of CW was segregated from the concentrated and neutralized salt waste which was being disposed along with lab waste and hot condensate. The CW was initially sent as a separate stream to the tank S-110 cascade (which already contained REDOX combined waste) while the concentrated and neutralized salt waste was sent to the tank S-101 cascade. This marks the point when these two major waste streams were sent to separate cascades.

After being sent to the tank S-110 cascade, through January 1954, the CW was then sent to the tank S-101 cascade (January 1954 to November 1954), then to the tank S-107 cascade (November 1954 to April 1955), and then sent to the tank S-104 cascade (April 1955 to August 1955). Tanks S-105 and U-110 received CW for short periods of time in May 1954 and September-October 1955, respectively. Coating removal waste from tank S-107 was transferred to tank S-106 in October 1955. From November 1955 to January 1956, CW was sent to tank S-107. During the period January 1956 to July 1957, the CW was directed to tank U-110. During this time waste was transferred out of tank U-110 to make space for additional waste.

Waste was transferred from tank U-110 to several tanks including tanks T-106, U-201 through U-204, U-109, and U-112. In July 1957, CW was transferred from tanks S-107 to U-107 in preparation for tank S-107 becoming the CW receiving tank. Tank S-107 continued to receive CW from August 1957 to the end of REDOX operations at the end of 1966. Coating removal waste accumulated in tank S-107 would be transferred from tank S-107 to other tanks, namely tanks U-107, U-108, T-101, T-102, S-104, S-105, S-111, T-105, T-106, and TX-115.

The discussion of CW from dejacketing aluminum clad fuel elements in Section 5.5.1.2 regarding composition and corrosion is applicable to CW generated as part of the REDOX process. No additional discussion regarding this waste stream is necessary beyond what was previously provided. Almost 99% of the nominally 22,000 tons uranium processed through REDOX during its operational life was aluminum clad.

5.5.3.4. Neutralized Zircaloy Cladding Removal Waste

During the last four years of REDOX' operational life, the facility began to process fuels that had zircaloy rather than aluminum cladding. Some of this fuel was delivered in sacrificial aluminum canisters that were dissolved in a manner similar to the aluminum clad fuel. That waste would be similar in chemical composition to the CW. However, the chemical process for removing zircaloy cladding from fuel was very different resulting in a very different cladding removal waste. The neutralized zircaloy cladding removal waste was generated from processing PRTR fuel, NPR fuel, and PWR Core 1 blanket fuel. These fuels made up roughly 1% of the total uranium tonnage processed through REDOX. Because the majority of zircaloy cladding removal waste originated from PUREX processing, the discussion of that waste type has been deferred to Section 5.5.4.3.

5.5.3.5. Concentrated and Neutralized Salt Waste

The following discussion of concentrated and neutralized waste transfers is based on waste status summary reports issued during the time of REDOX operation. In July 1953, disposal of concentrated and neutralized salt waste was segregated from the CW. The concentrated and neutralized salt waste was still being disposed along with laboratory waste and hot condensate. Laboratory waste was a relatively small volume and hot condensate contained relatively dilute concentrations of contaminants. The concentrated and neutralized salt waste was initially sent to the tank S-101 cascade. After this cascade was filled, the waste was directed to the tank U-110 cascade from January through April 1954. In April 1954 tank S-104 started to receive concentrated and neutralized salt waste and received it through June 1954. The first six tanks in SX Farm became operational in 1954. The tanks SX-101 through SX-103 cascade received concentrated and neutralized salt waste between June 1954 and February 1955 while the tanks SX-104 and SX-105 cascade received the waste between February and September 1955. Tank SX-106 was dedicated to the receipt of condensate from the other SX Farm tanks which were self-evaporating.

The last nine tanks of SX Farm were put into service starting with tank SX-109 in September 1955. Modifications were made to these tanks, primarily the addition of airlift

circulators, to address issues associated with self-concentrating waste. After tank SX-109 was initially filled, then tank SX-108 received waste starting in November 1955, tank SX-112 in February 1956, tank SX-107 in April 1956, tank SX-111 in June 1956, and tank SX-114 in November 1956. As these tanks self-evaporated, additional concentrated and neutralized salt waste was added to each of these tanks. No additional tanks were brought into service until waste was introduced into tank SX-113 in February 1958. Waste was then removed from tank SX-113 (to tank SX-103) in July 1958 because of a known bulge in the liner bottom and concern over stresses suffered by the liner and possible liner failure (HW-57249, *Interim Report on Displacement of the REDOX 113-SX Waste Storage Tank Liner*). Tanks U-101, U-102 and U-103 received concentrated and neutralized salt waste from other SX Farm tanks starting in May 1958, October 1958, and November 1958, respectively. Tank SX-115 was put into service in August 1958. Tank TX-105 received waste from tank SX-102 in July and August 1959. Finally, tank SX-110, the last empty SX Farm tank, was put into service in April 1960. Concentrated and neutralized waste stored in tank U-101 was moved to tank U-106 in July 1960. In July 1962, REDOX concentrated and neutralized waste was transferred from tank SX-102 to tank TX-101. Waste in tank TX-101 was subsequently moved to tank TX-104 in the first half of 1963, tank TX-106 in the second half of 1964, and tank TX-107 in the first half of 1965.

Coating removal waste was not sent to the last nine SX Farm tanks during the time they were receiving the concentrated and neutralized salt waste. This would mean that the waste would not initially contain any, or very little, nitrite ion which is present in the CW but not the salt waste. Because eight of these nine tanks have liner failures, it is of particular interest to know the start of operation, when the tanks started self-concentrating, and the time of first suspected failure of the tanks. This is presented in Table 5-23 below.

Table 5-23. Fill, Self-Concentration, and Suspected Leak Dates for 241-SX Tanks with Liner Failures

Tank	First Fill Date[1]	First Self-Concentrating Date	First Suspected Leak Date
SX-107	April 1956	June 1956[2] [2 months]*	March 1964[3] [95 months]*
SX-108	November 1955	February 1956[4] [3 months]*	December 1962[5] [85 months]*
SX-109	September 1955	February 1956[4] [5 months]*	January 1965[6] [112 months]*
SX-110	April 1960	January-June 1961[7] [9 months]*	Not suspected of leaking
SX-111	June 1956	November 1956[8] [5 months]*	May 1974[9] [215 months]*
SX-112	February 1956	March 1956[10] [1 month]*	January 1969[11] [155 months]*
SX-113	February 1958	May 1958[12] [3 months]*	July 1958[13] [5 months]*
SX-114	November 1956	June 1957[14] [7 months]*	August 1972[15] [189 months]*
SX-115	August 1958	January 1960[16] [17 months]*	March 1965[17] [79 months]*

1 HW-83906 E RD, *Chemical Processing Department 200 West Area Tank Farm Inventory and Waste Reports July 1961 Through 1965*
2 HW-43895, *Separations Section, Waste – Status Summary for June 1956.*
3 HW-81620, *Chemical Processing Department Monthly Report, March 1964.*
4 HW-41812, *Separations Section, Waste – Status Summary for February 1956.*
5 WHC-MR-0300, *Tank 241-SX-108 Leak Assessment.*
6 ARH-CD-261, *Thermal Conductivity of SX Tank Farm Soils.*
7 HW-71610, *Chemical Processing Department – Waste Status Summary January 1, 1961 through June 30, 1961.*
8 HW-47052, *Chemical Processing Department Waste – Status Summary, November 1, 1956 – November 30, 1956.*
9 ARH-CD-133B, *Operations Division Waste Status Summary, April 1, 1974 through June 30, 1974.*
10 HW-42394, *Separations Section, Waste – Status Summary for March 1956.*
11 ARH-1023-DEL, *Chemical Processing Division Daily Production Reports, October 1969 through December 1969.*
12 HW-56357, *Chemical Processing Department Waste Status Summary, May 1, 1958 – May 31, 1958.*
13 HW-57122, *Chemical Processing Department Waste Status Summary, July 1, 1958 – July 31, 1958*
14 HW-51348, *Chemical Processing Department Waste Status Summary June 1, 1957 through June 30, 1957.*
15 LET-081072, *TX-114-SX Leak Status and Recommendations.*
16 HW-63896, *Chemical Processing Department Waste Status Summary January 1-31, 1960.*
17 RL-SEP-297, *REDOX Weekly Process Reports January Through December 1965.*
*After first fill date

The REDOX flowsheet underwent several major changes throughout the plant's operational history. The composition of the concentrated and neutralized salt waste, based on the major flowsheets, contained the same major constituents within a moderately changing range of concentrations. Table 5-24 provides the flowsheet composition for concentrated and neutralized salt waste as depicted by the major flowsheets for the REDOX process. In March 1962 it was reported (HW-72890, *Chemical Processing Department Monthly Report, February, 1962*, p G-3) that laboratory studies indicated the amount of caustic required for salt waste neutralization could be reduced without affecting the chemical stability of the neutralized waste. The standard caustic addition for salt waste neutralization was reduced by 18% from that point forward. Lower caustic concentrations can be seen in the flowsheet compositions after 1962.

Table 5-24. Flowsheet-Based Composition of Concentrated and Neutralized Salt Waste from REDOX Processing

Component	Flowsheet Values (M)					
	HW-4 [ca. 1951]	HW-5 [ca. 1955]	HW-6 [ca. 1960]	HW-7 [ca. 1965]	HW-8 [ca. 1965]	HW-9 [ca. 1966]
$NaAlO_2$	1.28	1.29	0.93	1.01	1.17	1.2
Na_2CrO_4	--	0.16	0.18	--	--	--
$Na_2Cr_2O_7$	--	--	--	0.042	0.1	0.066
NaOH	1.59	1.21	1.44	1.13	0.44	0.69
$NaNO_3$	4.48	4.19	4.37	5.35	4.85	4.83
Na_2SO_4	--	0.023	0.02	0.042	0.028	0.031
$Fe(OH)_3$	--	0.0075	0.006	0.021	0.014	0.016
$Cr(OH)_3$	--	0.0025	0.003	0.12	0.014	0.045
H_2O	Balance	Balance	Balance	Balance	Balance	Balance
SpG	1.38	1.38	1.39	1.29	1.29	1.29
Reference	HW-18700, Table X-1	HW-38684	HW-66203	RL-SEP-243	RL-SEP-243	ISO-335

Supernatant samples were taken from tanks SX-101, SX-107, SX-108, and SX-114 in April 1961, prior to removal of the supernatant liquid from the tank (HW-69443, *Chemical Processing Department Monthly Report April, 1961*, p. G-5). These samples, presented in Table 5-25, represent the supernatant waste prior to pumping from the tank and represent liquid in equilibrium with the settled sludge. Table 5-25 shows that the tank SX-101 sample has a much higher nitrite and hydroxide concentration and a lower nitrate concentration than the other supernatant samples. The reason for this is not known. The differences may be attributed to some difference in operational conditions at REDOX. Higher nitrite could result from a reduction reaction in tank SX-101 where nitrate is reduced to nitrite, which is a relatively slow reaction, or ingrowth of nitrite from radiolysis of nitrate. Tank SX-101 had first received waste nearly seven years prior to sampling and not received fresh waste for at least five and a half years before sampling, which would have provided time for nitrite to build up in solution. Tanks SX-107, SX-108, and SX-114 had shorter time periods since first and last waste addition albeit still in terms of years. Tanks SX-107, SX-108 and SX-114 received first waste five, five and a half, and four and a half years, respectively. Regarding most recent waste additions direct from REDOX for tanks SX-107, SX-108 and SX-114, these occurred two and a quarter years, three and a quarter years, and about one year, prior to sampling, respectively.

Table 5-25. Waste Composition Results for Select 241-SX Tanks Containing Concentrated and Neutralized REDOX Waste

Tank	Layer	Date	Temp. (°C)	pH	$[OH^-]$ M	$[NO_2^-]$ M	$[NO_3^-]$ M
SX-101[1]	Supernatant above Sludge	April 1961	96	-	4.58	2.48	6.03
SX-107[1]	Supernatant above Sludge	April 1961	133	-	1.27	0.65	8.65
SX-108[1]	Supernatant above Sludge	April 1961	138	-	1.32	0.61	8.35
SX-114[1]	Supernatant above Sludge	April 1961	147	-	1.53	0.45	8.15

[1] Results were obtained from HW-69443, p. G-5.

Prior to REDOX operation, some preliminary corrosion resistance testing of welded mild steel and two types of stainless steel in synthetic REDOX stream 1A Column waste (1AW) neutralized to pH 0, 2, and 10 was carried out during 1949 (HW-14923, *Memorandum to File-Corrosion Rates of Mild and Stainless Steels Exposed in REDOX Stream IAW*). The stream composition tested was identified as from the ANL, June 1, 1948 flowsheet. This ANL flowsheet could not be found but a REDOX flowsheet from May 1949 based primarily on this ANL flowsheet is available (HW-13320, *REDOX Production Plant Chemical Flow Sheet*). The 1AW salt waste stream from HW-13320 and the estimated composition of the stream neutralized to pH 10, using 50% NaOH, is given below:

Constituent	1AW	Estimated 1AW Neutralized to pH 10
$Al(NO_3)_3 \cdot 9H_2O$	0.73 M	--
HNO_3	0.18 M	--
$NaNO_3$	0.11 M	2.04 M
$NaAlO_2$	--	0.63 M
NaOH	--	0.0001 M
H_2O	Balance	Balance

It was not stated that the simulated waste was concentrated for the testing and therefore would not be completely representative of the waste stream sent to tank farms. The pH of the solution was essentially constant throughout the duration of the test. The concentration of the solution was maintained by the use of a reflux condenser. The steel specimen was SAE 1020 plate that was hand welded by the metal arc process using a standard electrode for use in welding the material. The specimen size was 0.25 in. x 2 in. x 6 in. All welding was done under field conditions by qualified welders. All specimens were sandblasted, degreased, air dried, weighed to +/- 0.0001 gram and immediately exposed to the test environment. During testing, the specimens were partially immersed in the test solution which was maintained at 72°C. There was no mechanical aeration or agitation, however, the test solution was initially air saturated and convection currents, in effect, mildly agitated the system. Specimens were exposed for a total of 2.13 months. The uniform corrosion rate for the cumulative time period was 2.0 mil/yr. The remarks regarding the appearance of the corrosion coupon at the end of the exposure period stated,

> *Slight irregular rust formation vapor half, white crud formation liquid half, neither removable by H2O wash and bristle brush, the cleaning method for each exposure period. After final check the sample was cleaned by an acid dip... No correction factor was used. Specimen appearance was good.*

In 1950, more extensive study, prior to REDOX operation, of the corrosion resistance of several materials to then current (i.e., $BiPO_4$ process) and anticipated streams under specific conditions was performed and reported (HW-18595). The materials studied included stainless steel, SAE 1010 and SAE 1020 mild steel, and a number of protective coatings on SAE 1010 mild steel. Streams investigated included synthetic solutions of REDOX in-process waste streams, metal waste from $BiPO_4$ processing, and variations of REDOX column 1A and 1D waste (concentrated, neutralized, and concentrated and neutralized). The stream most closely

representing the concentrated and neutralized salt waste stream is the neutralized and concentrated 1AW-1DW stream tested at 170°F. The synthetic waste solution used in the testing is given below:

$NaNO_3$	29.10%	407.4 g/L	4.79 M
$NaAlO_2$	8.10%	113.4 g/L	1.38 M
NaOH	1.80%	25.2 g/L	0.63 M
Na_2SO_4	0.40%	5.6 g/L	0.039 M
$Na_2U_2O_7$-$6H_2O$	0.07%	0.98 g/L	0.001 M
$Na_2Cr_2O_7$-$2H_2O$	0.40%	5.6 g/L	0.026 M
NH_3	0.05%	0.7 g/L	0.04 M
$Cr(OH)_3$	0.03%	0.42 g/L	0.004 M
$Fe(OH)_3$	0.20%	2.8 g/L	0.026 M
NaCl	--		
H_2O	59.70%		
Assumed Density	1400 g/L		

General corrosion rates were measured for a roughly 130 day period for four different bare (i.e., no coating) SAE 1010 steel specimens in the synthetic concentrated and neutralized salt solution. Evaporation losses from the solution were replaced with distilled water. The pre-test pH of the solution was 10.0-10.7. Two of the specimens were prepared by sandblasting, one specimen was welded and sandblasted, and the fourth specimen was welded, stressed and sandblasted. The welded specimens "...were prepared from stock plate under field conditions by qualified welders using a Lincoln semi-automatic welding machine and Lincoln automatic rod type L-60. Standard procedures for welding this type material were followed" (HW-18595). The weld ran longitudinally through the center of the specimen. The welded and stressed specimen was pre-stressed into the shape of a U by bending through 180° with an inside radius of bend of ¾ in. Final stressing was accomplished by stainless steel nuts and bolts joining the legs of the U. The stainless steel was insulated from the carbon steel by means of lucite washers. The welded (non-stressed) and one of the sandblasted specimens were partially immersed in the solution while the stressed and welded specimen and the other sandblasted specimen were fully immersed in the solution. For all four specimens positive weight gain was recorded for the indicated general corrosion rate. This could be explained by the generation of a coating on the surface of the material that was not removed. The remarks for all four samples stated the specimens were corrosion resistant to this solution. Light uniform tarnish, or a whitish film, formed on the immersed portion with light uniform tarnish of the vapor half was described as well.

In 1955, a program was established to obtain corrosion rates of the material in use for waste storage tank construction, SAE 1020 steel, and three other candidate materials for future construction of storage tanks for neutralized process wastes (HW-37642, *Field Corrosion Tests in REDOX and PUREX Underground Waste Storage Tanks*). The original program was established to obtain corrosion rate data at 4, 8, 16, 32, 64, and 128 months. The material specimens were prepared as wrought, welded, wrought and stressed, and welded and stressed to represent various field conditions. Additionally, weld-metal samples of two different welding electrodes, normally used in fabrication, were also exposed. An assembly containing the

specimens was placed into REDOX waste storage tank SX-107. The assembly contained seven tubes, six for removal between 4 and 128 months and one spare. Each tube contains two sample cages, one suspended in the vapor phase and one submerged in the liquid in the tank. Each sample cage included five samples of SAE 1020 (two in wrought condition, one in welded condition, one in wrought and stressed condition, and one in welded and stressed condition) and two samples of welding electrodes normally used in fabrication of the tested materials. Data was sought regarding the rates of general corrosion, pitting, and possibility of SCC.

Although specimens were to be retrieved at various intervals, reported corrosion data was only found for specimens exposed for approximately one year (HW-53308, *Interim Report on the Examination for Corrosion Test Coupons Exposed in REDOX 107SX Process Waste Storage Tank (Rm 148)*). The exact time frame the specimens were in tank SX-107 is not known, but it is expected the specimens would have been installed around June 1955. This is based on the document describing the test (HW-37642 issued June 28, 1955) stating, "...one unit has been placed in a REDOX waste storage tank..." However, waste was not introduced into tank SX-107 until April 1956 (HW-42993, *Separations Section, Waste – Status Summary for April 1956*). The interim report on corrosion in tank SX-107 was issued in October 1957, so the statement regarding a one year exposure of the coupons to the waste seems reasonable. Between April 1956 and April 1957 the recorded waste temperature in the tank ranged from 117°F to 273°F with the lowest temperature at the beginning and highest temperature at the end of the period. Tank SX-107 received concentrated and neutralized salt waste from April 13 through June 9, 1956 and after beginning to self-concentrate was filled again to the same level between July 27 and August 2, 1956 (HW-50216) and later in August (HW-83906 B RD). The waste began to self-concentrate by July 1956 and continued to self-concentrate through the period of time the specimens were in the tank. Waste temperature at the bottom of the tank (2-3 in. off the bottom) in July 1956 was 250°F. The amount of waste sent to the tank between April and June 1956 is 600,000 gal. The volume of waste added in July and August is not known but it is probably on the order of 10-20% of the originally filled volume. The evaporated volume at the end of April 1957 was 312,000 gal or approximately half the original volume.

The composition of the waste was not given, but as a first approximation could be doubled although this does not consider solubility limitations of constituents or the dilution effect of "hot" condensate which was added along with salt waste and not tracked separately. A rough estimate of constituent concentrations can be determined by doubling the concentration of constituents in Table 5-24 for HW-5, which was the current flowsheet at the time tank SX-107 was being filled with salt waste. Not accounting for solubility limitations, the major constituents would roughly be 8.4 M sodium nitrate, 2.6 M sodium aluminate, and 2.4 M sodium hydroxide at the end of April 1957, the estimated end of the corrosion test.

The general corrosion rate is not given in the report, HW-53308, but it can be determined for wrought and welded specimens by weight loss and dimensional data by assuming the steel density and an exposure period of one year. General corrosion rate can be determined from weight loss by the equation

$$mpy = 61.02 \frac{W_l}{A \times \rho \times t}$$

where mpy stands for mil per year (corrosion rate), W_l is the weight loss in grams from the specimen, A is the original exposed area of the specimen in square inches, ρ is the density of the specimen in g/cm^3, and t is the exposure time in years.

The specimens are $^1/_8$-in. by ½-in. by 1-½ in. with a $^3/_{16}$-in. hole through one end from which the sample is suspended. The SAE 1020 steel specimens exposed in the liquid waste exhibited a general corrosion attack, evenly distributed over the entire surface. The vapor phase samples were attacked locally, but in the areas of attack the corrosion was more severe than was seen on the liquid phase coupons. The general corrosion rate in the liquid and vapor phase was below 1 mil/yr. The maximum pit penetration was 4.62 mils in the liquid phase and 7.26 mils in the vapor phase. Table 5-26 lists the measured general corrosion rate and pitting data for the specimens. Metallographic examination of a stressed specimen from this testing showed no indications of SCC.

Table 5-26. General and Pitting Corrosion Data for SAE 1020 Steel Coupons Exposed for One Year in 241-SX-107 REDOX Waste

Condition Location	Specimen	Corrosion Data			
		Weight Loss, g	General Corrosion Rate, mil/yr	Average Depth of 20 Deepest Pits, mil	Depth of Deepest Pit, mil
Vapor	Wrought, #29	0.1664	0.64	3.85	7.26
	Wrought, #31	0.0875	0.34	3.72	5.12
	Welded, #71	0.0134	0.052	1.96	2.64
	Welded & Stressed, #99	0.0218	--	2.77	4.85
	Stressed, #127	0.0319	--	1.90	3.30
Liquid	Wrought, #30	0.0367	0.14	1.59	2.14
	Wrought, #32	0.0381	0.15	1.67	1.98
	Welded, #72	0.1211	0.47	2.03	3.30
	Welded & Stressed, #100	0.0949	--	2.06	4.62
	Stressed, #128	0.1332	--	1.88	3.30

Data taken from HW-53308, Tables I & II.

Temperature

With the exception of the first 18 months of operation, temperature data has been located for operation of the S and SX Farm tanks during the time of REDOX operation. The first tank to receive concentrated and neutralized salt waste was tank S-101, in July 1953, and waste from tank S-101 then cascaded to tanks S-102 and S-103. Temperature data for these three tanks is included in Figure 5-32. Available temperature data from when tank S-101 was first filled is somewhat illegible (HW-83906 A RD), but does show between July 17 (last day tank level was 0) and July 27, 1953 the temperature increasing from 60°F to 134°F, averaging 7.4°F/day. Between July 29 and 30, 1953 the temperature in tank S-101 increased 14°F from 145°F to 159°F (14°F/day) and between August 18 and 19, 1953 the temperature increased 12°F from 192°F to 204°F (12°F/day).

Because waste was cascaded in the first five tanks of SX Farm, tanks SX-101 and SX-104, which were the first tanks in the cascades, had the highest maximum temperature for each cascade, as

shown in Figure 5-33. Initial temperature data wasn't found for tank SX-104 when that cascade was first filled. For tank SX-101 this data is available. Available temperature data from when tank SX-101 was first filled starts on May 20, 1954 with a temperature of 75°F and a liquid level of 3 in. The liquid level increased to nearly 10 ft on June 19, 1954 when the waste temperature reached 80°F (HW-83906 A RD). It is expected that this was a water addition but this could not be verified with available information. Temperatures raised gradually, typically less than 3°F per day, until July 22-23, 1954 when the recorded temperature went from 102°F to 145°F during which the tank level increased 5 in. No explanation is given for this rapid change. One possible explanation could be that the thermocouple was lowered from a location in the liquid to a location that had accumulated sludge at a higher temperature or sludge accumulated to cover the thermocouple.

A temperature chart from 1954-1955 (RPP-RPT-58371) shows that the thermocouples in tanks SX-101 and SX-104 were lowered on July 13, 1955 with significant step changes in temperatures, 15°F in tank SX-101 and 106°F in tank SX-104. Available temperature data after the step change in July 1954 in tank SX-101 shows a gradual increase in the maximum temperature typically less than 3°F per day and a steadying out of temperature in SX-104.

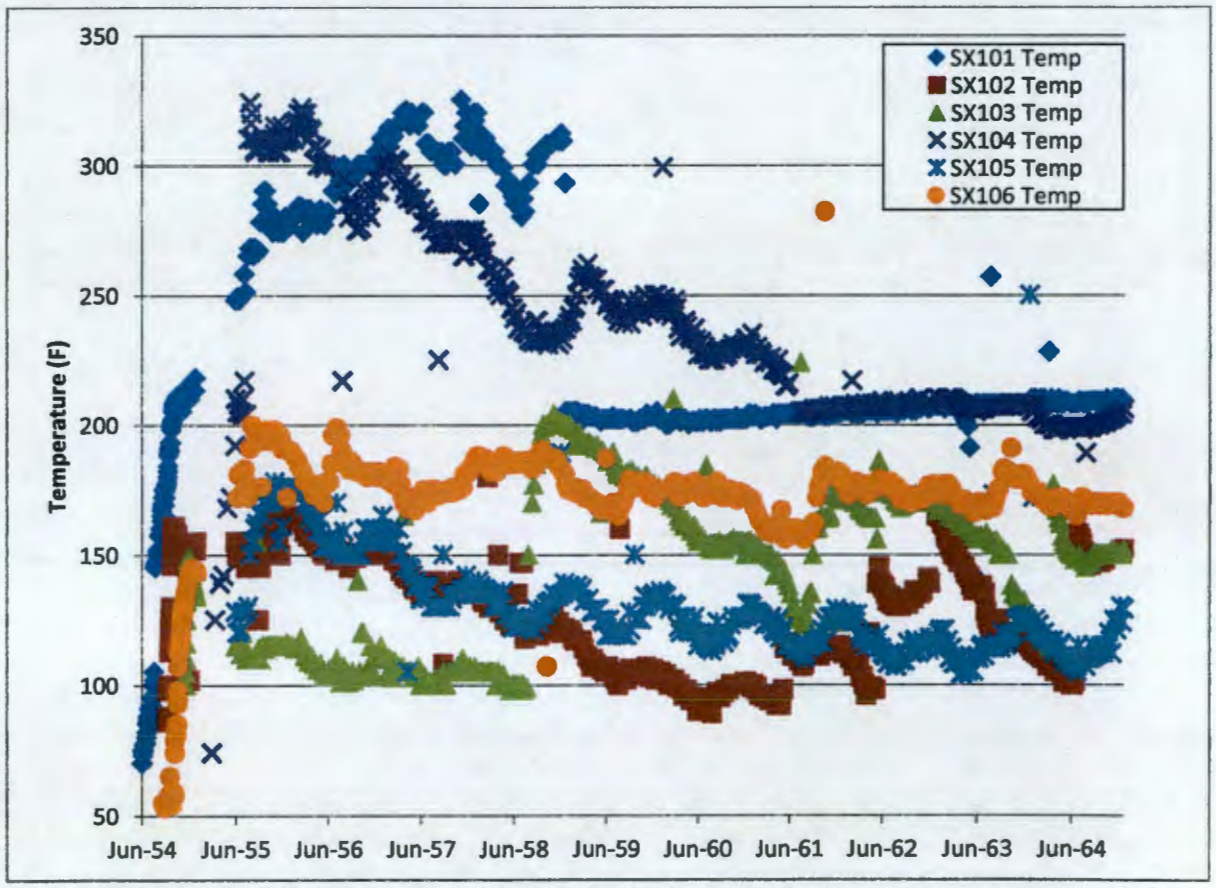


Figure 5-33. 241-SX-101 to 241-SX-106 Tank Content Maximum Temperatures at the Time of Filling with REDOX Waste, 1954-1964

In the last nine tanks of SX Farm, the waste was not cascaded so all tanks were exposed to higher temperatures. Temperature profiles for tanks SX-107 through SX-115 during the time of REDOX operation are shown in Figure 5-34. These temperatures were generally measured 2 to 3 in. from the tank bottom. The maximum temperature for each tank ranged from 234°F in tank SX-113 to 390°F (not shown on plot) in tank SX-107[5]. Tank SX-113 failed within five months of the first addition of waste and had not been completely filled.

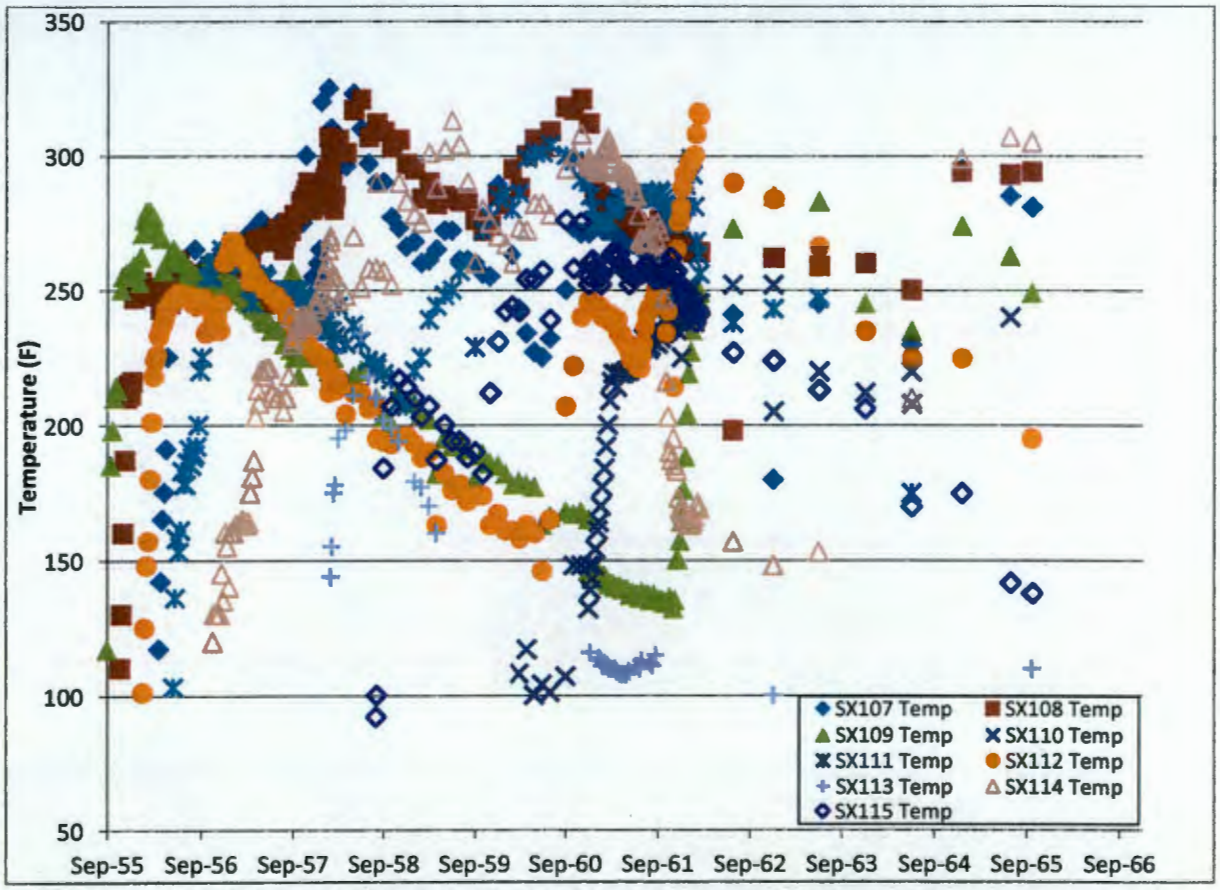


Figure 5-34. 241-SX-107 to 241-SX-115 Tank Content Maximum Temperatures at the Time of Filling with REDOX Waste, 1955-1965

Available maximum tank waste temperature and temperature rate of rise data of interest are tabulated for tanks that directly received either combined REDOX waste or concentrated and neutralized salt waste from REDOX (see Table 5-27). The tanks that received waste directly from REDOX include and SX Farms and the tanks U-110 through U-112 cascade.

[5] Two temperature readings of 390°F were recorded for SX-107 on February 5 and 12, 1958 but the temperature two weeks before was 320°F and one week after was 325°F so this temperature was not sustained for a very long time.

Table 5-27. Peak Temperature and Temperature Rate of Rise of Interest for Single-Shell Tanks Directly Receiving Combined REDOX Waste or Concentrated and Neutralized Salt Waste (2 Pages)

Tank	First Waste[1]	Temperature Rate of Rise[2]			Peak Temperature[2]	
		Change	Period	Rate	Date	Temp
S-101	18 Jul 53	75°F to 159°F	7/19/53– 7/30/53	7.6°F/day	various between 10/29/53 – 6/21/54	300°F+ offscale
		164°F to 246°F	8/8/53– 8/30/53	3.9°F/day		
		192°F to 204°F	8/18/53– 8/19/53	12°F/day		
S-102	8 Sep 53	70°F to 116°F	9/16/53– 9/23/54	6.6°F/day	various between 2/25/54 – 3/22/54	144°F
S-103	9 Nov 53	80°F to 129°F	12/7/53– 12/10/53	16°F/day	12/10/53	176°F[3], next highest temperature is 117°F
S-104	9 Feb 53	not available	--	--	various between 7/20/53 – 3/14/54 & 1/2/57	300°F or 300°F+ offscale
S-105	Apr 53	not available	--	--	12/6/53 – 12/8/53, 1/6/54-1/12/54, & 2/6/54	132°F
S-106	May 53	not available	--	--	6/5/57	160°F[3], next highest temperature is 117°F
S-107	25 Aug 52	not available	--	--	various between 4/17-24/54	300°F+ offscale
S-108	30 Oct 52	not available	--	--	various between 8/5/53 – 8/13/53	135°F
S-109	24 Dec 52	not available	--	--	8/15/53	115°F
S-110	Jan 52	not available	--	--	After 6/21/53[3] - 6/24-25/53	228°F
S-111	9 May 52	not available	--	--	After 6/21/53[3] – various between 11/21/53-12/5/53	119°F
S-112	25 Jul 52	not available	--	--	After 6/21/53[3] – 11/1/53	116°F
SX-101	19 May 54	65°F to 91°F	5/27/54– 7/1/54	0.74°F/day	11/6/57	325°F
SX-102	Sep 54	86°F to 158°F	9/9/54– 9/28/54	3.4°F/day	2/19/58	180°F
SX-103	Nov 54	100°F to 143°F	11/21/54– 11/28/54	6.1°F/day	7/20/61	224°F[3], next highest temperature is 210°F
SX-104	2 Feb 55	74°F to 125°F	3/1/55– 3/15/55	3.6°F/day	7/28/55	324°F
SX-105	11 May 55	130°F to 150°F	7/21/55– 7/28/55	2.9°F/day	12/26/63	250°F[3], next highest temperature is 189°F
SX-106	Jun 54	58°F to 74°F	10/8/54– 10/9/54	16°F/day	10/19/61	282°F[3], next highest temperature is 200°F
		94°F to 107°F	10/22/54– 10/23/54	13°F/day		
		58°F to 107°F	10/8/54– 10/23/54	3.3°F/day		
SX-107	3 Mar 56	191°F to 225°F	5/16/56– 5/23/56	4.9°F/day	2/5-12/58	390°F
		265°F to 390°F	1/15/58– 2/5/58	6.0°F/day		
SX-108	8 Nov 55	130°F to 160°F	11/24/55– 12/1/55	4.3°F/day	6/30/58 & 11/30/60	321°F
SX-109	20 Sep 55	117°F to 185°F	9/29/55– 10/13/55	4.9°F/day	12/31/62-1/3/63	285°F
SX-110	Nov 60	107°F to 148°F	9/30/60– 10/31/60	1.3°F/day	10/5/61, 7/25/62 & 12/31/62	252°F
SX-111	9 Jun 56	103°F to 136°F	6/13/56– 6/20/56	4.7°F/day	7/31/60	304°F
SX-112	13 Feb 56	101°F to 125°F	2/15/56– 2/22/56	3.4°F/day	3/8/62	316°F
SX-113	20 Feb 58	155°F to 175°F	3/5/58– 3/12/58	2.9°F/day	6/30/58	234°F
SX-114	Nov 56	135°F to 160°F	12/26/56– 1/2/57	3.6°F/day	6/30/59	313°F
SX-115	4 Nov 59	100°F to 184°F	9/2/58– 9/30/58	3.0°F/day	9/30/60	276°F
U-110	14 Jan 54	50°F to 202°F	1/27/54– 4/30/54	1.6°F/day	2/5-12/58	390°F
		128°F to 183°F	3/18/54– 4/5/54	3.1°F/day		

Table 5-27. Peak Temperature and Temperature Rate of Rise of Interest for Single-Shell Tanks Directly Receiving Combined REDOX Waste or Concentrated and Neutralized Salt Waste (2 Pages)

Tank	First Waste[1]	Temperature Rate of Rise[2]			Peak Temperature[2]	
		Change	Period	Rate	Date	Temp
		270°F to 287°F	12/18/59– 12/24/59	2.8°F/day		
		187°F to 217°F	1/31/63– 2/7/63	4.3°F/day		
U-111	Feb 54	65°F to 134°F	2/12/54– 3/25/54	1.7°F/day	9/24/58	317°F
		104°F to 116°F	3/9/54– 3/10/54	12°F/day		
		231°F to 274°F	1/7/59– 1/21/59	3.1°F/day		
U-112	Mar 54	60°F to 92°F	3/18/54– 3/29/54	2.9°F/day	9/30/60	276°F
		137°F to 219°F	12/14/61– 2/1/62	1.7°F/day		

[1]HW-83906 A-E RD or Monthly Waste Status Summary Reports for S and U Farm tanks, RHO-R-39, *Boiling Waste Tank Farm Operational History*, for SX Farm tanks.
[2]Data from waste level and temperature data sheets, see RPP-RPT-58371.
[3]Data point may be an outlier.

5.5.4 PUREX Process Waste Types (1956-1972)

This section of the document details wastes destined for single-shell waste storage tanks generated from the PUREX process between 1956 and 1972 (RPP-RPT-23177, *Origin of Waste in Tank 241-AW-105*). Irradiated nuclear fuel processing was restarted at PUREX in 1983 but all waste generated after 1980 was directed to DSTs rather than SSTs and therefore is outside the scope of this report.

The PUREX process was the second full scale solvent extraction separations process to recover plutonium and uranium from irradiated nuclear reactor fuel at Hanford. The PUREX facility provided a much higher throughput, and in less than five years of operation surpassed the combined total tons of uranium processed at T Plant, B Plant and REDOX (WHC-MR-0437, *A Brief History of the PUREX and UO_3 Facilities*). The PUREX plant exclusively processed aluminum clad irradiated nuclear fuel from its start of operation until mid-1967 when it also processed zircaloy clad fuel. The PUREX facility also processed thorium target material and a small amount of specialty fuels. Several modifications and flowsheet changes were made to the main process over the years. Information regarding the PUREX process, including changes impacting waste streams sent to the SSTs, and stream information for the major waste streams are provided below.

5.5.4.1. Process Description

The following process description is based primarily on the PUREX technical manual (HW-31000, *PUREX Technical Manual*, and RHO-MA-116, *PUREX Technical Manual*) and a variety of facility flowsheets (HW-24763, *PUREX Chemical Flowsheet HW #1,* HW-35225, *PUREX Chemical Flowsheet HW No. 4 – Increased PUREX Plant Capacity,* HW-40574, *PUREX Plant Flowsheet I (Startup),* HW-47889, *PUREX Phase II Proposed Flowsheet,* HW-52389-DEL, *PUREX Two-Cycle Flowsheet*, RL-SEP-381, *PUREX Plant Study Flowsheet 4.0 Capacity Factor*, ISO-705, *Proposed PUREX Flowsheet Dissolution of 0.947 Percent Enriched*

and 1.25-0.947 Percent Enriched "Spike" NPR Fuel Elements, ISO-1080-RD, *Reprocessing of PuO_2-UO_2 PRTR Fuel Elements in the PUREX Plant,* ARH-F-103, *PUREX Flowsheet Reprocessing N Reactor Fuels,* ARH-214, *PUREX Chemical Flowsheet – Processing of Aluminum-Clad Uranium Fuels,* ARH-1796, *Chemical Flowsheet for the PUREX Plant Second (2B Column) and Third Plutonium Solvent Extraction Cycles,* and ARH-2362, *PUREX Chemical Flowsheet for Processing N Reactor Fuels*). Changes to the flowsheet and operations associated with zircaloy clad fuel are based primarily on the updated PUREX technical manual, RHO-MA-116, which was issued in 1980.

The focus of the process description is initial operation with explanations of significant operational changes. Feed preparation was the first step of the PUREX process in which a solution containing uranium, plutonium, and fission products was prepared from the reactor-irradiated fuel. The fuel cladding removal and fuel dissolution processes for aluminum clad fuel are comparable to the processes performed as part of the $BiPO_4$ process and REDOX process described earlier. Zircaloy clad fuel, primarily from N Reactor, was processed through PUREX beginning in June 1967 (HNF-SD-WM-TI-794, *Activity of Fuel Batches Processed through Hanford Separations Plants, 1944 through 1989*, p. A-75). The subsequent portion of the PUREX process, solvent extraction, was designed to separate uranium and plutonium as product streams from the fission products with which they are associated in the irradiated nuclear fuel. The solvent extraction process separates the components (uranium, plutonium, fission products) by controlling their relative distribution between aqueous solutions and the immiscible organic solvent (TBP in a hydrocarbon diluent). This is performed by adjusting the valence state of the uranium and plutonium at different stages of the process where the organic and aqueous phases are contacted thus allowing distribution of the constituents between phases. This preferential distribution makes the separation of uranium, plutonium, and fission products from each other possible in the PUREX process. The organic solvent requires treatment to remove residual contaminants and degradation products. The principal acidic aqueous waste streams were concentrated while recovering the nitric acid for reuse in the process.

Figure 5-35 provides a simplified initial schematic identifying the major process steps and the waste streams of the PUREX process that are discharged to the SSTs. These waste streams are CW for both aluminum and zircaloy clad fuel, organic wash waste, and PUREX waste which is the highly active boiling waste containing the majority of the fission products. Coating removal waste was directed to tanks within C Farm and from there sent to other SSTs in C Farm and other farms. Organic wash waste was directed to tanks within the C Farm for a portion of the time during 1956, otherwise organic wash waste was sent to the boiling waste tanks where the water in the waste would boil off. The highly active boiling waste was sent to A Farm, then to AX Farm, and later to the DST farm, AY Farm.

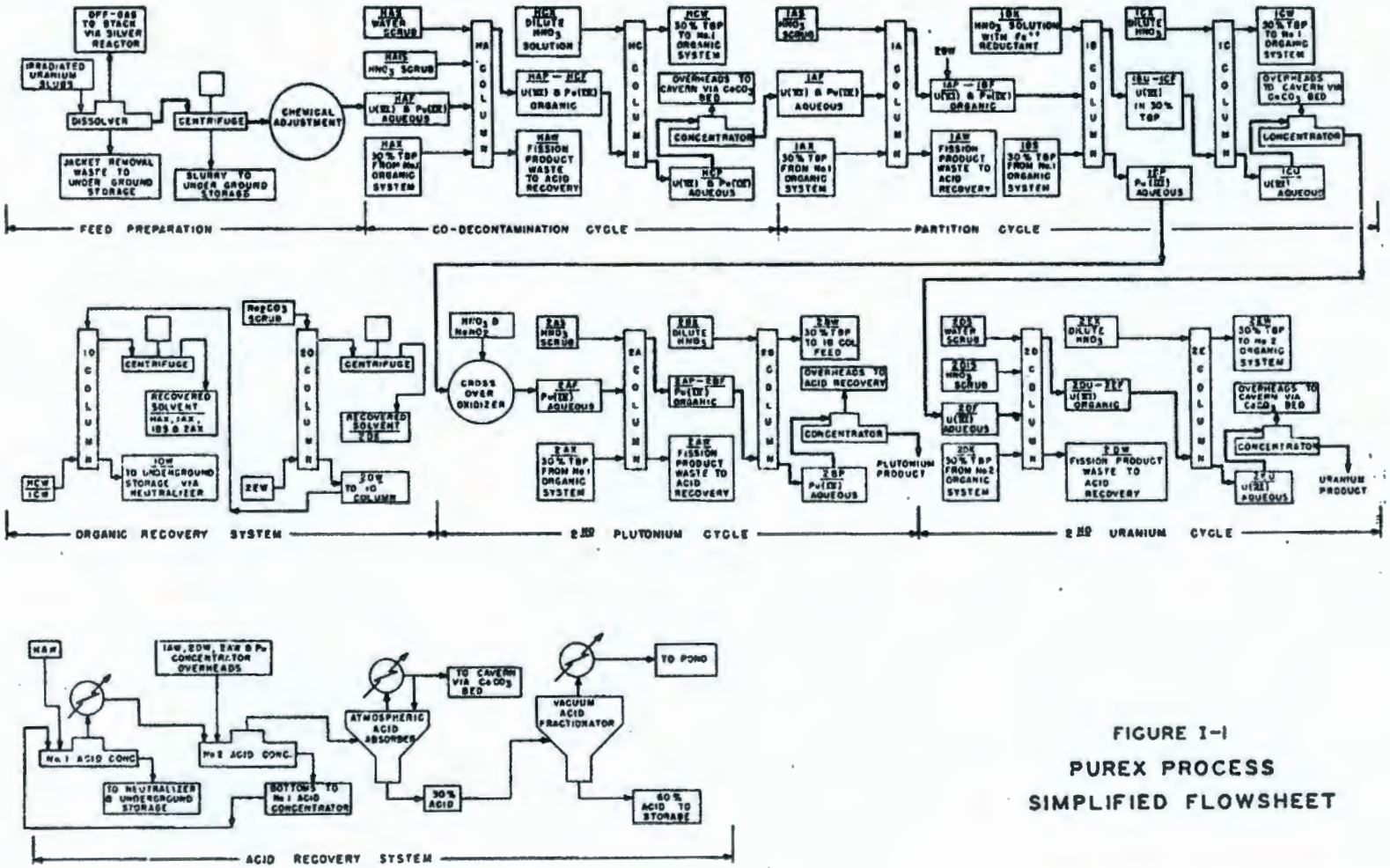


FIGURE I-1
PUREX PROCESS
SIMPLIFIED FLOWSHEET

Figure 5-35. PUREX Process Simplified Flowsheet, Circa 1955

Feed Preparation

The first step in the PUREX process was preparation of feed for the subsequent solvent extraction processes. Only aluminum clad fuel was processed from the start of operations in January 1956 through May 1967 (HNF-SD-WM-TI-794). In the feed preparation process, first the aluminum jacket and aluminum-silicon bonding layer surrounding the uranium is removed by preferentially dissolving the aluminum in a dissolver vessel with a solution of 10% (3.3 M) sodium hydroxide and 20% (3.0 M) sodium nitrate. This solution dissolves the aluminum jacket without dissolving any appreciable amount of the uranium and associated plutonium and fission products. This dissolved aluminum within the sodium hydroxide and sodium nitrate is removed from the dissolver and collected in a waste storage tank. The dissolver vessel containing the remaining uranium metal is then water washed and subsequently acid washed with a 5% nitric acid wash or a second water wash to remove residual material. The coating solution, and two wash solutions are combined for disposal to the tank farms. The combined solution is referred to as CW.

Beginning in June 1967, PUREX began processing zircaloy clad fuel in addition to aluminum clad fuel (HNF-SD-WM-TI-794). The decladding process for zircaloy clad fuel was significantly different than for aluminum clad fuel. The zircaloy cladding was removed via the Zirflex process (RHO-MA-116). The fuel was charged into a solution of 5.5 M ammonium fluoride and 0.5 M ammonium nitrate (AFAN) which was then brought to boiling via steam coils to dissolve the zircaloy. After dissolution of the zircaloy cladding surrounding the uranium the waste is removed from the dissolver and collected in a waste storage tank. The dissolver vessel, containing the remaining uranium metal, was then water washed to minimize free fluoride concentration within the dissolver. This water wash solution was then combined with the zircaloy cladding waste. The Zirflex process also resulted in about 1% of the uranium being converted to relatively insoluble uranium tetrafluoride. High fluoride content could increase uranium tetrafluoride formation and also lead to precipitation of ammonium hexafluorozirconate solids. To recover the solid uranium tetrafluoride in a soluble form, the solids in the dissolver was metathesized by 7 M potassium hydroxide producing hydrous uranium dioxide and potassium fluoride. The hydrous uranium dioxide was subsequently dissolved in nitric acid. After metathesis, the solution of potassium hydroxide and potassium fluoride were removed from the dissolver and stored for subsequent use. The dissolver contents were then water washed to remove residual metathesis solution and this water wash collected with the CW.

The collected CW and water washes from the dissolver were then centrifuged in two batches to separate uranium tetrafluoride solids from the waste supernatant liquid. The supernatant liquid discharged from the centrifuge was collected in a waste receiver tank that was prefilled with 19 M sodium hydroxide. As the waste was added to the sodium hydroxide the ammonia would be driven off from the waste and the pH of the waste would increase. The reaction of the CW with the sodium hydroxide would generate up to 50 vol% solids, primarily hydrated zirconium oxide. Transfer of this CW to underground storage required in-tank agitation at PUREX to ensure solids suspension and water flushing of the transfer line to clear any settled solids.

After cladding dissolution, the exposed uranium metal and accompanying plutonium and fission products were then dissolved in hot concentrated nitric acid. For zircaloy clad fuel aluminum, nitrate nonahydrate was first added to the dissolver to complex any residual fluoride before the

addition of nitric acid. As the dissolution first started water was added to the dissolver via the downdraft condenser. This water was added to scrub the dissolver offgas until boiling starts allowing reflux to the downdraft condenser. Dissolution occurs until change in specific gravity levels off and then water was added to the dissolver to cool and dilute the dissolver solution. The solution was then transferred to a storage tank and a second dissolution "cut" was made following the same process with the dissolver solution from the two cuts combined. Processing of aluminum clad fuel required subsequent centrifugation to remove a small amount of fine siliceous solids which could cause complications in solvent extraction (e.g., emulsification). The solids were residues from the aluminum-silicon bonding layer between the cladding and fuel core and impurities in the uranium core. The dissolver solution was processed through the centrifuge with the supernatant collected for subsequent treatment. The solids from the centrifuge were slurried out with water and ultimately collected with the CW. For aluminum clad fuel, the centrifuged dissolver solution was treated with sodium nitrite at elevated temperature to convert plutonium to the tetravalent state to allow for proper extraction during the solvent extraction decontamination cycle. The dissolver solution was chemically adjusted to make sure proper uranium and nitric acid concentrations were present for proper solvent extraction operation and additionally for zircaloy clad fuel that the proper aluminum to fluoride ratio was present.

Solvent Extraction

The solvent extraction system initially consisted of a decontamination cycle, partition cycle, a second uranium cycle, a second plutonium cycle, acid recovery, and organic recovery system. Subsequently a neptunium recovery cycle and third plutonium cycle were added and flowsheet and equipment modifications were made to increase capacity.

In the decontamination cycle the uranium and plutonium were first segregated from the bulk of the fission products in the HA column. The feed stream to the HA column was introduced approximately half way up the column where it would flow downward through the extraction portion of the column. The stream was contacted with an organic stream into which the uranium and plutonium would be extracted while the fission products for the most part remained in the aqueous phase which was directed to acid recovery. As the uranium and plutonium bearing organic stream rose through the column above the feed point it was contacted with a scrub solution which returned fission products that had entered the organic back to the aqueous phase. Roughly 99% of fission products were segregated from the uranium and plutonium in this column. The aqueous waste was collected for subsequent acid recovery. The organic stream containing the uranium and plutonium was subsequently sent to the HC column where the uranium and plutonium were stripped from the organic phase back into the aqueous phase in the presence of low concentration nitric acid. The organic phase from the HC column was sent to the organic recovery system. The aqueous phase from the HC column was sent to the tower section of a concentrator for removal of organic constituents. The aqueous phase flowed down the tower to the boiler where the stream was concentrated prior to subsequent partitioning of the uranium and plutonium.

In the partition cycle further decontamination from residual fission products was performed, plutonium was separated from uranium, and the uranium stream was concentrated prior to subsequent decontamination. The first column of the partition cycle was the IA column. The

concentrated stream from the decontamination cycle was fed to an intermediate point in the IA column and was operated in a manner similar to the HA column described above. The uranium and plutonium left in the organic phase from the top of the column while fission products left the bottom of the column in an aqueous waste stream. The aqueous waste stream from the IA column was sent to the acid recovery system. The organic overhead from the IA column was sent to the IBX extraction column along with recycled organic from the IBS scrub column and 2B column. The organic was contacted with a nitric acid, ferrous sulfamate stream which converted plutonium to the trivalent state which favored the aqueous phase. The uranium stayed in the organic phase which was then directed to the 1C column. Because of cell depth limitations, the originally planned IB column was split into two separate columns, the IBX and IBS columns. The plutonium bearing aqueous stream from the IBX column was sent to the IBS column where it was contacted with fresh organic that extracts residual uranium from the plutonium bearing aqueous stream. The organic stream from the IBS column was recycled to the IBX column as mentioned above and the plutonium bearing aqueous stream was collected in a tank for chemical adjustment prior to feeding to the final plutonium cycle. In the 1C column the uranium in the incoming organic feed stream from the IBX column was stripped back into the aqueous phase. The organic phase from the 1C column was sent to the organic recovery system. This aqueous phase bearing the uranium was sent to a concentrator for organic steam stripping and concentration prior to subsequent to processing through the final uranium decontamination cycle.

The final uranium decontamination cycle contains an extraction column, 2D, and strip column, 2E, that functioned like the HA and HC columns to produce a purified uranium product. The uranium-bearing aqueous stream from the partition cycle had ferrous sulfamate added for plutonium valence control prior to being fed to the 2D column. The feed was added near the middle of the column and the uranium was extracted to the organic as it fell through the bottom of the column. The organic phase for uranium decontamination came from a different organic system than that used in the rest of solvent extraction to reduce contamination of the final uranium product. The upper portion of the column was used to scrub fission products and plutonium from the organic as it rose through the column. The nitric acid solutions introduced in the 2D and 2E columns was fresh rather than recovered acid. This also reduced contamination of the final uranium product. The organic exiting the final uranium decontamination cycle was sent to a separate organic recovery system for removal of contaminants and degradation products prior to reuse. The uranium bearing aqueous product from the 2E column was steam stripped of organics and then concentrated in a concentrator.

The final plutonium decontamination cycle contained a collection tank where plutonium in the aqueous bottom stream from the IBS column was adjusted with nitric acid and sodium nitrite to the tetravalent state. The aqueous stream was fed to the midpoint of the 2A column where the plutonium was extracted into the organic phase. Above the feed point the organic was contacted with a scrub solution which removed the small amount of fission products that had also extracted into the organic phase. The organic overflowed to the 2B column where the plutonium was returned to the aqueous phase. After exiting the 2B column the plutonium-bearing aqueous stream was steam stripped of residual organic and then concentrated. The concentrated product was then placed in shipping containers.

The solvent used in the PUREX process was recycled repeatedly through the process and therefore accumulated contaminants and degradation products. The solvent used was 30 vol% TBP in an organic diluent. This diluent was initially a kerosene type diluent (identified as Shell kerosene fraction No. E-2342, similar to Shell Spray Base; or Phillips Soltrol 170) [HW-31000, p. 902-907]. This diluent was primarily composed of saturated aliphatic or napthenic hydrocarbons but contained small quantities of olefins, aromatics, and carboxylic acids which reacted to some extent with some of the PUREX process chemicals. In February 1963, the last of mixed diluent consisting of Shell-2342 and Soltrol-170 was introduced into the plant and a transition to all Soltrol-170 was started (HW-76848, *Chemical Processing Department Monthly Report, February, 1963*, p G-2). In mid-February 1966, the diluent Soltrol-170 was replaced with normal paraffin hydrocarbon (ISO-143, *Chemical Processing Division Monthly Report for February, 1966*).

To remove contaminants and degradation products accumulated from use, the solvent was treated by contacting it with an aqueous stream in a contactor and/or solvent extraction column. Organic used in the final uranium decontamination cycle was treated separately (in the second solvent recovery system) from the organic used in the remainder of the process (treated in the first solvent recovery system). The organic from the uranium decontamination cycle was contacted in the 2O solvent extraction column with a 0.24 M sodium carbonate aqueous stream to remove contaminants and degradation products. The organic from the decontamination cycle, partition cycle and plutonium cycles was contacted in the 1O solvent extraction column with either fresh sodium carbonate or used sodium carbonate from the second solvent recovery system. Later sodium carbonate and potassium permanganate were used in combination for the wash solution to aid in removal of certain contaminants (HW-49574, and HW-60116, *Description of PUREX Plant Process*).

By 1959, a more comprehensive solvent washing process was used for the first solvent recovery system (HW-60116) because of the more severe conditions to which the solvent was subjected. This consisted of first contacting the solvent with an alkaline-permanganate wash (solution of sodium carbonate and potassium permanganate), where the permanganate is reduced to manganese dioxide. The solvent is then washed with dilute nitric acid for removal of residual manganese dioxide and finally washed with dilute sodium carbonate. The second solvent recovery system was subsequently converted to provide the same treatment as the first solvent recovery system. Early on during PUREX operation, the used wash solution from the 2O solvent extraction columns at times was directed to the 1O solvent extraction column for use as the wash solution in that system. At other times fresh wash solution at similar or higher sodium carbonate concentration and with other chemicals (e.g., potassium permanganate) was used in the first solvent recovery system. There it would remove contaminants and degradation products from the balance of the organic used in the solvent extraction process. The aqueous waste streams from the solvent recovery systems were collectively referred to as organic wash waste (OWW). The OWW was sent to underground storage.

Acid Recovery System

The recovery of nitric acid in the PUREX process provided appreciable economic savings in terms of chemical (nitric acid and sodium hydroxide) procurement and radioactive waste storage

by providing recycled nitric acid for reuse in the process and coincidentally reducing the quantity of neutralized nitric acid, as sodium nitrate, disposed to underground storage tanks.

Originally the acid recovery system consisted of two acid concentrators, an acid adsorber and vacuum fractionator along with intermediate tankage. The first acid concentrator was used to concentrate the highly radioactive waste stream from the HA column. Water and nitric acid vapor were driven off in the overheads from the concentrator, condensed and routed to an accumulation tank. The bottoms stream from this concentrator was discharged to a receiver tank, neutralized and sent to boiling underground storage tanks (A Farm and later AX Farm). The second acid concentrator was used to concentrate the low activity waste streams and overheads from the first acid concentrator. The concentrated bottoms from this second acid concentrator are reused in the process. The overheads from this second concentrator were fed as vapor to the acid absorber. The acid absorber was an atmospheric pressure tower with bubble cap trays where the vapor was countercurrently contacted with water. This produced an overhead stream suitable for discharge and a 30% nitric acid bottom stream which was subsequently concentrated to 60% in the acid fractionator. The acid fractionator was a bubble cap tray tower operated at vacuum to produce a 60% nitric acid product at the bottom for reuse in the process. The vapor out the top of the column is condensed and discharged to ground. The vacuum acid fractionator was added to the process because of the potential for excessive corrosion of the acid absorber that was operated at atmospheric pressure.

Major Modifications

By February 1957, a proposed flowsheet was prepared for an increase of the PUREX throughput to a 4.0 capacity factor over the original design (HW-47889). This required a number of equipment and operational changes. The HC column was replaced by the HS column (new cartridge and organic continuous operation). The 1A column of the partition cycle was removed. Ion exchange purification of the final plutonium product was implemented. Sodium carbonate-potassium permanganate was used in the first solvent extraction treatment system. Aqueous wastes from the two separate solvent treatment systems were sent to underground storage rather than an attempt to reuse between the systems. The aqueous waste streams from the 2A column, 2D column, and plutonium ion exchange were concentrated in a backcycle waste concentrator for return to the HA column for recovery of products. Initial operations were at less than a 4.0 capacity factor increase.

During 1958, studies were undertaken to denitrate the 1WW stream via the addition of formaldehyde (HW-55941, *The Removal of Nitric Acid from PUREX Plant First Cycle Acid Waste by Reaction with Formaldehyde*). The advantage of this would be to limit the amount of nitrate present in the 1WW stream and the amount of sodium hydroxide that would have to be added to neutralize the stream for underground storage. By March 1962 formaldehyde denitration of the 1WW stream was tested within the PUREX plant (HW-73193 G, *Chemical Processing Department Monthly Report, March, 1962*). Performance of formaldehyde denitration resulted in higher than desired acidity in the waste (~3-4 M rather than the desired 1 M) and, when antifoam addition was interrupted, higher activity in the recovered acid (HW-76054, *Chemical Processing Department Monthly Report, December, 1962*, p. G-2). In February 1963, the use of sugar for denitration was tested in the plant with acid concentration in the 1WW reduced from 4.5 M to 0.70 M. (HW-76848, p. G-2). Sugar denitration was

subsequently used in the process. This allowed much higher concentrations of fission products relative to sodium nitrate present in the waste. For 1WW from zircaloy clad fuel, the aluminum concentration (present from aluminum nitrate nonahydrate [ANN] addition to complex fluoride) was limited to about 1 M before precipitation of aluminum would occur during sugar denitration (HW-79665, *Preliminary Study of Multiple Fuel Processing at the PUREX Plant*). It is interesting to note that after implementing sugar denitration, the 1WW waste was directed to tank A-105 (ruptured liner) and subsequently tank A-106 (tank with highest recorded waste temperature).

Development of a process to recover neptunium began in 1958 (HW-SA-2928, *New Neptunium Recovery Facility at the Hanford PUREX Plant*). Initially neptunium was recycled in the backcycle waste stream. Once the plant was shut down the accumulated neptunium was recovered via use of the final plutonium cycle. Subsequently continuous extraction equipment for neptunium recovery was installed to allow recovery of neptunium during operation of the balance of the PUREX plant. The processing consisted of collection in a dedicated solvent extraction cycle, subsequent decontamination in that solvent extraction cycle, and batch ion exchange for concentration and final purification of the final product. Continuous neptunium recovery had no significant impact on waste sent to underground storage.

From April 15, 1966 to August 20, 1966 the PUREX plant was dedicated to the performance of a campaign for processing 194 tons of thoria for the recovery of ^{233}U (ISO-419, *PUREX Plant Thorium Process Operation Report*). Major equipment changes included a new uranium product concentrator and cooler system and a new uranium purification and loadout system in N Cell, and extensive jumper additions and changes. Plant turnaround in preparation of the campaign included flushing the plant, equipment changes, operability testing, processing, post processing decontamination and flushing, equipment changes back to the original configuration, and operability testing for uranium fuel processing. From June 8, 1970 until January 16, 1971 the PUREX plant was dedicated to a second campaign for processing thoria. The plant processed 470 tons of thoria for the recovery of ^{233}U (ARH-2127, *PUREX Process Operation & Performance 1970 Thoria Campaign*). Major equipment changes include the installation of two new concentrators, a new downdraft condenser tower on one of the dissolvers, a new uranium product receiver-sampling tank, and a large number of jumper additions and changes. The solvent extraction flowsheet was based on the Thorex II flowsheet developed at Oak Ridge National Laboratory (ARH-2127). The first solvent extraction cycle was used for co-decontamination and partitioning of the thorium and uranium. Further decontamination was attained in one additional thorium cycle and two additional uranium cycles. The uranium was passed through a cation resin for final thorium absorption prior to concentration. During the first and second thoria campaigns (including pre and post flushes), 1,198,000 and 2,795,000 gal of waste were sent to underground storage, respectively (ISO-419, Section K; ARH-2127, Table X).

The PUREX plant was flushed and cleaned out in preparation for an extended shutdown in September 1972 (PPD-493-9 DEL, *Monthly Status and Progress Report September 1972*). The organic solutions were collected in the solvent recovery systems, washed and stored. Solvent extraction columns were consecutively flushed with caustic, tartaric acid, and oxalic-nitric acid flushes. Plutonium cycle equipment was flushed with caustic and tartaric acid.

Each of the major waste streams sent to SSTs are discussed below. The available compositional information, temperature data during storage, and corrosion testing data are provided for each stream.

5.5.4.2. Coating Removal Waste from Aluminum Clad Fuel

The discussion of CW from decladding aluminum clad fuel elements in Section 5.5.1.2 is applicable to CW generated as part of the PUREX process. No additional discussion regarding this waste stream composition is necessary beyond what was previously provided. From January 1956 until September 1972, when PUREX was placed in standby, CW from aluminum clad fuel was sent to C Farm tanks and from there also distributed among BX and BY Farm tanks. Some CW was also sent to T Farm (RL-SEP-821, *Chemical Processing Department Waste Status Summary July 1, 1965 through September 30, 1965*, ISO-806, *Chemical Processing Division Waste Status Summary, January 1, 1967 through March 31, 1967*, ISO-967, *Chemical Processing Division Waste Status Summary, April 1, 1967 through June 30, 1967*).

5.5.4.3. Coating Removal Waste from Zircaloy Clad Fuel

Up until the end of 1980, after which SSTs no longer received waste, 1770 metric tons zircaloy clad uranium from N Reactor had been processed. Of this, 231 metric tons were processed at REDOX (13%) and the remainder was processed through PUREX (HNF-SD-WM-TI-794). Small quantities of zircaloy clad PRTR fuel were also processed at PUREX during this time frame (March-June 1972) (PPD-493-3, *Monthly Status and Progress Report, March 1972*, PPD-493-4, *Monthly Status and Progress Report April 1972*, PPD-493-5, *Monthly Status and Progress Report May 1972*, PPD-493-6, *Monthly Status and Progress Report June 1972*). Other minor amounts of zircaloy clad fuel were also reprocessed. Coating removal waste from zircaloy clad fuels sent to SSTs was generated at PUREX from June 1967 until the summer of 1972, just before PUREX was placed in standby during September.

The chemical process for removing zircaloy cladding from fuel was very different from the process for aluminum cladding resulting in a very different cladding removal waste. Zircaloy clad fuel was declad via the Zirflex process. The following description is taken from RHO-MA-116. The Zirflex process is based on the dissolution of zirconium by fluoride. The process consists of a dissolution step followed by a metathesis step to recover the small amount of uranium and plutonium that dissolves along with the zirconium. Zircaloy cladding is dissolved from the fuel in boiling aqueous solution of 5.5 M ammonium fluoride and 0.5 M ammonium nitrate (AFAN). The decladding reaction occurs as:

$$Zr + 6NH_4F \rightarrow (NH_4F)_2ZrF_6 + 4NH_3 + 2H_2$$

Ammonia and hydrogen are evolved as gases during the reaction. Under certain conditions these gases can be flammable. In the presence of ammonium nitrate, hydrogen is converted to ammonia. In practice the overall reaction for dissolution of zirconium in the AFAN solution is:

$$Zr + 6NH_4F + 0.47NH_4NO_3 \rightarrow (NH_4F)_2ZrF_6 + 4.94NH_3 + 0.12H_2 + 1.41H_2O$$

The uranium metal, and plutonium (which acts similarly to uranium), of the fuel dissolves when exposed to the AFAN decladding solution. During dissolution roughly 1% of the uranium metal in the fuel elements was converted to relatively insoluble uranium tetrafluoride and a much smaller amount (about 0.1%) to more soluble uranium hexafluoride. The solubility of the uranium and plutonium is a function of the metal valence state, free fluoride in solution and temperature. These factors are controlled by sparging with steam rather than air to limit uranium conversion to the hexavalent state, limiting free fluoride at the end of the cladding dissolution step, and reducing the temperature of the decladding solution before removal from the dissolver. The remaining charge in the dissolver was water rinsed, with the water rinse subsequently added to the decladding solution. After water rinse, a solution of 7 M potassium hydroxide was added to the remaining fuel in the dissolver to metathesize the uranium and plutonium fluorides to oxides that were soluble in nitric acid. A portion of the used metathesis solution from the dissolver was then used for metathesis of uranium and plutonium solids in the decladding solution. The dissolver is rinsed after removing the metathesis solution and this rinse water is also processed with the decladding solution.

Because of the significant amount of uranium in the decladding solution and associated water rinse solutions, these streams were processed through a centrifuge to recover insoluble uranium and plutonium that was jetted out of the dissolver along with the solutions. The liquid from the centrifugation was collected in a waste receiver tank. The waste receiver tank was prefilled with concentrated sodium hydroxide (reverse strike) to drive off ammonia and increase the pH of the waste. The solids were collected from the centrifuge and metathesized with potassium hydroxide in a metathesis step to convert the solids to oxides that were soluble in nitric acid. After metathesis, the slurry was centrifuged to segregate the solids from the supernatant. The solids are collected and dissolved in nitric acid for subsequent combination with the dissolved uranium product from the dissolvers. The spent metathesis supernatant solution is collected in the same waste receiver tank as the decladding solution (described above) but processed separately.

The reaction of the decladding solutions and rinses with the sodium hydroxide results in up to 50 vol% solids, primarily hydrated zirconium oxide. This waste requires agitation for solid suspension in order to be transferred as a slurry to underground storage. Approximately 3,700 gal of decladding and rinse solutions are created per batch and a 530 gal line flush follows the waste discharge. The composition of the reacted decladding waste and rinses mixed with sodium hydroxide is given in the PUREX Technical Manual (RHO-MA-116, Table 4-3) as:

ZrO_2-$2H_2O$	0.17 M
NaF	1.2 M
$NaNO_3$	0.02 M
KF	0.004 M
NaOH	0.5 M
Solids	20 %

The spent metathesis supernatant solution associated with uranium solids in the decladding solution was nominally 2.7 M potassium hydroxide and 1.6 M potassium fluoride (RHO-MA-116, Table 4-4). Roughly 1070 gal of this spent solution and a 530 gal of line flush were produced batchwise. After metathesis, the slurry was centrifuged to segregate the solids from the supernatant. The solids are collected and dissolved in nitric acid for subsequent

combination with the dissolved uranium product from the dissolvers. The spent supernatant solution is collected in the same waste receiver tank as the decladding solution (described above) but processed separately.

Based on combining the decladding waste, spent metathesis supernatant solution, and line flushes, the composition of the combined streams would be:

ZrO_2-$2H_2O$	0.11 M
NaF	0.76 M
$NaNO_3$	0.013 M
KF	0.30 M
NaOH	0.32 M
KOH	0.50 M
Solids	20 %

Zircaloy clad PRTR fuel was also processed through PUREX (ISO-1080 RD, PPD-493-3, PPD-493-4, PPD-493-5, and PPD-493-6). Initial evaluation of processing PRTR fuel considered not centrifuging decladding waste since the centrifuges were not geometrically safe for the mixed oxide fuels. Otherwise, the cladding waste from this fuel would be similar to the decladding waste solutions from other Zirflex processing.

Coating removal waste from zircaloy clad fuel was not segregated in SST farms, but sent to tanks in C Farm that contained other waste types. During later processing (post 1980) of zircaloy clad fuel at PUREX, neutralized CW was sent to two DSTs, tanks AW-103 and AW-105 (RPP-22404, *Origin of Waste in Tank 241-AW-103*, Table 2). Sample analyses are available for a sample taken from tank AW-105 (Letter Report, M.S. Hanson to R.D. Wojtasek, "Characterization of Actual Zirflex Decladding Sludge", June 1986). The chemical composition from that letter report is repeated below for the liquid and solid phases:

Constituent	Supernatant	Sludge*
Fe^{+3}		0.32 mg/g sludge
Al^{+3}	0.02 M	0.96 mg/g sludge
Na^{+}	1.8 M	112. mg/g sludge
K^{+}	0.36 M	12.3 mg/g sludge
Ca^{+2}	0.36 M	0.20 mg/g sludge
F^{-}	0.62 M	75. mg/g sludge
NO_3^{-}	0.48 M	25. mg/g sludge^
NO_2^{-}	0.12 M	4.5 mg/g sludge^
SO_4^{-2}	0.12 M	85. mg/g sludge
PO_4^{-3}	<0.02 M	<25. mg/g sludge
CO_3^{-2}	0.94 M	63. mg/g sludge^
Cl^{-}	0.12 M	2. mg/g sludge
OH^{-}	0.76 M	--
NH_3	0.11 M	--
pH	13.2	--

* Values based on nitric acid digest of sludge.

^ Values based on water soluble portion of sludge per g of sludge. Nitrate, nitrite and carbonate are indeterminate via acid digest.

To simulate corrosion of the underground waste storage tanks, SAE 1020 mild steel coupons were exposed at 25 and 40°C to Zirflex decladding waste solution neutralized with 50 wt% NaOH to pH values between 5.5 and 9.3 (HW-61662, *Power Reactor Fuels Reprocessing Progress Report on Corrosion Studies*). Waste composition was not given as part of the results but would be expected to be similar to the composition given above. The corrosion data obtained indicated negligible attack on specimens exposed for five months to solutions at pH 8.5 and 9.3. Pitting attack was appreciable in solutions at lower pH. Exposure of 1020 mild steel specimens to boiling neutralized Zirflex waste solution was also performed, with negligible corrosion after two months of exposure. Tabulated results are provided in Table 5-28.

Table 5-28. Corrosion Rates of Mild Steel in Neutralized Zirflex Decladding Solution – Effect of pH

Temperature	pH	Corrosion Data			
		Weight Loss, g*		Maximum Pit Penetration, mil	
		Liquid	Interface	Liquid	Interface
25°C	5.5	0.470	0.431	6.5	5.5
	6.3	0.228	0.328	5.5	5.5
	6.9	0.172	0.337	5.5	5.0
	8.5	0.000	0.000	0.0	0.0
	9.3	0.000	0.000	0.0	0.0
40°C	5.5	1.084	0.898	13	14
	6.3	0.452	0.571	6.5	10.5
	6.9	0.175	0.491	3.0	6.0
	8.5	0.000	0.000	0.0	0.0
	9.3	0.000	0.000	0.0	0.0

Data taken from HW-61662, Table VIII.

* Weight loss data provided to demonstrate date trend with respect to pH. Specimen dimensions not given in report so general corrosion rate could not be determined.

5.5.4.4. Highly Active Waste

The highly active waste from the PUREX process was sent to tanks within A Farm from January 1956 through early 1965 (RL-SEP-659, *Chemical Processing Department Waste Status Summary January 1, 1965 through June 30, 1965*). After this time the highly active waste was sent to AX Farm until July-September 1969 (ARH-1200 C, *Chemical Processing Division Monthly Report Summaries, January 1972 – December 1973*). During this time some of the highly active waste was treated within PUREX for strontium and later strontium and cesium recovery (see Section 5.5.5.1). This section of the report only covers the highly active waste stream that was sent to the SSTs.

At the beginning of operations at PUREX, the bottoms stream from the first acid concentrator, 1WW, was discharged to a receiver tank, neutralized and sent to boiling underground storage tanks. This waste contained the concentrated fission products separated from the uranium and plutonium products. The waste was self-concentrating because the radioactive decay heat evaporated a portion of the water contained within the waste. No sample data was found from early processing but the flowsheet (HW-35225) current at the time PUREX was started provides

the estimated composition of neutralized waste sent to boiling underground storage tanks. The composition is repeated below:

Constituent	M
$NaNO_3$	2.1
Na_2SO_4	0.07
Na_2CO_3	0.1
$Fe(OH)_3$	0.035

By March 1962 formaldehyde denitration of the 1WW stream was tested within the PUREX plant (HW-73193 G) to increase acid recovery within PUREX and reduce the waste nitrate sent to underground storage. Formaldehyde denitration did not meet the expectations in terms of destruction of nitrate. In February 1963, the use of sugar for denitration was tested in the plant. Sugar denitration with acid concentration in the 1WW reduced from 4.5 M to 0.70 M. (HW-76848, p. G-2). Sugar denitration was subsequently used in the process. This allowed much higher concentrations of fission products relative to sodium nitrate present in the waste. Denitration consisted of collecting a batch of concentrated waste, heating to 95°C to 100°C, adding a 22 wt% sugar solution until the nitric acid concentration was less than 1 M, and was digested for 12 hours (RHO-MA-116). After digestion the waste would either be neutralized and sent to underground storage tanks or would remain as an acidic waste and sent to 244-AR vault for treatment prior to transfer to B Plant for cesium and strontium recovery.

Specifications and standards for operational control of A and AX Farm were issued in March 1965 (RL-SEP-269) including descriptions of the characteristics of the waste streams sent to these farms. The A and AX Farms received neutralized PUREX acid waste (PAW), fission product waste, OWW, and miscellaneous flushes and cell drainage. The neutralized PAW and fission product waste contain essentially all of the unrecovered fission products and the OWW is a dilute sodium carbonate-sodium nitrate solution containing manganese dioxide solids and decomposition products removed from the PUREX solvent. The PAW is denitrated to approximately 0.5 M free acid then neutralized to a pH of 10 with caustic. During self-concentration the percentage of solids in the waste increases. These solids settled out of the supernatant liquid as the waste aged and self-concentrated. Typical waste compositions for the supernatant liquid and sludge from neutralized PAW is listed in RL-SEP-269 and repeated below:

Constituent	Supernatant	Sludge
Fe^{+3}	--	0.04 g/g
Al^{+3}	--	0.02 g/g
Ni^{+2}	--	0.003 g/g
Cr^{+3}	--	0.003 g/g
Na^{+}	7.0 M	0.35 g/g
Ca^{+2}	--	0.0004 g/g
NO_3^{-}	0.7 M	0.05 g/g
NO_2^{-}	3.4 M	0.03 g/g
SO_4^{-2}	0.2 M	0.06 g/g
PO_4^{-3}	0.04 M	0.04 g/g

CO_3^{-2}	1.1	M	0.20	g/g
Cl^-	0.10	M	--	
OH^-	0.1	M	--	
SiO_2	--		0.002	g/g
MnO_2	--		0.0026	g/g

A few sample analyses of A and AX Farm supernatant liquid and sludge prior to sluicing for fission product recovery are available. These are presented below.

A PUREX tank farm sludge sample from tank A-102 was analyzed on May 31, 1963 (WHC-SD-WM-ER-308, *Supporting Document for the Historical Tank Content Estimate for A Tank Farm*) with the following results:

Constituent	g/g sludge
NO_3	0.0171
NO_2	0.0083
SO_4	0.113
CO_3	0.079
Na	0.246
Fe	0.055
Al	--
Cr	0.0001
Ni	0.0007
Si	0.01
Mn	0.01

PUREX tank farm supernatant solutions from tanks A-101, A-104 and A-106 were sampled on September 2, 1964 (RL-SEP-183 RD, *PUREX Tank Farm Supernatant Solution Composition*). The sample analyses were performed to help with ongoing research and development studies in support of waste management and fission product recovery activities. The sample composition is given below:

Constituent	241-A-101		241-A-104		241-A-106	
Na	6.52	M	6.52	M	6.95	M
NO_3	0.226	M	0.667	M	0.58	M
NO_2	3.36	M	3.42	M	3.35	M
SO_4	0.246	M	0.187	M	0.135	M
PO_4	0.0358	M	0.023	M	0.0095	M
Total Base	2.6	M	1.95	M	1.63	M
Total Anion (calculated)	4.04	M	4.62	M	4.32	M

Analytical results were reported for PUREX tank farm supernatant solutions from 241-A and 241-C tanks on May 27, 1969 via internal letter, "Ion Exchange Feed Samples" (Larkin 1969).

The sample analyses were performed to understand characteristics of remaining PSN waste to be processed through ion exchange for cesium recovery. The sample composition is given below:

Constituent	241-A-102*	241-A-103	241-C-101	241-C-103	241-A-106
Na	6.4 M	7.4 M	4.1 M	5.85 M	6.52 M
K	0.04 M	0.03 M	0.03 M	0.04 M	0.104 M
Al	0.01 M	0.007 M	0.04 M	0.01 M	0.002 M
pH	10.7	10.85	12.7	10.65	10.2

* Tank 241-A-102 contents a blend of 30% A-106 and 70% A-102.

