ENGINEERING CHANGE NOTICE

Page 1 of 7

☒ DM ☐ FM ☐ TM

1a. ECN 720332 R 0

1b. Proj. ECN W-NA - NA

2. Request Information Record Information on the ECN-1 Form	3a. Design Inputs -Record Information on the ECN-2 Form	3b. Design References - Record Information on the ECN-3 Form	3c. Engineering Evaluation / Estimate / Approval to Proceed w/ the Design - Record Information on the ECN-4 Form

4. Originator's Name, Organization, MSIN, & Phone No.
K. R. Sandgren, CH2M HILL Hanford Group, Inc., R1-49, 372-0371

5. USQ Number
No. TF - -
☒ N/A
Init. QKS Date ____

6. Date
3/22/2003

7. Title
Organic Complexant Topical Report

8. Bldg. / Facility No.
NA

9. Equipment / Component ID
NA

10. Approval Designator
NA

11. Document Numbers Changed by this ECN (For FM or TM Changes Record Information on the ECN-5 Form) Sheet and Rev.
HNF-3588, Rev. 0

12. Design Basis Documents?
☐ Yes ☒ No

13. Safety Designation
☐ SC ☐ SS ☐ GS
☒ N/A

14. Expedited / Off-Shift ECN?
☐ Yes ☒ No

15a. Work Package Number
NA

15b. Modification Work Completed
NA
Responsible Engineer / Date

15c. Restored to Original Status (TM)
NA
Responsible Engineer / Date

16. Fabrication Support ECN?
☐ Yes ☒ No

17. Description of the Change (Use ECN Continuation pages, as needed)
Revision of document to include analysis of inactive underground storage tanks and catch tanks.

18. Justification of the Change (Use ECN Continuation pages, as needed)
Changes were made to facilitate Office of River Protection (ORP) approval of the Tank Farms Documented Safety Analysis (DSA).

19. ECN Category
☒ Direct Revision
☐ Supplemental

ECN Revision Type
☐ Void/Cancel
☐ Closure
☐ Revision

20. Distribution (Name and MSIN)
See attached.

Release Stamp
DATE: MAR 22 2003
STA: 4
HANFORD RELEASE ID: 2

ENGINEERING CHANGE NOTICE

☒ DM ☐ FM ☐ TM

1a. ECN 720332 R 0

1b. Proj. ECN W-NA - NA

21. Design Check	22. Design Verification Required?	23. Closeout / Cancel / Void
Record Information on the ECN-6 Form NA	☐ Yes ☒ No If Yes, as a minimum attach the one page checklist from TFC-ENG-DESIGN-P-17.	☐ Yes ☒ No If Yes, Record Information on the ECN-7 Form and attach form(s).

24. **Revisions Planned** (Include a brief description of the contents of each revision)

NA

Note: All Revisions shall have the approvals of the affected organizations as identified in block 9 "Approval Designator," on page 1 of this ECN.

25a. **Commercial Grade Item Dedication Numbers** (associated with this design change)	25b. **Engineering Data Transmittal Numbers** (associated with this design change, e.g., new drawings, new documents)
NA	NA

26a. **Design Cost Estimate**	26b. **Materials / Procurement Costs**	26c. **Estimated Labor Hours**
NA	NA	NA

27. **Field Change Notice(s) Used?** (Used for ECN Revisions only)

☐ Yes ☒ No

If Yes, Record Information on the ECN-8 Form attach form(s) and identify permanent changes.

NOTE: ECN Revisions are required to record and approve all FCN's issued during the field modification work process. If the FCN's have not changed the original design media then they are just incorporated into the ECN file via an ECN revision. If the FCN did change the original design media then the ECN Revision will include the necessary engineering changes to the original design media changes.

28. **Approvals**

	Signature	Date
Design Authority		
Team Lead/Lead Engr.	J.M. Grigsby	3/22/03
Resp. Engineer	K. R. Sandgren	3/22/03
Resp. Manager	J.M. Grigsby	3/22/03
Quality Assurance		
IS&H Engineer		
NS&L Engineer		
Environ. Engineer		
Project Engineer		
Design Checker	J.M. Grigsby	3/22/03
Design Verifier		
Operations		
Radcon		
Other		
Other		

	Signature	Date
Originator/Design Agent		
Professional Engineer		
Project Engineer		
Quality Assurance		
Safety		
Designer		
Environ. Engineer		
Other		
Other		

DEPARTMENT OF ENERGY / OFFICE OF RIVER PROTECTION

Signature or a Control Number that tracks the Approval Signature

ADDITIONAL SIGNATURES

ECN - 1
ENGINEERING REQUEST FORM

☒ DM ☐ FM ☐ TM

1a. ECN 720332 R 0

1b. Proj. ECN W- -

Requestor's Name (Print)	Date	REA Reference
K. R. Sandgren	3/22/03	NA

Equipment Name	Estimated Need Date
Tank Farms	3/22/03

Problem/Issue Statement

See page 1, block 17.

Purpose for the Proposed Modification

See page 1, block 17.

Basis for the Estimated Need Date

Commitment to deliver DSA to ORP by 3/24/03

Requestor's Signature	Date	Requestor's Manager's Signature	Date
K. R. Sandgren	3/22/03		3/22/03

Responsible Manager Approval

Work Package Number (If Known)	Estimated Evaluation ROM Cost	CACN
NA	NA	501570

Process as a Simple Modification?	Assigned to (Team Lead)	Date
☒ Yes ☐ No	J.M. Grigsby	3/22/03

Responsible Manager's Signature		Date
	☒ Approve ☐ Reject	3/22/03

If rejected, explain reason for rejection:

(Once rejected the Responsible Manager returns the request to the Requestor's Manager)

Italicized text items need to be addressed. Standard text items need to be addressed as applicable to the problem/issue described.

ECN - 5 DRAWING / DOCUMENT CHANGE LIST FORM Sheet 1 of ECN – 5 Page 4 of 7	☒ DM ☐ FM ☐ TM	1a. ECN 720332 R 0 1b. Proj. ECN W- -

List of Engineering Drawings/Documents to be Modified (Use the attached checklist for guidance)

Dwg./Doc. Number (Sheet/Page, Rev)	Title/Type	Shared	Existing Change Document Nos.
HNF-3588, Rev. 0	Organic Complexant Topical Report	☐	
		☐	
		☐	
		☐	
		☐	
		☐	
		☐	
		☐	
		☐	
		☐	
		☐	
		☐	

Submitted to Document Service Center Prior to ECN Release?

☒ Yes ☐ No	Team Lead J.M. Grigsby	Date 3/22/03

List of Non-Engineering Documents Needed to be Modified

Document Number/Revision, Sheet/Page (If Available)	Document Title	Document Owner (Organization)	Individual Notified	Method	Date Notified

ECN - 5 DRAWING / DOCUMENT CHANGE LIST FORM Sheet 2 of ECN – 5 Page 5 of 7	☒ DM ☐ FM ☐ TM	1a. ECN 720332 R 0 1b. Proj. ECN W- -

Drawings/Documents to be Modified Checklist			
System Design Description	☐ Yes ☐ No ☒ N/A	Operating Procedure	☐ Yes ☐ No ☒ N/A
Functional Design Criteria	☐ Yes ☐ No ☒ N/A	System/Subsystem Specifications	☐ Yes ☐ No ☒ N/A
Functional Requirements	☐ Yes ☐ No ☒ N/A	Engineering Flow Diagram Drawing	☐ Yes ☐ No ☒ N/A
Operating Specification	☐ Yes ☐ No ☒ N/A	General Arrangement Drawing	☐ Yes ☐ No ☒ N/A
Criticality Specification	☐ Yes ☐ No ☒ N/A	Material Specification	☐ Yes ☐ No ☒ N/A
Conceptual Design Report	☐ Yes ☐ No ☒ N/A	Sampling Plan	☐ Yes ☐ No ☒ N/A
Detailed Design Report	☐ Yes ☐ No ☒ N/A	Inspection Plan	☐ Yes ☐ No ☒ N/A
Equipment Specification	☐ Yes ☐ No ☒ N/A	Radiation Control Procedure	☐ Yes ☐ No ☒ N/A
Procurement Specification	☐ Yes ☐ No ☒ N/A	Spare Parts List	☐ Yes ☐ No ☒ N/A
Construction Specification	☐ Yes ☐ No ☒ N/A	Test Specification	☐ Yes ☐ No ☒ N/A
Vendor Information	☐ Yes ☐ No ☒ N/A	Test Plan	☐ Yes ☐ No ☒ N/A
Operations / Maintenance Manual	☐ Yes ☐ No ☒ N/A	Acceptance Test Procedure	☐ Yes ☐ No ☒ N/A
Safety Analysis / FSAR / SAR / DSA	☒ Yes ☐ No ☐ N/A	Pre-Operational Test Procedure	☐ Yes ☐ No ☒ N/A
Technical Safety Requirement	☒ Yes ☐ No ☐ N/A	Operational Test Procedure	☐ Yes ☐ No ☒ N/A
Master Equipment List	☐ Yes ☐ No ☒ N/A	ASME Coded Item / Vessel	☐ Yes ☐ No ☒ N/A
Safety Equipment List	☐ Yes ☐ No ☒ N/A	Human Factor Consideration	☐ Yes ☐ No ☒ N/A
Radiation Work Permit	☐ Yes ☐ No ☒ N/A	Automated Control Configuration Procedure	☐ Yes ☐ No ☒ N/A
Environmental Requirement	☐ Yes ☐ No ☒ N/A	Computer / Automated Control Software Plan	☐ Yes ☐ No ☒ N/A
Environmental Permit	☐ Yes ☐ No ☒ N/A	Raceway / Cable Schedules	☐ Yes ☐ No ☒ N/A
Seismic / Stress / Structural Analysis	☐ Yes ☐ No ☒ N/A	Work Control Procedure	☐ Yes ☐ No ☒ N/A
Design Report	☐ Yes ☐ No ☒ N/A	Corrective Maintenance Procedure	☐ Yes ☐ No ☒ N/A
Interface Control Drawing	☐ Yes ☐ No ☒ N/A	Process Control Plan	☐ Yes ☐ No ☒ N/A
Calibration Procedure	☐ Yes ☐ No ☒ N/A	Process Control Procedure	☐ Yes ☐ No ☒ N/A
Preventive Maintenance Procedure	☐ Yes ☐ No ☒ N/A	Flow Sheet	☐ Yes ☐ No ☒ N/A
Engineering Procedure	☐ Yes ☐ No ☒ N/A	Purchase Requisition	☐ Yes ☐ No ☒ N/A
Security Plan	☐ Yes ☐ No ☒ N/A	Hazards Analysis	☒ Yes ☐ No ☐ N/A
Emergency Plan	☐ Yes ☐ No ☒ N/A	JCS PM Activity Datasheet	☐ Yes ☐ No ☒ N/A
	☐ Yes ☐ No ☐ N/A		☐ Yes ☐ No ☐ N/A
	☐ Yes ☐ No ☐ N/A		☐ Yes ☐ No ☐ N/A

ECN - 6 DESIGN CHECK LIST	☒ DM ☐ FM ☐ TM	1a. ECN 720332 R 0
Sheet 1 of ECN – 6 Page 6 of 7		1b. Proj. ECN W- -

Design Details/Attributes (to be filled out by the change originator) identified in the ECN.			
1. Issue/Problem Statement included	☒ Yes ☐ No ☐ N/A	21. Basis for Selected Alternative explained, including assumptions	☐ Yes ☐ No ☒ N/A
2. Safety/Commitment/Programmatic Impacts identified – NEPA Documentation completed	☐ Yes ☐ No ☒ N/A	22. Potential Component/System Impacts identified and resolved	☐ Yes ☐ No ☒ N/A
3. System/Equipment/Personnel Impacts identified	☐ Yes ☐ No ☒ N/A	23. Potential Software Impacts identified and resolved	☐ Yes ☐ No ☒ N/A
4. Technical Evaluation included	☒ Yes ☐ No ☐ N/A	24. Potential Safety Impacts are identified and resolved (e.g., energized electrical equipment)	☐ Yes ☐ No ☒ N/A
5. Compliance w/ Design Basis identified	☐ Yes ☐ No ☒ N/A	25. Modification is Constructible and can be implemented	☐ Yes ☐ No ☒ N/A
6. Assumptions/Sources clearly identified	☒ Yes ☐ No ☐ N/A	26. Design considers Operational Impacts	☐ Yes ☐ No ☒ N/A
7. Affected Documents and Databases clearly identified	☐ Yes ☐ No ☒ N/A	27. Contamination Controls are planned	☐ Yes ☐ No ☒ N/A
8. Inputs Verified	☒ Yes ☐ No ☐ N/A	28. Pre-Installation/Mockup/Prototype Testing planned	☐ Yes ☐ No ☒ N/A
9. Required Function(s) / changes clearly identified	☐ Yes ☐ No ☒ N/A	29. Sketches/Drawings for Tools/Fabricated Components included	☐ Yes ☐ No ☒ N/A
10. Safety Basis/Commitments/Concerns evaluated	☒ Yes ☐ No ☐ N/A	30. Hardware Design described	☐ Yes ☐ No ☒ N/A
11. Application of Industry Standards/Codes explained	☐ Yes ☐ No ☒ N/A	31. Software/Firmware Design described	☐ Yes ☐ No ☒ N/A
12. Proper Analytical Techniques employed	☒ Yes ☐ No ☐ N/A	32. Inspections (per Codes & Standards) / Quality Checks included	☐ Yes ☐ No ☒ N/A
13. Interfaces evaluated and identified	☐ Yes ☐ No ☒ N/A	33. Dimensions and Tolerances included	☐ Yes ☐ No ☒ N/A
14. Material/Component Compatibility evaluated	☐ Yes ☐ No ☒ N/A	34. Sketches/Drawings for Installation included	☐ Yes ☐ No ☒ N/A
15. ALARA/Radiological controls/chemical hazards evaluated	☐ Yes ☐ No ☒ N/A	35. Housekeeping/Personnel Safety Requirements identified	☐ Yes ☐ No ☒ N/A
16. Human/Machine Interface evaluated	☐ Yes ☐ No ☒ N/A	36. Walkdown(s) performed/Labeling Correct	☐ Yes ☐ No ☒ N/A
17. Program impacts evaluated	☐ Yes ☐ No ☒ N/A	37. Acceptance Test generated and Acceptance Criteria included	☐ Yes ☐ No ☒ N/A
18. Design Basis Calculations updated	☐ Yes ☐ No ☒ N/A	38. M&TE Requirements identified	☐ Yes ☐ No ☒ N/A
19. Alternatives described/evaluated and address resolution of problem	☐ Yes ☐ No ☒ N/A	39. Training/Qualification of Test Personnel identified	☐ Yes ☐ No ☒ N/A
20. Impacts on Maintenance and OPS described	☐ Yes ☐ No ☒ N/A	40. Safety and Hazards Analysis assessed	☒ Yes ☐ No ☐ N/A

Design Originator (Print/Sign)	**Date**
K. R. Sandgren K. R. Sandgren	3/22/03

Italicized text items need to be addressed. Standard text items need to be addressed as applicable to the change as described.

ECN - 6 DESIGN CHECK LIST	☒ DM ☐ FM ☐ TM	1a. ECN 720332 R 0
Sheet 2 of ECN – 6 Page 7 of 7		1b. Proj. ECN W- -

Design Check Method (Select method(s) and provide explanation of how to be performed):

☒ Peer Check	☐ Design Check Team*	☐ Other _____

Design Check Explanation:

Peer checker will verify that the document has been reviewed by a technical peer reviewer and approved by the author.

* Design check team members other than the originating organization normally should consist of personnel representing: Operations, Maintenance & Reliability Engineering, Maintenance Management, Maintenance Crafts, Safety, and Projects.

Design Check Details

Design inputs correctly identified?	☐ Yes ☐ No ☒ N/A	*Design changes properly documented?*	☐ Yes ☐ No ☒ N/A
Calculations checked and are correct?	☒ Yes ☐ No ☐ N/A	*Test procedures reviewed and are correct?*	☐ Yes ☐ No ☒ N/A
Design assumptions are stated and verified?	☒ Yes ☐ No ☐ N/A	*Is the design change adequate?*	☐ Yes ☐ No ☒ N/A
Design criteria incorporated into the design?	☐ Yes ☐ No ☒ N/A	*Is the design change complete?*	☐ Yes ☐ No ☒ N/A
Interfaces clearly identified in the design?	☐ Yes ☐ No ☒ N/A	*Is the design change correct?*	☐ Yes ☐ No ☒ N/A
EQRG pre-release review required?	☐ Yes ☒ No	EQRG Pre-release Approval	Date

Comments:

Reference TFC-ENG-DESIGN-P-17, Design Verification

Design Checker (Print/Sign)	***Date***
J. M. Grigsby	3/22/03

Italicized text items need to be addressed. Standard text items need to be addressed as applicable to the problem/issue described.

DISTRIBUTION SHEET

To	From	Page 1 of 1
Distribution	Nuclear Safety & Licensing	Date 03/22/2003
Project Title/Work Order		EDT No. N/A
HNF-3588, Rev. 1, "Organic Complexant Topical Report"		ECN No. 720332 R0

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Organic Complexant Topical Report

K. R. Sandgren
CH2M HILL Hanford Group, Inc.
Richland, WA 99352
U.S. Department of Energy Contract DE-AC27-99RL14047

EDT/ECN: ECN 720332-R0 UC: N/A
Cost Center: 7B300 Charge Code: 501570
B&R Code: N/A Total Pages: 372

Key Words:
Organic, complexant, red oil, bulk runaway, point source ignition, propagation, accident, consequence

Abstract:
This document summarizes the safety basis for resolving the organic complexant safety issue. Revision 1 of this document expanded the report to include inactive miscellaneous underground storage tanks and catch tanks, as well as, single-shell tanks, double-shell tanks, and double-contained receiver tanks.