PUREX tank farm sludge and supernatant that was originally in tank A-105, but then transferred to tank A-103 after failure of tank A-105, was sampled and analyzed on December 16, 1972. Those results (WHC-SD-WM-ER-308) are shown below:

Constituent	Supernatant	Hard Sludge	Fines
Fe	<0.00181 M	0.0870 g/g	0.0723 g/g
Al	0.026 M	<0.0675 g/g	0.0369 g/g
Si	<0.00196 M	0.0106 g/g	0.00949 g/g
Mn	0.00184 M	--	--
Na	3.47 M	--	0.0990 g/g
OH	0.914 M	--	--

PUREX tank farm sludge samples from AX Farm were sampled and analyzed during 1974 (WHC-SD-WM-ER-309, *Supporting Document for the Historical Tank Content Estimate for AX Tank Farm*). Those results are shown below:

Constituent	AX-102 [Sep 25, 1974]	AX-103 [Sep 19, 1974]	AX-104 [Jul 10, 1974]	AX-104 [Oct 14, 1974]
Fe	2.54 M	1.94 M	0.232 g/g	0.232 g/g
Al	--	1.05 M	0.032 g/g	--
Si	1.26 M	0.283 M	0.014 g/g	0.013 g/g
Cu	--	--	0.0048 g/g	--
Mg	0.044 M	0.056 M	0.0006 g/g	--
Mn	0.217 M	0.298 M	--	--
Ca	0.199 M	--	--	--
Ba	0.011 M	--	--	--

Tank waste average and maximum temperatures for the A and AX Farm tanks between 1957 and 1972 are provided in Figure 5-36 through Figure 5-38. Average temperature is not available for tanks AX-101 and AX-102 nor is the maximum temperature available for tank AX-104.

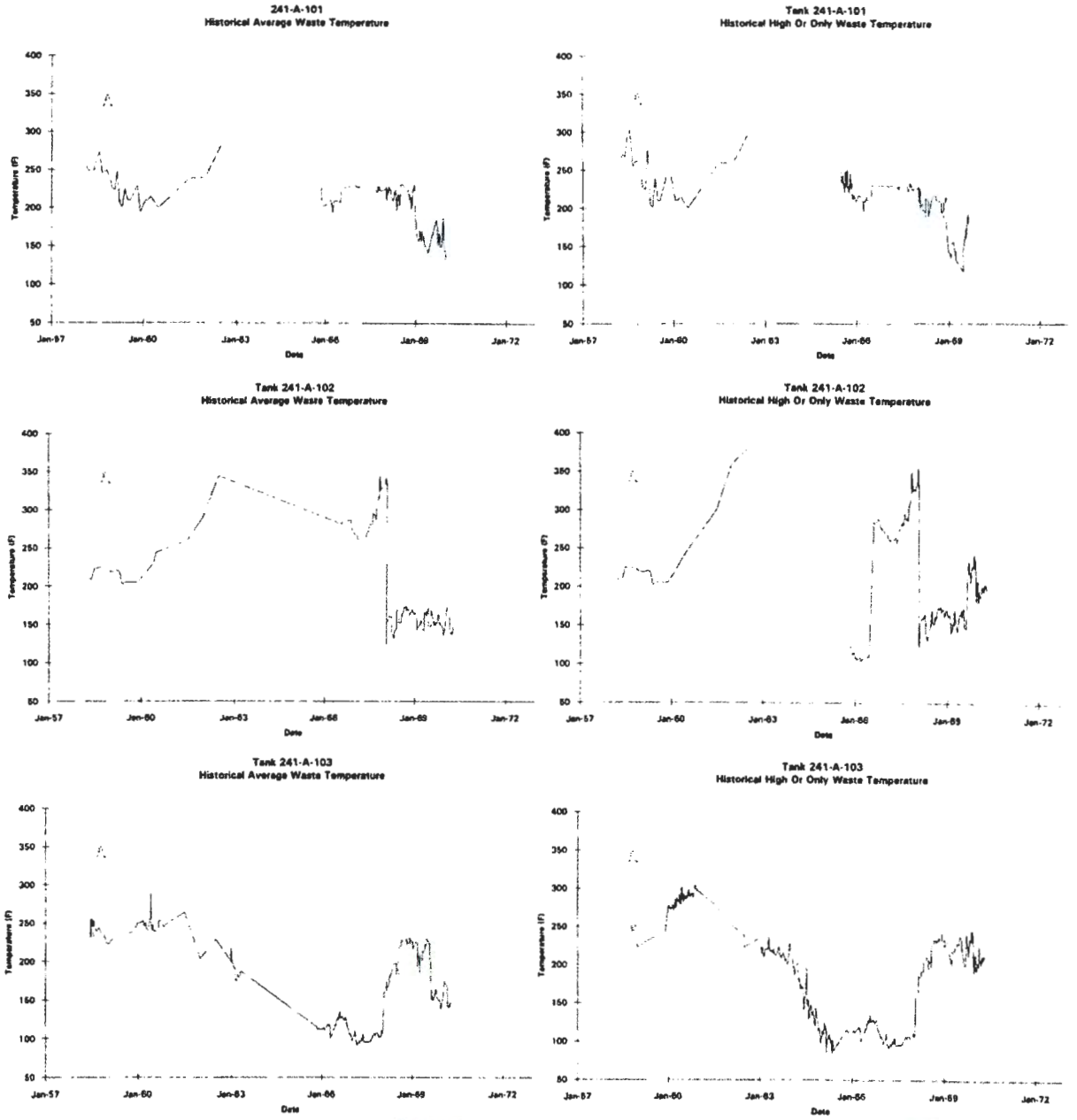


Figure 5-36. 241-A Tank Farm Waste Average and Maximum Temperatures, 1957 to 1972

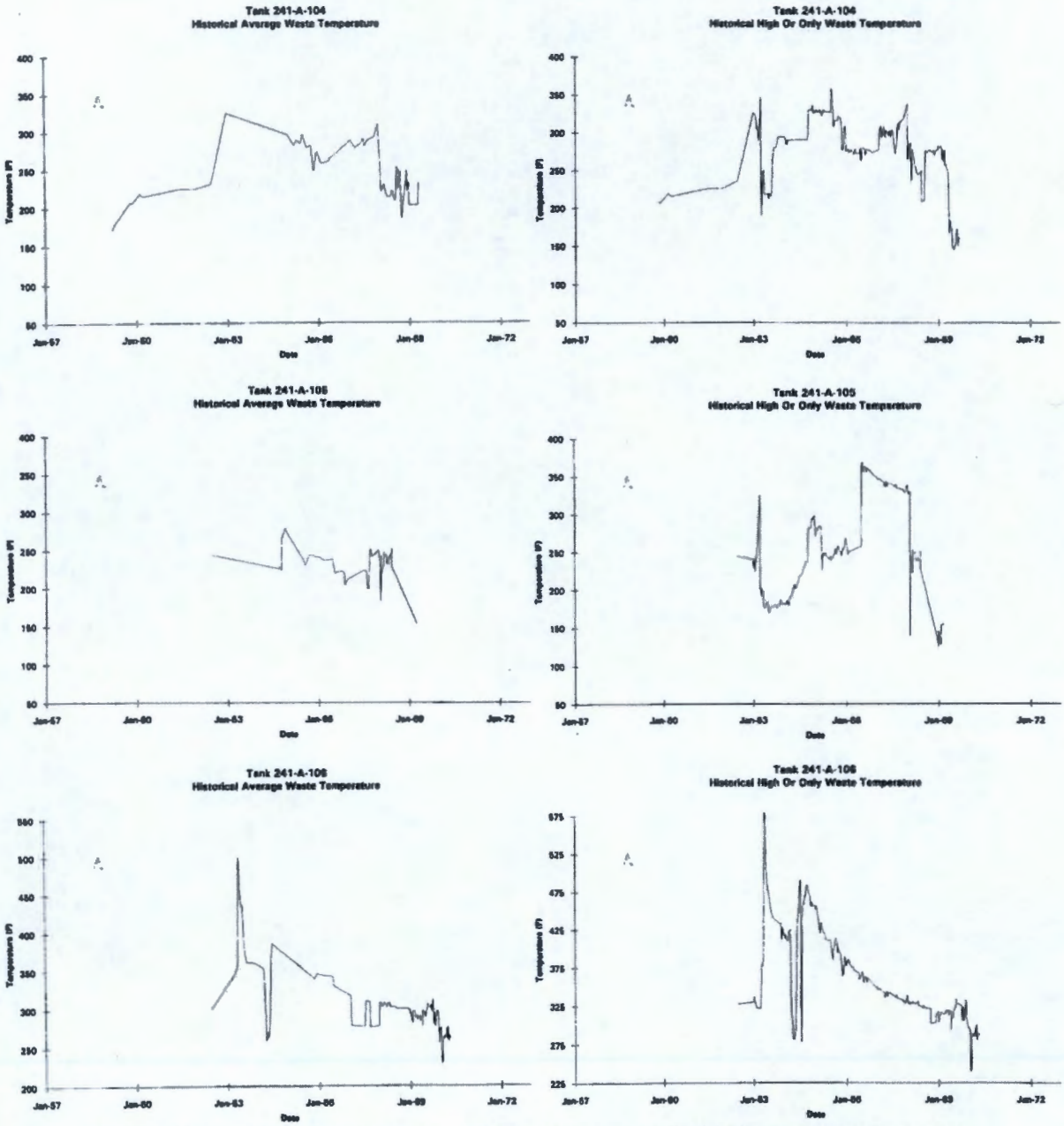


Figure 5-37. 241-A Tank Farm Waste Average and Maximum Temperatures, 1957 to 1972

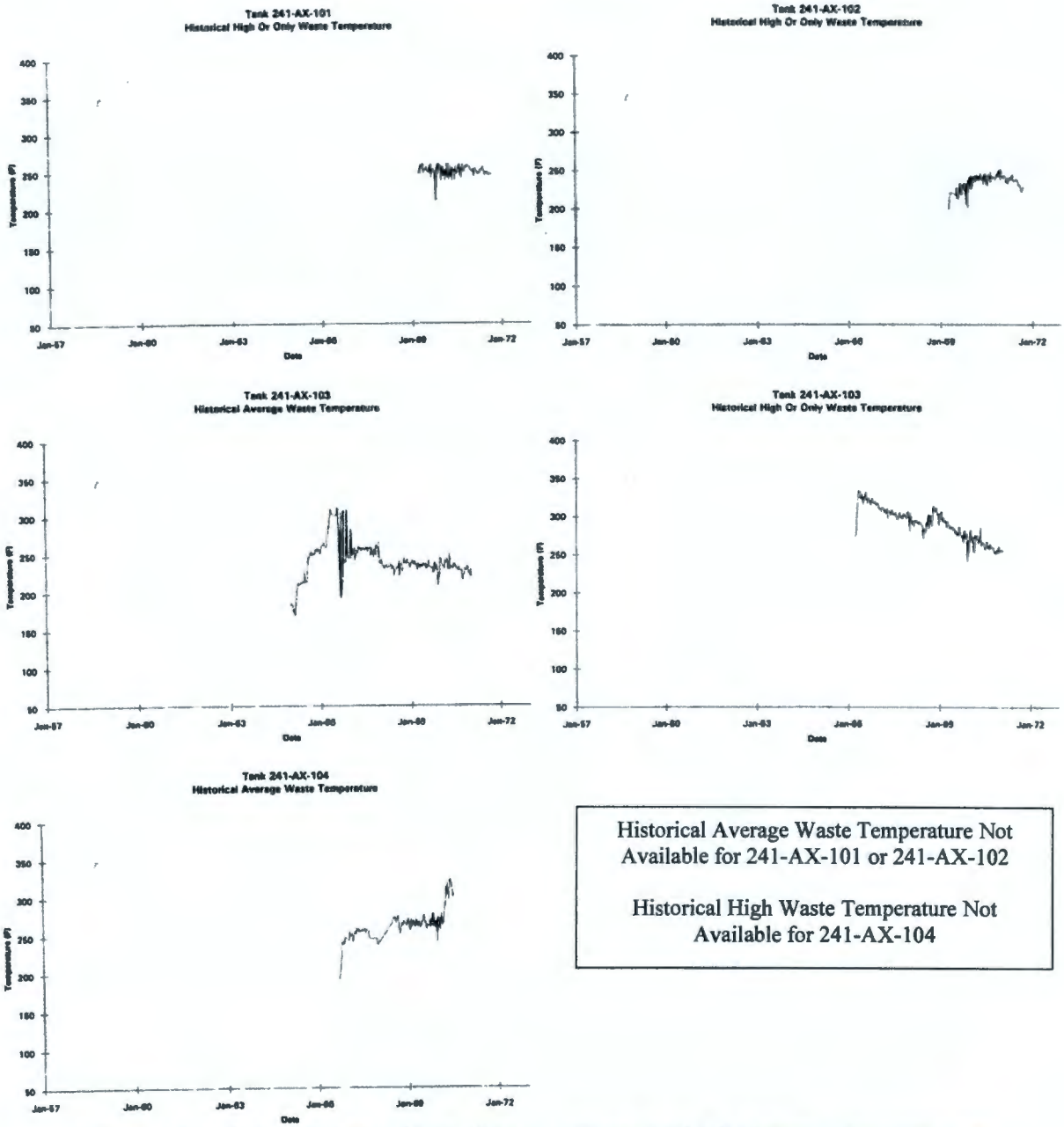


Figure 5-38. 241-AX Tank Farm Waste Average and Maximum Temperatures, 1957 to 1972

In 1952 a corrosion test was performed with sandblasted SAE 1010 low carbon steel specimens exposed to simulants of PUREX waste and concentrated PUREX waste at 250°F for 1000 hours (HW-26173, *Technical Activities Report, Metallurgy – Applied Research Unit, October 1952*). The test was performed to determine the corrosion rate of steel exposed to possible "hot spots" in storage tanks. General corrosion rates were very low, on the order of 10^{-5} in. per month for both normal and concentrated PUREX waste. A thin, tightly-adhering black-oxide coating

(presumably magnetite, Fe_3O_4) formed on the specimens in the concentrated PUREX waste, but not the normal PUREX waste. No pitting was observed on any of the specimens.

About the same time an investigation of the nature and extent of pitting to be expected in the vapor phase of mild steel tanks proposed for storing and concentrating the PUREX waste was performed over a three month period (HW-25858, *Technical Activities Report, Metallurgy-Applied Research Unit, September 1952*, HW-26892, *Progress Report, Chemical Development Separations Technology, January 31, 1953*). Mild steel coupons were sandblasted or polished and suspended over the waste solution/sludge that was heated to boiling. The test apparatus was outfitted with a condenser to reflux the evaporated solution. Examination of the data showed a decrease in pit penetration with time. The results of the vapor phase corrosion testing are presented in Table 5-29.

Table 5-29. General and Pitting Corrosion Rates of SAE 1010 Steel Coupons Exposed to Simulated PUREX Neutralized Waste Vapor Phase

Specimen	Type of Corrosion	Corrosion Rate Data, mil/yr		
		1 Month	2 Months	3 Months
Polished	Maximum Pit Penetration	2.3	1.3	0.76
	Average Pit Penetration	1.4	1.2	1.2
	Average Uniform Corrosion	0.73	0.24	0.11
Sandblasted	Maximum Pit Penetration	0.96	1.1	0.72
	Average Pit Penetration	0.48	0.72	0.48
	Average Uniform Corrosion	0.20	0.48	0.23

Data taken from HW-26892, p. 9. Values converted to mil/yr from inches/month in original table.

Also in 1952, longer term tests were performed with SAE 1010 specimens for liquid phase and vapor phase corrosion assessment in neutralized and concentrated PUREX waste at a temperature of 220°F (HW-32734). Polished and sandblasted specimens were tested. This test showed that SAE 1010 steel exposed to vapors over neutralized PUREX waste solution is subject to rather severe initial pitting attack, but that the rate of attack decreased rapidly with time. Polished and sandblasted specimens surfaces behaved similarly in resistance to pitting attack in the vapor environment. The general corrosion rate was low in the vapor phase and liquid phase. In examining the specimens it was noted that many of the pits that occurred around the support holes and in the region of the identification numbers, areas where the metal was cold worked. The results of the vapor phase corrosion testing are presented in Table 5-30.

Table 5-30. General and Pitting Corrosion Rates of SAE 1010 Steel Coupons Exposed to Simulated PUREX Neutralized Waste Liquid and Vapor Phase at 220°F

Condition Location	Specimen Surface	Exposure Period	Corrosion Data			
			General Corrosion Rate, mil/yr		Pit Penetration, mil	
			Average	Maximum	Average	Maximum
Vapor	Polished	1 month	0.73	1.03	1.7	2.0
		2 months	0.13	0.23	1.9	1.9
		3 months	0.11	0.17	1.5	1.9
	Fine Sand-blasted	1 month	0.20	0.23	1.7	2.0
		2 months	0.24	0.50	1.5	2.4
		3 months	0.23	0.29	1.6	2.0
		10 months	0.084	0.13	3.3	3.8
Liquid	Ordinary Sand-blasted	1 month	1.04	1.25	--	--
		2 months	0.25	0.29	--	--
		3 months	0.79	0.82	--	--

Data taken from HW-32734, Tables I & II.

The tested waste composition was not provided for any of the three corrosion tests mentioned above. It would be expected that the composition was similar to that predicted in the PUREX flowsheet available at that time, "PUREX Chemical Flowsheet HW #1", June 1952 (HW-24763). The available copy of that flowsheet is difficult to read so the reported values here may not be completely accurate. The composition of the neutralized 1WW stream is repeated below:

Constituent	M
$Fe(OH)_3$	0.08
$Na_2U_2O_7$	0.03
NaOH	0.21
$NaNO_3$	4.5
Na_2SO_4	0.88

During 1956 (February 6 – June 15), a 130-day field corrosion test was performed within tank A-101 (HW-49574) on specimens including SAE 1020 steel and all weld steels. The composition of the waste is not given and the amount of concentration the waste had undergone is not known. No sample analyses were found for this timeframe. The best estimate of the composition of the waste in tank A-101 at the time would be the flowsheet at that time for PUREX. Two flowsheets are provided in the initial PUREX technical manual (HW-31000) and the composition of the neutralized waste from each of those flowsheets is repeated below:

Constituent	HW #3 M	HW #4 M
$Na_2U_2O_7$	0.015	0.006
Na_2CO_3	--	0.1
$NaNO_3$	2.5	2.1
$Fe(OH)_3$	--	0.035
$Fe_2(SO_4)_3$	0.02	--
Na_2SO_4	0.02	0.07
NaOH	0.02	--

Sodium nitrite content wasn't provided for either flowsheet. The temperature of the waste is not known either. Waste status summary reports from March 1956 (HW-42394) showed tank A-101 was filled to 424,000 gal through March 21, 1956 when waste was routed to tank A-102 and that the waste volume remained at 424,000 gal through the end of the time the corrosion test apparatus was in the tank (HW-43895). No volume reduction due to evaporation was reported for tank A-101 until December 1956 (HW-47640, *Chemical Processing Department Waste-Status Summary December 1, 1956 – December 31, 1956*). This would indicate the waste was likely not boiling during the time the corrosion test specimens were in tank A-101. The general corrosion rate is not given in the report, HW-49574, but it can be estimated for wrought and welded specimens by weight loss and by assuming dimensional data and the steel density. Dimensional data is not given in the report but the program document describing the corrosion test (HW-37642) identifies that assemblies would be placed in a REDOX tank and PUREX tank. The corrosion results report for the REDOX tank (HW-53308) does specify the dimensions of the specimens in that tank. The weight of the specimens in the REDOX tank (tank SX-107) and the PUREX tank (tank A-101) were very nearly the same and so one can assume with relative confidence that the dimensions of the specimens were the same. Specimens were 1/8-in. thick by ½-in. wide by 1-½ in. long. General corrosion rate can be determined from weight loss by the equation

$$mpy = 61.02\frac{W_l}{A \times \rho \times t}$$

where mpy stands for mil per year (corrosion rate), W_l is the weight loss in grams from the specimen, A is the original exposed area of the specimen in square inches, ρ is the density of the specimen in g/cm^3 (assumed to be 7.85 g/cm^3), and t is the exposure time in years (130/365 days).

The SAE 1020 steel specimens exposed in the liquid waste exhibited greater general corrosion attack than comparable specimens exposed to the vapor. The general corrosion rate in the vapor phase was below 1 mil/yr. Unstressed specimens exposed to the liquid were at or below 1 mil/yr but stressed specimens exceeded 1 mil/yr. The depth of the deepest pits and average pit depth were greater in the SAE 1020 specimens in the liquid than the vapor phase. The maximum pit penetration was 3.215 mils in the liquid phase and 0.692 mils in the vapor phase. Maximum pit penetration was five times as severe and percent weight loss twice as great for the liquid phase all weld coupons as compared to the vapor phase. There was also greater liquid phase corrosion of the all weld coupons as compared to the vapor phase. Gas voids were noted on the all weld coupons exposed to the vapor phase.

Table 5-31 lists the measured general corrosion rate and pitting data for the SAE 1020 and all weld specimens. Other observations during examination indicated a severe pitting attack adjacent to the polytetrafluoroethylene washer in both vapor and liquid phase specimens, mainly on SAE 1020 steel coupons. These pits were not used in the calculation of maximum pit penetrations in Table 5-31 but they are reported separately in Table 5-32. Metallographic examination of SAE 1020 steel coupons showed slight signs of intergranular corrosion.

Table 5-31. General and Pitting Corrosion Data for SAE 1020 Steel Coupons Exposed for 130 Days in 241-A-101 PUREX Waste

Condition Location	Specimen	Corrosion Data			
		Weight Loss, g	General Corrosion Rate, mil/yr	Average Pit Penetration, mil	Depth of Deepest Pit, mil
Vapor	SAE 1020 Steel, #2	0.0269	0.79	0.450	0.692
	SAE 1020 Steel, #4	0.0129	0.51		0.628
	SAE 1020 Transverse Weld, #58	0.0200	0.74	0.450	0.460
	SAE 1020 Transverse Weld & Stress, #86	0.0162	0.89	0.450	0.560
	SAE 1020 Stressed, #114	0.0193	0.90	0.450	0.560
	60-16 All Weld, #562	0.0267	1.04	0.742	0.825 (Gas Void – 16.2)
	120-16 All Weld, #590	0.0061	0.23	0.295	0.330 (Gas Void – 2.55)
Liquid	SAE 1020 Steel, #1	0.0191	0.76	0.741	2.140
	SAE 1020 Steel, #3	0.0217	0.86		2.140
	SAE 1020 Transverse Weld, #57	0.0276	1.02	0.741	3.215
	SAE 1020 Transverse Weld & Stress, #85	0.0221	1.22	1.232	2.750
	SAE 1020 Stressed, #113	0.0297	1.39	1.419	2.573
	60-16 All Weld, #561	0.0429	1.68	2.990	3.830
	120-16 All Weld	0.0170	0.63	1.295	1.595

Data taken from HW-49574, Tables I, III, IV & VI.

Table 5-32. Pitting Corrosion Data Adjacent to Polytetrafluoroethylene Washers for SAE 1020 Steel Coupons Exposed 130 Days in 241-A-101 PUREX Waste

Condition Location	Specimen	Corrosion Data	
		Average Pit Penetration, mil	Depth of Deepest Pit, mil
Vapor	SAE 1020 Steel, #2	1.45	2.38
Liquid	SAE 1020 Steel, #1	1.585	2.485

Data taken from HW-49574, Table VII.

5.5.4.5. Organic Wash Waste

Organic wash waste was disposed to SSTs at various times by itself, in combination with the 1WW waste, and in combination with the CW from PUREX. Early in the operational life of PUREX, liquid waste disposal management identified that the OWW from the first and second solvent treatment cycles was sent to tank F-16 within PUREX for neutralization and then jetted to A Farm (HW-41837, *Liquid Waste Disposal Control at PUREX*). From June to December (except November) 1956, OWW was being directed to tanks C-110 and C-111 (HW-43895, HW-44860, *Separations Section, Waste – Status Summary for February 1956*, HW-45140, *Separations Section, Waste – Status Summary, August 1, 1956 – August 31, 1956*, HW-45738, *Separations Section, Waste – Status Summary for September 1956*, HW-46382, *Chemical Processing Department Waste – Status Summary, October 1, 1956-October 31, 1956*,

HW-47052, HW-47640). Waste status summary reports from early 1957 do not indicate where OWW was being directed but it is presumed that it was sent to A Farm. Starting with the July 1957 waste status summary record there is indication A Farm tanks received "carbonate wash" which would be consistent with the OWW composition (HW-51858, *Chemical Processing Department Waste Status Summary, July 1, 1957 – July 30, 1957*). When the highly active 1WW waste was sent to AX Farm, starting in 1965, OWW was sent to both A and AX Farms. Sometime between April and June 1968 until PUREX went into standby in 1972, OWW was routed back to C Farm tanks (ARH-721, *Chemical Processing Division Waste Status Summary, April 1, 1968 through June 30, 1968*).

Initially OWW streams were 2-1/2% sodium carbonate solutions (HW-31000, pp. 914, 915). By 1959, the treatment of the solvent in the first solvent recovery system included contacting with sodium carbonate-potassium permanganate, then contacting with nitric acid, and final contacting with sodium carbonate. The second solvent recovery system was still contacting the organic with sodium carbonate solution followed by centrifugation to remove solids.

In 1961, an investigation of evaporation of PUREX OWW included determining the average composition of the OWW solutions from G-8 (first solvent recovery system) and R-8 (second solvent recovery system) tanks within PUREX that were directed to underground storage (HW-71145, *Evaporation of PUREX Organic Wash Waste Solution*). Seven G-8 samples and one R-8 sample were collected over a one month period representing start-up, peak activity, and normal operation. Analytical results were provided in HW-71145 and are repeated below:

	G-8 Stream			R-8 Stream		
Constituent	**Aqueous**	**Organic**	**Solid**	**Aqueous**	**Organic**	**Solid**
Volume %	89.3 (75.3-97.8)*	4.1 (1.0-7.9)	6.6 (2.9-16.8)	98.2	1.3	0.4
K^+, M	0.0061 (<0.0026-0.0090)	--	--	0.0026	--	--
Na^+, M	0.18 (0.13-0.23)	--	--	0.48	--	--
Mn^{+2}, M	non-detect	--	--	non-detect	--	--
NO_3^-, M	0.031 (0.019-0.042)	--	--	--	--	--
CO_3^-, M	0.12 (0.06-0.18)	--	--	0.28	--	--
pH	9.6 (9.4-9.7)	--	--	--	--	--

* Values in parentheses show the range of reported values (typical).

Based on the sample analyses above, it is probable that the second solvent recovery treatment only consisted of sodium carbonate and potassium permanganate and did not include a cleanup step with nitric acid at the time the sampling was performed. This is inferred by the lack of nitrate in the R-8 sample.

As mentioned in the previous section, specifications and standards for operational control of A and AX Farms were issued in March 1965 (RL-SEP-269) including descriptions of the characteristics of the waste streams (PAW and OWW) sent to these farms. Typical waste compositions for the OWW circa 1965 is listed in RL-SEP-269 and repeated below:

Constituent	Concentration
Na^+	0.23 M
K^+	0.03 M
NO_3^-	0.06 M
CO_3^{-2}	0.075 M
OH^-	0.05 M
MnO_2	0.03 M

The Hanford Laboratories reported on a corrosion study (HW-70872, , p. C-12, HW-71222, *Hanford Laboratories Operation Monthly Activities Report*, p. C-4) of synthetic concentrated PUREX OWW to simulate corrosion that may take place under conditions expected during in-tank solidification (see Section 5.5.6.3). The study was performed to determine the corrosion of 1020 carbon steel during evaporation of the PUREX OWW. Synthetic OWW (2 M and subsequently 3 M total carbonate) was maintained at 100°C and sparged with CO_2 gas. The steel specimens were exposed to liquid, interface and vapor phases. The test duration was 840 hours for OWW at 2 M total carbonate. During that time the pH of the solution dropped from 11.0 to 8.9. Maximum corrosion rates as determined by weight loss were 0.05 mil/yr and 0.7 mil/yr for the liquid and vapor phases, respectively. A few broad shallow pits (ca. 0.5 mil) were noted on these specimens. Specimens exposed at the vapor-liquid interface were not preferentially attacked. A number of short term tests (24-78 hours) were also performed with erratic results. Whether or not attack occurred seemed to depend on surface conditions of the specimen. None of the specimens in the scaled, as-received condition were attacked in these short term tests. No significant change in liquid or vapor phase corrosion of the mild steel specimens was observed at an increased total carbonate concentration of 3 M (HW-71222).

5.5.4.6. Waste from Thoria Campaigns

During the first thoria campaign, April 15, 1966 to August 20, 1966, the PUREX plant discharged 1,198,000 gal of waste to underground storage (ISO-419, Section K). During the second thoria campaign, June 8, 1970 to January 16, 1971, the PUREX plant discharged 2,795,000 gal of waste to underground storage (ARH-2127, Table X). The waste consisted of flushes, sump waste, lab waste, CW, OWW, and highly active waste (1WW). The volume of waste by type for each campaign is presented below:

	Waste Volume to Underground Storage (gal)	
Waste Type	1966 Thoria Campaign	1970 Thoria Campaign
Pre-Campaign Flushes	318,000	360,000
Mid-Campaign Flushes	--	69,000
Post-Campaign Flushes	227,000	204,000
Sump Wastes	124,000	305,000
Lab and Miscellaneous	--	280,000
Coating Waste	55,000	370,000
Organic Wash Waste	357,000	980,000
1WW Highly Active Waste	117,000	227,000

Flushes of head end consisted of various solutions containing sodium nitrate, sodium hydroxide, nitric acid, potassium fluoride, and ANN (ISO-419, Table XIII). Flushes of solvent extraction consisted of nitric acid, oxalic acid-nitric acid, and tartaric-caustic solutions and water (ISO-419, Table XV). Sump waste would be intermittent and variable. Laboratory waste would vary depending on what analyses were being performed. No information was found on the composition of sump or laboratory waste.

Organic wash waste from the thoria campaigns was chemically similar to typical PUREX OWW. The waste generally consisted of dilute solutions of sodium nitrate, potassium nitrate, sodium carbonate, potassium permanganate, and manganese dioxide (ARH-2127, Figure II-E), except potassium permanganate was not used during the first thoria campaign (ISO-419, p. III-29). More frequent solvent wash changeouts were performed during the thoria campaigns than during typical uranium processing (ISO-419, p. III-29).

The thoria targets that were processed during the thoria campaigns were present within aluminum canisters. The canisters were dissolved using the standard aluminum coating removal flowsheet with extra caustic and nitrate to stabilize the CW (ISO-419, p. III-16).

The thoria material (powder or wafers) was dissolved with a nitric acid-potassium fluoride-aluminum nitrate solution (ARH-2127). The thoria is dissolved using 60 weight percent nitric acid. The potassium fluoride, at ~0.025 M F^-, provided a source of fluoride ion which increases the dissolution rate of the refractory thoria. To counteract the corrosive effect of fluoride on the stainless steel dissolver vessel, aluminum nitrate is added at a 4:1 aluminum to fluoride molar ratio (RL-SEP-267 PT1, *Engineering Study Thorium Processing – PUREX Part I-Flowsheet*). Due to the high nitric acid concentration and low thorium concentration of the dissolved thoria product, the solution was concentrated driving off nitric acid that was then recovered. The solution was then sent to solvent extraction for co-decontamination, partitioning, and purification of thorium and uranium products. No provision was made for waste backcycle. The waste stream from the HA column was sent to acid recovery and waste concentration. The concentrated and neutralized highly active waste stream during thoria processing is estimated in both RL-SEP-267 PT1 (1966 campaign) and ARH-2127 (1970 campaign) and these are presented below:

	Flowsheet-Based Neutralized 1WW Stream to Underground Storage Composition, M	
Constituent	1966 Thoria Campaign	1970 Thoria Campaign
Na^+	6.2	3.33
K^+	--	0.052
Al^{+3}	0.2	0.34
Fe^{+3}	0.05	0.023
NO_3^-	--	2.58
PO_4^{-3}	0.03	0.093
SO_4^{-2}	0.03	0.049
F^-	0.05	0.048
OH^-	--	0.047

No corrosion studies were found for carbon steel specimens assessing the impacts of 1WW waste from thoria processing sent to underground storage.

5.5.4.7. Miscellaneous Wastes

Along with the five waste types mentioned above, the PUREX plant generated other waste streams that were transferred to SSTs. Some streams may have been generated intermittently during the operational life of the facility while other streams may have been associated with discrete campaigns performed for short periods of time. Waste from cell floor drains, cell washes, decontamination operations in M cell, PUREX analytical laboratory waste, line flushes, and plant startup and shutdown wastes are examples of wastes generated intermittently during the operational life of the facility. Wastes from discrete campaigns include waste from early neptunium recovery operations, thorium campaigns, and specialty fuel campaigns at the end of operations in 1972.

Contaminated floor drain waste, cell wash waste, laboratory waste, and equipment flushes that ended up in underground storage tanks are generally low-activity wastes that were sent to the boiling waste tanks where the water would boil-off during self-concentration of the waste. Initially, tank TK-F18, the cell drain collection tank; tank TK-M1, the decontamination cell tank; and, tanks TK-U3 and TK-U4, laboratory waste tanks, could be discharged to a crib or to underground storage depending upon activity levels in the waste (HW-41837). For instance, cell drainage waste and dilute waste were specifically called out as being sent to tank A-102 in June 1960 (HW-66187, *Chemical Processing Department – Waste Status Summary*). An example of flushes would be the first and second solvent recovery system flushes performed nominally after processing 500 tons of uranium (RHO-MA-116, Table 4-41). Essential material flushes for the solvent recovery systems included nitric acid, sodium hydroxide, tartaric acid, and oxalic acid. These wastes would be neutralized prior to being sent to underground storage. Contaminated floor drain waste and cell wash waste are intermittent and variable. These streams were not tracked as separate streams being discharged to underground storage. These wastes are not considered as separate streams for the purpose of this report.

Waste from decontamination operations would be generated intermittently. The waste composition would be dependent upon the type of decontamination solution used and the radioactive and chemical contamination present on the equipment being decontaminated. The contamination would be dependent upon the portion of the process that the equipment came from. No specific compositional information was found for solutions used for decontamination operations.

Waste from plant startup and shutdown would be with process chemicals and or "cold" (i.e., not irradiated uranium fuel from a reactor) uranium depending on conditions. These wastes would be expected to have chemical similarities to the typical waste processed but relatively little radioactivity.

Approximately 52,000 gal of waste identified as "palm waste" was sent to tank C-112 in October 1959 (HW-62421, *Chemical Processing Department Waste Status Summary September 1-30, 1959*, HW-62723, *Chemical Processing Department Waste Status Summary,*

October 1- 31, 1959). "Palm" or "birch" was a term used to describe ^{237}Np. The main process would be shut down so neptunium, accumulated in the backcycle waste, could be extracted via the final plutonium cycle. The same chemicals used to separate plutonium from uranium in the PUREX process were used to separate neptunium from uranium and plutonium (HW-SA-2928). These chemicals would include sodium nitrite and nitric acid in the feed, dilute nitric acid scrub solution and dilute nitric acid strip solution (HW-49483-A, *The PUREX Process – A Solvent Extraction Reprocessing Method for Irradiated Uranium*). The specific compositional information was found for the waste solution from batch neptunium recovery, but it would be anticipated the stream would look like the backcycle waste stream or the typical 1WW stream if acid recovery were performed.

5.5.5 Fission Product Recovery Waste Types from B Plant (1961-1980)

This section of the document details wastes generated from fission product recovery process operations at B Plant between 1961 and 1980. Fission product recovery processes continued at B Plant beyond 1980 but waste generated was sent to DSTs after 1980 and are not included in this discussion. Fission product recovery operations that occurred at the Hot Semiworks, later renamed to Strontium Semiworks, are covered in Section 5.5.8.3.

The following description in this paragraph is primarily taken from RPP-16015, *Origin of Wastes in Single-Shell Tanks 241-B-110 and 241-B-111*, unless otherwise referenced. From August 1963 through June 1966, B Plant was used in conjunction with the PUREX facility, 244-CR Vault, and the 201-C Strontium Semiworks to separate strontium-90, cerium-144 and promethium-147 from high-level waste solutions. In B Plant strontium nitrate/rare earth nitrate solution was processed via precipitation and centrifugation to separate the strontium from the rare earths. The strontium solutions and rare earth solutions were separately transferred to 201-C for purification. Then, from July 1966 through December 1967, equipment was replaced within B Plant to expand the processing capability to include cesium removal from fission high-level waste solutions using ion exchange equipment. The strontium and rare earths processing equipment was also replaced to include only strontium removal using solvent extraction equipment, followed by precipitation and centrifugation equipment for purifying the strontium. From December 1967 to October 1983 cesium ion exchange was performed at B Plant. The B Plant solvent extraction equipment was first used, starting in January 1968, to purify the inventory of rare earth solutions (cerium and promethium) stored at B Plant. Separation of strontium from the strontium and rare earths solutions stored in 244-CR Vault was then conducted in March 1968 using the solvent extraction equipment. Strontium separation from high-level waste solutions using the solvent extraction equipment continued until 1977.

5.5.5.1. Process Description

Phase 1 Processing

Initial process operations (referred to as Phase I Processing) at B Plant from August 2, 1963 through June 1966 were for the purpose of separation of strontium and rare earth elements (cerium and promethium) (RPP-16015). Much of the following discussion of operations through

June 1966 is based on descriptions provided in RPP-16015. During this time B Plant was used in conjunction with PUREX, 244-CR Vault, and 201-C Strontium Semiworks. Although early tank-to-tank test sluicing occurred in 1964, retrieval of sludge via sluicing for strontium recovery did not occur until after this phase of B Plant operation for strontium and rare earth element separation (SD-WM-TI-302, Section 3). The feed stream to B Plant was the treated 1WW stream from PUREX. The 1WW stream is the concentrated high-level waste stream containing high concentrations of salt waste, the majority of fission products, iron, sulfate, and corrosion products (HW-83609, *A Summary of Hanford Laboratories Achievements in this Program Under General Electric, 1954 – 1964*). Because of the high sulfate content, a lead sulfate carrier precipitation process was developed and employed within PUREX to achieve a relatively high strontium recovery fraction. Strontium, cerium, and other rare earths can be precipitated from 1WW by adjustment of the sulfate ion and hydrogen ion concentrations. Strontium is precipitated as strontium sulfate and rare earths are precipitated as a double sulfate salt with sodium sulfate. By adding lead to precipitate lead sulfate as a carrier, the yield of strontium recovery was markedly improved (HW-69534, *Laboratory Development of a Carrier-Precipitation Process for the Recovery of Strontium from PUREX Wastes*). Initially tartaric acid, and later hydroxyacetic acid, was also added to complex iron and prevent its precipitation (HW-67728, *B-Plant Fission Product Flowsheets Parts 1 and 2*, HW-83609). The resulting sulfate precipitate containing the fission products is separated by centrifugation (HW-69011, *Project COC-897 – Title I Design Fission Product Storage in B-Plant*). A metathesis of the sulfate is made by addition of sodium hydroxide and sodium carbonate converting the strontium, lead, and fission products to insoluble carbonates which are more easily dissolved in nitric acid than the sulfates. The fission products were then dissolved in nitric acid (WHC-MR-0003, *Product Recovery and Utilization, Vol. 2 – Chapter Two: By-Product Recovery from High-Level Waste*) and transferred to 244-CR Vault pending transfer to B Plant for subsequent processing.

Initial processing at B Plant, in August 1963, separated strontium from cerium and other rare earths and recovered the strontium (HW-78817, *Chemical Processing Department Monthly Report, August, 1963*, HW-79768, *Chemical Processing Department Monthly Report for November, 1963*).. The first cerium-rare earth run was not completed until several months later in January 1964 (HW-80672, *Chemical Processing Department Monthly Report, January, 1964*). Within B Plant, the strontium is first separated from lead, cerium and other rare earth elements by reacting the acidic strontium nitrate and rare earth nitrate solution with 0.5 M oxalic acid to precipitate the rare earth elements and lead as oxalates leaving the strontium as a soluble nitrate in solution (HW-67728). The strontium nitrate solution was concentrated, stored in B Plant, and transferred periodically to the 201-C Strontium Semiworks for further purification. This portion of the process is provided in a contemporary flow diagram shown as Figure 5-39. Overheads from the concentration step were sent to a waste accumulation tank within B Plant.

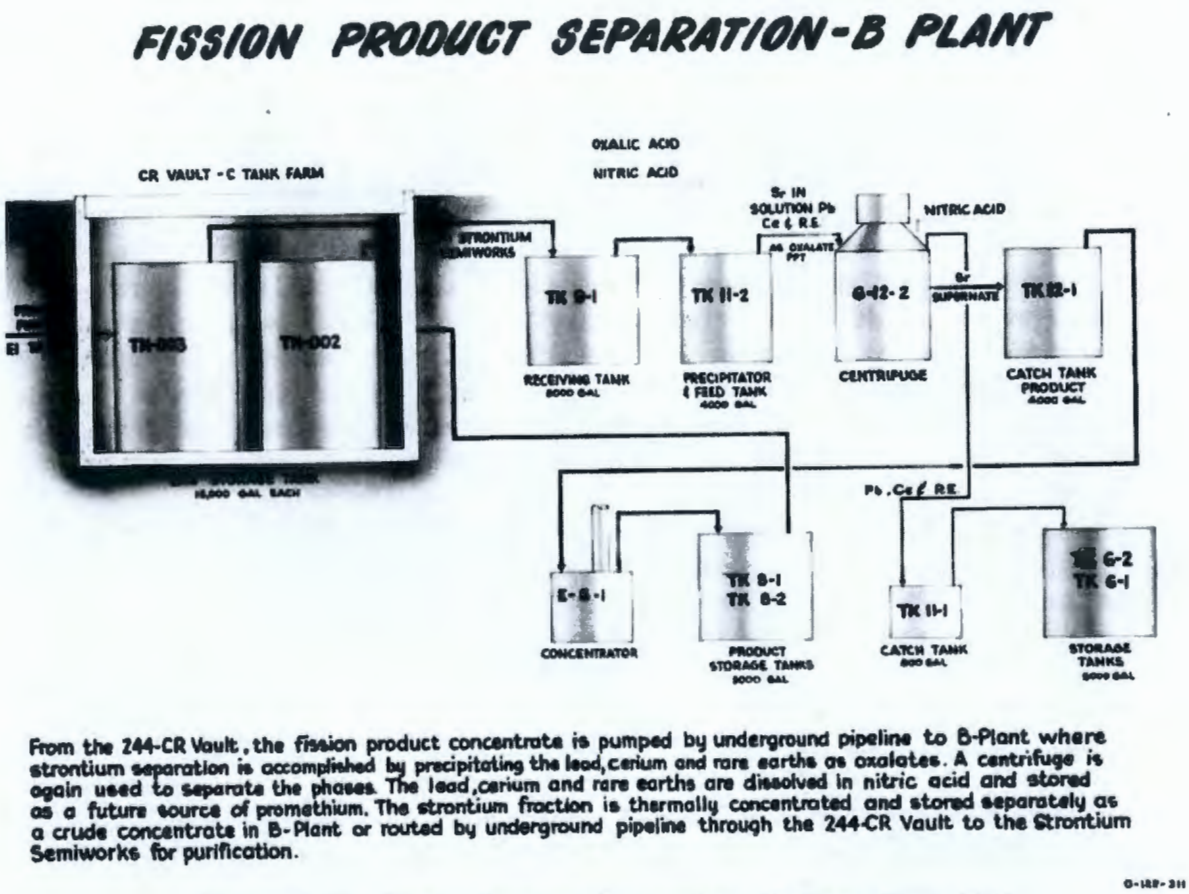


Figure 5-39. Fission Product Separation – B Plant Circa 1961

To recover the rare earth elements separate from cerium, the lead present in the solids was first removed allowing a higher concentration of rare earths in storage. The rare earth oxalate solids were mixed with caustic and heated which converted the lead to a soluble form, plumbite (PbO_2^{-2}), and converted the cerium and other rare earths to insoluble hydroxides (HW-81373, *Removal of Lead from B-Plant Cerium and Rare Earth Fractions*). The precipitated hydroxides were centrifuged and washed to segregate the soluble lead (50-60% of initial lead) from cerium and other rare earth hydroxides (HW-82526, *Chemical Processing Department Monthly Report, May 1964*). The lead bearing waste was sent to waste storage. The hydroxides were then dissolved with nitric acid. The cerium could then be separated from the other rare earths by precipitation of cerium peroxyacetate (IDMS Document, Accession Number 1012060589, *221-B Phase I Information Manual*). This is accomplished by the addition of a buffered hydrogen peroxide-sodium acetate solution to the rare earth nitrate solution. The solution is centrifuged and the supernatant solution containing the rare earths is concentrated and placed in storage (HW-67728). Overheads from the concentration step were sent to a waste accumulation tank in B Plant. The cerium peroxyacetate was dissolved in warm nitric acid. This cerium bearing waste stream was sent to waste storage.

Equipment Replacement

Equipment was replaced in B Plant during 1966 and 1967 to allow for solvent extraction of strontium and ion exchange of cesium.

Phase III Processing

Following equipment replacement within B Plant, during 1966 and 1967, a new phase of operations (referred to as Phase III) was started to recover strontium and cesium from waste. During this phase of operations at B Plant, fission product separation was performed on both high-activity wastes that were retrieved from underground waste storage tanks and from the acidic high-activity level liquid wastes generated at PUREX (WHC-MR-0003). The streams processed through B Plant for fission product recovery between 1967 and 1983 are:

- Current Acid Waste (CAW) – concentrated and denitrated acidic high-level waste from PUREX solvent extraction process (sometimes referred to as PAW for PUREX Acid Waste) either involving aluminum clad or zircaloy clad fuels. CAW from zircaloy clad fuels was sometimes referred to as Zirflex acid waste (ZAW).
- PUREX Acidified Sludge (PAS) – acidic waste resulting from acid dissolution of water-insoluble sludge solids sluiced from PUREX plant underground waste storage tanks (A and AX Farms).
- PUREX Supernate (PSN) – alkaline supernatant liquid pumped from PUREX plant underground waste storage tanks
- PUREX Sludge Supernate (PSS) – alkaline liquid resulting from water leaching the sludge solids remaining after removing PSN from PUREX plant underground waste storage tanks
- REDOX Supernate (RSN) – alkaline supernatant liquid pumped from the REDOX plant underground waste storage tanks.

The following process description is taken from WHC-MR-0003, ISO-100, *Waste Management Technical Manual,* SD-WM-PCP-002, *B Plant Current Acid Waste (CAW) Cesium and Strontium Recovery Draft Flowsheet*, RHO-F-6, *B Plant Cesium Clarification Flowsheet*, RHO-F-7, *Cell 18 Ion Exchange Flowsheet,* RHO-F-8, *Ion Exchange Flowsheet for Final Purification of B Plant Cesium*, RHO-F-9, *Waste Encapsulation and Storage Facility Cesium Flowsheet*, ARH-CD-691, *Strontium Recovery from PUREX Acidified Sludge*, and ARH-2973, *Sulfate Precipitation Flowsheet for Purification of Crude Strontium Products from B Plant Solvent Extraction*. The incoming feed types would be processed through head-end processes dependent upon the feed characteristics. All incoming feed streams were centrifuged to segregate solids from the liquid (WHC-MR-003). Subsequent cesium and strontium recovery processes required solids removal to avoid operating difficulties. The liquid portion would be transferred to storage for either subsequent separation of cesium and strontium (in the case of CAW), for strontium recovery (in the case of PAS), or for cesium recovery (in the cases of PSN, PSS and RSN). The segregated solids from the incoming streams contained strontium that was then metathesized from sulfate to carbonate for subsequent dissolution and recovery. The metathesis consisted of 0.5 M sodium hydroxide – 1 M sodium carbonate solution added to the segregated solids and heated to convert the solids. After the metathesis converted the fission

products from sulfates to carbonates, the waste metathesis solution was decanted and collected in waste tank TK-25-2 to be sent to underground storage in boiling waste tanks. The remaining solids were washed with 0.1 M sodium carbonate, settled, and then this wash solution was transferred to waste tank TK-25-2. The solids were then dissolved in nitric acid solution. Any residual solids (primarily siliceous solids) remaining after dissolution were slurried and ultimately sent to waste tank TK-25-2 for disposal. This B Plant head-end process for CAW is depicted in Figure 5-40. The figure also shows additional head-end processing prior to cesium recovery that is described in the following paragraph.

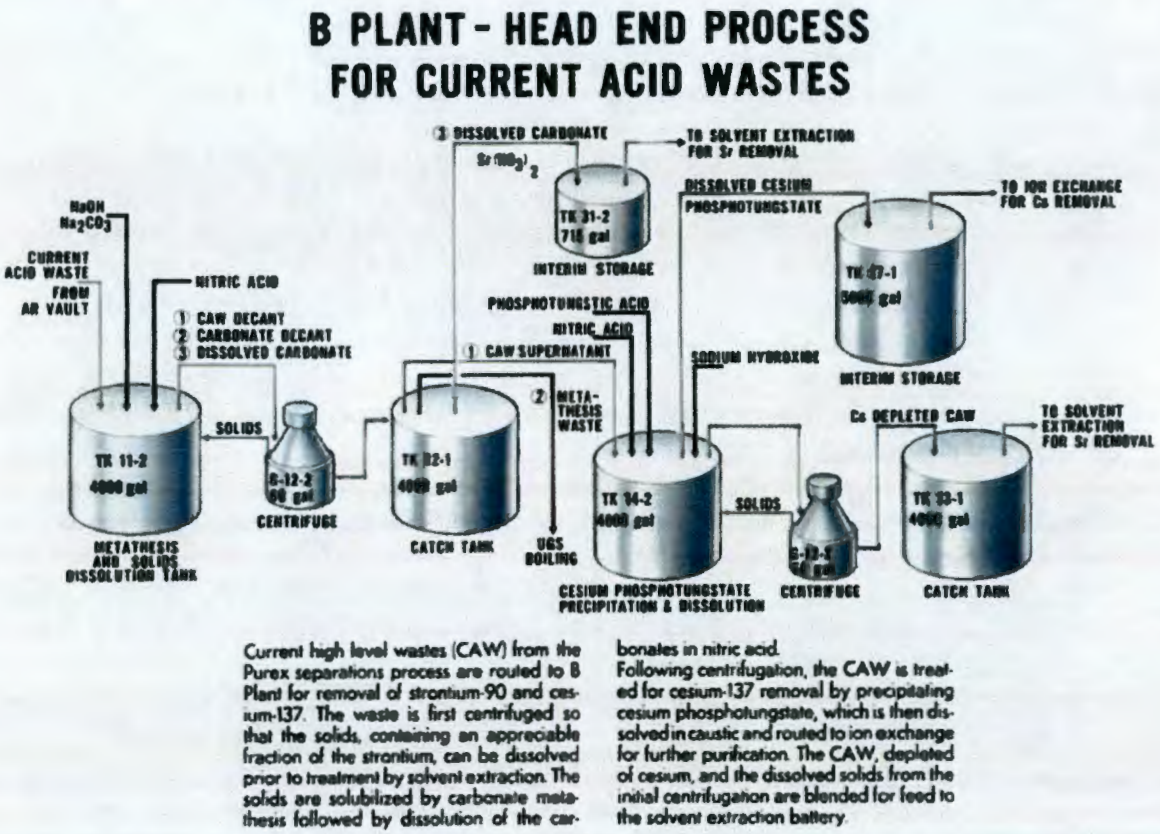


Figure 5-40. B Plant Head End Process for Current Acid Waste, Circa 1967

Cesium recovery within B Plant started on December 27, 1967 when alkaline supernatants stored in the SSTs were transferred to B Plant (HAN-99396-DEL, *Monthly Status and Progress Report, December 1967,* p. AIII-3). The following description of cesium recovery is largely taken from RHO-RE-SA-169, *Sixteen Years of Cesium Recovery Processing at Hanford's B Plant*, and WHC-MR-0003. The streams processed for cesium recovery included CAW, PSN, PSS, and RSN. All these streams were first centrifuged to separate solids from the cesium-bearing supernatant liquid as described above. The PSN, PSS and RSN streams were then ready for cesium recovery via ion exchange. For the CAW stream, the supernatant liquid first was treated with 0.10 M phosphotungstic acid (PTA) creating insoluble cesium phosphotungstate in a mild acid solution. The precipitate was triple washed with 1.0 M nitric acid - 0.2 M sodium gluconate

to remove strontium and metal (iron and zirconium) impurities. The cesium solids were then dissolved in 2.0 M sodium hydroxide, digested and then centrifuged. The cesium nitrate solution from CAW was then ready for cesium recovery. The supernatant liquid containing strontium was collected and sent to the solvent extraction feed tank. No waste streams were transferred to the tank farms from the PTA process.

Cesium recovery was via ion exchange. Inorganic (Linde AW-500, Zeolon-900) and then organic (Duolite ARC-359) resins were used over the years to recover the cesium, with changes being made to improve performance and alleviate operational problems. The feed stream containing cesium was fed to the ion exchange column to collect the cesium. The column would also collect sodium which was present in much higher concentration. The supernatant liquid effluent from the column was collected as waste in tank TK-18-1 (RHO-F-7). The column would be operated until breakthrough when feed to the column would be stopped. Following loading, the ion exchange column would be washed with 2000 gal of demineralized water which was then collected in tank TK-18-1 (RHO-F-7). After this a 0.2 M ammonium carbonate scrub solution was introduced to selectively remove sodium from the column (WHC-MR-0003). The scrub solution was collected in tank TK-18-1 (RHO-F-7). The volume used was dependent upon monitoring results (RHO-F-7) but consisted of at least seven column volumes and was followed by a demineralized water flush of the column (ISO-100). After sodium removal, the cesium was eluted from the column with a solution of 3 M ammonium carbonate and 2 M ammonium hydroxide, then concentrated and stored for subsequent purification. A simplified flow diagram of this process of the B Plant ion exchange process for cesium recovery is provided in Figure 5-41. Initially, the cesium was concentrated as carbonate, but after 1969, the cesium was converted to nitrate within the concentrator to allow the cesium to be more concentrated due to the higher solubility limit of cesium nitrate. The elution step also converted the resin to the ammonium form, in preparation for the next cesium loading cycle. If the new feed contained high aluminum concentrations, such as the RSN stream, the column would be subsequently washed with 2 M sodium hydroxide to convert the ion exchange resin to the sodium form to help prevent aluminum precipitation due to local pH changes upon ammonium ion exchange. Additionally, a water wash was added prior to the sodium scrub step when processing RSN feed. This step would hinder aluminum precipitation due to resulting pH changes. The flowsheet was generally the same for the various waste types (except as noted above) but the throughput was dependent upon cesium content and sodium to cesium ratio which varied appreciably between the waste types. The waste streams from cesium recovery include the supernatant liquid effluent from the ion exchange column, the water wash waste and sodium hydroxide wash for RSN, and

ion exchange cycle using feed from the cesium recovery process described in the above paragraph. After feeding the column to load it with cesium, the column was scrubbed to remove sodium, potassium and rubidium with dilute ammonium carbonate and ammonium hydroxide. The cesium was then eluted with concentrated ammonium carbonate – ammonium hydroxide flush solution. The solution with eluted cesium was concentrated, recovering the ammonium carbonate from the overheads. The waste stream from loading and the scrub solution were sent back to cesium recovery for recycle through the recovery process. If the streams contained low enough concentration of cesium they could alternately be processed as low level waste through the concentrator.

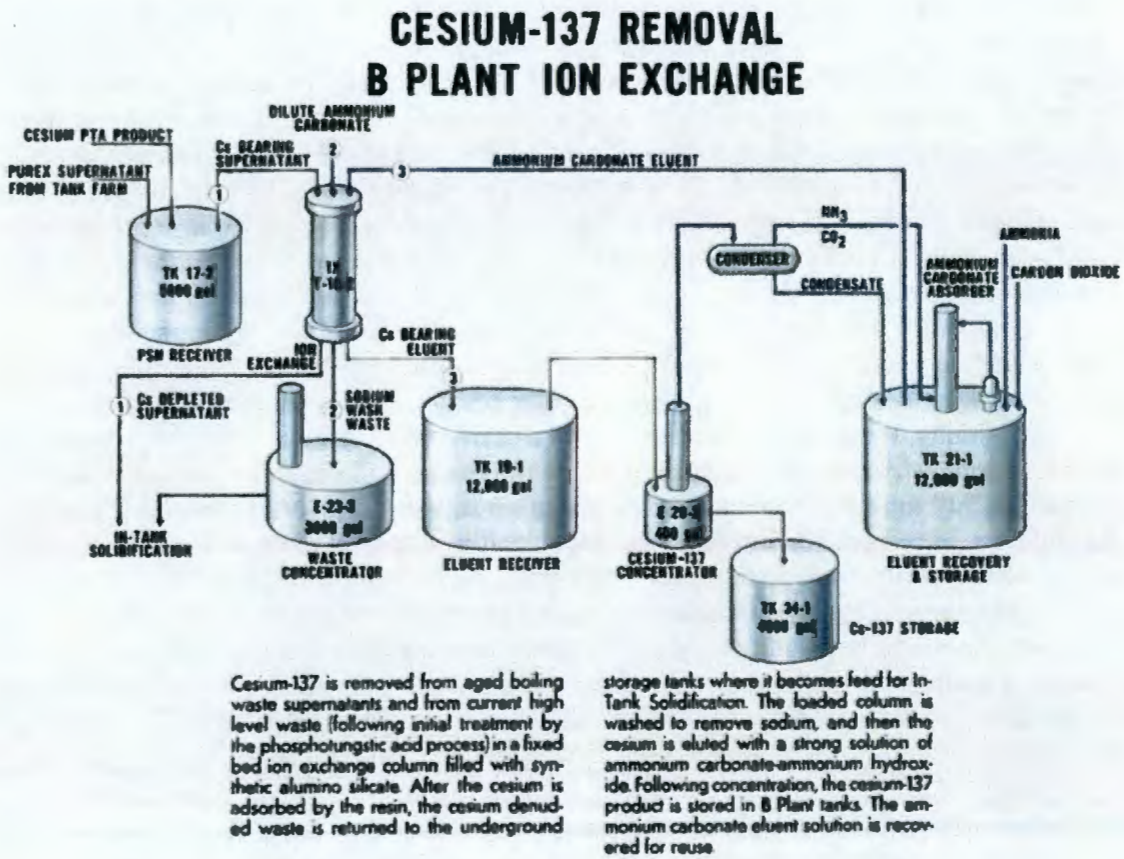


Figure 5-41. B Plant Cesium Recovery Ion Exchange Process, Circa 1967

The solvent extraction equipment installed at B Plant for strontium recovery was first operated at the end of January 1968 for the recovery of stored rare earth isotopes at B Plant (HAN-99604 DEL, *Monthly Status and Progress Report, January 1968*, p. AIII-3). Separation of strontium from the strontium and rare earth isotopes stored at 244-CR vault was subsequently performed in March 1968 (HAN-100127-DEL, *Monthly Status and Progress Report, March 1968*, p. AIII-3). The solvent extraction equipment first processed CAW to separate strontium in April 1968 (HAN-100357-DEL, *Monthly Status and Progress Report, April 1968*, p. AIII-3). Beginning in September 1968 acidification of PUREX sludge began, allowing subsequent processing of PAS

for removal of yttrium, traces of rare earths, and organic degradation products (ISO-100, p. 522). The organic is butted for return to the solvent extraction process. The aqueous waste streams from organic treatment are collected in a waste storage tank.

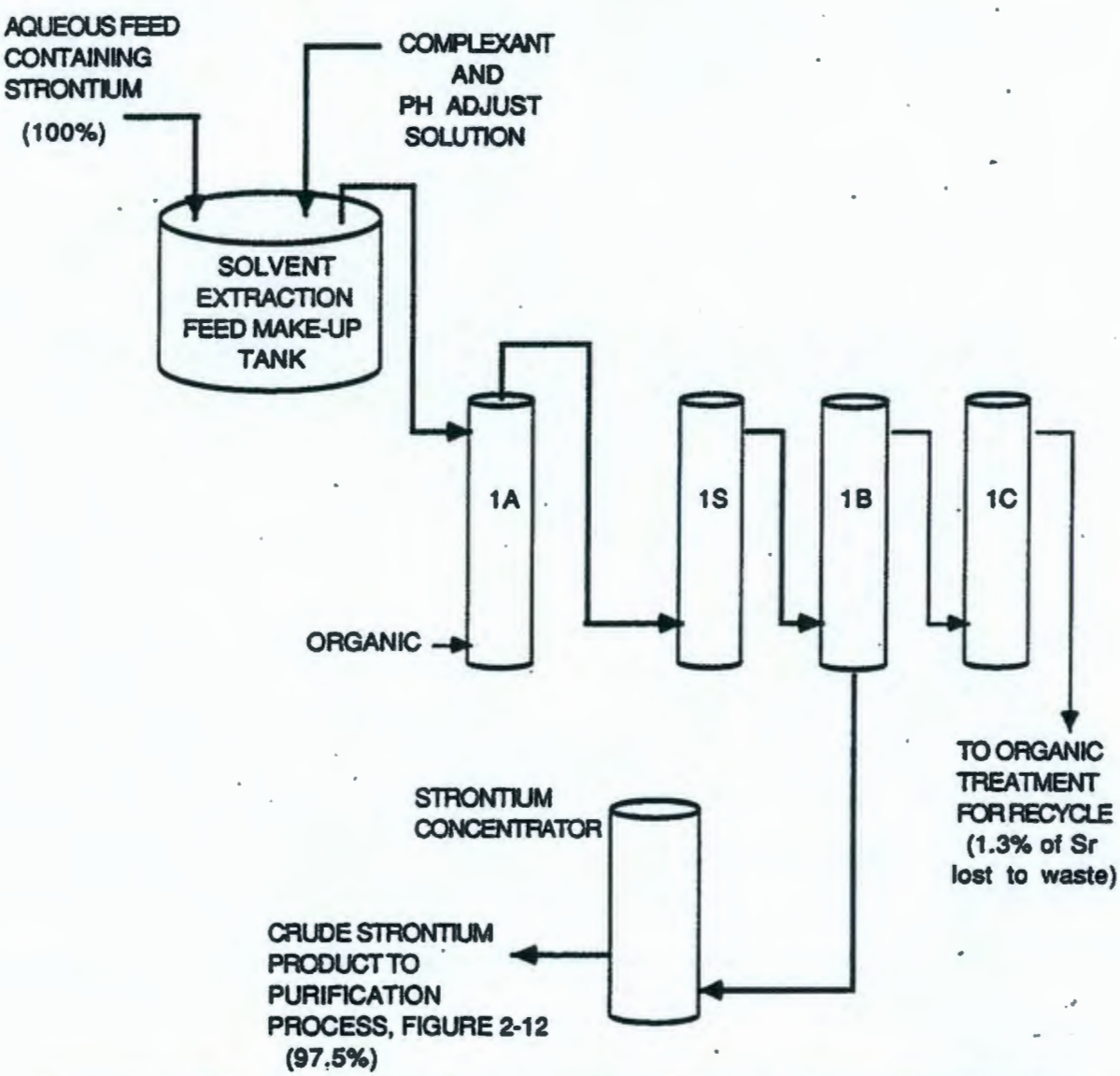


Figure 5-42. B Plant Strontium Recovery Solvent Extraction Process Simplified Flow Diagram

The strontium content of the crude strontium product from solvent extraction and concentration was only 5-15 percent of the cation weight, excluding sodium. This crude product was subsequently purified to prepare for encapsulation. Early purification was a two-step process consisting of sulfate precipitation followed by hydroxide precipitation. The sulfate precipitation process selectively precipitated strontium as sulfate with a first and second sulfate strike; centrifuged the material to separate solid with strontium and liquid with the impurities; washed

the precipitate to remove impurities; metathesized the strontium sulfate in sodium hydroxide and sodium carbonate to produce strontium carbonate; and, dissolved the strontium carbonate in dilute nitric acid. This process removed the bulk of most of the metallic cations present but left behind rare earths and barium. After sulfate precipitation the resulting strontium nitrate solution was further processed via hydroxide precipitation to remove about 90% of the remaining 3-5% metallic impurities. The hydroxide precipitation process removed the remaining impurities by addition of caustic to raise the pH to 10; agitate and digest to promote impurity precipitation; centrifuging the solids to separate the liquid and solid phases; water and dilute caustic washing of the solids to recover residual strontium; collection of strontium bearing liquid and washes; and, acidification of the strontium solution with nitric acid. This acidified product was allowed to concentrate by self-heating and in almost all cases was feed to the subsequent encapsulation process. In a few cases barium separation, via barium chromate precipitation, was also required prior to encapsulation.

Waste streams from the sulfate and hydroxide precipitation were returned to solvent extraction for strontium recovery. Recovery of strontium in B Plant was completed by the end of 1978, presenting a problem dealing with the large waste volume from sulfate and hydroxide precipitation. To address this, a new rare-earth precipitation process was used to recover the strontium as sulfate along with rare-earth sulfate as the carrier (see Figure 5-43). The solution was then centrifuged and the supernatant liquid was discharged to underground storage tanks. The solids were treated with sodium carbonate to convert the solids to carbonates, washed, agitated, settled and centrifuged. The liquids from this treatment were discharged to underground storage tanks. The strontium and rare-earth carbonates were dissolved in nitric acid and stored for subsequent treatment. Subsequent treatment consisted of ion exchange, but occurred after 1980 when incoming transfer were no longer being made to SSTs.

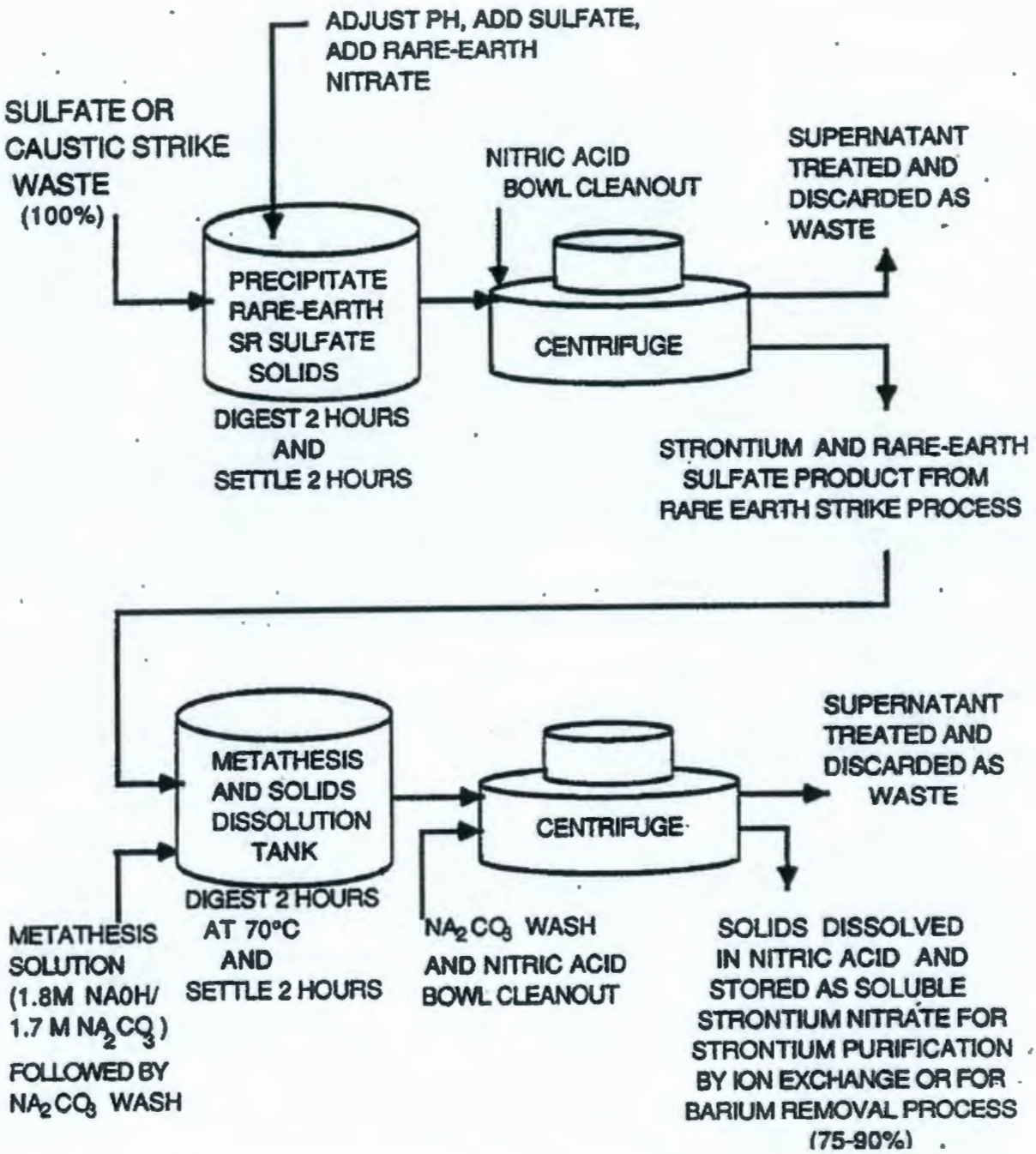


Figure 5-43. B Plant Strontium Purification Rare-Earth Sulfate Strike Process Simplified Flow Diagram

5.5.5.2. Major Waste Streams

Waste streams are described in terms of the phases of fission product recovery that occurred in B Plant. Each subsection below covers a particular phase at B Plant associated with fission product recovery.

5.5.5.2.1. Fission Product Waste During Phase I Operations, 1963-1966

During fission product recovery from 1963-1966, four waste streams were collected and accumulated within a waste storage tank in B Plant. These four waste streams were from the lead removal cycle, cerium separation cycle, concentrator overheads, and vessel ventilation. These wastes were accumulated and transferred to tank farms. The flowsheet composition of this accumulated waste from HW-67728 is:

NaOH	0.28 M
Na_2CO_3	0.039 M
$NaNO_3$	0.21 M
Specific Gravity	1.10

Waste coming from B Plant during this time was identified as fission product (FP) waste. The waste was sent to tank B-110 from start of operations until the end of 1964. From then until end of operation in June 1966, the waste was sent to tank B-111. Waste from tank B-110 was subsequently pumped from these tanks to tanks B-112, from B-112 to AX-101, and from tank AX-101 to tank AX-103. These five tanks are the only tanks identified in the monthly waste status summary reports as receiving FP waste from B Plant. Other SSTs received FP waste during this time frame but that FP waste came from Strontium Semiworks and not B Plant. None of the five tanks receiving FP waste from B Plant have probable liner failures.

5.5.5.2.2. Fission Product (FP) Waste During Equipment Replacement, 1966-1967

During the equipment replacement period (June 1966 to December 1967) between FP recovery phases, waste status summary reports show 367,000 gal of waste identified as FP waste was sent to tanks B-111 and B-110. This waste was likely waste from decontamination, flushing, and other operations associated with replacement of equipment in the various cells. This waste was subsequently sent to the B Plant cell 23 concentrator, E-23-3, for concentration. No compositional information was found for this waste. Again, neither of these tanks receiving FP waste from B Plant has a probable liner failure.

5.5.5.2.3. B Plant High-Level, B Plant Low-Level and B Plant Ion Exchange Waste during Phase III Operations, 1967-1980

During Phase III, FP recovery operations at B Plant there were a number of waste types generated at B Plant that were sent to the SSTs. Quarterly waste status summary reports used acronyms to describe waste streams sent to SSTs. Early on, at the end of 1967 through

March 1968, some waste from B Plant was still being identified as FP waste. Also, at the end of 1967, the concentrated low level waste from B Plant's E-23-3 concentrator was identified as B waste, a description later used for the high-level waste generated at B Plant. For the remainder of the operational period, there were three broad categories of generated waste streams: B Plant Low-Level Waste; Ion Exchange Waste; and, B Plant High-Level Waste. Each of these is described below.

B Plant Low-Level Waste

Streams containing small quantities of cesium and strontium were all sent through the waste concentration system in Cell 23 to be collected, blended, neutralized, and reduced in volume (WHC-MR-0003). These dilute waste streams from FP recovery (including cell drainage, condensate streams, encapsulation waste, and other miscellaneous streams) were collected in B Plant's tank TK-24-1, concentrated in the E-23-3 concentrator within B Plant, and the concentrated waste was collected in tank TK-23-1, the B Plant non-boiling waste concentrate tank (ISO-100, p 537). From TK-23-1, the waste would be transferred to the SSTs.

The waste streams from loading and the scrub solution for cesium purification, if they contained low enough concentration of cesium, could be processed as low-level waste through the concentrator. However, as described below, a waste stream in quarterly waste status summary reports identified as IX (or RIX or SIX) from B Plant were transferred directly to SSTs. A flowsheet from 1980 (RHO-F-7) does identify ion exchange waste that was collected in the waste disposal tank TK-18-1 as being pumped to TK-24-1, the low-level waste receiver tank that was the feed tank to the E-23-3 concentrator.

Waste collected in tank TK-24-1 was adjusted to a pH of at least 10 prior to being sent to the E-23-3 concentrator (ARH-CD-691, p 701). This was done to drive off ammonia in the concentrator overheads and to eliminate acid-base reactions within the concentrator.

No specific waste composition was found for B Plant low-level waste discharged from tank TK-23-1. The pH of the waste should have been at least 10 based on the requirement for pH adjustment of the feed to the E-23-3 concentrator.

B Plant Ion Exchange Waste

The waste streams from cesium recovery via ion exchange include the supernatant liquid effluent from the ion exchange column, water wash wastes, sodium scrub solution, and for RSN an additional sodium hydroxide wash waste. Waste transfers identified as ion exchange waste in waste status summary reports were listed as originating from tank TK-18-1 within B Plant. Waste in tank TK-18-1 could be sent to low-level waste receiver tank TK-24-1 for subsequent concentration in B Plant's E-23-3 concentrator or directly to underground storage tanks. Waste status summary reports identified IX waste as a stream separate from B Plant low-level waste that was concentrated in the E-23-3 concentrator. Available waste status summary reports through the end of 1976 show waste identified as ion exchange waste from B Plant being sent directly to underground storage tanks (ARH-CD-822 DEC, *Production and Waste Management Division Waste Status Summary December 1976*).

Waste streams associated with ion exchange at B Plant in quarterly waste status summary reports were referred to as IX, RIX and SIX, depending on the type of waste being processed through ion exchange. Most waste generated was simply identified as IX waste. This waste was ion exchange waste from treating PUREX waste which would include either processed CAW or PSN. Waste identified as RIX was ion exchange waste from REDOX supernatant. Waste identified as SIX was ion exchange waste from processing of sludge supernatant or PSS.

A flowsheet for cesium recovery from PUREX alkaline supernatant liquid (HW-78061, *Waste Management Program Process Flowsheets*, repeated in ISO-100) showed the following waste streams.

Constituent	Column Effluent, M	Water Wash Waste, M	Sodium Wash Eluent, M	Water Wash Waste, M	Combined, M
$NaNO_3$	0.58	--	--	--	0.43
$NaNO_2$	2.25	--	--	--	1.67
Na_2SO_4	0.10	--	--	--	0.074
Na_2CO_3	0.77	--	--	--	0.57
$(NH_4)_2CO_3$	--	--	0.2	--	0.03
NH_4OH	--	--	0.1	--	0.01
Relative Volume, gal	60,000	4,500	12,000	4,500	81,000

A flowsheet for cesium recovery from REDOX alkaline supernatant liquid (HW-78061, repeated in ISO-100) showed the following waste streams when treating supernatant from S Farm.

Constituent	Column Effluent, M	Wash Waste, M	Sodium Wash Eluent, M	Wash Waste, M	Combined, M
$NaNO_3$	3.53	--	--	--	2.61
$NaNO_2$	--	--	--	--	--
Na_2SO_4	--	--	--	--	--
Na_2CO_3	--	--	--	--	--
$(NH_4)_2CO_3$	--	--	0.2	--	0.03
NH_4OH	--	--	0.1	--	0.01
NaOH	1.59	0.01	--	1.	1.23
Al	0.37	--	--	--	0.27
Relative Volume, gal	60,000	4,500	12,000	4,500	81,000

A flowsheet for cesium recovery from REDOX alkaline supernatant liquid (HW-78061, repeated in ISO-100) showed the following waste streams when treating supernatant from SX Farm.

Constituent	Column Effluent, M	Wash Waste, M	Sodium Wash Eluent, M	Wash Waste, M	Combined, M
$NaNO_3$	2.62	--	--	--	1.94
$NaNO_2$	0.36	--	--	--	0.27
Na_2SO_4	0.03	--	--	--	0.02
Na_2CO_3	--	--	--	--	--
$(NH_4)_2CO_3$	--	--	0.2	--	0.03
NH_4OH	--	--	0.1	--	0.01
NaOH	0.93	0.01	--	1.	0.75
Al	0.84	--	--	--	0.62
Relative Volume, gal	60,000	4,500	12,000	4,500	81,000

A flowsheet with waste compositions for cesium recovery from processing sludge supernatant or PSS was not found.

B Plant High-Level Waste

The B Plant high level waste consisted of waste from head end processing, cesium clarification, and strontium recovery processing.

The head end process waste sent to B Plant high-level waste consisted of waste 0.5 M sodium hydroxide-1 M sodium carbonate metathesis solution, waste 0.1 M sodium carbonate wash solution, and residual solids (primarily siliceous solids) remaining after dissolution of metathesized solids (ISO-100, pp 506-508).

The residual solids from crude cesium product clarification were routed to high-level waste storage within B Plant. The composition of these solids, other than residual cesium content for process control purposes, could not be found in reviewed reports.

The strontium recovery waste sent to high-level waste storage consisted of the aqueous waste stream from 1A column, the aqueous waste stream from the 1C column, and the organic treatment waste. The aqueous waste stream from the bottom of the 1A column contained the majority of the contaminants and was by far the largest of the waste streams with about 16,000 gal produced per day during operation (ARH-CD-691, Figure 2). The aqueous waste stream from the 1C column consisted of a nitric acid stream used to further remove contaminants from the strontium-bearing organic stream. The aqueous waste from the 1C column was about 1,200 gal per day (ARH-CD-691, Figure 2). For cleanup of the organic after passing through solvent extraction, the stream was contacted with nitric acid-sodium nitrite to strip cerium from the organic stream and then with a sodium hydroxide-sodium tartrate wash solution for removal of yttrium, traces of rare earths, and organic degradation products and was butted to the desired nitrate concentration with nitric acid. The OWW consisted of about 2,650 gal per day (ARH-CD-691, Figure 2) and the organic butt waste was nominally 100 gal per day (ARH-CD-691, Figure 2). Concentrations of major constituents and volumes for these streams when processing PAS is shown below:

Constituent	1AW, M	1CP, M	OWW, M	Organic Butt, M	Combined
Al	0.0742	0.0052	0.0047	--	0.065
H^+	1E-05	1.5	--	--	--
Na^+	1.6	<1E-09	1.6	~7.	1.5
OH^-	--	--	1.3	--	0.17
NO3-	1.6[1]	--	--	~7.	1.32[1]
Specific Gravity	1.13	--	--	--	--
pH	4.5	--	--	3.5	--
Relative Volume, gal	16000	1200	2650	100	20000

[1] Assumed composition estimate based on sodium content. Not listed on flowsheet compositional information.

The 1AW and 1CP are accumulated in storage tanks and then transferred batchwise to a waste storage tank in B Plant. The OWW and Organic Butt Waste are transferred directly from the wash vessels to a waste storage tank in B Plant. The waste was adjusted if necessary to a minimum pH of 10. Early flowsheet reports show this waste being sent directly to boiling waste storage (ISO-100, HW-78061) while a later flowsheet shows the waste being concentrated first before being sent to boiling waste storage (ARH-CD-691). The flowsheet for concentration shows these major streams from solvent extraction being combined with some other dilute streams (e.g., cell drainage, encapsulation waste) and then concentrated to nominally 4 M sodium by controlling the bottoms specific gravity to 1.24 (ARH-CD-691). If concentrated to 4 M sodium, the nitrate concentration would be about 3.5 M and the hydroxide would be roughly 0.45 M. This waste was pumped from the concentrator via TK-23-1 to TK-25-2 from where it was transferred to a boiling waste tank.

5.5.6 Tank Farm Evaporation Process Waste Types (1951-1980)

In an effort to conserve tank storage volume and to convert the waste to a less mobile solid form, non-boiling liquid wastes were evaporated via various evaporation processes. These processes were operated from 1951 to beyond the end of waste additions to SSTs in 1980. A number of evaporation systems were employed during this time frame. The first method employed was atmospheric boiling of waste in purpose-built evaporators built adjacent to B Farm in 200 East Area and T Farm in 200 West Area. Subsequently, an in-tank solidification process was used within the BY Farm. Additional evaporative capacity was later added by using existing waste concentrators within the REDOX and B Plant canyon facilities. Finally, larger throughput evaporators, 242-S and 242-A, were built and operated. These evaporators operated under vacuum and could concentrate waste at lower temperature and return the concentrate to tanks for subsequent crystallization and precipitation of salt crystals. The equipment and process for concentrating waste for each of these systems is described in the subsections below. Waste composition information for feed to and bottoms from the various evaporators is provided along with any available corrosion and temperature data.

REDOX and PUREX generated waste referred to as boiling waste that would evaporate water via the radioactive decay heat present in the waste. No external heat was required to allow the waste to boil. These boiling wastes are discussed under the sections of this report having to do

with REDOX and PUREX operations and are not covered as part of this section (see sections 5.5.3 and 5.5.4, respectively).

5.5.6.1. 242-B and 242-T Atmospheric Evaporators Waste (1951-1955)

The 242-B and 242-T atmospheric evaporators were originally built to reduce the storage volume of 1C waste by boiling off water via evaporative concentration in an evaporator vessel with subsequent transfer of the bottoms stream to SSTs where crystallization and precipitation of salt cake would occur. The 242-T evaporator completed construction and was turned over to operations on April 27, 1951 (HW-20991-DEL, *Hanford Works Monthly Report for April 1951*, p. 54). The 242-B evaporator completed construction December 8, 1951 and was turned over to operations on December 14, 1951 (HW-23140-DEL, *Hanford Works Monthly Report for December 1951*, p. 34). The 242-B evaporator operated until October 28, 1954 (HW-45163-RD, *Tank Farm and Waste Evaporator Weekly Summary Process Unit Period 0200 12/31/53 to 0800 1/14/55*, p 71) and the 242-T evaporator operated until July 1955 (HW-38375-DEL, *Monthly Report Hanford Atomic Products Operation for July 1955*, p Ed-5). Subsequent operation of the 242-T evaporator, starting in 1965, is discussed in section 5.5.6.4.

Each atmospheric evaporator in 200 West and 200 East Area were built adjacent to existing SST farms. The dedicated feed tank to the 242-T evaporator was tank TX-118 and to the 242-B evaporator was tank B-106. Dilute waste would be sent to these feed tanks from the various tanks holding the waste.

A simplified schematic of the 242-T evaporator facility is provided in Figure 5-44 (RL-SEP-396, *242-T Evaporator Facility Information Manual*). The following description is excerpted from H-2-2028, *First Cycle Evaporation Schematic & Flow Diagram*, RL-SEP-396, and ARH-CD-178, *Operational Safety Analysis, 242-T Waste Evaporator*. The 242-B and 242-T evaporators employ a natural circulation evaporator system operating at atmospheric pressure to concentrate the radioactive salt waste solutions. The main process components of the evaporator system are the feed tank, pre-heater, evaporator vessel, cyclone separator, condenser, and condensate catch tanks. The 4,185 gal evaporator feed tank receives the dilute waste from the dedicated single-shell feed tank (tank B-106 or TX-118). The dedicated single-shell feed tank has a floating suction process feed pump with a nominal 20 gpm capacity. The feed tank has an overflow line that returns excess feed back to the dedicated single-shell feed tank. The feed from the feed tank is routed through two preheater tanks in series which are outfitted with double-helical coils. These coils receive a portion of the evaporator's steam condensate to provide preheat to the waste being fed to the evaporator. In the evaporator, the waste is maintained at its boiling temperature by four natural circulation vertical steam heated units. The pressure in the evaporator is controlled by the condenser temperature with a slight vacuum provided by jets installed at the condenser to remove non-condensables. Water vapor is drawn off into the condensing system and the waste concentrate flows by gravity out of the evaporator vessel bottom to the designated single-shell evaporator bottoms receiver. Entrained waste is removed from the water vapor via the cyclone separator. Later a packed scrubber with two, 6-in. layers of wire mesh packing was also added for additional deentrainment. Liquid collected in the cyclone separator, and later the packed scrubber, is directed to a small catch tank that gravity feeds back to the single-shell feed tank. The water vapor passing through the cyclone separator

passes to the shell side of the water-cooled condenser. The condensate flows by gravity to one of two catch tanks where the material can be sampled before being drained to an underground crib. If radioactivity exceeds operating limit, the condensate is diverted back to the single-shell feed tank. The boiling waste is maintained and collected condensate is sent to a crib for disposal and the concentrated waste is sent to a SST where the waste cools resulting in precipitation of salts. The evaporator systems also include a decontamination tank outside the building to introduce either sodium hydroxide or citric acid to the feed tank, evaporator, cyclone separator, and packed scrubber.

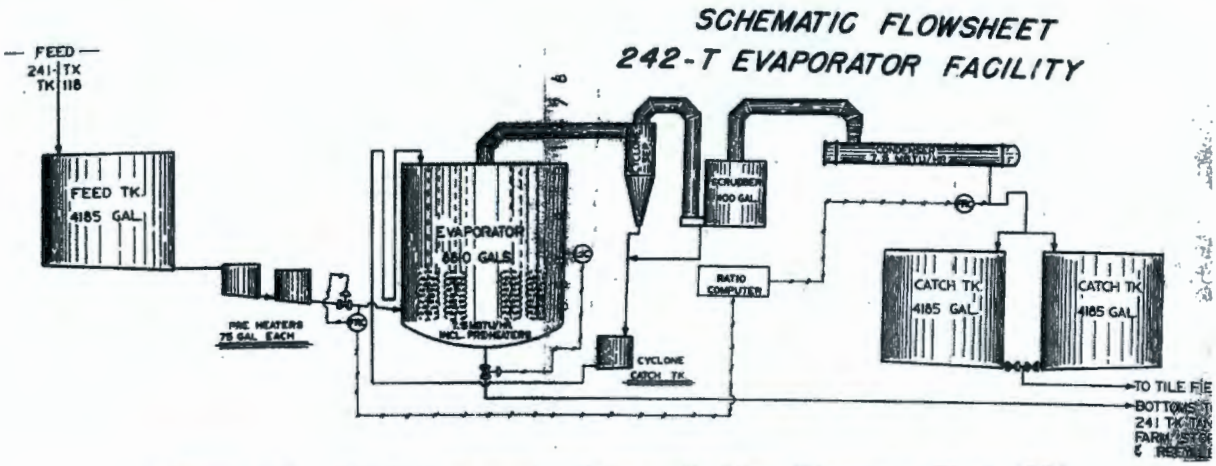


Figure 5-44. 242-T Evaporator Schematic Flow Diagram, Circa 1955

Scaling on the steam coils, steam coil failures, foaming and line plugging were not uncommon during the operation of the 242-B and 242-T evaporators. Generally, scale removal was performed by water or sodium hydroxide soaking of the coils after evaporation rates declined because of reduced heat transfer. Citric acid was also mentioned as a decontamination solution used. In December 1953, at both 242-B and 242-T, a commercial descaler "Socco" was added on a test basis at a rate of 1 quart per 10,000 gal to determine the effect on scale formation and evaporator performance (HW-45163-RD). It was documented that this was discontinued in January 1954, at least for 242-T. No information could be found on the composition of "Socco" descaler. Foaming agent was added on an as-needed basis when a foam detector indicated the presence of foam above the liquid in the evaporator. No information was found on the specific antifoaming agent used in the evaporator system. The corrosion implication of these chemicals is not known.

In 1949, prior to operation of the 242-B and 242-T evaporators, waste concentration studies were performed at Oak Ridge National Laboratories (ORNL) with a 50 gal sample of 1C waste sent from Hanford to ORNL (HW-14118, *Report of Visit to Oak Ridge National Laboratories to Investigate Problems Associated with Waste Concentration*). That testing does not identify the specific source tank for the 1C waste sent to ORNL but it was an actual waste sample rather than simulant, based on presented radioanalytical data. No chemical composition except pH or physical properties data except density are provided in the report HW-14118 describes initial 1C waste testing at ORNL. The waste would have consisted of combined 1C waste and CW since these streams weren't segregated until 1955 (see Section 5.5.1.2). The tested 1C waste had a pH

of 9.0 and an initial specific gravity of 1.110. When the waste was concentrated 5 to 1, the resulting pH was 8.5 and the specific gravity increased to 1.405. The average evaporation temperature during testing was 109°C (228°F). No corrosion testing was performed with the concentrated waste solution.

From the start of operation of both the 242-B and 242-T evaporators until February 1953, the evaporators concentrated 1C waste. The waste was typically concentrated in the range from 3 to 1 up to 4 to 1. During the original 1C waste evaporation, a marked reduction in the evaporation rate was frequently observed near 72 percent volume overhead to distillate (i.e., 3.57 to 1 concentration) (HW-25468, *Further Evaporation of Residual Solution from First Cycle Waste Evaporator*). It was suggested this was in part caused by crystallization of sodium sulfate and disodium phosphate on the coils. A sample of tank TX-116 evaporator bottoms solution identified the predominant salts in the evaporator bottoms solution from one pass concentration of first cycle concentration. That composition was identified as:

$NaNO_3$	540 g/L	6.35 M
Na_2SO_4	16 g/L	0.13 M
$Na_2HPO_4 \cdot 12H_2O$	29 g/L	0.08 M
$NaH_2PO_4 \cdot H_2O$	56 g/L	0.41 M

No information is given regarding sodium nitrite or sodium hydroxide, however, the pH of the solution is given as 6.79 (HW-25468, Table II).

In July 1952, a recommendation report (HW-24912, *Recommendations for Future use of First Cycle Waste Evaporators*) recognized that the original mission of concentrating 1C waste would be completed in 200 West Area by about August 1952 and 200 East Area by about July 1953. It was recommended that the remaining supernatant solution after once-concentrating 1C waste could be processed again through the evaporators. Additionally, it was recommended that TBP waste could be processed through the evaporators.

Laboratory studies of further evaporation of the supernatant liquid from a single pass of 1C waste through the evaporators were performed on tanks TX-116 and TX-117 supernatant to establish a method by which this material could be further reduced in volume (HW-25468). The waste temperature in tanks TX-116 and TX-117 at the time of sampling was 110°F and 100°F, respectively. Three months were required for the solution in tank TX-117 to cool from 100°C (212°F) to 38°C (100°F). Testing showed that evaporation of 40 volume percent of the material to condensate resulted in a slurry containing 40 volume percent solids. To avoid the formation of solids, it was found the solution could be evaporated to give up to 25 percent of the feed volume as condensate without crystallization at the boiling temperature. The bulk of the solids crystallizing was sodium nitrate and sodium hydrogen phosphate. The solubility of salts in the supernatant was examined in terms of temperature and pH. The report recommended that a second pass of 1C waste supernatant should be performed at the pH of the solution, namely in the range 6.5 to 7.0. It was also recommended to evaporate at 25 percent evaporation thus avoiding solids formation in the evaporator. A table of constituent concentrations before and after lab-scale evaporation of tank TX-116 supernatant is provided in HW-25468 and repeated below:

Ion	Collected TX-116 Supernatant [g/L]	Supernatant from TX-116 Evaporation [g/L]	Calculated analysis if no crystallization [g/L]
Sodium	150	193	200
Nitrate	397	413	529
Bismuth	<0.04	<0.04	--
Aluminum and Aluminate	0.04	0.04	0.05
Phosphate	46.4	62.0	62
Sulfate	10.7	7.47	14.3
Ferric Iron	<0.04	<0.04	--
pH	6.79	6.55	--

The results show that almost all crystallized salt is nitrate with the balance primarily being sulfate. At the pH tested, almost all the phosphate (~$^5/_6$) would be present as sodium dihydrogen phosphate with the balance mainly disodium monohydrogen phosphate. The remaining supernatant liquid after this second evaporation is 6.67 M nitrate, just slightly higher than the concentration reported after the first pass of evaporation.

In February 1953, both the 242-B and 242-T evaporators started to evaporate the supernatant solution remaining after the first pass of concentrating the 1C waste (HW-27288-DEL, *Hanford Works Monthly Report for February 1953*, p Ed-5). The re-evaporation of 1C waste at 242-T was completed June 20, 1953 (HW-28576-DEL, *Monthly Report Hanford Atomic Products Operation for June 1953*, p Ed-5) and at 242-B was completed July 9, 1953 (HW-28906, *Monthly Report Hanford Atomic Products Operation for July 1953*, p Ed-5). Concentration of the waste during this time frame ranged from nominally 20% volume reduction to 50% volume reduction.

Field corrosion tests of SAE 1020 steel polished and sandblasted specimens were performed with concentrated 1C waste (241-TX-117) for approximately seven months, starting November 24-25, 1952 (HW-30641). Unfortunately, it was not possible to recover the specimens in tank TX-117. The cause of the loss was unknown and no suggestion of the cause was given. No other corrosion information was located for concentrated 1C waste.

During May 1953, laboratory work was performed on reconcentration of stored TBP waste from tank T-109 (HW-28267-DEL, *Monthly Report Hanford Atomic Products Operation for May 1953*, p Fc-17). The work found that at 25°C the waste from tank T-109, before reconcentration, contained approximately 10 to 20 volume percent solids (no in-tank waste temperature was given). The work also found that single-batch concentration of the waste supernatant to 50 percent of the original volume gave a product with a boiling point of 107°C to 113°C containing 5 to 10 volume percent solids at that temperature and 60 to 70 volume percent solids at 25°C.

The evaporation of TBP waste began during July 1953 at 242-T (HW-28712, *Separations Section, Waste – Status Summary, June 30, 1953*) and September 1953 at 242-B (HW-29624, *Operations Section, Waste – Status Summary*). The 242-B and 242-T evaporators continued to operate evaporating TBP waste until October 1954 (HW-33544, *Separations Section,*

Waste-Status Summary for October 1954) and September 1954 (HW-33396, *Separations Section, Waste – Status Summary for Month of September 1954*), respectively. Concentration of the TBP waste during this time frame ranged from nominally 25% volume reduction to 50% volume reduction. This was the end of processing for the 242-B evaporator. No post-concentration compositional information could be found for solids or remaining supernatant liquid from TBP waste evaporation. Estimates of TBP waste composition prior to evaporation can be found in Section 5.5.2.2. Tri-butyl phosphate waste has a relatively high sodium nitrate concentration so one would expect the concentration of this waste would result in crystallization of sodium nitrate upon cooling. No corrosion testing information was found for the resulting crystallized solids or resulting supernatant liquid.

Steam coils were replaced in the 242-T evaporator and it was restarted in December 1954 (HW-34412, *Separations Section, Waste – Status Summary for December 1954*). The 242-T evaporator concentrated 1C waste until May 1955 (HW-37143, *Separations Section, Waste-Status Summary for May 1955*) and then transitioned to supernatant solution that remained after the first pass of concentrating the 1C waste. This processing continued until the end of then-current operations at 242-T in July 1955 (HW-38401, *Separations Section, Waste – Status Summary for July 1955*).

Evaporator bottoms were discharged from the evaporator at boiling conditions and sent to the receiving SSTs. Earlier it was shown the boiling point was nominally 110°C (230°F) for these wastes and that the waste cooled to about 38°C (100°F) within three months. Time then at elevated temperature would have been relatively short in comparison to the overall tank operational period. The tanks receiving evaporator bottoms from 242-B and 242-T during this time period are presented in Table 5-33.

Table 5-33. Tanks Receiving Evaporator Bottoms from 242-B and 242-T Atmospheric Evaporators Between 1951 and 1955

B-101	B-107 (liner leak)	BX-112	TX-114 (liner leak)
B-102	B-108	T-108	TX-116
B-103	B-109	T-109	TX-117
B-104	BX-110	TX-112	TX-118
B-105	BX-111	TX-113	TY-102

Based on those tanks identified as containing waste code EB (evaporator bottoms) as of July 1955 per HW-38401.

5.5.6.2. Waste Self-Concentration

Wastes from the REDOX process and PUREX process were referred to as self-concentrating or boiling wastes. These wastes typically were stored at higher temperatures than waste generated from previous processing operations. These wastes contained sufficient quantity and concentration of radionuclides which gave off enough decay heat to cause the waste to boil. As the waste boiled, water was driven off concentrating the chemical constituents present in the tank. Water, condensate, or dilute waste would be added to the tank to maintain waste temperature. Waste undergoing self-concentration is discussed in the sections dealing with

REDOX and PUREX operations (see Sections 5.5.3 and 5.5.4, respectively) and are not repeated here. Tanks that contained waste that was self-concentrating are listed in Table 5-34.

Table 5-34. Listing of Single-Shell Tanks That Underwent Self-Concentration

Tank	
SX-101	S-101
SX-104	S-104
SX-107*	U-110
SX-108	A-101
SX-109	A-102
SX-110	A-103
SX-111	A-104
SX-112	A-105
SX-113	A-106
SX-114	AX-101
SX-115	AX-102
	AX-103
	AX-104

*Tanks highlighted in red have probable liner leaks.

5.5.6.3. In-Tank Solidification Operations (1965-1974)

By the early 1960s, solidification of intermediate-activity wastes was a major goal of the Waste Management Program of the Chemical Processing Department (HW-68099, *CPD Waste Management Plant Improvement Program*, p. 5-6) at the Hanford Site. Increased volumes of PUREX CW, segregation of OWW, and B Plant FP waste, and then-recent tank failures in 200 West Area spurred the demonstration of in-tank solidification in a SST.

The in-tank solidification (ITS) prototype unit, referred to as ITS-1, was installed into tank BY-101 by the end of 1964. The ITS-1 system was first operated briefly on a test basis during December 1964 (RL-SEP-197, *Chemical Processing Department Monthly Report, December 1964*) and finally started up in full operation by March 19, 1965 (RL-SEP-405, *Chemical Processing Department Monthly Report for March, 1965*). The ITS-1 operated in tank BY-101 until early November 1966 (ISO-610 DEL). The unit was then moved to tank BY-102 where it began operation on November 23, 1966. The unit operated as ITS-1 until August 26, 1971 when it was converted to a cooler used in conjunction with ITS-2.

At the same time ITS-1 was first being operated, plans for second and third ITS systems were being put in place. Design criteria were established for a second ITS system, ITS-2, to be placed in tank BY-112 (RL-SEP-499, *Design Criteria for a Second In-Tank Waste Solidification System*). The major objectives of the second ITS system were: increased boil-off capacity to twice the design rate of the ITS-1 system; capability for a high degree of concentration; effective condensate decontamination; a simplification of off-gas handling; a safely operating system;

compatible with existing tank farms; and, earliest beneficial use at minimum cost. Laboratory findings showed that the necessary heating could be provided by immersing sheathed electrical heaters directly in the waste solution (HW-81481, *Waste Management Program Chemical Processing Department*). A circulator would still be required to mix the tank contents, but at a much lower air flow rate and at significantly reduced inlet air temperature. This simplified the demands for the off-gas treatment system by reducing air flow rate and also eliminated piping of the high temperature air above ground. The ITS-2 system was installed into tank BY-112 and acceptance and operability tested through November and early December 1967 (ARH-61-DEL, *Monthly Report, 200 Area Operation, November, 1967*, and ARH-62 DEL, *Monthly Report, 200 Area Operation, December, 1967*). The ITS-2 system was first operated December 7, 1967 (ARH-62 DEL) and reached boiling by February 15 and full operation by February 17, 1968 (ARH-301 DEL, *200 Areas Operation Monthly Report, February 1968*). The ITS-2 and ITS-1 systems were shut down on June 14, 1973 (ARH-2416 RD, *Chemical Processing Division Monthly Report Summaries, January 1972 – December 1973*). A timeline showing ITS-1 and ITS-2 operational highlights is shown in Figure 5-45.

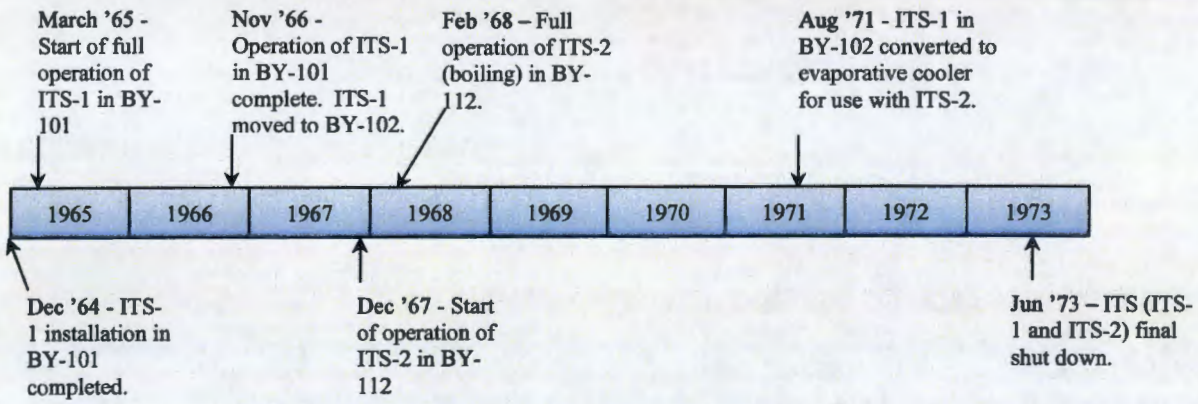


Figure 5-45. In-Tank Solidification Summary Operational Timeline

Design for a proposed third ITS system, to be located in TX Farm, was prepared (ISO-512, *Chemical Processing Division Monthly Report for September, 1966*, ISO-642). A low-wattage density electric immersion heater was installed in tank TX-114 in early December 1966 that was operated starting January 16, 1967 after troubleshooting the unit (ISO-707, *Chemical Processing Division Monthly Report for January, 1967*). Work associated with this third system (Project IAE-607) was placed on hold in January 1967 pending study of alternative waste volume reduction methods at reduced capital cost (ISO-707). Ultimately, predictions of waste storage requirements coupled with operating experience at ITS-1 and 242-T indicated that volume reduction goals could be met at a lower cost by increasing the capacities of ITS-1 and 242-T rather than completing ITS-3 and the ITS-3 project was canceled (ARH-905, *Evolution and Status of In-Tank Solidification*).

5.5.6.3.1. Process Description

ITS-1 Operational Description

The following operational description is excerpted from HW-83218, *First In-Tank Waste Solidification Unit Information Manual*, and other references as called out. The purpose of the project was to concentrate non-boiling waste in a SST through evaporation. Evaporation was achieved by sparging hot air into the waste solution. The design evaporation rate for the system was 10 gal per minute. A flow diagram for the initial ITS-1 is shown in Figure 5-46 (ISO-SA-1, *Operating Experience on In-Tank Solidification of Radiochemical Wastes*). Air at a nominal rate of 4200 SCFM was drawn through an inlet filter, air flow control valve and into a compressor. Inlet air was mixed with recycled hot air upstream of the compressor to maintain a constant inlet air temperature of 100°F for proper compressor operation. Air was compressed to 15-20 psig in order to overcome the hydrostatic head of the waste solution. The compressed air was directed to a 1440 kW electric heater where the air was heated to 1200°F. The heated, compressed air was directed through an insulated pipe which carried the air to a circulator located at the radial center of the tank about 4 ft above the tank bottom. The air was discharged at nominally 700°F into the waste solution heating the tank contents. The compressed air agitated the tank's contents and evaporated water as it cooled moving upward through the waste. The initial design solution temperature during operation was 170°F. Heat up rate of the waste solution was maintained at or below "…the maximum rate of 3°F per day as limited by tank thermal stress considerations" (RL-SEP-405). The moisture laden air leaving the waste solution entered the tank dome space where it entered a vent line where the air stream passed through a deentrainer, high efficiency filter, condenser, and finally an exhaust fan where the dehumidified air was discharged to the atmosphere. Plugging of the ventilation system was a common problem requiring flushing of various components with water and chemicals to remove solids.

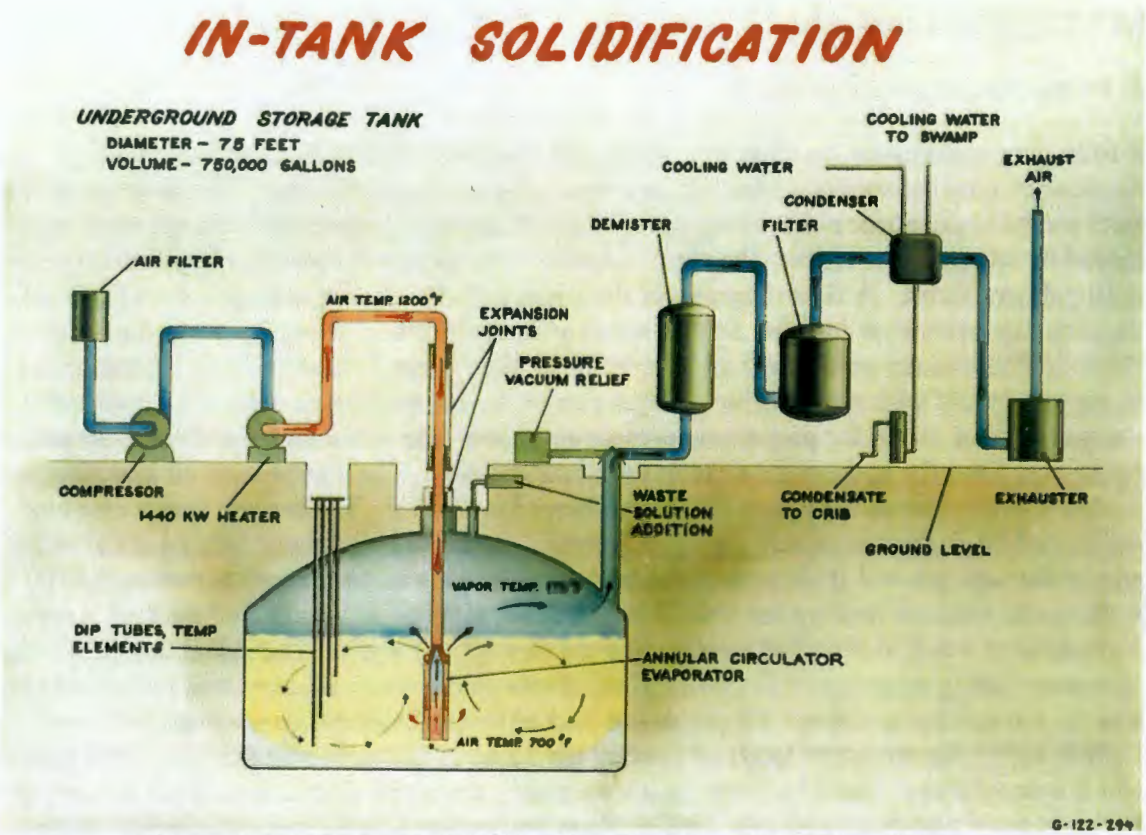


Figure 5-46. In-Tank Solidification Prototype Unit Flow Diagram

Roughly six months after start of ITS-1 operations, two prototype electric heaters were installed in the tank BY-101 east and west sluice pits (RL-SEP-706, *Chemical Processing Department Monthly Report for August, 1965*) to increase capacity and gain experience with electric immersion heaters (RL-SEP-755, *Chemical Processing Department Monthly Report for September, 1965*). The 240 kW heater failed after 480 hours of operation (RL-SEP-874-DEL, *Chemical Processing Department Monthly Report for November, 1965*). The reported reason for failure was due to overheating. The second heater failed after about six months due to accumulated sludge under and around the draft tube surrounding the electric heater (ISO-210-DEL, *Chemical Processing Division Monthly Report for March, 1966*). Solid samples taken from the heater were analyzed and found to contain a mixture of sodium nitrate, sodium carbonate, smaller amounts of sodium hydroxide and bicarbonate, and minor amounts of aluminum and silicon. The ITS unit in tank BY-101 was shut down November 3, 1966 and moved to tank BY-102 (ISO-610 DEL, *Chemical Processing Division Monthly Report for November, 1966*). About 119,000 gal of waste in tank BY-101 was pumped at an average rate of 400 gal per minute through heated lines to tank BY-105 (ISO-674, *Chemical Processing Division Waste Status Summary, October 1, 1966 through December 31, 1966*). The waste processed in tank BY-101 was identified as primarily sodium nitrate and carbonate solutions. Laboratory studies indicated the concentrated salt solution would not acquire enough waters of hydration upon cooling to completely solidify. A study of desiccants to bind the free water found that Portland cement in the ratio of 1.1 lb to 1 gal of waste concentrate would be adequate to solidify the waste. Cement and concentrate were alternately added to tank BY-105 for

improved mixing. Cement was transferred into the tank through three rotating nozzles using commercially available cement fluidization equipment. However, inaccurate measurement of sludge level and hence residual liquid in tank BY-105 prior to transfer of the ITS concentrate resulted in the transferred concentrate not fully solidifying upon cooling.

The ITS-1 equipment moved from tank BY-101 to tank BY-102 resumed operation November 23, 1966 (ISO-610 DEL). A year after start of operation of ITS-1 in tank BY-102, the deentrainer was converted to a scrubber humidifier by installing a water recirculation system to spray the top and bottom of the deentrainer pads (ARH-61-DEL). Also at that time, an ion exchange unit was installed to treat the condensate stream from the offgas. Initial operation of the unit resulted in reduction of the discharged Cs-137 with an average decontamination factor of 80 (ARH-61-DEL).

In February 1968, a Brink®[6] mist eliminator was installed between the deentrainer (converted to a scrubber humidifier) and the condenser (ARH-258-DEL, *Chemical Processing Division Daily Production Reports, January, 1968 through March, 1968*). Also near that time (March 1968) a 1000 kW immersion heater, in a 28-in. circulator (ARH-1381, *Electric Immersion Heater Failures in the Hanford Waste Solidification Program, Task Force Report*) was installed which was planned to double the evaporative capacity of the ITS-1 (ARH-258-DEL). A flow diagram showing this configuration for ITS-1 is given in Figure 5-47. Air flow at 37 cfm was continually maintained to the immersion heater circulator prior to immersion heater operation to ensure the agitation caused by the main heated air circulator would not plug the immersion heater circulator (ARH-1381). Air flow to the immersion heater circulator was maintained at 25-35 cfm during immersion heater operation (ARH-1381, Figure 18). In early May, the electric immersion heater's sheath cut out temperature limit was raised from 350°F to 360°F and ultimately to 500°F to allow continued operation as the heater sheath temperature increased. A maximum solution temperature of 208°F was recorded May 19-20 with a boiloff rate of about 10 gpm which was double the rate with just the air heater. Soon after peak temperature and boiloff rate was achieved the immersion heater was turned off due to high sheath temperature (exceeding 500°F) (ARH-458-DEL, *Chemical Processing Division Daily Production Reports, April, 1968 through June, 1968*). The immersion heater was removed at the end of June and ITS-1 continued with the air heater only (ARH-458-DEL).

[6] Brink is a registered trademark of E. I. du Pont de Nemours and Company or its affiliates, Wilmington, Delaware.

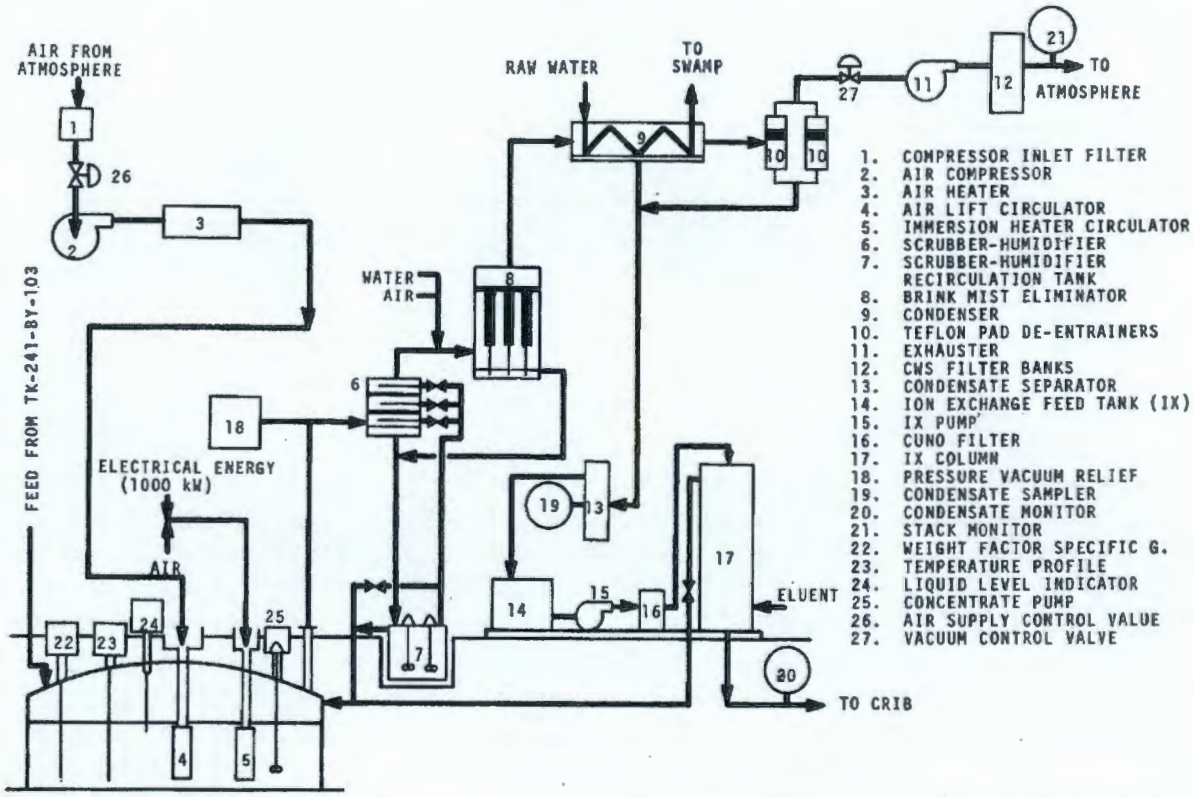


Figure 5-47. In-Tank Solidification Unit 1 (ITS-1) Flow Diagram During Operation in 241-BY-102

At the end of March 1970, ITS-1 was shut down due to a lack of feed (ARH-1526-1, *Chemical Processing Division Daily Production Reports, January, 1970 through March, 1970*). The unit was restarted May 1970 (ARH-1526-2, *Chemical Processing Division Daily Production Reports, April 1970 through June 1970*). Except for some down time associated with mechanical repairs, ITS-1 continued to operate as described until its operation as an evaporative cooler starting in August 1971 (see description below under "ITS-2 Operation with ITS-1 as a Cooler"). The ITS-1 system continued to operate as an evaporative cooler in combination with ITS-2 for the remainder of ITS-2 operations.

ITS-2 Operation

The second In-Tank Solidification unit (ITS-2) was installed in tank BY-112 via Project CAC-176 (ARH-405, *Project Proposal BY-Farm Concentrated Waste Recycle Facilities*). The purpose of the project was to concentrate waste in an underground storage tank to the point at which solidification would occur upon cooling (ARH-405). Waste was transferred from tank BY-112 to a concentrated bottoms receiver tank for subsequent cooling and solidification. The project was built to supplement the evaporative capacity of ITS-1 and the 242-T evaporator (ARH-387, *Process Specifications and Standards Second In-Tank Solidification Facility*). Evaporation was achieved within tank BY-112 by an electric immersion heater within a circulator located in the waste solution. Tank BY-111 was selected as the first concentrated

solution receiver (RL-SEP-499). Initial hot ITS bottoms transfer rates to tank BY-111 were limited to prevent thermal stressing of the tank (ARH-304 DEL, *200 Areas Operation Monthly Report, May 1968*). Very early on in operation it was recognized that a single bottoms receiver tank would severely limit operation of ITS-2 as solids would also build up in tank BY-112 and eventually limit circulator operation (ARH-405). A continuous recycle operating mode was selected to significantly defer the potential solids formation in tank BY-112. The continuous recycle operating mode is represented by the flow diagram in Figure 5-48. The initial design included use of tank BY-111 as the bottoms receiver from tank BY-112, with subsequent decant transfers of liquid from tanks BY-111 to BY-108, and from tanks BY-108 to BY-109, which was the feed tank to tank BY-112 (ARH-405). This recycled waste was mixed with new feed stock in tank BY-109 before being transferred to tank BY-112 for concentration. The design evaporation rate for the system was 20 gal per minute (RL-SEP-499). The moisture laden air leaving the waste solution from tank BY-112 entered the tank dome space where it entered a deentrainer, then to a vent line where the air stream passed through a condenser, deentrainer, cyclone separator, heater, high efficiency filter, and finally an exhaust fan where the dehumidified air was discharged to the atmosphere.

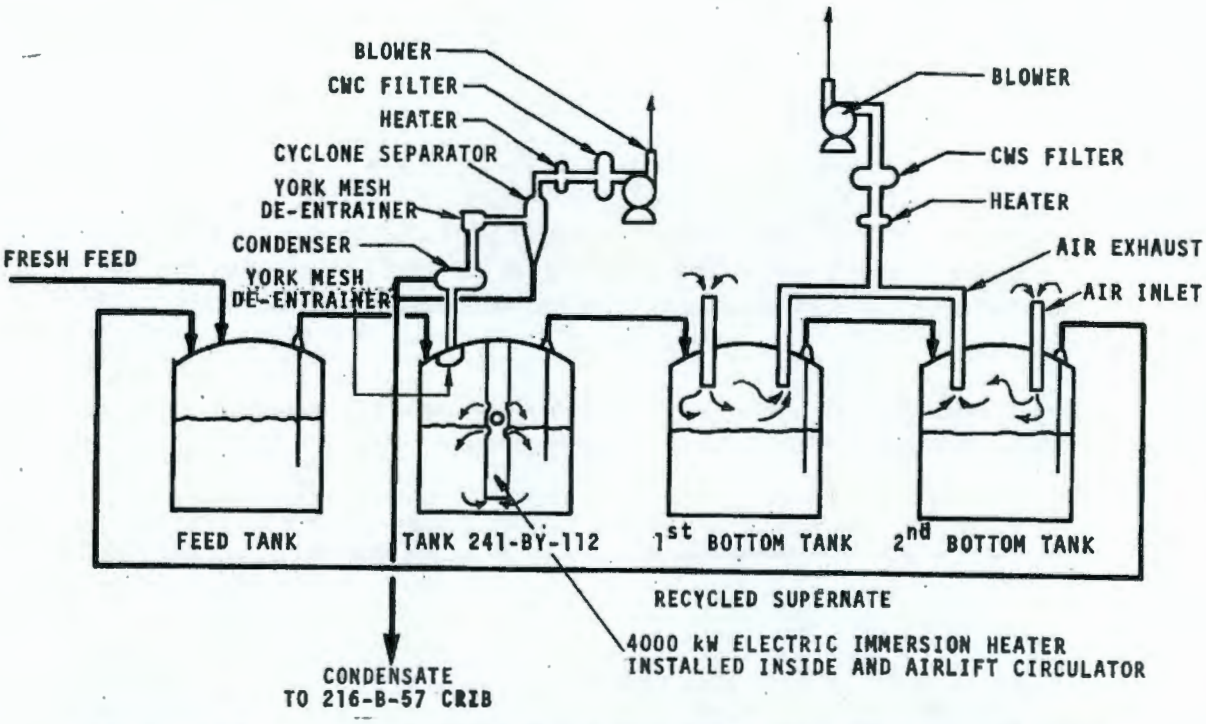


Figure 5-48. In-Tank Solidification Unit 2 (ITS-2) Simplified Flow Diagram

Additional tanks were identified to be incorporated into the ITS-2 waste recycle system (ARH-307 DEL, *200 Areas Operation Monthly Report, May 1968*). Tanks BY-110 and BY-107 were added in August 1968, tank BY-104 was introduced into bottoms service in June 1970 (ARH-1666 B, *Chemical Processing Division Waste Status Summary*), and tanks BY-105 and BY-106 entered bottoms service in August 1970 (ARH-1666 C, *Chemical Processing Division Waste Status Summary*). Tank BY-103, which had been the ITS-1 and ITS-2 feed tank, was introduced into bottom service in January 1971 (ARH-2074 A, *Chemical Processing Division*

Waste Status Summary) and tanks BX-111 and BX-110 were added during the Autumn 1971 (ARH-2074 D, *Chemical Processing Division Waste Status Summary*) and Winter 1972 (ARH-2456 A), respectively. This used all tanks in BY Farm for ITS-2 except tanks BY-101 and BY-102 which were concentrated via ITS-1.

The process specification for ITS-2 recognized large stresses could develop in the tank concrete walls and footings due to thermal gradients and imposed several temperature limits on operation of the ITS-2 (ARH-387):

- Maximum bulk temperature of the contents of any ITS-2 concentrate recycle tank shall be maintained below 230°F. The maximum bulk temperature in tank BY-112 shall be maintained below 250°F.
- Temperature changes at points below the liquid level shall be limited to a maximum of 5°F per day at temperature below 180°F or 3°F per day at temperatures above 180°F. A step change of 40°F may be made at temperatures below 180°F if no further temperature increases are made during the subsequent 8 day period.
- Temperature difference between the liquid and vapor phases shall not exceed 80°F.
- Vertical temperature gradient in the supernatant shall not exceed 20°F per ft.

ITS-2 Operation with ITS-1 as a Cooler

A process test was started August 26, 1971 to evaluate the use of ITS-1 equipment with the air heaters turned off to cool the supernatant by intimate contact of air with hot supernatant (ARH-2435, *Use of ITS-1 as an Evaporative Cooler*). The major advantages of using ITS-1 as an evaporative air cooler were found to be rapid and predictable salt precipitation. Cooling of the concentrated saturated solution precipitated solids which could be carried over by routine pumping to downstream tanks. Tank BY-102 contents temperature was normally maintained in the range of 135-150°F (ARH-2435). The ITS-1 cooler was operated as part of the bottoms cascade during its operation in combination with ITS-2. Available data shows that ITS-1 (tank BY-102) was operated as part of the following bottoms loops:

- BY-112 (ITS-2) → BY-110 → BY-107 → BY-104 → BY-102 (ITS-1) → BY-105 → BY-103 → BY-106 → BY-109 (Feed)
- BY-112 (ITS-2) → BY-110 → BY-107 → BY-104 → BY-102 (ITS-1) → BY-105 → BY-103 → BY-109 (Feed)
- BY-112 (ITS-2) → BY-107 → BY-104 → BY-102 (ITS-1) → BY-105 → BY-103 → BY-109 (Feed)

At the time that ITS-2 was being operated with ITS-1 as a cooler, the bottoms from ITS-2 would on occasion be diverted to other bottoms tanks not in the cascades shown above, namely a cascade to tank BX-111 followed by tank BX-110.

Waste evaporative units, including ITS-1 and ITS-2, in the 200 Areas were shut down on June 14, 1973 for an indeterminate period. The 242-S Evaporator-Crystallizer was placed in operation on "hot feed" on November 1, 1973, providing sustained condensate generation rates of 60 gpm. Because of this new waste evaporation capacity, layaway of the ITS-1 and ITS-2

units began in May 1974 (ARH-3067 RD, *Manufacturing and Waste Management Department-Monthly Report Summaries, January 1974 through December 1974*).

As mentioned previously, plugging of the ventilation system was a common problem requiring flushing of various components with water and chemicals to remove solids. These water and chemicals would typically end up in the ITS tanks (tanks BY-101, BY-102 or BY-112). Flushing of the ventilation system while ITS-1 was installed on tank BY-101 included solution of trisodium phosphate and dilute caustic. Flushes of the ventilation system during operation in tank BY-102 included using Turco 4518 (inhibited oxalic acid) and when that became ineffective 0.05-0.075 M sodium diethylenetriaminepentaacetate (DTPA). Later 0.25 M citric acid was also used to flush equipment. Oxalic acid can be corrosive to carbon steel at high enough concentrations. However, the addition of oxalic acid to the tank contents would neutralize the acid resulting in oxalate ion. Sodium DTPA forms a neutral pH solution. The citric acid would be converted to sodium citrate during the flushing or contact with the waste solution. All of these flush solutions would be present in very dilute quantities relative to the volume of the tank contents with which they combined.

5.5.6.3.2. In-Tank Solidification Waste Composition and Corrosion Data

Samples of saltcake and the mother liquor in tank BY-102 at the time of the electric immersion heater failure during June 1968 were analyzed for composition. The composition in g/gal and weight percent of dissolved salts is given in ARH-1381. The dissolved salts in the mother liquor are repeated in Table 5-35. The dissolved salts in the analyzed supernatant liquid from tank BY-102 would meet the waste chemistry limits established for DSTs provided the temperature was not above 212°F (OSD-T-151-00007, *Operating Specifications for the Double-Shell Storage Tanks*).

Table 5-35. In-Tank Solidification Unit 1 (ITS-1) Supernatant Liquor Composition Circa June 1968

Constituent	g/gal	Weight %	M
Mg^{+2}	<0.008	<0.0002	$<9x10^{-5}$
$Fe^{+2/+3}$	0.23	0.0055	0.0011
Na^{+}	1200	28.6	13.78
Ca^{+2}	<2	<0.05	<0.01
CO_3^{-2}	559	13.3	2.46
OH^{-}	352	8.4	5.47
NO_2^{-}	208	4.96	1.19
NO_3^{-}	1011	24.2	4.31
PO_4^{-3}	8	0.2	0.02
SO_4^{-2}	4.2	0.10	0.012
Cl^{-}	7.7	0.18	0.057
F^{-}	0.9	0.02	0.01
AlO_2	830	19.8	3.72
SiO_2	9.3	0.22	0.041

Data taken from ARH-1381, Table 4.

Samples of saltcake and the mother liquor in tank BY-112, after the time of the north quadrant electric immersion heater problems (June 1968), were analyzed for composition. The composition in g/gal and weight percent of dissolved salts is given in ARH-1381. The dissolved salts in the mother liquor are repeated in Table 5-36. The dissolved salts in the analyzed supernatant liquid from tank BY-102 would meet the waste chemistry limits established for DSTs (OSD-T-151-00007).

Table 5-36. In-Tank Solidification Unit 2 (ITS-2) Supernatant Liquor Composition Circa June 1968 (2 Pages)

Constituent	g/gal	Weight %	M
Mg^{+2}	<0.004	<0.0002	$<4X10^{-5}$
$Fe^{+2/+3}$	0.02	0.001	$9x10^{-5}$
Na^{+}	650	31.9	7.47
Ca^{+2}	<1	<0.05	<0.007
HCO_3^{-}	159	7.80	0.689
CO_3^{-2}	379	18.6	1.67
OH^{-}	168	8.24	2.61
NO_2^{-}	80	3.9	0.46
NO_3^{-}	530	26.0	2.26
PO_4^{-3}	8	0.4	0.02
SO_4^{-2}	1	0.05	0.003
Cl^{-}	7	0.3	0.05
F^{-}	1.5	0.074	0.021
AlO_2	54	2.6	0.24
SiO_2	0.38	0.019	0.0017

Data taken from ARH-1381, Table 6.

Samples of sludge, crust and supernatant liquid associated with the sludge and crust present in tank BY-112 during a period of pressurizations of the tank vapor space (January to March 1972) were analyzed for composition. The results are summarized in Table 5-37. The sludge was soluble in hot water and slightly soluble in hot dilute feed. The crust appeared to be much less water soluble than the sludge; none of the crust dissolved in dilute feed. Chemical analyses showed that the floating crust was markedly higher in carbonate and sulfate than the sludge. In comparing the sludge and crust to the supernatant liquid it can be seen that sodium, iron, silicon, nitrate, carbonate, sulfate, and phosphate are present at higher concentrations in the sludge and crust. Aluminum and nitrite are present at comparable or lower concentrations in the sludge and crust. The dissolved salts in the analyzed supernatant liquid meet the waste chemistry limits established for DSTs (OSD-T-151-00007).

Table 5-37. In-Tank Solidification Unit 2 (ITS-2) Supernatant Liquor, Sludge and Crust Composition Circa 1972

Constituent	Supernatant Liquor (M)	Sludge (M)	Crust (M)
Na	11.16	16.9	20.7
Fe	$<1.81x10^{-3}$	0.42	0.06
Al	2.05	1.71	0.58
Si	9.08x10-3	0.22	<0.03
NO_2	1.4	1.54	0.012
NO_3	2.1	6.17	4.33
CO_3	0.018	0.67	3.05
SO_4	0.05	0.12	0.46
PO_4	0.023	0.26	0.12
Total Acid Demand (TAD)*	7.20	8.11	9.84

* Total acid demand (TAD) includes all ions titratable by acid to the major pH break between pH 7 and 4. Ions that would be titrated by acid include OH^-, AlO_2^-, and CO_3^{-2}. Based solely on the listed Al and CO_3 concentrations given, the OH- concentration in the supernatant, sludge and crust would be 5.13 M, 5.73 M, and 6.21 M, respectively.

Data taken from Internal Memorandum, "Analysis of Tank 112-BY Sample", T.D. Anderson to J.S. Buckingham, April 4, 1972

In February-April 1969, stressed U-bend specimens of A515 Grade 60 steel specimens were subjected to simulated tank BY-112 waste solution at 170°F. The specimens had been pre-stressed at 30 percent above the ultimate yield strength. The test was terminated after eight weeks exposure, with no SCC occurring during the test (ARH-1102 DEL, *200 Areas Operation Monthly Report, March 1969* and ARH-1103 DEL, *200 Areas Operation Monthly Report, April 1969*). The composition of the simulated waste solution was not given. However, a simulant ITS bottoms supernatant liquid composition, based on a number of analyses of ITS bottoms tanks, was documented in 1972 as shown in Table 5-38.

Table 5-38. In-Tank Solidification Unit 2 (ITS-2) Bottoms Supernatant Liquid Simulant

Ionic Constituents	Weight %	Molarity, M
Na^+	--	9.95
Al	--	1.43
NO_2^-	--	1.00
NO_3^-	--	2.45
CO_3^{-2}	--	0.40
Total Acid Demand	--	7.72
Components	**Weight %**	**Molarity, M**
H_2O	55.0	--
$NaAlO_2$	8.3	1.43
$NaNO_2$	4.9	1.00
$NaNO_3$	14.7	2.45
Na_2CO_3	3.0	0.40
NaOH	12.1	4.27
Density	1.414 g/cc	

Data taken from Internal Memo, "Composition of Synthetic Recycle ITS Bottoms Supernatant", J.S. Buckingham to J.P. Knight, March 16, 1972.

5.5.6.4. 242-T Atmospheric Evaporator Waste (1965-1976)

After a ten year hiatus, the 242-T evaporator was returned to operation December 3, 1965 to reclaim storage space for non-boiling wastes (RL-SEP-913-DEL, *Chemical Processing Department Monthly Report for December, 1965*, p. 6). The description in Section 5.5.6.1 of the evaporator and its operation is similar to operation during this time period, except the evaporator was changed from batch operation to continuous operation with recycle. The evaporator concentrate is passed through two underground storage tanks in series where it cools and much of the salt crystallizes and settles to the bottom of the tanks. The salt-depleted supernatant liquid is then recycled and blended with fresh feed in a third underground waste tank which feeds waste to the concentrator. The initial boil off rate was nominally 10 gal per minute at a concentration factor of 4 to 1. The average boil off rate from 1965 through 1976 was 4.5 gal per minute during operation (ARH-CD-702-A, *Production and Waste Management Division Waste Status Summary January 1, 1976 through March 31, 1976*).

Initially, tank TX-116 received the bottoms from the 242-T evaporator and supernatant from tank TX-116 was transferred to tank TX-117. Then supernatant from tank TX-117 would be transferred back to feed tank TX-118. Tank TX-118 continued as the feed tank throughout the operation of the 242-T evaporator. As salt accumulated in the bottoms receiver tanks throughout TX Farm, additional TX Farm tanks would be used as bottoms receivers. By the end of 242-T operation, April 3, 1976, all tanks in TX Farm, except tank TX-101, were filled with evaporator bottoms from 242-T operations. In addition, tanks U-102, U-103, and U-105 were also used for 242-T evaporator bottoms and recycle. Tank TX-101 was used to receive the wastes from other tank farms that would then be transferred to tank TX-118 as feed to the 242-T evaporator.

The following operational description of waste types processed is based on waste status summary reports issued during the time of operation of the 242-T evaporator. From the restart of operation of the 242-T evaporator until December 1966, the evaporator concentrated TBP waste. Discussion of known information about concentration of TBP waste can be found in Section 5.5.6.1. From the beginning of 1967 to the end 1968 the 242-T evaporator received CW for concentration. Coating removal waste is described in Section 5.5.1.2. Beginning in 1969, supernatant liquid from evaporator bottoms and CW combined with OWW from PUREX were also concentrated at 242-T. In 1970 supernatant waste from REDOX and various B Plant wastes were also processed through the evaporator along with the other waste types previously concentrated. Waste processing at 242-T through the early 1970s included a significant amount of B Plant ion exchange waste and other B Plant waste.

In May 1973, discharge of high-risk Plutonium Finishing Plant (PFP or Z Plant) liquid waste to the soil column ended (ARH-CD-323, *Z Plant Liquid Waste Disposal through the 241-Z Vault*). The PFP high-salt and low-salt waste streams were combined in the 241-Z sump tanks and transferred to the 242-T Evaporator for neutralization and disposal within SSTs. In order to accommodate PFP waste, a waste receiver tank, tank R-1, located in the 242-TA vault was used to receive batchwise transfers of acidic waste from PFP's tank D-5 (ARH-CD-178). Waste in tank R-1 would then be pumped to a feed blend tank, tank B-1 located in the feed cell of the 242-T Evaporator building. A jet eductor in the evaporator feed line was used to draw the acid waste from tank B-1 into the evaporator feed stream where the acid was immediately neutralized. When the evaporator was not operating, its feed stream was recycled via a three-way valve to

tank TX-118 as necessary to dispose the generated waste from PFP. A schematic flow diagram showing the 242-T evaporator process around this time taken from ARH-CD-178 is shown in Figure 5-49.

Plutonium Finishing Plant waste is discussed in more detail in Section 5.5.8.1. As mentioned above the PFP waste was neutralized via mixing with existing SST waste from tank TX-118. Waste from the PFP was routinely concentrated at 242-T through the end of 242-T evaporator operation in 1976. After the end of evaporation operations PFP waste continued to be neutralized by mixing with existing waste from tank TX-118 using the B-1 tank in 242-T. This continued to occur until PFP waste was no longer sent to SSTs.

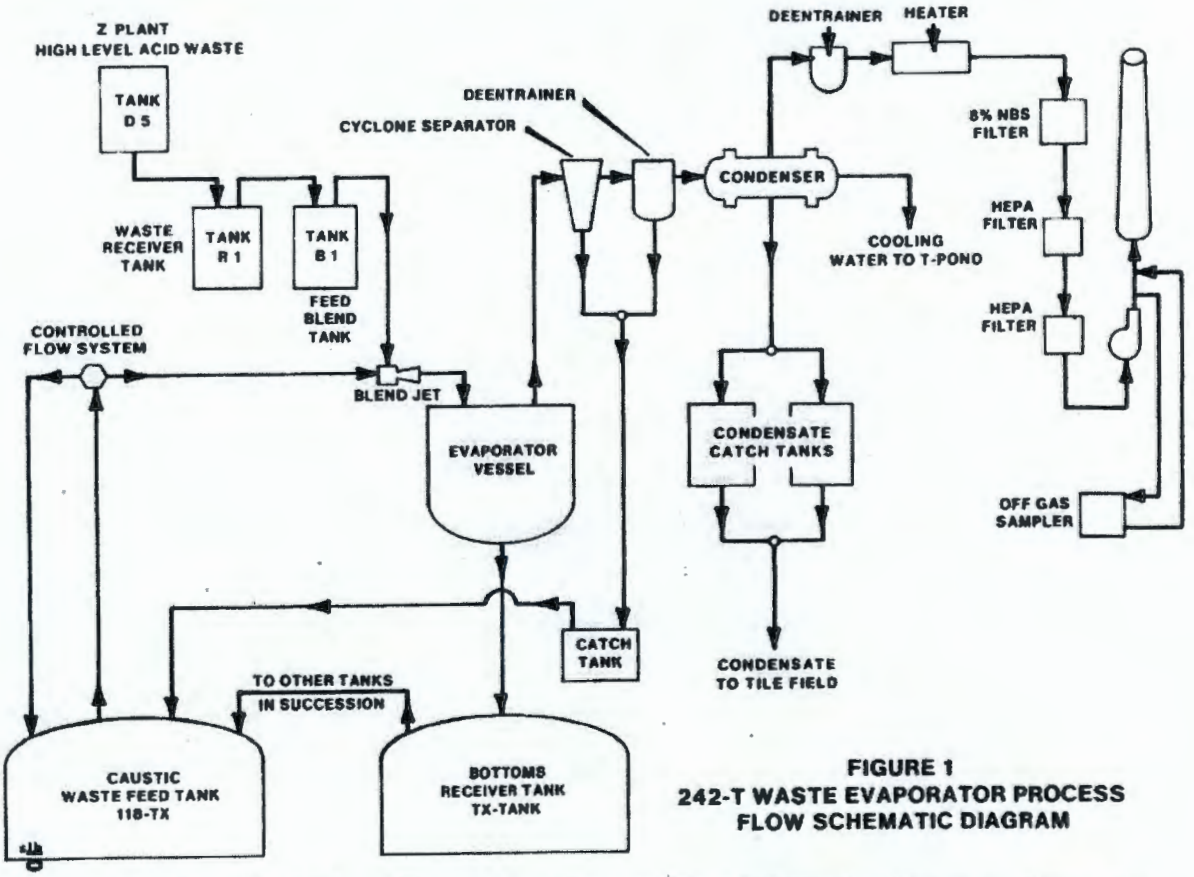


Figure 5-49. 242-T Waste Evaporator Process Flow Schematic Diagram, Circa 1974

Compositional information associated with processing of the various wastes would be dependent upon the specific types of waste and relative volumes of waste processed at a particular time. General compositional information (e.g., flowsheet composition) was not found for waste processed in the 242-T evaporator during this time period. Document ARH-CD-178 describes the feed material processed in the 242-T evaporator as alkaline solutions of sodium salts which contain radionuclides. The feed solutions' major components are water, sodium hydroxide, sodium nitrate, sodium nitrite, sodium aluminate, along with small quantities of sodium sulfate and sodium carbonate.

A large number of sample analyses are available for TX Farm tanks and the three tanks from U Farm associated with 242-T operations from 1965 to 1976. These sample analyses are primarily for the 242-T Evaporator feed tank, tank TX-118. These are provided in Table 5-39. The sample analyses for tanks TX-118 and TX-101 give an indication of the range of concentrations for major constituents being fed to the evaporator. In the table there are 70 analyses that contain nitrate and 55 that contain nitrate, nitrite, and hydroxide concentrations. Of those containing nitrate, nitrite, and hydroxide, 16 (29%) do not meet the DST waste chemistry limits for hydroxide, nitrite, or hydroxide and nitrite combined (OSD-T-151-00007). Of those containing nitrate but not nitrite and hydroxide, 9 (13%) exceed the maximum nitrate concentration (OSD-T-151-00007).

Table 5-39. 241-TX Tank Farm Sample Analyses During 242-T Atmospheric Evaporator Operation Between 1965 and 1976 (3 Pages)

Tank	Analysis Date[1]	Waste Type	pH	Concentration, M										
				Na	OH[2]	Al	NO_3[3]	NO_2[4]	PO_4	SO_4	CO_3	Cl	F	SpG
TX-101	10/24/75	Liquid[5]	10.90	3.58	1.33	0.026	1.60	0.26	0.015	--	0.296	<0.0075	0.0041	1.168
TX-101	10/25/76	Liquid	11.0	--	0.204	0.034	--	--	--	--	--	--	--	1.189
TX-102	9/24/65	--	--	9.91	1.65	1.35	4.39	--	--	--	1.04	0.031	0.0018	1.418
TX-102	3/30/76	Liquid	13.5	6.76	1.75	0.911	3.71	2.26	0.035	--	0.748	0.195	0.0012	1.456
TX-103	9/24/65	--	10.5	6.70	--	0.0007	5.71	--	--	--	0.142	0.006	--	1.329
TX-103	1/21/74	Slurry[5]	>11.9	9.31	2.18	--	--	--	0.086	--	--	--	--	--
TX-103	2/3/75	Slurry	--	--	2.86	--	--	--	--	--	--	--	--	1.5359
TX-103	3/30/76	Slurry	13.2	12.01	2.85	1.3	3.16	1.72	0.058	0.044	0.418	0.246	0.0016	1.4
TX-103	10/19/76	Slurry	13.8	9.8	2.6	1.39	3.1	2.32	<0.02	0.05	0.208	0.242	0.0012	1.43
TX-104	9/24/65	--	--	8.87	1.62	0.95	5.10	--	--	--	0.637	0.107	0.0010	1.382
TX-104	9/17/74	Liquid	13.1	6.58	0.82	0.352	2.79	0.192	0.009	0.025	0.088	--	0.075	1.2365
TX-104	9/17/76	Slurry	14.29	9.43	3.02	0.642	4.44	0.976	--	0.184	0.464	0.105	--	1.40
TX-105	1/21/74	Slurry	>11.8	13.82	2.96	--	--	--	0.139	--	--	--	--	--
TX-106	12/8/76	Liquid	13.5	9.19	4.99	1.61	0.285	1.13	<0.01	0.007	0.474	0.278	0.00009	1.437
TX-107	9/10/75	Liquid	--	--	0.23	--	2.84	0.555	0.041	--	0.319	--	--	--
TX-107	10/27/75	Liquid	14	7.69	1.67	0.561	3.92	0.655	0.027	--	0.184	--	0.0048	1.3804
TX-108	9/24/65	--	--	5.30	0.18	0.001	0.22	--	--	--	0.092	0.040	--	1.246
TX-108	1/21/75	Slurry	11.2	9.60	0.79	0.289	6.22/ 6.16[6]	0.374	0.062/ 0.939[6]	0.062	0.100	--	0.0052	1.403
TX-108	1/22/75	Slurry	--	--	0.84	--	--	--	--	--	--	--	--	1.4632
TX-108	3/16/76	Liquid	13	8.63	0.645	0.244	6.92	0.388	0.044	--	0.170	0.162	0.00008	1.358
TX-108	3/29/76	Liquid	13.3	0.334	0.367	0.249	5.62	0.31	0.062	0.24	0.311	0.43	0.00178	1.386
TX-109	9/24/65	--	9.0	2.52	--	0.344	1.82	--	--	--	0.270	0.004	0.026	1.138
TX-109	12/21/73	Slurry	8.6	5.54	--	--	--	--	0.256	--	--	--	--	--
TX-109	5/20/75	--	--	13.03	2.32	1.48	5.76	2.63	0.10	--	0.26	--	--	--
TX-109	8/27/75	Liquid	--	--	--	--	--	--	--	--	--	--	--	1.2395
TX-109	8/27/75	Liquid	--	--	--	--	--	--	--	--	--	--	--	1.2738
TX-109	9/3/75	Liquid	--	--	--	--	--	--	--	--	--	--	--	1.262
TX-109	9/10/75	Liquid	--	--	--	--	--	--	--	--	--	--	--	1.1263
TX-109	9/19/75	Liquid	--	--	--	--	--	--	--	--	--	--	--	1.3249
TX-109	9/19/75	Liquid	--	--	--	--	--	--	--	--	--	--	--	1.334
TX-109	10/2/75	Liquid	--	--	--	--	--	--	--	--	--	--	--	1.365
TX-109	10/20/75	Liquid	--	--	--	--	--	--	--	--	--	--	--	1.375
TX-109	10/27/75	Liquid	--	--	--	--	--	--	--	--	--	--	--	1.371
TX-109	11/6/75	Liquid	--	--	--	--	--	--	--	--	--	--	--	1.395
TX-109	11/26/75	Liquid	--	--	--	--	--	--	--	--	--	--	--	1.397
TX-109	12/3/75	Liquid	--	--	--	--	--	--	--	--	--	--	--	1.382
TX-109	12/3/75	Liquid	--	--	--	--	--	--	--	--	--	--	--	1.385
TX-109	12/3/75	Liquid	--	--	--	--	--	--	--	--	--	--	--	1.375
TX-109	12/17/75	Liquid	--	--	--	--	--	--	--	--	--	--	--	1.420
TX-109	1/12/76	Liquid	--	--	--	--	--	--	--	--	0.511	--	--	1.351
TX-109	1/14/76	Liquid	--	--	--	--	--	--	--	--	--	--	--	1.390
TX-109	1/21/76	Liquid	--	--	--	--	--	--	--	--	--	--	--	1.413
TX-109	2/2/76	Liquid	--	--	--	--	--	--	--	--	--	--	--	1.297
TX-109	2/13/76	Liquid	13.00	8.16	2.35	0.71	4.49	1.24	0.043	--	0.511	0.104	0.0050	1.398
TX-109	2/16/76	Liquid	--	--	--	--	--	--	--	--	--	--	--	1.444
TX-109	2/17/76	Liquid	--	--	--	--	--	--	--	--	--	--	--	1.390

Table 5-39. 241-TX Tank Farm Sample Analyses During 242-T Atmospheric Evaporator Operation Between 1965 and 1976 (3 Pages)

Tank	Analysis Date[1]	Waste Type	pH	Concentration, M										
				Na	OH[2]	Al	NO_3[3]	NO_2[4]	PO_4	SO_4	CO_3	Cl	F	SpG
TX-109	3/16/76	Liquid	--	--	--	--	--	--	--	--	--	--	--	1.432
TX-109	3/24/76	Liquid	12.90	8.86	1.08	0.67	4.64	1.34	0.045	0.12	0.541	0.111	0.0049	1.386
TX-109	9/17/76	Liquid	--	--	<0.019	0.34	3.76	0.414	--	--	0.323	--	--	1.376
TX-110	9/24/65	Slurry	10.3	6.61	--	0.0007	6.58	--	--	--	0.234	0.048	--	1.333
TX-110	3/31/75	Slurry	--	--	2.27	0.741	3.98	1.58	--	--	--	--	--	1.37
TX-111	9/24/65	Slurry	--	6.52	0.021	--	5.88	--	--	--	0.039	0.013	0.0105	1.032
TX-111	6/12/75	Slurry	14	11.52	2.11	1.30	5.10	2.55	0.115	--	0.250	--	0.0126	1.5559
TX-111	11/24/75	Liquid	--	--	--	--	--	--	--	--	--	--	--	1.328
TX-111	2/11/76	Liquid	--	--	1.03	--	2.32	1.39	0.044	--	0.323	--	--	--
TX-112	1/21/74	Slurry	>11.9	11.95	2.80	--	--	--	0.083	--	--	--	--	--
TX-113	1/18/74	Slurry	>11.1	9.69	2.0	--	--	--	0.074	--	--	--	--	--
TX-114	1/21/74	Liquid	11.45	5.57	1.57	--	--	--	0.019	--	--	--	--	--
TX-115	1/17/74	Slurry	>11.6	10.44	3.60	--	--	--	0.038	--	--	--	--	--
TX-117	7/20/71	--	13.2	11.6	1.00	--	6.67	0.72	--	--	--	--	--	--
TX-118[2]	9/24/65	Slurry	--	1.0	0.64	0.0012	0.27	--	--	--	0.036	0.011	--	1.041
TX-118[2]	9/24/65	Slurry	--	6.30	--	0.056	2.32	--	--	--	--	0.098	0.0234	1.266
TX-118	8/3/72	--	--	--	--	--	--	--	--	--	--	--	--	1.3975
TX-118	8/8/72	Slurry	--	--	--	--	--	--	--	--	--	--	--	1.4528
TX-118	8/10/72	Slurry	--	--	--	--	--	--	--	--	--	--	--	1.401
TX-118	11/20/72	Slurry	--	--	--	--	--	--	--	--	--	--	--	1.4415
TX-118	11/30/72	Slurry	--	--	--	--	--	--	--	--	--	--	--	1.425
TX-118	12/20/72	Slurry	--	--	--	--	--	--	--	--	--	--	--	1.4025
TX-118	1/15/73	Slurry	--	--	--	--	--	--	--	--	--	--	--	1.432
TX-118	1/18/73	Slurry	--	--	--	--	--	--	--	--	--	--	--	1.355
TX-118	2/1/73	Slurry	--	--	--	--	--	--	--	--	--	--	--	1.359
TX-118	2/21/73	Slurry	--	--	--	--	--	--	--	--	--	--	--	1.374
TX-118	3/5/73	Slurry	--	--	--	--	--	--	--	--	--	--	--	1.441
TX-118	3/20/73	Liquid	--	--	--	--	--	--	--	--	--	--	--	1.3777
TX-118	4/6/73	Slurry	--	--	--	--	--	--	--	--	--	--	--	1.3025
TX-118	4/19/73	Slurry	--	--	--	--	--	--	--	--	--	--	--	1.4038
TX-118	4/24/73	--	--	--	--	--	--	--	--	--	--	--	--	1.4035
TX-118	5/23/73	Slurry	--	--	--	--	--	--	--	--	--	--	--	1.373
TX-118	7/24/73	Slurry	--	--	--	--	--	--	--	--	--	--	--	1.4285
TX-118	1/21/74	Slurry	>12.4	20.06	2.34	--	--	--	0.0504	--	--	--	--	--
TX-118	2/11/74	Slurry	--	--	2.43	--	--	--	--	--	--	--	--	1.4710
TX-118	2/13/74	Slurry	--	--	2.35	--	--	--	--	--	--	--	--	1.4802
TX-118	2/26/74	Slurry	--	--	2.29	--	--	--	--	--	--	--	--	1.4907
TX-118	2/27/74	Slurry	--	--	2.15	--	--	--	--	--	--	--	--	1.4764
TX-118	3/25/74	Liquid	--	--	1.99	--	--	--	--	--	--	--	--	1.4300
TX-118	3/25/74	Liquid	10.8	--	1.83	--	--	--	--	--	--	--	--	1.4050
TX-118	3/29/74	Liquid	--	--	1.38	--	--	--	--	--	--	--	--	1.300
TX-118	4/12/74	Slurry	--	--	0.243	--	--	--	--	--	--	--	--	1.4381
TX-118	5/6/74	Slurry	--	--	2.07	--	--	--	--	--	--	--	--	1.3899
TX-118	5/6/74	Liquid	--	--	1.72	--	--	--	--	--	--	--	--	1.3283
TX-118	5/14/74	Slurry	--	--	3.45	--	--	--	--	--	--	--	--	1.4238
TX-118	5/23/74	Slurry	--	--	2.34	--	--	--	--	--	--	--	--	1.5320
TX-118	5/24/74	Slurry	--	--	1.72	--	--	--	--	--	--	--	--	1.4524
TX-118	6/10/74	Slurry	--	--	1.81	--	--	--	--	--	--	--	--	1.3812
TX-118	6/25/74	Liquid	--	--	1.34	--	--	--	--	--	0.0475	--	--	1.3995
TX-118	6/28/74	Liquid	--	--	2.98	--	--	--	--	--	--	--	--	1.3895
TX-118	8/2/74	Liquid	--	--	1.87	--	--	--	--	--	0.0127	--	--	1.427
TX-118	8/16/74	Liquid	--	--	2.86	--	--	--	--	--	--	--	--	1.4190
TX-118	10/14/74	Liquid	--	--	0.874	--	--	--	--	--	--	--	--	1.2859
TX-118	10/14/74	Liquid	--	--	1.58	--	--	--	--	--	--	--	--	1.4270
TX-118	10/14/74	Liquid	--	--	1.46	--	--	--	--	--	--	--	--	1.4864
TX-118	10/21/74	Slurry	--	--	1.97	--	--	--	--	--	--	--	--	1.5886
TX-118	10/21/74	Slurry	--	--	1.82	--	--	--	--	--	--	--	--	1.5554
TX-118	10/28/74	Liquid	--	--	1.32	--	--	--	--	--	--	--	--	1.420
TX-118	11/5/74	Liquid	--	--	1.37	--	--	--	--	--	--	--	--	1.426
TX-118	11/20/74	Liquid	--	--	1.27	--	--	--	--	--	--	--	--	1.4639
TX-118	11/25/74	Slurry	--	--	1.305	--	--	--	--	--	--	--	--	1.4404
TX-118	11/25/74	Liquid	--	--	0.759	--	--	--	--	--	--	--	--	1.3398
TX-118	12/6/74	Slurry	--	--	1.88	--	--	--	--	--	--	--	--	1.616

Table 5-39. 241-TX Tank Farm Sample Analyses During 242-T Atmospheric Evaporator Operation Between 1965 and 1976 (3 Pages)

Tank	Analysis Date[1]	Waste Type	pH	Concentration, M										
				Na	OH[2]	Al	NO_3[3]	NO_2[4]	PO_4	SO_4	CO_3	Cl	F	SpG
TX-118	12/17/74	Slurry	--	--	1.90	--	--	--	--	--	--	--	--	1.5234
TX-118	12/1874	Slurry	--	--	2.14	--	--	--	--	--	--	--	--	1.5732
TX-118	12/31/74	Slurry	--	--	2.08	--	--	--	--	--	--	--	--	1.618
TX-118	1/20/75	Slurry	--	--	2.28	--	--	--	--	--	--	--	--	--
TX-118	2/25/75	Slurry	14.0	10.64	1.74	1.19	4.27	2.35	0.0939	--	0.318	--	0.0079	1.5346
TX-118	2/25/75	Liquid	--	6.73	0.885	4.64	3.99	1.175	0.0508	--	0.277	--	--	1.346
TX-118	2/25/75	Liquid	--	8.34	1.43	0.983	4.21	1.89	0.0401	--	0.213	--	--	1.397
TX-118	3/31/75	Slurry	--	--	2.21	--	3.98	1.58	--	--	--	--	--	1.37
TX-118	4/23/75	Liquid	--	--	1.90	1.30	4.09	2.03	--	--	--	--	--	1.4637
TX-118	4/23/75	--	--	--	1.08	--	--	--	--	--	--	--	--	1.24
TX-118	5/2/75	--	--	--	2.03	1.08	4.62	2.03	--	--	--	--	--	--
TX-118	6/20/75	Slurry	--	--	0.696	0.440	2.31	1.09	0.0419	--	0.289	--	--	1.20
TX-118	7/10/75	--	--	--	1.98	0.292	3.67	0.506	0.0343	--	0.173	--	--	1.20
TX-118	8/20/75	Liquid	--	--	0.573	0.377	2.52	0.621	0.0476	--	0.191	--	--	1.2257
TX-118	8/22/75	--	--	--	0.735	0.363	2.42	0.746	0.0539	--	0.248	--	--	1.22
TX-118	8/22/75	--	--	--	0.932	0.543	2.56	0.936	0.0695	--	0.222	--	--	--
TX-118	8/22/75	--	--	--	**0.668**	0.180	3.55	**0.342**	0.0289	--	0.251	--	--	1.18
TX-118	8/22/75	--	--	--	**0.620**	0.136	3.37	**0.331**	0.0329	--	0.201	--	--	1.08
TX-118	8/22/75	--	--	--	**0.262**	0.147	2.44	**0.407**	0.0337	--	0.186	--	--	1.16
TX-118	9/3/75	Liquid	--	--	0.384	0.0796	1.60	0.277	0.0382	--	0.192	--	--	1.160
TX-118	9/3/75	Liquid	--	--	**<0.0095**	0.0345	1.30	**0.146**	0.0121	--	0.188	--	--	1.1225
TX-118	9/19/75	Liquid	--	--	**0.286**	0.0456	1.68	**0.196**	0.0160	--	0.238	--	--	1.1653
TX-118	9/24/75	Liquid	--	--	**0.005**	0.00783	2.65	**0.327**	0.0241	--	0.364	--	--	1.2367
TX-118	9/24/75	Liquid	--	--	**<0.005**	0.0232	1.53	**0.194**	0.0131	--	0.245	--	--	1.1586
TX-118	10/27/75	--	--	--	**0.409**	0.41	4.16	**0.031**	0.0285	--	0.17	--	--	1.175
TX-118	11/12/75	--	--	--	0.829	--	0.661	0.084	0.0062	--	0.114	--	--	--
TX-118	11/12/75	Liquid	--	--	**<0.005**	--	1.25	**0.134**	0.0107	--	0.240	--	--	--
TX-118	12/3/75	Liquid	--	--	0.619	0.477	2.88	0.741	0.0414	--	0.332	--	--	1.25
TX-118	12/11/75	Liquid	--	--	0.517	0.436	2.94	0.834	0.0387	--	0.376	--	--	1.272
TX-118	1/2/76	Liquid	--	--	0.371	0.281	2.25	0.686	0.0304	--	0.270	--	--	1.195
TX-118	1/5/76	Liquid	--	--	0.501	0.426	3.31	0.988	0.0378	--	0.358	--	--	1.255
TX-118	1/19/76	Liquid	--	--	1.0	0.638	4.36	0.999	0.0329	--	0.380	--	--	1.339
TX-118	2/2/76	Liquid	--	--	0.583	0.531	3.50	1.02	0.0417	--	--	--	--	1.308
TX-118	2/6/76	Liquid	--	--	0.761	0.466	3.09	0.740	0.0263	--	0.367	--	--	1.277
TX-118	2/11/76	Liquid	--	--	1.23	0.348	2.76	0.452	0.0143	--	0.373	--	--	1.178
TX-118	3/1/76	Liquid	--	--	0.828	0.461	3.11	0.916	0.0070	--	0.398	--	--	1.296
TX-118	3/16/76	Liquid	--	--	0.613	0.398	2.80	0.571	0.0025	--	0.381	--	--	1.289
TX-118	3/16/76	Liquid	--	--	0.89	--	3.48	0.87	0.0034	--	0.423	--	--	1.373
U-102	4/12/76	--	--	--	--	0.02	3.48	0.3	--	--	0.17	--	--	1.27
U-102	4/12/76	Slurry	--	5.4	--	4.2	3.9	--	0.1	--	--	--	--	1.60
U-102	4/12/76	Slurry	--	9.2	--	7.4	**8.9**	--	0.2	--	--	--	--	1.38
U-103	1/30/74	Liquid	11.25	6.94	1.48	0.432	4.58	--	4.79E-4	0.0206	0.148	--	9.42E-4	1.3220
U-103	9/20/76	--	--	--	2.23	0.378	2.95	0.610	--	0.038	0.35	--	--	1.305
U-103	9/20/76	Slurry	--	<0.6	--	5.7	0.6	--	0.03	<0.7	--	--	--	1.2278
U-105	4/16/76	Slurry	--	9.4	--	1.0	3.3	--	0.4	--	--	--	--	1.52

All data for TX Farm taken from WHC-SD-WM-ER-321, Rev 0, *Supporting Document for the Northwest Quadrant Historical Tank Content Estimate Report for TX-Tank Farm, Volume I & II.*

All data for U Farm taken from WHC-SD-WM-ER-325, Rev 0, *Supporting Document for the Southwest Quadrant Historical Tank Content Estimate Report for U-Tank Farm.*

1 Analysis date is date that analyses were performed at the laboratory and is not the sample date when the sample was collected from the tank. Sample date was not given in every instance of analyses.

2 Hydroxide concentrations shown in bold and shaded are less than the OSD-T-151-00007 double-shell tank waste chemistry lower limit for hydroxide concentration or in combination with nitrate concentrations are less than the lower limit for combined hydroxide and nitrite concentration relative to nitrate concentration.

3 Nitrate concentrations shown in bold and shaded exceed the OSD-T-151-00007 double-shell tank waste chemistry upper limit for nitrate concentration of 5.5 M.

4 Nitrite concentration shown in bold and shaded in combination with the hydroxide concentrations are less than the OSD-T-151-00007 double-shell tank waste chemistry lower limit for combined hydroxide and nitrite concentration relative to nitrate concentration.

5 Samples described as liquid contain less than 5% solids via visual observation while samples described as slurry contain 5% or greater solids via visual observation.

6 Samples taken at the same time but at different levels in the tank. Levels that samples taken at are not identified.

Decontamination and flushing of process cells, vessels, and piping was performed periodically with dilute solutions of citric acid, tartaric acid, caustic citrate, and caustic tartrate (ARH-CD-178). These decontamination and flushing solutions would be neutralized, if appropriate, and routed to TX Farm.

5.5.6.5. REDOX Concentrators (1967-1972)

The REDOX concentrators, D-12 and D-14, were used for volume reduction of dilute waste between 1967 and 1972. This included Battelle Northwest low-level wastes (see Section 5.5.9), N-Reactor decontamination flushes (ISO-713, *Chemical Processing Division Monthly Report for July, 1967*, HAN-98529-DEL, *Monthly Status and Progress Report*, ISO-714-DEL, *Chemical Processing Division Monthly Report for August, 1967*) (see Section 5.5.9), and 200 West Area decontamination wastes (ARH-721) (see Section 5.5.8.2). The D-12 and D-14 concentrators received wastes starting July 28, 1967 (ISO-714-DEL) and October 27, 1967 (HAN-98918-DEL, *Monthly Status and Progress Report – October 1967*, p AIII-3). Concentration of waste continued at REDOX until June 30, 1972 (ARH-2456 D).

The feed tank to the REDOX concentrators at the start of operations was tank T-105 and the waste was initially discharged to tank SX-105 until sometime between October and December 1968 (ARH-871, *Chemical Processing Division Waste Status Summary, July 1, 1968 through September 30, 1968*). The waste initially fed to the REDOX concentrators was a combination of 1C waste and Hanford Laboratory Operation (HLO) waste. Subsequently, decontamination waste, Battelle-Northwest laboratory (BNW) waste, and 100 N Area (N) waste were directed from other SSTs (e.g., T-108, T-112) to the REDOX concentrators, or in the cases of BNW and N waste it was more typical to send the waste directly to the REDOX concentrators. After tank SX-105 became filled with the evaporator bottoms from the REDOX concentrators, tank S-107 became the bottoms receiver and continued to receive bottoms until the end of operation of the REDOX concentrators for waste evaporation. Some of the evaporator bottoms in tank SX-105 were subsequently transferred to tanks U-107 (ARH-1200 A) and U-108 (ARH-1200 B). As tank S-107 became full, some of the evaporator bottoms waste in that tank was sent to tank U-107 (October-December 1969) and subsequently tank U-107 waste was transferred into tank U-109 (ARH-1200 D).

No sample analyses could be found for tanks SX-105, S-107, U-107, U-108 or U-109 for the time frame between 1967 and 1972. Sample analyses results were found circa 1974 but by then each of these tanks had either pumped some of the existing waste out or received additional waste streams.

It is worth noting that none of these five tanks receiving bottoms from the REDOX concentrators have probable liner failures.