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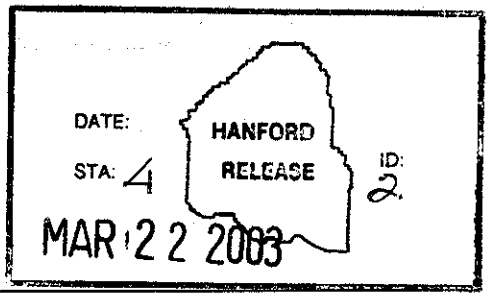

Release Approval Date Release Stamp

Approved For Public Release

RECORD OF REVISION

(1) Document Number: HNF-3588

(2) Title: Organic Complexant Topical Report

Change Control Record

(3) Revision	(4) Description of Change - Replace, Add, and Delete Pages	Authorized for Release	
		(5) Cog. Engr.	(6) Cog. Mgr. Date
0	(7) New document released via EDT #625109	WL Cowley	JE Meacham 11/98
1 RS	ECN #720332 RO Adds analysis of inactive miscellaneous storage tanks and catch tanks.	KR Sandgren K.R. Sandgren	JM Grigsby 3/22/03

HNF-3588
Revision 1

Organic Complexant Topical Report

Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management

CH2MHILL
Hanford Group, Inc.
Richland, Washington

Contractor for the U.S. Department of Energy
Office of River Protection under Contract DE-AC06-99RL14047

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HNF-3588
Revision 1

Organic Complexant Topical Report

Prepared by
K. R. Sandgren
CH2M HILL Hanford Group, Inc.

Date Published
March 2002

Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management

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Contractor for the U.S. Department of Energy
Office of River Protection under Contract DE-AC06-99RL14047

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ORGANIC COMPLEXANT TOPICAL REPORT

EXECUTIVE SUMMARY

This document updates information contained in the previous *Organic Complexant Topical Report*, HNF-3588, Revision 0 (Meacham et al. 1998). The status of tanks 241-C-106 and 241-AY-102 has been updated due to the transfer of waste from 241-C-106 to 241-AY-102.

This document summarizes the safety basis for resolving the Organic Complexant Safety Issue and closing the Condensed Phase Organic-Nitrate Unreviewed Safety Question for Hanford Site high-level waste single-shell tanks (SSTs), double-shell tanks (DSTs), double-contained receiver tanks (DCRTs), inactive miscellaneous underground storage tanks (IMUSTs), and catch tanks. Two distinct hazards were evaluated: spontaneous self-accelerating decomposition reactions in the bulk material (bulk runaway) and deflagration after being initiated by an ignition source (propagation).

Bulk runaway is not possible in the DSTs, DCRTs, and catch tanks because they contain predominantly aqueous wastes. Characterization data and calculations show that the available latent heat of water vaporization exceeds the theoretical chemical energy potential for these tanks. This was true even when the total organic carbon (TOC) in the tanks was assumed to be hydroxyethylethylenediaminetriacetic acid (HEDTA), the most energetic organic complexant discharged to the tanks.

Bulk runaway can be ruled out for the SSTs and many of the IMUSTs by comparing the time required to conduct heat from the tanks (time of cooling) with the storage time. Calculations for

the SSTs show that the time of cooling ranges from a few hours to 3.1 years. There have been no transfers of waste into the SSTs for about 17 years. Several times of cooling have passed over the last 17 years of storage, and no credible mechanisms to increase tank waste temperatures to bulk runaway reaction levels have been identified. Waste temperatures are decreasing consistent with the decrease in radioactive decay rates. Bulk runaway for the remainder of the IMUSTs can be ruled out with an examination of process history or by comparison to bounding SST waste.

Propagation is not possible in the DST, DCRT, and catch tank wastes because they contain significant water. Theoretical analyses and combustion testing show that propagation is not possible when the water concentration exceeds 20 wt%. Sample data and characterization show that the DST, DCRT, and catch tank wastes contain more than 20 wt% water. Some DSTs contain floating crusts that have less than 20 wt% water, but these crusts do not contain a significant amount of the organic complexant salts, because the complexants are highly soluble.

The organic complexants were sent to the single-shell tanks as dilute aqueous waste and are in waste matrices that include high concentrations of inerts and diluents (e.g., sodium carbonate, sodium sulfate, and hydroxy salts of aluminum, iron, and silicon). Sample data, process history, and combustion testing indicate that propagation is not possible in the SST and IMUST wastes. Tank wastes were screened using waste process histories, differential scanning calorimetry (DSC), and TOC measurements. The wastes with the highest DSC/TOC measurements were tested for propagation using adiabatic calorimetry. The waste samples were dried before testing, and none of the dried waste samples propagated. Fuel (sodium HEDTA) was added to the tank waste samples with the highest (bounding) TOC/energetics (AX-102 and U-106), to determine how much more fuel would be required before a dried waste sample would propagate. The dried

AX-102 waste sample required 31% more fuel, and the dried U-106 waste sample required 42% more fuel to support propagation.

Chemical speciation and testing of the waste samples revealed several phenomena that provide additional safety margin between tank waste conditions and the conditions that support combustion. In addition to containing fuel concentrations which were too low to sustain propagation, 45 tank wastes contain oxidizer concentrations that are too low to support propagation when sufficient fuel is **assumed** to be present. The open literature, simulant tests, and organic speciation of waste samples show that the organic complexants are decomposing to low energy byproducts (e.g., oxalate, formate, and carbonate) that do not propagate when tested.

Testing showed that the waste samples would not propagate even when the water was removed by drying at 105 °C. However, the extremely dry conditions in the propagation tests cannot occur under tank waste storage conditions, because the wastes contain hygroscopic salts that retain considerable water. Experiments on waste samples and modeling indicate that the organic complexant-bearing wastes will retain significant water during interim storage. Of the two tanks with the highest TOC/energetics, tank U-106 waste will retain more than 20 wt% water (20 wt% water prevented propagation at all TOC concentrations), and tank AX-102 waste will retain about 17 wt% water. This amount of water increases the theoretical requirement for propagation to 10.2 wt% TOC, which is more than a factor of two higher than the highest measured TOC concentration in AX-102 (3.7 wt%).

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LIST OF TERMS

ANOVA	analysis of variance
DCRT	double-contained receiver tank
DNFSB	Defense Nuclear Facilities Safety Board
DOE	U.S. Department of Energy
DSC	differential scanning calorimetry
DST	double-shell tank
ED3A	ethylenediaminetriacetic acid
EDDA	ethylenediaminediacetic acid
EDTA	ethylenediaminetetraacetic acid
HEDTA	hydroxyethylethylenediaminetriacetic acid
IDA	iminodiacetic acid
IMUST	inactive miscellaneous storage tank
NTA	nitrilotriacetic acid
PRSST	Propagating Reactive System Screening Tool
RSST	Reactive System Screening Tool
sd	standard deviation
SST	single-shell tank
TGA	thermogravimetric analysis
TOC	total organic carbon
USQ	Unreviewed Safety Question

DEFINITIONS

Bulk Runaway: The point at which the heat liberated from an exothermic chemical reaction exceeds heat loss to the environment. Temperatures within the reacting material grow exponentially and the chemical reaction cannot be stopped or slowed.

Characteristic Time of Adiabatic Runaway, τ_a: The time required to induce bulk runaway under adiabatic conditions.

Cooling Time, t_c: The time that elapses before the center of a slab experiences the effects of the relatively low temperatures at its boundaries. Bulk runaway is not possible if the finite time for the "adiabatic" central portion to reach infinity is greater than the time for heat conduction from the edge to influence the center. For one dimensional heat conduction in an infinite slab geometry, the cooling time is approximated by

$$t_c \approx \frac{L^2}{4\alpha}$$

where L (m) is the waste height and α ($m^2\ s^{-1}$) is the thermal diffusivity.

Fuel: Those organic complexant salts and their intermediate degradation products that support and/or contribute to propagation and combustion.

Propagation: A self-sustaining exothermic chemical reaction that passes through unreacted material after being initiated by an ignition source.

1.0 PURPOSE AND SCOPE

This document updates information contained in the previous *Organic Complexant Topical Report*, HNF-3588, Revision 0 (Meacham et al. 1998). The status of tanks 241-C-106 and 241-AY-102 has been updated due to the transfer of waste from 241-C-106 to 241-AY-102.

This document summarizes the safety basis for resolving the Organic Complexant Safety Issue and closing the Condensed Phase Organic-Nitrate Unreviewed Safety Question (USQ) for Hanford Site high-level waste single-shell tanks (SSTs), double-shell tanks (DSTs), double-contained receiver tanks (DCRTs), inactive miscellaneous underground storage tanks (IMUSTs), and catch tanks. The scope of this report, in revision 1, has been expanded to include interim waste storage in RPP owned IMUSTs as well as interim waste storage in SSTs, DSTs, DCRTs, and catch tanks. The document does not address other hazards that may be associated with these tanks (e.g., flammable gas deflagrations or organic solvent fires) except as these hazards relate to the Organic Complexant Safety Issue.

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2.0 BACKGROUND

Several waste generating processes were operated at the Hanford Site, including the bismuth phosphate process, the uranium recovery process, the REDOX process, the waste fractionization process, the PUREX process, and the processes conducted at the Plutonium Finishing Plant. The primary goal of these processes was to extract and/or process plutonium. Radioactive wastes from these processes are stored in underground tanks as alkaline slurries (Anderson 1990). There are 149 SSTs, 28 DSTs, six DCRTs, 45 IMUSTs, and 13 catch tanks.

Each of the waste-generating processes had a variety of waste streams (at least 49 different types have been identified), but the following broad categories can be established: (1) cladding (or coating) waste from the removal of the fuel element cladding; (2) metal waste from the processing of the fuel itself to remove the plutonium or other fissile material; (3) decontamination waste from the clean-out of the systems (this includes N Reactor decontamination waste); and (4) other miscellaneous waste, such as laboratory waste. Once the waste was generated and initially stored in the tanks, various other operations were performed, including removal/recovery of various materials (e.g., uranium, strontium, and cesium), evaporation, solidification, and settling.

The principal organic compounds sent to the waste tanks were divided into two classes: complexants (for chelating divalent, trivalent, and tetravalent cations) and extraction solvents. This document focuses on the organic complexant hazard; the organic solvent hazard is discussed in a separate report (Cowley et al. 2000).

The principal organic complexants were glycolic acid, citric acid, hydroxyethylethylenediamine-triacetic acid (HEDTA), and ethylenediaminetetraacetic acid (EDTA). The approximate quantities of complexants used are summarized in Table 2-1 (Allen 1976). Besides these complexants, others were also used such as nitrilotriacetic acid (NTA) and oxalic acid, but the quantities were relatively small and were not well quantified.

Table 2-1. Approximate Quantities of the Principal Organic Complexants Used at Hanford.

Complexant	Quantity (Metric Tons)
Glycolic Acid	880
Citric Acid	850
Hydroxyethylethylenediaminetriacetic Acid (HEDTA)	830
Ethylenediaminetetraacetic Acid (EDTA)	220

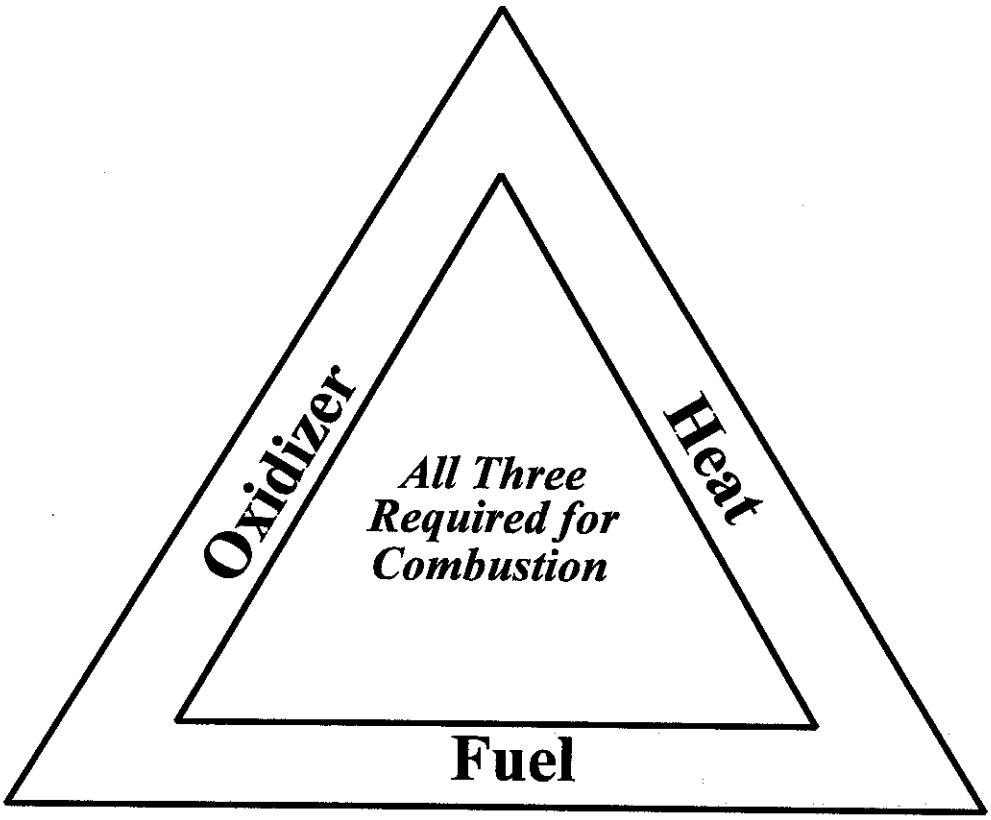
The organic complexants are in waste matrices that include inerts and diluents (e.g., water, excess sodium nitrate/nitrite, sodium carbonate, sodium sulfate, and hydroxy salts of aluminum, iron, and silicon) and potential oxidizers (sodium nitrate/nitrite). In the presence of oxidizing material such as sodium nitrate/nitrite, the complexant salts can be made to react exothermically by heating to high temperatures or by applying an electrical spark of sufficient energy.

2.1 APPROACH TO RESOLUTION OF THE ORGANIC SAFETY ISSUE

The approach to safety issue resolution centers on understanding the physicochemical properties of the complexant waste. To assess the organic-nitrate hazard, it is necessary to first define the physicochemical conditions that support combustion, and then to determine if these conditions exist in the tank waste.

There are two common hazards associated with the safe storage and handling of chemically reactive material (AIChE 1995): (1) spontaneous self-accelerating decomposition reactions in the bulk material (bulk runaway) and (2) deflagration after being initiated by an ignition source (propagation). However, as shown in the traditional fire triangle (Figure 2-1), fuel, oxidizer, and heat are all important parameters. If fuel, oxidizer, or heat (initiators) are not present in sufficient amounts, then a runaway or propagating reaction cannot occur.

Figure 2-1. Fire Triangle.



Safe storage is ensured if one of the three legs of the fire triangle is not sufficient. Bulk runaway is assessed in Section 3.0 and the assessment primarily shows that the heat (initiator) leg of the triangle is not sufficient because the decay and chemical heat can be safely conducted away. Propagation is assessed in Section 4.0 and the assessment shows that the fuel component of the fire triangle is not sufficient. Some tank wastes have low oxidizer concentrations in addition to low fuel concentrations.

2.2 UNREVIEWED SAFETY QUESTION

The first organic complexant hazard assessments focused on determining whether bulk runaway (see Section 3.0) could occur, similar to the 1957 accident at Kyshtym. A brief description and interpretation of the Kyshtym accident are provided in Appendix A. There are two important differences between Kyshtym and the waste stored at Hanford: (1) the Hanford tank wastes have radiolytic heatloads one to six orders of magnitude lower and (2) Hanford wastes contain inerts and diluents. Several early analyses (Beitel 1977, Fisher 1990, Turner and Miron 1994a, 1994b) examined organic-nitrate reaction onset temperatures and concluded that this type of accident could not occur at the Hanford Site because tank temperatures were well below that necessary for bulk runaway.

Subsequent studies examined a different accident scenario, propagation (see Section 4.0) (Webb 1996, Fauske et al. 1996). In this scenario, an external ignition source (e.g., lightning or welding slag) initiates a combustion front that propagates through the organic waste. A USQ evaluation on SSTs, DSTs, DCRTs, and IMUSTs (Farley and Dougherty 1996) determined that localized high energy ignition sources were credible, and that point source ignition of organic complexant waste was not adequately addressed in the then existing authorization basis. Consequently, a USQ was declared on these facilities in May 1996 for condensed-phase organic-nitrate reactions (Wagoner 1996). Revision 0 of this document was used as the technical basis for closing the USQ on condensed-phase organic-nitrate reactions in SSTs, DSTs, and DCRTs (Wagoner 1998). Revision 1 expands the scope of this document to include IMUSTs. It should be noted that the data used to close the USQ for DSTs, SSTs, and DCRTs in revision 0 was current as of 1998. The only active tanks that have been updated for revision 1 are C-106 and AY-102 to reflect the condition of C-106 after sluicing.

2.3 WATCH LIST

In November 1990, the Wyden Amendment [Public Law 101-510, Section 3137 (1990)] was enacted. This law required the identification of Hanford Site tanks that may have a serious potential for release of high-level waste due to uncontrolled increases of temperature or pressure. It was recognized that the organic complexants and organic solvents used at Hanford might contain sufficient energy to produce high temperatures or pressures, and an assessment of the waste tanks was made using a total organic carbon (TOC) concentration criterion.

Early experiments showed that a mixture containing 10 wt% sodium acetate (i.e., 3.0 wt% TOC) and sodium nitrate/nitrite would react violently at high temperatures (Fisher 1990). Using this 3 wt% TOC criterion, ten tanks were identified in the February 1991 report to Congress (Watkins 1991) that responded to the Wyden Amendment (tank C-103 was also included on this list because it contained a pool of organic solvent). A subsequent review of historical data (Toth et al. 1994) identified nine more tanks that might exceed the 3 wt% TOC criterion. Another organic solvent tank (C-102) was also added to the Watch List in May 1994 (Payne 1994), bringing the total number of Organic Watch List tanks to twenty.

The Organic Solvent Topical report (Cowley et al. 2000) was completed in May 1998. Analyses showed that the organic solvent hazard was adequately managed with the current authorization basis controls to reduce the risk from flame cutting and vehicle fuel fires. The report recommended removal of tanks C-102 and C-103 from the Watch List.

Tanks A-101, AX-102, B-103, S-102, S-111, SX-103, SX-106, T-111, TX-105, TX-118, TY-104, U-103, U-105, U-106, U-107, U-111, U-203, and U-204 were placed on the Organic Watch List because they were suspected to contain more than 3 wt% TOC. Sampling data, testing, and analyses presented in this report show that these tanks do not have a serious potential for release of high-level nuclear waste due to uncontrolled increases of temperature or pressure. Consequently, revision 0 of this document was used as the technical basis for removal of these 18 tanks from the Organic Watch List (Sohn 1999).

2.4 DNFSB RECOMMENDATION 93-5

In July 1993, the Defense Nuclear Facilities Safety Board (DNFSB) transmitted Recommendation 93-5 (Conway 1993) on the Hanford Waste Tank Characterization Studies to the U.S. Department of Energy (DOE). Recommendation 93-5 noted that insufficient tank waste technical information was available to ensure that Hanford Site wastes could be safely stored, and that associated operations could be conducted safely. As a result, the DNFSB recommended that the characterization effort be upgraded and expedited.

The DNFSB accepted an Implementation Plan (DOE 1994) in March 1994 (Conway 1994). Equipment upgrade difficulties and poor rotary-mode sampler reliability prevented completion of the commitments in the original implementation plan. Subsequent revision of the Implementation Plan (DOE 1996) focused characterization efforts on understanding safety-related phenomena to expedite resolution of the waste tank safety issues.

The Recommendation 93-5 Implementation plan (DOE 1996) has two deliverables associated with the organic complexant hazard: (1) a topical report describing the current understanding of the issue and future work for resolution (DNFSB Milestone 5.4.3.3a) and (2) a letter reporting results of testing to confirm safe storage criteria, organic solubility, and organic aging (DNFSB Milestone 5.4.3.3b). The first deliverable was met in June 1997 (Wagoner 1997), and revision 0 of this report was used to meet the second deliverable (Conway 1999).

3.0 BULK RUNAWAY

3.1 BULK RUNAWAY ACCIDENT SCENARIO

The scenario for bulk runaway is (1) waste drying or a loss of active cooling (on a tank with a high heatload) causes the waste to heat up to the self-accelerating decomposition temperature (AIChE 1995), (2) the chemical heating raises the waste temperature which in turn accelerates the chemical reaction, (3) this accelerating bulk runaway continues until the chemical reactants are consumed. The high temperatures and gases produced over-pressurize the tank and radioactive and toxic materials are released to the environment. This is analogous to the accident that occurred in 1957 at Kyshtym (see Appendix A).

3.2 BULK RUNAWAY SCREENING CRITERIA

3.2.1 Double-Shell Tank, Double-Contained Receiver Tank, and Catch Tank Bulk Runaway Screening Criteria

Catch Tanks, DCRTs, and DSTs contain mostly aqueous waste, and the available water provides a large heat sink for any exothermic chemical reactions that could occur. It is possible to rule out bulk runaway through a simple energy balance comparing the available theoretical chemical energy (ΔH_r), with the latent heat of water vaporization (ΔH_v) (latent heat is the energy required to change liquid water into vapor). That is, bulk runaway is not possible if

$$\Delta H_v > -\Delta H_r \qquad (3-1)$$

Heat generated by a chemical reaction would be absorbed by the surrounding water, and tank waste temperatures would remain below about 120 °C (the approximate boiling temperature of the supernatant). However, the DSTs are actively ventilated, and it is important to assess whether the decay heat will cause the waste liquid to boil if active ventilation were lost. Water vaporized by the decay heat (i.e., boiling and rapid water loss) would not be available to deter a bulk runaway. Empirical modeling of the relationship between headspace temperature and tank heatload suggest that the steady state headspace temperature can be estimated by the following equation (see Figure 3 in Kummerer 1995)

$$T_{v,p} \approx \frac{1}{2}\,\frac{Q H_s}{k_s A_t} + T_\infty \qquad (3-2)$$

where ($T_{v,p}$) is the steady-state temperature of the waste liquid under no active ventilation which would be about the same as the resulting tank headspace temperature, Q (W) is the total heat

flow rate (heatload), H_s (~ 4 m) is the height of tank overburden, k_s (1 W m^{-1} K^{-1}) is the overburden thermal conductivity (Bouse 1975), A_t (410 m^2) is the tank cross-sectional area, and T_∞ (14°C) is the average ambient temperature. The DSTs, DCRTs, and catch tanks are assessed for bulk runaway in Sections 3.3.1, 3.3.2, and 3.3.3, respectively.

Equation 3-2 provides a conservative assessment for the DSTs. The soil overburden above the DSTs ranges between two to three meters, but a bounding value of four meters is used in the equation. Convective heat losses under passive ventilation (which are not credited in Equation 3-2) would be greater in the DSTs than the SSTs. The DSTs have a 0.46 m (1.5 ft) annulus around the tank that allows for convective heat transfer out of the tank sides and bottom. A separate ventilation system also provides active ventilation in the annulus.

3.2.2 Single-Shell Tank and Inactive Miscellaneous Underground Storage Tank Bulk Runaway Screening Criteria

3.2.2.1 Chemical Heat Removal. Bulk runaway can occur when the chemical heat generation rate produced by an Arrhenius type reaction exceeds the rate of heat dissipation by conduction. Bulk runaway is not credible if heat dissipation exceeds heat generation. The safety criterion is therefore often expressed in terms of two characteristic time constants (see Appendix B for derivation of screening criteria):

$$\tau_a > \tau_c \qquad (3-3)$$

where τ_a is the characteristic time of adiabatic runaway and τ_c is the characteristic cooling time. For an infinite slab with thickness L, τ_c is given by Equation 3-4:

$$\tau_c \approx \frac{4\alpha t_c}{L^2} \approx 1 \qquad (3-4)$$

where L (m) is the total waste height, t_c (s) is the cooling time, and α (m^2 s^{-1}) is the thermal diffusivity. Rearranging Equation 3-4, the following is obtained:

$$t_c \approx \frac{L^2}{4\alpha} \qquad (3-5)$$

The time of cooling is the time that elapses before the center of the slab experiences the effects of the relatively low temperatures at its boundaries. Bulk runaway is not possible if the finite time for the "adiabatic" central portion to reach infinity is greater than the time for heat conduction from the edge to influence the center. Note that if one side of the slab were completely insulated,

the time of cooling would be L^2 divided by α instead of 4α. The actual waste tank characteristic times lie between these two values. In either case, the conclusions on bulk runaway remain unchanged (see Section 3.3.4 for calculations of t_c).

Calculation of the characteristic time of adiabatic runaway requires an understanding of the chemical kinetics associated with the organic waste. However, an assessment of the potential for bulk runaway can be done without calculating τ_a. Safe storage can be assessed by comparing the past storage time with the cooling time. That is, bulk runaway is not credible if the following safety criterion is satisfied:

$$t_s > t_c \qquad (3-6)$$

where t_s is the past storage time.

3.2.2.2 Decay Heat Removal. No radioactive waste has been added to the SSTs since 1980, and the major radioactive heat sources in the SSTs are ^{137}Cs and ^{90}Sr. Over the last 20 years, the decay heats have decreased about one-third, and the tank waste decay power continues to decline during storage. Similarly for IMUSTs, no radioactive waste has been added since 1985, with one exception. Tank 241-S-302A was not taken out of service until 1991. To determine if a bulk runaway accident is credible, it is necessary to assess whether heat from radioactive decay could increase tank waste temperatures to the self-accelerating decomposition temperature (i.e., bulk runaway temperature). Although bulk runaway temperatures for the organic tank wastes are not quantified, safe storage can be ensured if the temperatures are maintained below post-1980 temperatures. That is, if waste temperatures remain below previous historical temperatures (i.e., the peak temperature maintained for a duration equal to or greater than the time of cooling), then bulk runaway is not credible.

Hanford Site SSTs are either passively ventilated (heat is lost primarily through conduction) or actively ventilated (an exhauster is attached to increase air flow through the tank).

3.2.2.3 Passively Ventilated SSTs. For the passively ventilated tanks, an increase in waste temperature from decay heating would only occur if the thermal conductivity of the waste decreases (see discussions of tank A-101 in Appendix C). Thermal conductivity within the waste will decrease as a waste becomes drier (after stabilization); however, the waste temperature would increase only if the solid waste thermal conductivity decreases faster (as the waste becomes drier) than the volumetric heating rate decreases (from radioactive decay).

Tank waste temperatures will continue to decline if the temperature difference of a future dried out waste is less than the temperature difference of the waste tank in the current configuration. That is, waste temperatures will still be lower in its dried out state if the following is true:

$$q_0''' \frac{L^2}{2k_w} + q_0''' \frac{LH_s}{2k_s} > q_0''' (1 - Nt) \frac{L^2}{2k_d} + q_0''' (1 - Nt) \frac{LH_s}{2k_s} \qquad (3-7)$$

where q'''_0 (W m^{-3}) is the volumetric heating rate at time zero, L (m) is the waste height, k_w (1 W m^{-1} K^{-1}) is the thermal conductivity of the wet waste (Bouse 1975), H_s (m) is the height of the soil layer above the tank, k_s (W m^{-1} K^{-1}) is the thermal conductivity of soil, the quantity q'''_0 (1 - Nt) is the volumetric heating rate at time t with N (2.3 E-2 $year^{-1}$) being the decay constant, and k_d (W m^{-1} K^{-1}) is the thermal conductivity of the dried waste. From Equation 3-7, waste temperatures will continue to decline if the decrease in k_d is less than the decrease in decay power. The rate of decrease in decay power is constant, but the rate of decrease in k_d is a function of moisture loss from the waste (i.e., waste dry out).

Waste temperatures will continue to decline if moisture loss ($\dot{m}$) is less than the following (see Appendix B for derivation):

$$\dot{m} < \frac{k_w}{k_s} (1 - \epsilon) H_s A_t \rho_\ell N \qquad (3-8)$$

Where ϵ is the porosity of the dry waste (0.3) (Handy 1975), A_t (410 m^2) is tank cross-sectional area, and ρ_ℓ is the density of water (1000 kg m^{-3}). For the 1,000,000, 758,000 and 530,000 gallon tanks, $\dot{m}$ is about 26,000 kg $year^{-1}$. The upper bound for yearly moisture loss is less than 8,700 kg $year^{-1}$ (see Appendix D) for tank C-104, consequently the waste temperatures in passively ventilated tanks will continue to decrease for all solid waste inventories, consistent with tank farm observations.

For the smaller 55,000 gallon 200 series tanks, $A_t = 29$ m^2, and $\dot{m}$ is about 2000 kg $year^{-1}$. The upper bound for yearly moisture loss in the 200 series tanks is less than 200 kg $year^{-1}$ (see Appendix D), consequently the waste temperatures in passively ventilated tanks will continue to decrease for all solid waste inventories, consistent with tank farm observations.

3.2.2.4 Actively Ventilated SSTs. To assess the actively ventilated SSTs for bulk runaway, it is necessary to postulate what the waste temperatures would be if active ventilation were stopped. Empirical modeling of the relationship between headspace temperature and tank heatload suggest that the steady state headspace temperature under passive ventilation can be estimated by the following equation (see Figure 3 in Kummerer 1995):

$$T_{w,p} \approx (0.5) \frac{Q H_s}{k_s A_t} + T_\infty + (T_{w,a} - T_v) \qquad (3-9)$$

where $T_{w,a}$ is the waste temperature under active ventilation, and T_v is the average headspace temperature.

If the temperature after ventilation shutoff is less than the historical operating temperatures (i.e., the peak temperature maintained for a duration equal to or greater than the time of cooling), then bulk runaway is not credible. The SSTs are assessed for bulk runaway in Section 3.3.4.

3.2.2.5 Passively Ventilated IMUSTs. For IMUSTs, which are passively ventilated, an increase in waste temperature from decay heating would only occur if the thermal conductivity of

the waste decreases (see discussions of tank A-101 in Appendix C). Thermal conductivity within the waste will decrease as a waste becomes drier (after stabilization); however, the waste temperature would increase only if the solid waste thermal conductivity decreases faster (as the waste becomes drier) than the volumetric heating rate decreases (from radioactive decay).

Tank waste temperatures will continue to decline if the temperature difference of a future dried out waste is less than the temperature difference of the waste tank in the current configuration. That is, waste temperatures will still be lower in its dried out state if the following is true (for direct buried IMUSTs):

$$q_0''' \frac{L^2}{2k_w} + q_0''' \frac{L H_s}{2k_s} > q_0''' (1 - Nt) \frac{L^2}{2k_d} + q_0''' (1 - Nt) \frac{L H_s}{2k_s} \qquad (3-7)$$

where q_0''' (W m^{-3}) is the volumetric heating rate at time zero, L (m) is the waste height, k_w (W m^{-1} K^{-1}) is the thermal conductivity of the wet waste, H_s (m) is the height of the soil layer above the tank, k_s (W m^{-1} K^{-1}) is the thermal conductivity of soil, the quantity q_0''' (1 - Nt) is the volumetric heating rate at time t with N (2.3 E-2 $year^{-1}$) being the decay constant, and k_d (W m^{-1} K^{-1}) is the thermal conductivity of the dried waste. From Equation 3-7, waste temperatures will continue to decline if the decrease in k_d is less than the decrease in decay power. The rate of decrease in decay power is constant, but the rate of decrease in k_d is a function of moisture loss from the waste (i.e., waste dry out).

Waste temperatures will continue to decline if moisture loss ($\dot{m}$) is less than the following (see Appendix B for derivation):

$$\dot{m} < \frac{k_w}{k_s} (1 - \epsilon) H_s A_t \rho_\ell N \qquad (3-8)$$

If moisture loss is assumed to remain constant over time, then moisture loss ($\dot{m}$) can be related to the time required for waste dry out by:

$$\dot{m} = \frac{M_t}{t_d} \qquad (3-10)$$

Where M_t is the kilograms liquid within the tank and t_d is time required for the tank to reach dryout. Substituting and rearranging results in:

$$t_d > \frac{k_s M_t}{(1-\epsilon) k_w H_s A_t \rho_\ell N} \qquad (3-11)$$

Where ϵ is the porosity of the dry waste (0.3), A_t is tank cross-sectional area, and ρ_ℓ is the density of water (1000 kg m^{-3}). If we define the time to dry out based on decay heat (t_p) as:

$$t_p = \frac{k_s M_t}{(1-\epsilon) k_w H_s A_t \rho_\ell N} \qquad (3-12)$$

Waste temperatures will continue to decrease as long as the actual time required for dry out (t_d) exceeds time to dry out based on the decay power (t_p). Safe storage can be assessed by comparing the past storage time to the cooling time and the decay-based dry out time. Bulk runaway is not credible if the following is true:

$$t_s > (t_c + t_p) \qquad (3-13)$$

Where t_s is the past storage time.

3.3 ASSESSMENT OF TANKS FOR BULK RUNAWAY

3.3.1 Double-Shell Tank Bulk Runaway

The 28 DSTs were assessed for bulk runaway by comparing the available theoretical chemical energy (ΔH_r), with the available latent heat of water vaporization (ΔH_v). Waste characterization and transfer data were used to calculate TOC and water inventories. Total organic carbon inventories were converted to theoretical chemical energy inventories by multiplying by the heat of reaction for sodium acetate combustion with sodium nitrate, 2.7 E7 J per kg of carbon. Organic speciation shows that even the least aged waste sample has only 85% of the energy of sodium acetate (Section 4.4.4.3). Consequently, sodium acetate provides a conservative estimate of the heat of reaction. Water inventories were converted to energy inventories by multiplying by the latent heat of vaporization, 2.3 E6 J kg^{-1}. The sensible heat of water was conservatively excluded from the energy balance. Results are shown in Table 3-1.

The values of heatload (Q), TOC inventory, and water (H_2O) inventory in Table 3-1 are from Appendix E, and are considered the best estimates. Many values are sample based, but others were derived from samples taken in tanks which were subsequently transferred into another tank. While these values are estimates, the estimates are believed to be within 20% of the true value.

Table 3-1. Assessment of Double-Shell Tanks for Bulk Runaway. (2 sheets)

Tank	Q (W)	$T_{v,p}$ [1] (°C)	TOC (kg)	H_2O (kg)	$-\Delta H_r$ (J)	ΔH_v (J)
AN-101	269	15	1.1 E3	3.7 E5	3.0 E10	8.5 E11
AN-102	9,495	60	1.1 E5	2.8 E6	3.0 E12	6.3 E12
AN-103	10,957	67	1.3 E4	2.3 E6	3.5 E11	5.4 E12
AN-104	11,578	70	2.0 E4	2.9 E6	5.4 E11	6.6 E12
AN-105	9,948	63	3.0 E4	3.1 E6	8.1 E11	7.0 E12
AN-106	98	14	6.6 E2	1.4 E5	1.8 E10	3.1 E11
AN-107	9,795	62	1.6 E5	2.7 E6	4.3 E12	6.1 E12
AP-101	3,540	31	1.4 E4	3.3 E6	3.8 E11	7.6 E12
AP-102	4,434	36	1.4 E4	3.7 E6	3.8 E11	8.6 E12
AP-103	3	14	2.0 E1	1.0 E5	5.4 E8	2.3 E11
AP-104	2	14	1.6 E1	8.9 E4	4.3 E8	2.0 E11
AP-105	3,022	29	4.6 E3	1.8 E6	1.2 E11	4.2 E12
AP-106	206	15	1.8 E3	1.2 E6	4.9 E10	2,7 E12
AP-107	<1	14	3.4 E1	1.0 E5	9.2 E8	2.3 E11
AP-108	289	15	3.7 E3	9.0 E5	1.0 E11	2.1 E12
AW-101	8,847	57	1.0 E4	2.9 E6	2.7 E11	6.8 E12

Table 3-1. Assessment of Double-Shell Tanks for Bulk Runaway. (2 sheets)

Tank	Q (W)	$T_{v,p}$[1] (°C)	TOC (kg)	H_2O (kg)	$-\Delta H_r$ (J)	ΔH_v (J)
AW-102	869	18	3.9 E3	1.1 E6	1.1 E11	2.4 E12
AW-103	754	18	1.8 E3	1.3 E6	4.9 E10	3.0 E12
AW-104	1,292	20	1.9 E3	3.0 E6	5.1 E10	7.0 E12
AW-105	2,013	24	3.7 E3	1.5 E6	1.0 E11	3.5 E12
AW-106	845	18	3.1 E3	5.5 E5	8.4 E10	1.3 E12
AY-101	15,500	90	2.3 E4	3.0 E6	6.2 E11	7.0 E12
AY-102	50,500[2]	>120	7.5 E3[2]	1.9 E6[2]	2.0 E11	4.4 E12
AZ-101	77,618	>120	5.5 E3	2.9 E6	1.5 E11	6.7 E12
AZ-102	45,143	>120	7.2 E3	3.0 E6	1.9 E11	6.9 E12
SY-101	11,267	69	8.4 E3	2.6 E6	2.3 E11	5.9 E12
SY-102	501	16	4.4 E3	2.3 E6	1.2 E11	5.3 E12
SY-103	5,860	43	3.7 E4	1.7 E6	1.0 E12	4.0 E12

Notes: [1] Estimated tank waste headspace/liquid temperature under passive ventilation using Equation 3-2.
[2] Data from CHG 2000.