5.5.6.6. B Plant Cell 23 Concentrator (1967-1968)

The B Plant Cell 23 concentrator, E-23-3, was used for concentration of intermediate SST waste between October 30 or 31, 1967 (ISO-651-RD, *Fission Products Process Engineering Monthly*

Report 01/1967 thru 12/1967, p. 300 and ARH-60-DEL, *Monthly Report – 200 Areas Operation, October, 1967*, p. D-1) and February 2, 1968 (ARH-534, *Chemical Processing Division Waste Status Summary, January 1, 1968 through March 31, 1968*). The waste feed to the Cell 23 concentrator was accumulated FP waste that had been sent to tanks B-110, B-111 and B-112 starting in the second half of calendar year 1963 (HW-80379, *Chemical Processing Department – Waste Status Summary*, ARH-326, *Chemical Processing Division Waste Status Summary, October 1, 1967 through December 31, 1967*), and a mixture of TBP waste and primarily CW (~90%) stored in tank BX-102. The waste from tank BX-102 was concentrated for space recovery (HAN-99604, p AIII-4) and returned to tanks BX-101 and BX-104 (ARH-534, p 6).

No sample analyses could be found for B-110, B-111, or B-112 for the time frame between 1967 and 1968. Compositions of CW and TBP waste are described elsewhere in this report.

It is worth noting that none of these six tanks that either sent waste to or received bottoms from the B Plant Cell 23 concentrator have probable liner failures.

5.5.6.7. 242-S Vacuum Evaporator-Crystallizer Waste (1973-1980)

The 242-S vacuum evaporator-crystallizer was built to reduce the mobility of aqueous waste solutions which do not self-boil (ARH-MA-119, *242-S Evaporator-Crystallizer Information Manual*). The 242-S vacuum evaporator-crystallizer was built adjacent to S Farm. The dedicated single-shell feed tank to 242-S was tank S-102 until around February 1977 after which DST SY-102 was also used as a feed tank. Dilute waste would be sent to tank S-102 from various tanks holding the waste. The 242-S evaporator began hot operation on November 1, 1973 (ARH-2794-D) and continued to send evaporator bottoms to SSTs until 1980 when waste transfers into SSTs ended. The 242-S evaporator continued to operate after this time with DST SY-102 as the feed tank and concentrated wastes sent to DSTs.

The following description is excerpted from ARH-2907, *Operational Safety Analysis Report-242-S Evaporator-Crystallizer and Tank Farm Facilities*, and ARH-MA-119. The 242-S vacuum evaporator-crystallizer employs a forced-circulation, vacuum-evaporation system to concentrate radioactive salt waste solutions. The main process components of the system are the reboiler, vapor-liquid separator, recirculation pump and pipe loop, slurry product pump, primary condenser, jet-vacuum system, condensate collection tank, and ion exchange column. An isometric schematic of the 242-S vacuum evaporator-crystallizer process is provided in Figure 5-50 (ARH-2907). Feed for the evaporator is pumped from tank S-102 into the recirculation line on the upstream side of the reboiler. As the feed enters the recirculation line, it becomes blended with the main process slurry stream which flows to the reboiler. In the reboiler, the main process slurry stream is heated to a specified operating temperature, typically 130°F to 170°F. The heated slurry stream is discharged from the reboiler to the vapor-liquid separator vessel, which is maintained at approximately 0.8 pounds-force per square inch absolute (psia). Under this reduced pressure, a fraction of the water in the salt slurry concentrate flashes to steam and is drawn through two wire-mesh deentrainer pads and into the primary condenser. Process condensate formed in the primary condenser drains to a collection tank, from which it is pumped through the ion exchange column for removal of trace quantities of Cs-137. The process condensate is discharged to an underground crib. Vacuum in the vapor-liquid separator is

maintained via the primary condenser and process vapor line by a two-stage jet educator system. Motive steam from the primary jet and the secondary jet is discharged, respectively, to an intercondenser and an aftercondenser. Both vacuum-system condensers drain to the process condensate collection tank. As evaporation takes place in the vapor-liquid separator, further supersaturation occurs in the salt liquor slurry, which creates new salt crystal nuclei and promotes growth of existing crystals in the slurry liquor. The process slurry flows from the vapor-liquid separator to the recirculation pump suction via the separator vessel drop-out leg and the lower recirculation line. The recirculation pump discharges slurry back to the reboiler via the upper recirculation line, thus completing the process circuit. Production of crystal solids in the slurry liquor continues as further evaporation and crystallization takes place. The solids content of the slurry is controlled at about 30 volume percent by withdrawing a portion of the slurry stream from the upper recirculation line and pumping the slurry to underground storage tanks.

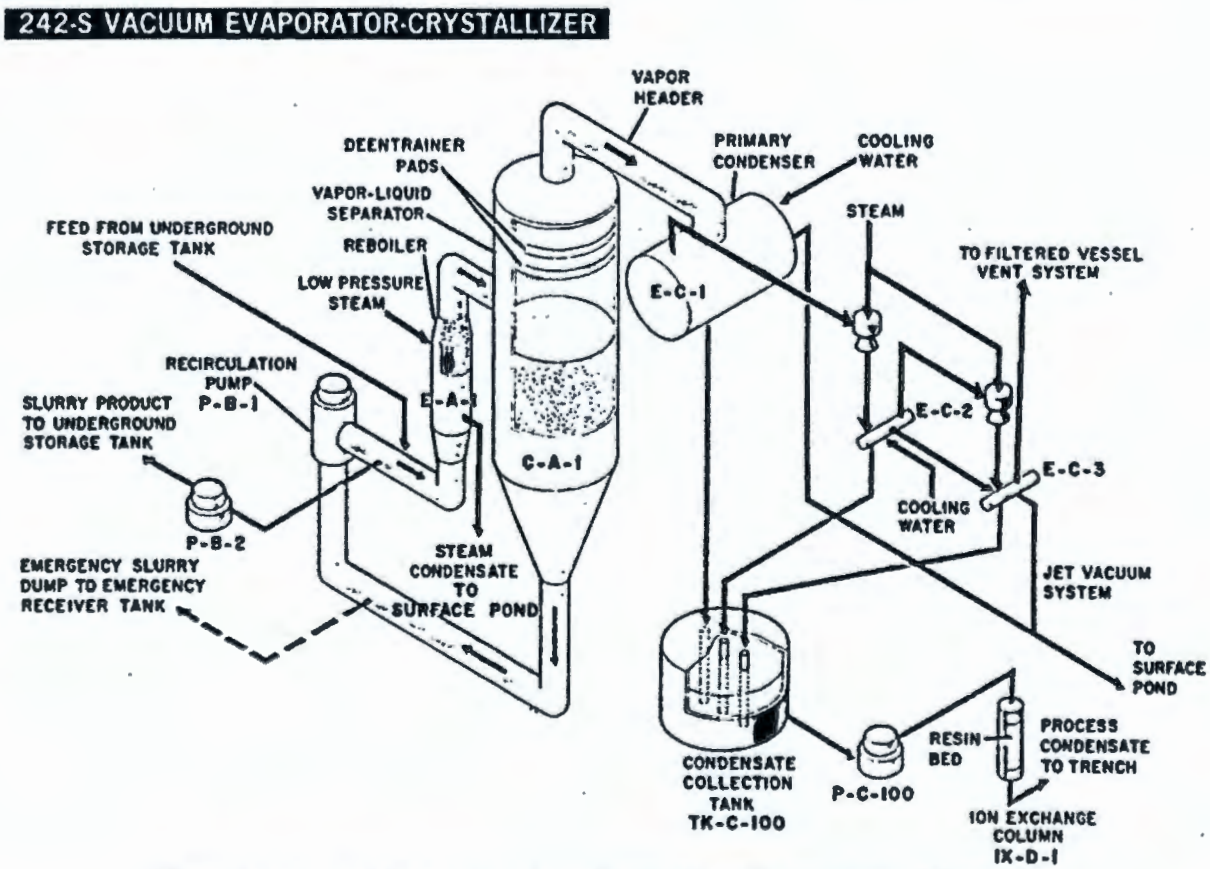


Figure 5-50. 242-S Evaporator Isometric Flow Diagram, Circa 1973

The feed to the evaporator from tank S-102 is a blend of unprocessed waste (i.e., not processed through 242-S) and recycled supernatant which has been decanted from the bottoms settling tanks in the S, SX, and later, U Farms. Unprocessed waste comes from a number of sources including stored non-boiling waste, new waste receipts, laboratory wastes, and residual liquor concentrates from other (i.e., not 241-S or 241-SX Farm) tank farms.

A decontamination tank was used to decontaminate and flush equipment for process efficiency improvement and maintenance activities. Dilute solutions of citric acid, tartaric acid, caustic citrate, and caustic tartrate are routinely used as the decontamination agents. The chemical solutions were neutralized or otherwise treated, as appropriate, and directed to SSTs followed by flush water. Sodium nitrate solution was used to regenerate the ion-exchange media. Anti-foaming agent was added on an as-needed basis from an anti-foam tank. No information was found on the specific antifoaming agent used in the evaporator system.

The processing of dilute radioactive waste solutions and the recycled supernatant liquid remaining after solids settle from the evaporator bottoms product in the 242-S evaporator would produce a solids primarily consisting of sodium nitrate, nitrite, and carbonate solids (ARH-F-104, *Partial Neutralization Flowsheet for Hanford Waste Liquors*). Subsequent to solids formation, saltwell pumping would be performed to remove interstitial liquid from the solids. Sodium aluminate solids have a characteristic extremely fine particle size and hold large amounts of interstitial liquid by capillary forces. Therefore, the precipitation of aluminate solids was avoided when possible. A method was developed to allow maximum volume reduction with conventional evaporation while avoiding formation of sodium aluminate solids. The method, referred to as partial neutralization or sometimes neutralization in transfer (WHC-SD-WM-TI-614, Rev 1, *Waste Status and Transaction Record Summary for the Southwest Quadrant of the Hanford 200 Area*, p. A-13), injects a mixture of nitric acid and potassium permanganate into the basic waste stream converting a portion of the sodium hydroxide to sodium nitrate. This partial neutralization results in a lower caustic concentration which increases the solubility of sodium aluminate and allows a larger quantity of water to be evaporated without precipitating aluminate solids. Potassium permanganate was added to suppress NO_x generation in the vapor phase.

The following description of partial neutralization is from ARH-F-104 and ARH-CD-783, *242-S Partial Neutralization Prototype*. Concentrated acid is pumped from a storage tank outside the 242-S building to an acid valve enclosure within 242-S. In the acid valve enclosure the acid is mixed with dilute potassium permanganate solution. The dilute acid and potassium permanganate solution is injected into the evaporator-crystallizer's 28-in. recirculation loop via a specially designed nozzle. A simplified process flow diagram (ARH-F-104) showing the partial neutralization flows in comparison to normal operation of the 242-S evaporative system is shown in Figure 5-51. The equipment and instrumentation installed to perform partial neutralization in the 242-S evaporator-crystallizer consists of:

- A 47,000 gal acid storage tank and instrument enclosure including two inline pumps, storage sump and sump pump
- Acid-resistant piping including jumpers in the pump room connecting to the recirculation loop
- Acid dilution system including acid valve enclosure located in the condenser room
- pH monitoring system
- NO_x monitoring system
- Corrosion monitoring systems.

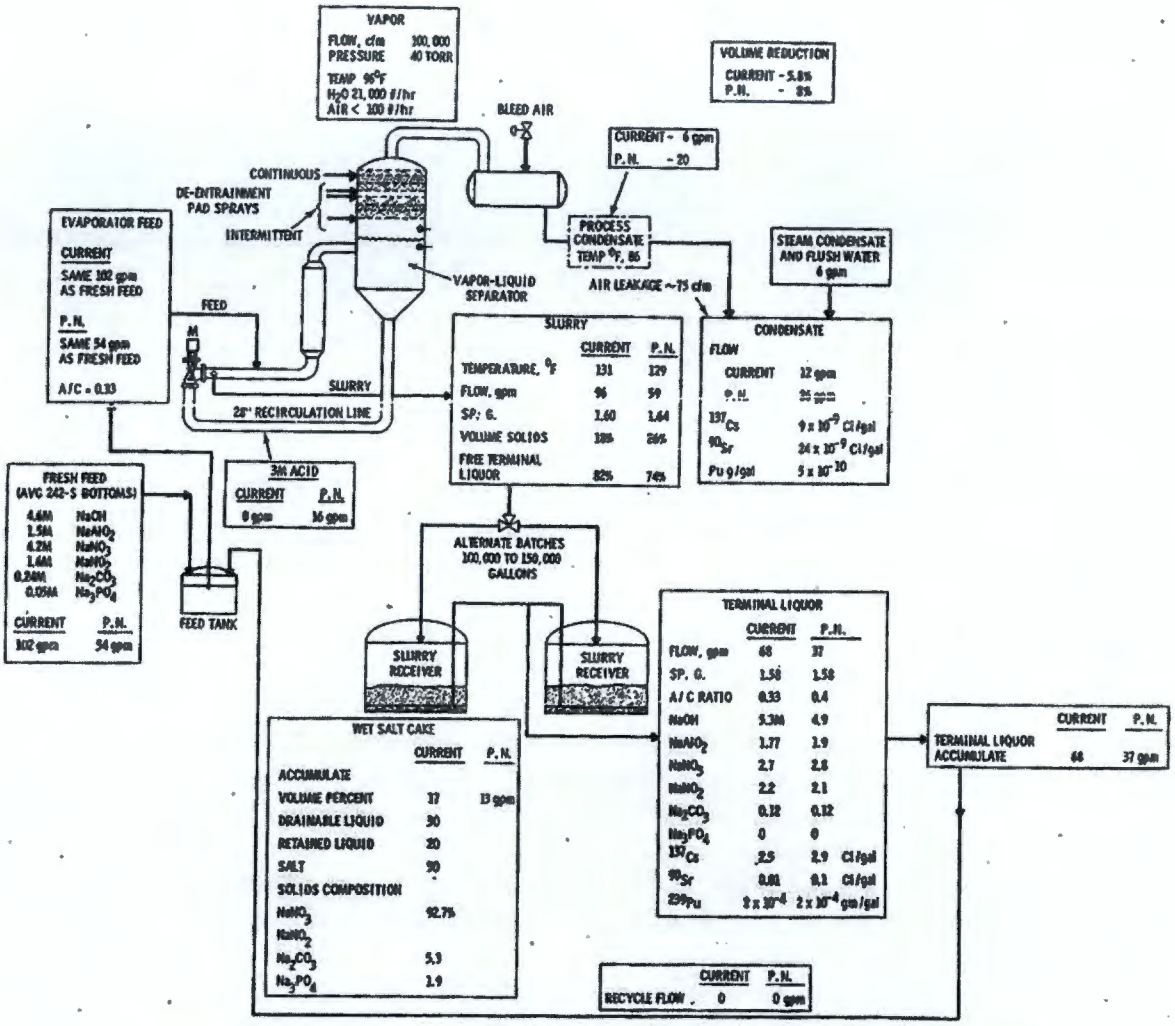


Figure 5-51. 242-S Evaporator Partial Neutralization Flow Diagram

A process test of the partial neutralization process was run during June 1975 at the 242-S vacuum evaporator. The first two production runs were performed November-December 1977 and January-February 1978 (Letter 60411-78-0534, *Partial Neutralization Prototype Facility Startup – Preliminary Report*). A third partial neutralization run was performed between July 30 and October 19, 1980 (RHO-CD-1515, *242-S Evaporator Crystallizer Third Partial Neutralization Campaign*). That is the last known partial neutralization runs occurring with bottoms discharged to SSTs. Waste transfers into SSTs were stopped at the end of 1980.

Feed materials processed in the 242-S evaporator-crystallizer are highly alkaline solutions of sodium salts which contain radionuclides (ARH-2907). Chemically the feed solutions are primarily composed of sodium hydroxide, sodium nitrate, sodium nitrite, sodium aluminate, sodium sulfate, and sodium carbonate. The approximate composition ranges of the evaporator feed stocks are shown below.

NaOH	2.5 - 12.5 M
$NaNO_3$	1.4 - 4.2 M
$NaNO_2$	0.3 - 1.4 M
$NaAlO_2$	0.3 - 1.2 M
Na_2SO_4	0.0 - 0.3 M
Na_2CO_3	0.0 - 0.5 M

Because the evaporator feed is a mixture of liquid wastes from several sources, the chemical composition of the feed stream fluctuates within the concentration range stated. Trace quantities of iron and chromium salts are occasionally encountered in low concentration in certain waste liquids. Process specifications and standards dictate that prospective feed stocks be chemically analyzed and tested prior to transfer to tank S-102.

Evaporator bottoms were discharged from the evaporator at boiling conditions and sent to the receiving SSTs. Earlier it was shown for the vacuum condition that the boiling point was typically 130°F to 170°F. Time then, at elevated temperatures, would have been relatively short in comparison to the overall tank operational period. The SSTs receiving evaporator bottoms from 242-S during this time period are presented in Table 5-40. Evaporator bottoms were first sent to tanks in S Farm (ARH-CD-133 B). During the second half of calendar year 1974 evaporator bottoms were then sent to SX Farm (ARH-CD-133 C, *Production and Waste Management Division Waste Status Summary, July 1, 1974 through September 30, 1974*). Tanks in U Farm received evaporator bottoms starting in the last quarter of calendar year 1975 (ARH-CD-336 D, *Production and Waste Management Division Waste Status Summary October 1, 1975 through December 31, 1975*). It is difficult to determine which tanks received bottoms from the 242-S evaporator after the first quarter of 1976 because of a change in the level of information reported in periodic tank waste status summary reports. Transfer records (WHC-SD-WM-TI-614, Rev 1) show that a number of tanks also contained a waste type designated as either PNF for partial neutralization feed or NIT for neutralization in transfer. These wastes identified as such were typically sent from tanks to either tank S-102 or later DST SY-102 which subsequently acted as the feed tank to 242-S.

Table 5-40. Single-Shell Tanks Receiving Evaporator Bottoms from 242-S Evaporator-Crystallizer Between 1973 and 1980

S-101	S-109	SX-102	U-106
S-103	S-110	SX-103	U-107
S-105	S-111	SX-104	U-108
S-106	S-112	SX-105	U-109
S-108	SX-101	U-105	U-111

Based on those tanks remarked as having 242-S bottoms & recycle in waste status summary reports between 1973 and 1976, listed in WHC-MR-0132 as 242-S bottoms or recycle, receiving bottoms from the second partial neutralization run per letter "242-S Second Partial Neutralization Production Run", C.A. Petersen to G.A. Olsen, February 13, 1978, or receiving bottoms from the third partial neutralization run per RHO-CD-1515.

A large number of sample analyses are available for the S, SX and U Farm tanks associated with 242-S operation from 1973 to 1980, primarily for the 242-S Evaporator feed tank, tank S-102. These are provided in Table 5-41. The sample analyses for tank S-102, as well as some of the analyses for other tanks, give an indication of the range of concentrations for major constituents

being fed to the evaporator. In the table there are 131 analyses that contain nitrate and 121 that contain nitrate, nitrite and hydroxide concentrations. Of those containing nitrate, nitrite and hydroxide, 16 (13%) do not meet the DST waste chemistry limits for hydroxide, nitrite, or hydroxide and nitrite combined (OSD-T-151-00007). Of those containing just nitrate but not nitrite and hydroxide, 19 (15%) exceed the maximum nitrate concentration (OSD-T-151-00007).

Table 5-41. 242-S Feed and Bottoms Receiver Tanks Sample Analyses During 242-S Operation Between 1973 and 1980 (4 Pages)

Tank	Analysis Date[1]	Waste Type	pH	Concentration, M										
				Na	OH[2]	Al	NO_3[3]	NO_2[4]	PO_4	SO_4	CO_3	Cl	F	SpG
S-101	12/20/74	Liquid[5]	14	2.9	0.415	0.333	1.53	0.197	0.0934	0.00878	0.111	--	0.00355	1.205
S-101	7/16/75	Slurry[5]	--	--	--	4.75	9.08	<0.2	0.08	--	--	--	--	1.52
S-101	11/19/75	Slurry	13.6	--	3.60	1.82	4.68	2.22	--	--	0.318	--	--	1.51
S-102	11/27/73	--	--	5.09	1.22	0.23	4.25	0.118	--	0.00988	0.019	--	0.00154	1.2297
S-102	11/27/73 & 12/7/73	Slurry	11.9	7.18/ 7.63[6]	1.51	0.367	3.05	0.088	0.112	0.0116	0.06	--	0.0051	1.2927
S-102	12/18/73	Liquid	11.4	5.43	1.22	0.23	4.25	0.118	--	0.00988	0.019	--	0.00154	1.2297
S-102	1/25/74	Liquid	10.5	--	--	--	--	--	--	--	--	--	--	1.4081
S-102	2/11/74	Liquid	11.6	--	--	--	--	--	--	--	--	--	--	1.303
S-102	2/22/74	Liquid	11.8	--	--	--	--	--	--	--	--	--	--	1.3868
S-102	2/25/74	Liquid	11.6	--	--	--	--	--	--	--	--	--	--	1.3315
S-102	3/7/74	Slurry	10.9	--	--	--	--	--	--	--	--	--	--	1.310
S-102	3/25/74	Liquid	12.1	--	--	--	--	--	--	--	--	--	--	1.204
S-102	3/25/74	Liquid	12.2	--	--	--	--	--	--	--	--	--	--	1.3463
S-102	4/17/74	Slurry	10.8	--	--	--	--	--	--	--	--	--	--	1.500
S-102	5/13/74	Slurry	12.4	6.66	4.52	0.62	2.51	0.69	0.0387	0.0532	0.259	--	0.0111	1.2839
S-102	5/22/74	Liquid	11.7	--	--	--	--	--	--	--	--	--	--	1.400
S-102	5/24/74	Liquid	12.3	--	--	--	--	--	--	--	--	--	--	1.2704
S-102	6/7/74	Liquid	11.8	--	--	--	--	--	--	--	--	--	--	1.4564
S-102	6/7/74	Liquid	12.1	--	--	--	--	--	--	--	--	--	--	1.3284
S-102	6/17/74	Liquid	12.6	6.92	2.78	0.671	2.56	0.958	0.0189	0.0420	0.176	--	0.00536	1.315
S-102	6/19/74	Slurry	12.3	--	--	--	--	--	--	--	--	--	--	1.2258
S-102	6/28/74	Liquid	11.6	--	--	--	--	--	--	--	--	--	--	1.5027
S-102	7/2/74	Liquid	11.9	--	--	--	--	--	--	--	--	--	--	1.0450
S-102	7/3/74	Liquid	11.0	--	--	--	--	--	--	--	--	--	--	1.4923
S-102	9/16/74	Liquid	13.2	6.13	1.53	0.501	1.60	0.87	0.00899	0.00394	0.175	--	0.0133	1.256
S-102	9/17/74	Liquid	11.5	--	--	--	--	--	--	--	--	--	--	1.4856
S-102	10/14/74	Liquid	11.5	--	--	--	--	--	--	--	--	--	--	1.4005
S-102	10/14/74	Liquid	11.6	--	--	--	--	--	--	--	--	--	--	1.3780
S-102	10/14/74	--	11.7	--	--	--	--	--	--	--	--	--	--	1.3360
S-102	10/14/74	Liquid	11.95	--	--	--	--	--	--	--	--	--	--	1.4450
S-102	10/21/74	Liquid	>12.8	12.51	3.65	1.34	3.29	1.89	0.0334	--	0.0103	--	0.00410	1.4669
S-102	10/21/74	Slurry	13.2	--	--	--	--	--	--	--	--	--	--	1.5311
S-102	10/21/74	Slurry	14	--	--	--	--	--	--	--	--	--	--	1.5357
S-102	10/21/74	Liquid	9.8	--	--	--	--	--	--	--	--	--	--	1.321
S-102	10/23/74	Slurry	14.0	--	--	--	--	--	--	--	--	--	--	1.4866
S-102	10/25/74	Liquid	14.0	--	--	--	--	--	--	--	--	--	--	1.5197
S-102	10/29/74	Slurry	10.1	--	--	--	--	--	--	--	--	--	--	1.3691
S-102	11/1/74	Slurry	13.8	--	--	--	--	--	--	--	--	--	--	1.3638
S-102	11/1/74	Slurry	13.8	--	--	--	--	--	--	--	--	--	--	1.484
S-102	11/4/74	--	12.0	--	--	--	--	--	--	--	--	--	--	1.4345
S-102	11/19/74	Liquid	13.8	--	--	--	--	--	--	--	--	--	--	1.407
S-102	11/19/74	Slurry	13.1	--	--	--	--	--	--	--	--	--	--	1.4554
S-102	11/26/74	Slurry	13.5	--	--	--	--	--	--	--	--	--	--	1.5142
S-102	12/4/74	Slurry	13.3	--	--	--	--	--	--	--	--	--	--	1.4327
S-102	12/17/74	Slurry	14	11.61	2.89	1.28	3.24	1.39	0.11	--	0.157	--	0.0105	1.4202
S-102	12/26/74	Slurry	14.0	--	--	--	--	--	--	--	--	--	--	1.4272
S-102	1/6/75	--	14.0	--	--	--	--	--	--	--	--	--	--	1.2582
S-102	1/6/75	Liquid	14.0	--	--	--	--	--	--	--	--	--	--	1.3476
S-102	1/6/75	Liquid	14.0	--	--	--	--	--	--	--	--	--	--	1.3476
S-102	1/6/75	Liquid	14.0	--	--	1.3	--	--	--	--	--	--	--	1.4346
S-102	1/20/75	Liquid	14.0	--	--	0.498	--	--	--	--	--	--	--	1.4586

Table 5-41. 242-S Feed and Bottoms Receiver Tanks Sample Analyses During 242-S Operation Between 1973 and 1980 (4 Pages)

Tank	Analysis Date[1]	Waste Type	pH	Concentration, M										
				Na	OH[2]	Al	NO_3[3]	NO_2[4]	PO_4	SO_4	CO_3	Cl	F	SpG
S-102	1/22/75	Liquid	14.0	--	--	1.29	--	--	--	--	--	--	--	1.6515
S-102	2/3/75	Slurry	13.2	--	--	--	--	--	--	--	--	--	--	1.4224
S-102	3/26/75	Liquid	13.3	--	--	0.884	--	--	--	--	--	--	--	1.4004
S-102	4/1/75	Slurry	12.7	--	--	1.08	--	--	--	--	--	--	--	1.34
S-102	4/1/75	Liquid	13.2	--	--	1.23	--	--	--	--	--	--	--	1.34
S-102	4/11/75	--	13.5	--	--	0.589	--	--	--	--	--	--	--	1.32
S-102	4/17/75	Slurry	--	10.29	--	1.40	3.18	<0.019	2.37	--	--	--	--	1.3
S-102	4/17/75	Slurry	--	0.296		25.59	--	0.022	0.091	--	--	--	--	1.5
S-102	4/23/75	Liquid	13.3	5.21	1.058	0.447	1.79	0.611	0.0326	--	0.14	--	0.00556	1.1914
S-102	4/23/75	--	12.8	--	--	0.978	--	--	--	--	--	--	--	1.36
S-102	4/30/75	--	13.0	--	2.69	0.0112	3.52	3.2	--	--	--	--	--	1.34
S-102	5/13/75	Liquid	13.0	--	1.16	0.448	1.61	0.818	--	--	--	--	--	1.2538
S-102	5/20/75	--	--	8.45	2.02	0.97	3.78	1.09	0.06	--	0.2	--	0.006	1.3
S-102	7/8/75	Liquid	12.8	--	2.84	0.818	3.19	1.43	--	--	--	--	--	1.38
S-102	7/8/75	Liquid	--	--	1.66	0.747	3.74	0.929	--	--	--	--	--	1.369
S-102	7/28/75	--	--	--	4.29	0.553/ 0.812[6]	2.63	2.38	--	--	0.223	--	--	1.5202
S-102	7/31/75	Slurry	13.5	--	1.74	1.00	2.92	1.15	--	--	--	--	--	--
S-102	7/31/75	--	13.5	--	1.57	0.898	4.2	1.36	--	--	--	--	--	1.35
S-102	7/31/75	Slurry	13.4	--	1.72	0.837	3.1	1.4	--	--	--	--	--	1.31
S-102	8/1/75	--	12.9	--	2.32	1.11	3.68	1.73	--	--	0.325	--	--	1.41
S-102	8/20/75	--	13	--	1.87	0.579	2.99	1.01	--	--	--	--	--	1.24
S-102	8/20/75	Slurry	12.8	--	--	0.742	5.17	1.12	--	--	--	--	--	1.32
S-102	8/22/75	Slurry	11.7	--	1.58	0.818	2.65	1.	--	--	--	--	--	--
S-102	8/22/75	Liquid	12.7	--	1.52	0.812	3.63	0.792	--	--	--	--	--	1.3612
S-102	8/22/75	--	--	--	2.24	1.09	2.92	1.44	--	--	0.263	--	--	1.34
S-102	9/19/75	Liquid	12.9	--	2.98	1.91	4.29	1.9	--	--	--	--	--	1.513
S-102	9/19/75	Liquid	12.5	--	2.18	1.11	3.4	1.59	--	--	--	--	--	1.395
S-102	9/19/75	Liquid	12.0	--	0.488	0.278	1.4	0.556	--	--	--	--	--	1.1716
S-102	9/19/75	--	10.0	--	2.34	1.07	2.98	1.82	--	--	0.258	--	--	1.4
S-102	9/22/75	Liquid	12.5	--	1.78	0.754	3.33	1.96	--	--	--	--	--	1.3662
S-102	9/23/75	Slurry	13.5	--	1.89	1.03	3.9	0.988	--	--	--	--	--	1.370
S-102	9/23/75	Liquid	12.7	--	1.07	0.514	1.98	1.21	--	--	--	--	--	1.2861
S-102	10/20/75	Liquid	14.0	9.93	2.63	1.13	3.64	1.87	0.0568	--	0.257	--	0.0134	1.580
S-102	10/20/75	Liquid	12.2	7.79	1.79	0.958	2.96	1.82	0.0292	--	0.463	0.11	0.00202	1.3308
S-102	10/20/75	Liquid	12.2	--	1.66	1.02	2.66	1.41	--	--	--	--	--	1.346
S-102	10/20/75	Liquid	13.0	--	1.94	1.09	2.92	1.79	--	--	--	--	--	1.398
S-102	11/6/75	Slurry	13.7	--	3.02	1.64	4.4	2.58	--	--	--	--	--	1.480
S-102	11/13/75	Slurry	13.3	--	1.98	0.826	3.3	1.52	--	--	--	--	--	1.320
S-102	11/18/75	--	14.0	--	2.42	1.17	7.64	5.44	--	--	0.181	--	--	1.420
S-102	11/21/75	--	13.5	--	2.	1.06	6.44	5.14	--	--	--	--	--	1.410
S-102	12/3/75	Slurry	12.7	7.6	0.97	0.444	1.99	0.596	0.0908	--	0.115	0.0504	9.72E-5	1.190
S-102	12/11/75	Slurry	12.7	8.48	1.31	0.842	3.5	1.34	0.0464	--	0.466	0.0861	9.85E-4	1.340
S-102	12/3/75	--	13.6	--	1.59	0.626	2.6	1.68	--	--	--	--	--	1.28
S-102	12/3/75	--	11.4	--	2.2	1.13	5.1	2.72	--	--	--	--	--	1.44
S-102	12/11/75	Slurry	13.5	--	1.66	0.99	4.4	2.	--	--	--	--	--	1.390
S-102	12/15/75	Slurry	11.7	--	1.8	0.914	4.44	2.22	--	--	--	--	--	1.430
S-102	1/8/76	--	13.3	--	1.7	0.923	4.29	3.48	--	--	--	--	--	1.38
S-102	1/15/76	--	14.0	--	1.53	0.982	4.3	1.7	--	--	--	--	--	1.38
S-102	1/19/76	Slurry	13.2	--	2.62	1.4	4.91	1.47	--	--	0.38	--	--	1.436
S-102	1/19/76	--	13.7	--	2.06	1.21	4.94	2.26	--	--	--	--	--	1.40
S-102	1/21/76	--	13.5	--	1.2	0.55	3.44	2.2	--	--	--	--	--	1.290
S-102	2/12/76	Liquid	12.8	7.5	1.57	0.823	2.92	1.77	0.0177	--	0.468	0.0904	4.19E-5	1.326
S-102	2/13/76	Liquid	13.0	8.1	1.33	0.978	3.9	1.75	0.104	--	0.442	0.154	0.00242	1.39
S-102	3/16/76	Liquid	13.2	5.21	1.21	0.565	2.76	1.27	0.0485	--	0.0138	0.0863	0.00354	1.2748
S-102	3/16/76	--	13.0	11.34	2.22	1.54	4.88	2.06	0.0678	0.0930	0.43	0.157	0.00150	1.4
S-102	4/27/76	Liquid	13.2	5.03	0.773	0.453	2.42	0.531	0.0470	--	0.238	0.0602	0.00938	1.250
S-102	4/5/79	Slurry	--	--	0.49	0.51	2.04/ 1.65[6]	1.55	0.12	0.27	0.62/ 0.56[6]	--	--	1.257
S-102	3/28/80	--	--	11.07	4.04	1.77	2.19	2.64	0.0502	0.0042	0.137	--	--	1.4018
S-103	10/5/73	Liquid	11	8.68	1.96	1.22	4.36	0.852	<3.77E-4	0.00878	0.042	--	0.00207	1.3517

Table 5-41. 242-S Feed and Bottoms Receiver Tanks Sample Analyses During 242-S Operation Between 1973 and 1980 (4 Pages)

Tank	Analysis Date[1]	Waste Type	pH	Concentration, M										
				Na	OH^{2}	Al	NO_3^{3}	NO_2^{4}	PO_4	SO_4	CO_3	Cl	F	SpG
S-103	1/21/74	Liquid	11.8	1.89	0.523	0.122	1.31	0.067	<3.77E-4	0.00612	0.011	--	5.26E-4	1.0742
S-103	12/6/74	Liquid	<14.5	3.84	1.18	0.471	1.43	0.579	0.0344	0.0121	0.0673	--	0.00427	1.235
S-105	10/5/73	Liquid	11.6	9.56	1.24	0.211	4.46	0.112	<3.77E-4	0.0113	0.034	--	0.00212	1.25
S-105	1/21/74	Slurry	11.5	9.14	2.83	0.578	6.24	0.37	<7.84E-4	0.0265	0.037	--	0.00603	1.4833
S-105	3/13/74	Liquid	--	11.37	6.46	1.69	1.95	0.99	0.029	0.021	0.073	--	--	1.46
S-105	8/21/74	Slurry	--	1.22	0.0126	0.00134	1.16	0.00373	--	--	0.0236	--	--	1.26
S-105	9/5/74	Liquid	--	11.17	6.47	1.69	1.94	1.00	--	--	0.0690	--	--	1.462
S-105	9/5/74	Slurry	--	15.66	0.158	0.0154	14.84	0.055	--	--	0.297	--	--	1.261
S-106	12/7/73	Liquid	11.6	8.32	1.28	0.195	4.16	0.165	<3.77E-4	0.0110	0.074	--	0.00179	1.2262
S-106	1/21/74	Slurry	10.7	10.94	2.86	0.758	5.66	0.296	<7.87E-4	0.0151	0.037	--	0.00255	1.49125
S-106	8/21/74	Slurry	--	1.51	0.0326	0.00961	1.36	0.00549	--	--	0.05	--	--	1.27
S-106	8/21/74	Liquid	--	10.06	5.33	1.56	2.49	0.656	--	--	0.0136	--	--	1.429
S-106	10/14/74	Liquid	11.42	0.107	0.0300	0.00136	0.0185	0.00261	4.05E-4	8.79E-4	0.00773	--	3.71E-4	1.0004
S-106	12/16/74	Slurry	14	14.20	5.20	1.45	2.90	1.02	0.0510	--	0.145	--	7.49E-4	1.5414
S-106	7/23/75	Slurry	--	15.53	2.46	0.94	7.39	1.04	0.233	--	1.515	--	--	1.59
S-106	7/23/75	Liquid	--	11.11	4.44	1.85	2.42	1.78	0.028	--	0.27	--	--	1.45
S-108	12/7/73	Liquid	11.5	8.14	1.43	0.224	4.46	0.127	<3.77E-4	0.00828	0.129	--	0.00255	1.2455
S-108	7/8/74	Liquid	--	11.17	5.08	1.55	2.6	1.94	--	--	--	--	--	1.513
S-109	12/18/73	Liquid	11.5	5.46	1.81	0.174	4.35	0.158	<3.77E-4	0.00980	0.024	--	0.00226	1.249
S-109	9/3/74	Slurry	--	12.48	0.63	0.148	11.14	--	--	--	0.280	--	--	1.1
S-109	9/16/74	Slurry	>13.1	10.45	5.57	1.19	4.82	1.76	0.146	0.0276	0.146	--	0.0188	1.7607
S-109	11/19/74	Slurry	14	--	5.07	--	--	--	--	--	--	--	--	1.6717
S-109	12/6/76	Slurry	--	19.33	0.224	0.280	10.96	0.387	0.00134	0.119	0.889	--	--	1.27
S-110	9/25/74	Slurry	--	--	--	8.02	--	--	--	--	--	--	--	1.7
S-110	9/25/74	Slurry	--	--	--	12.1	--	--	--	--	--	--	--	1.53
S-110	12/17/74	Slurry	14	11.82	3.19	1.48	3.72	1.65	0.00636	--	0.203	--	0.00395	1.536
S-111	5/29/74	Slurry	--	1.27	0.41	7.90	0.54	0.018	0.00247	0.00190	0.128	--	--	1.348
S-111	8/21/74	Slurry	--	0.88	0.137	0.0231	0.679	0.0321	--	--	0.0845	--	--	1.704
S-111	8/21/74	Slurry	--	9.69	3.80	1.34	2.90	1.65	--	--	--	--	--	1.414
S-111	12/16/74	Slurry	>13.4	23.84	5.16	1.34	4.91	2.761	0.00452	--	0.293	--	0.00510	1.7953
S-111	2/28/77	Slurry	--	12.87	0.33	1.36	7.73	0.71	0.0119	0.0441	2.00	--	--	1.41
S-111	8/25/78	Liquid	--	11.0	3.68	1.5	1.95	1.82	0.0874	0.0318	0.082	--	--	1.5
S-111	8/25/78	Liquid	--	9.6	3.77	1.88	0.75	1.74	0.4	0.011	0.21	--	--	1.46
S-112	1/7/74	Liquid	12.2	4.95	1.26	0.348	2.83	0.118	<3.77E-4	0.0160	0.014	--	0.00295	1.1739
S-112	7/8/74	Liquid	--	11.43	5.72	1.19	2.5	2.02	--	--	--	--	--	1.501
S-112	12/9/74	--	13.7	--	4.54	--	--	--	--	--	0.293	--	--	1.5909
S-112	12/10/74	--	--	15.22	1.43	0.42	9.01	0.586	0.0636	--	1.80	--	--	1.304
SX-101	11/13/74	--	--	18.81	0.29	0.22	17.06	0.12	--	--	0.56	--	--	1.65
SX-101	11/20/74	Liquid	12.5	5.62	0.984	1.46	3.06	0.379	0.0286	--	0.212		0.00815	1.318
SX-101	12/4/78	Liquid	--	6.36	--	1.95	1.82	2.45	0.046	--	--	--	--	1.76
SX-101	2/7/79	--	--	--	5.20	1.40	3.44	2.46	0.094	<0.006	--	--	--	--
SX-101	7/14/80	Liquid	--	--	0.253	0.0756	1.115	0.171	0.0746	--	0.054	--	--	1.060
SX-101	10/29/80	Liquid	--	0.87	0.419	0.0365	0.199	0.0883	0.0216	--	0.0320	--	--	1.020
SX-101	10/29/80	Liquid	--	1.07	0.368	0.0672	0.299	0.145	0.0362	--	0.0430	--	--	1.028
SX-102	10/14/74	Liquid	13.3	5.81	0.51	0.22	1.29	0.0962	0.0231	0.0771	0.610	--	0.0354	1.2239
SX-102	11/26/74	--	--	9.11	--	5.77	--	--	0.004	0.037	--	--	--	1.74
SX-102	11/26/74	--	--	3.61	--	5.12	--	--	0.015	0.021	--	--	--	1.90
SX-102	3/18/75	--	--	20.97	0.50	0.25	18.40	0.40	0.045	--	0.59	--	--	1.829
SX-102	5/25/75	--	--	9.59	2.71	0.75	1.88	1.18	0.07	0.29	1.14	--	--	1.88
SX-102	5/25/75	--	--	10.29	2.85	0.38	1.65	0.81	<0.3	0.31	1.99	--	--	1.3
SX-102	9/7/77	--	--	--	--	0.66	1.1	--	0.0370	<0.65	--	--	--	--
SX-103	6/10/75	Slurry	--	--	--	4.8	17.3	0.2	--	--	--	--	--	1.53
SX-103	6/10/75	Liquid	--	8.02	0.964	0.39	5.59	--	--	--	0.538	--	--	1.38
SX-103	3/18/76	--	--	17.55	0.36	0.23	15.69	0.39	0.0195	--	0.39	--	--	1.601
SX-103	12/8/76	Slurry	--	10.15	0.0044	0.242	6.92	0.383	0.027	0.044	0.50	--	--	0.84
SX-103	12/16/77	Slurry	--	24	--	0.80	--	--	0.011	<0.89	--	--	0.0390	--
SX-104	10/21/74	Slurry	>13.10	10.09	1.52	0.00996	5.81	0.529	0.0141	0.0323	0.204	--	0.0120	1.4618
SX-104	12/16/74	Slurry	--	13.50	--	3.53	--	--	<0.07	0.024	--	--	--	1.62
SX-104	10/23/75	Slurry	--	--	1.34	1.02	6.06	0.7073	--	--	--	--	--	--
SX-104	12/18/75	--	13.5	12.48	2.36	1.48	4.54	2.66	--	--	0.768	0.174	--	1.490
SX-104	Mar-Apr/77	--	--	15.71	1.64	1.65	11.21	0.755	0.088	0.0217	0.695	0.0392	--	1.39

Table 5-41. 242-S Feed and Bottoms Receiver Tanks Sample Analyses During 242-S Operation Between 1973 and 1980 (4 Pages)

Tank	Analysis Date[1]	Waste Type	pH	Concentration, M										
				Na	OH[2]	Al	NO_3[3]	NO_2[4]	PO_4	SO_4	CO_3	Cl	F	SpG
SX-105	10/4/74	Slurry	--	--	--	14.34	--	--	--	--	--	--	--	1.77
SX-105	10/4/74	Slurry	--	--	--	13.59	--	--	--	--	--	--	--	1.71
SX-105	11/19/74	Slurry	>13.2	7.22	1.44	0.597	3.71	0.443	0.00211	--	0.275	--	0.0368	1.3444
SX-105	12/18/75	Slurry	13.8	12.52	2.32	1.41	5.08	2.78	--	--	0.788	--	--	1.5
SX-105	3/29/77	Slurry	--	11.06	**0.312**	1.18	**11.28**	**0.092**	--	0.276	0.53	0.0598	0.00112	1.06
U-105	4/16/76	Slurry	--	9.4	--	1.0	3.3	--	0.4	--	--	--	--	1.52
U-105	4/5/77	Slurry	--	23.0	--	1.0	4.2	--	0.3	<0.6	--	--	--	1.72
U-105	1/10/78	Slurry	--	24.0	--	1.2	--	--	0.035	<0.46	--	--	--	--
U-105	12/4/78	Slurry	--	26.06	1.14	0.72	4.81	1.48	0.0512	0.253	1.46	--	--	1.62
U-106	2/26/74	Liquid	12.4	5.73	1.18	0.54	4.09	0.124	0.0124	0.0210	0.0693	--	0.00145	1.3058
U-108	1/21/74	Liquid	11.6	0.515	**<0.01**	<0.0076	0.381	**0.00317**	0.137	0.00493	0.024	--	0.0127	1.0056
U-108	9/29/75	Slurry	--	2.90	**0.0022**	1.36	0.190	**0.026**	0.854	--	0.0593	--	--	0.898
U-109	12/15/75	Liquid	--	5.99	1.31	0.342	3.08	0.628	0.0476	--	0.243	--	--	1.24
U-109	12/15/75	Slurry	--	5.13	0.263	1.79	0.494	0.122	--	--	0.0238	--	--	1.05
U-111	9/29/75	Slurry	--	5.35	0.136	1.47	0.085	0.118	1.26	--	0.617	--	--	0.908
U-111	10/21/75	Liquid	12.8	2.33	**0.635**	0.0559	1.81	**0.0659**	0.0174	--	0.0364	0.0301	0.0194	1.1178

All data for 241-S farm tanks taken from WHC-SD-WM-ER-323, Rev 0, *Supporting Document for the Southwest Quadrant Historical Tank Content Estimate Report for S-Tank Farm.*

All data for 241-SX farm tanks taken from WHC-SD-WM-ER-324, Rev 0, *Supporting Document for the Southwest Quadrant Historical Tank Content Estimate Report for SX-Tank Farm.*

All data for 241-U farm tanks taken from WHC-SD-WM-ER-325, Rev 0, *Supporting Document for the Southwest Quadrant Historical Tank Content Estimate Report for U-Tank Farm.*

1 Analysis date is date that analyses were performed at the laboratory and is not the sample date when the sample was collected from the tank. Sample date was not given in every instance of analyses.

2 Hydroxide concentrations shown in bold and shaded are less than the OSD-T-151-00007 double-shell tank waste chemistry lower limit for hydroxide concentration or in combination with nitrate concentrations are less than the lower limit for combined hydroxide and nitrite concentration relative to nitrate concentration.

3 Nitrate concentrations shown in bold and shaded exceed the OSD-T-151-00007 double-shell tank waste chemistry upper limit for nitrate concentration of 5.5 M.

4 Nitrite concentration shown in bold and shaded in combination with the hydroxide concentrations are less than the OSD-T-151-00007 double-shell tank waste chemistry lower limit for combined hydroxide and nitrite concentration relative to nitrate concentration.

5 Samples described as liquid contain less than 5% solids via visual observation while samples described as slurry contain 5% or greater solids via visual observation.

6 Second result is a rerun of the analysis.

5.5.6.8. 242-A Vacuum Evaporator-Crystallizer Waste (1977-1980)

The 242-A vacuum evaporator-crystallizer began operating March 18, 1977 with an original design life of 10 years (WHC-SD-WM-ER-310, Rev 0, *Supporting Document for the Historical Tank Content Estimate for B Tank Farm – Work Order ER4945*, p. 22, and ARH-LD-227 B, *Atlantic Richfield Hanford Company Monthly Report March 1977*, p. 22). The 242-A evaporator-crystallizer shared design and operational features with the 242-S evaporator-crystallizer. The description of the 242-S vacuum evaporator-crystallizer is also applicable to 242-A, and the reader is referred to Section 5.5.6.7 for that description. Although a conceptual design was prepared to install systems for partial neutralization at 242-A the project never proceeded (Letter G Burton Jr to L.J. Adams, US ERDA, "Request for Directive Partial Neutralization Facilities for the 242-A Evaporator-Crystallizer (Project B-134)", November 11, 1976).

Early on during processing of wastes through 242-A the evaporated waste was sent to storage in tanks in A and AX Farms. Tank A-102 operated as a feed tank and tanks A-101, A-103, A-106, AX-101, AX-102, and AX-103 received bottoms from 242-A. A number of sample analyses are available for the A and AX Farm tanks associated with 242-A operation from 1977 to 1980.

These are provided in Table 5-42. The sample analyses give an indication of the range of concentrations for major constituents being fed to the evaporator as well as the concentrated product. In the table there are 43 analyses that contain nitrate and 42 analyses that contain nitrate, nitrite and hydroxide concentrations. All of these meet the DST waste chemistry limits for nitrate, hydroxide, nitrite, or hydroxide and nitrite combined (OSD-T-151-00007).

Table 5-42. 242-A Feed and Bottoms Receiver Tanks Sample Analyses During 242-A Operation Between 1977 and 1980

Tank	Analysis Date[1]	Waste Type	pH	Concentration, M										
				Na	OH[2]	Al	NO_3[3]	NO_2[4]	PO_4	SO_4	CO_3	Cl	F	SpG
A-101	10/2/79	Liquid[2]	--	--	0.126	0.0256	0.0420	0.0479	0.00142	--	0.0610	--	--	0.9952
A-101	10/3/79	Liquid	--	--	0.518	0.274	0.0772	0.421	0.00212	--	0.0010	--	--	1.052
A-101	11/2/79	--	--	9.01	2.31	1.26	2.27	1.58	0.037	--	0.75	--	--	1.378
A-101	8/22/80	--	--	--	0.675	0.379	2.48	0.952	0.045	--	0.52	--	--	1.2916
A-101	9/22/80	--	--	--	3.06	1.364	2.72	2.04	0.016	--	0.98	--	--	1.344
A-101	9/22/80	--	--	--	3.15	1.758	2.298	2.565	0.33	--	0.156	--	--	1.144
A-101	9/22/80	--	--	--	3.874	1.36	2.53	1.438	0.125	--	0.089	--	--	1.449
A-101	10/13/80	--	--	13.36	4.2	2.54	2.11	3.79	0.08	--	0.24	--	--	1.306
A-101	10/13/80	--	--	11.79	3.51	2.185	2.02	3.26	0.23	--	0.06	--	--	1.277
A-101	10/22/80	--	--	8.51	3.51	1.53	1.89	1.11	0.05	--	0.16	--	--	1.445
A-101	11/10/80	--	--	12.11	2.45	1.51	2.77	2.22	0.08	0.13	1.33	--	--	1.58
A-101	11/10/80	--	--	9.32	2.31	1.21	2.67	2.22	0.09	0.01	0.31	--	--	1.43
A-101	11/10/80	--	--	12.96	2.45	1.59	3.07	2.28	0.09	0.15	1.5	--	--	1.65
A-101	11/10/80	--	--	10.74	2.51	1.67	3.2.4	2.4	0.08	--	0.34	--	--	1.47
A-101	11/11/80	--	--	17.11	3.51	1.95	3.66	3.01	0.12	--	2.31	--	--	1.85
A-101	11/11/80	--	--	12.27	3.12	2.08	3.48	2.94	0.13	--	0.13	--	--	1.45
A-102	7/17/80	--	--	--	0.738	0.268	0.942	0.594	0.0346	--	0.110	--	--	1.1554
A-102	7/17/80	--	--	--	0.622	0.291	0.879	0.603	0.0374	--	0.120	--	--	1.1572
A-102	7/17/80	--	--	--	0.622	0.410	0.996	0.599	0.0362	--	0.110	--	--	1.1554
A-102	8/4/80	Liquid	--	--	1.24	0.546	1.50	0.433	0.0594	--	0.240	--	--	1.180
A-102	8/4/80	Liquid	--	--	1.27	0.521	1.67	--	0.0591	--	0.230	--	--	1.199
A-102	12/23/80	--	--	11.41	3.31	2.42	2.06	3.22	0.04	--	0.14	--	--	1.44
A-102	12/23/80	--	--	10.57	3.12	1.92	1.91	3.13	0.07	--	0.14	--	--	1.452
A-103	8/2/79	--	--	--	1.48	0.888	3.	1.68	0.039	<0.030	0.8	--	--	1.398
A-103	3/20/80	--	--	--	0.74	0.55	1.92	1.24	0.0817	--	0.340	--	--	1.24
A-103	3/20/80	--	--	--	1.67	1.14	3.17	4.89	0.0707	--	0.521	--	--	1.417
A-103	9/12/80	--	--	--	2.85	0.4	3.42	2.20	--	--	0.38	--	--	1.436
A-103	9/22/80	--	--	--	2.85	0.400	3.42	2.20	0.063	--	0.380	--	--	1.436
A-103	10/2/80	--	--	--	1.96	1.21	3.23	1.65	0.58	--	0.31	--	--	1.402
A-106	10/27/79	Liquid	--	--	1.01	0.724	1.331	0.739	0.0869	--	--	--	--	1.194
A-106	5/23/80	--	--	10.25	2.36	1.00	1.40	3.10	0.129	--	0.90	--	--	1.39
AX-101	10/7/80	--	--	--	3.18	1.87	1.85	2.91	0.073	--	0.115	--	--	1.395
AX-101	11/11/80	--	--	13.07	3.69	2.23	1.66	5.14	0.07	--	0.07	--	--	1.36
AX-101	11/11/80	--	--	10.44	3.67	2.06	1.69	2.59	0.07	--	0.108	--	--	1.391
AX-102	1/23/80	--	--	3.20	0.572	0.0371	0.865	0.443	0.100	--	0.490	--	--	1.113
AX-102	1/23/80	--	--	--	<0.5	0.215	4.12	1.98	0.0488	--	0.95	--	--	1.404
AX-102	2/22/80	--	--	2.80	0.329	0.070	0.725	0.267	0.0142	0.187	0.490	--	0.0074	1.088
AX-102	2/22/80	--	--	2.72	0.172	0.147	0.717	0.268	0.0138	0.164	0.52	--	0.0074	1.071
AX-103	3/14/79	Liquid	--	--	0.856	0.621	1.98	1.04	--	--	0.19	--	--	--
AX-103	8/6/79	--	--	--	2.35	1.52	3.47	1.445	--	--	0.26	--	--	1.443
AX-103	8/6/79	--	--	--	0.66	0.44	1.06	1.01	--	--	0.05	--	--	--
AX-103	4/27/80	Liquid	--	--	2.31	1.05	2.02	1.43	0.0430	--	0.49	--	--	1.274
AX-103	4/27/80	Liquid	--	--	2.47	1.11	2.58	1.67	0.0426	--	1.10	--	--	1.376

All data for 241-A farm tanks taken from WHC-SD-WM-ER-308, Rev 0, Supporting Document for the Northeast Quadrant Historical Tank Content Estimate Report for A-Tank Farm, Westinghouse Hanford Company, Richland WA, September 1994.

All data for 241-AX farm tanks taken from WHC-SD-WM-ER-309, Rev 0, Supporting Document for the Northeast Quadrant Historical Tank Content Estimate Report for AX-Tank Farm, Westinghouse Hanford Company, Richland WA, September 1994.

1 Analysis date is date that analyses were performed at the laboratory and is not the sample date when the sample was collected from the tank. Sample date was not given in every instance of analyses.

2 Samples described as liquid contain less than 5% solids via visual observation.

5.5.6.9. Corrosion Study of Steel Tank Liners Exposed to Simulated Evaporated Waste

A report, BNWL-1869, *Corrosion of Mild Steel Tank Liners Exposed to Simulated Solidified Alkaline High-Level Waste*, was prepared to document the corrosiveness of simulated solidified waste on Hanford's SST mild steel liners. The corrosiveness of solidified waste was largely unknown at the time of the study (October 1974) and little subsequent information has been found in this area. The study examined the effects of variation in major chemical constituents of the solid waste, residual water content, and temperature. Test specimens were exposed for periods of 7, 12 and 22 months to evaluate general corrosion, pitting corrosion and SCC.

The various waste simulants were prepared by evaporating solutions of each of the compositions, drying, and then adding water resulting in the desired quantity of free water. Composition of the waste simulants tested is provided in Table 5-43. Each waste simulant was placed in a welded metal container along with corrosion specimens of ASTM A-283, Grade C, used for weight loss determination, pitting intensity and notched and pre-cracked c-ring specimens to evaluate SCC. The closed containers were held at 60°C, 80°C, and 95°C. The closed containers were opened at one to two month intervals. A strong odor of ammonia was detected when containers holding high-alkali waste were opened. At high pH, iron in the presence of nitrate or nitrite is expected to proceed as

$$3Fe + NaOH + NaNO_2 + 3H_2O \rightarrow Na_2FeO_2 + 2Fe(OH)_2 + NH_3$$

Table 5-43. Waste Compositions Examined for Corrosion from Solidified Alkaline Waste

Constituent	Composition (g/L) of Constituents for Indicated Waste							
	I-OH	II-OH	I-PO_4	II-PO_4	I-SO_4	II-SO_4	I-NO_3	II-NO_3
NaOH	400	200	40	20	40	20	40	20
$NaAlO_2$	139	139	139	139	139	139	139	139
$NaNO_3$	366	366	366	366	366	366	1131	749
$NaNO_2$	90	90	90	90	90	90	90	90
Na_2CO_3	170	170	170	170	170	170	170	170
NaCl	12	12	12	12	12	12	12	12
Na_2SiO_3	1	1	1	1	1	1	1	1
Na_3PO_4	--	--	492	246	--	--	--	--
Na_2SO_4	--	--	--	--	639	320	--	--

Data taken from BNWL-1869.

Specimens were removed from test apparatuses and corrosion rates were obtained by weight loss determinations and pit depths obtained by microscopic measurement. General corrosion rates and pit depth for the three test temperatures are tabulated by waste composition in Table 5-44 and Table 5-45, respectively. General corrosion rates in high-alkaline waste, up to 4.7 mils per year, were one to two orders of magnitude greater in high-alkaline waste than low-alkaline waste. Pitting attack occurred on all specimens exposed to high-alkaline waste but on none of the specimens exposed to low-alkaline waste. Pitting frequency was subjectively described as quite high on specimens exposed to high-alkaline waste without giving a quantitative population density. Maximum pit depth observed after 22 exposure months ranged from 8 to 20 mils. The pitting rate appeared approximately linear with respect to time. Inspection of the steel containers housing the specimens showed no preferential attack at the waste-vapor interface. No

preferential attack was associated with the weld metal areas of the containers. Stress corrosion cracking did not occur in the c-ring specimens at any of the waste compositions. A few tests were duplicated in open systems with condensers and the results obtained were similar to the results from the closed system tests.

Table 5-44. Corrosion Rates of Mild Steel Exposed to Simulated Solidified Alkaline Waste

Waste[1]	Water, wt%	Average General Corrosion Rate, mil/yr								
		60°C			80°C			95°C		
		7 mo.	12 mo.	22 mo.	7 mo.	12 mo.	22 mo.	7 mo.	12 mo.	22 mo.
I-OH	5	1.1	--	0.7	0.8	2.9	2.0	0.5	0.4	0.7
II-OH	5	1.8	1.3	2.0 (1.5)[2]	1.5	1.6	2.1	0.6	0.5	1.0
I-OH	15	2.6	1.4	2.4	2.4	4.2	1.6	0.8	0.4	0.9
II-OH	15	2.2	1.7	4.7 (1.5)[2]	2.7	2.6	1.4	1.1	0.5	1.4
I-PO_4	5	<0.01	--	<0.01	<0.01	0.02	0.01	0.08	0.2	0.01
II- PO_4	5	<0.01	0.03	<0.01	<0.01	0.01	0.01	--	0.05	--
I- PO_4	15	<0.01	0.01	0.01	<0.01	0.02	0.01	0.07	0.05	0.01
II- PO_4	15	<0.01	0.01	0.01	<0.01	--	0.01	0.09	0.06	0.01
I-SO_4	5	--	--	0.01[2]	0.02	0.02	0.01	--	--	--
II- SO_4	5	--	--	0.05[2]	0.02	--	--	--	--	--
I- SO_4	15	--	--	--	0.05	0.02	--	--	--	--
II- SO_4	15	--	--	0.02[2]	0.02	0.02	--	--	--	--
I-NO_3	5	--	--	--	0.02	0.01	--	--	--	--
II- NO_3	5	--	--	--	0.01	0.08	0.01	--	--	--
I- NO_3	15	--	--	--	0.02	--	--	--	--	--
II- NO_3	15	--	--	--	0.06	--	--	--	--	--
II-OH[3]	5	--	1.7[2]	--	--	2.3	0.01	--	--	--
II-OH[4]	5	--	--	1.8	--	--	--	--	--	--

Data recreated from BNWL-1869.

1 Waste compositions shown in Table 5-43.
2 Open system using water-cooled condenser
3 1% fluoride added as NaF
4 Waste contained no nitrite

Table 5-45. Pitting Intensity of Mild Steel Exposed to Simulated Solidified Alkaline Waste

Waste[2]	Water, wt%	Pit Depth, mils[1]								
		60°C			80°C			95°C		
		7 mo.	12 mo.	22 mo.	7 mo.	12 mo.	22 mo.	7 mo.	12 mo.	22 mo.
I-OH	5	2 (4)	5 (7)	9 (15)	4 (5)	7 (12)	13 (20)	2 (4)	3 (6)	7 (12)
I-OH	15	1 (1)	3 (4)	6 (8)	4 (6)	7 (10)	7 (10)	2 (4)	3 (3)	6 (8)
II-OH	5	1 (1)	4 (4)	8 (10)	0 (0)	7 (10)	12 (17)	0 (0)	3 (3)	8 (14)
II-OH	15	0 (0)	1 (2)	4 (8)	0 (0)	5 (7)	14 (20)	5 (9)	1 (2)	8 (12)

Data recreated from BNWL-1869.

1 Values given are the average depth of ten measurements. Parenthetical values represent the maximum pit depth found.
2 Waste compositions shown in Table 5-43.

5.5.7 In-Farm Processes

A number of in-farm processes were performed on waste present in SSTs that created waste streams that although similar to the source could be chemically different enough to warrant consideration. These processes include a number of evaporation processes to concentrate waste, in-farm scavenging of waste from the metal recovery process, nitrate leaching of REDOX waste, and PUREX sludge washing. Because of the large number and variety of evaporation processes employed both with in-farm facility and ex-farm facilities, these processes were combined into Section 5.5.6. The remaining in-farm processes are described below.

5.5.7.1. In-Farm Scavenging Process

From the start of the TBP plant until late September 1954 when in-plant scavenging started, metal recovery wastes from the TBP plant were stored in the SSTs after neutralization and concentration (HW-33536, *Nickel Ferrocyanide Scavenging Flowsheet for Neutralized Concentrated RAW*). Aqueous waste approximately equal in volume to that of the metal waste processed for uranium recovery resulted from the metal recovery process (HW-31442, *Removal of Cesium from Uranium Recovery Process Wastes*). These aqueous wastes were sufficiently radioactive that they had to be returned to SSTs rather than discharged to the ground. The alkaline insoluble solids in this waste settled out in the tanks over time. Some of the supernatant liquid underwent further concentration at the tank farm atmospheric evaporators. The concentrate from the tank farm evaporators was stored separately or mixed with similarly concentrated $BiPO_4$ 1C waste (including CW). Scavenging of these waste streams was predicted to be able to process roughly 17 million gal of waste with the possibility of freeing up 15 million gal of tank space. In-farm scavenging started at 244-CR vault in November 1955 (HW-38955-REV). There were also plans to convert 242-T for in-farm scavenging (HW-38955-REV) but no record was found of this ever being the case.

5.5.7.1.1. In-Farm Scavenging Process Description

In-farm scavenging operating procedure, HW-38955-REV, identified three methods of scavenging based on scavenging studies performed on 24 tanks. The waste composition varied depending upon the waste treatment conditions in the TBP plant, and this in turn resulted in variations of the methods employed for scavenging the waste. In all methods the waste was first adjusted to or maintained at a pH of 9.3 ± 0.7 by addition of nitric acid or sodium hydroxide.

The first method was employed for waste neutralized to a relatively high pH (greater than 11). These wastes contained little strontium and therefore, nickel ferrocyanide scavenging alone was used. After neutralization of the waste to pH 9.3, sodium ferrocyanide was added to 0.005 M. Then nickel sulfate was added to 0.005 M. The waste was agitated and then sent to an underground storage tank for settling of the solids before cribbing the supernatant liquid.

The second method was employed for waste neutralized to a lower pH (8 to 10). Generally, this waste contained a higher concentration of strontium which required scavenging. This second method was the same as the first method but after nickel sulfate addition, 0.01-0.03 M calcium

nitrate was also added to the waste. The waste was then agitated and sent to an underground storage tank for settling of the solids before cribbing the supernatant liquid.

The final method was employed for wastes that were already scavenged in the TBP plant, but that did not contain sufficiently low strontium concentration to allow cribbing. After neutralization of the waste to pH 9.3, 0.01-0.03 M calcium nitrate was added to the waste. The waste was agitated and sent to underground storage for settling of solids before cribbing the supernatant liquid.

5.5.7.1.2. Process Waste from In-Farm Scavenging of TBP Waste

A flowsheet for nickel ferrocyanide scavenging of neutralized concentrated RAW stream (RA column effluent from the metal recovery first solvent extraction column) is provided in HW-33536. The flowsheet identifies the formation of a sludge containing 0.025 M ferrocyanide ion and 0.025 M nickel ferrocyanide. The ferrocyanide ion is listed along with nickel ferrocyanide because the specific anions associated with the ferrocyanide were not known but believed to include cesium and iron complexes. The sludge was present with a large amount of supernatant liquid. The given composition of the supernatant liquid from the flowsheet is shown below:

SO_4^{-2}	0.35 M
PO_4^{-3}	0.24 M
NO_3^-	6.2 M
Cl^-	0.021 M
Na^+	7.42 M
K^+	0.02 M

No corrosion testing data was found for process waste from in-farm scavenging of TBP waste. The composition of the supernatant liquid from the in-farm scavenging flowsheet is comparable to the simulated TBP waste stream for which corrosion testing was performed (HW-30041) as documented in Section 5.5.2.2.

Storage temperature data was not located for storage of in-farm scavenging of TBP waste. Studies showed little effect of temperature on the final decontamination obtained on wastes, but higher temperatures appeared to improve the settling rate of the sludge (H-38955-REV, *In-Farm Scavenging Operating Procedure*). The operating procedure did not specify a temperature for processing or discharging the waste back to SSTs for sludge settling.

5.5.7.2. 241-SX Nitrate Leaching Process

In the 202-S REDOX separation facility, the first step to prepare the radioactive slugs for uranium-plutonium-fission-product separation was the removal of the aluminum jacket from each slug, which was performed in the head-end dissolvers. The aluminum slug jacket was removed by dissolution in a solution consisting of about 10% sodium hydroxide and 20% sodium nitrate ($NaNO_3$) at boiling temperatures. The sodium nitrate served to suppress the formation of

hydrogen, which would otherwise evolve in high concentrations (HW-18700-DEL, p. 303). Commercial $NaNO_3$ was used for suppression prior to 1963, however the REDOX chemical flowsheet discusses the change from using commercial $NaNO_3$ to using recovered $NaNO_3$ from dissolved tank farm sludge waste on January 13, 1963 (RL-SEP-243, p. 7). This change is represented in comparing REDOX Flowsheets 7 and 8. The nitrate addition to the dissolver changes from fresh $NaNO_3$ in Flowsheet 7 to the use of 4.50 M tank farm $NaNO_3$ in Flowsheet 8 (RL-SEP-243, p. 13-19). The process and known chemical composition of waste in tanks that underwent nitrate leaching are discussed in this section.

5.5.7.2.1. Nitrate Leaching Process Description

The process of nitrate recycling from SX Farm tanks is of interest as a potential contributing factor to tank failure. The preparation of a solution with relatively high concentration of sodium nitrate and low hydroxide and nitrite solution within SSTs could point to nitrate-induced SCC. It should be noted that the nitrate leaching from tanks within SX Farm is separate from the aluminum nitrate recovery system for the REDOX solvent extraction process.

Extensive information about the specific process of nitrate recycling has not been found in the Hanford document systems. The primary source of information has been the Waste Status Summary reports, which were released every six months from 1962 to 1965 (HW-83906-E-RD) and the REDOX weekly readings and reports from 1964 through 1965 (HW-80202, *REDOX Weekly Process Reports January Through December 1964*, and RL-SEP-297). Figure 5-52 below shows the flow diagram for the nitrate recycle system (IDMS document number 34213-1, *Sodium Nitrate Recycle Flow Diagram*). This figure remains the only visual representation found showing nitrate recycling operations and only depicts the transfer route from the SX Farm to the REDOX dissolvers. The date of publication is unknown.

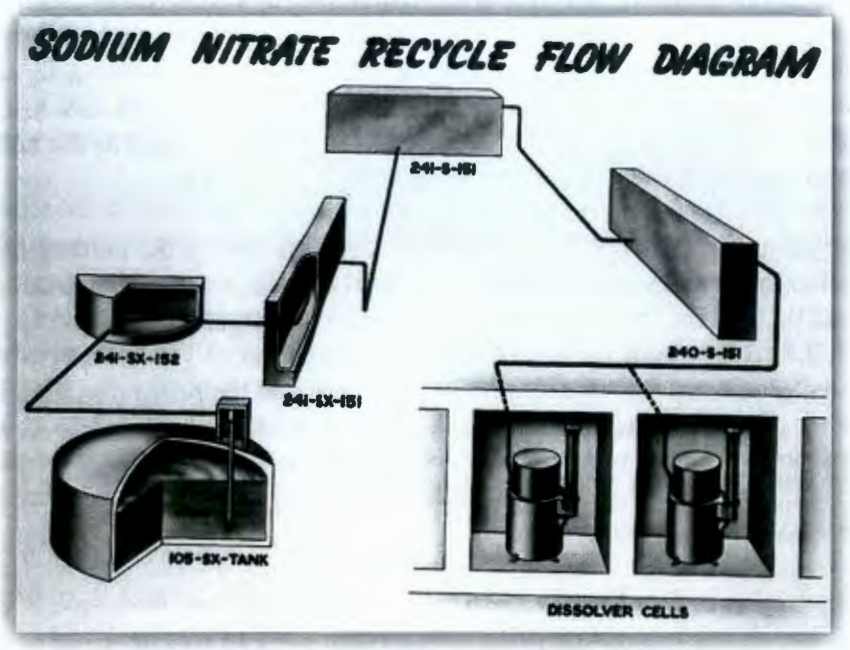


Figure 5-52. Sodium Nitrate Recycle Flow Diagram (IDMS document number 34213-1)

Based on weekly REDOX tank readings, the process of nitrate waste leaching involved first pumping the SST down to the apparent sludge depth, which equated to a waste level between 3 and 4 ft. The tank would then be filled to a liquid level of about 10 ft with condensate from tank SX-106, which was the condensate receiver tank for the self-boiling tanks in SX Farm. Exact operations during the sodium nitrate dissolution are unknown, but the sludge was likely mixed with condensate using ALCs. The September 1961 REDOX monthly report discusses investigations to determine how well sludge can be dissolved or slurried in tank SX-114 using ALCs (HW-71187, *Chemical Processing Department Monthly Report September, 1961*, p. G-4). The results from the ALC dissolution test are discussed in the January 1962 REDOX monthly report and show that eighty percent of the sludge volume has been dissolved, which suggests the test was a success and that ALCs were then used in the proceeding nitrate recycle process (HW-72551, *Chemical Processing Department Monthly Report January, 1962*, p. G-4).

The condensate used for dissolution would remain in the tank between one and three months, at which time the nitrate leachate would be pumped to the feed tank for the REDOX plant and the leached tank would be returned to service to receive REDOX waste for self-concentration. A total volume of about 200,000 gal of recovered nitrate leachate was pumped from each tank during leaching while the nitrate feed tank to REDOX was pumping out sodium nitrate leachate at an average of around 10,000 gal per month. The chemical composition results from sampling of supernatant, sludge, and leachate waste forms are shown in the next section.

Document RHO-R-39, released in 1969, provides a boiling waste tank operational history table outlining the usage of SX, A, and AX Farm tanks. The table contains a column describing whether $NaNO_3$ was leached from the sludge in a given tank, which is one of the few resources directly addressing nitrate leaching. According to RHO-R-39, tanks SX-107, SX-108, SX-114,

and SX-115 were nitrate leached, however when comparing to Waste Status Summary reports, it appears the table is incomplete. The Waste Status Summary reports provide information about transfers into and out of SX Farm tanks and are considered the most reliable information regarding nitrate leaching. Based on these reports, tanks SX-107, SX-108, SX-111, SX-114, and SX-115 were all nitrate leached. In addition, tank SX-105 was later used as the holding and feed tank for leached nitrate sent to the 202-S dissolvers in REDOX plant.

When nitrate recycling first began in 1963, tank SX-114 was used as the holding tank for nitrate leachate from other tanks and was also used as the feed tank for nitrate to REDOX plant (HW-83906-E-RD). The first tank to be nitrate leached was actually tank SX-114, which was leached through the ALC testing conducted in the fourth quarter of 1961. Approximately eighty percent of the sludge volume was dissolved during the test and the result was nitrate leachate. The second tank to be nitrate leached was tank SX-108 with its leachate sent to tank SX-114 in 1962. Once recycling of nitrate was started in 1963, monthly summaries show sodium nitrate being pumped from tank SX-114 to REDOX plant. Nitrate was next leached from tank SX-107 and sent to tank SX-114 during early 1963.

In May 1963, the feed tank for nitrate waste to REDOX was changed from tank SX-114 to tank SX-105. Therefore, all leached nitrate being held in tank SX-114 was removed and sent to tank SX-105. Tank SX-105 subsequently began sending batches of sodium nitrate to the dissolvers in the REDOX plant (HW-83906-E-RD). During 1964, transfers from tank SX-105 to send sodium nitrate to REDOX were continued while the tank also received leached sodium nitrate from tanks SX-111 and SX-115. Tank SX-105 remained the sodium nitrate feed tank for REDOX until the third quarter of 1966 when the process was shut down. Figure 5-53 shows a timeline of the nitrate recycling operations.

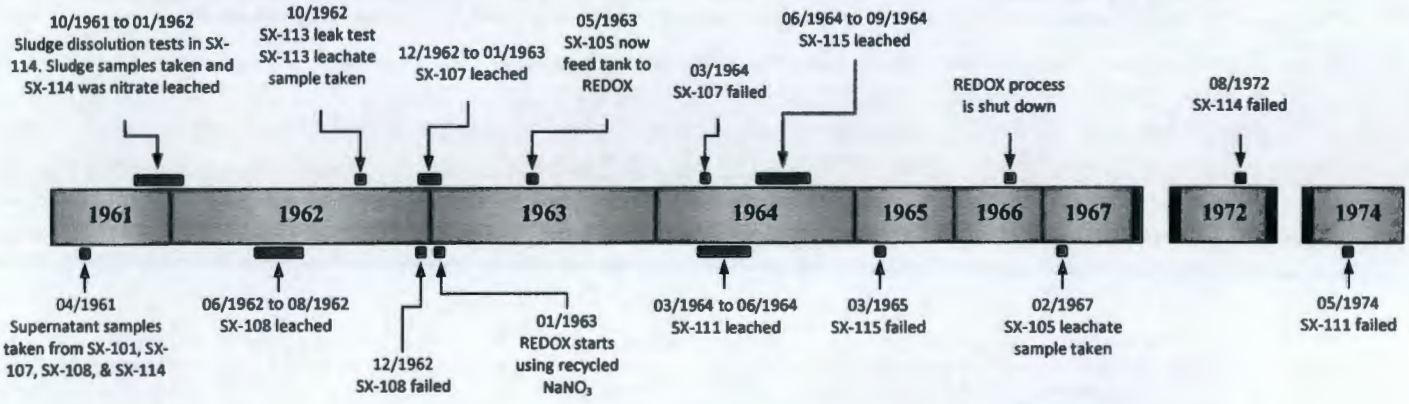


Figure 5-53. Timeline of Nitrate Recycle Operations

It should be noted that there are three additional instances of nitrate leaching mentioned in various reports, but supporting documents suggest they did not happen. The Chemical Processing Department Waste Summary shows that both tanks SX-106 and SX-115 had waste sent directly to the 202-S dissolvers in the REDOX plant in early 1963 (HW-78279, *Chemical Processing Department Waste Status Summary for 01/01/1963 Through 06/30/1963*). This information is suspect since the Waste Status Summary reports and REDOX Weekly Readings

do not show waste being pumped from tanks SX-106 or SX-115 to REDOX. Tank SX-106 was used as the condensate collection tank and likely would not have been leached of nitrate, especially since tank SX-114 was deemed to be the single feed tank to the 202-S dissolvers at the time. Tank SX-115 was, in fact, nitrate leached in 1964 according to the Waste Status Summaries, which would make the scenario of nitrate waste also being pumped from tank SX-115 to REDOX in 1963 to be highly unlikely.

According to ARH-R-43, tank SX-112 was also said to have been nitrate leached between its first filling in 1958 and its second filling in 1966. However, based on Waste Status Summary reports, monthly reports, and liquid level measurements, there is no evidence of leaching from tank SX-112. Therefore, it does not appear the information regarding leaching of tanks SX-106, SX-112, or the first leaching of tank SX-115 is accurate. Table 5-46 is a composite of various data sources and provides an overall summary for all tanks in SX Farm with regard to nitrate leaching.

Table 5-46. Overall Summary of the 241-SX Tank Farm With Respect to Nitrate Leaching

Tank	$NaNO_3$ Leached? (order)	Date Leached	Confirmed Leaker?	Est. Failure Date[1]
SX-101	No	-	No	-
SX-102	No	-	No	-
SX-103	No	-	No	-
SX-104	No	-	No	-
SX-105	No	-	No	-
SX-106	No	-	No	-
SX-107	Yes (3)	January 1963	Yes	March 1964
SX-108	Yes (2)	August 1962	Yes	December 1962
SX-109	No	-	Yes	February 1965
SX-110	No	-	No	-
SX-111	Yes (4)	June 1964	Yes	May 1974
SX-112	No	-	Yes	January 1969
SX-113	No	-	Yes	June 1958
SX-114	Yes (1)	October 1961	Yes	August 1972
SX-115	Yes (5)	September 1964	Yes	March 1965

[1] Estimated failure dates were adopted from the *Hanford SX-Farm Leak Assessments Report*, RPP-ENV-39658.

5.5.7.2.2. Sodium Nitrate Waste from Leaching

The waste sample analysis from SX Farm tanks during the period of nitrate leaching is not extensive, but the limited data available serves to represent an estimated chemical composition of certain tanks prior to, during, or after nitrate leaching. The collective analytical results of SX Farm sample analyses during nitrate leaching and contemporary REDOX waste chemical composition as stated from Flowsheets 7 and 8 are shown in Table 5-47.

Table 5-47. Waste Composition Results for 241-SX Tanks During the 1960s

Source	Layer	Date	Temp. (°C)	pH	$[OH^-]$ M	$[NO_2^-]$ M	$[NO_3^-]$ M	$[NO_2^-]/[NO_3^-]$
Sample Analytical Results Prior to Nitrate Leaching								
SX-101[1]	Supernatant above Sludge	April 1961	96	-	4.58	2.48	6.03	0.41
SX-107[1]	Supernatant above Sludge	April 1961	133	-	1.27	0.65	8.65	0.08
SX-108[1]	Supernatant above Sludge	April 1961	138	-	1.32	0.61	8.35	0.07
SX-114[1]	Supernatant above Sludge	April 1961	147	-	1.53	0.45	8.15	0.06
Sample Analytical Results During or After Nitrate Leaching								
SX-114[2]	Partially Dissolved Sludge Leachate	October 1961	124	12.2	0.16	0.05	1.64	0.03
SX-114[2]	Partially Dissolved Sludge Leachate	November 1961	102	11.7	0.22	0.07	3.47	0.02
SX-113[3]	Dissolved Sludge Leachate	October 1962	47	-	0.4	0.1	4.2	0.02
SX-105[5]	Dissolved Sludge Leachate	January 1966	49	11.4	0.52	0.18	4.23	0.04
Flowsheet Conditions								
Flowsheet 7[4]	-	January 1965	-	-	1.13	-	5.35	-
Flowsheet 8[4]	-	January 1965	-	-	0.44	-	4.85	-

[1] Results were obtained from HW-69443, p. G-5.
[2] Results were obtained from HW-71895, *Chemical Processing Department Monthly Report November, 1961*, p. G-4.
[3] Results were obtained from HW-75714, *Leak Testing of the 113-SX Tank*, p. 4.
[4] Results were obtained from RL-SEP-243, p. 13-19.
[5] Results were obtained from ISO-708-DEL, *Chemical Processing Division Monthly Report for February, 1967*, p. G-4.

Supernatant samples were taken from tanks SX-101, SX-107, SX-108, and SX-114 in April 1961 prior to removal of the supernatant liquid from the tank (HW-69443, p. G-5). These samples represent the waste that would have been pumped from the tanks prior to condensate addition and sludge dissolution and are provided for comparison.

Supernatant liquid from dissolved sludge samples were taken from tank SX-114 while testing the use of ALCs for sludge dissolution, with one sample taken in October 1961 and the other taken in November 1961 (HW-71895, p. G-4). It should be noted that the sample results, as reported from HW-71895, provided a "free caustic" concentration as well as a pH and the two values seemingly do not match up, as hydroxide concentrations of 0.16 M and 0.22 M would equate to pH values of about 13.2 and 13.3, respectively. However, the values were entered into Table 5-47 exactly as they were reported in the monthly report with both a pH and a hydroxide concentration.

A sample to determine characteristics of tank farm nitrate was taken from tank SX-105 while the tank was being used as the nitrate feed tank to REDOX in January 1966 (ISO-708-DEL, p. G-4). The resulting analysis is shown in Table 5-47. This sample can be seen to match up reasonably well with the tank SX-113 sample, which provides greater confidence in the expected composition of the leachate for all nitrate leached tanks. As mentioned previously, the reported values for "free caustic" concentration and pH do not seem to match up, as a hydroxide

concentration of 0.52 M would equate to a pH of about 13.7. However, the values were entered into Table 5-47 exactly as they were reported in the monthly report with both a pH and a hydroxide concentration.