From Table 3-1, the available latent heat of water vaporization (ΔH_v) exceeds the theoretical chemical energy potential ($-\Delta H_r$) for all the DSTs. Bulk runaway is not possible under current waste storage conditions. Waste transfers will not change the results of this assessment because incoming waste streams will maintain the balance between latent heat of water vaporization and theoretical chemical energy (i.e., $\Delta H_v > -\Delta H_r$). The minimum water concentration in a potential incoming transfer is about 50 wt%, and the corresponding latent heat of vaporization would be 1.6 E6 J per kg of waste. The theoretical chemical energy of the incoming waste stream would have to exceed 1.6 E6 J per kg of waste to begin to shift the current balance. The TOC equivalent (using the heat of combustion of sodium acetate with sodium nitrate, 2.7 E7 J per kg of carbon) is about 5.9 wt% or 71 g of TOC per liter. The frequency distribution of the TOC has been analyzed and shown to average only 5.2 g of TOC per liter, with none of the analyzed concentrations exceeding 40 grams TOC per liter (see Section 4.3.3.2). Therefore, waste transfers within the tank farm facilities are not a credible threat to change the balance between the latent heat of vaporization and the theoretical chemical energy.

The DSTs are actively ventilated, and it is important to assess whether the decay heat will cause the water to boil if active ventilation were lost. Water vaporized by the decay heat would not be available to deter a bulk runaway. Liquid waste temperatures under passive ventilation ($T_{v,p}$) were estimated using Equation 3-2 (see Table 3-1). The waste liquid temperatures in three DSTs, AY-102, AZ-101, and AZ-102, might eventually exceed the boiling point of the supernatant (about 120 °C) if active ventilation were lost. However, any organic complexant that wasn't

already oxalate in tanks AY-102, AZ-101, and AZ-102 would be quickly oxidized to carbonate and oxalate at the high temperatures and high dose rates (Camaioni et al. 1998).

For tank AZ-101, the estimated water quantity is about 2.9 E6 kg and the corresponding latent heat of vaporization is about 6.7 E12 Joules. Considering that about 56,000 W is removed by boiling (total heat load - heat load required for bulk boiling), the time to dry out tank AZ-101 is about 4 years. Assuming that all of organic is converted to oxalate (a conservative assumption since experimental results show that the TOC is about equally converted to carbonate and oxalate from thermal decomposition), the temperature rise from oxidation of this oxalate would be negligible. The heat of reaction for oxalate combustion with sodium nitrate is 6.94 E6 J/kg of carbon (Burger 1993). From Appendix E, the estimated TOC inventory in tank AZ-101 is about 5,500 kg, and the sludge inventory is 1.3 E6 kg. Assuming a heat capacity of 1500 J/kg-K, the temperature rise would be about 19 °C.

$$\frac{(5{,}500\,\text{kg of carbon})\ (6.94\,\text{E6 J/kg of carbon})}{(1500\,\text{J/kg of waste- K})\ (1.3\,\text{E6 kg of waste})} \approx 19\,\text{K} \qquad (3-14)$$

Results for tank AZ-102 are similar. The estimated time to remove the available water (about 3 E6 kg) is over 9 years. From Appendix E, the estimated TOC content in tank AZ-102 is about 7,200 kg, and the sludge inventory is 8.1 E5 kg. The corresponding temperature rise would be about 41 °C.

$$\frac{(7{,}200\,\text{kg of carbon})\ (6.94\,\text{E6 J/kg of carbon})}{(1500\,\text{J/kg of waste- K})\ (8.1\,\text{E5 kg of waste})} \approx 41\,\text{K} \qquad (3-15)$$

Tank AY-102 can be analyzed similarly. The time to dry out tank AY-102 is about 5 years, based on the available water (1.9 E6 kg). Tank AY-102 received a large quantity of waste from Tank C-106. The post transfer heat load is reported in the Best Basis Inventory (CHG 2000) as is a post-transfer sampling event that shows a TOC content of 7,500 kg of carbon in AY-102. The corresponding temperature rise would be 39 °C.

$$\frac{(7{,}500\,\text{kg of carbon})\ (6.94\,\text{E6 J/kg of carbon})}{(1500\,\text{J/kg of waste- K})\ (8.9\,\text{E5 kg of waste})} \approx 39\,\text{K} \qquad (3-16)$$

Waste transfers do not change the results of the DST assessment as long as the total heatload will not cause the waste supernatant to boil. The heatload required for bulk boiling can be calculated from Equation 3-2 by setting $T_{v,p}$ equal to 120 °C and solving for Q (21,700 watts). If the heatload in a DST exceeds 21,700 watts, then the tank needs to be evaluated for bulk runaway as described above for tanks AY-102, AZ-101, and AZ-102.

3.3.2 Double-Contained Receiver Tank Bulk Runaway

The six DCRTs were assessed for bulk runaway by comparing the specific theoretical chemical energy ($\Delta \hat{H}_r$) with the specific latent heat of water vaporization ($\Delta \hat{H}_v$). Waste characterization and transfer data were used to calculate TOC and water concentrations. Total organic carbon concentrations were converted to specific theoretical chemical energy by multiplying by the heat of reaction for sodium acetate combustion with sodium nitrate, 2.7 E7 J per kg of carbon. The specific water energy is simply the water concentration multiplied by the latent heat of water vaporization, 2.3 E6 J kg^{-1}. Results of the assessment are shown in Table 3-2.

The waste temperature under passive ventilation ($T_{v,p}$) was calculated using the value Q and the waste depth (L), and $T_{v,p}$ is within 25% of the true value. The values H_r and H_v are simple multipliers of TOC and H_2O and are within about 20% of the true value. As the difference between H_r and H_v are an order of magnitude, a shift of 20% in the values will not change the conclusions.

Table 3-2. Assessment of Double-Contained Receiver Tanks for Bulk Runaway.

Tank	TOC (wt%)	Water (wt%)	$-\Delta \hat{H}_r$ (J kg^{-1})	$\Delta \hat{H}_v$ (J kg^{-1})
244-A	0.2	97	5.4 E4	2.2 E6
244-BX	0.3	50	8.1 E4	1.2 E6
CR-003-TK	0.18	60	4.8 E4	1.4 E6
244-S	0.02	92	5.4 E3	2.1 E6
244-TX	0.018	88	4.8 E3	2.0 E6
244-U	NA	NA	NA	NA

Notes: NA = not applicable, 244-U has not been used yet for waste transfers.

From Table 3-2, the specific latent heat of water vaporization ($\Delta \hat{H}_v$) exceeds the specific theoretical chemical energy ($\Delta \hat{H}_r$) for the DCRT wastes by about two orders of magnitude. Bulk runaway reaction scenarios are not credible for the DCRTs.

3.3.3 Catch Tank Bulk Runaway

Catch tanks are underground storage tanks used to collect small amounts of liquid. Waste sources include rain water, snow melt, de-entrainer flush, diversion box drainage, condensate from aging waste tanks, and drainage from the cross site transfer line pit. These waste streams have a high water content, and would contain only small concentrations of organic. Three of the 12 active catch tanks have sample data, and the results are shown in Table 3-3. The high water and low TOC concentrations indicate no potential for bulk runaway reactions in the catch tanks. Process histories (Table 3-4) indicate that the catch tanks received little, if any, organic complexants and the three tanks sampled bound the ten unsampled tanks.

Table 3-3. Assessment of Catch Tanks for Bulk Runaway.

Tank	TOC (wt%)	Water (wt%)	$-\Delta \hat{H}_r$ (J kg^{-1})	$\Delta \hat{H}_r$ (J kg^{-1})
A-302-A	0.017	99	4.6 E3	2.3 E6
ER-311	0.010	98	2.7 E3	2.2 E6
U-301-B	<0.004	99	<1 E3	2.3 E6

Table 3-4. Description of Catch Tank Use and Process Histories.

Tank	Function
AX-152	Diversion box drain – rain, de-entrainer flush, snow melt
AZ-151	Diversion box drain and AZ loop seal
AZ-154	AZ-102 heating coil steam condensate. Now empty, steam is off.
A-350	Collects drainage from A farm – rain, flush water
A-302-A	Diversion box drain – flush water and leaks from A-151 PUREX waste
AR-204	Receives waste from railroad cars during unloading and transfers the waste to the double shell tanks.
A-417	A-702 process condensate – condensate from the aging waste tanks
ER-311	Diversion box drain – B-Plant flush and condensate from ER-151 and ER-152
TX-302-C	TX-154 diversion box drain – rain, snow melt
U-301-B	Diversion box drain – processing and decontamination mixed waste solutions from U-151 and U-152, rain, snow melt
UX-302-A	Diversion box drain – snow melt, rain
S-304	Diversion box drain – rain
Vent Station Catch Tank	Drainage from cross-country transfer line pit.

3.3.4 Single-Shell Tank Bulk Runaway

All of the SSTs are evaluated for bulk runaway in this section. The analysis differs between tanks that are passively ventilated and tanks that are actively ventilated. Therefore, the analysis for bulk runaway is divided into two sections, passively ventilated tanks and actively ventilated tanks.

3.3.4.1 Passively Ventilated Tanks. Most of the SSTs (134 out of 149) are passively ventilated, which assures that decay heat removal is entirely by passive means. From the discussion in Section 3.2, temperatures in the tank waste will continue to decline, even as the waste slowly dries and the thermal conductivity decreases. This is true even if the tank is interim stabilized.

The conclusion that the time-averaged annual temperatures in the passively ventilated tanks are continuing to decline is also corroborated by the tank temperature trends over the past fifteen years. The historical temperature data show that the time-averaged annual temperatures within the solid waste are slowly decreasing (Brevick et al. 1994a, 1994b, 1994c, 1994d, 1994e, 1994f,

1994g, 1994h, 1994i, 1994j, 1994k, 1994l). Examination of tank headspace temperatures also indicate waste temperatures and heatloads are decreasing. Some specific aspects that may influence this trend are discussed in Appendix C, using tank A-101 as an example. Waste temperatures after interim stabilization have also continued to decline, consistent with the principal heatload from radioactive decay rates (Lechelt 1995). Of the 149 SSTs, 118 have been interim stabilized as part of an ongoing program.

Passively ventilated SSTs are assessed in Tables 3-5, 3-6, 3-7, and 3-8. Results show that a bulk runaway accident can be ruled out in connection with chemical heating. The times of cooling (t_c) are well below the 20 years of waste storage time. The largest t_c was about 3.1 years for tank A-101. The heat from chemical reactions in the wastes is safely removed by passive conductive means through the waste. That is, the values of t_c are much smaller than the corresponding adiabatic chemical runaway times since no bulk runaways occurred during the Hanford waste storage period.

Table 3-5. Assessment of Passively Ventilated 1,000,000 Gallon SSTs for Bulk Runaway.

Tank	Waste Height[1] (m)	t_c (years)	Tank	Waste Height[1] (m)	t_c (years)
A-101	8.8	3.1	AX-101	6.9	1.9
A-102	0.37	0.0055	AX-102	0.4	0.0052
A-103	3.4	0.47	AX-103	1.0	0.044
A-104	0.3	0.0030	AX-104	0.06	0.00015
A-105	0.2	0.0014	SX-113	0.37	0.0055
A-106	1.2	0.057	SX-115	0.24	0.057

Notes: [1] Data from Kummerer (1995).
t_c calculated using Equation 3-5; thermal diffusivity $\alpha = 2$ E-7 $m^2 s^{-1}$.

3.3.4.2 Actively Ventilated Tanks. There are fifteen actively ventilated SSTs (C-105, C-106, SX-101, SX-102, SX-103, SX-104, SX-105, SX-106, SX-107, SX-108, SX-109, SX-110, SX-111, SX-112, and SX-114). The assessment for seven of these tanks is straight forward; tanks SX-107 through SX-114 do not contain sufficient organic material to fuel a bulk runaway. Characterization data, waste transfer records (Agnew et al. 1996), and waste process histories (Brevick et al. 1997) indicate negligible TOC is contained in tanks SX-107 through SX-114. Furthermore, tanks SX-107, SX-108, SX-109, and SX-112 stopped receiving waste transfers before organic complexants were used at the Hanford Site in 1968 (see Appendix F).

For tanks C-105 and SX-101 through SX-106, it is necessary to calculate the time of cooling, t_c, and to determine what the time average temperature in the waste tanks would be under passive ventilation alone, $T_{w,p}$. Results are summarized in Table 3-9. Excluding tank C-106, the characteristic times of cooling are sufficiently short (much less than the storage time of over 17 years), and the temperatures under passive ventilation are less than the historical high

temperatures (T_{hist}), (i.e., the peak temperature maintained for a duration equal to or greater than the time of cooling). Therefore, bulk runaway is not credible for tanks C-105, and SX-101 through SX-106.

Table 3-6. Assessment of Passively Ventilated 758,000 Gallon SSTs for Bulk Runaway.

Tank	Waste Height[1] (m)	t_c (years)	Tank	Waste Height[1] (m)	t_c (years)
BY-101	3.6	0.52	TX-101	1.0	0.041
BY-102	3.4	0.44	TX-102	1.2	0.060
BY-103	3.9	0.60	TX-103	1.6	0.11
BY-104	3.3	0.44	TX-104	0.8	0.025
BY-105	4.6	0.82	TX-105	5.8	1.3
BY-106	6.1	1.5	TX-106	4.4	0.77
BY-107	2.6	0.27	TX-107	0.5	0.011
BY-108	2.3	0.21	TX-108	1.4	0.082
BY-109	4.1	0.66	TX-109	3.8	0.55
BY-110	3.8	0.57	TX-110	4.5	0.79
BY-111	4.4	0.77	TX-111	3.6	0.52
BY-112	2.9	0.33	TX-112	6.2	1.5
S-101	4.1	0.68	TX-113	5.8	1.3
S-102	5.3	1.1	TX-114	5.1	1.0
S-103	2.5	0.24	TX-115	6.1	1.5
S-104	2.9	0.33	TX-116	6.0	1.4
S-105	4.4	0.77	TX-117	6.0	1.4
S-106	5.2	1.1	TX-118	3.0	0.36
S-107	3.6	0.52	TY-101	1.3	0.068
S-108	5.8	1.3	TY-102	0.8	0.025
S-109	5.4	1.2	TY-103	1.7	0.11
S-110	6.6	1.7	TY-104	0.6	0.015
S-111	5.7	1.3	TY-105	2.3	0.21
S-112	6.1	1.4	TY-106	0.3	0.0044

Notes: [1] Data from Kummerer (1995).
t_c calculated using Equation 3-5, thermal diffusivity $\alpha = 2$ E-7 $m^2 s^{-1}$.

Table 3-7. Assessment of Passively Ventilated 530,000 Gallon SSTs for Bulk Runaway.

Tank	Waste Height[1] (m)	t_c (years)	Tank	Waste Height[1] (m)	t_c (years)
B-101	1.2	0.060	C-108	0.8	0.023
B-102	0.5	0.0093	C-109	0.8	0.023
B-103	0.7	0.021	C-110	2.0	0.16
B-104	3.6	0.52	C-111	0.7	0.021
B-105	3.0	0.36	C-112	1.2	0.052
B-106	1.3	0.066	T-101	1.4	0.082
B-107	1.7	0.11	T-102	0.5	0.0093
B-108	1.1	0.044	T-103	0.4	0.0071
B-109	1.4	0.074	T-104	4.3	0.74
B-110	2.5	0.24	T-105	1.1	0.047
B-111	2.4	0.22	T-106	0.4	0.0063
B-112	0.5	0.0093	T-107	1.9	0.14
BX-101	0.6	0.014	T-108	0.6	0.015
BX-102	1.0	0.041	T-109	0.7	0.021
BX-103	0.8	0.025	T-110	3.7	0.55
BX-104	1.1	0.047	T-111	4.4	0.77
BX-105	0.7	0.018	T-112	0.8	0.027
BX-106	0.6	0.015	U-101	0.4	0.0071
BX-107	2.4	0.24	U-102	3.7	0.52
BX-108	0.4	0.0071	U-103	4.5	0.79
BX-109	2.0	0.16	U-104	1.3	0.068
BX-110	2.0	0.16	U-105	4.1	0.66
BX-111	2.3	0.21	U-106	2.3	0.21
BX-112	1.7	0.11	U-107	3.9	0.60
C-101	1.0	0.041	U-108	4.5	0.80
C-102	4.1	0.68	U-109	4.5	0.79
C-103	2.1	0.18	U-110	1.9	0.15
C-104	2.9	0.33	U-111	3.2	0.41
C-107	3.3	0.44	U-112	0.6	0.016

Notes: [1] Data from Kummerer (1995).

Table 3-8. Assessment of Passively Ventilated 55,000 Gallon SSTs for Bulk Runaway.

Tank	Waste Height[1] (m)	t_c (years)	Tank	Waste Height[1] (m)	t_c (years)
B-201	3.8	0.58	T-201	3.8	0.58
B-202	3.6	0.51	T-202	2.8	0.31
B-203	6.7	1.8	T-203	4.6	0.84
B-204	6.6	1.7	T-204	5.0	0.99
C-201	0.3	0.0044	U-201	0.7	0.021
C-202	0.2	0.0016	U-202	0.7	0.021
C-203	0.7	0.021	U-203	0.5	0.0085
C-204	0.5	0.0085	U-204	0.5	0.0085

Notes: [1] Data from Kummerer (1995).
t_c calculated using Equation 3-5; thermal diffusivity $\alpha = 2$ E-7 $m^2 s^{-1}$.

Table 3-9. Assessment of Actively Ventilated SSTs for Bulk Runaway.

Tank	Waste Height[1] (m)	T_v[1] (°C)	T_w[1] (°C)	Heat Load[1] (W)	T_{hist}[2] (°C)	$T_{w,p}$[3] (°C)	t_c (years)	Bulk Runaway Credible
C-105	1.58	28	32	7,300	69	54	0.099	No
SX-101	4.36	30	53	3,700	81	55	0.77	No
SX-102	5.15	33	64	4,400	93	66	1.1	No
SX-103	6.16	47	79	8,100	98	86	1.5	No
SX-104	5.79	29	74	3,600	93	77	1.3	No
SX-105	6.43	30	81	3,700	96	83	1.6	No
SX-106	5.09	28	42	3,200	57	44	1.0	No

Notes: [1] Data from Kummerer (1995).
[2] Data from Brevick et al. (1994f and 1994h).
[3] Calculated using Equation 3-7.
t_c calculated using Equation 3-5, thermal diffusivity $\alpha = 2$ E-7 $m^2 s^{-1}$.

Tank C-106 was analyzed for bulk runaway potential in 1997 (Meacham et al. 1997). Due to its high heat load it required water for cooling. Consequently, tank C-106 contains an appreciable amount of water, and bulk runaway was ruled out based on an energy balance between the latent

heat of water (ΔH_v) and chemical energy potential (ΔH_r). The results of this analysis are shown in Table 3-10.

Table 3-10. Assessment of Tank C-106, Before Transfer, for Bulk Runaway.

Tank	Q (W)	$T_{v,p}$[1] (°C)	Oxalate[2] (kg)	H_2O (kg)	$-\Delta H_r$ (J)	ΔH_v (J)
C-106	32,200	>120	6.0 E4	1.9 E5	7.2 E10	4.4 E11

Notes: [1]Estimated tank waste headspace/liquid temperature under passive ventilation using Equation 3-2.
[2]TOC = (0.27) (kg Oxalate).

Speciation of organic in C-106 showed that the TOC was almost all low energy oxalate (Campbell et al. 1996). The oxalate inventory was converted to theoretical chemical energy inventory by multiplying by the heat of reaction for sodium oxalate combustion with sodium nitrate, 1.2 E6 J per kg of oxalate (Burger 1993). Water inventory was converted to energy inventory by multiplying by the latent heat of vaporization, 2.3 E6 J kg^{-1}. The sensible heat of water was conservatively excluded from the energy balance.

Between November 1998 and October 1999, approximately 80% of the waste in tank C-106 was transferred to tank AY-102 (Cuta et al. 2000). The post-transfer heat load in C-106 was analyzed and was shown to be insufficient to cause the waste to self-boil. Table 3-11 shows a post-transfer analysis of tank C-106.

Table 3-11. Assessment of Tank C-106, After Transfer, for Bulk Runaway.

Tank	Q[1] (W)	$T_{v,p}$[2] (°C)	Oxalate[3] (kg)	H_2O[1,4] (kg)	$-\Delta H_r$ (J)	ΔH_v (J)
C-106	2,600	27	6.0 E4	7.1 E4	7.2 E10	1.6 E11

Notes: [1] Data from Ogden et al. 2000.
[2] Estimated tank waste headspace/liquid temperature under passive ventilation using Equation 3-2.
[3] Conservative assumption that no oxalate was transferred to AY-102.
[4] Conservative assumption that the fraction of water contained in the waste did not increase after transfer.
[5] Data from Cuta et al. 2000.

From Table 3-11, the latent heat of water vaporization (ΔH_v) exceeds the theoretical chemical energy potential ($-\Delta H_r$) in C-106. Bulk runaway is not possible under current waste storage conditions. Even if active ventilation was lost, the heat load remaining would be insufficient to boil off the water. Due to the reduced heat load, controls are no longer required for C-106 to prevent a bulk chemical runaway.

3.3.5 Inactive Miscellaneous Underground Storage Tank Bulk Runaway

To be considered an IMUST a tank must be physically or administratively isolated, potentially contain radioactive material, at least partially below grade, and is not located within a major facility. There are currently 45 RPP "owned" IMUSTs. These tanks consist of catch tanks,

diverter tanks, settling tanks, underground drain tanks, flush tanks, decontamination tanks, receiver tanks, and vault tanks. Seven of these tanks have also collected more than one designation over the years. Specifically, tank 200-W-7 is referred to as 243-S-TK-1 in some documents, 216-BY-201 is also known as 241-BY-201, 241-B-301 is also called 241-B-301B, 241-C-301 corresponds to 241-C-301C, 241-SX-302 is sometimes called SX-304, 241-T-301B sometimes has the "B" designation dropped, and 241-TX-302XB has an alias of 241-TX-302.

3.3.5.1 Storage Time Assessment. The IMUSTs are passively ventilated assuring that decay heat removal is entirely by passive means. From the discussion in section 3.3.3.5, temperatures in the tank waste will continue to decline, even as the thermal conductivity decreases, if the past storage time (t_s) exceeds the sum of the cooling time (t_c) and decay-based dry out time (t_p). The mass of liquid within each tank (M_t) was found by summing the mass of supernatant with the mass of interstitial liquid assuming a void space of 0.3. Table 3-12 shows the IMUSTs that were assessed in this fashion. Bulk runaway is not credible for these tanks.

Table 3-12. Assessment of Inactive Miscellaneous Underground Storage Tanks for Bulk Runaway. (2 sheets)

Tank	Waste Height (in)	M_t (kg)	t_c [1] (yr)	t_p [2] (yr)	t_s (yr)
240-S-302	20.4[3]	379	0.30	0.11[4]	13[5]
241-A-302B	30[5]	9,535	0.24	6.97[4]	20[5]
241-B-301	2.75[7]	2,040	0.0002	1.42[4]	16[5]
241-B-302B	35[5]	16,833	0.30	6.54[4]	15[5]
241-BX-302A	10.25[5]	948	0.30	0.29[4]	15[5]
241-BX-302B	18[5]	1,435	0.0083	1.34[4]	15[5]
241-BX-302C	16[6]	1,586	0.0065	1.49[4]	15[5]
241-C-301	53.5[6]	15,804	0.073	11.0[4]	17[5]
241-S-302A	--[8]	530	0.29	0.16[4]	9[5]
241-SX-302	14.25[6]	2,347	0.0052	0.50[4]	16[5]
241-TX-302A	21.5[6]	2,896[6]	0.012	0.88[4]	18[5]
241-TX-302B	14.75[6]	1,427	0.0056	0.56[4]	16[5]
241-TX-302B(R)	96[9]	45,425	0.24	16.9[3,4]	46[5]

Table 3-12. Assessment of Inactive Miscellaneous Underground Storage Tanks for Bulk Runaway. (2 sheets)

Tank	Waste Height (in)	M_t (kg)	t_c[1] (yr)	t_p[2] (yr)	t_s (yr)
241-TX-302XB	6.5[6]	1,049	0.0011	0.39[4]	15[6]
241-TY-302A	6.75[6]	511	0.0012	0.15[5]	19[5]
241-Z-8	7[5]	568	0.24	0.65[5]	38[5]

Notes:
1 t_c calculated using thermal diffusivity of 2 E-7 $m^2 s^{-1}$.
2 Waste dry out calculated using (3-12) with A_t from Caldwell et al. (1993).
3 Interstitial liquid estimated in Caldwell et al. (1993).
4 Data on soil depth from reference drawings given in Caldwell et al. (1993).
5 Data from Caldwell et al. (1993).
6 Data from Neilsen (1992).
7 Data from Stabilization Evaluation Form Tank B-301-B, completed by Allen Alstad (1985).
8 Liquid volume estimated after filling with grout to prevent leakage (Neilsen 1992).
9 Assumes a completely full tank.

3.3.5.2 Isolation Date Assessment. A number of tanks can be evaluated based on process history such as the date they were taken out of service. Complexants were not used in quantity, outside of C Plant, until 1968 (ERDA 1975). Tanks that did not receive waste from C Plant and were taken out of service prior to 1968 do not contain complexants. Table 3-13 lists the tanks that were taken out of service before 1968 that process history shows did not receive waste from the C Plant. Bulk chemical runaway is not credible for these tanks.

Table 3-13. Inactive Miscellaneous Underground Storage Tanks Isolated Prior to 1968.

Tank	Out of Service Date[1]	Tank	Out of Service Date[1]
241-ER-311A	1954	244-TXR-002	1956
244-BXR-001	1957	244-TXR-003	1956
244-BXR-002	1957	244-UR-001	1957
244-BXR-003	1957	244-UR-002	1957
244-BXR-011	1956	244-UR-003	1957
244-TXR-001	1956	244-UR-004	1957

Notes:
1 Data from Caldwell et al. (1993).

3.3.5.3 Special Case Tanks. The seventeen remaining IMUSTs required individual assessments. The process history of each of these tanks was examined and the potential sources of waste analyzed.

Tank 200-W-7. 200-W-7 is a catch tank previously associated with a personnel decontamination facility. The only input to this IMUST was effluent from personnel decontamination from the Decontamination Trailer. This tank contains soap, water, and low levels of contamination rinsed from onsite workers per a review of process records documented in Stickney et al. 1998. This tank is also known as 243-S-TK-1. Due to the low levels of contamination present, bulk chemical runaway is not credible.

Tank 209-E-TK-111. Tank 209-E-TK-111 is a drain tank formerly associated with the Critical Assembly Room (CAR). The tank was used to hold condensate from the facility prior to its release to a crib. This tank was routinely sampled prior to discharge. The present contents of the tank are estimated to consist of residual water from the condensate collection and low levels of plutonium (Stickney et al. 1998). Complexants were not produced or used in the CAR (Caldwell et al. 1993). Because complexants are not present in the condensate, bulk chemical runaway is not credible.

Tank 216-BY-201. 216-BY-201 is a supernatant disposal flush tank located between the 241-BY Tank Farm and the 216-B Cribs. This tank is also known as 241-BY-201. 216-BY-201 received waste from the 241-BY tanks and the TBP waste line en-route to the 216-B Cribs (Stickney et al. 1998). The contents of 216-BY-201 are bound by the contents of the 241-BY Tanks. Process history and sampling data of the 241-BY tanks show that an organic complexant reaction cannot be initiated. Therefore, bulk chemical runaway is not credible in 216-BY-201.

Tanks 231-W-151-001 and 231-W-151-002. The 231-W-151 tanks (231-W-151-001 and 231-W-151-002) received waste from about 75 floor drains in Building 231-Z. Drainage was received into 231-W-151-002, which overflowed into 231-W-151-001. The overflow from 231-W-151-001 emptied to crib 216-Z-7. By 1974 the inlets to these tanks had been blanked off. Process history does not support the presence of organic salts per a review of process records documented in Caldwell et al. 1993. Therefore, bulk chemical runaway is not credible for these tanks due to insufficient organic complexants.

Tanks 241-AX-151CT, 241-AX-151-TK-D, 241-AX-151-TK-E, 241-AX-151-TK-F, and 241-AX-151-TK-G. The 241-AX-151 diverter station is a partially below grade structure. It station consists of four diverter tanks that were used in the routing of liquids around the 241-AX Tank Farm, and a catch tank (241-AX-151CT) that received run-off and spills or leakage from transfers and line flushes. The contents of the diverter tanks (241-AX-151-TK-D, -TK-E, -TK-F, and -TK-G) will reflect the contents of the 241-AX Tank Farm. While it cannot be determined which transfers had spills to the catch tank, it is expected that the contents are bound by the composition of the wastes in the 241-AX Tank Farm (Stickney et al. 1998). Process history, sample analysis, and propagation testing of the wastes in the 241-AX Tank Farm show that an organic complexant reaction cannot be initiated. Consequently, bulk chemical runaway is not credible in 241-AX-151CT, 241-AX-151-TK-D, 241-AX-151-TK-E, 241-AX-151-TK-F, and 241-AX-151-TK-G.

Tanks 241-BY-ITS2-TK-1 and 241-BY-ITS2-TK-2. These tanks were components of the ITS-2 In-Tank Solidification System. ITS-2 was used to remove water and other volatile components from 241-BY-112. Tank 241-BY-ITS2-TK-1 is a vapor condenser and received condensate from the heated in ground waste tank. Organic complexants are extremely low volatility, therefore the condensate would have a lower content of complexant than the source tank. Since process history and sample data shows the source tank (241-BY-112) to have low complexant concentrations (section 4.5.4), bulk chemical runaway is not credible in 241-BY-ITS2-TK-1. Tank 241-BY-ITS2-TK-2 is a heater flush tank that received decontamination solution after cleaning the ITS-2 heater assemblies. The composition of the contents is bound by the contents of 241-BY-112. Therefore, bulk chemical runaway is not credible in 241-BY-ITS2-TK-2.

Tanks 241-S-302B and 241-TY-302B. Tanks 241-S-302B and 241-TY-302B were isolated and stabilized in 1984. The stabilization evaluation forms listed them as completely empty based on solids and liquid level measurements (Neilsen 1992). Since both these tanks were found to be empty, a bulk chemical runaway scenario is not credible for these tanks.

Tank 241-T-301B. Tank 241-T-301B is a catch tank that received drainage from four diversion boxes: 241-T-151, 241-T-152, 241-T-153, and 241-T-252 (Caldwell et al. 1993). 241-T-301B collected runoff, leaks, and line flushes associated with waste transfers in the T Tank Farm. The contents of 241-T-301B are thus bound by the contents of the T Tank Farm. The heat load for all the tanks in the T Tank Farm has been shown to be insufficient to cause bulk chemical runaway, therefore bulk chemical runaway is not credible for this catch tank.

Tank 242-T-135. The 242-T-135 tank is a decontamination liquid storage tank. It provided decontamination solutions to the feed tank, evaporator, cyclone separator, and scrubber of the 242-T Evaporator. 242-T-135 was not used for processing or collecting waste (Stickney et al. 1998). Since process history shows that this tank does not contain a radiological heatload, bulk chemical runaway is not credible.

Tank 242-TA-R1. 242-TA-R1 is a receiver tank located at the bottom of the 242-TA receiver vault. Tank 242-TA-R1 was used to neutralize Z-Plant acid waste. The composition of the waste is known from process design criteria. The waste did not contain organics (Stickney et al. 1998). Therefore, process history of Z-Plant shows that 242-TA-R1 did not receive complexant bearing waste. Consequently, bulk chemical runaway is not credible.

Bulk chemical runaway is not possible in any of the 45 IMUSTs. A tank-by-tank summary of the analysis that lead to this conclusion is given in Table 3-14.

Table 3-14. Bulk Chemical Runaway Analysis Summary for All Inactive Miscellaneous Underground Storage Tanks.

Tank	Result	Tank	Result	Tank	Result
200-W-7	1	241-BX-302B	3	241-TY-302B	6
209-E-TK-111	2	241-BX-302C	3	241-Z-8	3
216-BY-201	1	241-BY-ITS2-TK-1	1	242-T-135	2
231-W-151-001	2	241-BY-ITS2-TK-2	1	242-TA-R1	2
231-W-151-002	2	241-C-301	3	244-BXR-001	5
240-S-302	3	241-ER-311A	5	244-BXR-002	5
241-A-302B	3	241-S-302A	3	244-BXR-003	5
241-AX-151-CT	4	241-S-302B	6	244-BXR-011	5
241-AX-151-TK-D	4	241-SX-302	3	244-TXR-001	5
241-AX-151-TK-E	4	241-T-301B	3	244-TXR-002	5
241-AX-151-TK-F	4	241-TX-302A	3	244-TXR-003	5
241-AX-151-TK-G	4	241-TX-302B	3	244-UR-001	5
241-B-301	3	241-TX-302B(R)	3	244-UR-002	5
241-B-302B	3	241-TX-302XB	3	244-UR-003	5
241-BX-302A	3	241-TY-302A	3	244-UR-004	5

Notes:
[1] Assessment of waste transfer records and process history indicate low complexant content.
[2] Assessment of process history indicates complexants were not constituents of source waste.
[3] Assessment of the storage time shows that it exceeds the cooling and waste decay dry out time.
[4] Assessment of process history, sample analysis, and propagation testing indicates the waste will not react.
[5] Tank received no waste after complexants were introduced in 1968 (ERDA 1975).
[6] Process records indicate these tanks to be empty (Neilsen 1992).

3.4 BULK RUNAWAY HAZARD POTENTIAL AND ACCIDENT FREQUENCY

There is no potential for bulk runaway under current waste storage conditions. Analyses show that interim stabilization, waste drying by evaporation, and loss of active ventilation could not initiate a bulk runaway.

3.5 BULK RUNAWAY CONTROLS

No active controls are required to prevent bulk runaway under current waste storage conditions and tank configurations. Waste transfers do not change the results of this assessment if the total heatloads remain below about 21,700 watts. However, if waste transfers increase the heatload to above 21,700 watts, then the tank needs to be evaluated for bulk runaway as described in Section 3.3.1 for tanks AY-102, AZ-101, and AZ-102.

Operations that could significantly increase bulk waste temperatures (e.g., retrieval), or operations that could significantly lower the ability of a tank to dissipate heat (e.g., installation of an insulating barrier) require analyses to conclude that bulk runaway is not possible under any new conditions.

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4.0 PROPAGATION

The propagation accident scenario, screening criteria, waste assessment, hazard potential, and controls are summarized in this section. The derivation and basis for the screening criteria are described in Appendix G.

4.1 PROPAGATION ACCIDENT SCENARIO

The scenario for point source ignition is the following: (1) combustible waste is created by concentrating and drying the organic complexants stored in the tanks; (2) an ignition source of sufficient energy and temperature contacts the combustible waste and a propagating reaction is initiated; (3) the combustion front spreads through the waste over-pressurizing the tank, and radioactive and toxic materials are released to the environment; and (4) the reaction continues until all contiguous combustible waste is consumed.