According to the August 1962 monthly report, a sludge sample was taken from tank SX-108 which would represent the waste composition at the time of leaching (HW-74804, *Chemical Processing Department Monthly Report For August, 1962*, p. G-6), but the results were not found in records. Tank SX-115 was also sampled in September 1964 which also would represent the waste composition at the time of leaching. Unfortunately, the compositional results from the sampling only contain data on radioactivity, specific gravity, and sodium hydroxide concentration (BNWL-CC-701, *Characterization of Subsurface Contamination in the SX Tank Farm*, p. 10).

5.5.7.3. PUREX Sludge Washing Supernatant Liquid

The following is excerpted from WHC-MR-0003. The PUREX sludge supernatant liquid (PSS) is the cesium-rich, aqueous leach solution resulting from the washing and settling of the PUREX sludge. It contains about 5-10% of the cesium stored in the underground tank. This solution was used to wash the slurry in the receiving tank after the sludge was hydraulically mined from the underground storage tanks for FP recovery (see Section 5.5.5). This washing step removed the soluble salts such as sodium nitrate, sodium nitrite, and sodium carbonate from the sludge, along with the small amount of cesium that was occluded in the sludge. This leach water was then recirculated to the underground storage tanks to be used in the mining operation. The composition of the PSS is given in Table 5-48.

Table 5-48. PUREX Sludge Supernatant (PSS) Liquid Waste Composition

Constituent	Molarity, M
Na^+	1.8-5.4
Al	0.005-0.04
Ba	0.013
CrO_4	0.002-0.004
SiO_2	0.005
OH^-	0.08-0.5
NO_3^-	0.9-4.2
NO_2^-	0.2-0.5
SO_4^-	0.25-0.4
Cl^-	0.002
CO_3^{-2}	0.24-0.7

Data taken from WHC-MR-0003, Table 2.5.

A sample of PSS from tank AX-103 was analyzed October 14, 1974 (WHC-SD-WM-ER-309) with the following results:

Constituent	M
$NaNO_3$	0.14
$NaNO_2$	1.36
Na_2SO_4	0.19
Na_2CO_3	0.40
$NaAlO_2$	0.022
NaOH	0.77
Na_3PO_4	0.013
Si	2.78E-4

The sample nitrite and hydroxide concentrations are higher and nitrate concentration is lower than the flowsheet values in Table 5-48.

Although not PSS, per se, water leach of the sludge in tank A-103 was performed during 1962-1963 with sample analyses showing the composition of the supernatant as a function of time (HW-77828). This supernatant might be considered comparable to PSS. After removal of the supernatant, six feet of hot water was added to tank A-103 in July 1962. Samples were collected periodically over the next 283 days. The composition as a function of time is shown below:

Sample No.	1	6	9	10	11	12
Height Above Sludge	36"	36"	36"	36"	40"	12"
Days After H_2O Add	10	52	127	232	283	283
Constituent						
Na^+, M	0.38	1.78	2.19	3.25	3.20	3.09
OH^-, M	0.11	0.16	--	--	1.06	1.02
NO_2^-, M	0.17	0.27	0.25	0.99	0.79	0.75
CO_3^{-2}, M	0.0017	0.25	--	--	--	--
NO_3^-, M	0.0040	0.70	0.74	0.56	0.72	0.67

5.5.8 Other 200 Area Process Facility Waste Types

The 200 Areas of the Hanford Site also included additional operations generating appreciable quantities of waste sent to SSTs. These operations include the PFP, decontamination processes from U Plant and T Plant, and pilot testing and demonstration and fission product separation at Hot Semiworks/Strontium Semiworks. Each of these three operations is described below in the context of operations and the possible link to common factors contributing to SST liner failure.

5.5.8.1. Plutonium Finishing Plant Waste (1973-1980)

In May 1973, discharge of high-risk PFP liquid waste to the soil column ended (ARH-CD-323). The PFP high-salt and low-salt acidic waste streams were combined in the 241-Z sump tanks and transferred to the 242-T Evaporator for neutralization and disposal within SSTs. The PFP waste was neutralized via mixing with existing SST waste from tank TX-118. Waste from the PFP was routinely concentrated at 242-T through the end of 242-T evaporator operation. After the end of

evaporation operations PFP waste continued to be neutralized by mixing with existing waste from tank TX-118 using the B-1 tank in 242-T. This continued to occur until PFP waste was no longer sent to SSTs.

Prior to the decision to transfer PFP waste to SSTs, an evaluation of alternative methods to deal with high-salt and low-salt waste (ARH-2292, *Liquid Waste Effluents from Plutonium Finishing Facility*) identified seven main streams/chemical additions that made up high-salt waste and five main streams that made up low-salt waste. The high-salt and low-salt waste streams generally contained nitric acid, aluminum and aluminum-fluoride compounds, metallic nitrates, sodium nitrate, and sodium sulfate. Report ARH-2292 provides an estimated composition for combined high-salt and low-salt waste before and after neutralization with caustic. The estimated composition before neutralization is:

HNO_3	417	g-mol/hr	0.621	M
$Al(NO_3)_3$	379	g-mol/hr	0.564	M
$AlF(NO_3)_2$	223	g-mol/hr	0.332	M
$Mg(NO_3)_2$	60	g-mol/hr	0.089	M
$Ca(NO_3)_2$	40	g-mol/hr	0.060	M
$Fe(NO_3)_3$	8	g-mol/hr	0.012	M
$NaNO_3$	71	g-mol/hr	0.106	M
KNO_3	27	g-mol/hr	0.040	M
Na_2SO_4	6	g-mol/hr	0.009	M
$UO_2(NO_3)_2$	0.25	g-mol/hr	0.0004	M
Flow	672	L/hr		

To neutralize the waste above would require 3049 g-mol/hr of NaOH. For discussion purposes, using 50 wt% NaOH (19 M) to neutralize the waste would require 160 L/hr caustic. The estimated composition after neutralization using 50 wt% caustic, assuming additive volumes, is:

$NaNO_3$	2295	g-mol/hr	2.76 M
$NaAlO_2$	602	g-mol/hr	0.72 M
NaF	223	g-mol/hr	0.27 M
$Mg(OH)_2$	60	g-mol/hr	0.07 M
$Ca(OH)_2$	40	g-mol/hr	0.05 M
$Fe(OH)_2$	8	g-mol/hr	0.01 M
KNO_3	27	g-mol/hr	0.03 M
Na_2SO_4	6	g-mol/hr	0.007 M
Flow	832	L/hr	

Report, ARH-CD-323, provides limited sample data on chemical composition and volume of the PFP waste generated and sent to tank D-5 (tank from which transfers were made to 242-T Evaporator) for batches of waste between August 1974 and October 1974. The minimum, average, and maximum molar concentration of hydronium ion, aluminum ion and fluoride ion during this time frame is:

	Minimum	Average	Maximum
H^+	0.047 M	0.251 M	0.875 M
Al^{+3}	0.0242 M	0.209 M	0.391 M
F^-	0.001 M	0.022 M	0.06 M

These concentrations are lower than estimated in ARH-2292 and show a smaller ratio of fluoride ion to aluminum ion.

The same report, ARH-CD-323, also provides an estimate of PFP waste composition and volume that is pumped to the 242-T Evaporator via the D-5 tank in 241-Z vault. Plutonium Finishing Plant performed several different operations that each generated different volumes and compositions of waste. Variation of flow rates and chemical composition are the major changes introduced by operating different processes. These processes can be separated into the following six modes:

- Button or nitrate feed
- Slag and crucible feed
- Scrap feed
- A-Line operation
- C-Line operation
- Incinerator operation

The estimated flow rate and composition of each of the six modes is listed below in Table 5-49.

Table 5-49. Estimated Tank D-5 Composition and Flow Rates by Plutonium Finishing Plant Operating Mode

Mode	Concentration, M										Flow
	H^+	Na^+	K^+	Al^{+3}	CO_3^{-2}	F^-	NO_3^-	$AlF(N0_3)_2$	AlF_2NO_3	OH^-	(gal/wk)
Button or Nitrate Feed	0.30	0.60	0.045	0.30	0.03	0.05	1.75	--	--	--	16,400
Slag and Crucible Feed[1]	0.30	0.60	0.09	0.30	0.03	0.05	1.75	--	--	--	16,400
Scrap Feed[2]	0.30	0.60	0.045	>0.30	0.03	>0.05	1.75	--	--	--	16,400
A-Line Operation	--	--	--	--	--	--	--	--	--	--	--
C-Line Operation[3]	2.8	--	--	--	--	--	2.8	1.23	1.23	--	2,700
Incinerator Operation[4]	0.05	0.8	--	--	--	--	0.8	--	--	--	536

Values taken from ARH-CD-323, Table III.

1 Slag and crucible feed also includes Fe^{+3}, Cr^{+3}, Ni^{+2}, Ca^{+2}, Mg^{+2} that totals to 0.5 M

2 Scrap feed is essentially the same as button or nitrate feed except for variation in Al^{+3}, Fe^{+3}, F^-, Cr^{+3} and Ni^{+2} concentrations, that will generally be higher and will vary as the scrap feedstock changes.

3 After May 1973 until 1980, C-Line operation only occurred during July and August 1973 so waste contribution was minimal (HNF-EP-0924, *History and Stabilization of the Plutonium Finishing Plant (PFP) Complex, Hanford Site*)

4 The incinerator did not operate after disposal of PFP waste to single-shell tanks (HNF-EP-0942).

Because the PFP waste is intimately mixed and quickly reacts with alkaline waste from tank TX-118 before entering a SST, it never enters a SST as a unique waste stream but in combination with whatever stream with which it is mixed. No corrosion data specific to neutralized PFP

waste or PFP waste in combination with alkaline tank waste has been found in available records. Compositional information for TX Farm tanks during the time that PFP waste was sent to SSTs is available in Section 5.5.6.4.

5.5.8.2. Decontamination Waste (1957-1976)

Little information is available for waste described as decontamination waste. From the completion of the uranium metal recovery operations in April 1957 until 1958, U Plant was the primary facility used for decontamination operations (HW-50089, and WHC-MR-0452, *A Brief History of the T Plant Facility at the Hanford Site*, Addendum 1). No description of decontamination operations at U Plant were found but the acid and caustic solutions remaining from uranium recovery were left in the storage tanks for use in decontamination operations (HW-50089). Starting in November 1957, waste described as "TBP" waste was sent from U Plant to tank TX-118 (HW54067, *Chemical Processing Department Waste Status Summary, November 1, 1957 – November 30, 1957*, HW-83906 C RD) although this was about seven months after U Plant was flushed of uranium. It is thought that this waste, described as being from U Plant, was likely decontamination waste. Waste from U Plant was sent to tank TX-118 until at least March 1960 (HW-64810, *Chemical Processing Department Waste Status Summary, March 1 – 31, 1960*). A portion of this waste was subsequently transferred to tank TY-104 in August 1959 (HW-61952, *Chemical Processing Department Waste Status Summary, August 1, 1959 – August 31, 1959*).

The following description comes from WHC-MR-0452, Addendum 1. In 1958 T Plant replaced U Plant as the center for decontamination in the 200 Areas. Highly contaminated items were decontaminated in the 221-T canyon while very large and less contaminated items were decontaminated in the 2706-T annex at T Plant. The decontamination operation carried out in T Plant involved several processes including flushing, sand blasting, steam blasting, pressure washing, and scrubbing. During the initial years at T Plant, decontamination usually began with a strong nitric acid flush followed by a caustic wash. The caustic wash could include sodium phosphate, boric acid, EDTA, sodium dichromate, sodium tartrate or sodium citrate in addition to sodium hydroxide. Early on decontamination solutions were sent to soil cribs. The EDTA and tartrate adversely affected adsorption of the rinsate materials on the soil column. High-pressure sprays at times used 1,1,1-trichloroethane or perchloroethylene and detergents that were generally chloride based. By the mid-1960s, commercially prepared and trademarked chemical mixtures had replaced most of the simpler chemicals used earlier. Many of the commercial products were based on oxalic acid, phosphates, nitric acid-ferrous ammonium sulfate combinations, potassium permanganate and sodium bisulfate, with some unknown additives. No specific compositional information was found for decontamination waste.

A waste transfer sent to tank T-111 in December 1959 is identified as being from T Plant without identifying the waste as decontamination waste (HW-63559, *Chemical Processing Department Waste Status Summary December 1-31, 1959*). It is thought this waste was decontamination waste. Subsequently in March 1960 a transfer was made from T Plant to tank T-112 without being identified as decontamination waste, although it is likely that it was (HW-64810). These wastes are identified as being pumped from T Plant to tank T-111 (or tank T-112) and then pumped from tank T-112 to a crib. This waste is assumed to be quite low in radioactivity to

allow cribbing of the cascaded waste. According to waste status summary reports, the first waste identified as decontamination waste from T Plant was sent to the tank farms during January 1961 as a transfer from T Plant to tank TX-118 (HW-83906 D RD, HW-71610). Some of the waste sent to tank TX-118 was subsequently transferred to tanks TY-103, TY-104 and TX-108 (HW-83906 D RD, HW-72625, *Chemical Processing Department – Waste Status Summary*, RL-SEP-260, *Chemical Processing Department Waste Status Summary, July 1, 1964 through December 31, 1964*). Waste from T Plant was subsequently transferred to tank U-107. The waste transfer summary reports are not clear on how long waste is transferred from T Plant to the SSTs but it is at least midway through 1976.

Waste sent to tank TX-118, unless subsequently transferred out of the tank, would be fed to the 242-T evaporator which concentrated dilute wastes between 1965 and 1976. Discussion of the 242-T evaporator and the associated waste is discussed in Section 5.5.6.4. Waste sent to tank U-107 would be transferred to a number of tanks but generally ended up in tank S-102, the feed tank to the 242-S Evaporator/Crystallizer. Discussion of the 242-S Evaporator/Crystallizer and the associated waste concentrated there is discussed in Section 5.5.6.7.

5.5.8.3. Hot Semiworks/Strontium Semiworks (1953-1967)

The description of the Hot Semiworks/Strontium Semiworks in this section is taken from RPP-RPT-23177 (unless otherwise referenced) which provides operational details based on reference sources contemporary to those operations. The Hot Semiworks was constructed in the 200 East Area in 1951-1952 as a research and test facility for the REDOX and TBP Plant chemical separations processes. Original operation of the facility from November 1952 to October 1953 was as a pilot facility researching and demonstrating REDOX separations processes. The radioactive waste from the REDOX process research test runs was concentrated and transferred to TK-70 (or CX-70) at the Hot Semiworks 241-CX tank farm facilities. The waste in TK-70 was eventually retrieved and transferred to DST AW-105. Monthly waste status summary reports from May 1953 (HW-28377, *Separations Section Waste Status Summary, May 31, 1953*) to September 1954 (HW-33396) identify that miscellaneous waste from TBP and Hot Semiworks were designated to be sent to tanks BY-111 and BY-112 via cascade. During this time tank BY-111 was full and tank BY-112 was partially full but did not see any increase in volume. Rather the volume reading for tank BY-112 was 6,000 gal less in September 1953 (HW-29624, *Separations Section, Waste – Status Summary*) than in August 1953 (HW-29242) and was otherwise unchanged, indicating no waste receipts in these tanks over this time period. The waste from Hot Semiworks during REDOX process research and demonstration will not be considered as a contributing factor to liner failure.

The facility was modified in 1953 and operated from May 1955 through March 1956 as a research and demonstration facility for the PUREX separations process. After PUREX process research and development activities, the facility underwent a maintenance program and then placed in standby in July 1957. Radioactive wastes from the PUREX process research test runs were concentrated and transferred to tanks C-201 through C-204. The waste in these four tanks was eventually transferred to either tanks C-104 or C-109. None of the C Farm, 200-Series tanks or tanks C-104 or C-109 have probable tank liner failures. The waste from Hot Semiworks

during PUREX process research and demonstration will not be considered as a contributing factor to liner failure.

The Hot Semiworks was reactivated in 1961, renamed Strontium Semiworks, and used until 1967 to separate fission products from various high-level waste solutions. The modifications made to the facility included incorporating solvent extraction and ion exchange columns for demonstrating strontium purification processing. From May 1961 to October 1961, strontium separation was demonstrated for PUREX waste. The Strontium Semiworks along with B Plant, PUREX head-end, and 244-CR vault were used from 1961 to 1967 to separate strontium-90, cesium-137, cerium-144, and promethium-147 from various waste solutions. Solvent extraction equipment was operated under various flowsheet conditions to purify separate batches of strontium-90, cerium-144, and promethium-147. The Strontium Semiworks was also used, in conjunction with the 801-C cask station, to demonstrate separation of technetium-99 from alkaline high-level waste solutions in two different campaigns. Additionally, the installed solvent extraction equipment was used to purify a solution containing a mixture of americium, cerium, and rare earths originally from the REDOX facility. Tanks C-107, C-108, C-109, C-111, and C-112 all received highly radioactive waste solutions from the Strontium Semiworks from 1961 through 1967. None of these C Farm tanks have probable tank liner failures.

The only available corrosion data found for any of the waste generated from the Hot Semiworks or Strontium Semiworks was from a monthly activities report for the Hanford laboratories operation (HW-70165, *Hanford Laboratories Operation Monthly Activities Report, June, 1961*, p. C-8).

> *Corrosion rates were determined for 1020 mild steel exposed to simulated HSW waste from strontium recovery operations. Liquid phase corrosion rates (at 80 C and boiling) were less than 0.1 mil/m in highly alkaline wastes (pH 11.2). However, in simulated wastes at pH 7, the liquid phase rate at 80 C was 5.6 mils/mo. In another test, the waste was made 0.25 M in sodium carbonate and adjusted to pH 7 (simulating reduction of pH of an alkaline waste by generation of carbon dioxide). Corrosion of 1020 steel in this waste at 80 C was 10 mils/mo. These results emphasize the need to keep these wastes strongly alkaline to counteract possible reduction of pH due to radiolytic decomposition of organic material present.*

The waste from Hot Semiworks during fission product recovery will not be considered as a contributing factor to liner failure.

5.5.9 Miscellaneous Waste Types

A number of other miscellaneous waste types and additions were made to various SSTs over their operational lifetime. These wastes and additions are discussed below.

Miscellaneous Radioactive Wastes

Some of the larger miscellaneous waste streams include Battelle-Northwest waste (BNW), Hanford Laboratories waste (HLO) or 222-S Laboratory waste (LW), and 100-N Area waste (N). The BNW and HLO or LW wastes would be expected to vary greatly in composition and concentration of constituents depending on the specific operations or analytical procedures being performed at any time. The 100-N Area waste stream is thought to be approximated by a description of phosphate/sulfate waste generated at N Reactor as described in PNL-6152, *Long-Term Performance Assessment of Grouted Phosphate/Sulfate Waste from N Reactor Operations*. The waste described in that report is composed of three waste streams that originate at the N Reactor of the Hanford Site. The three streams are phosphate waste, sulfate waste, and sandfilter backwash. The phosphate waste is produced during periodic reactor decontamination using a commercial decontamination agent that contain phosphoric acid, citric acid, and trace amounts of other chemicals. The resulting waste is a dilute aqueous solution of trisodium phosphate and citrate containing trace amounts of inorganic chemicals and radioactive elements. Sulfate waste comes from sulfuric acid used to regenerate cation ion-exchange resins and sodium hydroxide used to regenerate anion ion-exchange resins. These resins are used to remove radionuclides from recirculated fuel storage basin water. The sulfuric acid, sodium hydroxide, and rinse water are combined to form dilute sodium sulfate solution that is adjusted to a pH of 12. The fuel storage basin water cleanup also includes a sandfilter that is periodically backflushed to remove entrained solids. Flushing of the sandfilter forms a dilute slurry.

Miscellaneous wastes would be mixed with other waste types in tanks and because of their dilute nature would typically end up being concentrated in any of the various waste evaporators used to reduce waste volume in the SSTs (see Section 5.5.6). Considering that these miscellaneous wastes were not stored in dedicated waste storage tanks and would generally undergo concentration along with other wastes, it is extremely difficult to assess the impact of these miscellaneous waste streams in terms of SST liner failures. Miscellaneous radioactive wastes will not be considered as a contributing factor to liner failure.

Miscellaneous Non-Radioactive Additions

Portland cement was added to tank BY-105, receiver tank for ITS-1 operation, in an attempt to prevent a liquid phase from separating as the tank contents cooled and solidified. Portland cement was added in the ratio of 1.1 lbs cement per gal of concentrated waste (ISO-610 DEL). However, inaccurate measurement of sludge level and hence residual liquid in tank BY-105 prior to transfer of the ITS concentrate resulted in the transferred concentrate not fully solidifying upon cooling (ISO-642-DEL). Portland cement in contact with water creates an alkaline solution that is generally not harmful to carbon steel.

Diatomaceous earth additions were made to six SSTs (ARH-CD-222, *Characterization of the Effects of Diatomaceous Earth Additions to Hanford Wastes*). Initially, a technique was needed to immobilize a liquid heel in a tank which could not be removed by then-existing pumping techniques (i.e., turbine pump with floating suction) which left several inches of liquid supernatant in the waste storage tank. Methods were developed to accomplish the in-situ adsorption of the supernatant liquid and the process was demonstrated on two tanks containing saltcake (tank TX-116 and TX-117) in late 1970 and early 1971. The process was also applied to

four known or suspected leaking tanks containing sludge (tanks BX-102, TY-106, SX-113 and U-104) during the first half of 1972. Since that time pumping from screened saltwells was developed to remove supernatant and drainable interstitial liquid. Diatomaceous earth is 92.3 wt% silicon dioxide, 1.1 wt% aluminum oxide, 2.0 wt% ferric oxide, 0.9 wt% calcium oxide, and 0.4 wt% magnesium oxide with 3.1 wt% loss on ignition. Primarily two chemical reactions may occur when waste liquor reacts with diatomaceous earth. The first is between sodium aluminate and silica

$$NaAlO_2 + SiO_2 + 0.7H_2O \rightarrow NaAlSiO_4 \cdot 0.7H_2O$$

and the second is between sodium hydroxide and silica

$$2NaOH + SiO_2 \rightarrow Na_2SiO_3 + H_2O$$

The product of the first reaction is cancrinite and the second is sodium silicate. Sodium silicate solution is used in some applications as a corrosion inhibitor.

5.5.10 Operational Service

During the 1990's waste transaction summaries were prepared for the purpose of estimating tank chemical and radionuclide inventories (WHC-SD-WM-TI-615, Rev 1, *Waste Status and Transaction Record Summary for the Northeast Quadrant of the Hanford 200 Area*). This effort included a review of tank receipt, transfer and discharge transactions to derive a list of qualified fill records. That derivation resulted in among other things a tabulation of the "total traffic" for each SST. Document WHC-SD-WM-TI-615 describes total traffic as, "The volume in kgal of all xins from processes and rec[eipt]'s from other tanks for each tank throughout its history." The term xins was defined in that document as the addition of primary waste from a plant and includes waste returning from secondary processing operations. The total traffic or volumetric throughput for each SST as reported in WHC-SD-WM-TI-615 is tabulated below in Table 5-50.

Table 5-50. Single-Shell Tank Total Waste Volumetric Throughput

Tank	Total Traffic (kgal)	Tank	Total Traffic (kgal)	Tank	Total Traffic (kgal)	Tank	Total Traffic (kgal)
A-101	20479	BY-101	9472	SX-101	10865	TX-101	19881
A-102	70773	BY-102	21730	SX-102	14271	TX-102	7942
A-103	18113	BY-103	26540	SX-103	7772	TX-103	8324
A-104	18472	BY-104	6359	SX-104	7320	TX-104	4910
A-105	5978	BY-105	7527	SX-105	10357	TX-105	9026
A-106	38259	BY-106	10928	SX-106	31229	TX-106	9929
AX-101	14992	BY-107	13767	SX-107	4387	TX-107	4992
AX-102	11617	BY-108	13354	SX-108	4696	TX-108	4968
AX-103	14636	BY-109	33344	SX-109	2894	TX-109	6650
AX-104	5887	BY-110	11919	SX-110	7146	TX-110	6789
B-101	8196	BY-111	10878	SX-111	6219	TX-111	3992
B-102	4150	BY-112	38966	SX-112	3792	TX-112	4008
B-103	11644	C-101	4216	SX-113	724	TX-113	5942
B-104	3988	C-102	19621	SX-114	7926	TX-114	4871
B-105	7013	C-103	10317	SX-115	2044	TX-115	6934
B-106	17459	C-104	25704	T-101	6378	TX-116	4129
B-107	4254	C-105	27117	T-102	3128	TX-117	8395
B-108	5003	C-106	11221	T-103	5192	TX-118	78553
B-109	4911	C-107	4374	T-104	3460	TY-101	4195
B-110	8386	C-108	6745	T-105	5870	TY-102	1934
B-111	8764	C-109	4980	T-106	3192	TY-103	13345
B-112	8801	C-110	3730	T-107	4729	TY-104	4291
B-201	59	C-111	6023	T-108	3833	TY-105	6237
B-202	270	C-112	6791	T-109	2465	TY-106	5053
B-203	317	C-201	277	T-110	22535	U-101	5238
B-204	372	C-202	264	T-111	21953	U-102	7049
BX-101	27709	C-203	200	T-112	25206	U-103	9806
BX-102	10161	C-204	252	T-201	55	U-104	3544
BX-103	35868	S-101	11543	T-202	118	U-105	5770
BX-104	28571	S-102	80822	T-203	173	U-106	4705
BX-105	13140	S-103	13511	T-204	55	U-107	17346
BX-106	16205	S-104	3497			U-108	8737
BX-107	2368	S-105	1990			U-109	6196
BX-108	2740	S-106	1735			U-110	4112
BX-109	7599	S-107	17873			U-111	9540
BX-110	3014	S-108	3951			U-112	1004
BX-111	3122	S-109	3622			U-201	49
BX-112	1213	S-110	15389			U-202	51
		S-111	3983			U-203	46
		S-112	3165			U-204	15

Data taken from WHC-SD-WM-TI-615, Rev. 1, Table 3a.
Tanks highlighted in red are tanks with probable liner failures.

5.6 TANK EXTERNAL ENVIRONMENT

Of the mechanisms external to the tank liner that have been considered, only pressurization external to the tank liner is considered a potentially likely contributing factor to liner failure.

Historical information regarding external pressurization and tank liner bulges is presented in the subsection below.

5.6.1 Pressurization External to Tank Liner

An external pressure source acting on the tank bottom liner could impart a significant force on the steel plate resulting in increased stresses and temporary or permanent deformation of the liner. An external pressurization could occur if vapor or gas was trapped such that it could not escape or escape at a rate quickly enough to eliminate pressurization resulting in a liner bulge. For clarification, liner bulging from external pressurization as discussed in this section of the report is different than the small discontinuous ripples of probably less than a few inches in height observed during construction. Bulging is typically indicated by the degree of bottom liner uplift of more than several inches over a relatively larger area after the tank is filled or partially filled. A bulge in a tank liner may result in the direct failure of the liner or cause enough stress or other effects on the steel liner plates and welds that they become more susceptible to the effects of corrosion. Experience indicates that bulging tends to be a dynamic phenomenon, and it is possible that a tank with no measured bulge at one point in time may actually have had a displaced liner that was not detected at another time. This makes identifying tanks with liner bulges difficult.

An external pressure source acting on the tank bottom liner from vapor or gas requires three factors to allow pressurization to occur: a source of water or a substance with a substantial vapor pressure underneath the liner; temperature to support vapor or gas formation; and, sealing or trapping the formed gas or vapor. Under a given hydrostatic head, liquid water will vaporize at the saturation temperature. The initial recommended limitation for waste temperatures in self-boiling tanks was 250°F in order to prevent bulging of the tank bottom liner (HW-59919, p 7). High temperature of the liner could release excess or even bound water for the grout cap directly below the liner. Heating of the tank above this temperature was to be delayed for as long as possible to allow depletion of the moisture from the grout. This temperature limitation assumes that the moisture will not remain sealed or trapped between the liner and the concrete but rather find a way out over time. A tight fit of the liner in the concrete would limit means of vapor escape around the liner, causing pressure upwards on the bottom of the tank. A faster rate of temperature rise in the waste could cause expansion of the steel liner before the concrete wall expands forcing a tighter fit between the two. The rounded bottom knuckle in Type I, II and III tanks may have allowed for an easier path for vapor to escape around the liner, unlike the flat bottom tanks (SX and A Farms) that do not allow for easy vapor escape. The bottom plate in these designs is completely captured between the concrete basemat and wall (see Figure 5-9 and Figure 5-10). In addition, the SX Farm design for the top of the liner resulted in a seal between the exterior of the liner and the concrete wall, as shown in Figure 5-54. This did not allow for any communication between the exterior of the tank liner and the interior of the tank liner.

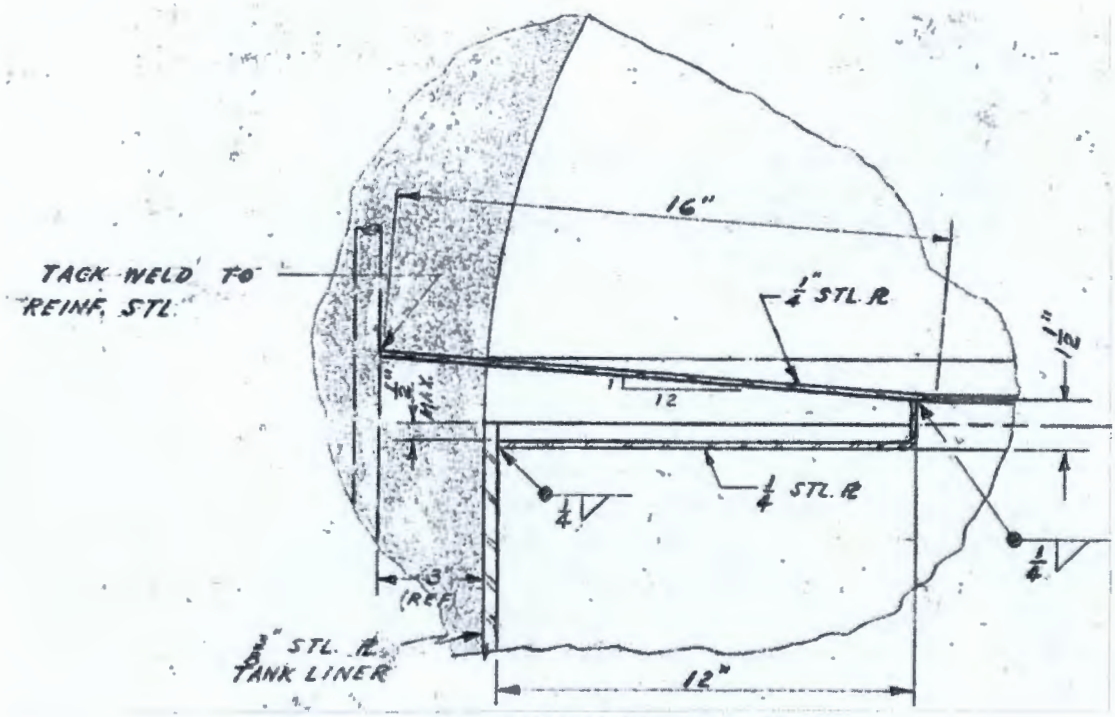


Figure 5-54. 241-SX Tank Liner Top Design

With the exception of tank U-104, known bulging liners have only occurred in SSTs in SX and A Farms, both of which received boiling waste. AX Farm also received boiling waste but there was no indication of bulging tank bottom liners in this tank farm. In AX Farm, the tanks had channels underneath the bottom tank liner and these channels provided an exit path for gases and vapors that may have formed under the liner. It has been reported that upon warming of tank AX-104 over 800 gal of liquid were collected from the installed drainage laterals under the tank (ARH-76, *Design Considerations for the 241-AY Tank Farm*, p 7). Table 5-51 provides a tabulation of the information related to possible liner bulges in 241-SX and 241-A Farms and tank U-104. The majority of the information in the table comes from the leak cause and location reports for 241-SX (RPP-RPT-54910), 241-A (RPP-RPT-54912), and 241-U (RPP-RPT-54915) tank farms. Leak cause and location reports for other tanks and tank farms indicate liner bulging was not found in any other tanks investigated. Photos of tank U-112 in RPP-RPT-54915 show ridges in solids on the tank bottom that seem to follow weld lines. Although ridges along the weld line could result in increased stress, the cause likely would be from fabrication rather than external pressurization and is not addressed here.

Table 5-51. Indications of Possible Bulged Liners for Select Single-Shell Tanks

Tank	Indications of Possible Bulged Liner					Tank Failed	Source
	Photo shows bulge	Bottom Depth Sounding	Tilted ALC	Broken ALC Guy Rod	Bent Pipe		
SX-101	Not Inspected	Unknown	N/A	N/A	No	No	SX-101 photo mosaic 3-10-89
SX-102	Not Inspected	Unknown	N/A	N/A	No	No	SX-102 photo mosaic 1-7-88
SX-103	Not Inspected	Unknown	N/A	N/A	No	No	SX-103 photo mosaic 12-17-87
SX-104	Not Inspected	Unknown	N/A	N/A	No	No	SX-104 photo mosaic 9-8-88
SX-105	Not Inspected	Unknown	No	N/A	No	No	SX-105 photo mosaic 6-15-88
SX-106	Not Inspected	Unknown	N/A	N/A	No	No	SX-106 photo mosaic, 6-1-89
SX-107[1]	No	No	No	Yes	No	Yes	RPP-RPT-54910
SX-108	No	Yes, +2.5 ft	No	Yes	Yes	Yes	RPP-RPT-54910
SX-109	No	No	No	No	Yes	Yes	RPP-RPT-54910
SX-110	No	No	No	Yes	Yes	No	Photo 763161-28CN, 776538-6CN
SX-111	No	No	No	Yes	Yes	Yes	RPP-RPT-54910
SX-112[2]	No	No	No	Yes	Yes	Yes	RPP-RPT-54910
SX-113	No	Yes,+4 ft	No	Yes	No	Yes	RPP-RPT-54910
SX-114	No	No	No	Yes	No	Yes	RPP-RPT-54910
SX-115	No	Yes, +0.25 ft	No	Yes	Yes	Yes	RPP-RPT-54910
A-101	No	Unknown	No	Yes	No	No	Photo 7510221-18CN, 19CN, 20CN,
A-102	No, Localized Distortions	Unknown	No	Yes	Yes	No	Photos 770225-24CN, 768029-7CN, 768029-9CN
A-103	No, Localized Distortions	No	No	Yes	No	No	770807-1CN, 7611266-24CN
A-104	No	No	No	Yes	Yes	Yes	RPP-RPT-54912, 8604129-15CN, 16CN
A-105	Yes	Yes, +8.5 ft	Yes	Yes	Yes	Yes	RPP-RPT-54912, Photo 8605560-28CN
A-106	No	No	No	Yes	No	No	Photo 92352-19CN
U-104	Yes	Yes, +5 ft	N/A	N/A	No	Yes	RPP-RPT-54915

[1] Documentation regarding a bulge in SX-107 is conflicting. RHO-R-39 and ARH-R-43 state a bulge was found. Monthly report ARH-1100 identifies the presence of a bent piping. Monthly report ARH-1105, five months later, identified that liner and sludge elevations in SX-107 indicate no bulge existed at that time. A review of photographs documented in RPP-RPT-54910 showed, "There were no photographs that indicated the presence of bent piping as stated in ARH-1100." Based on this information, no primary indication of a liner bulge exists.

[2] Historical documentation regarding a bulge in SX-112 is inconclusive. RHO-R-39 and ARH-R-43 state a bulge was found. ARH-R-43 states that thermocouples were installed and the tank bottom was mapped after a significant liquid level drop in the tank. Documentation of the results of the tank bottom mapping could not be found. Monthly report ARH-1100 reported that photographs were taken that "…showed twisted and broken pipes and equipment…". Based on this information, no primary indication of a liner bulge exists.

Photos showing a bulge or bottom depth soundings with positive displacement of a tank bottom are primary indications (i.e., direct physical evidence) of a bulging liner bottom. Tilted ALCs, broken guy rods on ALCs, and bent piping are secondary indications (i.e., inferred evidence, effects could have been caused by other factors) of a bulging liner bottom. Eleven tanks have only secondary indication of possible bulged bottom liner: SX-107, SX-109, SX-110, SX-111, SX-112, SX-114, A-101, A-102, A-103, A-104, and A-106. Five tanks are known to have bulged liners based on a primary indication: U-104, SX-108, SX-113, SX-115, and A-105. For these five tanks with known liner bulges, a more descriptive history of the liner bulging is presented.

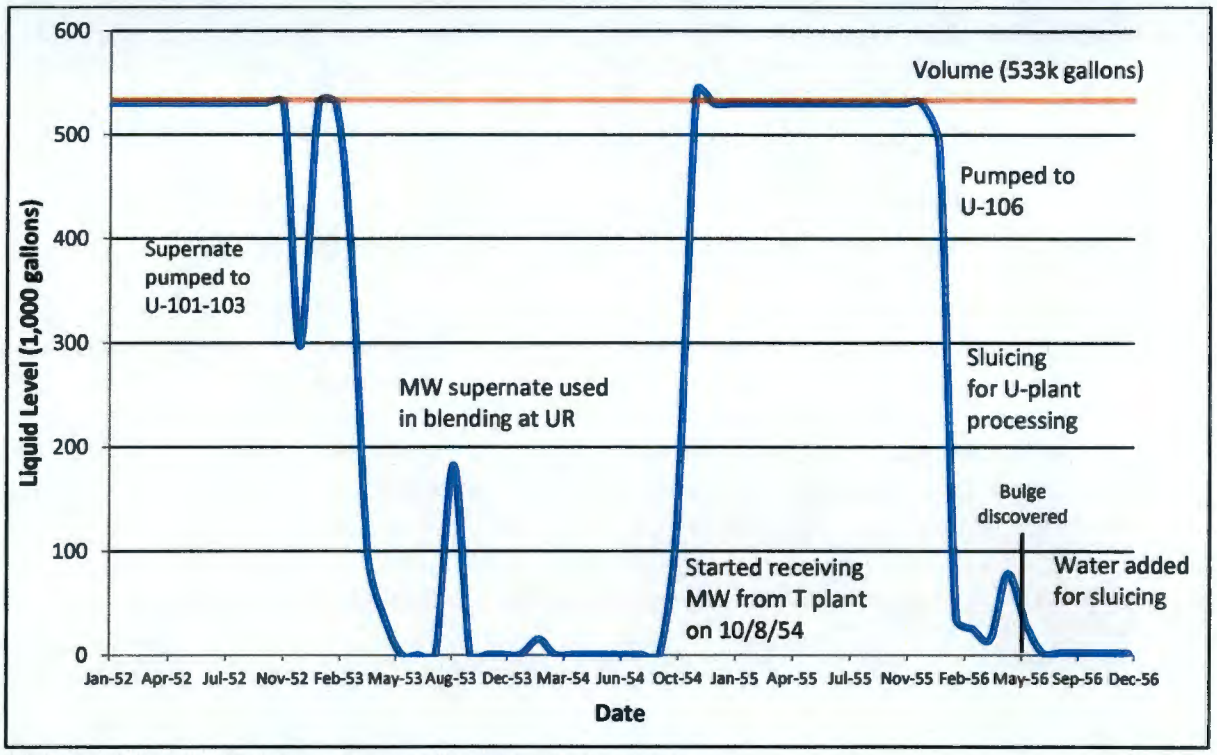
5.6.1.1. Tank 241-U-104

Tank U-104 was first filled with metal waste from the $BiPO_4$ process in July 1947 and was filled by December 1947 (WHC-MR-0132). The waste remained in the tank until 1953 when the waste was sluiced for uranium metal recovery at the TBP Plant. The tank was empty until filled again with metal waste between October 8 and November 11, 1954 (HW-33544 and HW-33904, *Separations Section, Waste – Status Summary for November 1954*). Waste was pumped from tank U-104 to U-106 in January 1956 and sluicing began during February 1956 (HW-41038, *Separations Section, Waste – Status Summary for January 1956*, and HW-41812). A document on the history of tank U-104 (Bayless to Roberts, "History of the 104-U Tank", February 9, 1961) identifies that sluicing was discontinued on May 3, 1956 and the following day attempts were made to install a heel jet in the tank but the assembly was approximately 3 ft too long. This could be an indication of the presence of a bulge. Bayless identifies inspections were done between May 4 and July 30, 1956 revealing a bulge, but this author could find no other documentation to corroborate inspections other than the information presented in the following paragraph.

Sluicing of tank U-104 for uranium metal recovery restarted on the 4-12 shift, July 5, 1956 (HW-44024-RD, *Weekly Summary 6/29/56 to 7/6/56*). Operations were discontinued at 1:00 AM the next morning when acidic solution similar to feed overflowed onto the ground from the UR-151 diversion box (HW-44024-RD, *Weekly Summary 6/29/56 to 7/6/56*). The U-104 tank was water-sluiced for an hour each shift until normal sluicing was resumed July 10 (HW-44024-RD, *Weekly Summary 7/6/56 to 7/13/56*). The following week, "The 104-U tank was sluiced for only a short time…(because) there appears to be a leak in the 104-U tank so sluicing operations have been suspended while this is being investigated" (HW-44024-RD, *Weekly Summary 7/13/56 to 7/20/56*). On July 26, a periscope was installed in the tank to allow inspection of the tank (HW-44024-RD, *Weekly Summary 7/20/56 to 7/27/56*) and "…inspections of the tank revealed a definite bulge in the center of the tank and what appeared to be a split in the steel plates of the bulged portion" (HW-44024-RD, *Weekly Summary 7/27/56 to 8/3/56*). "On August 15th photographs were taken of the interior of the 104-U tank for Engineering studies of the bottom bulge. Electrodes have been installed at both ends of the tank and reference points established in an effort to determine if a leak is actually present" (HW-44024-RD, *Weekly Summary 8/10/56 to 8/17/56*). "Photographs of the 104-U tank…indicate that the bottom of the tank is bulged in several places but that there are also several low spots in the center of the tank. No rupture or crack is evident from the pictures

received" (HW-44024-RD, *Weekly Summary 8/17/56 to 8/24/56*). During the week of August 24-31, "Investigation of the leakage of the 104-U tank was continued. Water was added to the tank and electrode readings taken each shift. No decrease in level was noted" (HW-44024-RD, *Weekly Summary 8/24/56 to 8/31/56*).

Figure 5-55, below, shows the liquid level and operations pertaining to tank U-104 from April 1952 to December 1956.



*Referenced from the *Waste Status Summary Separations Sections* reports.

Figure 5-55. Plot of Liquid Levels in Tank U-104 Prior to Bulge

The Separations Technology section's monthly report for August 1956 state that the mild steel liner is buckled upward (HW-45115 H, *Separations Technology Section Monthly Report-August 1956*). "Electrode measurements indicate that the center of the tank is approximately five feet higher than it should be. The photographs do not show that the liner is ruptured; however, about one-half of the tank surface is covered with liquid and could not be observed" (HW-45115-H, p. Fc-14 and Fc-15).

Temperature data is not available during the time of the second sluicing of tank U-104. However, some temperature data is available for other tanks containing metal waste. Figure 5-24 and Figure 5-25 show waste temperatures for tanks containing metal waste. The first tank in a cascade (such as tanks U-101, U-104 or TX-101) has higher temperatures than downstream tanks in the cascade. The peak temperature occurred roughly one year or a little longer after filling (tank U-104 was about 8 months, TX-101 was about 20 months, and BX-101 was about 19 months). The peak recorded temperature found in searched records for the first tank of a metal

waste cascade was 216°F in tank BX-101. The supernatant liquid was removed from tank U-104 approximately 14 months after being filled, which is about the point in time one would expect near-peak temperatures within the waste. With the reduction in hydrostatic head, by pumping off the supernatant liquid in January 1956 prior to sluicing, the required partial pressure to overcome the hydrostatic head would have been significantly lower. At the end of February 1956, tank U-104 contained 35,000 gal of waste (HW-41812) which would be equivalent to roughly 8 in. above the bottom of the knuckle or 20 in. of total waste. At a temperature of 216°F the partial pressure of water is about 1.07 atm or 30 in. of water gauge. So one could postulate that the reduced hydrostatic head in combination with high temperature of the waste could have led to a condition where water under the liner was vaporized resulting in bulging of the liner. However, no direct data is available (actual waste level, waste density, waste temperature, or liner temperature) to corroborate this postulate. No other plausible postulates have been identified.

This postulate was also put forth in a 1959 document, HW-59919, regarding limitations for storing waste from separations plants in existing storage tanks. That report stated

> *The instability of the bottoms of the 113-SX and the 104-U tank is postulated to have been caused by vaporization of moisture present in the two-inch layer of grout trapped between the steel liner and the asphaltic membrane. When this vaporization pressure, caused by elevated temperature, beneath the liner exceeds the hydrostatic load on the liner, there is a possibility for the liner to become unstable and to deform upward developing a reversed dish gas dome when the moisture vaporizes.*

5.6.1.2. Tank 241-SX-108

Tank SX-108 was constructed from 1953 to 1954 and started receiving REDOX concentrated and neutralized salt waste on November 8, 1955 (RHO-R-39). Like all other SX Farm tanks (except tanks SX-107, SX-109, SX-110 and SX-115) tank SX-108 was not preheated or pre-filled with a liquid heel prior to use (RHO-R-39). On or about November 17, 1955 the waste temperature in tank SX-108 was about 110°F and by December 15 the waste temperature was about 210°F, equivalent to a 3.6°F/day temperature rise (see RPP-RPT-58371). Between January 4 and 11, 1956 the temperature of the waste in tank SX-108 increased from 216°F to 248°F or a 4.6°F/day temperature rise (see RPP-RPT-58371). The waste temperature stabilized (only gradual increase) beyond this point indicating concentration of the waste and self-boiling. At the end of January 1956, the liquid volume in the tank was 554,000 gal (HW-41038). The tank continued to receive REDOX concentrated and neutralized salt waste and condensate from SX-106 as the waste continued to boil and self-concentrate (WHC-MR-0132).

The following description is from WHC-MR-0300.

> *The tank was pumped out in... 1962, following standard practices for tank farm operation. Water was used to dissolve sodium nitrate from the residual solids, allowing the dissolved nitrate to be recycled to the Redox process. The tank was refilled in 1963, on its normal operation schedule.*

The first indications of a possible leak in Tank SX-108 were recorded in December 1962 when minor levels of radiation were detected in two laterals. Further monitoring detected no increase and the tank was kept in service.

Increased radiation was detected in the laterals in August 1964,...By December 1965, however, the lateral readings had leveled off. The tank had also been isolated and operated on total reflux to allow observation of the liquid level in the tank; no leakage could be detected in this manner, within the accuracy of the readings.

In March 1967, because of renewed activity in the laterals, Tank SX-108 was declared leaking. The supernatant liquor was pumped out, and the tank was taken out of service. No further transfers of liquids were made, in or out. When cooling was required, an induced-draft ventilation system was provided.

The September 1967 monthly report for 200 Areas operations (ARH-59-DEL, *Monthly Report – 200 Areas Operation, September 1967*) identifies that in an effort to increase knowledge about the sludge characteristics, eight, 2-in. holes were drilled through the tank dome to map the sludge level, tank sludge samples and measure temperatures. When thermocouple probes were installed in the new 2-in. inspection risers, it was found that six of the probes rested on the liner above its expected elevation and the maximum liner rise that was detected was about 2 ½ ft., in the northeast quadrant. The report postulates, "Additionally, the sludge contour pattern does not match the contour of the bulged liner, thus indicating the upheaval is of sufficient age to allow a complete redistribution of the sludge." The October 1967 monthly report for 200 Area operations (ARH-60-DEL) describes photographs taken in tank SX-108 confirming the location of the bulged bottom as indicated by skewing of pipes and raised circulators.

5.6.1.3. Tank 241-SX-113

Tank SX-113 was constructed from 1953 to 1954 and started receiving REDOX concentrated and neutralized salt waste on February 20, 1958 (HW-57249, *Interim Report on Displacement of the REDOX 113-SX Waste Storage Tank Liner*). Tanks receiving boiling waste before and including SX-113 were not preheated prior to use (RHO-R-39). With the exception of tank A-104, tanks receiving boiling waste after tank SX-113 were preheated prior to use to minimize heat transfer stresses.

After initially receiving waste, thermocouple temperatures rose from 42°F (ambient air inside the tank) on February 26, 1958 to ~155°F one week later on March 5, 1958 (RHO-CD-1172, *Survey of the Single-Shell Tank Thermal Histories*). Tank SX-113 received approximately 483 kgal of REDOX HLW through June 2, 1958 with continuous self-boiling commencing April 22, 1958 (HW-57249 page 4). From HW-57249,

During the initial filling of the 113-SX tank, started on February 20, 1958, it was observed that the volume received in the tank exceeded slightly the volume sent, a condition not uncommon where interchange of water vapor is possible. Attempts, on May 28, 1958, to install an experimental, replaceable air-lift circulator in the newly-activated 113-SX storage tank failed when the circulator encountered an

obstruction. Subsequent soundings through several nearby openings in the tank indicated the steel lining of the tank to be elevated to a height greater than four feet above its original position. Measurements in several other tanks in the SX farm revealed no similar abnormality. Routing of waste to the 113-SX tank was terminated on June 2, 1958. During a seven-day period starting June 11, 1958, the liner returned to its original position with an apparent net loss in volume of approximately 63,000 gallons. The volume remaining following the collapse of the liner, however, was in good agreement with the volume sent, indicating the liner was probably intact.

It should be pointed out that a small rupture or crack in the liner which only passed a small amount of waste could have been present without being noticed.

An interim report on displacement of the tank SX-113 liner (HW-57249) stated that the tank liner returned to its original position between June 11 and June 18, 1958. At this time the measured waste temperature increased from 231°F to 236°F and the measured waste height decreased from 13 ft 11 in. to 11 ft 5½ in. The return of the liner to its position wasn't due to a reduction in partial pressure of water (temperature increased not decreased) or an increase in counteracting hydrostatic head (liquid level decreased not increased and no waste was added). The most likely explanation is that a buildup of pressure on the underneath of the liner was either relieved through some vent path in the liner or concrete surrounding the liner.

In response to bulging of the bottom liner upward away from the concrete foundation in tank SX-113, report HW-57274 was prepared to explain the likely phenomenon causing the bulging. It was postulated that the cause was trapped gas below the liner that pressurized causing the liner to dish upward. The report goes on to state, "It is possible that the reason the phenomenon of dishing was not observed previously on other tanks, may be that this was the first tank in which the junction between the concrete shell and steel liner was vapor tight…"

Some possible explanations for the receding of the bulge in tank SX-113, and possibly other tanks were described by L.E. Brownell. As strain on the bottom of the tank increased, vapor could have been released suddenly, causing the steel liner return to rest on the concrete bottom. Bending stresses would have produced large plastic strains, leading to the failure of the weld at the junction of the steel shell and bottom liner. As explained earlier, fillet welds used in SX Farm and A Farms would have been more susceptible to failure under large strains.

Welding inspector, F.H. Waldrep, stated that in his opinion, part of the bottom joint would be expected to fail if the bottom liner was raised to a height of 4 ft. The rupture of a weld would allow for the vapor to escape and a reduction in the liner bulge (see Figure 5-56). Another means of vapor escape could be under the steel liner as a result of a blow-out of the asphalt sealing of the shell. In this case, the liner could maintain integrity if the vapor was released slowly over an extended period of time. This theory could explain why tank SX-110 and possibly other sound tanks may have experienced a bulge but was able to maintain leak tightness. A third method of vapor release could be the buckling of the lower stiffener, allowing vapor to escape between the liner and concrete shell. The liner would be deformed inward, and could possibly be still intact. The most probable type of vapor escape in the tanks would be the rupture of a joint (HW-57274, p. 5).

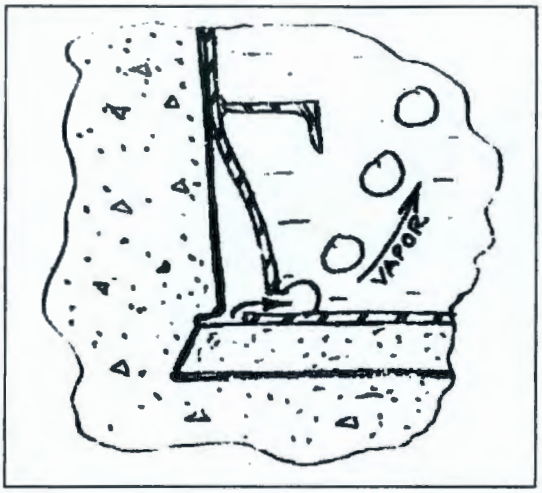


Figure 5-56. Vapor Escape through Rupture of a Joint (HW-57274 Fig. 8)

Brownell concluded that the design of SX and A Farms did not provide an allowance for thermal expansion of the bottom of the tank liner. Earlier tanks of BX Farm design (see drawing H-2-602, *Composite Tank Typical Details Concrete 241-BX*) and TX Farm design (see report HW-37519) had two features that allowed for thermal expansion. First a layer of asphalt and gunite on the outside of the steel shell permitted some expansion of bottom and shell before being stopped by the restraint of the reinforced concrete shell. Second, the 4-ft radius at the lower corner was particularly useful in transfer of compressive stress in the bottom liner around the arc so as to relieve the stress by lifting the shell of the tank. These were good design features which were eliminated in the SX Farm tanks (see drawing H-2-39511) and PUREX tanks (see drawing H-2-55911). If either a radius in the lower corner or the asphalt had been retained in the later designs there would have been some provision for thermal expansion of the bottom steel liner relative to the concrete tank. These problems are of special importance when the tank is filled with hot fluid having temperature above the boiling point of water. (HW-57274, p. 13)

A test was performed to determine if vapor pressure could be developed from the vaporization of moisture contained in the Portland cement grout used in SX Farm. One sample reached maximum pressures of 15.9 and 16.0 psig (30.6 and 30.7 psia, respectively) during two separate heating cycles at temperatures up to 240°F. As stated above, saturation temperature of steam at 21.5 psia is 232°F. The grout was able to produce a vapor pressure higher than what is indicated in the steam tables. (HW-60556, *Portland Cement Grout Vapor Pressure-Temperature Test,* H.W. Stivers, p. 5)

5.6.1.4. Tank 241-SX-115

Tank SX-115 was constructed from 1953 to 1954 and started receiving REDOX HLW on August 29, 1958 (see RPP-RPT-58371). Tank SX-115 was preheated by adding water, condensate from tank SX-106 and REDOX waste. After initially receiving waste, thermocouple temperatures rose from 100°F on September 3, 1958 to 209°F on October 15, 1958 (see

RPP-RPT-58371) for an average temperature rise of 2.6°F/day. The only description of bulging associated with tank SX-115 is presented in the October 1958 Chemical Processing Department monthly report (HW-58051-DEL, *Chemical Processing Department Monthly Report for October 1958*, p. J-8).

> *Settling of sludge in the 115-SX tank, currently being heated up for active service, caused the temperature measured at the one-inch level to rise approximately 15 F above the temperature at the four-inch level and about 30 F higher than the average liquid temperature. When minor variations in liquid level were observed on October 13, a sounding of the tank bottom was made which indicated the liner to be raised three inches above its original elevation which had been confirmed by soundings made as late as October 2. The injection of approximately 90,000 gallons of water into the tank reduced the average solution temperature... Concurrently the tank liner returned to within a half-inch of its original position and remained there throughout the report period...*

No other details have been found regarding this event. Later photos taken in February 1972 (Photograph 720766-32CN) show bent piping on a ALC#4. This could infer that the bulge in tank SX-115 was greater than 3 in. but this cannot be confirmed.

5.6.1.5. Tank 241-A-105

The next two paragraphs are paraphrased from ARH-78. The first addition to tank A-105 was 6 in. of water prior to tank farm startup in 1955. The water was added to protect against bottom uplift from operation of the active ventilation exhauster. The level gradually increased to 18 in. in May 1962 due to water additions to various vapor seals. Tank A-105 was first filled with 330,000 gal aged supernatant from tank A-103 in May of 1962 over a period of 20 days. The tank temperature increased 18°F (10°C) to 133°F (56°C) during this time period, or 0.9°F/day (0.5°C/day). On July 27, 1962 an additional 330,000 gal of supernatant were added from tank A-103 resulting in an additional 14°F (8°C) temperature rise. From July 27 to December 12, 1962 about 63,000 gal of supernatant were removed from A-105. On December 12, 1962 about 252,000 gal of supernatant were added from A-101 with a 25°F (14°C) temperature rise. This waste was blended with ALCs and then 490,000 gal transferred to C-103. Following this transfer, the remaining contents were pumped to tank A-101 until only a 10-in. heel remained in A-105. In January 1963, hot condensate was added to A-105 in preparation for receipt of PUREX self-boiling waste raising the waste temperature from 122°F (50°C) to 144°F (62°C). The tank contents were brought up to boiling temperature at a nearly uniform rate with full-level waste, reaching boiling on March 5, 1963. On November 19, 1963, radiation was noted in one lateral. The liquid level was reduced by self-concentration to 260 in., below the level a few months before the leak was detected. Radiation intensity in the lateral subsided indicating the leak had stopped because of self-sealing or because the liquid was below the leak point. The tank level was maintained at 260 in. and waste added to concentrate the supernatant to the 7.0 M sodium operating limit, which was reached about September 1, 1964. The liquid level was then permitted to increase, maintaining 7.0 M sodium, with the waste level reaching the postulated leak level in October 1964. There was no indication of leakage at that time and

the tank was filled to capacity in December 1964. On January 28, 1965, a sudden steam release occurred in tank A-105.

In response to the steam bump an air sparger was fabricated for insertion in the tank in order to minimize the accumulation of superheat within the supernatant. Prior to installing the air sparger it was decided to probe the area because an obstruction had been encountered at that riser during a sludge measurement. The probing of the area confirmed that an obstruction existed about 8 ft above the tank bottom's normal position. Pressure readings on the ALCs dip tubes indicated the #1 and #2 circulators were either 6 ft higher or all the air lines to the circulators were broken. The static pressure readings coupled with the physical detection of an obstruction under the location the air sparger was going to be added left little doubt that the tank bottom was bulged. Many mechanisms causing the bulge were considered but reduced to two possibilities: differential thermal expansion between the concrete wall and bottom liner plate; and, lifting of the liner plate by water vapor trapped between the bottom liner and concrete. Engineering calculations showed that thermal forces could not create an uplift in excess of 1.9 ft. This left uplift by water vapor as the primary mechanism. It was determined a temperature of 250°F would produce water vapor pressure that would counterbalance the hydrostatic head of the waste in the tank and higher temperatures could generate steam pressures which could cause the liner to lift. Temperature data showed 250°F was reached in October 1964 when the tank was 80 percent filled.

In an effort to learn more about the effect of pressure on the bottom of the waste tank liner, a scale model of the tank liner was built and pressure was applied to the bottom until the tank liner failed (RL-SEP-630). A 0.096 to 1 scale model of the tank A-105 liner was pressurized on the bottom until it bulged and failed. Part of the tank wall bent inward at the first stiffener ring allowing the bottom to bulge upward over an area about three feet across. Then five minutes later it bulged slightly more and ruptured adjacent to the weld at the bottom-to-side joint. This break was about 2 in. long. It could not be concluded that the actual tank joint would fail under similar circumstances but it was thought that it was a good possibility that it would.

From in-tank inspections, it is theorized that vapor pressure forced the steel floor upward, and tension apparently caused it to rip roughly $^{2}/_{3}$ the way around the tank (TRAC-0022, *An Estimate of Bottom Topography, Volume and Other Conditions in Tank 105-A, Hanford, Washington*). It appears that the parting usually occurred at the 90° weld at the junction of the floor and the wall. However, the parting did not occur until the floor liner had been partially elevated, the steel wall had been bent upward, and the edge of the liner had been rolled downward (TRAC-0022). Figure 5-57 shows the assumed tear in the liner from the in-tank inspections.

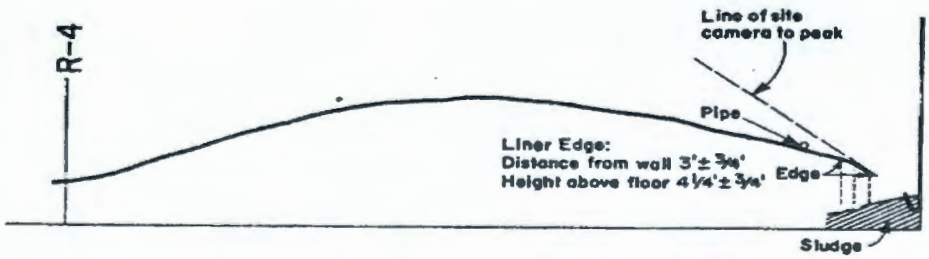


Figure 5-57. Rupture of Liner in Tank A-105 (TRAC-0022)

6.0 COMMON FACTORS ANALYSIS

This section contains the data and analysis of factors that may have contributed to SST liner failure. The section is broken into six segments. The first segment describes the approach to performing the common factors analysis including limitations of this approach. The second through sixth segment provide analysis of possible liner failure mechanisms organized according to categories of tank design, procured materials, tank construction, operational service aspects, and external environmental conditions. These categories are directly related to the categorization of mechanisms first introduced in Section 4.0. The historical information collected in Section 5.0 is used as the data for analysis. When data is not available or incomplete and analysis cannot be performed, this fact is recognized for the particular mechanism being considered. In these cases, qualitative or subjective discussions of the particular mechanism may be included.

6.1 ANALYTICAL METHODS FOR EVALUATING COMMON FACTORS

Developing statistically significant samples to identify common factors is one of the major constraints to this analysis. Attempts to sort the SSTs into groups based on possible factors often result in small sample sizes that are not statistically significant. Also, lack of complete data associated with a particular mechanism does not allow one to provide a true representation of the SST population. No causal inference can be made for a variable for which no measurable data is available. That being said, performing an analysis of variance, where possible, does allow one to determine whether or not the population of SSTs which includes a particular mechanism has a statistically different mean than the remainder of the SST population that does not include that mechanism.

The common factors analysis, where possible, will rely on the chi-square statistic for dichotomous categorical data. Dichotomous categorical data can only have two possible outcomes as opposed to continuous numerical data. The dichotomous categories of interest for this report are "probable liner failure" and "liner failure not known". The chi square statistic compares the counts of categorical responses between two groups. Where possible, the chi-square statistic p-value is used to determine whether an association exists between a factor and liner failure at a particular level of significance, α. For this analysis the selected level of significance is 0.05, a typically reported high-confidence value. A p-value greater than 0.05 leads to failing to reject the null hypothesis (i.e., there is no statistically significant difference between the samples). A p-value less than 0.05 leads to rejecting the null hypothesis (i.e., there is a statistically significant difference between the samples). This level of significance, α=0.05, will result in assuming an association exists between a particular factor and liner failure 1 out of 20 times when no such association actually exists. The chi-square value is calculated by the following summation:

$$\chi^2 = \sum \frac{(Observed\ Frequency - Expected\ Frequency)}{Expected\ Frequency}$$

The observed frequency is simply the sample value while the expected frequency is determined by the formula

$$Expected\ Frequency = \frac{Row\ Subtotal \times Column\ Subtotal}{Sample\ Total}$$

Observed and expected frequencies are shown below in Table 6-1 for a 2x2 matrix. The formula for expected frequency in each matrix location is written out explicitly using the observed frequencies. This can easily be expanded for larger matrices.

Table 6-1. Sample Observed and Expected Frequencies Involved in 2x2 Chi-Square Testing

Observed Frequency of Data	**Probable Liner Failure**	**Liner Failure Not Known**	**Total**
Factor Present	a	b	$a+b$
Factor Absent	c	d	$c+d$
Total	$a+c$	$b+d$	$a+b+c+d$
Expected Frequency of Data	Probable Liner Failure	Liner Failure Not Known	Total
Factor Present	$\frac{(a+b)\times(a+c)}{(a+b+c+d)}$	$\frac{(a+b)\times(b+d)}{(a+b+c+d)}$	$a+b$
Factor Absent	$\frac{(c+d)\times(a+c)}{(a+b+c+d)}$	$\frac{(c+d)\times(b+d)}{(a+b+c+d)}$	$c+d$
Total	$a+c$	$b+d$	$a+b+c+d$

The value returned as χ^2 can be compared to lookup values in readily available tables showing the χ^2 value for various p-values dependent upon the degrees of freedom. When there is one independent variable then the degree of freedom is one.

The use of the chi-square test to approximate the level of significance depends on both the sample size and the number of cells. A widely used rule of thumb (*Some Methods for Strengthening the Common Chi-Square Test* [Cochran 1954]) states that the chi-square test is adequate if no expected cell frequency is less than one and no more than 20% are less than five. Because the chi-square tests performed in this analysis are typically (but not always) 2x2 tests, each test will only consist of four cells and therefore all cells will have to have expected values greater than five to be considered adequate. For samples that are deemed as not adequate, different testing is required.

An exact test, generally used, is Fisher's exact test. Fisher's exact test is computationally more involved but does not include the limitations of small sample sizes or small values associated with the chi-square test. The Fisher's exact test relies on calculating the hypergeometric probability of the sample data. The hypergeometric probability of the outcome of the sample values in Table 6-1 is given as

$$p = \frac{(a+b)!\,(c+d)!\,(a+c)!\,(b+d)!}{a!\,b!\,c!\,d!\;\;(a+b+c+d)!}$$

The hypergeometric probability of the particular outcome is summed with all other equally likely or less likely hypergeometric probabilities where the row and column subtotals are identical to the particular outcome of interest. The summation of these probabilities is the two-sided p-value.

It must be recognized that the evaluation of factors to determine whether they are the cause of SST liner failures is not based on performing well controlled experiments. Rather the evaluation is based on the available data for systems in which control for any particular factor was never employed. Because of this and the large number of variables being considered, some of those factors (variables) may be common to certain subpopulations. Variables correlated with a particular variable of interest are called confounding variables. Because of the relatively large number of variables, there is a greater chance for the presence of confounding variables. The presence of confounding variables may provide false results, demonstrating a variable of interest is related to liner failure when in fact the confounding variable is indeed the cause of the liner failure. This may be particularly troubling if there is no measurable data for the confounding variable.

6.2 ANALYSIS OF TANK DESIGN FEATURES

This section addresses the various design factors that may have contributed to liner failures. Aspects of tank design are important to investigate because they represent the possibility that some tanks may have been inherently at risk for failure before storing waste. This can also be important in determining whether certain conditions observed in the tanks were more detrimental because of distinguishing design features.

6.2.1 Lack of Post-Weld Stress Relieving

As previously mentioned (see Section 4.1.1), SCC in nuclear waste storage tanks was first recognized as a significant concern in 1962 when four tanks at the Savannah River Site were discovered to have cracks (SRNL-STI-2012-00745). Subsequently, tanks constructed at Savannah River Site underwent thermal stress relief of the tank liners to prevent cracking. All SSTs at Hanford were constructed before the benefit of stress relieving tanks in order to stop SCC was understood. Post-weld stress relieving was not specified for any of Hanford's SSTs.

Because no SST was post-weld stress relieved, no quantitative evaluation can be made regarding whether or not lack of post-weld stress relieving was a common factor related to liner failure. It is well understood though that residual stress or stress intensity must be present above a particular threshold to allow SCC to occur in a given material exposed to a specific environment (see Section 4.4.9.4). Therefore, for situations where SCC is considered the likely mechanism of failure, one can infer that large enough residual post-weld stresses were present to allow SCC to occur, thus making lack of post-weld stress relieving a common factor. Unfortunately, there is

no means to determine whether or not the residual stresses in any individual SST were indeed large enough for SCC to occur.

6.2.2 Liner Bottom to Wall Transition Design

Historically, the liner bottom to wall transition design used in SX and A Farms, consisting of double fillet welds at a corner joint, has been suggested as a factor resulting in liner failure. Section 5.2.2 discusses the details of the various weld designs used in the SSTs over the years. The weld design used in each tank farm was investigated by looking at the differences between the transition design and type of weld used to make the connection between the bottom and wall of the steel liner. Table 6-2 shows the transition design and weld type used in the construction of each tank farm as well as the number of confirmed leakers from each farm.

Table 6-2. Bottom to Wall Transition Design Used to Construct the Single-Shell Tanks

Tank Farm	Transition Shape	Transition Weld	Reference	Failed Tanks
T	Large Radius Knuckle	Butt weld	HW-1946, Drawings D-2, D-23	2/16
U			HW-1946, Drawings D-2, D-23	3/16
B			HW-1946, Drawings D-2, D-23	1/16
C			HW-1946, Drawings D-2, D-23	2/16
BX			HW-1946, Drawings D-2, D-23	0/12
TX			HW-3061, H-2-809	2/18
BY			HW-3783, H-2-1313	1/12
S			HW-3937, H-2-1784	0/12
TY			HW-4696, H-2-2245	4/6
SX	Corner Joint – Near Orthogonal	Fillet Weld	HW-4957, H-2-39511	8/15
A	Corner Joint – Orthogonal	Fillet Weld	HWS-5614, H-2-55911	2/6
AX	Small Radius Knuckle	Butt weld	HWS-8237, H-2-44562	0/4

Because there are only four tanks in AX Farm, the sample size for the small radius, butt welded knuckle is too small to provide meaningful statistical information. Comparison can be made between the larger populations of butt welded, large radius knuckle transitions and the fillet welded corner joint design. Performing a chi-square test with the values presented in Table 6-3 results in a p-value of 6.7E-05. Since the p-value is less than the selected significance level, $\alpha=0.05$, we reject the null hypothesis. In other words there is a statistically significant difference in the proportion of liner failures between tanks with fillet welded, corner joint designs and those with butt welded, large radius knuckle designs.

Table 6-3. Bottom to Wall Transition Design Liner Failure Rate Observational Data

	Probable Liner Failure	Liner Failure Not Known	Total
Large Radius Knuckle, Butt Welded	15	109	124
Corner Joint, Fillet Welded	10	11	21
Total	**25**	**120**	**145**

The above chi-square test does not account for any confounding factors. Later in this report (see Section 6.5.6.1) it is shown that waste composition and temperature likely played a significant role via nitrate-induced SCC in liner failures in TY and SX Farm. However, since SCC requires both a particular environment and the presence of stress or stress intensity above a particular level, both these factors in tandem would be required to cause SCC. Thus, the confounding factor may be the presence of an environment required for SCC.

The design of SX and A Farm tanks' liner bottom to wall transition is likely not the only contributing cause of failure of the tanks, however, it may be a significant contributor. When combined with harsh conditions such as high temperature and stresses, the liner design could be a compounding factor leading to the failure of the liner. The design of the transition including the weld type required made the liners more susceptible to fatigue and stresses. Lack of radiographic inspection of the transition and spot radiographic examination of other welds in the SX and A Farm tanks also brings into question the level of integrity in the welds.

Based on the available information it appears that the liner bottom to wall transition design is a common factor contributing to liner failure.

6.2.3 Exterior Finish of Tank Liner

The absence of an asphaltic membrane on the exterior of the tank liner has been considered a possible common factor resulting in liner failure (see Section 4.1.3). The asphaltic membrane is meant to provide waterproofing of the exterior of the liner. Additionally, the asphalt is considered yielding allowing for some expansion of the liner material due to heating during operation. Section 5.2.3 discusses the use and details of any external layers between the tank liner and the concrete wall of the tank. The design used in each tank farm was investigated by looking at the differences between the methods and materials used on the exterior of the liner. Table 6-4 shows the bottom and wall exterior liner design used in the construction of each tank farm as well as the number of confirmed leakers from each farm.

Table 6-4. Exterior Liner Finish Design Used for the Single-Shell Tanks

Tank Farm	Bottom Liner Exterior	Sidewall Exterior	Reference	Failed Tanks
241-T, 100-Series	3-ply asphalt membrane below 2 in. grout layer	3-ply asphalt membrane protected by cement mortar or gunite	HW-1946, Drawing D-2	2/12
241-U, 100-Series				3/12
241-B, 100-Series				1/12
241-C, 100-Series				2/12
241-BX				0/12
241-T, 200-Series	Direct contact with concrete	1 in. thick Banrock metal mesh blanket	HW-1946, Drawing D-20	0/4
241-U, 200-Series				0/4
241-B, 200-Series				0/4
241-C, 200-Series				0/4
241-TX	3-ply asphalt membrane below 2 in. grout layer	3-ply asphalt membrane protected by gunite	HW-3061, H-2-809	2/18
241-BY			HW-3783, H-2-1313	1/12
241-S			HW-3937, H-2-1784	0/12
241-TY			HW-4696, H-2-2245	4/6
241-SX		Direct contact with concrete	HW-4957, H-2-39511	8/15
241-A			HWS-5614, H-2-55911	2/6
241-AX	Direct contact with concrete		HWS-8237, H-2-44562	0/4

In terms of providing waterproofing of the exterior of the liner and allowing for thermal expansion, the Type II and Type III tanks are the only tanks that have a continuous asphaltic membrane surrounding the bottom and sidewall of the tank liner. Comparison can be made between those tanks and all other tanks. Performing a chi-square test with the values presented in Table 6-5 results in a p-value of 0.126. Since the p-value is greater than the selected significance level, α=0.05, we accept the null hypothesis. In other words there is no statistically significant difference in the proportion of liner failures in tanks with continuous asphaltic membranes compared to those tanks with partial or no asphaltic membranes.

Table 6-5. Asphaltic Exterior Finish Liner Design Failure Rate Observational Data

	Probable Liner Failure	Liner Failure Not Known	Total
Continuous Asphaltic Membrane	15	93	108
Partial (Bottom Only) or No Asphaltic Membrane	10	31	41
Total	**25**	**124**	**149**

One can also consider the population of tanks that have provisions allowing for thermal expansion of the tank liner, without also accounting for waterproofing as done above. The Type I, II and III tanks have a yielding material (i.e., asphalt or Banrock) on the sidewall as opposed to direct contact of the tank liner with the rigid concrete shell. This should allow for some thermal expansion of the cylindrical shell portion of the tank liner at a reduced stress level. Comparison can be made between all tanks with a yielding material on the sidewall and all other tanks. Performing a chi-square test with the values presented in Table 6-6 results in a p-value of 6.6×10^{-4}. However, the expected values for the chi-square test do not meet one of the general rules of thumb for chi-square testing (i.e., no more than 20% of expected values are less than five). Therefore, the chi-square test should not be used. Performing Fisher's exact test, the

calculated p-value is 0.0019. Since the p-value is less than the selected significance level, α=0.05, we reject the null hypothesis. In other words there is a statistically significant difference in the proportion of liner failures in tanks with yielding exterior finish surrounding the cylindrical portion of the tank liner compared to those tanks with a rigid exterior finish. At this point it is important to point out that the presence of a yielding material on the exterior of the tank liner sidewall is only significant in preventing a liner failure if the tank is subjected to thermal expansion through a rapid rate of temperature rise. Rapid rate of temperature rise is analyzed in section 6.5.2.2. That analysis finds that lack of adequate data does not allow determination of whether or not a high temperature rate of rise is a common factor contributing to liner failure. Therefore, the presence of a yielding material, which would allow for thermal expansion of the tank liner, cannot be determined without also knowing associated temperature rate of rise data, which is unavailable.

Table 6-6. Yielding Exterior Finish Surrounding Cylindrical Shell Portion of Liner Failure Rate Observational Data

	Probable Liner Failure	Liner Failure Not Known	Total
Asphalt or Banrock Surrounding Cylindrical Shell Portion of Liner	15	109	124
Liner Wall in Direct Contact with Concrete	10	15	25
Total	**25**	**124**	**149**

Based on the available information it appears that it is indeterminate whether the type of exterior finish applied to the tank liner is or is not a common factor contributing to liner failure.

6.2.4 Gas Vent Path below Tank Liner

It is possible that the lack of a vent path for transfer of gases and vapors that may form below the bottom tank liner may have played a role in contributing to liner failures (see Section 4.1.4). One can examine this information to determine whether there is a difference in liner failure rate based on the presence or lack of a vent path. Table 6-7 provides the liner failure rates for tanks with a gas vent path underneath the tank bottom liner and for those without a vent path. The expected values from the chi-square test include one value (out of 4) which is less than 5 and one value that is less than one, and therefore the sample does not meet two of the general rules for chi-square testing (i.e., no more than 20% of the expected values are less than 5 and no values less than 1). Thus, the results of the chi-square testing generally would not be considered relevant. Performing Fisher's exact test, the calculated p-value is 1.0. Because the p-value is greater than the selected significance level, α=0.05, we accept the null hypothesis. In other words there is no statistically significant difference in the proportion of liner failures in tanks which had a gas vent path below the tank liner and those that did not.

Table 6-7. Effect of Gas Vent Path on Failure Rate Observational Data

	Probable Liner Failure	Liner Failure Not Known	Total
Vent Path Present	0	4	4
Vent Path Absent	25	120	145
Total	**25**	**124**	**149**

From a qualitative standpoint it makes logical sense that the presence of a gas vent path below the bottom tank liner would prevent gas buildup under the tank bottom liner. However, one cannot infer from this that not having a vent path causes gas buildup under the tank bottom liner. Further, there is no indication that any gas pressurization under the tank liner always results in liner failure. That being said, pressurization under the bottom of the tank liner has been linked to the failure of at least one SST liner (tank A-105). In that situation, if a vent path had been present it is likely that any trapped gases could have vented from underneath the tank rather than building to a pressure causing failure of the liner. The lack of a vent path may result in the presence of a mechanism (i.e., pressurization under the tank bottom liner) that causes liner failure but the lack of the vent path does not directly by itself result in that mechanism occurring. Other contributory conditions must be present for gas or vapor to form and the lack of a vent path may in certain instances allow a high enough pressurization to occur to result in liner failure. The analysis of pressurization external to the tank liner as a common factor in liner failure is covered in Section 6.6.

Based on the above discussion and the available information it does not appear that the lack of a gas vent path below the tank liner is a common factor contributing to liner failure. Rather, lack of a vent path may contribute to an external pressurization mechanism that could result in liner failure.

6.3 ANALYSIS OF PROCURED TANK MATERIALS

The SST liner consists of continuously welded plate with side wall reinforcement consisting of angle rings stitch welded to the interior walls of the liner. In Section 4.2 it was determined that the basic properties of the liner plate material or manufacturing defects in that plate could be areas of concern associated with liner failure. Specific properties of the liner material are analyzed below as potential common factors. Information on manufacturing defects of the liner material could not be found in the searched records. Qualitative discussions of liner material and weld material defects are also provided.

6.3.1 Properties of Liner Material

In Section 5.3.1 it was determined that four possible factors associated with the physical, mechanical and chemical properties of the liner material could be potential common factors contributing to liner failure: carbon equivalent; yield strength; steel grade; and liner thickness. The subsections below contain the analysis for each of those four factors.

6.3.1.1. Carbon Equivalent

The information in Section 5.3.1 regarding carbon equivalent shows that there can be a significant difference between the carbon equivalent value based on maximum compositional limits and actual compositional information. The available compositional information for the earlier tank farms is significantly different from the maximum compositional information, demonstrating that it is not appropriate to use maximum compositional limits as surrogates for actual compositional information when considering material weldability and propensity for cold cracking. Also, it is not appropriate to make comparisons between actual compositional information for some tanks and maximum compositional limits for the remaining tanks. That being said, one can still look at the available information and decide if any conclusions can be drawn. Table 6-8 summarizes the failures and failure rates considering both available liner composition information and specified maximum compositional information. The failure rate data with and without compositional information is charted in Figure 6-1.

Table 6-8. Failures and Failure Rates as a Function of Liner Plate Carbon Equivalent

	Carbon Equivalent Using Available Liner Composition Information								
	0.12[1]	**0.14[1]**	**0.22[2]**	**0.24[2]**	**0.29[1]**	**–**	**0.35[2]**	**0.36[2]**	**–**
Failed	8	2	0	4	1		0	10	
Not Failed	68	16	12	2	11		4	11	
Failure Rate	0.11	0.11	0.0	0.67	0.083		0.0	0.48	
	Carbon Equivalent Using Maximum Specified Composition Information								
	–	**–**	**0.22**	**0.24**	**–**	**0.32**	**0.35**	**0.36**	**0.42**
Failed			0	4		2	8	10	1
Not Failed			12	2		16	72	11	11
Failure Rate			0.0	0.67		0.11	0.10	0.48	0.083

[1] Carbon Equivalent value based on available material compositional information.

[2] Carbon Equivalent value based on specified compositional limits.