4.2 PROPAGATION SCREENING CRITERIA

In contrast to bulk runaway, a deflagration propagates by thermal energy transfer (AIChE 1995). Given the presence of an adequate amount of oxidizer ($NaNO_3/NaNO_2$) and an ignition source, sustained propagation depends on the fuel concentration and the absence of diluents such as water. Conditions that could support combustion were examined both theoretically (Section 4.2.1) and experimentally (Section 4.2.2).

4.2.1 Theoretical Fuel and Moisture Requirements

Conditions that could support combustion were examined theoretically and the derivation is shown in Appendix G. The minimum theoretical chemical energy (in MJ per kg of waste) necessary to sustain propagation is given by Equation 4-1:

$$-\Delta H_{min} > 1.2 + 4.5\, x_w \qquad (4-1)$$

Where x_w is the mass fraction of water. For dry material, the x_W term drops out and the minimum chemical energy is simply 1.2 MJ kg^{-1}. This criterion is consistent with the 0.71 to 1.25 MJ kg^{-1} (170 to 300 cal g^{-1}) range found in the literature for materials susceptible to propagation (AIChE 1995). However, direct testing of the materials is recommended to determine a more accurate threshold for propagation (AIChE 1995).

The criterion for propagation can also be expressed in terms of TOC concentration considering sodium acetate as a representative organic. The equivalent TOC (fuel) concentration is simply the minimum energy requirement ($-\Delta H_{min}$) divided by the heat of reaction ($-\Delta H_{rx}$) for sodium

acetate combustion with sodium nitrate [about 27.1 MJ kg^{-1} from Burger (1993)]. It is also important to note that Equation 4-1 is not appropriate for values of x_w greater than about 0.2, since the liquid phase now becomes the continuous phase (Fauske et al. 1996). For such conditions the contact temperature T_i will not exceed the boiling point of the salt solution (about 120 °C) which is well below T_{ig} values of interest. Therefore, the criterion for propagation in terms of wt% TOC (as sodium acetate) becomes

$$\text{wt\% TOC (as Sodium Acetate)} > (4.5 + 17\,x_w)\,; \quad \text{where } x_w < 0.2 \qquad (4-2)$$

4.2.2 Experimental Fuel and Moisture Requirements

The measurements made with various organic waste simulants are summarized in this section. Measured quantities of key interest include ignition and combustion temperatures, the fuel concentration required to support propagating reactions, and the water concentration that will inhibit propagation. A summary of key data is provided below; further details are provided in Appendix G, and in Fauske et al. (1996) and Fauske (1996a, 1996b).

4.2.2.1 Reactive System Screening Tool Combustion Tests with Waste Simulants. Organic complexant-sodium nitrate/nitrite mixtures were tested in the Reactive System Screening Tool (RSST) (Fauske and Leung 1985). In these tests, sizeable samples (about 10 grams) were heated at 1 °C min^{-1} under low heat loss conditions. Results are shown in Table 4-1. As the sample was heated to above the reaction onset temperature, the thermal energy produced by the reaction caused the sample to self-heat. The rate and extent of this self-heating provide direct evidence of the character of the reaction that has taken place.

Two distinct types of behavior were seen depending on sample reactivity: (1) a relatively slow heat-up rate that is typical of an Arrhenius or bulk runaway reaction (any material that contains chemicals that react exothermically will exhibit this behavior) and (2) a sharp transition to a very high self-heating rate indicating ignition and the passing of a reaction front. For materials that exhibit this behavior, propagation is possible given a sufficient initiator.

It is important to note that the onset of propagating reactions in the RSST tests occurs when the entire sample has essentially reached the ignition temperature. This is in contrast to the tube propagation tests discussed in Section 4.3.2.2, in which propagation can occur at ambient waste temperature given an adequate ignition source. The organic simulant tests included a 4:1 mass ratio of nitrate to nitrite. Table 4-1 shows that the lowest ignition temperature was about 220 °C, which is more than 100 °C higher than the maximum waste temperatures.

It may also be noted from Table 4-1 that several compounds did not support propagation, including dibutyl and tributyl phosphates, or their salts such as aluminum and sodium dibutyl phosphate. This behavior can be related to early decomposition of these compounds (in the 150 to 200 °C temperature range) both with and without the presence of the nitrate-nitrite

oxidizer. Sodium oxalate also did not support propagation, even under stoichiometric fuel-oxidizer conditions.

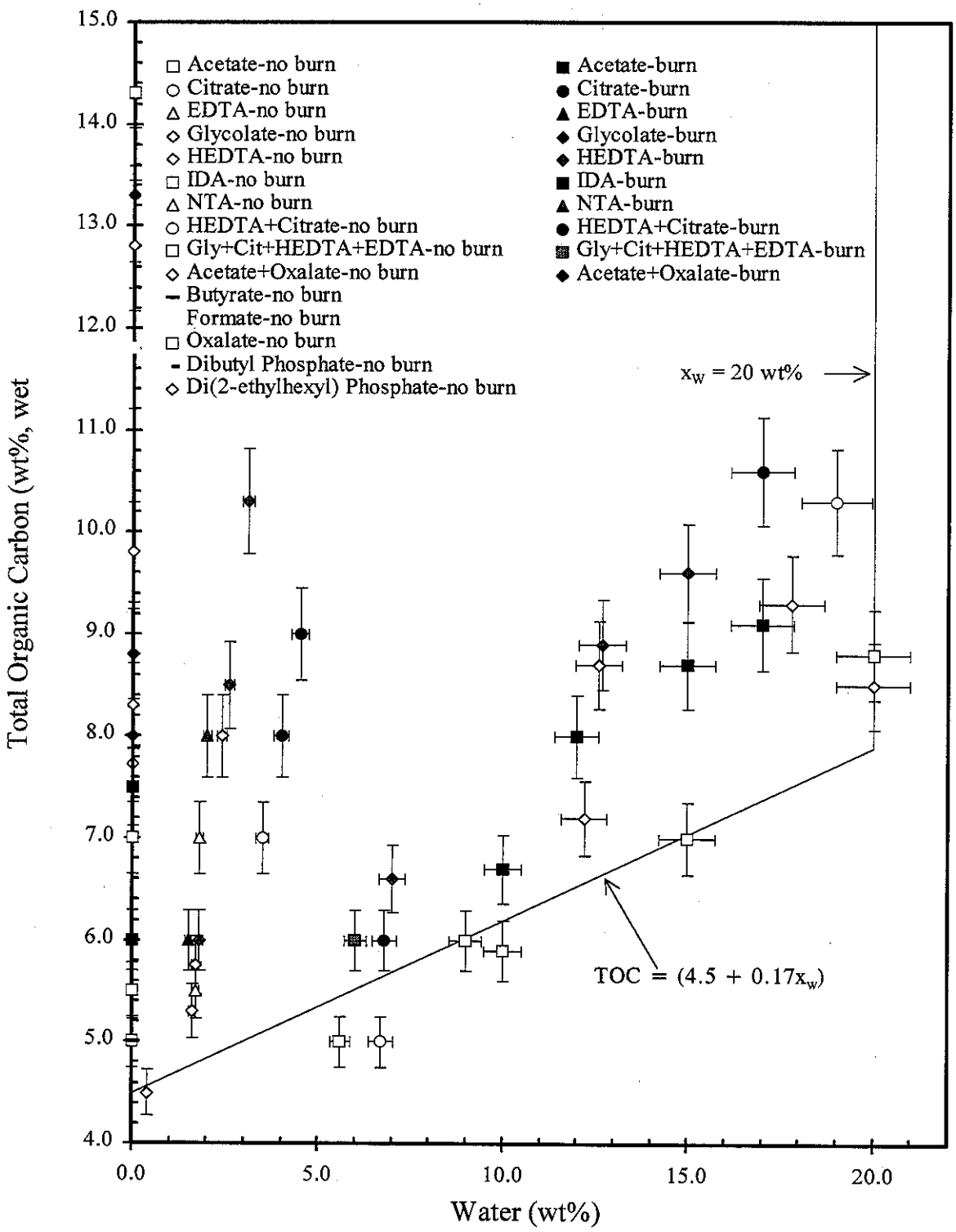
Table 4-1. Summary of RSST Tests on Organic Simulants[1].

TOC (wt%, dry)	Description	Propagation Observed	Ignition Temperature (°C)
3.5	Sodium Acetate	No	NA
5.0[2]	Sodium Acetate	No	NA
6.0	Sodium Acetate	Yes	300
7.0	Sodium Acetate	Yes	300
8.0	Sodium Citrate	Yes	230
6.0[3]	Sodium HEDTA	Yes	220
14[4]	Sodium Oxalate	No	NA
5.0	Sodium Stearate	No	NA
6.0	Sodium Stearate	No	NA
9.0	Sodium Stearate	Yes	260
5.0	Sodium HEDTA + Sodium Citrate	Yes	230
6.0	Sodium Glycolate + Sodium Citrate + Sodium HEDTA + Sodium EDTA	Yes	230
11	Tributyl Phosphate	No	NA
7.9	Aluminum Dibutyl Phosphate	No	NA
9.3	Sodium Dibutyl Phosphate	No	NA

Notes: NA = Not Applicable.
[1] Data from Fauske (1994), Fauske (1996a), and Fauske et al. (1996).
[2] This test was repeated six times. Sodium hydroxide (0.7 and 1.4 molar) was added to two of the tests with no change in results (Fauske 1994).
[3] This test was repeated three times with different inerts added to the mixture. No changes in propagation were observed, but ignition temperatures increased when several inerts were added (Fauske 1996a).
[4] Stoichiometric mixture of fuel and oxidizer.

4.2.2.2 Propagation Tests with Waste Simulants. The effect of water on propagation was evaluated with tube propagation tests. The test apparatus consisted of a thin, insulated stainless-steel cylinder, 25 mm in diameter and 100 mm tall, filled with the test material (see Appendix G). The reaction was ignited at the top, and the progress of the reaction, if any, was monitored by four thermocouples spaced 20 to 30 mm apart. Again, one of two distinct behaviors was observed. The reaction proceeded to the bottom of the cylinder in samples capable of supporting a propagation. If the reaction would not ignite or failed to sustain combustion, the sample did not support propagation. Results are summarized in Figure 4-1, and experimental details are provided in Appendix G.

Figure 4-1. Tube Propagation Test Results for Organic Waste Simulants.



Examining Figure 4-1, test results showed that more than 4.5 wt% TOC was required to support propagation. The TOC concentration required to support propagation increased with the water content of the mixture, and all of the mixtures that supported propagation exceeded the theoretical fuel-water criterion. Stoichiometric mixtures of fuel and oxidizer failed to propagate when 20 wt% water was present.

The amount of TOC required for propagation varied based on energetics. More energetic compounds required lower TOC concentrations (e.g., HEDTA and EDTA), while less energetic compounds required higher TOC concentrations (e.g., NTA). Several compounds did not sustain propagation, even when no water was added to the mixture. Compounds that did not support propagation included butyrate, formate, oxalate, dibutyl phosphate, and di(2-ethylhexyl) phosphate.

The simulant tests provide a conservative evaluation of the organic hazard. The condition for fuel and oxidizer reactions are optimized by the fuel-to-oxidizer ratio, thorough mixing, use of small particles, and absence of complex mixtures of diluents. Many of the diluents are known to form hydrates that tightly bind water (e.g., hydroxy salts of aluminum and iron). However, all possible components and mixtures of waste components cannot be evaluated so potential catalysis or synergistic effects (e.g., low melting eutectic mixtures) cannot be ruled out based on the simulant tests. Therefore, propagation tests were conducted on waste samples and the results are discussed in Section 4.4.4.5. Simulants with compositions approximating those found in tanks were tested and no catalytic or synergistic effects were found (Appendix G).

4.3 PHENOMENA THAT FURTHER MITIGATE THE COMPLEXANT HAZARD

4.3.1 Tank Waste Oxidizer Concentration

As shown earlier in the traditional fire triangle (Figure 2-1), fuel, oxidizers, and heat (initiators) must all be present in sufficient quantities to sustain propagation. In addition to having low fuel concentrations, sampling data and testing show that some tanks also have low oxidizer concentrations. That is, even if it were assumed that these tanks contained more than 4.5 wt% TOC, they do not have sufficient oxidizer (sodium nitrite/nitrate) to combust with the minimum required fuel concentration.

For complete combustion, the stoichiometry for oxidation of sodium acetate by sodium nitrate or nitrite is the following (Burger 1993):

$$NaC_2H_3O_2 + 1.6\,NaNO_3 = 1.3\,Na_2CO_3 + 0.7\,CO_2 + 1.5\,H_2O + 0.8\,N_2 \qquad (4-3)$$

$$NaC_2H_3O_2 + 2.67\,NaNO_2 = 1.83\,Na_2CO_3 + 0.17\,CO_2 + 1.5\,H_2O + 1.33\,N_2 \qquad (4-4)$$

The stoichiometry for combustion varies for different organic compounds, and the oxidizer concentration requirements range between 0.25 grams of sodium nitrate per gram of sodium oxalate to 2.17 grams of sodium nitrate per gram of sodium HEDTA. Oxidizer requirements for the complexants and their degradation products are shown in Table 4-2.

Table 4-2. Stoichiometric Oxidizer (Sodium Nitrate/Nitrite) Requirement for Combustion.

Fuel	Sodium Nitrate Requirement (g of $NaNO_3$/g of TOC)	Sodium Nitrite Requirement (g of $NaNO_2$/g of TOC)
Sodium Oxalate	1.8	2.5
Sodium Formate	1.9	2.5
Sodium IDA	2.6	3.5
Sodium Citrate	3.1	4.2
Sodium Glycolate	3.3	4.4
Sodium NTA	3.5	4.7
Sodium Acetate	4.1	5.5
Sodium EDTA	4.3	5.8
Sodium HEDTA	5.0	6.7

The stoichiometric sodium nitrate and sodium nitrite requirements for 4.5 wt% TOC as sodium acetate (the minimum theoretical fuel concentration that supports propagation) are 26 and 35 wt%, respectively. Comparing the stoichiometric oxidizer requirements with the sodium nitrate and sodium nitrite tank waste concentrations from characterization data (Kupfer and Leclair 1997), 45 tanks contain waste that is low in oxidizer if they hypothetically contained 4.5 wt% TOC (Table 4-3).

Table 4-3. Tank Wastes with Low Oxidizer (Sodium Nitrate/Nitrite) Concentrations.

Tank	Tank	Tank	Tank	Tank
A-104	BX-102	C-105	C-204	T-112
A-105	BX-103	C-106	SX-113	T-201
AW-105	BX-104	C-107	T-102	TX-109
AX-104	BX-106	C-108	T-103	TY-104
AY-102	BY-102	C-109	T-105	U-110
B-108	BY-112	C-111	T-106	U-201
B-109	C-102	C-201	T-107	U-202
B-201	C-103	C-202	T-109	U-203
BX-101	C-104	C-203	T-110	U-204

4.3.2 Organic Aging

Experiments, theory, and analyses of tank samples indicate that organic complexants decompose to low energetic products under the chemical and radiological conditions found in the Hanford Site tanks. This process, called aging, substantially lowers the energy content and ultimately eliminates the hazards associated with organic complexants. The organic complexants age to low energy compounds (such as formate, oxalate, and carbonate) which do not support propagation.

The complexant-containing wastes have been stored in tanks for more than 20 years. During that time, the organic complexants were exposed to radiation, temperatures of up to 140 °C (284 °F), and a reactive chemical environment. The wastes contain high concentrations of hydroxide, nitrate, nitrite, aluminate, and transition metal oxides including noble metals, radioactive elements (e.g., uranium, plutonium, cesium, and strontium), and many other species that could act as catalysts or promoters that affect aging pathways or outcomes.

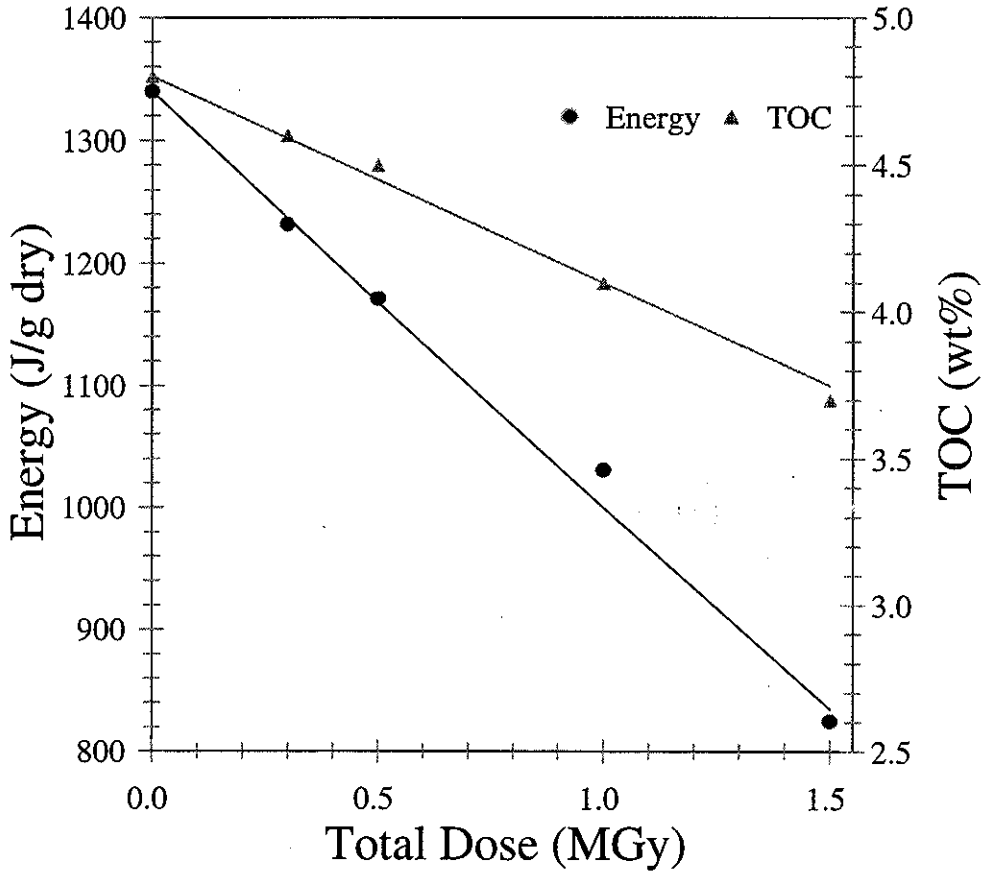
4.3.2.1 Parameters Affecting the Rate of Aging. Extensive studies of both thermal and radiolytic degradation reactions of organic complexants have been performed (Ashby et al. 1993, 1994, Barefield et al. 1995, 1996, Meisel et al. 1991a, 1991b, 1992, 1993, 1997, Camaioni et al. 1994, 1995, 1996, 1998). Several studies of nonradioactive waste simulants (Delegard 1987, Ashby et al. 1994, Meisel et al. 1993) show that organic complexants are sensitive to temperature and will decompose thermally. An early study by Delegard (1987) reported that HEDTA and glycolate degraded thermally producing hydrogen, nitrogen, nitrous oxide, and ammonia gases. Products identified included ethylenediaminetriacetate (ED3A) and oxalate from HEDTA, and oxalate from glycolate. Ashby et al. (1994) reported that thermal aging of HEDTA produced ethylenediaminediacetate (EDDA), iminodiacetate (IDA), glycine, and

formate in addition to ED3A and oxalate. Glycolate aged to produced formate and oxalate. These reactions required nitrite and were found to be catalyzed by aluminum species. Citrate was shown to decompose thermally producing oxalate and acetate (Ashby et al. 1994). The reaction was found to be catalyzed by hydroxide.

Experiments with waste simulants (Camaioni et al. 1994, 1995, 1996, 1998) show that organic complexants age to lower energy products when subjected to thermal and radiolytic conditions analogous to tank waste environments. In these experiments, the waste simulants were heated and irradiated, and the products were measured. The simulant was indicative of the waste from B Plant (Carlson and Babad 1996) and contained many inorganic species including nitrate, nitrite, hydroxide, and iron and aluminum species, and the major organic complexants, HEDTA, EDTA, citrate, and glycolate.

Results (Figure 4-2) show that the energy and TOC concentration decreased at different rates. While the TOC decreased to 78% of its original concentration, the energy decreased to 62% of its original value. This is because some products like oxalate have a low chemical energy potential but take some time to be converted to carbonate. Principal aging products included carbonate, formate, oxalate, and chelator fragments such as ED3A, NTA, IDA, and EDDA (Camaioni et al. 1998). Analyses of tank waste samples show these same degradation products.

Figure 4-2. Decrease in Energy and Total Organic Carbon Concentration as a Function of Total Dose for B Plant Process Flow Sheet Waste Simulant.



4.3.2.2 Confirmation of Organic Aging from Waste Sample Data. Many tank waste samples have been analyzed for TOC and oxalate ion (an aging byproduct), and wastes with high TOC concentrations were extensively analyzed for other organic constituents. The results show that the organic complexants are being oxidized to less energetic compounds and in some cases, the original complexants have been almost completely converted to oxalate and carbonate ions.

Tanks with Oxalate Data. The oxalate ion content can be determined by ion chromatography, which is routinely performed on tank waste to determine the concentrations of the major inorganic anions. In Table 4-4, the oxalate ion data have been compiled and compared with the measured TOC content for the 32 SSTs with more than 0.1 wt % TOC.

Table 4-4. Total Organic Carbon and Oxalate in Single-Shell Tanks.

Tank	Mean TOC[1] (wt%, wet)	TOC Inventory[2] (kg)	Oxalate Inventory[3] (kg)	Average TOC as Oxalate[4] (wt%)(sd)[5]
A-101	0.31	19,600	31,300	44 (7)
A-102	1.11	3,910	3,140	22 (2)
AX-101	0.62	3,050	4,250	38 (33)
AX-102	1.87	3,290	1,450	12 (1)
AX-103	0.52	3,260	5,130	43 (2)
BX-110	0.15	2.070	4,710	62 (34)
BY-101	0.48	12,300	33,400	74 (25)
BY-102	0.38	6,940	30,400	>99 (33)
BY-104	0.67	6,810	13,100	52 (21)
BY-105	0.73	24,200	84,300	95 (52)
BY-106	0.51	11,500	31,800	75 (15)
BY-107	0.52	7,630	22,000	79 (19)
BY-108	0.39	5,820	9,750	46 (11)
BY-109	0.33	11,900	37,100	85 (70)
BY-110	0.64	16,700	26,300	43 (11)
BY-111	0.55	16,700	52,800	86 (33)
BY-112	0.71	13,600	47,700	96 (44)
C-104	1.00	16,100	6,390	11 (4)
C-106	1.34	15,200	60,200	>99 (25)
S-101	0.22	5,160	10,200	52 (38)
S-102	0.33	11,800	25,400	57 (17)
S-106	0.23	6,110	13,000	58 (16)
S-107	0.20	4,150	10,200	67 (11)
S-111	0.17	6,600	17,300	71 (19)
SX-101	0.53	15,800	32,400	56 (41)
SX-106	0.39	13,300	17,600	36 (39)
U-102	0.74	15,900	10,300	18 (3)
U-103	0.64	24,000	7,690	9 (2)
U-105	1.23	30,200	24,100	22 (3)
U-106	2.16	29,600	12,700	12 (2)
U-107	0.18	4,950	6,860	38 (16)
U-108	0.42	12,900	12,700	27 (3)

Notes: [1] Mean TOC concentration calculated from the best basis inventory.
[2] TOC inventory presented in the current tank characterization reports.
[3] Oxalate ion inventory calculated from the information in the current tank characterization reports.
[4] Average % carbon as oxalate ion evaluated from inventory or sampling data.
[5] Uncertainty calculated using the following:

$$sd = \sqrt{\left(\frac{a}{b}\right)^2\left(\frac{\sigma_a}{a}\right)^2 + \left(\frac{b}{a}\right)^2\left(\frac{\sigma_b}{b}\right)^2}$$

where sd = standard deviation, a = TOC measurements, and b = oxalate measurements.

The sample-based mean TOC concentrations and TOC inventories (Kupfer and Leclair 1997) are shown in the first two columns of Table 4-4. The sample-based oxalate ion inventories, and the average percentage of organic carbon in the form of oxalate ion are tabulated in the next two columns. The standard deviations (sd) for the TOC and oxalate analyses provided in the characterization reports were used to estimate the uncertainty in the percentage of organic carbon in oxalate.

Seven of the 32 tanks shown in Table 4-4 had oxalate concentrations sufficient to account for more than 75 % of the TOC (tanks BY-102, BY-105, BY-107, BY-109, BY-111, BY-112 and C-106). Ten tanks had oxalate concentrations sufficient to account for 50 to 75 % of the measured TOC (BX-110, BY-101, BY-104, BY-106, S-101, S-102, S-106, S-107, S-111, and SX-101). Fourteen tanks had oxalate concentrations sufficient to account for 10 to 50 % of the TOC (A-101, A-102, AX-101, AX-102, AX-103, BY-108, BY-110, C-104, SX-106, U-102, U-105, U-106, U-107, and U-108).

Aging converts the original organic complexants into an array of new compounds and eventually provides carbonate as the final product. Oxalate and formate, which are eventually oxidized to carbonate ion, are the major organic products of the aging reactions. When their concentrations are high and they account for the major portion of the organic content, it is evident that the aging process has occurred to a significant extent. Additional organic speciation was performed on wastes with relatively high TOC to examine the intermediate organic compounds formed during the aging process.

Detailed Organic Speciation. Tank wastes speciated thoroughly include A-101, A-102, AN-107, AW-101, AX-102, BY-102, BY-104, BY-105, BY-107, BY-110, C-104, C-105, C-201, S-102, U-105, U-106, U-107, and U-108. Analyses show that these wastes contain some of the original complexants (i.e., citrate, EDTA, glycolate, and HEDTA), but these complexants have aged producing degradation products such as acetate, formate, IDA, NTA, and oxalate. Table 4-5 lists the major species identified in the waste samples.

The speciation results shown in Tables 4-4 and 4-5 are consistent with laboratory aging studies showing degradation of complexants to chelator fragments and carboxylate salts such as oxalate and formate. Oxalate persists in the wastes at higher concentrations than formate and many other chelator fragments. The slow rate of oxalate oxidation to carbonate is probably due to its low solubility. Oxidation of the organic species mainly occurs in the aqueous phase. Therefore, oxidation rates of oxalate are limited by its insolubility in tank supernatant and interstitial liquids.

4.3.2.3 Conclusion on Organic Waste Aging. The organic complexants stored in the Hanford Site waste tanks have aged and are continuing to age to lower energy compounds. The rate of aging is sensitive to both temperature and dose rates. Analyses of tank waste samples corroborate aging and indicate the formation of oxalate and other aging byproducts.

Table 4-5. Organic Species in Waste Samples.

Tank	Segment	TOC (wt%)	Acetate (wt%)	Citrate (wt%)	Glycolate (wt%)	Formate (wt%)	Oxalate (wt%)	EDTA (wt%)	HEDTA (wt%)	IDA (wt%)	NTA (wt%)
A-101	10	1.2	0.21	ND	ND	0.27	3.8	0.02	ND	ND	ND
A-102	1	1.0	0.17	0.13	0.004	0.17	1.4	ND	ND	ND	ND
AN-107	1	3.2	---*	0.60	0.79*	0.52	1.8	0.22	0.05	0.33	0.05
AW-101	21	1.5	0.09	0.02	0.05	0.10	1.1	ND	ND	ND	0.01
AX-102	1	3.5	ND	0.51	0.08	0.48	1.8	0.31	0.15	1.2	ND
BY-102	4	1.9	0.01	ND	ND	0.004	6.8	ND	ND	ND	ND
BY-104	6	1.8	ND	3.0	ND	ND	5.4	ND	ND	ND	ND
BY-105	1	0.2	0.11	0.21	ND	0.09	ND	ND	ND	ND	ND
BY-107	1	0.9	0.14	ND	ND	0.06	2.6	ND	ND	ND	ND
BY-110	4	2.1	0.05	ND	ND	ND	3.7	ND	ND	ND	ND
BY-110	7	0.8	0.09	ND	ND	0.04	9.5	ND	ND	ND	ND

4.3.3 Organic Solubility

The organic complexants used at the Hanford Site are extremely soluble and were originally disposed to the tanks as aqueous (liquid) waste. Because of waste storage operations, the liquid complexant wastes have been mixed with other (non-complexant) waste and partially evaporated (either in situ or using evaporators) to reduce their volumes. If the organic fuel remains in the liquid, then combustion is not possible. Furthermore, the organic complexant inventory in a tank can be decreased by pumping the tank liquids, reducing or eliminating the organic complexant hazard completely. Experiments with waste simulants and analyses of tank waste samples indicate that most of the organic complexants and energetic chelator fragments remain in the tank supernatants and interstitial liquid.

4.3.3.1 Parameters Affecting Organic Solubility. The amount of organic complexant in solution is dictated by the solubility limits at tank temperatures. Waste simulant experiments have investigated the solubility of organic compounds in the highly saline liquid wastes. The sodium salt of the organic compound being tested was always present as a crystalline solid during the measurements to ensure saturation of the aqueous solution. In the first experiments, only one organic compound was used in each mixture to simplify the analyses. This prevented interferences and eliminated the need for separations before analysis. Progressively, more complex mixtures were examined. Results are shown in Table 4-6.

Table 4-6. Solubility of Complexants in Waste Simulant Solutions.

Compound	Solubility in Solution Containing 4.0 Molar $NaNO_3$ and 0.97 Molar $NaNO_2$		Solubility in Solution Containing Saturated $NaNO_3$ and 2.0 Molar $NaNO_2$	
	(moles L^{-1})	(g of TOC L^{-1})	(moles L^{-1})	(g of TOC L^{-1})
Acetate	4.0 - 8.0	96 - 192	3.8 - 5.4	91 - 130
Butyrate	2.6 - 4.0	125 - 192	2.2 - 3.5	106 - 168
Citrate	0.6 - 1.2	43 - 86	0.35 - 0.63	25 - 45
EDTA	0.7 - 1.4	84 - 168	0.83 - 1.0	100 - 120
Formate	6.8 - 9.8	82 - 118	6.6 - 8.5	79 - 102
Glycolate	4.4 - 5.8	106 - 140	3.6 - 4.2	86 - 101
HEDTA	1.5 - 1.8	180 - 216	1.1 - 1.2	131 - 143
NTA	1.3 - 1.7	94 - 122	0.81 - 1.2	58 - 86
Oxalate	0.0042 - 0.015	0.1 - 0.36	0.0012 - 0.0039	0.029 - 0.094
Mixture[1]	---[1]	140 - 220	---[1]	120 - 180

Notes: Solubility in simulant solutions at 25 to 50 °C and hydroxide concentrations from 3 E-5 to 2.0 Molar (M).

[1] Saturated complexant salt mixtures contained 0.36 - 0.54 M EDTA, 0.15 - 0.19 M citrate, 2.0 - 2.5 M gylcolate, 0.1 - 0.33 M NTA, 0.3 M Na_2CO_3, 0.05 M Na_2SO_4, 0.1 M Na_3PO_4, 0.005 M aluminin, 0.005 M iron, 0.005 M chromium, 0.005 M bismuth, 0.005 M calcium, 0.005 M nickel, and 0.005 M zirconium.

Solubilities in Table 4-6 were measured in simulated supernatant solutions containing sodium nitrate, sodium nitrite, and sodium hydroxide. Two simulant solutions were used that represented solutions typical of interstitial liquids in saltcake waste tanks. The first was a mixture containing 4.0 molar sodium nitrate, 0.97 molar sodium nitrite, and sodium hydroxide ranging from 3 E-5 to 2.0 molar. The second simulant was a mixture containing 2.0 molar sodium nitrite, saturated sodium nitrate, and sodium hydroxide ranging form 0.1 to 2.0 molar. The solubility experiments were conducted over a 25 to 50 °C temperature range. Details of the solubility experiments are provided in Barney (1994, 1995, 1996, 1997).

From Table 4-6, the major organic complexants (citrate, EDTA, glycolate, and HEDTA) and aging byproducts (acetate, formate, and NTA) remain soluble, even in the basic, highly saline simulant solutions. The exception to this is oxalate, which has solubilities two orders of magnitude lower than the other organic compounds tested. It is important to note that oxalate did not support propagation even under stoichiometric conditions (see Appendix G).

4.3.3.2 Confirmation of Organic Solubility from Waste Sample Data. Many tank waste liquid samples have been analyzed for TOC. The TOC concentrations have been collected for 61 tanks. These include SSTs (Van Vleet 1993a) and DSTs (Van Vleet 1993b). The frequency distribution for these 61 tanks is shown in Figure 4-3. As shown in Figure 4-3, no concentration exceeded 40 g L^{-1}, and 55 of the 61 measurements (90%) are below 15 g L^{-1}. The TOC concentrations in the liquid samples from the SSTs average 5.2 ± 1.1 g L^{-1} (at the 95% confidence level) (Toth et al. 1995). At these TOC concentrations, only oxalate would exceed its solubility limit and exist as a solid phase. Organic speciation of the waste liquid and solid (separated by centrifugation) samples from tanks with the highest TOC corroborates that the energetic complexants are contained in the aqueous phase. It should be noted that the energetic complexants degrade into less reactive compounds (Section 4.3.2.2). Results are shown in Figure 4-4.

Figure 4-3. Distribution of TOC Concentrations in Supernatant Solutions for 61 Tanks.