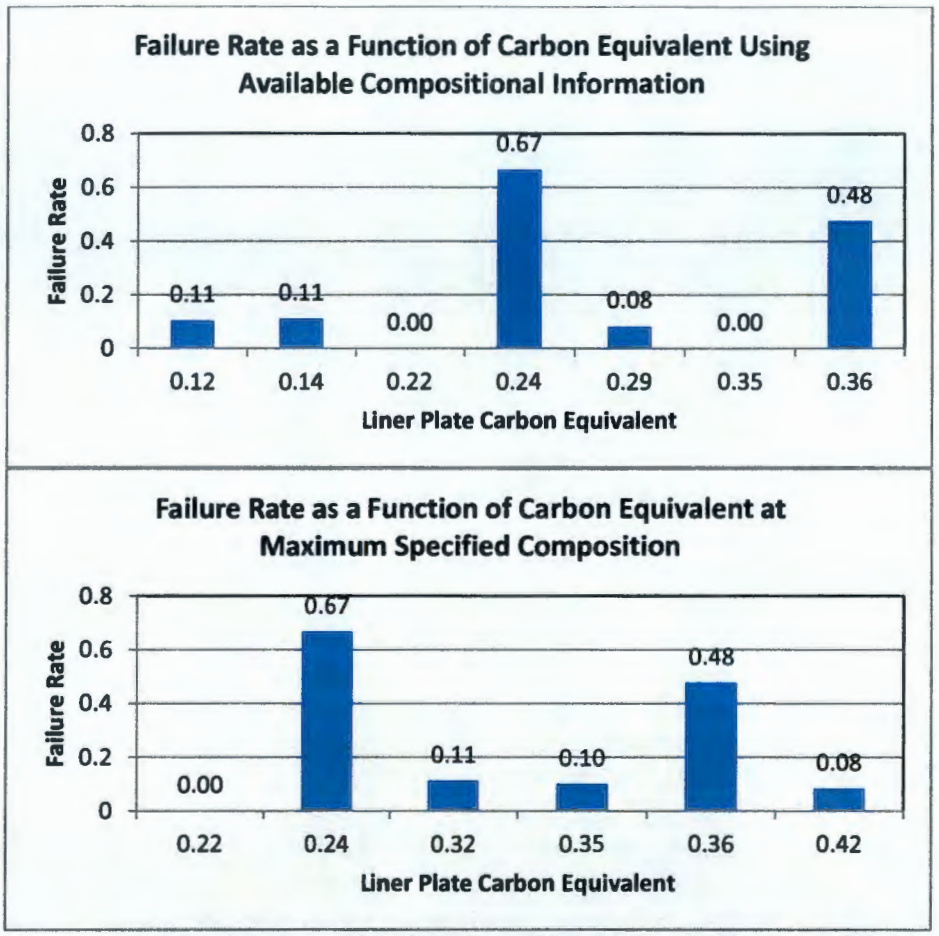


Figure 6-1. Tank Liner Failure Rate as a Function of Liner Plate Carbon Equivalent, with and without Compositional Information

In examining the data in Table 6-8 there are a relatively large number of values for the carbon equivalent. Because there is large variation in the carbon equivalent, the sample size for most categories is quite small making it difficult to provide meaningful statistical information. Considering either maximum specified compositional limits by themselves or in combination with available compositional information, the expected values for a chi-square test do not meet the general rules of thumb for chi-square testing (i.e., no more than 20% of expected values are less than five and/or no value less than one). Therefore, the chi-square test cannot provide meaningful statistical information.

Taking a more general (rather than statistical) view on weldability, liner plates with higher carbon equivalent values would be expected to be more at risk, with respect to cold crack formation in the liner resulting in liner failure. However, the available data regarding failure rates as a function of carbon equivalent value does not appear to support this hypothesis. One explanation might be based on the fact that the calculated carbon equivalent value where actual compositional information is available is less (by 0.13-0.23) than the value based solely on maximum specified compositional limits. Thus for those tank farms where actual compositional information is not available, it should be expected that the actual carbon equivalent value, based

on actual composition, is lower than shown for the maximum specified compositional limit. This would result in a more favorable view of the weldability of the material. Another explanation is that there is no appreciable difference in the weldability between any of the liner plates used based on the range of carbon equivalent used. An example of subjective weldability ratings based on carbon equivalent taken from "Flat Rolling Fundamentals" is shown in Table 6-9.

Table 6-9. Weldability as a Function of Carbon Equivalent

Carbon Equivalent (CE)	Weldability[1]
Up to 0.35	Excellent
From 0.36 to 0.40 included	Very Good
From 0.41 to 0.45 included	Good
From 0.46 to 0.50 included	Fair
Over 0.50	Poor

[1] from Flat Rolling Fundamentals, V.B. Ginzburg, R. Ballas, CRC Press, 2000.

Based on the ratings in Table 6-9 no distinction is made in weldability if the carbon equivalent is 0.35 or less. The maximum specified compositional limit for nearly all the tank liner plates is 0.35 or less. There are twelve tanks with a maximum specified compositional limit resulting in a carbon equivalent of 0.36 which just exceeds the best weldability category in Table 6-9. Carbon equivalent for these twelve tanks based on actual composition would be expected to be 0.35 or less. So based on the example subjective categorization, no appreciable difference is expected in weldability between any of the liner plates used for the various SSTs.

A related subject to carbon equivalent is preheat and interpass temperature requirements during welding. Steels with higher carbon equivalent values typically require higher preheat and interpass temperatures during welding to avoid the potential for forming cracks. This topic as it relates to weld defects during fabrication is discussed in Section 6.4.3.

Based on the available information and discussion presented it does not appear that the liner plate carbon equivalent value is a common factor contributing to liner failure.

6.3.1.2. Yield Strength

In Section 4.4, the only mechanical failure mechanism considered potentially likely is high temperature-induced failure which is analyzed in Section 6.5.2.1. The consideration of the liner plate's yield strength as a factor affecting liner failure is not tied directly to mechanical failure due to operational load combinations exceeding the material's yield strength. Rather, yield strength may be used as a surrogate for grain size. As mentioned in Section 5.3.1, a fine grain size has been shown to increase the resistance to SCC of carbon steels in solutions containing nitrates (McCafferty 2010, p. 336). Based on the Hall and Petch effect, there is an inverse relationship between grain size and yield strength. Thus carbon steels with higher yield strengths would have a lesser propensity to failure via SCC.

Table 5-6 shows that four different minimum yield strength values exist for the liner plates used in construction of the SSTs. The tank liner failure rate at each of these four minimum yield strengths is depicted in a histogram (see Figure 6-2).

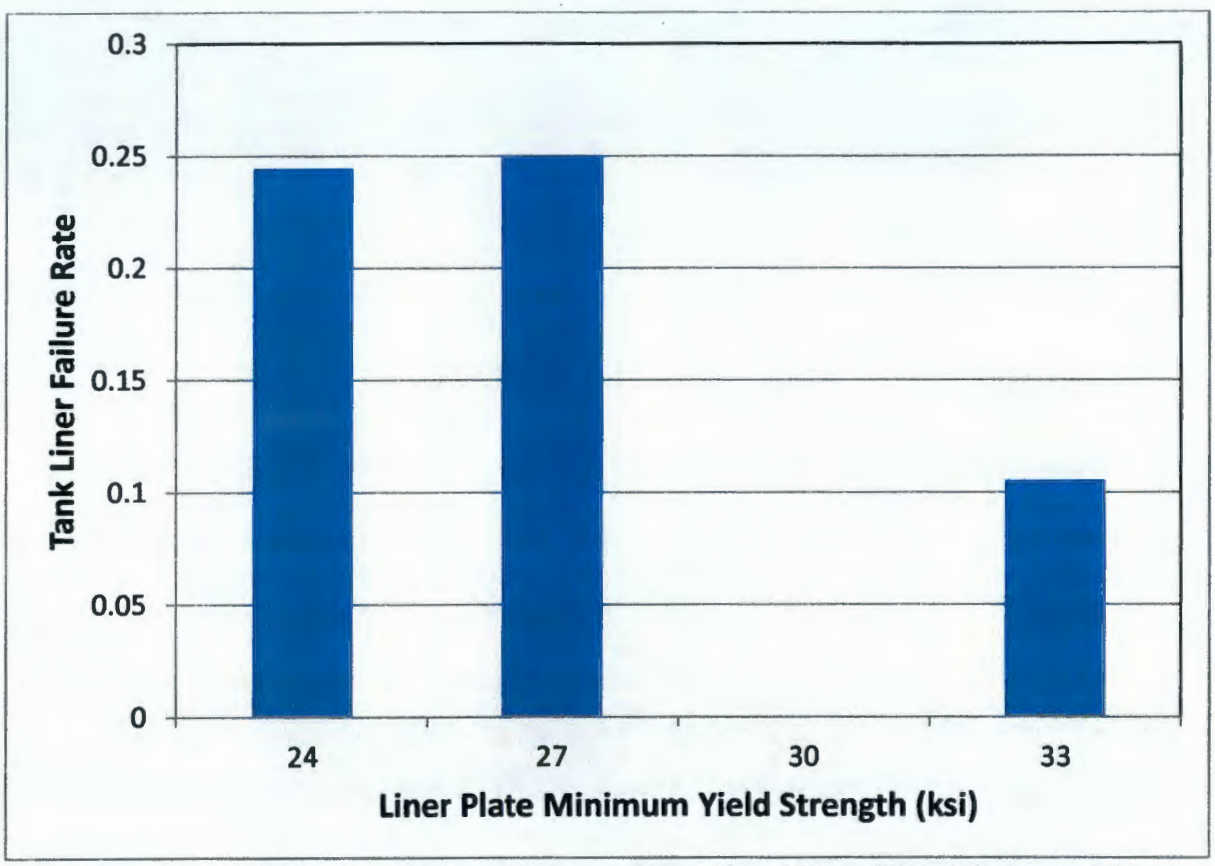


Figure 6-2. Tank Liner Failure Rate as a Function of Liner Plate Minimum Yield Strength

There is an apparent break in the failure rate between liner plates with a minimum yield strength of 27 ksi and 30 ksi. The data can be evaluated statistically using a chi-square test. The null hypothesis can be stated that there is no difference in failure rate for a liner plate with a minimum yield strength less than or equal to 27 ksi compared to greater than 27 ksi. Performing a chi-square test with the values presented in Table 6-10 results in a p-value of 0.017. Since the p-value is less than the selected significance level, $\alpha=0.05$, we reject the null hypothesis. In other words there is a statistically significant difference in the proportion of liner failures in tanks with liner plate having a minimum yield strength no more than 27 ksi as compared to those tanks with liner plate having a minimum yield strength greater than 27 ksi.

Table 6-10. Liner Plate Minimum Yield Strength Observational Data

	Probable Liner Failure	Liner Failure Not Known	Total
Yield Strength ≤ 27 ksi	17	52	69
Yield Strength > 27 ksi	8	72	80
Total	**25**	**124**	**149**

It is important to note that a confounding factor may be present that is directly correlated with yield strength. The above chi-square test does not account for any confounding factors. Because the yield strength is used as a surrogate for grain size, which is considered a factor in SCC, it is instructive to examine data for those tanks where waste constituent concentrations are known to cause SCC (see Section 6.5.6). Thus the confounding factor may be the presence of an environment conducive to SCC.

6.3.1.3. Material Standard and Grade

It is possible that the standard and grade of steel used to construct the liner may have played a role in contributing to the liner failures (see Section 4.2). The liner material used in each tank farm was investigated by looking at the differences between the steel standards and grades and the proportion of liner leaks through each steel standard and grade. Table 6-11 shows the liner material used in the construction of each tank farm as well as the number of confirmed leakers from each farm.

Note that when looking at the steel liner grade, it does not distinguish a unique, singular cause for failure because all tanks in a given farm were built with the same steel grade and each farm that had tank failures also had tanks that did not fail. Therefore, liner failure cannot be explained solely by the steel liner grade itself, but it may have a compounding effect when other operational conditions were applied to a tank with a particular steel grade.

Table 6-11. Steel Liner Material Used to Construct the Single-Shell Tanks

Tank Farm	Year Built	Liner Material	Reference	Failed Tanks
A	1954	A283-52T, Grade B, C	HWS-5614	2/6
AX	1963	A201-61T, Grade A	HW-72780 & HWS-8237	0/4
B	1943	A7-39	HW-1946	1/16
BX	1946	A7-39	HW-1946	0/12
BY	1948	A285-46, Grade A, B, C	HW-3783	1/12
C	1943	A7-39	HW-1946	2/16
S	1950	A283-46T, Grade B	HW-3937	0/12
SX	1953	A283-52T, Grade A, B	HW-4957	8/15
T	1943	A7-39	HW-1946	2/16
TX	1947	A285-46	HW-24800-35 & H-2-809	2/18
TY	1951	A283-49T, Grade B	HW-4696	4/6
U	1943	A7-39	HW-1946	3/16

Because there is large variation in the standard and grade of steel liner material used, the sample size for any standard and grade is quite small (except for A7-39 used in the first five tank farms) making it difficult to provide meaningful statistical information. Even if one combines all grades and specific years into a single collective standard (i.e., A7, A283, A285, A201), the expected values for a chi-square test do not meet the general rules of thumb for chi-square testing (i.e., no more than 20% of expected values are less than five and no value less than one).

By looking only at the percentage of liner failures for each standard, regardless of the year of the standard or the grade, the use of A283 steel liners appear to be a significant factor contributing to liner failure with a total leak percentage of 36%. In comparison, only 11% of the A7 liners, 10%

of the A285 liners, and 0% of the A201 liners have failures. The overall percentage of SSTs with liner failures is 17%. Because the tank liners made from steel specified to ASTM standards A7, A285, and A201 had liner failure percentages less than the overall percentage, these standards would not be considered contributing factors.

A closer examination of A283 steel by year of specification can be performed to determine if there are differences in failure percentages between the various issue years of the standard. The tanks made with A283-46T plate had a failure percentage of 0%, A283-49T plate had a failure percentage of 67%, and A283-52T plate had a failure percentage of 48%. At this point it is noteworthy to point out that these three standards had identical acceptable production processes (open-hearth or electric furnace), the same chemical composition requirements, and the same tensile and bending properties by grade. Based on the requirements of the specifications, there are no obvious differences in specified requirements between the different years of the specification that would account for the different percentage failures. This leads one to either consider that there is some material variable which is not accounted for in the standard that causes the difference in failure rates, or that there is some other variable which is confounding the failure rate percentage data. It is shown later, in section 6.5.6.1, that nitrate-induced stress corrosion cracking was likely responsible for liner failure in ten of the 12 liners of A283-49T and A283-52T material. Nitrate-induced stress corrosion cracking confounds the role of material standard and grade in contributing to liner failure. Finally, the sample size of any material standard and grade is too small to make a reasonable statement regarding whether or not the material standard and grade is a contributing factor in causing liner failure.

Based on the available information a determination cannot be made whether or not the liner plate standard and grade is a common factor contributing to liner failure.

6.3.1.4. Liner Plate Thickness

It is possible that the thickness of the liner plate used to construct the various SSTs may have played a role in contributing to the liner failures (see Section 4.2). The liner material thickness specified in each tank farm is available from construction drawings. One can examine this information to determine whether there is a difference in liner failure rate based on these liner plate thickness differences. Table 6-12 shows the liner material thicknesses specified in the construction of each tank farm as well as the number of confirmed leakers from each farm.

Table 6-12. Steel Liner Material Used to Construct the Single-Shell Tanks (2 Pages)

Tank Farm	Year Built	Liner Thickness	Reference	Failed Tanks	Percent Failed
B, 100-Series	1943	¼ in. bottom and wall, $^5/_{16}$ in. knuckle	Drawing D-2	1/12	16.7%
C, 100-Series				2/12	
T, 100-Series				2/12	
U, 100-Series				3/12	
B, 200-Series	1943	¼ in. all plate	Drawing D-20	0/4	0%
C, 200-Series				0/4	
T, 200-Series				0/4	
U, 200-Series				0/4	
BX	1946	$^3/_8$ in. bottom, $^5/_{16}$ in. knuckle, ¼ in. wall	H-2-602, H-2-696[1]	0/12	0%

Table 6-12. Steel Liner Material Used to Construct the Single-Shell Tanks (2 Pages)

Tank Farm	Year Built	Liner Thickness	Reference	Failed Tanks	Percent Failed
TX	1947	$^3/_8$ in. bottom and knuckle, $^5/_{16}$ in. lower wall, ¼ in. upper wall	H-2-809	2/18	14.6%
BY	1948		H-2-1313	1/12	
S	1950		H-2-1784	0/12	
TY	1951		H-2-2245	4/6	
SX	1953	$^3/_8$ in. all plate	H-2-39511	8/15	40.0%
A	1954		H-2-55911	2/6	
AX	1963		H-2-44562	0/4	

Note: [1] *Steel Plate Details 75 Foot Tank 241-BX.*

Because there is large variation in the combination of liner plate thicknesses used in different portions of the tank, the sample size for any combination is relatively small. In addition, a couple of the liner thickness categories have no failures which put the validity of the chi-square test into question. In fact, the sample does not meet one of the general rules for chi-square testing (i.e., 3 out of 10 of the expected values [which is greater than 20%] are less than 5). Therefore, the chi-square test cannot provide meaningful statistical information.

By looking only at the percentage of liner failures for each combination of liner plate thicknesses, the use of all $^3/_8$ in. plate for the entire liner appears to be a significant factor contributing to liner failure with a total leak percentage of 40%. In comparison, the overall percentage of SSTs with liner failures is 17%. However, it should be pointed out that all the tanks constructed with all $^3/_8$ in. plate are also the tanks with boiling waste (high temperature and high temperature rate of rise). In addition, the SX Farm tanks have a high percentage of tanks exposed to waste known to cause nitrate-induced SCC (see Section 6.5.6). These confounding variables, the inability to control for confounding variables, and the relatively small sample populations make it impossible to determine whether liner plate thickness did contribute to liner failure. Based on the available information it is indeterminate whether liner plate thickness is a common factor contributing to liner failure.

6.3.2 Liner Plate Defects

Steel liner plate defects could not be eliminated from consideration as a potentially likely factor contributing to liner failure (see Section 4.2.2). However, no relevant information was found regarding the types and severity of defects present in the steel used to construct the SSTs in the various tank farms. Because no defect information is available, no quantitative evaluation can be made regarding whether or not the presence of liner plate defects was a common factor related to liner failure. Based on the lack of information a determination cannot be made whether or not the presence of liner plate defects is a common factor contributing to liner failure.

6.3.3 Weld Material Defects

Weld material defects could not be eliminated from consideration as a potentially likely factor contributing to liner failure (see Section 4.2.3). However, no relevant information was found regarding the types and severity of defects present in the weld material used to construct the SSTs in the various tank farms. Because no defect information is available, no quantitative

evaluation can be made regarding whether or not the presence of weld material defects was a common factor related to liner failure. Based on the lack of information a determination cannot be made whether or not the presence of weld material defects is a common factor contributing to liner failure.

6.4 ANALYSIS OF TANK CONSTRUCTION ASPECTS

This section addresses the various construction aspects of the SSTs that may have contributed to liner failures. Aspects of tank construction are important to investigate because they represent the possibility that some tanks may have been inherently at risk for failure before storing waste. This can also be important in determining whether certain conditions observed in the tanks were more detrimental because of distinguishing design features.

In Section 4.3 it was determined that brittle fracture during cold-weather construction or weld joint defects could be areas of concern associated with liner failure. Brittle fracture of the tank liner material during cold weather construction is analyzed below as a potential common factor. Complete information is not available on weld joint defects with weld information only available for a limited number of tank farms. A qualitative discussion of weld joint defects is provided.

6.4.1 Brittle Fracture or Crack Propagation Due to Cold Weather Construction

Construction of the steel liner during temperatures below the minimum design metal temperature of 18°F has been considered a possible common factor resulting in liner failure (see Section 4.3.1). Construction activities on the steel liner may result in impacts to the liner (e.g., dropped tools, impacts from equipment on vehicles, crane activities, etc.) by considering if the temperature during the construction period was ever below 18°F. A refinement to this would be to determine the number of construction hours by farm during which the environmental temperature was less than 18°F. However, daily construction reports, by tank, and hourly temperature data during the construction period are not available and such a refinement is not possible.

If an impact occurred to the steel liner while the temperature was below the minimum design metal temperature, there is the possibility of brittle fracture. Section 5.4.1 discusses the details of construction history during cold weather and the possibility of brittle fracture. Table 6-13 shows the number of confirmed leakers from each farm and highlights the tank farms during which cold-weather construction occurred.

Table 6-13. Minimum Environmental Temperatures During Liner Construction and Steel Liner Failures of Single-Shell Tanks

Tank Farm	Approximate Liner Construction Start[1]	Approximate Dome Construction End[1]	Minimum Temperature During Period	Failed Tanks
A	April 1954	October 1954	14°F	2/6
AX	November 1963	June 1964	7°F	0/4
B	July 1944	October 1944	12°F	1/16
BX	April 1947	September 1947	32°F	0/12
BY	December 1949	May 1949	-2°F	1/12
C	August 1944	November 1944	>18°F	2/16
S	December 1950	May 1951	6°F	0/12
SX	October 1953	March 1954	-6°F	8/15
T	May 1944	August 1944	12°F	2/16
TX	March 1948	July 1948	13°F	2/18
TY	July 1951	October 1951	4°F	4/6
U	March 1944	August 1944	>18°F	3/16

[1] Dates were estimated using construction photographs.

If impact during low temperature construction conditions was the cause of liner failure, it might be expected that a leak would occur early on in storage operations. Only two tanks, A-105 and SX-113, failed within two years of first waste storage. In other words, only 10% of the probable liner failures that occurred in tank farms with cold-weather construction were early on during the tanks operational history. If early failure of tanks is an indicator of failure from impact at low temperatures, then qualitatively it does not appear that brittle fracture from cold-weather construction is significant. It is impossible, due to lack of records, to definitively determine whether impact to a tank liner at a temperature below its minimum design metal temperature occurred in any given tank, or whether any impacts that may have occurred contributed as a primary cause of liner leaks.

Comparison can be made between those tanks for which liner construction occurred below and above the minimum design metal temperature of 18°F. Performing a chi-square test with the values presented in Table 6-14 results in a p-value of 0.252. Since the p-value is greater than the selected significance level, $\alpha=0.05$, we accept the null hypothesis. In other words there is no statistically significant difference in the proportion of liner failures in tanks which the liners were constructed during cold temperatures (≤18°F) than warm temperatures. Based on the available information it appears that cold-weather construction is not a common factor contributing to liner failure.

Table 6-14. Brittle Fracture Failure Rate Observational Data

	Probable Liner Failure	Liner Failure Not Known	Total
Construction Below 18°F	20	85	105
Construction Above 18°F	5	39	44
Total	**25**	**124**	**149**

6.4.2 Cold Working and Strain Aging

Based on construction specifications for the SST farms, cold working of the SST liners included rolling or pressing of the large radius knuckle plates of the Type I, II and III tanks. Two separate cold working processes identified in construction specifications were different among the various SST farms. These processes were stress-relieving of shop-fabricated knuckle sections and peening of intermediate pass welds.

Some knuckle plates were stress-relieved after forming, but there is no indication that this occurred in all cases. Strain aging may have occurred when cold worked knuckles that were not stress relieved were subjected to moderately elevated temperatures during operation. If a liner included knuckles that were not stress relieved after forming, there is the possibility of strain aging affecting the leak tightness of the tank liner.

Another source of cold working for some of the tanks was tied to the requirement for peening of intermediate pass welds. Peening was performed in an attempt to relieve stresses and limit deformation of the tank liner but could have hidden or formed cracks depending on the care under which the peening was performed. Peening of weld passes may have also impacted the leak tightness of the liner (positively if stress were relieved or negatively if cracks were hidden or formed).

Section 5.4.2 discusses the details of cold working and strain aging as inferred from the SST construction specifications. Table 6-15 shows the number of confirmed leakers from each farm and highlights the tank farms with knuckles, whether the knuckles were stress relieved, and whether intermediate welds were peened.

Table 6-15. Cold Working Specified in Single-Shell Tank Construction Specifications

Tank Farm	Construction Specification	Knuckle (Yes/No)	Knuckle Stress Relieved (Yes/No)	Intermediate Welds Peened (Yes/No)	Failed Tanks
A	HWS-5614	No	N/A	No	2/6
AX	HWS-8237	Yes	No	No	0/4
B	HW-1946	Yes	No	No	1/16
BX	HW-1946	Yes	No	No	0/12
BY	HW-3783	Yes	Yes	No	1/12
C	HW-1946	Yes	No	No	2/16
S	HW-3937	Yes	Yes	Yes	0/12
SX	HW-4957	No	N/A	No	8/15
T	HW-1946	Yes	No	No	2/16
TX	HW-3061	Yes	No	No	2/18
TY	HW-4696	Yes	Yes	Yes	4/6
U	HW-1946	Yes	No	No	3/16

For those tanks which contained knuckles, comparison can be made between those tanks for which the knuckles were stress relieved after forming and those that were not (or for which no such requirements were given). Performing a chi-square test with the values presented in Table 6-16 for tank liner failures for tanks with knuckles that were or were not stress-relieved results in a p-value of 0.336. The expected values from the chi-square test include one value (out of 4) which is less than 5, and therefore the sample does not meet one of the general rules for

chi-square testing (i.e., no more than 20% of the expected values are less than 5). Thus, the results of the chi-square testing generally would not be considered relevant. Performing Fisher's exact test, the calculated p-value is 0.341, very nearly the same as from the chi-square test. Because the p-value is greater than the selected significance level, α=0.05, we accept the null hypothesis. In other words there is no statistically significant difference in the proportion of liner failures in tanks in which the knuckles were or were not stress-relieved as part of shop fabrication. Based on the available information it appears that not stress-relieving knuckles as part of shop fabrication is not a common factor contributing to liner failure.

Table 6-16. Knuckle Stress Relieving Failure Rate Observational Data

	Probable Liner Failure	Liner Failure Not Known	Total
Knuckle Stress-Relieved	10	88	98
Knuckle Not Stress-Relieved	5	25	30
Total	**15**	**113**	**128**

Comparison can also be made between those tanks for which peening of intermediate pass welds was specified and those for which it was not. Performing a chi-square test with the values presented in Table 6-17 for tank liner failures for tanks with weld peening performed compared to those for which weld peening was not performed results in a p-value of 0.510. The expected values from the chi-square test include one value (out of 4) which is less than 5, and therefore the sample does not meet one of the general rules for chi-square testing (i.e., no more than 20% of the expected values are less than 5). Thus, the results of the chi-square testing generally would not be considered relevant. Performing Fisher's exact test, the calculated p-value is 0.507, very nearly the same as from the chi-square test. Because the p-value is greater than the selected significance level, α=0.05, we accept the null hypothesis. In other words there is no statistically significant difference in the proportion of liner failures in tanks in which peening of the intermediate welds was specified. Based on the available information it appears that intermediate weld peening is not a common factor contributing to liner failure.

Table 6-17. Weld Peening Failure Rate Observational Data

	Probable Liner Failure	Liner Failure Not Known	Total
Weld Peening Specified	4	14	18
Weld Peening Not Specified	21	110	131
Total	**25**	**124**	**149**

6.4.3 Weld Joint Discontinuities and Defects

The information in Section 5.4.3 regarding preheat and interpass temperatures shows that there can be a significant difference in these recommended temperatures whether maximum compositional limits or actual compositional information is used. The available compositional information for the earlier tank farms is significantly different from the maximum compositional information, demonstrating that it is not appropriate to use maximum compositional limits as surrogates for actual compositional information when considering preheat and interpass temperatures for welding. Also, it is not appropriate to make comparisons between actual

compositional information for some tanks and maximum compositional limits for the remaining tanks. That being said, one can still look at the available information and decide if any conclusions can be drawn. Table 6-18 summarizes the failures and failure rates as a function of preheat and interpass temperature considering both available liner composition information and specified maximum compositional information. The failure rate data with and without compositional information is charted in Figure 6-3. As previously mentioned in Section 5.4.3, early single-shell tank farms were welded without specifying temperature limitations, and later tank farms were welded using qualitative ("...warm to the hand...") and subsequently quantitative ("...not...less than 40 F..."). These specifications would have been inadequate relative to the recommended preheat and interpass temperatures below.

Table 6-18. Failures and Failure Rates as a Function of Liner Plate Preheat and Interpass Temperature Assuming High Restraint Employed During Welding

	Recommended Preheat and Interpass Temperature Based on Available Liner Composition Information					
	<65°F	**65°F**	**150°F**	**220°F**	**280°F**	**320°F**
Failed	8	1	2	4	0	10
Not Failed	56	11	40	2	4	11
Failure Rate	0.13	0.08	0.05	0.67	0.00	0.48
	Recommended Preheat and Interpass Temperature Based on Maximum Specified Composition Information					
	<65°F	**65°F**	**150°F**	**220°F**	**280°F**	**320°F**
Failed	--	--	--	4	0	21
Not Failed	--	--	--	14	4	106
Failure Rate	--	--	--	0.22	0.00	0.17

In examining the data in Table 6-18 and Figure 6-3 there are six different values for the recommended preheat and interpass temperature. Because there is large number of categories, the sample size for most categories is quite small making it difficult to provide meaningful statistical information. Considering either maximum specified compositional limits by themselves or in combination with available compositional information, the expected values for a chi-square test do not meet the general rules of thumb for chi-square testing (i.e., no more than 20% of expected values are less than five and/or no value less than one). Therefore, the chi-square test cannot provide meaningful statistical information.

Taking a more general (rather than statistical) view on whether there is a relationship between recommended preheat and interpass temperature and weld defects, liner plates with higher recommended temperatures would be expected to be more at risk, with respect to weld defects. If no actual compositional information was available the data shows all SSTs would have required significant preheat and interpass temperatures relative to what was specified for construction (i.e., no requirement given or "warm to touch"). Using available compositional information though shows that about half the tanks would have been adequately preheated at 65°F or less. If actual compositional information was available for all tanks one would expect more tanks would have lower recommended preheat and interpass temperatures. Unfortunately, no data is available to support this hypothesis.

Based on the available incomplete compositional information and discussion presented, it does not appear that the use of recommended preheat and interpass temperatures is useful in determining whether weld defects are a factor contributing to liner failure.

6.5 ANALYSIS OF OPERATIONAL SERVICE ASPECTS

This section addresses the various operational service aspects of the SSTs that may have contributed to liner failures. Aspects of tank operation are important to investigate because they represent the possibility that some tanks may have been at risk for failure because of the waste stored in the tanks or the method in which the waste was stored.

In Section 4.4 it was determined that low-cycle fatigue, high temperature-induced failure (high temperature and high rate of rise), and several corrosion mechanisms were areas of potential concern associated with liner failure. Corrosion mechanisms to be analyzed include general corrosion and pitting corrosion due to the liquid waste, crevice corrosion, SCC, concentration cell corrosion, vapor space general and pitting corrosion, and differential temperature cell corrosion.

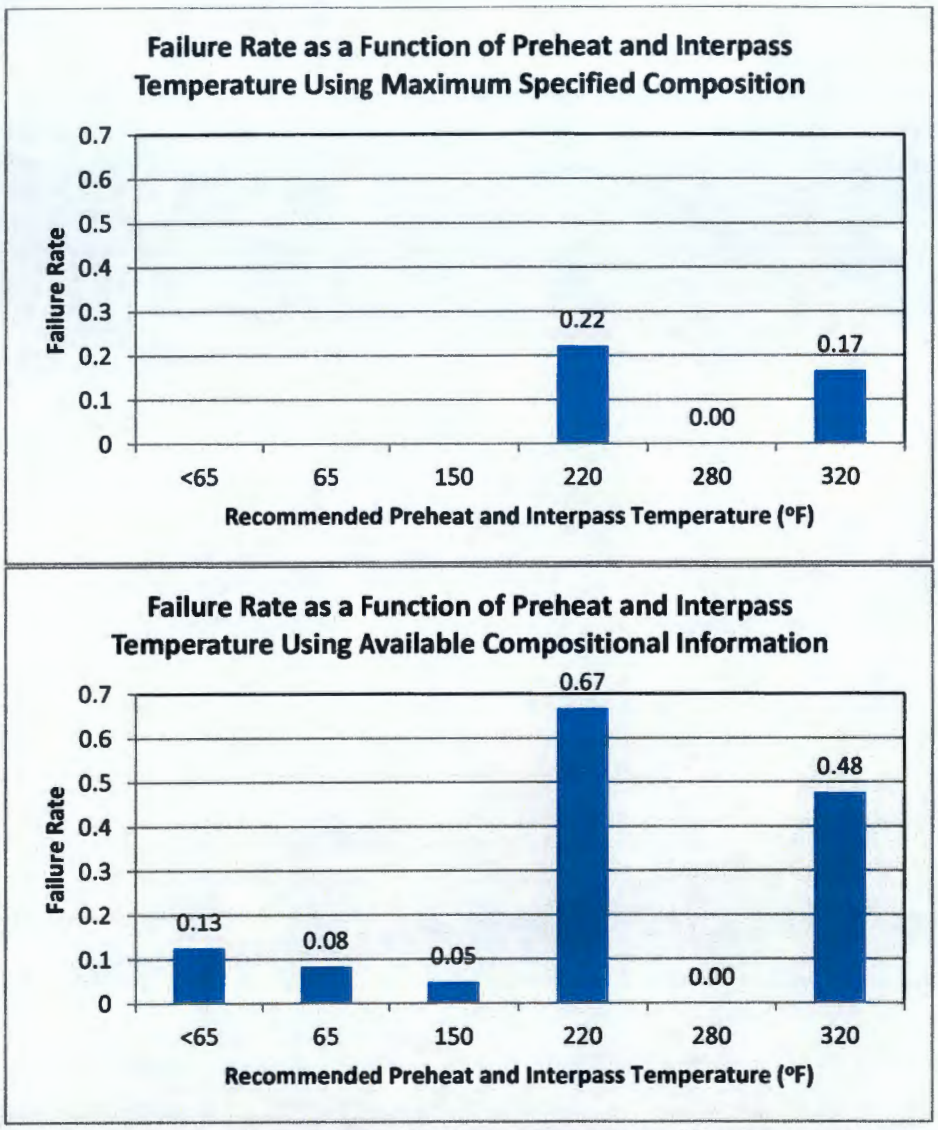


Figure 6-3. Tank Liner Failure Rate as a Function of Preheat and Interpass Temperature, with and without Available Compositional Information

6.5.1 Low-Cycle Fatigue

Operational cycling from tank fill and empty cycles during which the liners are subject to contraction and expansion and associated mechanical and thermal stresses has been identified as a possible liner failure mechanism (see Section 4.4.2). If operational cycling were considered a possible failure mechanism, then increased operational cycles would be hypothesized to cause more liner failures. Section 5.5.10 provides a tabulation of volumetric throughput information for each SST. That tank volumetric throughput information has been normalized to each tank's volume and plotted as a bar chart from greatest to least throughput in Figure 6-4. The graph shows that five of the 25 tanks with probable liner failures had relatively large volumetric throughput of waste (17.6 or higher) while the remaining 20 tanks had relatively small

volumetric throughput (8.2 or lower). There is a significant gap between the large and small volumetric throughput values, making it difficult to determine where in the range of that gap it would be appropriate to distinguish between what is considered a low or high throughput. One could look at the extremes of the gap region (<17.6 or >8.2 as the range) and the midpoint and see if that difference in the relative populations results in different chi-square test results. These possible variations in how the population is split are presented in Table 6-19.

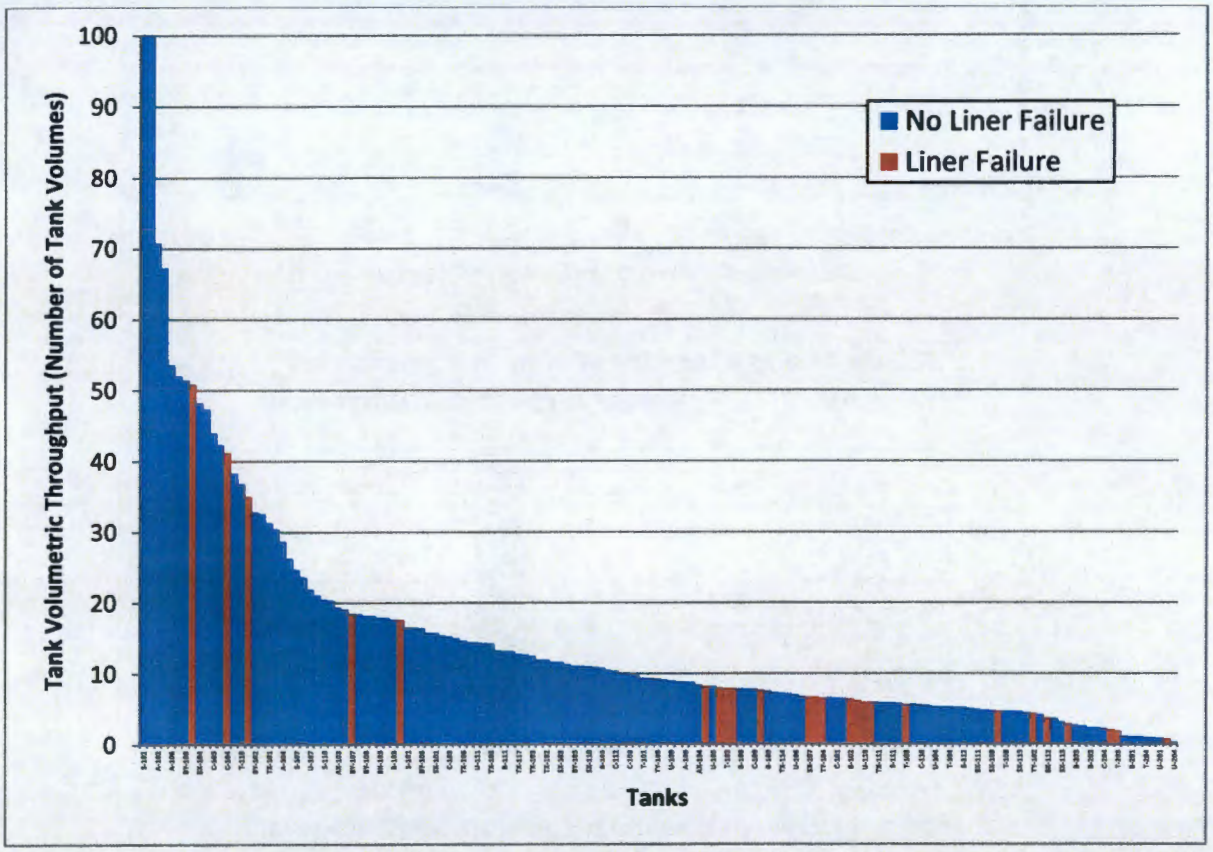


Figure 6-4. Tank Volumetric Throughput in Number of Tank Volumes for Single-Shell Tanks

Table 6-19. Tank Volumetric Throughput Observational Data

Observational Data Assuming Relatively Large Population of High Throughput Tanks			
	Probable Liner Failure	**Liner Failure Not Known**	**Total**
Throughput ≤ 8.2 tanks	20	47	67
Throughput > 8.2 tanks	5	77	82
Total	**25**	**124**	**149**
Observational Data Assuming Relatively Small Population of High Throughput Tanks			
	Probable Liner Failure	**Liner Failure Not Known**	**Total**
Throughput ≤ 17.6 tanks	20	91	111
Throughput > 17.6 tanks	5	33	38
Total	**25**	**124**	**149**
Observational Data Assuming Equal Populations of High and Low Throughput Tanks			
	Probable Liner Failure	**Liner Failure Not Known**	**Total**
Throughput ≤ 9.2 tanks	20	55	75
Throughput > 9.2 tanks	5	69	74
Total	**25**	**124**	**149**

Performing a chi-square test with the three populations presented in Table 6-19 results in the following p-values:

Population	p-value
Large Population of High Throughput Tanks	0.00011
Small Population of High Throughput Tanks	0.489
Equal Populations of High and Low Throughput Tanks	0.00115

Considering the above p-values, there is a significant difference in the value depending on how the populations are split. As mentioned previously, no basis exists for selecting how to split the population. Therefore, selecting how to split the population is arbitrary and that selection has an impact on the result of the test, using our selected significance level, $\alpha=0.05$. In examining the data above it is clear that regardless of how the population is split, the population of tanks with less throughput has a higher failure rate than tanks with greater throughput. This is contrary to the original hypothesis that greater throughput would result in a higher failure rate.

Based on the available information it appears that low-cycle fatigue is not a factor contributing to liner failure.

6.5.2 Temperature-Induced Failure

High temperatures or high temperature rate of rise within SSTs potentially can create conditions under which a mechanical or chemical tank liner failure mechanism is more likely to occur. Two high temperature related conditions have been identified as potential mechanisms that could contribute to tank liner failure. The conditions considered are high temperature and temporal gradient (temperature rate of rise) within the waste and tank structure (see Section 4.4.3). Each of these will be discussed below.

6.5.2.1. High Temperature-Induced Failure

As operating temperature increases within the tanks, thermal stresses can increase within the tank liner and chemical processes (e.g., corrosion) can accelerate. The last three SST farms constructed, SX, A and AX Farms, are described as self-concentrating or boiling waste tank farms because of the intention of storing self-boiling waste in these tank farms from REDOX and PUREX. In addition, some tanks in S and U Farms received self-boiling waste from REDOX. In comparison, waste generated prior to REDOX was well below a point of self-boiling. This waste at times was heated to boiling (e.g., evaporation processes) but the waste would self-cool in a period of a few months as the thermal heat dissipated. The nominal maximum operating temperature of the first nine tank farms is 180°F for sludge and supernatant (ARH-76). The nominal maximum operating temperature of SX, A, and AX Farms is 300-310°F for sludge and 240°F supernatant (ARH-76).

Table 5-34 identifies the SSTs that underwent self-concentration. In all, 24 tanks underwent self-concentration with 11 of these tanks having liner failures. Comparison of liner failure rates can be made between those tanks that contained self-concentrating waste and those that did not. Performing a chi-square test with the values presented in Table 6-20 for tank liner failures for tanks with and without self-concentrating waste results in a p-value of 3.2×10^{-5}. The expected values from the chi-square test include one value (out of 4) which is less than 5, and therefore the sample does not meet one of the general rules for chi-square testing (i.e., no more than 20% of the expected values are less than 5). Thus, the results of the chi-square testing generally would not be considered relevant. Performing Fisher's exact test, the calculated p-value is 2.2×10^{-4}. Because the p-value is less than the selected significance level, $\alpha=0.05$, we reject the null hypothesis. In other words, there is a statistically significant difference in the proportion of liner failures in tanks which contained self-concentrating waste and those that did not. Based on the available information it appears that storing high temperature self-concentrating waste is a common factor contributing to liner failure.

Table 6-20. Self-Concentrating Waste Failure Rate Observational Data

	Probable Liner Failure	Liner Failure Not Known	Total
Self-Concentrating (Boiling) Waste	11	13	24
Non-Boiling Waste	14	111	125
Total	**25**	**124**	**149**

6.5.2.2. Rapid Rate of Temperature Rise Induced Failure

The 1959 report (HW-59919) defining physical limitations for the existing SSTs included a recommended maximum rate of temperature rise for liquid waste. A maximum uniform temperature rise of 2°F/day or 40°F incremental rise followed by four weeks at a static temperature was recommended. The purpose of these recommendations was to minimize cracking in the concrete and to minimize the thermal stress in the steel liner plate. The 2°F/day temperature rise resulted in a nearly uniform temperature gradient across the concrete wall of 25°F/ft (HW-59658, *Heat Transfer Study for Self-Boiling Radioactive Wastes*) and minor thermal expansion compressive stress on the bottom liner. Document HW-56821 showed that a

25°F and 175°F instantaneous temperature rise within a tank (waste introduction) resulted in a 5,000 psi and 33,000 psi compressive stress on the bottom liner, respectively. A 40°F instantaneous temperature rise would then result in a nominal 8,000 psi compressive stress on the bottom plate, which is well below the yield strength (nominally 24,000 to 33,000 psi, see Table 5-6). The actual stress at which buckling of the bottom liner would occur can be significantly less than the critical compressive stress (~0.2) and is dependent upon several factors specific to a particular liner including thickness, radius, imperfections and discontinuities (Hutchinson 2010, *Knockdown Factors for Buckling of Cylindrical and Spherical Shells Subject to Reduced Biaxial Membrane Stress*).

Temperature rate of rise data for waste types are tabulated in Table 6-21. The data comes from Figure 5-24, Figure 5-25, Figure 5-26, Figure 5-27, Figure 5-28, Figure 5-29, and Table 5-27 and from RHO-CD-1172 for tanks A-103 and A-105 and ARH-258 for tank BY-112. Notably no tank temperature rate of rise data is available for high temperature bottoms from atmospheric evaporators (242-B, 242-T) discharged to SSTs. The waste discharged from the atmospheric evaporators at nominally 230°F which would result in heating of the receiving tank. The temperature rise would be dependent upon the initial temperature and waste volume in the receiving tank.

The information in Table 6-21 does indicate that temperature rate of rise for waste from $BiPO_4$ processing wastes were relatively very low in comparison to later waste types. Temperature rate of rise from REDOX and PUREX waste was relatively high, but the tanks encountering the highest temperature rate of rise (tanks S-101, S-103, SX-106, and U-111 all over 10°F/day) do not have probable liner failures. Also, operation of the ITS-2 unit in tank BY-112, which does not have a probable liner failure, resulted in a high temperature rate of rise for that tank. One may try to infer from these tanks that temperature rate of rise may not be a factor contributing to liner failure. However, the lack of complete temperature rate of rise information among all tanks does not make it possible to make this statement. Based on the lack of information a determination cannot be made whether or not the presence of a high temperature rate of rise is a common factor contributing to liner failure.

Table 6-21. Tank Temperature Rate of Rise Data (2 Pages)

Waste Type	Tank	Starting		Ending		Rate of Rise
		Temperature	Date	Temperature	Date	
Bismuth Phosphate Metal Waste	T-101	132°F	8/21/1945	166°F	3/24/1946	0.2°F/day
	TX-101	110°F	11/30/1949	128°F	2/28/1950	0.2°F/day
	B-103	83°F	12/24/1945	102°F	1/22/1946	0.7°F/day
	BX-101	130°F	7/21/1950	170°F	12/1/1950	0.3°F/day
Bismuth Phosphate First Cycle & Coating Waste	TX-109	135°F	12/31/1949	142°F	1/31/1950	0.2°F/day
	B-107	90°F	8/21/1945	96°F	9/20/1945	0.2°F/day
	BX-110	95°F	11/30/1949	105°F	12/31/1949	0.3°F/day
	BX-110	125°F	4/26/1950	138°F	5/26/1950	0.6°F/day
Bismuth Phosphate Second Cycle Waste	T-110	72°F	4/26/1950	90°F	5/26/1950	0.6°F/day
	B-111	59°F	4/26/1950	78°F	5/26/1950	0.6°F/day
REDOX Concentrated & Neutralized	S-101	75°F	7/19/1953	159°F	7/30/1953	7.6°F/day
		164°F	8/8/1953	246°F	8/30/1953	3.9°F/day
		192°F	8/18/1953	204°F	8/19/1953	12°F/day

Table 6-21. Tank Temperature Rate of Rise Data (2 Pages)

Waste Type	Tank	Starting		Ending		Rate of Rise
		Temperature	Date	Temperature	Date	
Waste (No Coating Waste)	S-102	70°F	9/16/1953	116°F	9/23/1953	6.6°F/day
	S-103	80°F	12/7/1953	129°F	12/10/1953	16°F/day
	SX-101	65°F	5/27/1954	91°F	7/1/1954	0.7°F/day
	SX-102	86°F	9/9/1954	158°F	9/28/1954	3.4°F/day
	SX-103	100°F	11/21/1954	143°F	11/28/1954	6.1°F/day
	SX-104	74°F	3/1/1955	125°F	3/15/1955	3.6°F/day
	SX-105	130°F	7/21/1955	150°F	7/28/1955	2.9°F/day
	SX-106	58°F	10/8/1954	74°F	10/9/1954	16°F/day
		94°F	10/22/1954	107°F	10/23/1954	13°F/day
		58°F	10/8/1954	107°F	10/23/1954	3.3°F/day
	SX-107	191°F	5/16/1956	225°F	5/23/1956	4.9°F/day
		265°F	1/15/1958	390°F	2/5/1958	6°F/day
	SX-108	130°F	11/24/1955	160°F	12/1/1955	4.3°F/day
	SX-109	117°F	9/29/1955	185°F	10/13/1955	4.9°F/day
	SX-110	107°F	9/30/1960	148°F	10/31/1960	1.3°F/day
	SX-111	103°F	6/13/1956	136°F	6/20/1956	4.7°F/day
	SX-112	101°F	2/15/1956	125°F	2/22/1956	3.4°F/day
	SX-113	155°F	3/5/1958	175°F	3/12/1958	2.9°F/day
	SX-114	135°F	12/26/1956	160°F	1/2/1957	3.6°F/day
	SX-115	100°F	9/2/1958	184°F	9/30/1958	3.0°F/day
	U-110	50°F	1/27/1954	202°F	4/30/1954	1.6°F/day
		128°F	3/18/1954	183°F	4/5/1954	3.1°F/day
		270°F	12/18/1959	287°F	12/24/1959	2.8°F/day
		187°F	1/31/1963	217°F	2/7/1963	4.3°F/day
	U-111	65°F	2/12/1954	134°F	3/25/1954	1.7°F/day
		104°F	3/9/1954	116°F	3/10/1954	12°F/day
		231°F	1/7/1959	274°F	1/21/1959	3.1°F/day
	U-112	60°F	3/18/1954	92°F	3/29/1954	2.9°F/day
		137°F	12/14/1961	219°F	2/1/1962	1.7°F/day
PUREX Waste	A-103	80°F	5/28/1956	215°F	6/30/1956	4.1°F/day
		105°F	2/6/1968	165°F	2/23/1968	3.5°F/day
	A-105	263°F	3/1/1963	295°F	3/12/1963	2.9°F/day
		295°F	3/20/1963	323°F	3/26/1963	4.7°F/day
		119°F	1/31/1963	191°F	2/25/1963	2.9°F/day
In-Tank Solidification #2	BY-112	188°F	2/4/1968	198°F	2/5/1968	10°F/day

6.5.3 General Corrosion

General corrosion information is available for a number, but not all, of the major waste streams introduced into the SSTs. The majority of general corrosion rate information is based on historical testing with waste simulants representing the major constituents present in the waste stream. Some field corrosion testing is also available. General corrosion data has been reported for the liquid waste, solid waste, solid-liquid interface, liquid-vapor interface, and vapor above the waste. This section of analysis only examines data for liquid and solid waste. The liquid-vapor data, solid-liquid interface data, and vapor data are analyzed in Sections 6.5.7.1, 6.5.7.2, and 6.5.8, respectively.

Combined general corrosion data is presented in Table 6-22. Almost all general corrosion rates are less than 1 mil/yr and some are considerably less than 1 mil/yr. At a general corrosion rate of 1 mil/yr, half a ¼-in. thick steel tank liner would be corroded away in 125 years. The notable exceptions are PUREX neutralized acid waste tested in tank A-101 with up to 1.68 mil/yr, high hydroxide (5-10 M) solidified waste at 4.7 mil/yr, and pH 7 Hot Semiworks waste. The PUREX neutralized acid waste with a corrosion rate slightly greater than 1 mil/yr is likely not of concern. Fission product recovery was being performed on PUREX waste, so the time of exposure within a SST liner would have been relatively short duration, say twenty years. The high hydroxide solidified waste is of interest because the waste was made to simulate dried out waste reconstituted with some water. This could be considered more similar to current conditions in stabilized SSTs after saltwell pumping than historical waste types. Although this is very limited data, stabilized SST waste with a high hydroxide concentration (5-10 M) may have a relatively high corrosion rate, greater than 1 mil/yr. The low pH Hot Semiworks waste emphasize the effect of pH and the need to keep certain wastes alkaline to counteract possible reduction of pH.

In 1983, results of year-long testing of simulants for DST waste were reported including data on uniform corrosion (PNL-4727, *Double-Shell Slurry Low Temperature Corrosion Tests*). The waste testing included a wide range of compositions for major constituents also found in SST waste. The composition range of the waste tested is shown below in Table 6-23. There were roughly 50 compositions tested with steel specimens of A-537, Grade 1 (steel used in DST farms, 241-AN and 241-AW and later 241-AP [RPP-RPT-55983, *241-AP Tank Farm Construction Extent of Condition Review for Tank Integrity*]) and A-516 (representative of earlier SSTs having 0.12-0.13%C, 0.86-0.93%Mn, 0.25-0.26%Si and steel used in 241-SY [RPP-RPT-54819, *241-SY Tank Farm Construction Extent of Condition Review for Tank Integrity*]). Several trends were noticed in the general corrosion rate data. Corrosion rates generally increased with increasing temperature and decreased with longer exposure duration, generally due to formation of a protective oxide coating. The corrosion rate is strongly influenced by the hydroxide concentration, with the corrosion rate decreasing with decreasing hydroxide concentration. For all combinations of solution chemistries and temperatures up to 212°F during 12 months exposure, uniform corrosion rates were less than 1 mil/yr. At temperature of 140°C (284°F) only one composition (0.1 M OH^-, 0.2 M F^-, 2.5 M NO_3^-, 0.01 M NO_2^-, 0.5 M Al, 0.6 M citrate) had a corrosion rate in excess of 1 mil/yr, and suffered severe localized attack. Currently, the temperature of waste in most SSTs, with the exception of SX Farm, is less than nominally 100°F. Currently, within SX Farm the temperature of waste is less than nominally 180°F.

Table 6-22. General Corrosion Rate Data for Wastes Stored in Single-Shell Tanks

Process	Waste Type	Actual Waste or Simulant	Exposure Period	Temperature	Condition/ Location	General Corrosion Rate (mil/yr)	Reference
Bismuth Phosphate	Metal Waste	Simulant, pH 10	7.4-7.6 months	72°C	Liquid	Gain	HW-18595, App I, Table I
	Metal Waste	Simulant, pH 11	7.4-7.5 months	72°C	Liquid	Gain	HW-18595, App I, Table I
	Metal Waste	Simulant, pH 10.5	424-472 hrs	102°C (boiling)	Liquid	0.08-0.09	HW-24136, Table 3
	First Cycle	Simulant, pH 6	3-6 months	80°C	Liquid	0.04-0.12	HW-26202, Table 3
	First Cycle	Simulant, pH 7	3-6 months	80°C	Liquid	0.01-0.10	HW-26202, Table 3
	First Cycle	Simulant, pH 8	3-6 months	80°C	Liquid	0.06-0.10	HW-26202, Table 3
	First Cycle & Coating Waste	Actual, TX-109	7 months (11/52-6/53)	--	Liquid	0.10-0.28	HW-30641, Table 1
Uranium Recovery (TBP Process)	TBP	Simulant, pH 7	1-3 months	30°C	Liquid	0.08-0.12	HW-30041
	TBP	Simulant, pH 8	1-3 months	30°C	Liquid	0.06-0.19	HW-30041
	TBP	Simulant, pH 9	1-3 months	30°C	Liquid	0.07-0.22	HW-30041
REDOX	REDOX	Actual (SX-107)	1 year	121-134°C	Liquid	0.14-0.47	HW-53308, Tables I& II
PUREX	Neutralized Acid Waste	Simulant	1-3 months	104°C	Liquid	0.25-1.04 (0.29-1.25)	HW-32734, Table I
	Neutralized Acid Waste	Actual, A-101	130 days (2/6/56-6/15/56)	--	Liquid	0.63-1.68	HW-49574, Tables I & III
	Organic Wash Waste	Simulant, pH 8.9-11.0	840 hours	100°C	Liquid	(0.05)	HW-70872, p. C-12
Evaporator Processes	High Hydroxide Solidified Waste	Simulant	7-22 months	60-95°C	Solid with 5-15% water	0.01-4.7	BNWL-1869, Table II
	High Phosphate, Sulfate, or Nitrate Solidified Waste	Simulant	7-22 months	60-95°C	Solid with 5-15% water	<0.01-0.09	BNWL-1869, Table II
Hot Semiworks	Hot Semiworks Waste	Simulant, from Sr recovery operations, pH 7	--	80°C	Liquid	67-120	HW-70165, p. C-8
	Hot Semiworks Waste	Simulant, from Sr recovery operations, pH 11.2	--	80°C - boiling	Liquid	<1.2	HW-70165, p. C-8

References: HW-18595, *Corrosion of REDOX Waste Storage Tank Construction Materials*

Table 6-23. Double-Shell Tank Corrosion Testing Composition Range

Constituent	Composition Range (M)
OH^-	0.5 - 10.0
NO_3^-	1.0 - 8.0
NO_2^-	0.2 - 10.0
AlO_2^-	0.0 - 5.0
CO_3^{-2} (2 fixed values)	0.2 or 0.25
PO_4^{-3}	0.0 - 2.0
EDTA/HEDTA	0.0 - 1.0
Citrate (3 fixed values)	0.0, 0.2 or 0.6
SO_4^- (single value)	0.05

Reference PNL-4727, Table 1

Based on the available information above it appears that general corrosion is not a factor contributing to liner failure. The relatively low corrosion rates indicate long periods of time would be required to fail a tank liner via general corrosion. Continuing decrease in waste temperatures should reduce general corrosion rates. However, the presence of waste with high concentration of hydroxide ion or relatively low pH waste may be problematic long term.

6.5.4 Pitting Corrosion

Pitting corrosion information is available for a few, but not all of the major waste streams introduced into the SSTs. The majority of pitting corrosion rate information is based on testing with waste simulants representing the major constituents present in the waste stream. Some field corrosion testing is also available. Pitting corrosion data has been reported for the liquid waste, solid waste, solid-liquid interface, liquid-vapor interface, and vapor above the waste. This section of analysis only examines data for liquid and solid waste. The liquid-vapor interface pitting corrosion data, solid-liquid interface pitting corrosion data, and vapor pitting corrosion data are analyzed in Sections 6.5.7.1, 6.5.7.2, and 6.5.8, respectively.

Combined liquid-phase pitting corrosion data is presented in Table 6-24. With the exception of PUREX-generated, higher pH, neutralized Zirflex decladding solution, all pitting corrosion rates are greater than 1 mil/yr and some are considerably greater than 1 mil/yr. For testing in actual tank waste, average pitting rates were on the order of 5 mil/yr or less, except for PUREX neutralized acid waste which had an average pitting rate of 8.97 mil/yr. In general, tested simulants have higher average and maximum pitting rates than actual waste. For TBP waste simulants, short duration (1 month) pitting rates are higher than longer duration (3 months) pitting rates. The pitting rate associated with high hydroxide solidified waste is of interest because the waste was made to simulate dried out waste reconstituted with some water. This could be considered more similar to current conditions in stabilized SSTs after saltwell pumping than historical waste types. Although this is very limited data, stabilized SST waste with a high

hydroxide concentration (5-10 M) may have a relatively high pitting rate, on the order of 7-8 mil/yr. PUREX neutralized acid waste also has a relatively high pitting rate. The PUREX OWW has a relatively high pitting rate but it is based on short duration (35 days) testing and may not be representative of longer term pitting.

Table 6-24. Liquid Phase Pitting Corrosion Rate Data for Wastes Stored in Single-Shell Tanks (2 Pages)

Process	Waste Type	Actual Waste or Simulant	Exposure Period	Temperature	Condition/ Location	Average (Maximum) Pit Depth (mil)	Average (Maximum) Pitting Rate (mil/yr)	Reference
Bismuth Phosphate	First Cycle & Coating Waste	Actual, TX-109	7 months (11/52-6/53)	--	Liquid	1.7 (2.0-2.1)	2.8-3.0	HW-30641, Table 1
Uranium Recovery (TBP Process)	TBP	Simulant, pH 7	1 month	30°C	Liquid	--	6.1-12.2 (8.0-17.9)	HW-30041
	TBP	Simulant, pH 7	3 months	30°C	Liquid	--	5.5 (6.6-9.1)	HW-30041
	TBP	Simulant, pH 8	1 month	30°C	Liquid	--	8.8-15.4 (12.2-34.6)	HW-30041
	TBP	Simulant, pH 8	3 months	30°C	Liquid	--	4.6-9.5 (5.2-10.9)	HW-30041
	TBP	Simulant, pH 9	1 month	30°C	Liquid	--	7.3-11.4 (9.8-14.2)	HW-30041
	TBP	Simulant, pH 9	3 months	30°C	Liquid	--	5.4-10.4 (7.1-12.5)	HW-30041
REDOX	REDOX (excluding Coating Waste)	Actual, SX-107	1 year	121-134°C	Liquid	1.59-2.06 (1.98-4.62)	1.59-2.06	HW-53308, Table II
PUREX	Neutralized Zirflex Decladding Solution	Simulant, pH 5.5	5 months	25-40°C	Liquid	(6.5-13.)	(16-31)	HW-61662, Table VIII
	Neutralized Zirflex Decladding Solution	Simulant, pH 6.3	5 months	25-40°C	Liquid	(5.5-6.5)	(13-16)	HW-61662, Table VIII
	Neutralized Zirflex Decladding Solution	Simulant, pH 6.9	5 months	25-40°C	Liquid	(3.0-5.5)	(7.2-13)	HW-61662, Table VIII
	Neutralized Zirflex Decladding Solution	Simulant, pH 8.5	5 months	25-40°C	Liquid	0	0	HW-61662, Table VIII
	Neutralized Zirflex Decladding Solution	Simulant, pH 9.3	5 months	25-40°C	Liquid	0	0	HW-61662, Table VIII
	Neutralized Acid Waste	Actual, A-101	130 days (2/6/56-6/15/56)	--	Liquid	0.741-2.99 (2.14-3.83)	2.224-8.97 (6.42-11.49)	HW-49574, Tables IV & VI
	Neutralized Acid Waste	Actual, A-101	130 days (2/6/56-6/15/56)	--	Liquid, adjacent to PTFE washer	1.585 (2.485)	4.755 (7.455)	HW-49574, Table VII
	Organic Wash Waste	Simulant, pH 8.9-11.0	840 hours	100°C	Liquid	~0.5	~5.2	HW-70872, p. C-12
Evaporator Processes	High Hydroxide	Simulant	7 months	60-95°C	Solid with 5-15% water	0-5 (0-9)	0-8.6 (0-15)	BNWL-1869, Table

Table 6-24. Liquid Phase Pitting Corrosion Rate Data for Wastes Stored in Single-Shell Tanks (2 Pages)

Process	Waste Type	Actual Waste or Simulant	Exposure Period	Temperature	Condition/ Location	Average (Maximum) Pit Depth (mil)	Average (Maximum) Pitting Rate (mil/yr)	Reference
	Solidified Waste							III
	High Hydroxide Solidified Waste	Simulant	12 months	60-95°C	Solid with 5-15% water	1-7 (2-12)	1-7 (2-12)	BNWL-1869, Table III
	High Hydroxide Solidified Waste	Simulant	22 months	60-95°C	Solid with 5-15% water	4-14 (8-20)	2.2-7.6 (4.4-11)	BNWL-1869, Table III

Pitting corrosion control limits have been developed to inhibit pitting in dilute nitrate solutions (less than 1 M) in the Savannah River Site's waste storage tanks (WSRC-MS-2003-00882). Pitting has not been observed in the Savannah River Site wastes above 1 M nitrate because of the associated high concentration of hydroxide which prevents pitting. The pitting corrosion control limits for dilute nitrate solutions established at the Savannah River Site are shown in Table 6-25.

Table 6-25. Dilute Nitrate Pitting Corrosion Control Limits

For $[NO_3^-]$ & $[OH^-]$ Range	Parameter	Limit
$0.02M<[NO_3^-]<1.0M$ & $[OH^-]<1.0$ M	$[OH^-]$	1.0 M
	OR	
	$[NO_2^-]$	$0.038x[NO_3^-]x10^{1.64}$
$[NO_3^-]\leq 0.02M$ & $[OH^-]<1.0$ M	$[OH^-]$	1.0 M
	OR	
	$[NO_2^-]$	$0.00076x10^{1.64}$

Reference WSRC-MS-2003-00882, Table 2.

To determine whether the potential for pitting from dilute nitrate solutions may occur in Hanford SSTs, the criteria in Table 6-25 can be compared against the waste composition information presented in Table 5-39, Table 5-41, Table 5-42, and Table 6-27 (see Section 6.5.6) for liquid (supernatant) samples. The specific criteria considered are minimum hydroxide or minimum nitrite concentration when the nitrate concentration is less than 1.0 M. If either criterion is satisfied, pitting would not be expected. These comparisons are made in Table 6-26. For any composition with both the nitrate and hydroxide concentration less than 1.0 M, those values are shaded in gray regardless of the nitrite concentration. For those compositions with both nitrate and hydroxide concentration less than 1.0 M and nitrite concentration less than the minimum limit from Table 6-25, the nitrite concentration is also shaded gray. The following waste types had samples, simulants, or flowsheet values that exceeded one of the considered criteria:

- $BiPO_4$ – CW circa 1945, flowsheet
- PUREX – Neutralized Zircaloy Cladding Removal Waste Supernatant, based on AW-105 sample results ca. 1986 and flowsheet values
- Evaporation Processes –242-S, and 242-A, samples
- In-Farm Process – PUREX sludge washing, flowsheet minimum

Although CW circa 1945 does not meet the dilute nitrate limits to inhibit pitting corrosion, CW was combined with 1C waste until 1955 and would not have been disposed to a tank as a separate waste stream. By the time of the 1951 $BiPO_4$ flowsheet, the CW stream shows compliance with the dilute nitrate limits to inhibit pitting corrosion. Early CW which was discharged along with 1C waste should not be a concern for pitting corrosion due to dilute nitrate concentration.

PUREX neutralized zircaloy cladding removal waste, based on sample and flowsheet values, does not meet the dilute nitrate criteria to inhibit pitting corrosion. The simulant neutralized Zirflex decladding solution did not show pitting at pH of 8.5 or higher (see Table 6-24). The pH of the sample from DST AW-105 was 13.2. Coating removal waste from zircaloy clad fuel was not segregated in SST farms, but sent to tanks in C Farm that contained other waste types. The likelihood of pitting occurring in SSTs that received PUREX neutralized zircaloy cladding removal waste seems low.

Evaporator feed samples were sometimes dilute waste and it would be anticipated that at times these streams would not meet the pitting criteria. The available evaporator feed samples typically met the criteria limiting pitting from dilute nitrate, inferring dilute nitrate solutions were not long term concerns from the standpoint of extended environments conducive to pitting.

PUREX sludge washing flowsheet minimum values do not meet dilute nitrate pitting limits but the sole sample available shows much higher nitrite concentration which would alleviate any concern for pitting.

Table 6-26. Comparison of Waste Stream Compositions to Criteria for Limiting Pitting Corrosion in Dilute Nitrate Solutions (6 Pages)

Process	Waste Type	Data Type	$[NO_3^-]$	$[NO_2^-]$	$[OH^-]$	Req'd $[NO_2^-]$
Bismuth Phosphate	Coating Removal Waste, ca. 1945	Flowsheet	0.83	0.62	0.39	1.38
	Coating Removal Waste, ca. 1951	Flowsheet	0.73	0.81	1.09	--
	Metal Waste Supernatant, T-101 ca 1947	Sample	0.085	--	--	--
	Metal Waste Supernatant, T-102 ca 1947	Sample	0.771	--	--	--
	Metal Waste Supernatant, T-103 ca 1947-48	Sample	0.603	--	--	--
	Metal Waste Supernatant, 241-T Composite ca 1947-48	Sample	0.543	--	--	--
	Metal Waste Supernatant, U-103 ca 1948-49	Sample	0.37	--	--	--
	Metal Waste Supernatant, U-103 ca 1948-49	Sample	0.39	--	--	--
	Metal Waste Simulant, Average	Simulant	0.52	--	--	--
	First Cycle Waste, ca. 1951	Flowsheet	1.5	--	--	--
	First Cycle Waste, ca. 1954	Flowsheet	1.83	--	--	--
	Combined First Cycle and Coating Removal Waste	Flowsheet	1.4	0.056	0.075	--
	Second Cycle Waste	Flowsheet	1.01	--	--	--
	224 Waste	Flowsheet	0.68	--	--	--
Uranium Recovery	TBP Waste Prior to In-Plant Scavenging, HW-4	Flowsheet	6.19	--	0.08	--
	TBP Waste Prior to In-Plant Scavenging, HW-5	Flowsheet	6.19	--	0.08	--

Table 6-26. Comparison of Waste Stream Compositions to Criteria for Limiting Pitting Corrosion in Dilute Nitrate Solutions (6 Pages)

Process	Waste Type	Data Type	$[NO_3^-]$	$[NO_2^-]$	$[OH^-]$	Req'd $[NO_2^-]$
(TBP Process)	TBP Waste Post In-Plant Scavenging	Flowsheet	3.3	--	--	--
REDOX	REDOX Combined Waste	Simulant	3.85	0.087	1.33	--
	REDOX Concentrated and Neutralized Salt Waste, HW-4	Flowsheet	4.48	--	1.59	--
	REDOX Concentrated and Neutralized Salt Waste, HW-5	Flowsheet	4.19	--	1.21	--
	REDOX Concentrated and Neutralized Salt Waste, HW-6	Flowsheet	4.37	--	1.44	--
	REDOX Concentrated and Neutralized Salt Waste, HW-7	Flowsheet	5.35	--	1.13	--
	REDOX Concentrated and Neutralized Salt Waste, HW-8	Flowsheet	4.85	--	0.44	--
	REDOX Concentrated and Neutralized Salt Waste, HW-9	Flowsheet	4.83	--	0.69	--
	REDOX Concentrated and Neutralized Salt Waste Supernatant Liquid, SX-101 ca. 1961	Sample	6.03	2.48	4.58	--
	REDOX Concentrated and Neutralized Salt Waste Supernatant Liquid, SX-107 ca. 1961	Sample	8.65	0.65	1.27	--
	REDOX Concentrated and Neutralized Salt Waste Supernatant Liquid, SX-108 ca. 1961	Sample	8.35	0.61	1.32	--
	REDOX Concentrated and Neutralized Salt Waste Supernatant Liquid, SX-114 ca. 1961	Sample	8.15	0.45	1.53	--
PUREX	Neutralized Zircaloy Cladding Removal Waste Supernatant, AW-105 ca. 1986	Sample	0.48	0.12	0.76	0.80
	Neutralized Zircaloy Cladding Removal Waste Supernatant	Flowsheet	0.013	--	0.82	0.03
	Highly Active Waste, ca. 1955	Flowsheet	2.10	--	--	--
	Highly Active Waste Supernatant Liquid, ca. 1965	Flowsheet	0.70	3.40	0.10	1.16
	Highly Active Waste Supernatant Liquid, A-101 ca. 1964	Sample	0.226	3.36	--	--
	Highly Active Waste Supernatant Liquid, A-104 ca. 1964	Sample	0.667	3.42	--	--
	Highly Active Waste Supernatant Liquid, A-106 ca. 1964	Sample	0.58	3.35	--	--
	Highly Active Waste Supernatant Liquid, A-103 (from A-105) ca. 1972	Sample	--	--	0.914	--
	Highly Active Waste, HW #3, ca. 1956	Flowsheet	2.5	--	0.02	--
	Highly Active Waste, HW #4, ca. 1956	Flowsheet	2.1	--	--	--
	Organic Wash Waste, G-8 ca. 1961	Sample	0.031	--	--	--
	Organic Wash Waste, ca. 1965	Flowsheet	0.06	--	0.05	0.10
	Thoria Campaign Waste, ca. 1970	Flowsheet	2.58	--	0.047	--
Fission Product Recovery (B Plant)	Phase I Operations Waste	Flowsheet	0.21	--	0.28	0.35
	Phase III Ion Exchange Waste, PUREX alkaline supernatant	Flowsheet	0.43	1.67	0.01	0.71
	Phase III Ion Exchange Waste, 241-S REDOX alkaline supernatant	Flowsheet	2.61	--	1.24	--
	Phase III Ion Exchange Waste, 241-SX REDOX alkaline supernatant	Flowsheet	1.94	0.27	0.75	--
	Phase III High Level Waste, Not Concentrated	Flowsheet	1.32	--	0.17	--
	Phase III High Level Waste, Concentrated	Flowsheet	3.52	--	0.45	--
Evaporation Processes	242-B and 242-T Evaporators Bottoms, 1951-55, TX-116 Supernatant Pre-Evaporation	Sample	6.40	--	--	--

Table 6-26. Comparison of Waste Stream Compositions to Criteria for Limiting Pitting Corrosion in Dilute Nitrate Solutions (6 Pages)

Process	Waste Type	Data Type	$[NO_3^-]$	$[NO_2^-]$	$[OH^-]$	Req'd $[NO_2^-]$
	242-B and 242-T Evaporators Bottoms, 1951-55, TX-116 Supernatant Post-Evaporation	Sample	6.66	--	--	--
	In-Tank Solidification Waste, ITS-1 BY-102 Supernatant ca. 1968	Sample	4.31	1.19	5.47	--
	In-Tank Solidification Waste, ITS-2 BY-112 Supernatant ca. 1968	Sample	2.26	0.46	2.61	--
	In-Tank Solidification Waste, ITS-2 BY-112 Supernatant ca. 1972	Sample	2.1	1.4	--	--
	In-Tank Solidification Waste, ITS-2 Bottoms Supernatant ca. 1972	Simulant	2.45	1.0	4.27	--
	242-T - TX-101	Sample	1.6	0.26	1.33	--
	242-T - TX-101	Sample	--	--	0.204	--
	242-T - TX-102	Sample	3.71	2.26	1.75	--
	242-T - TX-104	Sample	2.79	0.192	0.82	--
	242-T - TX-106	Sample	0.285	1.13	4.99	--
	242-T - TX-107	Sample	2.84	0.555	0.23	--
	242-T - TX-107	Sample	3.92	0.655	1.67	--
	242-T - TX-108	Sample	6.92	0.388	0.645	--
	242-T - TX-108	Sample	5.62	0.31	0.367	--
	242-T - TX-109	Sample	4.49	1.24	2.35	--
	242-T - TX-109	Sample	4.64	1.34	1.08	--
	242-T - TX-109	Sample	3.76	0.414	--	--
	242-T - TX-111	Sample	2.32	1.39	1.03	--
	242-T - TX-114	Sample	--	--	1.57	--
	242-T - TX-118	Sample	--	--	1.99	--
	242-T - TX-118	Sample	--	--	1.83	--
	242-T - TX-118	Sample	--	--	1.38	--
	242-T - TX-118	Sample	--	--	1.72	--
	242-T - TX-118	Sample	--	--	1.34	--
	242-T - TX-118	Sample	--	--	2.98	--
	242-T - TX-118	Sample	--	--	1.87	--
	242-T - TX-118	Sample	--	--	2.86	--
	242-T - TX-118	Sample	--	--	0.874	--
	242-T - TX-118	Sample	--	--	1.58	--
	242-T - TX-118	Sample	--	--	1.46	--
	242-T - TX-118	Sample	--	--	1.32	--
	242-T - TX-118	Sample	--	--	1.37	--
	242-T - TX-118	Sample	--	--	1.27	--
	242-T - TX-118	Sample	--	--	0.759	--
	242-T - TX-118	Sample	3.99	1.175	0.885	--

Table 6-26. Comparison of Waste Stream Compositions to Criteria for Limiting Pitting Corrosion in Dilute Nitrate Solutions (6 Pages)

Process	Waste Type	Data Type	$[NO_3^-]$	$[NO_2^-]$	$[OH^-]$	Req'd $[NO_2^-]$
	242-T - TX-118	Sample	4.21	1.89	1.43	--
	242-T - TX-118	Sample	4.09	2.03	1.9	--
	242-T - TX-118	Sample	2.52	0.621	0.573	--
	242-T - TX-118	Sample	1.6	0.277	0.384	--
	242-T - TX-118	Sample	1.3	0.146	--	--
	242-T - TX-118	Sample	1.68	0.196	0.286	--
	242-T - TX-118	Sample	2.65	0.327	0.005	--
	242-T - TX-118	Sample	1.53	0.194	0.005	--
	242-T - TX-118	Sample	1.25	0.134	--	--
	242-T - TX-118	Sample	2.88	0.741	0.619	--
	242-T - TX-118	Sample	2.94	0.834	0.517	--
	242-T - TX-118	Sample	2.25	0.686	0.371	--
	242-T - TX-118	Sample	3.31	0.988	0.501	--
	242-T - TX-118	Sample	4.36	0.999	1.	--
	242-T - TX-118	Sample	3.5	1.02	0.583	--
	242-T - TX-118	Sample	3.09	0.74	0.761	--
	242-T - TX-118	Sample	2.76	0.452	1.23	--
	242-T - TX-118	Sample	3.11	0.916	0.828	--
	242-T - TX-118	Sample	2.8	0.571	0.613	--
	242-T - TX-118	Sample	3.48	0.87	0.89	--
	242-T - U-103	Sample	4.58	--	1.48	--
	242-S - S-101	Sample	1.53	0.197	0.415	--
	242-S - S-102	Sample	4.25	0.118	1.22	--
	242-S - S-102	Sample	2.56	0.958	2.78	--
	242-S - S-102	Sample	1.6	0.87	1.53	--
	242-S - S-102	Sample	3.29	1.89	3.65	--
	242-S - S-102	Sample	1.79	0.611	1.058	--
	242-S - S-102	Sample	1.61	0.818	1.16	--
	242-S - S-102	Sample	3.19	1.43	2.84	--
	242-S - S-102	Sample	3.74	0.929	1.66	--
	242-S - S-102	Sample	3.63	0.792	1.52	--
	242-S - S-102	Sample	4.29	1.9	2.98	--
	242-S - S-102	Sample	3.4	1.59	2.18	--
	242-S - S-102	Sample	1.4	0.556	0.488	--
	242-S - S-102	Sample	3.33	1.96	1.78	--
	242-S - S-102	Sample	1.98	1.21	1.07	--
	242-S - S-102	Sample	3.64	1.87	2.63	--
	242-S - S-102	Sample	2.96	1.82	1.79	--

Table 6-26. Comparison of Waste Stream Compositions to Criteria for Limiting Pitting Corrosion in Dilute Nitrate Solutions (6 Pages)

Process	Waste Type	Data Type	$[NO_3^-]$	$[NO_2^-]$	$[OH^-]$	Req'd $[NO_2^-]$
	242-S - S-102	Sample	2.66	1.41	1.66	--
	242-S - S-102	Sample	2.92	1.79	1.94	--
	242-S - S-102	Sample	2.92	1.77	1.57	--
	242-S - S-102	Sample	3.9	1.75	1.33	--
	242-S - S-102	Sample	2.76	1.27	1.21	--
	242-S - S-102	Sample	2.42	0.531	0.773	--
	242-S - S-103	Sample	4.36	0.852	1.96	--
	242-S - S-103	Sample	1.31	0.067	0.523	--
	242-S - S-103	Sample	1.43	0.579	1.18	--
	242-S - S-105	Sample	4.46	0.112	1.24	--
	242-S - S-105	Sample	1.95	0.99	6.46	--
	242-S - S-105	Sample	1.94	1	6.47	--
	242-S - S-106	Sample	4.16	0.165	1.28	--
	242-S - S-106	Sample	2.49	0.656	5.33	--
	242-S - S-106	Sample	0.0185	0.0026	0.03	0.03
	242-S - S-106	Sample	2.42	1.78	4.44	--
	242-S - S-108	Sample	4.46	0.127	1.43	--
	242-S - S-108	Sample	2.6	1.94	5.08	--
	242-S - S-109	Sample	4.35	0.158	1.81	--
	242-S - S-111	Sample	1.95	1.82	3.68	--
	242-S - S-111	Sample	0.75	1.74	3.77	--
	242-S - S-112	Sample	2.83	0.118	1.26	--
	242-S - S-112	Sample	2.5	2.02	5.72	--
	242-S - SX-101	Sample	3.06	0.379	0.984	--
	242-S - SX-101	Sample	1.82	2.45	--	--
	242-S - SX-101	Sample	1.115	0.171	0.253	--
	242-S - SX-101	Sample	0.199	0.0883	0.419	0.33
	242-S - SX-101	Sample	0.299	0.145	0.368	0.50
	242-S - SX-102	Sample	1.29	0.0962	0.51	--
	242-S - SX-103	Sample	5.59	--	0.964	--
	242-S - U-106	Sample	4.09	0.124	1.18	--
	242-S - U-108	Sample	0.381	0.0032	--	--
	242-S - U-109	Sample	3.08	0.628	1.31	--
	242-S - U-111	Sample	1.81	0.0659	0.635	--
	242-A - A-101	Sample	0.042	0.0479	0.126	0.07
	242-A - A-101	Sample	0.077	0.421	0.518	0.13
	242-A - A-102	Sample	1.5	0.433	1.24	--
	242-A - A-102	Sample	1.67		1.27	--

Table 6-26. Comparison of Waste Stream Compositions to Criteria for Limiting Pitting Corrosion in Dilute Nitrate Solutions (6 Pages)

Process	Waste Type	Data Type	$[NO_3^-]$	$[NO_2^-]$	$[OH^-]$	Req'd $[NO_2^-]$
	242-A - A-106	Sample	1.331	0.739	1.01	--
	242-A - AX-103	Sample	1.98	1.04	0.856	--
	242-A - AX-103	Sample	2.02	1.43	2.31	--
	242-A - AX-103	Sample	2.58	1.67	2.47	--
In-Farm Process	In-Farm Scavenging Waste	Flowsheet	6.2	--	--	--
	241-SX Nitrate Leaching Waste, Partially Dissolved Sludge Leachate SX-114 Oct. 1961	Sample	1.64	0.05	0.16	--
	241-SX Nitrate Leaching Waste, Partially Dissolved Sludge Leachate SX-114 Nov. 1961	Sample	3.47	0.07	0.22	--
	241-SX Nitrate Leaching Waste, Dissolved Sludge Leachate SX-113 ca 1962	Sample	4.2	0.1	0.4	--
	241-SX Nitrate Leaching Waste, Dissolved Sludge Leachate SX-105 ca 1967	Sample	4.23	0.18	0.52	--
	PUREX Sludge Washing Supernatant Liquid, Minimum	Flowsheet	0.9	0.2	0.08	1.49
	PUREX Sludge Washing Supernatant Liquid, Maximum	Flowsheet	4.2	0.5	0.5	--
	PUREX Sludge Washing Supernatant Liquid, AX-103 ca. 1974	Sample	0.14	1.36	0.77	0.23

From a qualitative perspective, the available liquid-phase pitting corrosion data shows corrosion rates generally between 2-15 mil/yr (excluding low pH neutralized Zirflex decladding solution and results from 1 month or less exposure period). Most historical composition data found does not indicate a concern when compared to dilute nitrate pitting corrosion control limits. The limited information does not eliminate liquid-phase pitting corrosion as a possible concern relative to liner failure. Unfortunately, there is inadequate information to quantitatively determine whether liquid-phase pitting corrosion is significant or to come to a meaningful conclusion regarding liquid-phase pitting corrosion. The role of pitting corrosion in SST liner failure is indeterminate.

6.5.5 Crevice Corrosion

As previously mentioned (Section 4.4.9.3), crevice corrosion can occur in regions where a small volume of solution cannot readily mix with the bulk solution, including between overlapping steel sheets (e.g., stiffener rings stitch-welded on the tank interior wall) or under corrosion products, sludge or other deposits during stagnant periods. These areas were identified as possible regions for crevice corrosion.

Review of historical data did not uncover any crevice corrosion testing of wastes sent to the SSTs. This was also the case as documented in previous reviews of historical corrosion data (ARH-ST-111, *Compilation of Hanford Corrosion Studies*) and corrosion behavior (WHC-EP-0722). Studies of carbon steel under conditions representative of sludge washing did identify crevice corrosion attack under gasketed surfaces on fully immersed coupons (TWRS PP-94-025, *Sludge Washing Materials Study: The Behavior of Carbon Steel in a Dilute Waste Environment*). The two solutions in which crevice attack was observed contained low

concentration of hydroxide and nitrate/nitrite ratios >10 (Solution 1 = 0.025 M NO_2^-, 0.393 M NO_3^-, 0.026 M OH^-; Solution 2 = 0.10 M NO_2^-, 1.00 M NO_3^-, 0.10 M OH^-).

The limited information does not eliminate crevice corrosion as a possible concern relative to liner failure. In fact dilute compositions may be particularly aggressive in terms of causing crevice corrosion. Although crevice corrosion is a possible contributing factor to liner failure, there is inadequate information available to make such a determination.

6.5.6 Stress Corrosion Cracking

Stress corrosion cracking (SCC) requires a susceptible material with the simultaneous presence of a sustained tensile stress and an aggressive environment (BNL-52527). The aggressive environments considered for contributing to liner failure are nitrate, hydroxide, and carbonate solutions. To analyze these environments, compositional information of the major waste streams identified in Section 5.5 is tabulated below in Table 6-27. Because of the extensive listing of evaporator bottoms samples for 242-T, 242-S and 242-A, the previously tabulated compositional information for those wastes are cross-referenced to the appropriate tables elsewhere in the report.

Table 6-27. Waste Compositions for Major Waste Streams Discharged to Single-Shell Tanks Based on Sample Analyses, Flowsheets, and Simulaut Testing (3 Pages)

Process	Waste Description	Data Type	Na	AlO_2	SiO_3	U	NO_3	NO_2	OH	SO_4	PO_4	HCO_3	CO_3	Bi	Ce	Zr	Fe	Cr	NH_4	SiF_6	La	F	K	Ca	Mn	C_2O_4	Cl	Reference
Bismuth Phosphate	Coating Removal Waste, ca. 1945	Flowsheet	2.68	0.82	0.01	--	0.83	0.62	0.39	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	HW-10475-C DEL, Chapter IV; DUH-1687
	Coating Removal Waste, ca. 1951	Flowsheet	3.87	1.16	0.04	--	0.73	0.81	1.09	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	HW-23043
	Metal Waste Supernatant, T-101 Jul. 1947	Sample	--	--	--	0.0282	--	--	--	0.296	0.405	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	HW-14157
	Metal Waste Supernatant, T-101 Aug. 1947	Sample	--	--	--	0.0244	--	--	--	--	0.369	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	HW-14157
	Metal Waste Supernatant, T-101 ca 1947	Sample	3.06	--	--	0.0282	0.085	--	--	0.248	0.33	--	0.45	--	--	--	--	--	--	--	--	--	--	--	--	--	--	HW-14157
	Metal Waste Supernatant, T-102 Jul. 1947	Sample	--	--	--	0.101	--	--	--	0.282	0.33	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	HW-14157
	Metal Waste Supernatant, T-102 Aug. 1947	Sample	--	--	--	0.0916	--	--	--	--	0.304	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	HW-14157
	Metal Waste Supernatant, T-102 ca 1947	Sample	2.92	--	--	0.0903	0.771	--	--	0.177	0.263	--	0.507	--	--	--	--	--	--	--	--	--	--	--	--	--	--	HW-14157
	Metal Waste Supernatant, T-103 Jul. 1947	Sample	--	--	--	0.112	--	--	--	0.26	0.358	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	HW-14157
	Metal Waste Supernatant, T-103 Aug. 1947	Sample	--	--	--	0.103	--	--	--	--	0.341	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	HW-14157
	Metal Waste Supernatant, T-103 ca 1947-48	Sample	3.31	--	--	0.111	0.603	--	--	0.225	0.267	--	0.912	--	--	--	--	--	--	--	--	--	--	--	--	--	--	HW-14157
	Metal Waste Supernatant, 241-T Composite ca 1947-48	Sample	3.41	--	--	0.08	0.543	--	--	0.278	0.347	--	0.715	--	--	--	--	--	--	--	--	--	--	--	--	--	--	HW-14157
	Metal Waste Supernatant, U-103 ca 1948-49	Sample	1.48	--	--	0.084	0.37	--	--	0.115	0.105	--	0.33	--	--	--	--	--	--	--	--	--	--	--	--	--	--	HW-14157
	Metal Waste Supernatant, U-103 ca 1948-49	Sample	1.61	--	--	0.084	0.39	--	--	0.115	0.105	--	0.3	--	--	--	--	--	--	--	--	--	--	--	--	--	--	HW-14157
	Metal Waste Simulant, Average	Simulant	4.13	--	--	0.26	0.52	--	--	0.27	0.27	--	0.725	--	--	--	--	--	--	--	--	--	--	--	--	--	--	HW-18595
	First Cycle Waste, ca. 1951	Flowsheet	2.00	--	--	--	1.5	--	--	0.05	0.28	--	--	0.01	0.0002	0.0003	0.02	0.003	0.12	0.03	--	--	--	--	--	--	--	HW-23043
	First Cycle Waste, ca. 1954	Flowsheet	2.31	--	--	--	1.83	--	--	0.077	0.254	--	--	0.018	0.0001	0.0002	0.036	0.002	0.137	0.032	--	--	--	--	--	--	--	HW-33184
	Combined First Cycle and Coating Removal Waste	Flowsheet	2.20	0.08	0.0028	--	1.4	0.056	0.075	0.046	0.26	--	--	0.012	0.0002	0.0003	0.023	0.0029	0.11	0.028	--	--	--	--	--	--	--	HW-23043
	Second Cycle Waste	Flowsheet	1.63	--	--	--	1.01	--	--	0.038	0.247	--	--	0.006	--	--	0.033	0.001	0.103	0.026	--	--	--	--	--	--	--	HW-23043
	224 Waste	Flowsheet	1.60	--	--	--	0.68	--	--	0.0036	0.032	--	--	0.0056	--	--	--	0.0033	0.0067	--	0.0035	0.29	0.22	--	0.006	0.015	--	HW-23043
Uranium Recovery (TBP Process)	TBP Waste Prior to In-Plant Scavenging, HW-4	Flowsheet	7.83	--	--	0.0026	6.19	--	0.08	0.398	0.268	--	--	--	--	--	0.024	--	--	--	--	--	--	--	--	--	0.022	HW-18169
	TBP Waste Prior to In-Plant Scavenging, HW-5	Flowsheet	7.96	--	--	0.0026	6.19	--	0.08	0.346	0.136	--	--	--	--	--	0.024	--	--	--	--	--	--	--	--	--	0.022	HW-18232
	TBP Waste Post In-Plant Scavenging	Flowsheet	4.10	--	--	0.0007	3.3	--	--	0.24	0.13	--	--	--	--	--	0.02	--	0.06	--	--	--	0.02	--	--	--	--	HW-30399
REDOX	REDOX Combined Waste	Simulant	6.76	1.28	0.001	0.001	3.85	0.087	1.33	0.049	--	--	--	--	--	--	0.025	0.050	0.049	--	--	--	--	--	0.006	--	0.02	HW-22834
	Coating Removal Waste	see above																										N/A
	Neutralized Zircaloy Cladding Removal Waste	see below																										N/A
	REDOX Concentrated and Neutralized Salt Waste, HW-4	Flowsheet	7.35	1.28	--	--	4.48	--	1.59	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	HW-18700
	REDOX Concentrated and Neutralized Salt Waste, HW-5	Flowsheet	7.06	1.29	--	--	4.19	--	1.21	0.023	--	--	--	--	--	--	0.0075	0.1625	--	--	--	--	--	--	--	--	--	HW-38684
	REDOX Concentrated and Neutralized Salt Waste, HW-6	Flowsheet	7.14	0.93	--	--	4.37	--	1.44	0.02	--	--	--	--	--	--	0.006	0.183	--	--	--	--	--	--	--	--	--	HW-66203
	REDOX Concentrated and Neutralized Salt Waste, HW-7	Flowsheet	7.66	1.01	--	--	5.35	--	1.13	0.042	--	--	--	--	--	--	0.021	0.204	--	--	--	--	--	--	--	--	--	RL-SEP-243
	REDOX Concentrated and Neutralized Salt Waste, HW-8	Flowsheet	6.72	1.17	--	--	4.85	--	0.44	0.028	--	--	--	--	--	--	0.014	0.214	--	--	--	--	--	--	--	--	--	RL-SEP-243
	REDOX Concentrated and Neutralized Salt Waste, HW-9	Flowsheet	6.91	1.20	--	--	4.83	--	0.69	0.031	--	--	--	--	--	--	0.016	0.177	--	--	--	--	--	--	--	--	--	ISO-335
	REDOX Concentrated and Neutralized Salt Waste Supernatant Liquid, SX-101 ca. 1961	Sample	--	--	--	--	6.03	2.48	4.58	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	HW-69443
	REDOX Concentrated and Neutralized Salt Waste Supernatant Liquid, SX-107 ca. 1961	Sample	--	--	--	--	8.65	0.65	1.27	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	HW-69443
	REDOX Concentrated and Neutralized Salt Waste Supernatant Liquid, SX-108 ca. 1961	Sample	--	--	--	--	8.35	0.61	1.32	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	HW-69443
	REDOX Concentrated and Neutralized Salt Waste Supernatant Liquid, SX-114 ca. 1961	Sample	--	--	--	--	8.15	0.45	1.53	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	HW-69443
PUREX	Coating Removal Waste	see above																										N/A

Table 6-27. Waste Compositions for Major Waste Streams Discharged to Single-Shell Tanks Based on Sample Analyses, Flowsheets, and Simulant Testing (3 Pages)

Process	Waste Description	Data Type	Na	AlO_2	SiO_2	U	NO_2	NO_3	OH	SO_4	PO_4	HCO_3	CO_3	Bi	Ce	Zr	Fe	Cr	NH_4	SiF_6	La	F	K	Ca	Mn	C_2O_4	Cl	Reference
	Neutralized Zircaloy Cladding Removal Waste Supernatant, AW-105 ca. 1986	Sample	1.80	0.02	--	--	0.48	0.12	0.76	0.12	--	--	0.94	--	--	--	--	--	0.11	--	--	0.62	0.36	0.36	--	--	0.12	HW-61662
	Neutralized Zircaloy Cladding Removal Waste Supernatant	Flowsheet	1.09	--	--	--	0.013	--	0.82	--	--	--	--	--	--	--	--	--	--	--	--	1.06	0.8	--	--	--	--	RHO-MA-116
	Highly Active Waste, ca. 1955	Flowsheet	2.44	--	--	--	2.10	--	--	0.07	--	--	0.10	--	--	--	0.035	--	--	--	--	--	--	--	--	--	--	HW-35225
	Highly Active Waste Supernatant Liquid, ca. 1965	Flowsheet	7.00	--	--	--	0.70	3.40	0.10	0.20	0.04	--	1.10	--	--	--	--	--	--	--	--	--	--	--	--	--	0.1	RL-SEP-269
	Highly Active Waste Supernatant Liquid, A-101 ca. 1964	Sample	6.52	--	--	--	0.226	3.36	--	0.246	0.0358	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	RL-SEP-183 RD
	Highly Active Waste Supernatant Liquid, A-104 ca. 1964	Sample	6.52	--	--	--	0.667	3.42	--	0.187	0.023	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	RL-SEP-183 RD
	Highly Active Waste Supernatant Liquid, A-106 ca. 1964	Sample	6.95	--	--	--	0.58	3.35	--	0.135	0.0095	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	RL-SEP-183 RD
	Highly Active Waste Supernatant Liquid, A-102 ca. 1969	Sample	6.4	0.01	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	Larkin (1969)
	Highly Active Waste Supernatant Liquid, A-103 ca. 1969	Sample	7.4	0.007	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	Larkin (1969)
	Highly Active Waste Supernatant Liquid, C-101 ca. 1969	Sample	4.1	0.04	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	Larkin (1969)
	Highly Active Waste Supernatant Liquid, C-103 ca. 1969	Sample	5.85	0.01	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	Larkin (1969)
	Highly Active Waste Supernatant Liquid, A-106 ca. 1969	Sample	6.52	0.002	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	Larkin (1969)
	Highly Active Waste Supernatant Liquid, A-103 (from A-105) ca. 1972	Sample	3.47	0.026	--	--	--	--	0.914	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	0.0018	--	--	WHC-SD-WM-ER-308
	Highly Active Waste, HW #3, ca. 1956	Flowsheet	2.59	--	--	0.03	2.5	--	0.02	0.06	--	--	--	--	--	--	0.04	--	--	--	--	--	--	--	--	--	--	HW-31000
	Highly Active Waste, HW #4, ca. 1956	Flowsheet	2.45	--	--	0.012	2.1	--	--	0.07	--	--	--	--	--	--	0.035	--	--	--	--	--	--	--	--	--	--	HW-31000
	Organic Wash Waste, G-8 ca. 1961	Sample	0.18	--	--	--	0.031	--	--	--	--	--	0.12	--	--	--	--	--	--	--	--	--	0.0061	--	--	--	--	HW-71145
	Organic Wash Waste, R-8 ca. 1961	Sample	0.48	--	--	--	--	--	--	--	--	--	0.28	--	--	--	--	--	--	--	--	--	0.0026	--	--	--	--	HW-71145
	Organic Wash Waste, ca. 1965	Flowsheet	0.23	--	--	--	0.06	--	0.05	--	--	--	0.075	--	--	--	--	--	--	--	--	--	0.03	--	0.03	--	--	RL-SEP-269
	Thoria Campaign Waste, ca. 1966	Flowsheet	6.20	0.2	--	--	--	--	--	0.03	0.03	--	--	--	--	--	0.05	--	--	--	--	0.05	--	--	--	--	--	RL-SEP-267 PT 1
	Thoria Campaign Waste, ca. 1970	Flowsheet	3.33	0.34	--	--	2.58	--	0.047	0.049	0.093	--	--	--	--	--	0.023	--	--	--	--	0.048	0.052	--	--	--	--	ARH-2127
Fission	Phase I Operations Waste	Flowsheet	0.568	--	--	--	0.21	--	0.28	--	--	--	0.039	--	--	--	--	--	--	--	--	--	--	--	--	--	--	HW-67728
Product	Phase II Equipment Replacement Waste	data not found																										N/A
Recovery	Phase III Low Level Waste	data not found																										N/A
(B Plant)	Phase III Ion Exchange Waste, PUREX alkaline supernatant	Flowsheet	3.39	--	--	--	0.43	1.67	0.01	0.074	--	--	0.6	--	--	--	--	--	0.07	--	--	--	--	--	--	--	--	HW-78061
	Phase III Ion Exchange Waste, 241-S REDOX alkaline supernatant	Flowsheet	3.84	0.27	--	--	2.61	--	1.24	--	--	--	0.03	--	--	--	--	--	0.07	--	--	--	--	--	--	--	--	HW-78061
	Phase III Ion Exchange Waste, 241-SX REDOX alkaline supernatant	Flowsheet	3.00	0.62	--	--	1.94	0.27	0.75	0.02	--	--	0.03	--	--	--	--	--	0.07	--	--	--	--	--	--	--	--	HW-78061
	Phase III High Level Waste, Not Concentrated	Flowsheet	1.5	0.065	--	--	1.32	--	0.17	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	ARH-CD-691
	Phase III High Level Waste, Concentrated	Flowsheet	4	0.173	--	--	3.52	--	0.45	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	ARH-CD-691
Evaporation	242-B and 242-T Evaporators Bottoms, 1951-55, TX-116 Supernatant Pre-Evaporation	Sample	6.52	0.0015	--	--	6.40	--	--	0.111	0.488	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	HW-25468
Processes	242-B and 242-T Evaporators Bottoms, 1951-55, TX-116 Supernatant Post-Evaporation	Sample	8.39	0.0015	--	--	6.66	--	--	0.078	0.653	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	HW-25468
	In-Tank Solidification Waste, ITS-1 BY-102 Supernatant ca. 1968	Sample	13.78	3.72	--	--	4.31	1.19	5.47	0.012	0.02	--	2.46	--	--	--	0.0011	--	--	--	--	0.01	--	--	--	--	0.057	ARH-1381
	In-Tank Solidification Waste, ITS-2 BY-112 Supernatant ca. 1968	Sample	7.47	0.24	--	--	2.26	0.46	2.61	0.003	0.02	0.689	1.67	--	--	--	9E-05	--	--	--	--	0.021	--	--	--	--	0.05	ARH-1381
	In-Tank Solidification Waste, ITS-2 BY-112 Supernatant ca. 1972	Sample	11.16	2.05	--	--	2.1	1.4	--	0.05	0.023	--	0.018	--	--	--	--	--	--	--	--	--	--	--	--	--	--	ARH-1381
	In-Tank Solidification Waste, ITS-2 Bottoms Supernatant ca. 1972	Simulant	9.95	1.43	--	--	2.45	1.0	4.27	--	--	--	0.40	--	--	--	--	--	--	--	--	--	--	--	--	--	--	Buckingham, 1972

Table 6-27. Waste Compositions for Major Waste Streams Discharged to Single-Shell Tanks Based on Sample Analyses, Flowsheets, and Simulant Testing (3 Pages)

Process	Waste Description	Data Type	Na	AlO_2	SiO_2	U	NO_3	NO_2	OH	SO_4	PO_4	HCO_3	CO_3	Bi	Ce	Zr	Fe	Cr	NH_4	SiF_6	La	F	K	Ca	Mn	C_2O_4	Cl	Reference
	242-T Evaporator Bottoms, 1965-1976	see Table 5-39																										N/A
	REDOX Concentrators Waste	data not found																										N/A
	B Plant Concentrator E-23-3 Waste	data not found																										N/A
	242-S Evaporator Bottoms	see Table 5-41																										N/A
	242-A Evaporator Bottoms	see Table 5-42																										N/A
	Simulated Evaporated Solid Waste	see Table 5-43																										
In-Farm Processes	In-Farm Scavenging Waste	Flowsheet	7.42	--	--	--	6.2	--	--	0.35	0.24	--	--	--	--	--	--	--	--	--	--	--	0.02	--	--	--	0.021	HW-33536
	241-SX Nitrate Leaching Waste, Partially Dissolved Sludge Leachate SX-114 Oct. 1961	Sample	--	--	--	--	1.64	0.05	0.16	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	HW-71895
	241-SX Nitrate Leaching Waste, Partially Dissolved Sludge Leachate SX-114 Nov. 1961	Sample	--	--	--	--	3.47	0.07	0.22	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	HW-71895
	241-SX Nitrate Leaching Waste, Dissolved Sludge Leachate SX-113 ca 1962	Sample	--	--	--	--	4.2	0.1	0.4	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	HW-75714
	241-SX Nitrate Leaching Waste, Dissolved Sludge Leachate SX-105 ca 1967	Sample	--	--	--	--	4.23	0.18	0.52	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	ISO-708-DEL
	PUREX Sludge Washing Supernatant Liquid, Minimum	Flowsheet	1.8	0.005	--	--	0.9	0.2	0.08	0.25	--	--	0.24	--	--	--	--	0.002	--	--	--	--	--	--	--	--	0.002	WHC-MR-0003
	PUREX Sludge Washing Supernatant Liquid, Maximum	Flowsheet	5.4	0.04	--	--	4.2	0.5	0.5	0.4	--	--	0.7	--	--	--	--	0.004	--	--	--	--	--	--	--	--	0.002	WHC-MR-0003
	PUREX Sludge Washing Supernatant Liquid, AX-103 ca. 1974	Sample	3.511	0.022	--	--	0.14	1.36	0.77	0.19	0.013	--	0.4	--	--	--	--	--	--	--	--	--	--	--	--	--	--	WHC-SD-WM-ER-309
Other Wastes	Plutonium Finishing Plant Waste	combined with other wastes before storage in single-shell tanks																										N/A
	Decontamination Waste	data not found																										N/A
	Hot Semiworks/Strontium Semiworks	not considered																										N/A
	Battelle-Northwest Waste	data not found, waste composition variable																										N/A
	Hanford Laboratories Waste	data not found, waste composition variable																										N/A
	222-S Laboratory Waste	data not found, waste composition variable																										N/A
	100-N Area waste	dilute waste combined with other wastes																										N/A

6.5.6.1. Nitrate-Induced Stress Corrosion Cracking

As mentioned in Section 4.4.9.4, nitrate-induced SCC is a well-known and documented cause of liner failure for non-stress-relieved carbon steel tanks containing basic radioactive waste. Specifications have been developed to minimize the threat of SCC in Hanford's DSTs (OSD-T-151-00007, RPP-RPT-47337). The technical bases for the operating specification document contain limits for avoiding SCC due to high nitrate and low hydroxide and nitrite concentrations. Based on the current DST operating specifications, OSD-T-151-00007, the following waste chemistry limits are provided in Table 6-28.

Table 6-28. General Waste Chemistry Limits for Double-Shell Tanks

For $[NO_3^-]$ Range	Variable	For Waste Temperature (T) Range		
		T<167°F	167°F ≤T≤212°F	T>212°F
$[NO_3^-]\leq 1.0$ M	$[OH^-]$	0.010M≤$[OH^-]$≤8.0M	0.010M≤$[OH^-]$≤8.0M	0.010M≤$[OH^-]$≤8.0M
	$[NO_2^-]\leq 1.0$ M	0.011M≤$[NO_2^-]$≤5.5M	0.011M≤$[NO_2^-]$≤5.5M	0.011M≤$[NO_2^-]$≤5.5M
	$[NO_3^-]/([OH^-]+[NO_2^-])$	<2.5	<2.5	<2.5
1.0M<$[NO_3^-]$≤ 3.0M	$[OH^-]$	0.1$[NO_3^-]$≤$[OH^-]$≤10.M	0.1$[NO_3^-]$≤$[OH^-]$≤10.M	0.1$[NO_3^-]$≤$[OH^-]$≤4.0M
	$[OH^-]+[NO_2^-]$	≥0.4$[NO_3^-]$	≥0.4$[NO_3^-]$	≥0.4$[NO_3^-]$
$[NO_3^-]$ > 3.0 M	$[OH^-]$	0.3M≤$[OH^-]$≤10.M	0.3M≤$[OH^-]$≤10.M	0.3M≤$[OH^-]$<4.0M
	$[OH^-]+[NO_2^-]$	≥1.2M	≥1.2M	≥1.2M
	$[NO_3^-]$	≤5.5M	≤5.5M	≤5.5M

Information in table taken from OSD-T-151-00007, Rev. 12, Table 1.5.1-1.

Subsequent to development of the operating specifications in OSD-T-151-00007, self-cooling of the waste provided an opportunity to adjust the chemistry control limits based on the available empirical evidence. For nitrate-rich waste these specifications, documented in RPP-RPT-47337, are shown below in Table 6-29.

Table 6-29. Proposed Specification for Control of Stress Corrosion Cracking for Nitrate Ion-Rich Waste in Double-Shell Tanks

Specification Criteria	Limit
Maximum Temperature	50°C
Maximum Nitrate Ion	6.0 M
Maximum Hydroxide Ion	6.0 M
Minimum pH	11
Minimum Nitrite Ion	0.05 M
Minimum Nitrite/Nitrate Ion Ratio	0.15

Information from RPP-RPT-47337, Rev. 0, Table 3-8.

To determine whether the potential for nitrate-induced SCC may occur, the criteria in Table 6-28 and Table 6-29 can be compared against the waste composition information presented in Table 5-39, Table 5-41, Table 5-42, and Table 6-27 for liquid (supernatant) samples. The specific criteria considered are maximum nitrate concentration of 5.5 M (Table 6-28 limit umbrellas 6.0 M limit in Table 6-29), hydroxide plus nitrite to nitrate ratio as a function of nitrate concentration (from Table 6-28), and minimum nitrite to nitrate ratio of 0.15 (from Table 6-29). These three specific criteria do not have a temperature dependence, and thus temperature is not considered as part of this analysis. These comparisons are made in Table 6-30 with those values

exceeding a criteria shaded in gray. The following waste types had samples, simulants, or flowsheet values that exceeded one of the considered criteria:

- $BiPO_4$ – combined 1C and CW, flowsheet
- Uranium recovery – TBP waste prior to in-plant scavenging, flowsheet
- REDOX – concentrated and neutralized salt waste, flowsheet and samples
- PUREX – highly active waste, flowsheet
- PUREX – Thoria campaign waste from 1970, flowsheet
- Fission Product Recovery – Phase III ion exchange waste, flowsheet
- Fission Product Recovery – Phase III high level waste, flowsheet
- Evaporation Processes – 242-B, 242-T, 242-S, and 242-A, samples
- In-Farm Process – scavenging waste, flowsheet
- In-Farm Process – nitrate leaching, samples
- In-Farm Process – PUREX sludge washing, flowsheet

Table 6-30. Comparison of Waste Stream Compositions to Criteria for Limiting Nitrate-Induced Stress Corrosion Cracking (7 Pages)

Process	Waste Description	Data Type	$[NO_3]$	$[NO_2]$	[OH]	$([OH]+[NO_2])/[NO_3]$	$[NO_2]/[NO_3]$
Bismuth Phosphate	Coating Removal Waste, ca. 1945	Flowsheet	0.83	0.62	0.39	1.22	0.75
	Coating Removal Waste, ca. 1951	Flowsheet	0.73	0.81	1.09	2.60	1.11
	Metal Waste Supernatant, T-101 ca. 1947	Sample	0.085	--	--	--	--
	Metal Waste Supernatant, T-102 ca. 1947	Sample	0.771	--	--	--	--
	Metal Waste Supernatant, T-103 ca. 1947-48	Sample	0.603	--	--	--	--
	Metal Waste Supernatant, 241-T Composite ca. 1947-48	Sample	0.543	--	--	--	--
	Metal Waste Supernatant, U-103 ca. 1948-49	Sample	0.37	--	--	--	--
	Metal Waste Supernatant, U-103 ca. 1948-49	Sample	0.39	--	--	--	--
	Metal Waste Simulant, Average	Simulant	0.52	--	--	--	--
	First Cycle Waste, ca. 1951	Flowsheet	1.5	--	--	--	--
	First Cycle Waste, ca. 1954	Flowsheet	1.83	--	--	--	--
	Combined First Cycle and Coating Removal Waste	Flowsheet	1.4	0.056	0.075	0.09	0.04
	Second Cycle Waste	Flowsheet	1.01	--	--	--	--
	224 Waste	Flowsheet	0.68	--	--	--	--
Uranium Recovery (TBP Process)	TBP Waste Prior to In-Plant Scavenging, HW-4	Flowsheet	6.19	--	0.08	0.01	--
	TBP Waste Prior to In-Plant Scavenging, HW-5	Flowsheet	6.19	--	0.08	0.01	--
	TBP Waste Post In-Plant Scavenging	Flowsheet	3.3	--	--	--	--
REDOX	REDOX Combined Waste	Simulant	3.85	0.087	1.33	0.37	0.02
	REDOX Concentrated & Neutralized Salt Waste, HW-4	Flowsheet	4.48	--	1.59	0.35	--
	REDOX Concentrated & Neutralized Salt Waste, HW-5	Flowsheet	4.19	--	1.21	0.29	--
	REDOX Concentrated & Neutralized Salt Waste, HW-6	Flowsheet	4.37	--	1.44	0.33	--
	REDOX Concentrated & Neutralized Salt Waste, HW-7	Flowsheet	5.35	--	1.13	0.21	--
	REDOX Concentrated & Neutralized Salt Waste, HW-8	Flowsheet	4.85	--	0.44	0.09	--
	REDOX Concentrated & Neutralized Salt Waste, HW-9	Flowsheet	4.83	--	0.69	0.14	--
	REDOX Concentrated & Neutralized Salt Waste Supernatant Liquid, SX-101 ca. 1961	Sample	6.03	2.48	4.58	1.17	0.41
	REDOX Concentrated & Neutralized Salt Waste Supernatant Liquid, SX-107 ca. 1961	Sample	8.65	0.65	1.27	0.22	0.08

Table 6-30. Comparison of Waste Stream Compositions to Criteria for Limiting Nitrate-Induced Stress Corrosion Cracking (7 Pages)

Process	Waste Description	Data Type	$[NO_3]$	$[NO_2]$	[OH]	$([OH]+[NO_2])/[NO_3]$	$[NO_2]/[NO_3]$
	REDOX Concentrated & Neutralized Salt Waste Supernatant Liquid, SX-108 ca. 1961	Sample	8.35	0.61	1.32	0.23	0.07
	REDOX Concentrated & Neutralized Salt Waste Supernatant Liquid, SX-114 ca. 1961	Sample	8.15	0.45	1.53	0.24	0.06
PUREX	Neutralized Zircaloy Cladding Removal Waste Supernatant, AW-105 ca. 1986	Sample	0.48	0.12	0.76	1.83	0.25
	Neutralized Zircaloy Cladding Removal Waste Supernatant	Flowsheet	0.013	--	0.82	63.08	--
	Highly Active Waste, ca. 1955	Flowsheet	2.10	--	--	--	--
	Highly Active Waste Supernatant Liquid, ca. 1965	Flowsheet	0.70	3.40	0.10	5.00	4.86
	Highly Active Waste Supernatant Liquid, A-101 ca. 1964	Sample	0.226	3.36	--	14.87	14.87
	Highly Active Waste Supernatant Liquid, A-104 ca. 1964	Sample	0.667	3.42	--	5.13	5.13
	Highly Active Waste Supernatant Liquid, A-106 ca. 1964	Sample	0.58	3.35	--	5.78	5.78
	Highly Active Waste Supernatant Liquid, A-103 (from A-105) ca. 1972	Sample	--	--	0.914	--	--
	Highly Active Waste, HW #3, ca. 1956	Flowsheet	2.5	--	0.02	0.01	--
	Highly Active Waste, HW #4, ca. 1956	Flowsheet	2.1	--	--	--	--
	Organic Wash Waste, G-8 ca. 1961	Sample	0.031	--	--	--	--
	Organic Wash Waste, ca. 1965	Flowsheet	0.06	--	0.05	0.83	--
	Thoria Campaign Waste, ca. 1970	Flowsheet	2.58	--	0.047	0.02	--
Fission Product Recovery (B Plant)	Phase I Operations Waste	Flowsheet	0.21	--	0.28	1.33	--
	Phase III Ion Exchange Waste, PUREX alkaline supernatant	Flowsheet	0.43	1.67	0.01	3.91	3.88
	Phase III Ion Exchange Waste, 241-S REDOX alkaline supernatant	Flowsheet	2.61	--	1.24	0.48	--
	Phase III Ion Exchange Waste, 241-SX REDOX alkaline supernatant	Flowsheet	1.94	0.27	0.75	0.53	0.14
	Phase III High Level Waste, Not Concentrated	Flowsheet	1.32	--	0.17	0.13	--
	Phase III High Level Waste, Concentrated	Flowsheet	3.52	--	0.45	0.13	--
Evaporation Processes	242-B and 242-T Evaporators Bottoms, 1951-55, TX-116 Supernatant Pre-Evaporation	Sample	6.40	--	--	--	--
	242-B and 242-T Evaporators Bottoms, 1951-55, TX-116 Supernatant Post-Evaporation	Sample	6.66	--	--	--	--

Table 6-30. Comparison of Waste Stream Compositions to Criteria for Limiting Nitrate-Induced Stress Corrosion Cracking (7 Pages)

Process	Waste Description	Data Type	$[NO_3]$	$[NO_2]$	[OH]	$([OH]+[NO_2])/[NO_3]$	$[NO_2]/[NO_3]$
	In-Tank Solidification Waste, ITS-1 BY-102 Supernatant ca. 1968	Sample	4.31	1.19	5.47	1.55	0.28
	In-Tank Solidification Waste, ITS-2 BY-112 Supernatant ca. 1968	Sample	2.26	0.46	2.61	1.36	0.20
	In-Tank Solidification Waste, ITS-2 BY-112 Supernatant ca. 1972	Sample	2.1	1.4	--	0.67	0.67
	In-Tank Solidification Waste, ITS-2 Bottoms Supernatant ca. 1972	Simulant	2.45	1.0	4.27	2.15	0.41
	242-T - TX-101	Sample	1.6	0.26	1.33	0.99	0.16
	242-T - TX-101	Sample	--	--	0.204	--	--
	242-T - TX-102	Sample	3.71	2.26	1.75	1.08	0.61
	242-T - TX-104	Sample	2.79	0.192	0.82	0.36	0.07
	242-T - TX-106	Sample	0.285	1.13	4.99	21.47	3.96
	242-T - TX-107	Sample	2.84	0.555	0.23	0.28	0.20
	242-T - TX-107	Sample	3.92	0.655	1.67	0.59	0.17
	242-T - TX-108	Sample	6.92	0.388	0.645	0.15	0.06
	242-T - TX-108	Sample	5.62	0.31	0.367	0.12	0.06
	242-T - TX-109	Sample	4.49	1.24	2.35	0.80	0.28
	242-T - TX-109	Sample	4.64	1.34	1.08	0.52	0.29
	242-T - TX-109	Sample	3.76	0.414		0.11	0.11
	242-T - TX-111	Sample	2.32	1.39	1.03	1.04	0.60
	242-T - TX-114	Sample	--	--	1.57	--	--
	242-T - TX-118	Sample	--	--	1.99	--	--
	242-T - TX-118	Sample	--	--	1.83	--	--
	242-T - TX-118	Sample	--	--	1.38	--	--
	242-T - TX-118	Sample	--	--	1.72	--	--
	242-T - TX-118	Sample	--	--	1.34	--	--
	242-T - TX-118	Sample	--	--	2.98	--	--
	242-T - TX-118	Sample	--	--	1.87	--	--

Table 6-30. Comparison of Waste Stream Compositions to Criteria for Limiting Nitrate-Induced Stress Corrosion Cracking (7 Pages)

Process	Waste Description	Data Type	$[NO_3]$	$[NO_2]$	[OH]	$([OH]+[NO_2])/[NO_3]$	$[NO_2]/[NO_3]$
	242-T - TX-118	Sample	--	--	2.86	--	--
	242-T - TX-118	Sample	--	--	0.874	--	--
	242-T - TX-118	Sample	--	--	1.58	--	--
	242-T - TX-118	Sample	--	--	1.46	--	--
	242-T - TX-118	Sample	--	--	1.32	--	--
	242-T - TX-118	Sample	--	--	1.37	--	--
	242-T - TX-118	Sample	--	--	1.27	--	--
	242-T - TX-118	Sample	--	--	0.759	--	--
	242-T - TX-118	Sample	3.99	1.175	0.885	0.52	0.29
	242-T - TX-118	Sample	4.21	1.89	1.43	0.79	0.45
	242-T - TX-118	Sample	4.09	2.03	1.9	0.96	0.50
	242-T - TX-118	Sample	2.52	0.621	0.573	0.47	0.25
	242-T - TX-118	Sample	1.6	0.277	0.384	0.41	0.17
	242-T - TX-118	Sample	1.3	0.146	--	0.11	0.11
	242-T - TX-118	Sample	1.68	0.196	0.286	0.29	0.12
	242-T - TX-118	Sample	2.65	0.327	0.005	0.13	0.12
	242-T - TX-118	Sample	1.53	0.194	0.005	0.13	0.13
	242-T - TX-118	Sample	1.25	0.134	--	0.11	0.11
	242-T - TX-118	Sample	2.88	0.741	0.619	0.47	0.26
	242-T - TX-118	Sample	2.94	0.834	0.517	0.46	0.28
	242-T - TX-118	Sample	2.25	0.686	0.371	0.47	0.30
	242-T - TX-118	Sample	3.31	0.988	0.501	0.45	0.30
	242-T - TX-118	Sample	4.36	0.999	1.0	0.46	0.23
	242-T - TX-118	Sample	3.5	1.02	0.583	0.46	0.29
	242-T - TX-118	Sample	3.09	0.74	0.761	0.49	0.24
	242-T - TX-118	Sample	2.76	0.452	1.23	0.61	0.16
	242-T - TX-118	Sample	3.11	0.916	0.828	0.56	0.29

Table 6-30. Comparison of Waste Stream Compositions to Criteria for Limiting Nitrate-Induced Stress Corrosion Cracking (7 Pages)

Process	Waste Description	Data Type	$[NO_3]$	$[NO_2]$	[OH]	$([OH]+[NO_2])/[NO_3]$	$[NO_2]/[NO_3]$
	242-T - TX-118	Sample	2.8	0.571	0.613	0.42	0.20
	242-T - TX-118	Sample	3.48	0.87	0.89	0.51	0.25
	242-T - U-103	Sample	4.58	--	1.48	0.32	
	242-S - S-101	Sample	1.53	0.197	0.415	0.40	0.13
	242-S - S-102	Sample	4.25	0.118	1.22	0.31	0.03
	242-S - S-102	Sample	2.56	0.958	2.78	1.46	0.37
	242-S - S-102	Sample	1.6	0.87	1.53	1.50	0.54
	242-S - S-102	Sample	3.29	1.89	3.65	1.68	0.57
	242-S - S-102	Sample	1.79	0.611	1.058	0.93	0.34
	242-S - S-102	Sample	1.61	0.818	1.16	1.23	0.51
	242-S - S-102	Sample	3.19	1.43	2.84	1.34	0.45
	242-S - S-102	Sample	3.74	0.929	1.66	0.69	0.25
	242-S - S-102	Sample	3.63	0.792	1.52	0.64	0.22
	242-S - S-102	Sample	4.29	1.9	2.98	1.14	0.44
	242-S - S-102	Sample	3.4	1.59	2.18	1.11	0.47
	242-S - S-102	Sample	1.4	0.556	0.488	0.75	0.40
	242-S - S-102	Sample	3.33	1.96	1.78	1.12	0.59
	242-S - S-102	Sample	1.98	1.21	1.07	1.15	0.61
	242-S - S-102	Sample	3.64	1.87	2.63	1.24	0.51
	242-S - S-102	Sample	2.96	1.82	1.79	1.22	0.61
	242-S - S-102	Sample	2.66	1.41	1.66	1.15	0.53
	242-S - S-102	Sample	2.92	1.79	1.94	1.28	0.61
	242-S - S-102	Sample	2.92	1.77	1.57	1.14	0.61
	242-S - S-102	Sample	3.9	1.75	1.33	0.79	0.45
	242-S - S-102	Sample	2.76	1.27	1.21	0.90	0.46
	242-S - S-102	Sample	2.42	0.531	0.773	0.54	0.22
	242-S - S-103	Sample	4.36	0.852	1.96	0.64	0.20

Table 6-30. Comparison of Waste Stream Compositions to Criteria for Limiting Nitrate-Induced Stress Corrosion Cracking (7 Pages)

Process	Waste Description	Data Type	$[NO_3]$	$[NO_2]$	[OH]	$([OH]+[NO_2])/[NO_3]$	$[NO_2]/[NO_3]$
	242-S - S-103	Sample	1.31	0.067	0.523	0.45	0.05
	242-S - S-103	Sample	1.43	0.579	1.18	1.23	0.40
	242-S - S-105	Sample	4.46	0.112	1.24	0.30	0.03
	242-S - S-105	Sample	1.95	0.99	6.46	3.82	0.51
	242-S - S-105	Sample	1.94	1	6.47	3.85	0.52
	242-S - S-106	Sample	4.16	0.165	1.28	0.35	0.04
	242-S - S-106	Sample	2.49	0.656	5.33	2.40	0.26
	242-S - S-106	Sample	0.0185	0.00261	0.03	1.76	0.14
	242-S - S-106	Sample	2.42	1.78	4.44	2.57	0.74
	242-S - S-108	Sample	4.46	0.127	1.43	0.35	0.03
	242-S - S-108	Sample	2.6	1.94	5.08	2.70	0.75
	242-S - S-109	Sample	4.35	0.158	1.81	0.45	0.04
	242-S - S-111	Sample	1.95	1.82	3.68	2.82	0.93
	242-S - S-111	Sample	0.75	1.74	3.77	7.35	2.32
	242-S - S-112	Sample	2.83	0.118	1.26	0.49	0.04
	242-S - S-112	Sample	2.5	2.02	5.72	3.10	0.81
	242-S - SX-101	Sample	3.06	0.379	0.984	0.45	0.12
	242-S - SX-101	Sample	1.82	2.45	--	1.35	1.35
	242-S - SX-101	Sample	1.115	0.171	0.253	0.38	0.15
	242-S - SX-101	Sample	0.199	0.0883	0.419	2.55	0.44
	242-S - SX-101	Sample	0.299	0.145	0.368	1.72	0.48
	242-S - SX-102	Sample	1.29	0.0962	0.51	0.47	0.07
	242-S - SX-103	Sample	5.59	--	0.964	0.17	--
	242-S - U-106	Sample	4.09	0.124	1.18	0.32	0.03
	242-S - U-108	Sample	0.381	0.00317	--	0.01	0.01
	242-S - U-109	Sample	3.08	0.628	1.31	0.63	0.20
	242-S - U-111	Sample	1.81	0.0659	0.635	0.39	0.04

Table 6-30. Comparison of Waste Stream Compositions to Criteria for Limiting Nitrate-Induced Stress Corrosion Cracking (7 Pages)

Process	Waste Description	Data Type	$[NO_3]$	$[NO_2]$	[OH]	$([OH]+[NO_2])/[NO_3]$	$[NO_2]/[NO_3]$
	242-A - A-101	Sample	0.042	0.0479	0.126	4.14	1.14
	242-A - A-101	Sample	0.0772	0.421	0.518	12.16	5.45
	242-A - A-102	Sample	1.5	0.433	1.24	1.12	0.29
	242-A - A-102	Sample	1.67	--	1.27	0.76	--
	242-A - A-106	Sample	1.331	0.739	1.01	1.31	0.56
	242-A - AX-103	Sample	1.98	1.04	0.856	0.96	0.53
	242-A - AX-103	Sample	2.02	1.43	2.31	1.85	0.71
	242-A - AX-103	Sample	2.58	1.67	2.47	1.60	0.65
In-Farm Processes	In-Farm Scavenging Waste	Flowsheet	6.2	--	--	--	--
	241-SX Nitrate Leaching Waste, Partially Dissolved Sludge Leachate SX-114 Oct. 1961	Sample	1.64	0.05	0.16	0.13	0.03
	241-SX Nitrate Leaching Waste, Partially Dissolved Sludge Leachate SX-114 Nov. 1961	Sample	3.47	0.07	0.22	0.08	0.02
	241-SX Nitrate Leaching Waste, Dissolved Sludge Leachate SX-113 ca 1962	Sample	4.2	0.1	0.4	0.12	0.02
	241-SX Nitrate Leaching Waste, Dissolved Sludge Leachate SX-105 ca 1967	Sample	4.23	0.18	0.52	0.17	0.04
	PUREX Sludge Washing Supernatant Liquid, Minimum	Flowsheet	0.9	0.2	0.08	0.31	0.22
	PUREX Sludge Washing Supernatant Liquid, Maximum	Flowsheet	4.2	0.5	0.5	0.24	0.12
	PUREX Sludge Washing Supernatant Liquid, AX-103 ca. 1974	Sample	0.14	1.36	0.77	15.21	9.71

6.5.6.1.1. Bismuth Phosphate – Combined First Cycle and Coating Removal Waste

From the start of the $BiPO_4$ operation until 1955, the CW was routinely discharged in batches to the same tank used for collection of the 1C waste. Based on WHC-MR-0132, 37 separate SSTs received combined 1C and CW up until 1955 and for 32 of those tanks it was the first waste type received. Those tanks are listed in Table 6-31. Tanks with probable liner leaks are highlighted in red in the table. Tanks that first received combined 1C and CW from the $BiPO_4$ process are footnoted as such. These tanks are of interest because residual fabrication tensile stresses may be higher than remaining tensile stresses in tanks having previously received waste. Both of these conditions will be considered.

Table 6-31. Listing of Single-Shell Tanks That Received Combined First Cycle and Coating Removal Waste from the Bismuth Phosphate Process

Tank		
B-104	BY-106*	T-104*
B-105	BY-107*	T-105
B-106	BY-108*	T-106
B-107*	BY-110*	T-107*
B-108*	C-107*	T-108*
B-109*	C-108*	T-109*
BX-107*	C-109*	TX-109*
BX-108*	C-110*	TX-110*
BX-109*	C-111*	TX-111*
BX-110*	C-112*	TX-112*
BX-111*		TX-114*
BX-112*		TX-118*
		U-110*
		U-111*
		U-112*

* First waste received in this tank was combined first cycle and coating removal waste.
Tanks highlighted in red have probable liner leaks.

Of the 37 tanks that received combined 1C and CW generated from the $BiPO_4$ process, five of these tanks have liner failures. Of the 32 tanks that first received combined 1C and CW generated from the $BiPO_4$ process, four of these tanks have liner failures. Comparison of liner failure rates can be made between those tanks that contained combined 1C and CW from the $BiPO_4$ process and those that did not. This test can be performed separately for all tanks receiving this waste and for tanks that first received this waste.

Performing a chi-square test with the values presented in Table 6-32 for tank liner failures for all tanks that did and did not receive combined 1C and CW from the $BiPO_4$ process results in a p-value of 0.54. Because the p-value is greater than the selected significance level, $\alpha=0.05$, we accept the null hypothesis. In other words, there is no statistically significant difference in the proportion of liner failures in tanks which received combined 1C and CW from the $BiPO_4$ process and those that did not. Based on the available information it appears that receiving and

storing combined 1C and CW from the $BiPO_4$ process at any time prior to liner failure is not a common factor contributing to liner failure.

Performing a chi-square test with the values presented in Table 6-32 for tank liner failures for tanks that first received combined 1C and CW from the $BiPO_4$ process results in a p-value of 0.46. Because the p-value is greater than the selected significance level, α=0.05, we accept the null hypothesis. In other words there is no statistically significant difference in the proportion of liner failures in tanks which first received combined 1C and CW from the $BiPO_4$ process and those that did not. Based on the available information it appears that receiving and storing combined 1C and CW from the $BiPO_4$ process as the first waste type for a tank is not a common factor contributing to liner failure.

Table 6-32. Combined Bismuth Phosphate First Cycle and Coating Removal Waste Receiving Tank Failure Rate Observational Data

	Probable Liner Failure	Liner Failure Not Known	Total
All Tanks That Received $BiPO_4$ Combined 1C and CW	5	32	37
Tanks That Did Not Receive $BiPO_4$ Combined 1C and CW	20	92	112
Total	**25**	**124**	**149**
	Probable Liner Failure	**Liner Failure Not Known**	**Total**
Tanks That First Received $BiPO_4$ Combined 1C and CW	4	28	32
Tanks That Did Not First Receive $BiPO_4$ Combined 1C and CW	21	96	117
Total	**25**	**124**	**149**

6.5.6.1.2. Uranium Recovery – Tri-Butyl Phosphate Waste Prior to In-Plant Scavenging, Flowsheet

From June 1952 until September 1954, TBP waste, prior to in-plant scavenging, was discharged in SSTs. Based on WHC-MR-0132, 27 separate SSTs received TBP waste prior to in-plant scavenging. However, two of those tanks, BY-109 and TX-115, were homogenized supernatant temporary storage tanks (SD-WM-TI-302, Table 2.1), so although they were listed as containing TBP waste, they contained collected supernatant from the tanks in support of sluicing for metal waste sludge removal and were not chemically similar to TBP waste. Those two tanks are not included as containing TBP waste prior to in-plant scavenging. The remaining 25 tanks are listed in Table 6-33. Tanks with probable liner leaks are highlighted in red in the table. Tanks that first received TBP waste prior to in-plant scavenging are footnoted as such. These tanks are of interest because residual fabrication tensile stresses may be higher than remaining tensile stresses in tanks having previously received waste. Both of these conditions will be considered.

Table 6-33. Listing of Single-Shell Tanks That Received Tri-Butyl Phosphate Waste Prior to In-Plant Scavenging

Tank		
B-106	C-105	T-107
BX-107	C-106	T-108
BX-108	C-107	T-109
BX-109	C-108	TX-118
BY-107	C-109	TY-103*
BY-108	C-110	TY-104*
C-101	C-111	TY-105*
C-102	C-112	TY-106*
C-103		

* First waste received in this tank was TBP waste generated prior to in-plant scavenging.
Tanks highlighted in red have probable liner leaks.

Of the 25 tanks that received TBP waste prior to in-plant scavenging, six of these tanks have liner failures. Of the four tanks that first received TBP waste prior to in-plant scavenging, all of these tanks have liner failures. Comparison of liner failure rates can be made between those tanks that contained TBP waste prior to in-plant scavenging and those that did not. This test can be performed separately for all tanks receiving this waste and for tanks that first received this waste.

Performing a chi-square test with the values presented in Table 6-34 for tank liner failures for all tanks that did and did not receive TBP waste prior to in-plant scavenging results in a p-value of 0.29. The expected values from the chi-square test include one value (out of 4) which is less than 5, and therefore the sample does not meet one of the general rules for chi-square testing (i.e., no more than 20% of the expected values are less than 5). Thus, the results of the chi-square testing generally would not be considered relevant. Performing Fisher's exact test, the calculated p-value is 0.38. Because the p-value is greater than the selected significance level, α=0.05, we accept the null hypothesis. In other words, there is no statistically significant difference in the proportion of liner failures in tanks which received TBP waste prior to in-plant scavenging and those that did not. Based on the available information it appears that receiving and storing TBP waste generated, prior to in-plant scavenging being performed, at any time prior to liner failure is not a common factor contributing to liner failure.

Performing a chi-square test with the values presented in Table 6-34 for tank liner failures for tanks that first received TBP waste prior to in-plant scavenging results in a p-value of 6.3×10^{-6}. The expected values from the chi-square test include two values (out of 4) which are less than 5 and one value less than one, and therefore the sample does not meet the general rules for chi-square testing (i.e., no more than 20% of the expected values are less than 5, and no values less than 1). Thus, the results of the chi-square testing generally would not be considered relevant. Performing Fisher's exact test, the calculated p-value is 6.4×10^{-4}. Because the p-value is less than the selected significance level, α=0.05, we reject the null hypothesis. In other words, there is a statistically significant difference in the proportion of liner failures in tanks which first received TBP waste prior to in-plant scavenging and those that did not. Based on the available

information it appears that tanks receiving and storing TBP waste prior to in-plant scavenging as the first waste type for a tank is a common factor contributing to liner failure.

Table 6-34. Tri-butyl Phosphate Waste Prior to In-Plant Scavenging Receiving Tank Failure Rate Observational Data

	Probable Liner Failure	Liner Failure Not Known	Total
All Tanks That Received TBP Waste Prior to In-Plant Scavenging	6	19	25
Tanks That Did Not Receive TBP Waste Prior to In-Plant Scavenging	19	105	124
Total	**25**	**124**	**149**
	Probable Liner Failure	**Liner Failure Not Known**	**Total**
Tanks That First Received TBP Waste Prior to In-Plant Scavenging	4	0	4
Tanks That Did Not First Receive TBP Waste Prior to In-Plant Scavenging	21	124	145
Total	**25**	**124**	**149**

6.5.6.1.3. REDOX – Concentrated and Neutralized Salt Waste, Flowsheet and Samples

Starting in July 1953, disposal of REDOX concentrated and neutralized salt waste in SSTs was segregated from the REDOX CW. Based on WHC-MR-0132, 32 separate SSTs received REDOX concentrated and neutralized salt waste after June 1953 and for 17 of those tanks it was the first waste type received. Those tanks are listed in Table 6-35. Tanks with probable liner leaks are highlighted in red in the table. Tanks that first received combined 1C and CW from the $BiPO_4$ process are footnoted as such. These tanks are of interest because residual fabrication tensile stresses may be higher than remaining tensile stresses in tanks having previously received waste. Both of these conditions will be considered.

Table 6-35. Listing of Single-Shell Tanks That Received Segregated REDOX Concentrated and Neutralized Salt Waste, July 1953 and Beyond

Tank		
SX-101*	SX-112*	U-101
SX-102*	SX-113*	U-102
SX-103*	SX-114*	U-103
SX-104*	SX-115*	U-106
SX-105*	TX-101	U-110
SX-107*	TX-102	U-111
SX-108*	TX-104	U-112
SX-109*	TX-105	U-201*
SX-110*	TX-106	U-202*
SX-111*	TX-107	U-203*
--	TX-115	U-204

* First waste received in this tank was REDOX concentrated and neutralized salt waste.
Tanks highlighted in red have probable liner leaks.

Of the 32 tanks that received REDOX concentrated and neutralized salt waste, 11 of these tanks have liner failures. Of the 17 tanks that first received combined 1C and CW generated from the $BiPO_4$ process, eight of these tanks have liner failures. Comparison of liner failure rates can be made between those tanks that contained REDOX concentrated and neutralized salt waste and those that did not. This test can be performed separately for all tanks receiving this waste and for tanks that first received this waste.

Performing a chi-square test with the values presented in Table 6-36 for tank liner failures for all tanks that did and did not receive REDOX concentrated and neutralized salt waste results in a p-value of 0.0026. Because the p-value is less than the selected significance level, α=0.05, we reject the null hypothesis. In other words, there is a statistically significant difference in the proportion of liner failures in tanks which received REDOX concentrated and neutralized salt waste and those that did not. Based on the available information it appears that receiving and storing REDOX concentrated and neutralized salt waste at any time prior to liner failure is a common factor contributing to liner failure.

Performing a chi-square test with the values presented in Table 6-36 for tank liner failures for tanks that first received REDOX concentrated and neutralized salt waste results in a p-value of 3.9×10^{-4}. The expected values from the chi-square test include one value (out of 4) which is less than 5, and therefore the sample does not meet one of the general rules for chi-square testing (i.e., no more than 20% of the expected values are less than 5). Thus, the results of the chi-square testing generally would not be considered relevant. Performing Fisher's exact test, the calculated p-value is 1.9×10^{-3}. Because the p-value is less than the selected significance level, α=0.05, we reject the null hypothesis. In other words, there is a statistically significant difference in the proportion of liner failures in tanks which first received REDOX concentrated and neutralized salt waste and those that did not. Based on the available information it appears that tanks receiving and storing REDOX concentrated and neutralized salt waste as the first waste type for a tank is a common factor contributing to liner failure.

Table 6-36. REDOX Concentrated and Neutralized Salt Waste Receiving Tank Failure Rate Observational Data

	Probable Liner Failure	Liner Failure Not Known	Total
All Tanks That Received REDOX Concentrated and Neutralized Salt Waste	11	21	32
Tanks That Did Not Receive REDOX Concentrated and Neutralized Salt Waste	14	103	117
Total	**25**	**124**	**149**
	Probable Liner Failure	**Liner Failure Not Known**	**Total**
Tanks That First Received REDOX Concentrated and Neutralized Salt Waste	8	9	17
Tanks That Did Not First Receive REDOX Concentrated and Neutralized Salt Waste	17	115	132
Total	**25**	**124**	**149**

6.5.6.1.4. PUREX – Highly Active Waste, Flowsheet

The highly active waste from the PUREX process was sent to tanks within A Farm from January 1956 through early 1965 (RL-SEP-659). After this time the highly active waste was sent to AX Farm until July-September 1969 (ARH-1200 C). The early flowsheet compositions of highly active waste do not include any indication of the nitrite content of the waste. Later standards from 1965 (RL-SEP-269) show the stored waste as having high nitrite content (> 3.0 M) which is consistent with supernatant samples available during that timeframe.

The two tanks that have probable liner failures in A and AX Farms are tanks A-104 and A-105. It is known that the failure of the A-105 liner was a catastrophic failure not directly caused by SCC. However, it is not known if SCC may have played a role leading to the catastrophic failure.

Performing a chi-square test with the values presented in Table 6-37 for tank liner failures for tanks that received PUREX highly active waste results in a p-value of 0.78. The expected values from the chi-square test include one value (out of 4) which is less than 5, and therefore the sample does not meet one of the general rules for chi-square testing (i.e., no more than 20% of the expected values are less than 5). Thus, the results of the chi-square testing generally would not be considered relevant. Performing Fisher's exact test, the calculated p-value is 0.68. Because the p-value is greater than the selected significance level, α=0.05, we accept the null hypothesis. In other words, there is no statistically significant difference in the proportion of liner failures in tanks which received PUREX highly active waste and those that did not. Based on the available information it appears that receiving and storing PUREX highly active waste is not a common factor contributing to liner failure.

Table 6-37. PUREX Highly Active Waste Tank Failure Rate Observational Data

	Probable Liner Failure	Liner Failure Not Known	Total
All Tanks That Received PUREX Highly Active Waste	2	8	10
Tanks That Did Not Receive PUREX Highly Active Waste	23	116	139
Total	**25**	**124**	**149**

* Tank A-105 excluded from consideration because catastrophic liner failure not caused by stress corrosion cracking.

6.5.6.1.5. PUREX – Thoria Campaign Waste from 1970, Flowsheet

During the second thoria campaign, June 8, 1970 to January 16, 1971, the PUREX plant discharged 2,795,000 gal of waste to underground storage (ARH-2127, Table X) including pre- and post-flushes. This waste was discharged to tank C-104. Waste status summary report for July-September 1970 (ARH-1666 C) shows waste from tank C-104 transferred to tanks BX-101 and BX-103 and from tanks BX-103 to BY-102 and BY-109 which were ITS-1 and the ITS-2 feed tank, respectively. None of these tanks have probable liner failures. Waste status summary report for October-December 1970 (ARH-1666 D) shows waste from tank C-104 transferred to tanks BX-101 then to BX-103 and BX-106. The thoria campaign waste from C-104 represented 40% of the total waste volume transferred into BX-101 with the remainder coming from B Plant ion exchange waste (50%) and concentrated bottoms from the B Plant E-23-3 concentrator via B-101 (10%). From BX-103 waste was transferred to BY-102 and BY-109 which were ITS-1 and the ITS-2 feed tank, respectively. From BX-106 waste was transferred to TY-103 and finally to TY-104. This waste was mixed with other waste along the way as it was transferred between tanks. Most notably during October-December 1970, the Thoria campaign waste was combined with Fission Product Recovery ion exchange waste (see Section 6.5.6.1.6 below) in tank BX-101.

Of the tanks mentioned above, tanks TY-103 and TY-104 have probable liner failures. However, making a direct tie between thoria campaign waste and liner failures in TY-103 and TY-104 is not possible. It is indeterminate whether PUREX thoria campaign waste from 1970 was a factor contributing to liner failure.

6.5.6.1.6. Fission Product Recovery – Phase III ion exchange waste, flowsheet

The only Phase III fission product recovery ion exchange waste that has a composition within the range that can cause SCC is the SX Farm REDOX alkaline supernatant liquid (see Table 6-30). As demonstrated in Section 5.5.5.2.3, the ion exchange process resulted in the feed stream being stripped of cesium and combined with column wash materials consisting of caustic, ammonium hydroxide and ammonium carbonate. The combination of the eluent stream and wash streams resulted in a waste stream with diluted nitrate and nitrite concentrations and slightly increased the relative concentration of hydroxide to nitrate and nitrite. The composition, except for the addition of ammonium, was still very similar to the original 241-SX REDOX alkaline supernatant liquid. Based on monthly waste status summary reports, the 241-SX REDOX alkaline supernatant was processed through B Plant ion exchange from the first quarter of

calendar year 1971 through the third quarter of calendar year 1972. The REDOX concentrated and neutralized salt waste was transferred to tank BX-104 for processing through B Plant ion exchange. The REDOX ion exchange waste was then transferred from B Plant to tank BX-101. Waste from tank BX-101 would be transferred to various tanks including back to the SX Farm tanks, BY Farm tanks for evaporation via ITS-1 and/or ITS-2, TX Farm tanks for evaporation in 242-T. Neither tank BX-101 nor BX-104 is a tank with a probable liner failure.

The analysis of REDOX concentrated and neutralized salt waste (primarily disposed in SX Farm) has already been addressed in Section 6.5.6.1.3. The ion exchange flowsheet does not materially affect the likelihood of SCC associated with the REDOX concentrated and neutralized salt waste. The tank directly receiving the ion exchange waste from processing 241-SX REDOX alkaline supernatant, BX-104, is not a tank with a probable liner failure. Ion exchange waste from fission product recovery is not considered a common factor contributing to SST liner failure.

6.5.6.1.7. Fission Product Recovery – Phase III high level waste, flowsheet

B Plant waste or B Plant high level waste was first identified as a separate waste stream in December 1967 (ARH-326) destined for boiling waste tanks (i.e., A and AX Farms). B Plant high level waste from phase III operations was first generated in early 1968 (ARH-534). Available waste status summary reports and historical waste transfer documents (WHC-MR-0132, WHC-SD-WM-TI-615) show that B Plant high level waste was transferred to every tank in A and AX Farms except for tanks A-104 and A-105. B Plant high level waste was also transferred to DST AY-101 during the last three quarters of calendar year 1971 and all of 1972. None of the SSTs that received B Plant high level waste from phase III fission product recovery have probable tank liner failures. Therefore, this waste type is not considered a common factor contributing to liner failure.

6.5.6.1.8. Evaporation Processes – 242-B, 242-T, 242-S, and 242-A, samples

Based on WHC-MR-0132, approximately 60 separate SSTs received concentrates from evaporation processes. Four tanks with probable liner leaks received concentrates from evaporation processes: B-107; TX-107; TX-114; and, BY-103. The failure rate for tanks receiving evaporator concentrates (7%) is less than half the nominal failure rate for all SSTs (17%). It is not certain that the evaporation concentrates contributed to the failure of the tank liner in any of these four instances of liner failure (e.g., TX-107 contained REDOX concentrated and neutralized salt waste which is considered a common factor contributing to liner failure). Evaporator concentrates from evaporator processes are not considered a common factor contributing to liner failure.

6.5.6.1.9. In-Farm Process – Scavenging Waste, Flowsheet

The flowsheet for nickel ferrocyanide scavenging of neutralized concentrated RAW stream (RA column effluent from the metal recovery first solvent extraction column) (HW-33536) identifies the addition of ferrocyanide ion resulting in the formation of a sludge containing 0.025 M

ferrocyanide ion and 0.025 M nickel ferrocyanide. There is no available information showing a connection between ferrocyanide and SCC. Except for the scavenging chemical additions, the composition of the process waste after scavenging is the same as the TBP waste prior to in-plant scavenging. The analysis of TBP waste prior to in-plant scavenging as a potential common factor contributing to liner failure has already been addressed in Section 6.5.6.1.2. The in-farm scavenging process does not materially affect the likelihood of SCC associated with TBP waste prior to in-farm scavenging. In-farm scavenging is not considered a common factor contributing to SST liner failure.

6.5.6.1.10. In-Farm Process – Nitrate Leaching, Samples

A summary of nitrate leaching operations including the date of condensate addition, leach date, temperature of each tank at the time of nitrate leaching, believed failure date, and total leach time are shown in Table 6-38. It should be noted that the temperatures for the tanks dropped significantly when the nitrate-bearing sludge was leached, as expected due to the high volume addition of condensate. However, the tanks remained at relatively high temperatures, which may be conducive to SCC. In addition, tank SX-105 was later used as the holding and feed tank for leached nitrate sent to the 202-S dissolvers in REDOX plant.

Table 6-38. Nitrate Leach Date and Corresponding Temperature for 241-SX Tanks

Tank	$NaNO_3$ Leach Order	Water Addition	Date Leached	$NaNO_3$ Leaching Time (days)	Temperature (°C)	Confirmed Leaker?	Est. Failure Date[1]
SX-107	3	December 1962	January 1963	39	87	Yes	March 1964
SX-108	2	June 1962	August 1962	63	73	Yes	December 1962
SX-111	4	March 1964	June 1964	83	87	Yes	May 1974
SX-114	1	-	October 1961	150[2]	102	Yes	August 1972
SX-115	5	June 1964	September 1964	104	81	Yes	March 1965

[1] Obtained from the *Hanford SX-Farm Leak Assessments Report*, RPP-ENV-39658

[2] Represents the Sludge Dissolution Test time as the test procedure resulted in nitrate leaching (HW-72551, p. G-4).

Evidence shows that five total tanks were nitrate leached from SX Farm and a sixth tank was used for nitrate waste storage and feed to REDOX plant. All five of the nitrate leached tanks are confirmed leakers and the estimated failure dates occur after nitrate leaching. The nitrate leaching may have produced a nitrate ion rich solution that contained insufficient nitrite and hydroxide concentrations to inhibit SCC at the tank temperatures.

Performing a chi-square test with the values presented in Table 6-39 for tank liner failures for tanks that contained nitrate leaching waste results in a p-value of 8.5×10^{-6}. The expected values from the chi-square test include one value (out of 4) which is less than 5, and therefore the sample does not meet one of the general rules for chi-square testing (i.e., no more than 20% of the expected values are less than 5). Thus, the results of the chi-square testing generally would not be considered relevant. Performing Fisher's exact test, the calculated p-value is 4.9×10^{-4}. Because the p-value is less than the selected significance level, $\alpha=0.05$, we reject the null hypothesis. In other words, there is a statistically significant difference in the proportion of liner failures in tanks which contained waste from nitrate leaching and those that did not. Based on

the available information it appears that receiving and storing waste from nitrate leaching is a common factor contributing to liner failure.

Table 6-39. Nitrate Leaching Waste Tank Failure Rate Observational Data

	Probable Liner Failure	Liner Failure Not Known	Total
All Tanks That Contained Nitrate Leaching Waste	5	1	6
Tanks That Did Not Contain Nitrate Leaching Waste	20	123	143
Total	**25**	**124**	**149**

6.5.6.1.11. In-Farm Process – PUREX sludge washing, flowsheet

PUREX sludge supernatant (PSS) waste was first identified as a separate waste stream in the quarter ending September 1969 (ARH-1200 C). The first receipt of PSS waste was during January-March 1971 (ARH-2074 A). The waste was initially transferred from 244-AR vault to tank C-106 and then to C-105 which acted as a feed tank to B Plant where the cesium was removed from the waste. Beginning later in 1971 the waste was also stored in tanks C-103 and A-102. Beginning in January-March 1973 (ARH-2794 A) PSS waste was transferred from 244-AR vault to tank A-104. Starting in 1973 PSS waste was also stored in tanks AX-101, AX-103 and AX-104. In 1974 and 1975 PSS waste was stored in tank A-103. Tank A-104 stopped receiving PSS waste when a leak was detected in the tank in April 1975 (RPP-RPT-54912). After the leak in tank A-104, PSS waste from 244-AR vault was sent to tank AX-103. In 1976 some PSS waste was also transferred to tank C-104 and from there to tank SX-106 (ARH-CD-702 B) but this was a minor amount (about 150,000 gal between the two tanks) that would have been mixed in with the other waste types. Transfer records after June 1976 are not as clear regarding which tanks received PSS waste. It is expected that tank AX-103 continued to receive the PSS waste from 244-AR vault and send the waste to tank C-105 which provided feed for cesium recovery at B Plant. Sluicing of the A and AX Farm tanks was completed in April 1978 (SD-WM-TI-302). The tanks that contained PSS waste (except tanks C-104 and SX-106 which were only small quantities that mixed with other wastes) are listed in Table 6-40. Tanks with probable liner leaks are highlighted in red in the table.

Table 6-40. Listing of Single-Shell Tanks That Received PUREX Sludge Supernatant Waste

Tank		
C-103	A-102	AX-101
C-105	A-103	AX-103
C-106	A-104	AX-104

Tanks highlighted in red have probable liner leaks.

Of the nine tanks that received PSS waste, two of these tanks have probable liner failures. Comparison of liner failure rates can be made between those tanks that contained PSS waste and those that did not. Performing a chi-square test with the values presented in Table 6-40 for tank liner failures for all tanks that did and did not receive PSS waste results in a p-value of 0.65. The

expected values from the chi-square test include one value (out of 4) which is less than 5, and therefore the sample does not meet one of the general rules for chi-square testing (i.e., no more than 20% of the expected values are less than 5). Thus, the results of the chi-square testing generally would not be considered relevant. Performing Fisher's exact test, the calculated p-value is 0.65. Because the p-value is greater than the selected significance level, α=0.05, we accept the null hypothesis. In other words, there is no statistically significant difference in the proportion of liner failures in tanks which received PSS waste and those that did not. Based on the available information it appears that receiving and storing PSS waste is not a common factor contributing to liner failure.

6.5.6.1.12. Summary of Nitrate-Induced Stress Corrosion Cracking by Waste Type

Eleven waste types were identified as having compositions that did not meet one or more criteria associated with preventing stress corrosion cracking. The failure rates of tank liners containing each of these waste types have been evaluated in the above subsections to determine whether each waste type may be considered a common factor contributing to tank liner failure. A summary of those findings is presented in Table 6-41 below. Only three waste types are considered as likely contributing to tank liner failure. REDOX concentrated and neutralized salt waste and waste from in-farm nitrate leaching are considered likely contributors. Uranium recovery TBP waste is also considered a likely common factor when it was the first waste introduced to a tank, but not when subsequently added to a tank that had already received another waste type. The likelihood of waste from the PUREX 1970 thoria campaign being a common factor was indeterminate. All other waste types analyzed were considered unlikely as common factors contributing to liner failure.

Table 6-41. Summary of Nitrate-Induced Stress Corrosion Cracking by Waste Type

Liner Failure Mechanisms	Indeterminate	Unlikely	Likely
Bismuth Phosphate Combined First Cycle and Coating Removal Waste		X	
Uranium Recovery TBP Waste Prior to In-Plant Scavenging		X (Later Waste in Tank)	X (1st Waste in Tank)
REDOX Concentrated and Neutralized Salt Waste			X
PUREX Highly Active Waste		X	
PUREX 1970 Thoria Campaign Waste	X		
Fission Product Recovery Phase III Ion Exchange Waste		X	
Fission Product Recovery Phase III High Level Waste		X	
Evaporation Processes Waste		X	
In-Farm Scavenging Waste		X	
In-Farm Nitrate Leaching			X
In-Farm PUREX Sludge Washing Waste		X	

6.5.6.2. Caustic Cracking

As mentioned previously in Section 4.4.9.4, caustic SCC of carbon steel occurs over a wide range of caustic concentrations, with even a few weight percent of caustic able to cause cracking under appropriate conditions. As caustic concentration increases, carbon steel is susceptible to caustic SCC at lower temperatures. Under appropriate environmental conditions, caustic SCC is inhibited by the presence of nitrate (BNL-52527). However, at high enough caustic concentration and temperature caustic SCC can still occur.

Testing of 10 M hydroxide solutions with various concentrations of nitrate (1-5 M) and nitrite (0.2-5.3 M) showed cracking at 180°C with moderate nitrate concentration (1-5 M) and low nitrite concentration (0.2 M) (SD-WM-TI-161, *Section on Tank Corrosion Study High Temperature Tests Eight Month Evaluation*). Caustic cracking was also reported at 140°C with 5 M sodium hydroxide, 0.3 M sodium nitrate, and 0.2 M sodium nitrite (PNL-4727). Double-shell tank waste chemistry limits were established (OSD-T-151-00007) to protect against caustic cracking at high temperatures and high caustic concentration and to protect against excessive general corrosion at intermediate temperatures and caustic concentrations. To protect against caustic cracking at higher temperature, sodium hydroxide is limited to 4.0 M above 100°C (SD-WM-TI-150, *Technical Basis for Waste Tank Corrosion Specifications*). At lower temperatures sodium hydroxide is limited to 10.0 M. For non-stress-relieved tanks recommendations were made for limiting sodium hydroxide at 10.0 M to a temperature of 70-80°C rather than 100°C (PNL-4727).

Examining the waste composition information presented in Table 5-39, Table 5-41, Table 5-42, and Table 6-27 for liquid (supernatant) samples, identifies only two samples (from tank S-105, see Table 5-41) that exceed 6 M sodium hydroxide. These samples have moderate nitrate (~2 M) and nitrite (~1 M) concentrations. Four other samples exceed 5 M sodium hydroxide but these also all have moderate nitrate and nitrite concentrations as well. Another four samples exceed 4 M sodium hydroxide but these all have moderate or high (i.e., higher than sodium hydroxide) nitrate and/or nitrite concentrations as well.

Sample	OH^- [M]	NO_3^- [M]	NO_2^- [M]	From
ITS-2 bottoms supernatant, BY-112, ca. 1972	4.27	2.45	1.0	Table 6-27
S-106 liquid, ca. 1975	4.44	2.42	1.78	Table 5-41
SX-101 supernatant sample, ca. 1961	4.58	6.03	2.48	Table 6-27
TX-106 liquid, ca. 1976	4.99	0.285	1.13	Table 5-39
S-108 liquid, ca. 1974	5.08	2.6	1.94	Table 5-41
S-106 liquid, ca. 1974	5.33	2.49	0.656	Table 5-41
ITS-1 supernatant, BY-101, ca. 1968	5.47	4.31	1.19	Table 6-27
S-112 liquid, ca. 1974	5.72	2.5	2.02	Table 5-41
S-105 liquid, ca. 1974	6.46	1.95	0.99	Table 5-41
S-105 liquid, ca. 1974	6.47	1.94	1.00	Table 5-41

The bottoms from ITS-2 and the 242-T evaporator exceeded 212°F (100°C), while ITS-1 was nominally operated around 170°F (77°C). The 242-S evaporator operated under vacuum resulting in a bottoms discharge temperature around 131°F (55°C). None of the source tanks in the listing above have probable liner failures.

Considering the available data, it appears there is little likelihood that conditions existed to allow caustic cracking to occur in any of the SSTs. Appreciable quantities of nitrate and nitrite were present in those few instances where sodium hydroxide concentration exceeded 4.0 M at temperatures above 80°C. For the one instance where nitrite concentration was below 1.0 M, the anticipated temperature would have been no more than 131°F (55°C). Caustic cracking is not considered to be a likely contributing factor causing liner failure.

6.5.6.3. Carbonate-Induced Stress Corrosion Cracking

As mentioned in Section 4.4.9.4, concentrated carbonate/bicarbonate solutions at pH greater than 9.3, can induce SCC and some studies indicate SCC could be produced in more dilute solutions, down to 0.25 N mixtures. High pH carbonate/bicarbonate-induced SCC occurs in a narrow range of potentials. In a solution of 0.5 M sodium bicarbonate and 1 M sodium carbonate solution at 75°C, cracking occurs between approximately -0.7 V (vs. SCE) and -0.6 V (vs. SCE) (NWMO TR-2010-21).

Examining the waste composition information presented in Table 5-39, Table 5-41, Table 5-42, and Table 6-27 identifies eight waste types with at least one instance greater than 0.25 N carbonate/bicarbonate:

- $BiPO_4$ metal waste supernatant;
- PUREX neutralized zircaloy cladding removal waste supernatant;
- PUREX highly active waste supernatant;
- PUREX OWW;
- B Plant ion exchange waste from processing PUREX alkaline supernatant;
- ITS-1 and ITS-2 waste;
- 242-T evaporator waste; and,
- 242-A evaporator waste.

Of these, only ITS-1 and ITS-2 waste samples exceeded 1.5 M carbonate/bicarbonate. The ITS-1 and ITS-2 samples had nitrate and hydroxide concentrations in excess of the carbonate and substantial nitrite concentrations (0.46 M or greater).

No studies were found specifically examining carbonate-induced SCC from any wastes discharged to SSTs. The only corrosion study found related to high carbonate waste was for synthetic concentrated PUREX OWW to simulate corrosion that may take place under conditions expected during in-tank solidification. These studies looked at 2 M and 3 M carbonate but did not provide any discussion regarding SCC.

Because of the limited information available regarding carbonate-induced SCC, no determination can be made whether it was a contributing factor causing liner failure.

6.5.7 Concentration Cell Corrosion

Localized attack on carbon steel can occur where concentration gradients can develop in the environment in contact with the steel. These concentration gradients can develop an electrolytic cell with discrete anodic and cathodic regions. If the potential difference is great enough the anodic region will corrode preferentially. A concentration cell may form anywhere a concentration difference exists in an electrolyte that will cause corrosion. In SSTs, these areas could include the LAI, solid-liquid interface, differential solid-solid interface with two different solid compositions, stagnant solids layer. Each of these will be discussed below.

6.5.7.1. Liquid-Air Interface (LAI) Corrosion

Local differences in pH at a stagnant LAI with lower pH values at the surface of the waste (e.g., from water evaporation and recondensation at the surface or carbon dioxide absorption at the waste surface from the air space) can cause pitting. Reactions involving carbon dioxide in the air and hydroxide could have an effect on the corrosiveness of a thin liquid layer that migrates up the steel surface above the bulk solution. It is possible that corrosion would be localized owing to a difference in local corrosiveness of the environment.

Limited data was found regarding LAI corrosion within SSTs. The general corrosion data and pitting corrosion data for LAI are shown in Table 6-42 and Table 6-43, respectively.

The available general corrosion data associated with LAI corrosion show relatively low general corrosion rates. Two of the REDOX waste simulants do show general corrosion rates in excess of 1 mil/yr but these are associated with broad ranges of rates and relatively short duration tests. The number of waste types for which information is available is limited.

The available pitting corrosion data associated with LAI corrosion show some significant pitting corrosion rates, albeit the reported rates are only for simulants and not actual waste. The $BiPO_4$ metal waste simulant results are of little utility because of the extremely short exposure period. With the exception of $BiPO_4$ 1C waste simulant, there is no time-dependent data which makes it impossible to determine whether the pitting rate is declining with time. For the $BiPO_4$ 1C simulant, it is clear that there is a reduction in pitting rate at the LAI as a function of time between 3 and 6 months. Regarding the high pitting rates associated with the neutralized Zirflex decladding solution at relatively low pH, it is important to point out that sample analysis for neutralized Zirflex decladding solution shows a much higher pH of 13.2 (Letter Report, M.S. Hanson to R.D. Wojtasek, "Characterization of Actual Zirflex Decladding Sludge", June 1986). The available data show no LAI pitting corrosion for neutralized Zirflex decladding solution at higher pH.

The available LAI corrosion data is limited in terms of the waste types examined. Because of the limited nature of the data, no quantitative evaluation, and therefore, no determination can be made regarding whether or not LAI corrosion was a contributing factor related to liner failure.

Table 6-42. General Corrosion Rate Data at Liquid-Air Interface for Single-Shell Tank Waste

Process	Waste Type	Actual Waste or Simulant	Exposure Period	Temperature	Condition/ Location	General Corrosion Rate (mil/yr)	Reference
Bismuth Phosphate	Metal Waste	Simulant, pH 10	7.4-7.6 months	72°C	Partially Immersed	Gain - 0.14	HW-18595, App I, Table I
	Metal Waste	Simulant, pH 11	7.4-7.5 months	72°C	Partially Immersed	Gain - 0.09	HW-18595, App I, Table I
	First Cycle	Simulant, pH 6	3-6 months	80°C	Liquid-Vapor Interface	0.06-0.37	HW-26202, Table 3
	First Cycle	Simulant, pH 7	3-6 months	80°C	Liquid-Vapor Interface	0.01-0.12	HW-26202, Table 3
	First Cycle	Simulant, pH 8	3-6 months	80°C	Liquid-Vapor Interface	0.01-0.25	HW-26202, Table 3
REDOX	REDOX	Simulant, pH 11	1000 hrs	82-104°C	Liquid-Vapor Interface	0.07-0.49	HW-26201, Table 1
	REDOX	Simulant, pH 12	1000 hrs	82-104°C	Liquid-Vapor Interface	0.23-1.56	HW-26201, Table 1
	REDOX	Simulant, pH 13	1000 hrs	82-104°C	Liquid-Vapor Interface	0.08-3.43	HW-26201, Table 1

Table 6-43. Pitting Corrosion Data at Liquid-Air Interface for Single-Shell Tank Waste (2 Pages)

Process or Source	Waste Type	Actual Waste or Simulant	Exposure Period	Temperature	Condition/ Location	Average Pit Depth (Max Pit Depth) (mil)	Average (Max) Pitting Rate (mil/yr)	Reference
Bismuth Phosphate	Metal Waste	Simulant, pH 10.5	424-472 hours	102°C (boiling)	Liquid-Vapor Interface	0.7-1.3 (0.8-1.7)	13-26	HW-24136, Table 3
	First Cycle	Simulant, pH 6	3 months	80°C	Liquid-Vapor Interface	0.91-1.18	3.6-4.7	HW-26202, Table 5
	First Cycle	Simulant, pH 6	6 months	80°C	Liquid-Vapor Interface	1.06-1.38	2.1-2.8	HW-26202, Table 5
	First Cycle	Simulant, pH 7	3 months	80°C	Liquid-Vapor Interface	1.38-1.62	5.5-6.5	HW-26202, Table 5
	First Cycle	Simulant, pH 7	6 months	80°C	Liquid-Vapor Interface	1.22-1.70	2.4-3.4	HW-26202, Table 5
	First Cycle	Simulant, pH 8	3 months	80°C	Liquid-Vapor Interface	1.70-1.85	6.8-7.4	HW-26202, Table 5
	First Cycle	Simulant, pH 8	6 months	80°C	Liquid-Vapor Interface	0.87-1.06	1.7-2.1	HW-26202, Table 5
PUREX	Neutralized Zirflex Decladding Solution	Simulant, pH 5.5	5 months	25-40°C	Liquid-Vapor Interface	(5.5-14.)	(13-34)	HW-61662, Table VIII

Table 6-43. Pitting Corrosion Data at Liquid-Air Interface for Single-Shell Tank Waste (2 Pages)

Process or Source	Waste Type	Actual Waste or Simulant	Exposure Period	Temperature	Condition/ Location	Average Pit Depth (Max Pit Depth) (mil)	Average (Max) Pitting Rate (mil/yr)	Reference
	Neutralized Zirflex Decladding Solution	Simulant, pH 6.3	5 months	25-40°C	Liquid-Vapor Interface	(5.5-10.5)	(13-25)	HW-61662, Table VIII
	Neutralized Zirflex Decladding Solution	Simulant, pH 6.9	5 months	25-40°C	Liquid-Vapor Interface	(5.0-6.0)	(12-14)	HW-61662, Table VIII
	Neutralized Zirflex Decladding Solution	Simulant, pH 8.5	5 months	25-40°C	Liquid-Vapor Interface	0	0	HW-61662, Table VIII
	Neutralized Zirflex Decladding Solution	Simulant, pH 9.3	5 months	25-40°C	Liquid-Vapor Interface	0	0	HW-61662, Table VIII

6.5.7.2. Solid-Liquid Interface Corrosion

As solids in the SST waste precipitated from the liquid phase and settled, a solid-liquid interface would form within the tank. Over time, local differences in composition could occur between interstitial liquid in equilibrium with solids and the supernatant liquid above. This difference in composition could cause a concentration cell between the interstitial liquid and supernatant liquid resulting in corrosion within the anodic layer. Very limited data was found, specifically only for REDOX waste, regarding solid-liquid interface corrosion within SSTs. The general corrosion data and pitting corrosion data for solid-liquid interfaces are shown in Table 6-44 and Table 6-45, respectively.

Table 6-44. General Corrosion Rate Data at Solid-Liquid Interface for Single-Shell Tank Waste

Process	Waste Type	Actual Waste or Simulant	Exposure Period	Temperature	Condition/ Location	General Corrosion Rate (mil/yr)	Reference
REDOX	REDOX	Simulant, pH 11	1000 hrs	82-104°C	Liquid-Sludge	0.02-0.19	HW-26201, Table 1
	REDOX	Simulant, pH 12	1000 hrs	82-104°C	Liquid-Sludge	0.16-4.37	HW-26201, Table 1
	REDOX	Simulant, pH 13	1000 hrs	82-104°C	Liquid-Sludge	0.08-1.01	HW-26201, Table 1
	REDOX (including Coating Waste)	Actual, S-104	9 months	149°C +	Liquid-Sludge	0.36-0.56	HW-32755, Table II

Table 6-45. Pitting Corrosion Data at Solid-Liquid Interface for Single-Shell Tank Waste

Process or Source	Waste Type	Actual Waste or Simulant	Exposure Period	Temperature	Condition/ Location	Average Pit Depth (Max Pit Depth) (mil)	Average (Max) Pitting Rate (mil/yr)	Reference
REDOX	REDOX (including Coating Waste)	Actual, S-104	9 months	149°C +	Liquid-Sludge	1.9-3.0 (2.1-4.0)	2.5-4.0 (2.8-5.3)	HW-32755, Table II

One REDOX simulant showed a general corrosion rate in excess of nominally 1 mil/yr, actual waste showed general corrosion less than 1 mil/yr. Maximum pitting rates over a 9 month period for actual REDOX waste, including CW, were nominally 5 mil/yr. No information is available on pit growth with age or pitting cessation.

Although solid-liquid interface corrosion is a possible contributing factor to liner failure there is inadequate information available to make such a determination.

6.5.7.3. Solid-Solid Interface Corrosion

Tanks which received different waste types containing settled solids layers can result in a solid-solid interface where the composition is different between the two solid layers. This difference in composition can cause a concentration cell between the interstitial liquid of two adjacent layers of solids within the tank. This concentration difference could result in corrosion (e.g., general, pitting, SCC) within the anodic layer. Information was not found regarding investigation of solid-solid interface corrosion within SSTs.

Solid-solid interface corrosion would require receipt of different waste types into a given tank. Tank farm history (WHC-MR-0132) shows that only 14 SSTs either contained a single waste type for the entirety of its operational life or prior to failure of the tank. Those tanks are: T-201 through T-204, TX-116, TX-117, TY-105, TY-106, SX-107 through SX-109, SX-112, SX-113, and SX-115. The last eight of the listed tanks have failed liners most likely caused by nitrate-induced stress corrosion cracking.

Comparison can be made between those tanks which only received one waste type and those that received multiple waste types. Multiple waste types are necessary to provide conditions that could result in solid-solid corrosion. Performing a chi-square test with the values presented in Table 6-46 for tank liner failures for tanks with a single waste type results in a p-value of 2.17E-05. The expected values from the chi-square test include one value (out of 4) which is less than 5, and therefore the sample does not meet one of the general rules for chi-square testing (i.e., no more than 20% of the expected values are less than 5). Thus, the results of the chi-square testing generally would not be considered relevant. Performing Fisher's exact test, the calculated p-value is 3.28E-04. Because the p-value is less than the selected significance level, α=0.05, we reject the null hypothesis. In other words there is a statistically significant difference in the proportion of liner failures in tanks which contained a single waste type. However, the presence of a single waste type results in a significantly higher failure rate than multiple waste types with multiple solid layers. As mentioned previously, this higher failure rate is likely due to the presence of an environment conducive to nitrate-induced stress corrosion cracking. The failure rate of tank liners with multiple solid waste layers (17/135) is less than the overall tank liner failure rate (25/149). Based on the available information solid-solid interface corrosion is not a common factor contributing to liner failure.

Table 6-46. Single Waste Type Failure Rate Observational Data

	Probable Liner Failure	Liner Failure Not Known	Total
Single Waste Type and Solids	8	6	14
Multiple Waste Type and Solids Layers	17	118	135
Total	**25**	**124**	**149**

6.5.8 Vapor Space Corrosion

General and pitting corrosion information is available for several but not all of the major waste streams introduced into the SSTs. The majority of general corrosion rate information is based on testing with waste simulants representing the major constituents present in the waste stream, but some data for actual waste is also available. This section of analysis only examines data for vapor space corrosion. Corrosion data for liquid waste, solid waste, liquid-vapor interface, and solid-liquid interface are analyzed elsewhere. General corrosion data and pitting corrosion data for the vapor space over various waste types is tabulated in Table 6-47 and Table 6-48, respectively.

Some data trends can be seen in the tabulated vapor space general corrosion data. General corrosion rates in the vapor space are typically lower (or comparable) in actual waste than the corresponding simulant waste. General corrosion rates for available actual wastes are less than nominally 1 mil/yr. Simulants of $BiPO_4$ 1C waste and REDOX waste had general corrosion rates in excess of 1 mil/yr but these corrosion rates decreased with an increase in the exposure period. Very low corrosion rates were found for TBP waste, which was tested at a much lower temperature than the other waste types presented. From a qualitative perspective, the available vapor space general corrosion data does not support vapor space corrosion being a contributing

factor to liner failure. However, the available data is incomplete and a more quantitative determination cannot be made.

Table 6-47. Vapor Space General Corrosion Rate Data for Single-Shell Tank Waste

Process	Waste Type	Actual Waste or Simulant	Exposure Period	Temperature	Condition/ Location	General Corrosion Rate (mil/yr)	Reference
Bismuth Phosphate	First Cycle	Simulant, pH 6	1 month	80°C	Vapor	5.0-6.7	HW-26202, Table 4
	First Cycle	Simulant, pH 6	2 months	80°C	Vapor	1.7-3.2	HW-26202, Table 4
	First Cycle	Simulant, pH 6	3 months	80°C	Vapor	2.0-2.9	HW-26202, Table 4
	First Cycle	Simulant, pH 7	1 month	80°C	Vapor	3.1-4.2	HW-26202, Table 4
	First Cycle	Simulant, pH 7	2 months	80°C	Vapor	1.2-1.3	HW-26202, Table 4
	First Cycle	Simulant, pH 7	3 months	80°C	Vapor	0.2-0.8	HW-26202, Table 4
	First Cycle	Simulant, pH 8	1 month	80°C	Vapor	2.5-3.1	HW-26202, Table 4
	First Cycle	Simulant, pH 8	2 months	80°C	Vapor	0.6-0.8	HW-26202, Table 4
	First Cycle	Simulant, pH 8	3 months	80°C	Vapor	0.2-1.0	HW-26202, Table 4
	First Cycle & Coating Waste	Actual, TX-109	7 months (11/52-6/53)	--	Vapor	0.04-0.16	HW-30641, Table 1
Uranium Recovery (TBP Process)	TBP	Simulant, pH 7	1 month	30°C	Vapor	0.06	HW-30041
	TBP	Simulant, pH 7	3 months	30°C	Vapor	0.006	HW-30041
	TBP	Simulant, pH 8	1 month	30°C	Vapor	0.014-0.019	HW-30041
	TBP	Simulant, pH 8	3 months	30°C	Vapor	0.019-0.024	HW-30041
	TBP	Simulant, pH 9	1 month	30°C	Vapor	0.019-0.024	HW-30041
	TBP	Simulant, pH 9	3 months	30°C	Vapor	0.006-0.036	HW-30041
REDOX	REDOX	Simulant, pH 11	1000 hrs	82-104°C	Vapor	1.37-5.74	HW-26201, Table 1
	REDOX	Simulant, pH 12	1000 hrs	82-104°C	Vapor	0.84-4.08	HW-26201, Table 1
	REDOX	Simulant, pH 13	1000 hrs	82-104°C	Vapor	0.67-3.43	HW-26201, Table 1
	REDOX	Actual (SX-107)	1 year	not known	Vapor	0.052-0.64	HW-53308, Tables I& II
PUREX	Neutralized Acid Waste	Simulant	1-3 months	Boiling	Vapor	0.11-0.73	HW-26892, p. 9
	Neutralized Acid Waste	Simulant	1-3 months	104°C	Vapor	0.11-0.73 (0.17-1.03)	HW-32734, Table I
	Neutralized Acid Waste	Actual, A-101	130 days (2/6/56-6/15/56)	--	Vapor	0.23-1.04	HW-49574, Tables I & III
	Organic Wash Waste	Simulant, pH 8.9-11.0	840 hours	100°C	Vapor	(0.7)	HW-70872, p. C-12

Some trends can be identified by examining the tabulated vapor space pitting corrosion data. A number of trends are similar to the trends found for vapor space general corrosion. Pitting corrosion rates in the vapor space are typically lower (or comparable) in actual waste than the corresponding simulant waste. For all tests extended over a time period (i.e., between 1 and 3 months), pitting corrosion rates decrease with time. One can infer from this that pits will not continue to grow at the rate shown at the end of the period studied but at some lower rate. Pitting rates for periods examined for all waste types, both actual and simulant, were in excess of 1 mil/yr. Pitting rates for specimens in actual waste tanks are based on longer exposure periods than simulants. Correspondingly, the pitting rate is lower for longer exposure periods with actual waste than for shorter exposure periods with simulants. No information is available on long term (beyond the 3 months examined) pit growth with age or pitting cessation. The lower test temperature for TBP waste did not result in an appreciably lower pitting corrosion rate in comparison to tests of other waste types at much higher temperatures.

From a qualitative perspective, the available vapor space pitting corrosion data shows higher corrosion rates than general corrosion and numbers reported are generally between 1-10 mil/yr. The limited information does not eliminate vapor space pitting corrosion as a possible concern relative to liner failure. Unfortunately, there is inadequate information to quantitatively determine whether vapor space pitting corrosion is significant or to come to a meaningful conclusion regarding vapor space pitting corrosion.

6.5.9 Differential Temperature Cell Corrosion

In tanks with settled solids layers a differential temperature exists between the settled solids and the supernatant liquid directly above the solid. Convective currents allow a more uniform temperature throughout the supernatant liquid while conductive heat transfer through the solids results in a temperature gradient through the solid layer. Information was not found regarding investigation of differential temperature cell corrosion within SSTs. Every tank has some settled solids present within the tanks so some level of differential temperature is to be expected in every tank. Incomplete temperature profile data (both temporally and spatially) for SSTs do not allow for a total analysis of differential temperatures within tanks. So neither adequate differential temperature data nor differential temperature cell corrosion data are available.

Although differential temperature cell corrosion is a possible contributing factor to liner failure there is no information available to make such a determination.

Table 6-48. Vapor Space Pitting Corrosion Rate Data for Single-Shell Tank Waste

Process or Source	Waste Type	Actual Waste or Simulant	Exposure Period	Temperature	Condition/ Location	Average Pit Depth (Max Pit Depth) (mil)	Average (Max) Pitting Rate (mil/yr)	Reference
Bismuth Phosphate	Metal Waste	Simulant, pH 10.5	424-472 hours	102°C (boiling)	Vapor	0.8-1.2 (0.9-1.8)	14-24	HW-24136, Table 3
	First Cycle	Simulant, pH 6	1 month	80°C	Vapor	1.42-1.46	17-18	HW-26202, Table 5
	First Cycle	Simulant, pH 6	2 months	80°C	Vapor	1.62-2.17	9.7-13	HW-26202, Table 5
	First Cycle	Simulant, pH 6	3 months	80°C	Vapor	2.09-2.24	8.4-9.0	HW-26202, Table 5
	First Cycle	Simulant, pH 7	1 month	80°C	Vapor	1.97-2.20	24-26	HW-26202, Table 5
	First Cycle	Simulant, pH 7	2 months	80°C	Vapor	2.13-2.17	13	HW-26202, Table 5
	First Cycle	Simulant, pH 7	3 months	80°C	Vapor	0.67-2.17	2.7-8.7	HW-26202, Table 5
	First Cycle	Simulant, pH 8	1 month	80°C	Vapor	1.62	19	HW-26202, Table 5
	First Cycle	Simulant, pH 8	2 months	80°C	Vapor	1.22-1.26	7.3-7.6	HW-26202, Table 5
	First Cycle	Simulant, pH 8	3 months	80°C	Vapor	0.51-1.02	2.0-4.1	HW-26202, Table 5
	First Cycle & Coating Waste	Actual, TX-109	7 months (11/52-6/53)	--	Vapor	1.2-1.7 (1.5-2.0)	2.0-2.8	HW-30641, Table 1
Uranium Recovery (TBP Process)	TBP	Simulant, pH 7	1 month	30°C	Vapor	--	9.6-10. (11-13)	HW-30041
	TBP	Simulant, pH 7	3 months	30°C	Vapor	--	5.6-9.1 (7.9-13)	HW-30041
	TBP	Simulant, pH 8	1 month	30°C	Vapor	--	4.9-12. (7.1-14)	HW-30041
	TBP	Simulant, pH 8	3 months	30°C	Vapor	--	5.6-6.5 (7.9-10.)	HW-30041
	TBP	Simulant, pH 9	1 month	30°C	Vapor	--	7.2-8.9 (8.5-12)	HW-30041
	TBP	Simulant, pH 9	3 months	30°C	Vapor	--	4.4-9.2 (4.6-11)	HW-30041
REDOX	REDOX (excluding Coating Waste)	Actual, SX-107	1 year	not known	Vapor	1.90-3.85 (2.64-7.26)	1.90-3.85 (2.64-7.26)	HW-53308, Tables II
PUREX	Neutralized Acid Waste	Simulant	1 month	Boiling	Vapor	--	0.48-1.4 (0.96-2.3)	HW-26892, p. 9
	Neutralized Acid Waste	Simulant	2 months	Boiling	Vapor	--	0.72-1.2 (1.1-1.3)	HW-26892, p. 9
	Neutralized Acid Waste	Simulant	3 months	Boiling	Vapor	--	0.48-0.76 (0.72-1.2)	HW-26892, p. 9
	Neutralized Acid Waste	Simulant	1 month	104°C	Vapor	1.7 (2.0)	20 (24)	HW-32734, Table II
	Neutralized Acid Waste	Simulant	2 months	104°C	Vapor	1.5-1.9 (1.9-2.4)	9.0-11 (11-14)	HW-32734, Table II
	Neutralized Acid Waste	Simulant	3 months	104°C	Vapor	1.5-1.6 (1.9-2.0)	6.0-6.4 (7.6-8.0)	HW-32734, Table II
	Neutralized Acid Waste	Simulant	10 months	104°C	Vapor	3.3 (3.8)	4.0 (4.6)	HW-32734, Table II
	Neutralized Acid Waste	Actual, A-101	130 days (2/6/56-6/15/56)	--	Vapor	0.295-0.742 (0.330-0.825)	0.828-2.08 (0.927-2.32)	HW-49574, Tables IV & VI

6.6 ANALYSIS OF EXTERNAL ENVIRONMENTAL ASPECTS

The only identified possible external environmental failure mechanism is pressurization external to the tank liner. This mechanism is discussed below.

6.6.1 Pressurization External to Tank Liner

With the exception of tank U-104, known bulging liners have only occurred in SSTs in SX and A Farms, both of which received boiling waste. Table 5-51 identifies five tanks that have primary indications (i.e., direct physical evidence via photo or tank bottom sounding) of a bulging liner bottom. All five of these tanks have liner failures. Additionally, eleven more tanks have secondary indications (i.e., inferred evidence such as tilted ALCs, broken guy rods on ALCs, and bent piping; which could have been caused by other factors). Of these eleven tanks an additional six tanks have liner failures. It should be noted that the presence of a secondary indication does not mean that an external pressurization occurred in a particular tank, nor does the absence of a secondary indication mean that an external pressurization did not occur. Tank U-104 had primary indication (photo) of a bulging liner but no secondary indication. Type II and Type III tanks with probable liner failures were reviewed for indications of bulging but the larger population of these tanks was not reviewed for the presence of bulges. The results of this analysis should be viewed in the light of this information.

Failure rates can be compared for those tanks with primary indications of external pressurization and those for which no primary indication is present. Performing a chi-square test with the values presented in Table 6-49 for tank liner failures for tanks with primary indication of an external pressurization results in a p-value of 4.1×10^{-7}. The expected values from the chi-square test include two values (out of 4) less than 5, and therefore the sample does not meet one of the general rules for chi-square testing (i.e., no more than 20% of the expected values are less than 5). Thus, the results of the chi-square testing generally would not be considered relevant. Performing Fisher's exact test, the calculated p-value is 9.3×10^{-5}. Because the p-value is less than the selected significance level, $\alpha=0.05$, we reject the null hypothesis. In other words, there is a statistically significant difference in the proportion of liner failures in tanks in which there is a primary indication of external pressurization. Based on the available information it appears that primary indication of external pressurization is a factor contributing to liner failure.

Table 6-49. Primary Indication of External Pressurization Liner Failure Rate Observational Data

	Probable Liner Failure	Liner Failure Not Known	Total
Primary indication of bulge	5	0	5
No primary indication of bulge	20	124	144
Total	**25**	**124**	**149**

Comparison can also be made between those tanks for which primary and/or secondary indication of an external pressurization exist or don't exist. Performing a chi-square test with the values presented in Table 6-50 for tank liner failures for tanks with and without primary and/or secondary indication of an external pressurization results in a p-value of 3.9×10^{-9}. The expected values from the chi-square test include one value (out of 4) less than 5, and therefore the sample

does not meet one of the general rules for chi-square testing (i.e., no more than 20% of the expected values are less than 5). Thus, the results of the chi-square testing generally would not be considered relevant. Performing Fisher's exact test, the calculated p-value is 8.2×10^{-7}. Because the p-value is less than the selected significance level, $\alpha=0.05$, we reject the null hypothesis. In other words there is a statistically significant difference in the proportion of liner failures in tanks in which primary and/or secondary indication of external pressurization exists. Based on the available information it appears that external pressurization is a factor contributing to liner failure.

Table 6-50. Primary and/or Secondary Indication of External Pressurization Liner Failure Rate Observational Data

	Probable Liner Failure	Liner Failure Not Known	Total
Primary indication of bulge	11	5	16
No primary indication of bulge	14	119	133
Total	**25**	**124**	**149**

7.0 CONCLUSIONS

Based on a literature review of documents concerned with tank failure mechanisms, an extensive listing of potential liner failure mechanisms were identified that could reasonably cause or play a role in causing liner failure in a SST based on the design, materials, construction and operation of the SSTs. Each of these potential mechanisms was further evaluated in greater detail as it applied specifically to the SSTs to determine whether the particular mechanism was improbable or possible. This initial examination between improbable and possible only determined whether conditions existed that could lead to the failure mechanism rather than whether the mechanism was a common factor contributing to tank liner failure. In general, a mechanism was considered improbable if it was known that the conditions necessary for the mechanism to occur did not exist in the SSTs. If it was unknown whether the conditions existed under which the mechanism could occur or it was known the necessary conditions existed, a mechanism was considered possible. Of the potential mechanisms examined, 28 failure mechanisms were identified as being possible. Explanations are given why the remaining identified failure mechanisms are considered improbable.

Available historical information was examined for SSTs relative to the 28 possible failure mechanisms. A statistical analysis was attempted to determine what factors were significant in causing SST liner failures. Adequate historical information was not available for 14 of the 28 possible failure mechanisms in order to make any determination on whether the failure mechanism was a likely or unlikely common factor contributing to liner failure. Of the remaining 14 failure mechanisms evaluated, six mechanisms were evaluated as likely common factors contributing to liner failure. A listing of the 28 failure mechanisms as well as whether each was a likely or unlikely common factor or it was indeterminate is presented in Table 7-1.

Table 7-1. Analysis Results of Possible Failure Mechanisms (2 Pages)

Liner Failure Mechanisms	Indeterminate	Unlikely	Likely
Design and Design Modification Flaws			
Lack of Post-Weld Stress Relieving			X
Liner Bottom to Wall Transition Design			X
Exterior Finish of Tank Liner	X		
Lack of Vent Path for Gases Formed Below Tank Liner		X	
Procured Material Defects			
Properties of Liner Materials			
Carbon Equivalent		X	
Yield Strength			X
Material Standard and Grade	X		
Liner Plate Thickness	X		
Steel Liner Plate Defects	X		
Weld Material Defects	X		
Tank Fabrication Defects			
Brittle Fracture or Crack Propagation During Fabrication		X	
Cold Working and Strain Aging (shop fabricated knuckles and weld peening)		X	
Weld Joint Discontinuities and Defects	X		
Operational Service Related Failure Mechanisms			
Low-Cycle Fatigue		X	
Temperature Induced Failure			

Table 7-1. Analysis Results of Possible Failure Mechanisms (2 Pages)

Liner Failure Mechanisms	Indeterminate	Unlikely	Likely
Rate of Rise	X		
High Temperature			X
Corrosion			
General or Uniform Corrosion		X	
Pitting Corrosion	X		
Crevice Corrosion	X		
Stress-Corrosion Cracking			
Nitrate-Induced			X[1]
Caustic Cracking		X	
Carbonate-Induced	X		
Concentration Cell Corrosion			
Liquid-Air Interface	X		
Solid-Liquid Interface	X		
Solid-Solid Interface		X	
Vapor Space Corrosion	X		
Differential Temperature Cell Corrosion	X		
External Environmental Failure Mechanisms			
Pressurization External to Tank Liner			X

[1] Nitrate-induced stress-corrosion cracking is likely for three waste types: TBP waste if it is the first waste in a tank; REDOX concentrated and neutralized salt waste; and, in-farm nitrate leaching. Nitrate-induced SCC is unlikely for other waste types considered, except for PUREX 1970 Thoria Campaign waste for which the analysis was indeterminate.

Some general conclusions regarding this work are listed below:

- Small sample sets of tanks with and without a particular mechanism present limit the confidence one has in the results.
- Because the evaluations are based on field data rather than carefully controlled "experiments", a number of confounding variables may be present that mask the real common factors contributing to liner failure.
- Precise identification of the cause of each of the 25 probable liner failures is not possible with the available information.
- Lack of post-weld stress relieving and tank liner bottom to wall transition design for Type IV tanks are likely design and construction features contributing to certain SST liner failures.
- Little information regarding the properties of the materials used for the SST liners generally do not allow one to determine the role played by the materials in liner failure.
- Yield strength, which may be considered a surrogate for grain size, appears to be a common factor contributing specifically to liner failure due to nitrate-induced SCC. Because of the presence of confounding factors, it is not possible to determine this unequivocally.
- High operational temperature associated with boiling waste is a likely common factor contributing to liner failure.
- The only form of corrosion that is known to be a common factor contributing to liner failure is nitrate-induced SCC. Stress corrosion cracking requires an appropriate aggressive environment (chemistry, high temperature) and tensile stress in the liner (lack of post weld stress relieving, steel grain size, high temperature). The waste types associated with nitrate-induced SCC are:

- Uranium Recovery TBP waste, provided this waste was the first waste introduced to the SST. If TBP waste was subsequently added to a tank that previously held another waste type, there is no such relationship to liner failure.
- REDOX concentrated and neutralized waste, when not combined with CW. The REDOX concentrated and neutralized waste was first sent to the same single-shell tank as CW but after roughly one and a half years of REDOX operation discharge of the two streams was segregated.
- In-farm nitrate leaching waste. REDOX concentrated and neutralized waste sludge was dissolved to recover sodium nitrate solution for use in dissolving aluminum cladding from irradiated fuel elements at the REDOX facility.
- The in-farm nitrate leached tanks also received REDOX concentrated and neutralized waste prior to nitrate leaching making these waste types confounding variables to each other.

- Identifying the commonality of half the possible failure mechanisms is not possible due to the lack of detailed historical information related to the procured materials, tank fabrication, waste operations and chemical compositions within the tanks.

Table 7-2 shows the six mechanisms that are likely common factors to liner failure in single-shell tanks. For clarity, the nitrate-induced stress corrosion cracking mechanism is split into three entries to account for the three different waste types causing nitrate-induced SCC. With the exception of the lack of post-weld stress relieving, none of these factors were present in all 25 tanks with probable liner failures. The comment section of the table shows that all of the factors, except TBP waste as the first waste in a tank causing nitrate-induced SCC, are present in tanks in 241-SX tank farm. And with the exception of containing waste causing nitrate-induced SCC, all the factors are present in tanks in 241-A tank farm. Generally, the operational mechanisms (i.e., high temperature, nitrate-induced stress corrosion cracking, external pressurization) do not show up or show up infrequently in the earliest single-shell tanks.

Table 7-2. Applicability of Probable Failure Mechanisms to Single-Shell Tanks (2 Pages)

Condition	Liner Failure		Comments
	Probable	Not Likely	
Lack of Post-Weld Stress Relieving			
Tank Not Stress Relieved	**25**	**124**	None of the single-shell tanks were post-weld stress relieved. Because of this, there is no way of quantifying the impact on tank liner failure. Post-weld residual stress is considered a significant source of tensile stress in the steel liner which is necessary for stress-corrosion cracking. This was also the case in tank liner failures at the Savannah River Site.
Tank Stress Relieved	0	0	
Liner Bottom to Wall Transition Design			
Large Radius Knuckle	15	109	Relatively weak orthogonal fillet weld joints were used in the 21 tanks of 241-SX and 241-A tank farms. The failure rate in these two tank farms is much higher than the overall population failure rate. Tanks with small and large radius knuckles and relatively strong butt weld joints were used in all other tank farms.
Orthogonal Joint	**10**	**11**	
Small Radius Knuckle	0	4	

Table 7-2. Applicability of Probable Failure Mechanisms to Single-Shell Tanks (2 Pages)

Condition	Liner Failure		Comments
	Probable	Not Likely	
Yield Strength			
Yield Strength ≤27 ksi	**17**	**52**	Lower minimum yield strength material (≤ 27 ksi) found in 241-TX, 241-BY, 241-S, 241-TY, 241-SX, and 241-A tank farms. Yield strength may be considered a surrogate for grain size with inverse relationship between yield strength and grain size. Larger grain size lowers the resistance to stress corrosion cracking of carbon steel in nitrate solutions. Because of the presence of confounding factors, it is not possible to determine this unequivocally.
Yield Strength > 27 ksi	8	72	
High Temperature			
Boiling Waste	**11**	**13**	Boiling waste was stored in the 10 tanks of 241-A and 241-AX, 11 of the 15 tanks in 241-SX (all but SX-102, SX-103, SX-105, SX-106), and in S-101, S-104 and U-104. Waste typically contained a layer of settled sludge on the tank bottom. These solids were at higher temperatures than the liquid because of conductive heat transfer in the solids. Higher temperatures are associated with higher stresses in the tank liner and can also initiate or generate faster rates of corrosion including stress corrosion cracking
Non-Boiling Waste	14	111	
Nitrate-Induced Stress Corrosion Cracking – TBP Waste as First Waste in Tank			
First Waste is TBP Waste	**4**	**0**	Tanks 241-TY-103, -104, -105, and -106 were the only tanks that first received TBP waste generated prior to in-plant scavenging. All of these tanks have probable liner leaks. TBP waste contained high nitrate concentration, but low hydroxide concentration and little or no nitrite, conducive to stress corrosion cracking.
First Waste Not TBP Waste	21	124	
Nitrate-Induced Stress Corrosion Cracking – Received REDOX Concentrated and Neutralized Salt Waste			
Received REDOX Waste	**11**	**21**	The tanks listed in Table 6-35 identify the 32 tanks that received REDOX concentrated and neutralized salt waste segregated from coating waste. These tanks are in 241-SX, 241-TX and 241-U farms. Eight of the 11 probable failures are in 241-SX, with one in 241-TX and two in 241-U. REDOX concentrated and neutralized salt waste contained high nitrate concentration, but low hydroxide and nitrite concentrations, conducive to stress corrosion cracking.
Did Not Receive REDOX Waste	14	103	
Nitrate-Induced Stress Corrosion Cracking – Contained Nitrate Leaching Waste			
Contained Nitrate Leaching Waste	**5**	**1**	Tanks 241-SX-107, -108, -111, -114 and -115 were the only tanks at which nitrate leaching of sludge from REDOX concentrated and neutralized waste was performed. All of these tanks have probable liner failures. Additionally, 241-SX-105 held the waste from nitrate leaching but did not have a liner failure. Waste from nitrate leaching contained high nitrate concentration, but low hydroxide and nitrite concentrations, conducive to stress corrosion cracking.
Did Not Contain Nitrate Leaching Waste	20	123	
Pressurization External to Tank Liner Resulting in Bulged Liner			
Primary Indication of Bulge	**5**	**0**	Tanks U-104, SX-108, SX-113, SX-115, A-105 all have primary indication of a bulged liner (through photographic evidence or tank bottom depth sounding). A bulge can result in a tear in the liner or increased stresses. All of these tanks have probable liner leaks. Other tanks may have bulged, but documentation providing primary indication of a bulge was not found. See section 5.6.1 for details.
No primary Indication of Bulge	20	124	

The identification of SCC as a common factor is in some conflict with historical corrosion testing reported for many waste types and storage conditions that generally showed favorable

results. These tests, especially those related to SCC were limited and lack the sensitivity of modern corrosion testing. Therefore testing of select waste types, using modern testing methods designed to detect SCC, is planned to gauge their propensity for SCC.

This analysis identifies that general corrosion is unlikely and pitting and crevice corrosion is indeterminate in causing single-shell tank liner failures. Historical test results for general and pitting corrosion are available for the major waste types and generally show low rates. Lack of corrosion test data for certain waste types and lack of data covering all waste conditions results in a level of uncertainty in understanding the full extent of past corrosion. Based on available historic sample data, a small fraction of the waste material samples would not meet current DST corrosion prevention specifications which are preventive of general corrosion (< 1 mil/yr), pitting corrosion and stress-corrosion cracking. While most waste types tested showed low rates for general corrosion and pitting, relatively high rates (up to ~5 mil/yr) of general corrosion were seen in tests intended to represent evaporated tank waste with very high hydroxide concentrations (~5-10 M).

The reader is reminded that there are limitations on this analysis.

- Many tanks are awaiting a formal leak assessment, per TFC-ENG-CHEM-D-42, and the presence of a liner leak is currently inconclusive. Those tanks have been treated as sound tanks for the purpose of the statistical analysis performed in this document. The actual categorization of those tanks will require a formal leak assessment. The number of additional tanks with probable liner failures is indeterminate and could have an impact on this analysis.
- Some tanks considered sound for this analysis may have undetected liner flaws (e.g., pits, cracks). Waste released from a liner may be contained by the asphalt or concrete shell or a past liner leak may have been too small to detect or may have been plugged by waste solids.

Nonetheless, based on available data, the results represent the best effort to identify the mechanism(s) most likely contributing to SST liner failure and to determine mechanisms common or broadly applicable across groups of SSTs.

8.0 RECOMMENDATIONS

The M-045-91F-T02 target date contains language to provide recommendations as appropriate, such as enhanced leak detection, monitoring, and mitigation (LDMM) activities. There are no findings or conclusions from this common factors analysis that would influence current LDMM activities. As such, there is no basis for specific recommendations with respect to enhanced LDMM associated with SSTs. Below are recommendations associated with this common factors analysis and the related conclusions.

It is noteworthy to mention that half the possible failure mechanisms identified could not be adequately evaluated due to the unavailability of information necessary to determine the role of the mechanism in contributing to liner failure. The lack of information was either due to the information not being maintained or catalogued or due to the lack of collecting such information. This included the lack of complete material records, construction records, operational data and sample results. However, there was also no recognition of the potential for certain failure mechanisms to occur and thus no information was ever collected relevant to the mechanism. Ongoing and future efforts should focus on maintaining complete and accurate records.

- Complete records of material properties used in construction of any future tanks should be maintained not only for the operational life but beyond to aid in any similar efforts as undertaken for this report.
- Archival specimens of materials used in construction of any future tanks should be maintained to aid in subsequent forensic investigations.
- Complete construction records of any future tanks should be maintained for the operational life and beyond to aid in similar efforts as undertaken for this report.
- Complete operational data records should be maintained for the operational life and beyond for any future tanks.
- Sample information and analytical results should be maintained for the operational life and beyond for any future tanks.
- Mechanisms that were identified as indeterminate should be evaluated to consider whether useful information could be collected in terms of understanding the likelihood of the failure mechanism in contributing to liner failure. This would most likely be useful in the area of corrosion mechanisms (e.g., pitting and crevice corrosion) rather than material properties or construction records.

The likely common factors contributing to liner failure can be considered as static or transient. Static factors (i.e., do not change with time) are related to tank design and construction, and include bottom to wall transition design, lack of post-weld stress relieving, and procured liner initial yield strength. For these factors it is important to recognize how they may apply to future designs rather than how they can be adjusted to limit the possibility of a future of existing SST liner failure.

- The bottom to wall transition in any future design needs to eliminate the build up of any deleterious stresses in the liner.
- The importance of properly performing post-weld stress relieving is important in reducing the possibility of SCC in future tanks.

- Material selection for any future tanks is critical in assuring as long a life as possible.

Transient factors (i.e., do change with time) are operational in nature, and include high operating temperature, aggressive chemical environments, or conditions allowing external pressurization. For these factors it is important to consider how they may affect future storage of waste in the SSTs. There are certain things to consider about these transient factors.

- Waste temperatures are declining as radioactive decay continues. Generally, although not always, reduced temperatures result in a lower rate or likelihood of corrosion mechanisms.
- Blending of waste types among tanks generally diminishes the aggressive nature of an individual waste type.
- Continued radiolysis of nitrate results in nitrite production and also ammonia production. Continued nitrite production should lessen the future possibility of SCC.
- Hydroxide in the SST waste is depleted through destruction by reaction with atmospheric carbon dioxide to make carbonate. It was noted in Section 5.5.6.9 that solid waste simulants reconstituted with water that was high in hydroxide was generally the most aggressive waste in terms of general and pitting corrosion. A lowering of hydroxide while maintaining a high pH could lessen future corrosion. However, continued hydroxide depletion that results in a lowering of the pH of waste, especially near the liquid waste surface could negatively impact future corrosion rates.

The following recommendations are made in consideration of corrosion testing to better understand current threats to liner integrity.

- Although most historical waste types were supported by favorable corrosion testing, currently stored waste in single-shell tanks that is expected to be of concern from a corrosion standpoint should be tested to understand the current impact to liner integrity. This corrosion testing of potentially aggressive waste layers has been initiated and is ongoing (RPP-PLAN-50077, *Test Plan to Evaluate the Propensity for Corrosion in Single-Shell Tanks*).
- Past waste types that may have been conducive to concentration cell corrosion under stiffener rings should be evaluated. It is worth noting that additional consideration is already being given to corrosion testing of this design feature suspected of causing localized concentration cell corrosion. Corrosion testing is being integrated into the overall DST and SST corrosion testing program.
- Confirmatory testing of select waste types using modern testing methods is planned to gauge their propensity for SCC. This testing will use simulants based on compositions provided in this document and be conducted at temperatures representative of historical storage conditions. This testing is integrated with ongoing DST corrosion testing. The waste types selected for confirmatory testing will include Uranium Recovery TBP waste, REDOX concentrated and neutralized waste, and nitrate leaching waste.

The uncertainty in the outcome of tanks recommended for future SST leak assessments done per TFC-ENG-CHEM-D-42 process is recognized as an uncertainty in the results of this analysis. In the event that most tanks that go through the TFC-ENG-CHEM-D-42 process are indeed found

to be considered sound, then it does not make sense to revisit this failure analysis. If a large number of tanks are identified as having liner leaks, then it would be necessary to assess whether or not any benefit would be derived from revisiting this analysis. Such a determination would need to be made in the future depending upon the number of tanks found to have liner failures.

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APPENDIX A

HISTORICAL DISCUSSION OF TANK INTEGRITY

During initial operation of the SSTs, no specific assignment of responsibility existed to formally evaluate collected liquid level data with the intention of identifying unexplained changes or trends that could be associated with a suspected leak (TID 26431, *Report on the Investigation of the 106 T Tank Leak at the Hanford Reservation, Richland*). In general, anomalous data (e.g., indication of a bulged liner, unexplained liquid level decrease, increase in drywell monitoring count rate) would be cause for investigation to determine whether the data was indicative of a tank leak. The first known tank to be investigated for a suspected leak was tank U-104, during August 1956 (HW-44024-RD) because of the presence of a bulged liner. Shortly after this, an estimate was made of what might constitute a significant leak (i.e., entering the regional groundwater table) (LET-120756, *Underground Storage Tank Leak Detection*). The value of 50,000 gal was established to limit the leak volume to something less than what would be expected to reach the groundwater table. The value was based on a number of assumptions including a factor of ¼ to account for actual conditions varying from theoretical conditions assumed in the estimate. Although the evaluation estimated a leak of 50,000 gal could be tolerated it was recommended "...immediate action be taken to transfer or immobilize waste in a tank as soon as definite evidence of a leak is detected."

By 1957, after identification of the U-104 bulged liner, work responsibility was identified for groups concerned with detecting leaks in underground storage tanks (HW-51026). At that time, expected accuracy of liquid level measurements was +/- 1 in. and two successive measurements outside that range would require certain actions (e.g., remeasurement, increased frequency of liquid level measurements). It was concluded that weekly liquid level measurements were probably satisfactory in detecting liquid loss before a significant leak occurred. During operation of the SSTs, tanks would be removed from service if either a liquid level decrease was observed *or* if drywell readings indicated a tank leak. A tank was determined to be a leaker if there was conclusive evidence of a leak, which often meant both a liquid level decrease and elevated radiation readings were observed in an adjacent drywell. In the fifteen year period between 1958 and 1972 there were 13 confirmed leakers identified, averaging about one per year (REP-032780, *Assessment of the Surveillance Program of the High-Level Waste Storage Tanks at Hanford*). In 1968 the first tank with questionable integrity was identified, and by 1972, within five years, 13 tanks were identified as having questionable integrity (REP-032780).

In 1973 the largest leak from a tank, T-106, occurred. Part of the reason for the size of the leak was the failure to promptly review liquid level and radiation level data. If the leak had been recognized at the earliest possible time, it was anticipated the volume of leaked material would have been limited to 30,000 to 40,000 gal (TID-26431). After the significant leak, estimated at 115,000 gal, from T-106 (discovered in June 1973), a review was undertaken of liquid level and leak detection data on a tank by tank basis. This review was initiated June 15, 1973, to be updated annually via a report (RHO-CD-213, *Waste Storage Tank Status and Leak Detection Criteria – 200 West Area*). The purpose of the report was to describe the nature, scope and frequency of the surveillance employed, to state action criteria for response to data deviations and to present the results of the data review. At the time of the leak in tank T-106, a computer automated surveillance system (CASS) was being installed in the tank farms for the purpose of interfacing tank liquid level gauges and thermocouples to a computer for the purpose of collecting data, detect abnormal conditions and alarm in the event, and to provide daily control

reports (TID 26431, Exhibit K). Initially, not all data was collected electronically, and that data was entered manually into the computer (REP-032780).

Various systems of classification have been applied to the waste storage tanks over the years to describe the status of each of the tanks. A variety of systems have alternatively conveyed operational availability (active, inactive, etc.), condition of contents (static storage, boiling waste storage, etc.) or content immobilization (interim stabilized, interim isolated, etc.). Some of these systems would not make distinctions between operational status and tank soundness. A listing of various classification systems used for operational status classification during the 1970s through the present is provided in Table A-1. The classifications during the 1970s through 1980, were originally listed in REP-032780. Subsequent classifications are derived from subsequent sources.

Generally, categories of sound and confirmed leaker have always been present with variations in other categories. Additional categories had been added and removed over time. In 1974 a three category system was developed: sound; questionable integrity; and, confirmed leaker. This three category system was described in terms of confidence intervals in 1980 (RHO-CD-213, p. 00-00-21). For a sound tank it was stipulated that it could be concluded with 95 percent or better confidence that the tank was sound. For a confirmed leaker it was stipulated that it could be concluded with 95 percent or better confidence that the tank was a leaker. A tank with questionable integrity then covered the broad range between these two extremes and all other tanks between these two ends of the spectrum were put into this broad category. The discussion regarding defining these three categories recognized that these definitions, based on qualitative confidence intervals, had to rely on subjective determinations.

Periodic reviews of the classification of questionable integrity (QI) tanks were conducted, as in the case of the 1980 review documented in RHO-CD-896. However the reviews and analyses were conducted in order to determine whether the tank should remain QI or if there was sufficient evidence to be reclassified as a confirmed leaker. Through this process, tanks would not be determined sound and removed from the QI list once added. RHO-CD-896 states that if there was any indication of failure of integrity, then the tank was classified as confirmed leaker or questionable integrity, pumped to a minimum heel, and no longer used to store liquid waste. RHO-CD-896 went on to state that from an operational viewpoint there were really only sound tanks and all other tanks.

As of November 21, 1980 all SSTs were declared to be inactive (RHO-CD-14, WHC-EP-0182-28, *Tank Farm Surveillance and Waste Status Summary Report for July 1990*). An inactive tank was defined as, "a tank which has been removed from liquid-processing service, pumped to minimum supernatant liquid heel, and is awaiting or is in the process of being stabilized and interim isolated, (and) includes all tanks not in active or active restricted categories." In November 1980, 34 were questionable integrity, 24 were leakers while the remainder were labeled as inactive without explicitly stating whether the tank was sound, although this is the assumption (RHO-CD-14). This classification scheme continued until September 1984, when 31 tanks were identified as having questionable integrity and 29 were identified as leakers (RHO-RE-SR-14 September 1984).

Table A-1. Past Variation in Tank Operational Classifications Regarding Integrity

Categories of Operational Classification									
Sound	**Border -line**	**Dormant**	**Suspect**	**Restricted Use**	**Questionable or Questionable Integrity**	**Assumed Leaker**	**Confirmed (Declared) Leaker**	**Other**	**Source**
X			X	X			X		(1)
X (Active)				X (Active)	X (Inactive)		X	Inactive	(2)
X (Active)					X (R. 1-10-79)		X		(3)
X (Active)				X (Active)				Inactive	(4)
X					X		X		(5)
X (Active)				X (Active)	X (Inactive)		X	Inactive	(6)
X (Active)				X (Active)	X (Inactive)		X	Inactive	(7)
X	X	X	X				X		(8) [1971-72]
X	X	X	X				X		(8) [1972-73]
X			X	X			X		(8) [1972-73]
X					X		X		(8) [1973-74]
X			X				X		(8) [1974]
X (Active)					X		X	Inactive	(8) [1974-80]
X (Deactivated)					X		X	Inactive	(9) [1980-84]
X (Inactive)						X		Stabilized	(10) [1984-present]

Sources:

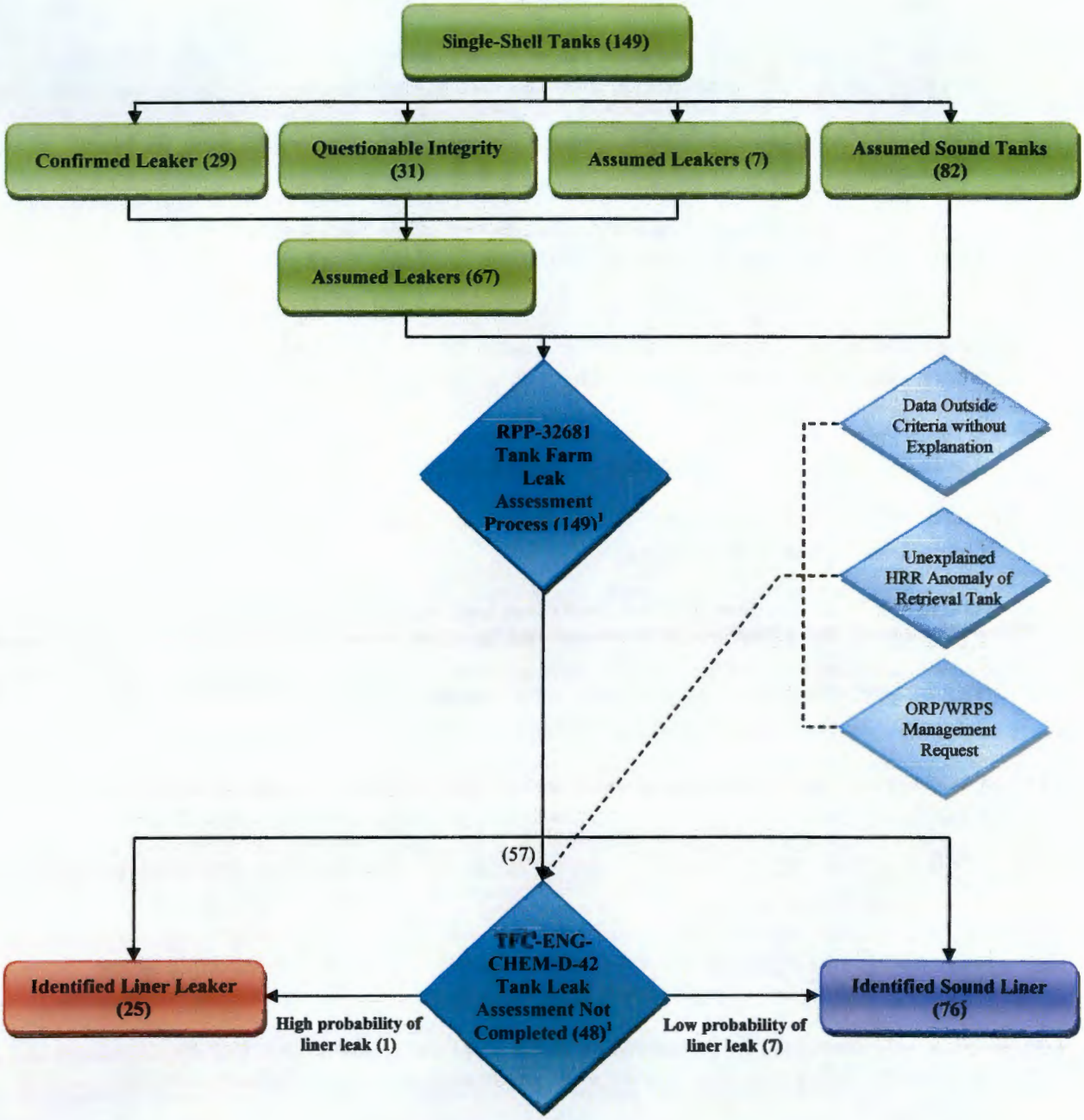
(1) Letter, Richards (ARHCO) to Fremling (DOE-RL), 8-31-73, "Waste Storage Tank Leak Detection Methods and Criteria"; Attachment dated 10-18-73, "Leak Categorization Summary – Revision 1"
(2) RHO-CD-213, Rev 1-1-77, p. 00-00-08
(3) RHO-CD-213, pp. 00-02-01 through 00-02-05, Rev 1-10-79
(4) RHO-CD-430, Surveillance and Maintenance Program Plan, 10-30-78, pp. A-2 through A-10, Rev 4-13-79
(5) RHO-MA-151, *Specifications and Standards for the Operation of Radioactive Waste Tank Farms and Associated Facilities*, Section B, p. 3-1 (and other sections.
(6) Rockwell Hanford Operations Briefing to DOE-EV Assessment Group 10-11-79.
(7) RHO-CD-14, *Waste Status Summary-December 1979*, dated 1-11-79 (sic), pp. 45-48.
(8) RHO-CD-896, *Review of Classification of Nine Hanford Single-Shell 'Questionable Integrity' Tanks*, Appendixes A and D.
(9) RHO-RE-SR-14, *Waste Status Summary - September 1984*, p. 5, dated October 9, 1984.
(10) RHO-RE-SR-14, *Waste Status Summary – October 1984*, p. 5, dated October 31, 1984.

In October 1984, classifications used in RHO-RE-SR-14, monthly waste status summary reports, were changed and the confirmed leaker and questionable integrity classifications were eliminated. The new categories used were sound, assumed leaker, and stabilized. The definition of sound remained consistent with past definition relying on a 95 percent or greater confidence

that the tank was sound. The assumed leaker category was defined as, "A tank for which there is an indication of a breach of integrity. Such a tank exhibits surveillance parameter changes that exceed stated criteria limits and result in a less than 95 percent confidence that it is sound." This assumed leaker category was a significant change, because it no longer distinguished between whether there was a 95 percent or higher confidence that a tank had leaked or whether a lower level of confidence existed. The classification of stabilized was defined as, "The condition of an inactive waste storage tank following removal of all supernatant (free-standing) and interstitial (in places separating the salt crystals) liquid that is technically practical to remove." Although the definitions were not explicit in terms of mutual exclusivity, these three classifications were used mutually exclusively. The instituted hierarchy was that any tank that was stabilized would be identified as such regardless of whether it was sound or an assumed leaker, then the remaining tanks would be identified as either sound or assumed leaker.

During 1988, the status of assumed leakers was modified to include interim stabilized tanks, no longer making the two categories mutually exclusive (WHC-EP-0182-9, *Tank Farm Surveillance and Waste Status Summary Report for December 1988*). However, the "sound" and "assumed leaker" classifications were mutually exclusive and accounted for all 149 single-shell tanks. During 1988 the definitions used to describe assumed leakers and sound tanks were modified. The definition for "sound" relied on surveillance data showing no indication of loss of liquid attributed to a breach of integrity but eliminated the 95% or greater confidence level statement from the definition (WHC-EP-0182-1, *Tank Farm Surveillance and Waste Status Summary Report for April 1988*, WHC-EP-0182-8, *Tank Farm Surveillance and Waste Status Summary Report for November 1988*). Similarly the definition for "assumed leaker" relied on surveillance data indicating a loss of liquid due to a breach of integrity but also eliminated the less than 95% confidence level that the tank was sound. At the end of 1988 there were 66 single-shell tanks that were assumed leakers. In October 1992, tank 241-T-101 was declared an assumed leaker, bringing the total number of assumed leakers to 67 (WHC-EP-0182-55, *Tank Farm Surveillance and Waste Status Summary Report for October 1992*). The total number of reported assumed single-shell tank leakers held constant until recently. As of September 2014, D-42 analyses were completed for eight tanks, the integrity status of C-105 was changed to assumed leaker and the integrity status for tanks A-103, AX-102, AX-104, C-110, C-111, SX-104, and SX-110 were changed to sound, bringing the number of assumed leaking tanks to 61(HNF-EP-0182, Rev. 321, *Waste Tank Summary Report for Month Ending September 30, 2014*).

Figure A-1 demonstrates the designation path for SSTs as "assumed liner leaker" or "sound" as it relates to this evaluation. As previously mentioned, tanks historically have been designated as "sound" or "assumed leaker" in HNF-EP-0182 and predecessor documents which had classified "assumed leakers" as "confirmed leaker" or "questionable integrity". Regardless of this previous historical status, SSTs were evaluated through the process laid out in RPP-32681, *Process to Assess Tank Farm Leaks in Support of Retrieval and Closure Planning*. The process documented in RPP-32681 was developed to provide updated estimates of tank farm leak loss inventories. In order to establish leak loss inventories, the source of tank farm leaks needed to be established or confirmed based on existing information and emergent field data. Because the assessments identify leak sources, tanks were either confirmed to be "sound" or "assumed liner leaker" or a recommendation was made to perform a formal integrity assessment per TFC-ENG-CHEM-D-42 (see Table 2-2).



(1) The RPP-32681 process recommended 57 tanks be assessed via the TFC-ENG-CHEM-D-42 process. Nine of these 57 have been assessed leaving 48 to be assessed. Four of these 48 tanks have already been retrieved (C-201; C-202, C-203, C-204) and may not be assessed. Two of the 48 tanks are currently being assessed (T-102 and T-105).

Figure A-1. Flow Diagram Illustrating the Evolution of the Twenty-Five SSTs with Liner Leaks

References

HNF-EP-0182, 2013, *Waste Tank Summary Report for Month Ending May 31, 2013*, Rev. 302, Washington River Protection Solutions, Richland, Washington.

HW-44024-RD, 1956, *TBP Plant and Tank Farm Weekly Summary – Process Unit – 6-29-56 thru 8-31-56*, General Electric Company, Richland, Washington.

HW-51026, 1957, *Leak Detection – Underground Storage Tanks,* General Electric, Richland, Washington.

LET-120756, 1956, *Underground Storage Tank Leak Detection,* Radiological Design & Development Facilities Engineering Operation, Richland, Washington.

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REP-032780, 1980, *Assessment of the Surveillance Program of the High-Level Waste Storage Tanks at Hanford,* U.S. Department of Energy, Richland, Washington.

RHO-CD-14, 1981, *242-T Evaporator Facility Shutdown/Standby Plan*, Rockwell Hanford Operations, Richland, Washington.

RHO-CD-213, 1977, *Waste Storage Tank Status and Leak Detection Criteria – 200 West Area*, Rockwell Hanford Operations, Richland, Washington.

RHO-CD-896, 1980, *Review of Classification of Nine Hanford Single-Shell "Questionable Integrity" Tanks,* Rockwell Hanford Operations, Richland, Washington.

RHO-MA-151, 1979, *Specifications and Standards for the Operation of Radioactive Waste Tank Farms and Associated Facilities,* Rockwell Hanford Operations, Richland, Washington.

RHO-RE-SR-14, 1987, *Waste Status Summary, February 1987,* Rockwell Hanford Operations, Richland, Washington.

RPP-32681, 2013, *Process to Assess Tank Farm Leaks in Support of Retrieval and Closure Planning*, Rev. 2, Washington River Protection Solutions LLC., Richland, Washington.

TID 26431, 1973, *Report on the Investigation of the 106 T Tank Leak at the Hanford Reservation, Richland, Washington,* U.S. Atomic Energy Commission, Richland, Washington.

WHC-EP-0182-1, 1988, *Tank Farm Surveillance and Waste Status Summary Report for April 1988*, Westinghouse Hanford Company, Richland, Washington.

WHC-EP-0182-8, 1988, *Tank Farm Surveillance and Waste Status Summary Report for November 1988,* Westinghouse Hanford Company, Richland, Washington.

WHC-EP-0182-9, 1988, *Tank Farm Surveillance and Waste Status Summary Report for December 1988*, Westinghouse Hanford Company, Richland, Washington.

WHC-EP-0182-28, 1990, *Tank Farm Surveillance and Waste Status Summary Report for July 1990*, Westinghouse Hanford Company, Richland, Washington.

WHC-EP-0182-55, 1992, *Tank Farm Surveillance and Waste Status Summary Report for October 1992,* Westinghouse Hanford Company, Richland, Washington.

APPENDIX B

MEETING MINUTES

washington river protection solutions

MEETING SUMMARY

From: T. J. Venetz
Phone: 376-9669
Location: Ecology Office
Date: October 15, 2014
Subject: SST Common Factors and Leak Summary Report

To: Distribution

Jim Alzheimer, ECOLOGY*
Jeff Lyons, ECOLOGY*
Mike Barnes, ECOLOGY*
Joe Caggiano, ECOLOGY*
Alan Carlson, WRPS*
Dennis Washenfelder, WRPS/AEM*
Dan Baide, WRPS*
Crystal Girardot, WRPS
Don Harlow, WRPS/AEM*
Jeremy Johnson, ORP*
Ted Venetz, WRPS*

*Attended Meeting

PURPOSE:

The purpose of this meeting was to discuss status of the SST Common Factors report being prepared to satisfy the M-045-91F-T02 target and the overall SST Leak Integrity Summary Report that will be submitted for approval for the M-045-91F interim milestone. The Summary Report will capture and summarize the information submitted under the T02 through T04 targets. It was also mentioned that the SST Leak Cause, Locations, and Leak Rate – Summary Report to satisfy the M-045-91F-T04 target was transmitted to ORP for submittal to Ecology

SST Common Factors Status (91F-T02 Target)

Comments were solicited on the common factors analysis presentation that was made to the Single-Shell Tank Expert Panel in August and previously distributed to Ecology. The complete list of failure mechanisms was distributed and the general approach for the analysis was described.

Ecology asked about how much good quality information was found as part of this effort. Some short comings are acknowledged in that area. There are gaps in the historical record, such as data on material of construction, weld repair rates and operating records. Another example could be historical analysis of failures that are later thought have reached accurate conclusions. The common factors report will include an extensive discussion of historical information related to the failure mechanisms, with original references where possible. A suggestion was made that if new tanks were constructed, there should a better effort to maintain the historical record, both in aspects of construction (materials and potential defects) and in tank operating histories.

There are other limitations in the analysis. These include small sample sets, both in failed tanks and sound tanks along with multiple potential causes. Some tanks may have liner flaws (pits, cracks) but no waste loss has been detected (no waste detected ex-situ, waste level change is insignificant, or waste is contained by asphalt or concrete) so these tanks are considered sound.

For this report, tanks identified as needing a formal leak assessment per the TFC-ENG-CHEM-D-42 process are treated as sound tanks in the statistical analysis. There is no intention to update the common factors analysis as these D-42s are completed. If tanks that were assumed to be sound for this analysis are later determined to be leaking as result of a future D-42 assessment that could change the statistics slightly, but the overall assessment of likely SST failure mechanisms is not expected to change.

The common factors analysis has spawned corrosion testing as part of the integrated DST/SST corrosion testing effort, which is guided by the DST Expert Panel Oversight Committee (EPOC). The initial tests are stress corrosion cracking tests on the three most aggressive waste types: TBP Waste, REDOX waste and nitrate leached REDOX waste.

Ecology questioned why the mechanism titled Improper or Inadequate Procedures was judged unlikely. Although early specifications were later judged insufficient based on current knowledge, their impact was addressed in earlier sections of the analysis. No other inadequacies were identified, other than those previously addressed.

If findings from the analysis could be identified as practices to avoid in new tank construction, they should be identified. Knowing the historical waste characteristics is not necessarily indicative of future corrosion threats. Many of the factors likely to be judged significant in past failures, such as high operating temperature, high rate of temperature rise, and storage of certain corrosive waste types are no longer active as failure mechanisms. Future failure mechanisms may be different than past mechanisms.

Ecology asked if risk factors from this study (such as tanks with bad designs or operating histories) could be used to alter retrieval sequence. WRPS indicated the results can be fed back into the retrieval planning process.

Ecology suggested that, in light of delays in retrieval schedules, information from the common factors analysis be incorporated into retrieval sequence, especially if predictive failure is possible. They suggested the Expert Panel could help in understanding the predictive risk and that the IQRPE could benefit from the information in the 2018 SST Integrity Assessment.

The entire common factors document will be very large. Ecology requested a summary presentation, with ability to delve deeper into details if desired. WRPS indicated the document should be ready for review in early December.

SST Leak Integrity Summary Report (M-045-91F)

The outline for the summary document was provided for review and comment. It was stated that probably two more meetings would be held, one early January after target summaries and appendixes were completed and another in March to discuss recommendations and conclusions.

Additional Discussion

Ecology indicated they have been asked to revisit the A/AX TWRPS in regard to decisions about the amount of waste to be left in the tank. They questioned if the Expert Panel could help with this. WRPS indicated some members probably could be helpful, but that the request should be directed to the Vadose Zone group not SST Integrity.

Mention was made of the tank A-106 sidewall coring test report, which is being finalized. Ecology indicated a briefing on that subject was not required. Due to concerns about potential damage in the tank previously cored (tank SX-115); Ecology suggested that SX-115 be re-cored. WRPS indicated that excessive core damage noted during tank SX-115 coring was likely the result of the improvised coring setup, which used a standard wall coring bit. WRPS agreed to send the SX-115 core drilling report.

ACTIONS:

1. All: Review and provide comment on the Leak Summary Outline
   Status: Complete
2. Venetz: Provide the SX-115 coring report.
   Status: Complete.

APPENDIX C

EVALUATION OF ISSUES ASSOCIATED WITH MATERIALS USED IN ASME CODE CONSTRUCTION

C.1 ASME BOILER AND PRESSURE VESSEL CODE, SECTION II, PART D, NONMANDATORY APPENDIX A

The ASME B&PV Code, Section II – Materials is a service section for reference by the ASME B&PV Code construction sections. The section provides tables of material properties including allowable, design, tensile and yield stress values, physical properties and external pressure charts and tables. Section II, Part D – Properties contains appendices which contain criteria for establishing allowable stress, the bases for establishing external pressure charts, and information required for approval of new materials. Part D, Nonmandatory Appendix A, Issues Associated with Materials Used in ASME Code Construction, provides an extensive listing of potential issues to be considered as part of good engineering judgment during design of any ASME B&PV Code component. The listing of issues identifies items that could result in potential change in the material's properties or performance related to fabrication, installation or service.

It is important to note that the single-shell tanks were not built to the ASME B&PV Code nor is there any intention to infer that the tanks should have considered the list of issues associated with materials of construction as identified in the ASME B&PV Code. A number of the issues were not known or understood at the time of construction of the various single-shell tanks or do not apply to the materials of construction or service conditions. Rather, the listing provides a convenient extensive list of potential issues to consider that may have contributed to SST liner failure.

C.2 IDENTIFICATION OF ISSUES FROM NONMANDATORY APPENDIX A POTENTIALLY APPLICABLE TO SINGLE-SHELL TANK LINERS

The list of issues identified in ASME B&PV Code, Section II, Part D, Nonmandatory Appendix A was examined to determine which of the listed issues might be potential SST liner failure mechanisms requiring consideration in this report. A cross-check of each potential issue from the nonmandatory appendix to potential SST liner failure mechanisms listed in Section 4.0 of this report is provided in the table below.

Table C-1. Evaluation of Applicability of Issues Associated with Materials Used in ASME Code Construction to Single-Shell Tanks (6 Pages)

Issue Category	Definition	Conditions	Applicability & Report Section
Metallurgical Changes that Can Occur in Service			
Graphitization	Some portion of the carbon, present in the iron carbide of carbon steels, dissociates from carbides and forms separate particles of free carbon or graphite.	Occurs in prolonged operating temperature range of 800°F to 1,100°F and can result in substantial loss of strength and ductility.	Not applicable due to lower service temperature of SSTs
Spheroidization (Softening)	Some portion of the carbon, present in the iron carbide of carbon steels, is altered from a planar shape to a lower energy spheroidal shape.	Occurs in prolonged operating temperature range of 800°F to 1,100°F and can result in loss of room temperature and elevated temperature strength but increase in ductility.	Not applicable due to lower service temperature of SSTs
Temper embrittlement	For low alloy steels, the preferential segregation of certain residual and surface-active elements (e.g., phosphorous,	Occurs in some low alloy steels during long-time exposure in the temperature range of 650°F to	Not applicable due to material type and lower service

Table C-1. Evaluation of Applicability of Issues Associated with Materials Used in ASME Code Construction to Single-Shell Tanks (6 Pages)

Issue Category	Definition	Conditions	Applicability & Report Section
	arsenic, antimony, and tin) to the grain boundaries.	1,100°F.	temperature of SSTs
Strain aging	Age-hardening phenomena in which the tensile strength and hardness of a cold-worked material are increased and ductility. Commonly due to precipitation of nitrides at dislocations and other crystalline defects.	Requires previous plastic deformation. Occurs when exposed to moderately elevated temperatures. Nitride precipitation more prevalent in pre-1980 carbon steels where control of the nitrogen content of the steel was less effective.	See Sections 4.3.2, 4.4.3, and 4.5.3. Strain aging can occur after cold working (see below)
Cold working (Cold strain)	Plastic deformation below the transformation or recrystallization temperature in which the material is hardened by the strain but the ductility of the material decreases.	Requires deformation of component.	See Section 4.3.2 for construction. See Section 4.5.3 for liner bulging. See Section 4.4.3 for liner expansion from transient temperature gradients
Relaxation cracking (Strain-induced precipitation hardening)	Temper-resistant particles precipitate at excess defect sites generated by cold or warm working operations increasing the materials creep strength and hardness.	Occurs in cold-worked or warm-worked austenitic materials subsequently heated to 950°F to 1,400°F.	Not applicable due to material type and lower service temperature of SSTs
885°F embrittlement	Carbide, nitride, or silicide precipitation in some stainless steels at elevated temperature which increases material hardness and decreases tensile ductility and toughness. The maximum embrittlement occurs at 885°F	Occurs in certain stainless steels exposed to elevated temperatures as low as 500°F.	Not applicable due to material type and lower service temperature of SSTs
Sigma phase embrittlement	Hard and brittle iron-chromium intermetallic compound forms.	Occurs in certain high alloy steels after prolonged exposure at temperatures ranging from 1,050°F to 1,700°F.	Not applicable due to material type and lower service temperature of SSTs
Laves phase precipitation	Precipitation of Laves phase due to exposure of certain alloys to elevated temperature. Laves phase precipitates within the grains or intergranularly forming into globular particles or into platelets.	May occur during exposure of austenitic stainless steels containing molybdenum, titanium, and niobium or other alloys in the temperature range from 1,100°F to 1,600°F.	Not applicable due to material type and lower service temperature of SSTs
Sensitization	Precipitation of chromium carbides along the grain boundaries of austenitic and ferritic/martensitic stainless steels.	May occur during exposure for significant periods of time in the temperature range of about 1,000°F to 1,550°F.	Not applicable due to material type and lower service temperature of SSTs
Thermal aging embrittlement	General term covering several types of thermally induced embrittlement.	Necessary conditions depend on the particular mechanism.	See following four rows for specific types covered
Blue brittleness	Accelerated form of strain-age embrittlement characterized by an increase in strength and marked decrease in ductility and toughness.	Can occur when plain carbon steel and some alloy steels are heated into the temperature range of 450°F to 750°F.	Not applicable due to lower service temperature of SSTs
Quench-age embrittlement	Occurs in low carbon steels when the material undergoes hardening in response to the precipitation of carbides at existing dislocations due to differences in the solid solubility of carbon in ferrite at different temperatures. Hardness of the steel increases and ductility decreases.	Can occur during rapid cooling from temperatures slightly below the lower critical transformation temperature (around 1020°F) at which the solubility of carbon is substantially greater than at room temperature. An aging period of several weeks at room	See Section 4.2.2

Table C-1. Evaluation of Applicability of Issues Associated with Materials Used in ASME Code Construction to Single-Shell Tanks (6 Pages)

Issue Category	Definition	Conditions	Applicability & Report Section
		temperature is required for maximum embrittlement.	
Stress-relief embrittlement	Rapid precipitation of temper-resistant phases during early stages of heat treatment or elevated temperature service leading to intergranular cracking within the higher-strength portions of material.	Occurs in low alloy structural and pressure vessel steels, ferritic creep-resisting steels, austenitic stainless steels, and some nickel-base alloys.	Not applicable due to material type and lack of post weld heat treatment of SSTs
Tempered-martensite embrittlement	Ferrite networks that develop due to the precipitation of cementite platelets along prior-austenite grain boundaries	Affects quenched and tempered high-strength low alloy steels over the temperature range of 400°F to 700°F.	Not applicable due to material type and lower service temperature of SSTs
Radiation embrittlement	Loss in toughness and ductility with accompanying gain in strength from atomic dislocations from radiation exposure such as high levels of high-energy neutrons.	Requires exposure to intense radiation field such as high levels of high-energy neutrons.	See Section 4.4.10
Solidification cracking in nickel alloys	Alloying element or impurities present in weldments of nickel-base alloys segregate and form low-melting-point liquid films on grain boundaries.	May occur during welding of nickel-base alloys as macroscopic solidification cracks along the weld centerline or as microfissures within the weld metal.	Not applicable due to material type of SSTs
Uniform Corrosion			
General corrosion and wastage	Uniform wall thinning proceeding without any obvious signs of localized attack.	May occur depending on environment, temperature, and material type.	See Section 4.4.9.1
Atmospheric corrosion	Material cross-section is reduced as the result of the corrosive nature of the atmosphere.	Atmosphere considered to be the vapor space above the waste within the tank.	See Section 4.4.9.9
Galvanic corrosion	When dissimilar metals are in electrical contact in an electrolyte, the less noble metal is attacked to a greater degree and more noble metal to a lesser degree than if they were exposed alone.	Requires dissimilar metals to be present.	See Section 4.4.13
Stray current corrosion	Damage to material due to the influence of electric currents from a source external to the affected component (typically extraneous current in the earth).	Most frequently seen in buried cast iron, carbon steel, and low ally steel component, which are more commonly buried.	Not applicable; tank liner is not in contact with the surrounding soil but isolated via the concrete tank.
High temperature corrosion	Attack of a metal surface when the material is exposed to an oxidizing gas at elevated temperature.	Requires exposure to an oxidizing gas at high temperature.	Not applicable; operational conditions do not exist.
Soil corrosion	Deterioration of a metal when exposed to soil.	Requires exposure to soil.	See Section 4.5.2
Caustic corrosion (Caustic attack)	Metal attack that occurs when caustic salts concentrate on a surface.	Commonly encountered in steam- or water-side boilers where caustic salts concentrate under deposits (e.g., phosphate) formed on evaporative tubing surface. Caustics are added to control pH and protect tube surfaces from acidic attack.	Not applicable; conditions of a boiler do not apply to SSTs. General corrosion from caustic and caustic stress corrosion cracking considered separately.
Carbon dioxide corrosion	Metal attack when carbon dioxide dissolves in water forming carbonic acid which corrodes the metal.	Requires fluid medium in which carbonic acid will form.	Not applicable; highly caustic wastes in SSTs result in carbonate forming not

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Issue Category	Definition	Conditions	Applicability & Report Section
			carbonic acid.
Concentration cell corrosion	Corrosion damage when an electrolytic cell develops, the electromotive driving force of which is caused by local difference in the concentration of some component of the electrolyte.	Requires fluid medium with differing concentrations or a metal part partially submerged in an electrolyte with vapor present above.	See Section 4.4.9.8
Differential-temperature cell corrosion	Occurs when different parts of the same metal are immersed in an electrolyte that varies in temperature from one location to another.	Requires temperature difference in an electrolyte in which the metal is immersed.	See Section 4.4.9.10
Molten salt corrosion	Corrosion damage due to attack by molten salt in contact with the metal surface. Corrosion can be uniform or any of a number of localized forms depending on the system.	System that contains molten salt.	Not applicable; molten salt not used in SSTs.
Liquid metal corrosion	Corrosion damage due to exposure to liquid metals.	System that uses liquid metal such as liquid sodium, sodium-potassium, mercury, lead-bismuth, etc.	Not applicable; liquid metal not used in SSTs.
Localized Corrosion			
Pitting corrosion	Corrosion confined to a point or small area in which the ratio of the depth of the attack is large relative to the surface area.	Local breakdown of passive film followed by formation of an electrolytic cell.	See Section 4.4.9.2
Filiform corrosion	Material deterioration that occurs under coating, usually organic in nature, taking the form of randomly distributed threadlike filaments.	Generally occurs when coated material is exposed to temperatures in the range of 70°F to 95°F at relative humidity levels between 60% and 95%.	Not applicable; paint applied in SSTs below water line removed by waste.
Crevice corrosion	Localized attack of a metal surface that occurs when the surface is located immediately adjacent to an area that is shielded from full exposure to the environment by another material.	Narrow openings or gaps between metal-to-metal or nonmetal-to-metal components. Can be unintentional crevices such as cracks, laps or seams or under deposits.	See Section 4.4.9.3
Microbiologically influenced corrosion	Deterioration of metal as the result of the metabolic activity microorganisms.	Localized under deposits or tubercles that are used by the organisms to sustain their metabolic activity. Particularly occurs in intermittent, stagnant or low-flow conditions.	See Section 4.4.9.5
Metallurgically Influenced Corrosion			
Intergranular corrosion (Intercrystalline corrosion or Intergranular attack)	Attack occurring preferentially at its grain boundaries, usually with slight or negligible attack on the adjacent grain surfaces.	Grain boundary or the material immediately adjacent to the grain boundary is less resistant to certain contaminants, due to local concentration or loss of particular elements. Occurs in stainless steel and aluminum alloys.	Not applicable due to material type of SSTs
Dealloying corrosion (e.g., Decarburization)	Selective attack of one or more components of a metal solid solution where it is preferentially removed, leaving behind an altered (weakened) residual structure. Decarburization is the preferential removal of carbon from carbon steel.	Requires high temperature and exposure to hydrogen or oxidizing atmosphere.	Not applicable; operational conditions do not exist in SSTs.
Grooving	Redistribution of manganese sulfide along the weld line during welding leading to local enrichment in sulfur which can	Typically occurs in electric resistance welded carbon steel pipe exposed to aggressive aqueous coolants.	Not applicable to SSTs; applicable to electric resistance

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Issue Category	Definition	Conditions	Applicability & Report Section
	behave as a dissimilar metal couple. This can lead to selective attack of the sulfur enriched anodic zone in the presence of an electrolyte.		welded pipe
Mechanically Assisted Corrosion			
Velocity-affected corrosion	General term to define the attack that occurs on materials immersed in a flowing medium. This can either be in a slow to stagnant fluid or swift-moving fluid.	In slow-moving and stagnant liquids, loosely adherent solid corrosion products can deposit on component surfaces and aggravate corrosion. In closed systems, corrosion inhibitors can lose their effectiveness under low flow conditions or stagnant legs. In swift-moving liquid, dissolved metal ions may be carried away before protective films can reform on the surface, resulting in a continuous high rate of attack.	Typically, swift-moving fluid conditions do not exist in SSTS. Stagnant conditions exist in SSTs and are covered as part of crevice corrosion under Section 4.4.9.3
Erosion-corrosion	Damage to metals when particles transported in a liquid impinge on a component surface removing the protective surface film.	Solid particles present in a flowing liquid medium.	See Section 4.4.9.7
Impingement corrosion	Attack of a material surface caused by the impingement on that surface of turbulent flowing liquids.	Most frequently occurs where there is a sharp change in fluid direction such as in impellers or at a partial blockage in straight pipe sections	See Section 4.4.9.7
Cavitation erosion	Attack of a material surface caused by localized forming and collapsing gas bubbles under conditions of changing pressure in the liquid in contact with the affected material surface.	Requires localized change in pressure in response to change in the operating environment.	Not applicable; operational conditions don't exist in SSTs
Corrosion fatigue	Damage that occurs through the interaction of repeated or fluctuating stresses and a corrosive environment, with damage occurring at lower stress levels or fewer cycles than would be required in the absence of the corrosive environment.	Requires corrosive environment and repeated fluctuating cycles of stress.	See Section 4.4.9.6
Environmentally Induced Embrittlement and Cracking			
Stress corrosion cracking (SCC) • Transgranular • Intergranular • Irradiation-assisted	Simultaneous action of a corrosive environment at a critical concentration and a sustained tensile stress of sufficient magnitude on a susceptible material that causes cracking.	Can occur in mild chemical environments at tensile stresses well below the yield strength of the metal. Transgranular SCC associated with higher stress levels. Intergranular SCC typically occurs near welds, in heat-affected zones or base metal where heating has altered the material structure. Irradiation-assisted SCC requires high levels of neutron bombardment.	See Section 4.4.9.4
Hydrogen damage	General term covering several types of degradation where hydrogen is the principal degrading agent.	Necessary conditions depend on the particular mechanism.	See Section 4.4.8
Hydrogen embrittlement	Induced low ductility or hydrogen-induced cracking in metals resulting from the absorption of hydrogen.	Can occur by a very small amount of hydrogen (i.e., a few parts per million). Occurrence increases with increased strength in carbon steel.	See Section 4.4.8.1

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Issue Category	Definition	Conditions	Applicability & Report Section
Hydrogen-induced blistering	Formation of blisters below the surface of a metal due to excessive internal hydrogen pressure.	Hydrogen may be generated during cleaning, pickling, plating, corrosion, etc.	See Section 4.4.8.2
Cracking from precipitation of internal hydrogen	Localized hydrogen embrittlement resulting from the concentration of internal hydrogen.	Can occur during cooling after forging or rolling or upon cooling after welding if metal is supersaturated in hydrogen.	See Section 4.4.8.3
Hydrogen attack (high-temperature damage)	Decarburization and fissuring at grain boundaries or by bubble formation in the metal matrix. Hydrogen can combine with carbon to form methane which diffuses to grain boundaries where it causes fissuring.	Results from exposure at high temperature and pressure to a hydrogen-rich environment	Not applicable; operational conditions do not exist in SSTs
Cracking from hydride formation	Hydrogen absorbed in the melted metal matrix (e.g., during melting or welding) is converted to a hydride form upon cooling. Hydride can also form during corrosion processes.	Unique to a variety of transition, rare-earth, and alkaline-earth metals. Typically elevated temperature exposure is required.	Not applicable due to material type and lower service temperature of SSTs
Liquid metal embrittlement	Decrease in ductility of a metal caused by contact with a liquid metal.	Requires presence of a liquid metal environment.	Not applicable; operational conditions do not exist.
Caustic embrittlement	Obsolete historical term denoting a form of caustic-induced stress corrosion cracking in carbon steel or iron-chromium-nickel alloys.	In carbon steel most frequently encountered in concentrated hydroxide solutions at temperatures of 400°F to 480°F.	See Section 4.4.9.4
Flow-assisted corrosion	Chemical attack on metals resulting in the local dissolution of the protective oxide film and the simultaneous sweeping away of metal ions from the exposed surface by the flowing liquid.	Requires flowing system.	Not applicable; operational conditions do not exist.
Sulfur embrittlement	Embrittlement from nickel combining with sulfur at elevated temperatures to form a brittle sulfide.	Nickel and nickel-based alloys subjected to sulfur.	Not applicable due to material type of SSTs
Mechanical Damage Mechanisms			
Fretting and wear	Damage to the solid surface, generally involving progressive loss of material due to relative motion between two contacting surfaces.	Wear between tight-fitting surfaces subjected to oscillation at small amplitudes.	See Section 4.4.6
Thermal fatigue	Fracture resulting from the presence of temperature gradients that vary with time to produce cyclic stresses in a structure.	Requires mechanical restraint and temperature change.	See Section 4.4.1
Dynamic loading	Application of moving, sometimes high-velocity stress, that can produce high strain rates in the affected component.	Dynamic loading may range from mild application of cyclic loads during normal operation to severe impact loads.	See Section 4.5.3 for dynamic loading associated with liner bulging. No other dynamic loads identified.
Anisotropy	Directional dependence of properties.	For polycrystalline cubic metals, anisotropy is not significant.	Not applicable due to material type of SSTs