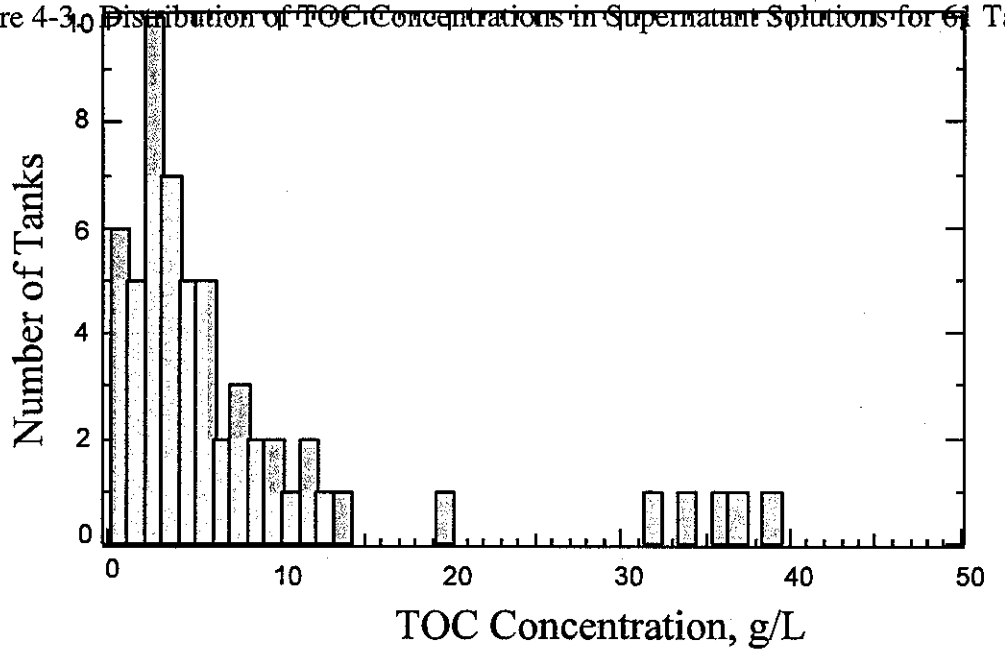
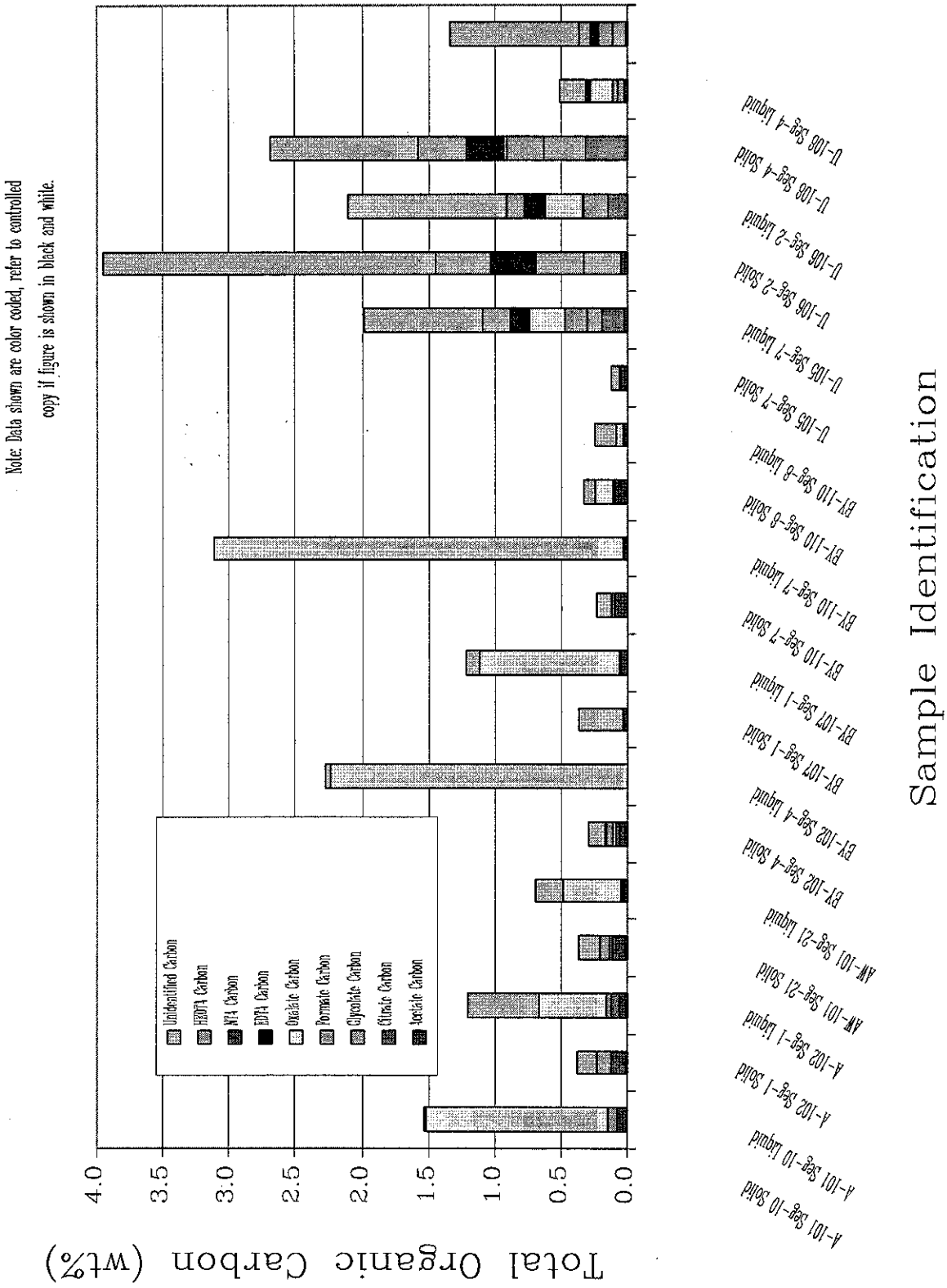


Figure 4-4. Comparison Between Organic Species in Liquid and Solid Phases.



From Figure 4-4, the solid waste fractions contained most of the oxalate, and the liquid fractions contained significantly higher concentrations of the complexants (citrate, EDTA, glycolate, and HEDTA) and their energetic degradation products (acetate, formate, and NTA). Some residual was also found in the solid samples because centrifugation did not completely separate the liquid and solid fractions (the centrifuged solids still contained 10 - 40 wt% water after separation). A small amount of complexants might also be adsorbed on the waste particles. Simulant experiments showed that adsorption would account for less than 0.1 wt% TOC.

4.3.3.3 Conclusions on Organic Solubility. High solubilities will prevent precipitation of the complexants and energetic chelator fragments from tank solutions. The TOC analyses of actual tank supernatant samples are much lower than the TOC ranges for the simulated supernatant solutions saturated (at the solubility limit) with the organic salts. This is true even if all the dissolved carbon in a given tank sample contained only one of the compounds tested (an unlikely situation). Comparison of liquid and solid waste samples show that the complexants and energetic chelator fragments are retained in the aqueous phase and would be moved as liquid is transferred from the tanks. Low energy oxalate is present in the waste solid samples; however, even stoichiometric oxalate-nitrate mixtures failed to propagate when tested (see Appendix G).

4.3.4 Tank Waste Water Retention and Dryout

Propagation test results on waste samples (see Section 4.4.4.5) showed that no tank waste samples support propagation even when the water was removed by drying at 105 °C. However, the extremely dry conditions in the propagation tests cannot occur under tank waste storage conditions, because the wastes contain hygroscopic salts that retain considerable water. Water retention provides an added safety margin between the tank waste conditions and the conditions necessary for propagation.

Experiments and modeling (Appendix D) were used to estimate water retention during interim storage for those SST wastes with the highest complexant concentration. Waste samples were exposed to water vapor at a range of partial pressures that would be typical of the actual exposure range during storage. Water partial pressure at Hanford varies seasonally from a winter average low of 3.8 torr to a summer average high of 7.9 torr. These experiments established the water content of the waste samples as a function of the partial pressure of water vapor. The tests were performed at the temperature measured by the uppermost thermocouple located in the solid waste; temperatures ranged from 20 to 41 °C.

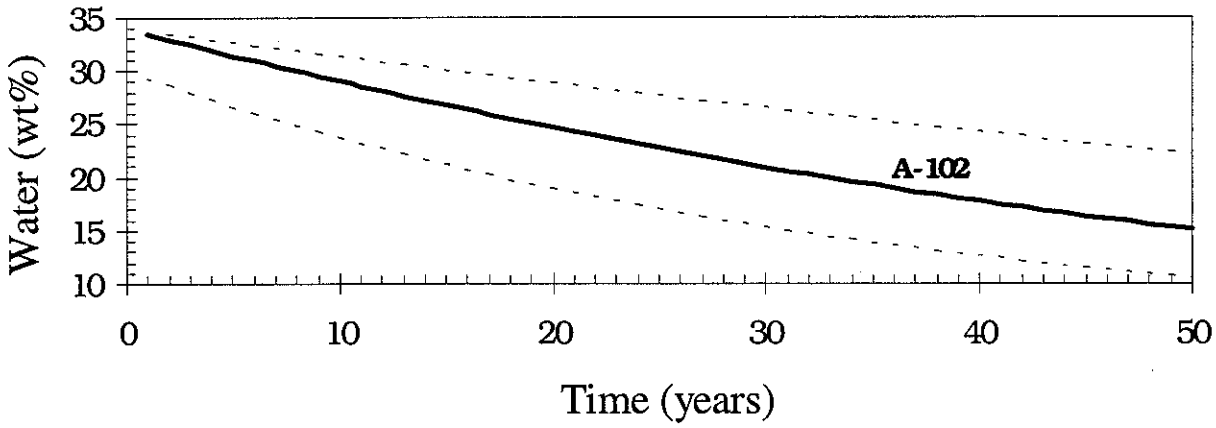
The rate at which air is exchanged between the tank headspaces and the atmosphere was studied using a tracer gas. Inert tracer gas (helium or sulfur hexafluoride) was injected into the tank headspace and the concentration measured periodically. Ventilation rates varied significantly from tank to tank with lower rates in U Farm (2.2 - 8.5 m^3/hour) than in A and AX Farms (17 - 42 m^3/hour). Tank headspace humidities were also measured so that the water loss from a tank could be calculated.

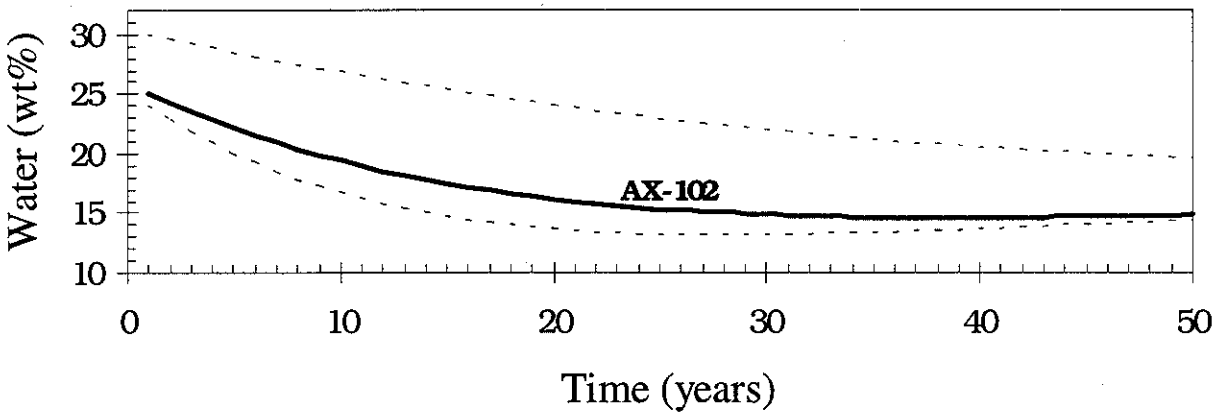
The information obtained from the water partial pressure experiments, headspace breathing rate tests, and headspace humidity measurements were combined into mathematical models of the waste-tank headspace system to estimate the rate of water loss from the tanks. The models predicted the long-term water content of the wastes, and results are shown in Figure 4-5. The

rate of waste dry out is most dependent on the rate of headspace breathing, and the upper and lower dashed-lines in Figure 4-5 represent dry out at the upper and lower bound breathing rates.

From Figure 4-5, tanks C-104, U-105, and U-106 would retain more than 30 wt% water over the next fifty years under current storage conditions. The theoretical criterion and experiments show that more than 20 wt% water prevents propagation at all TOC concentrations. Tank A-102 and AX-102 wastes retain about 17 wt% water. Using the theoretical criterion, 17 wt% water increases the TOC requirement for propagation to 7.4 wt% TOC, which is a factor of two higher than the highest measured TOC concentration in tank AX-102 waste (3.7 wt%), and about a factor of four higher than the highest measured TOC concentration in tank A-102 waste (1.8 wt%). Figure 4-6 in Section 4.4.4.1 and Table 4-16 in Section 4.4.4.5 show the range of TOC measurements for the tanks.

Figure 4-5. Projected Waste Dry Out for Tank Wastes With High Total Organic Carbon.





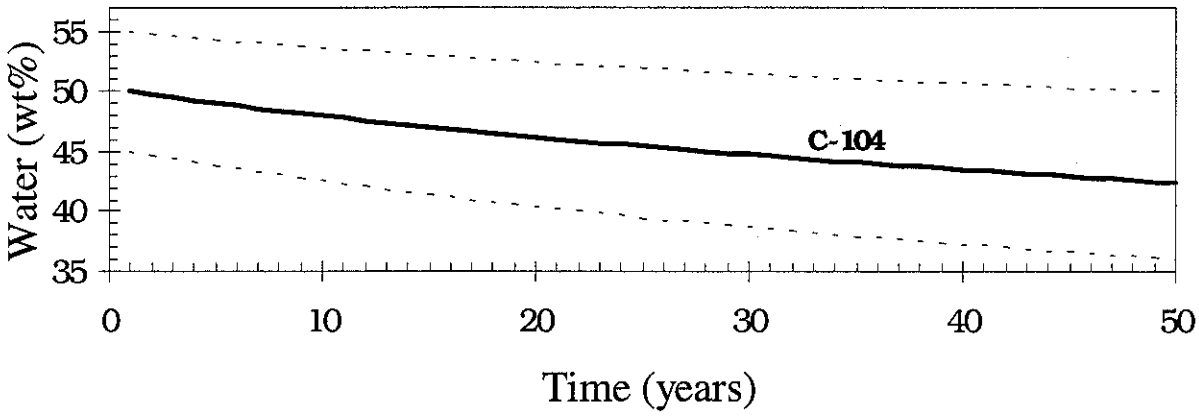
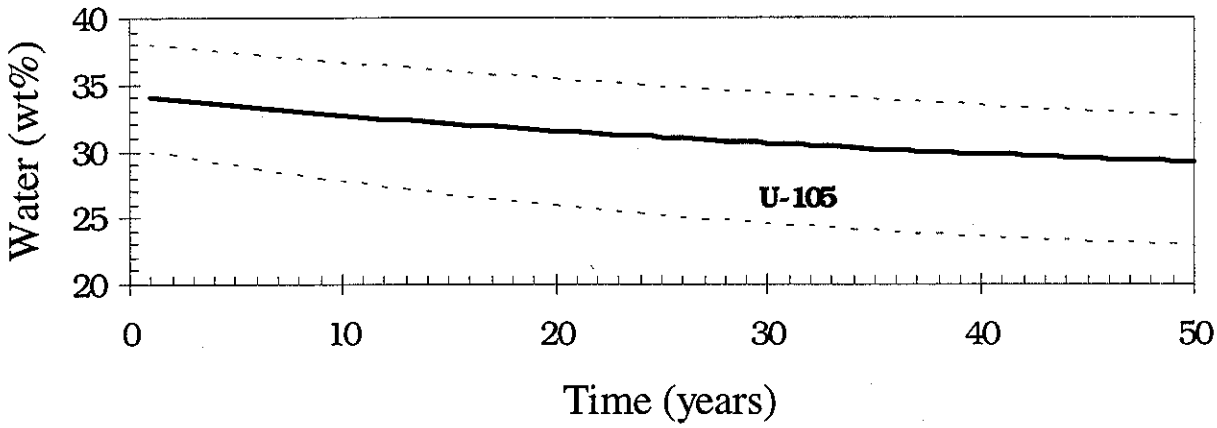
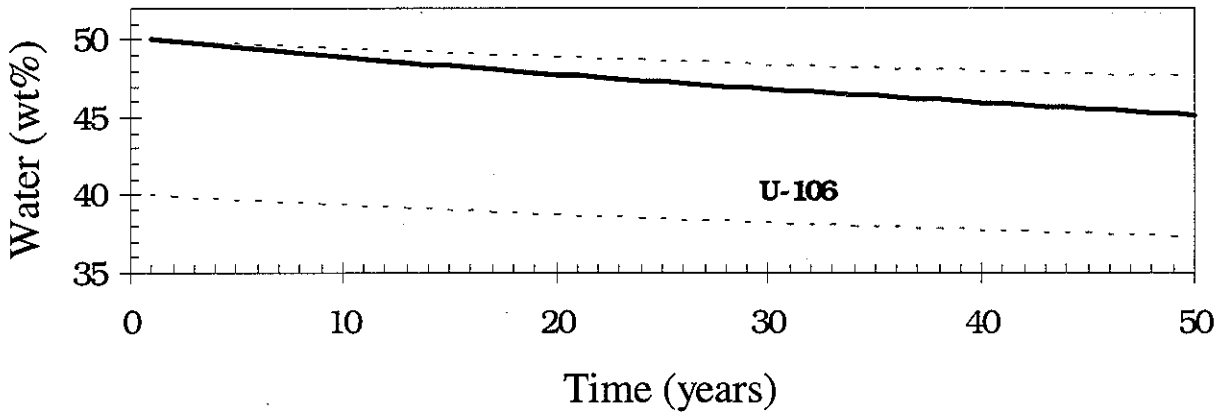
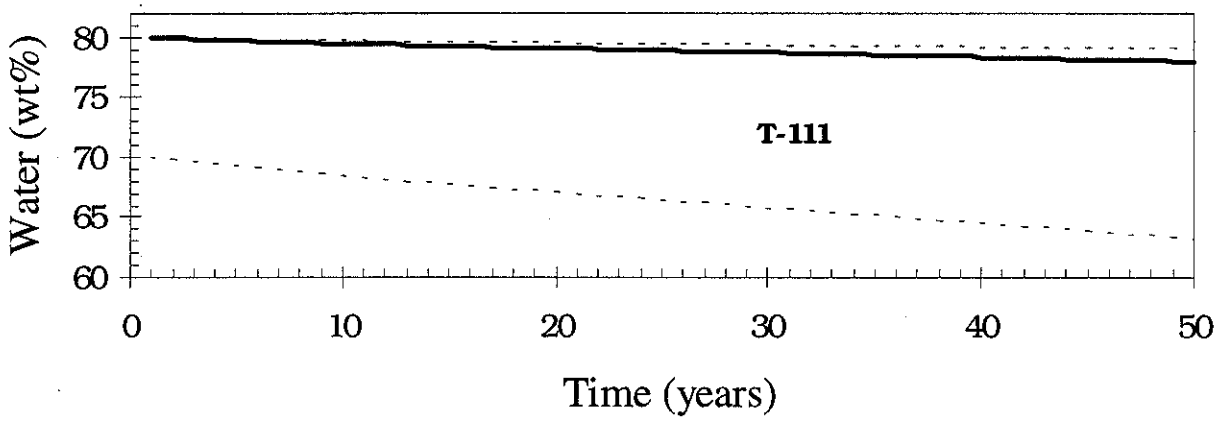


Figure 4-5. Projected Waste Dry Out for Tank Wastes With High Total Organic Carbon (Continued).







4.4 ASSESSMENT OF TANK WASTE FOR PROPAGATION

4.4.1 Double-Shell Tank Waste Propagation

The DSTs were constructed to provide intermediate storage of high-level radioactive waste, including waste capable of boiling from radioactive decay (aging waste) and waste not capable of boiling (non-aging waste). There are 28 DSTs, with 25 located in five tank farms in the 200 East Area and three located in one farm in 200 West Area. A major operational difference between the DSTs and SSTs is that the DSTs have only stored liquid wastes and slurries. There have been no operations that were intended to dry waste below 20 wt% water and no operations are planned as part of the interim storage mission. Therefore, DSTs do not pose a hazard for propagation during the interim storage mission.

Table 4-7 shows the range of moisture and TOC concentrations in DSTs. These values confirm the conclusion stated above. However, there are some unique situations where solids have precipitated, forming either a low porosity sludge or a floating crust layer. These solid phases can have low moisture concentrations even though the bulk average moisture concentration is relatively high. Because the organic complexants are highly soluble (see discussion on organic solubility in Section 4.3.3), the organic fuel would not be present in significant quantities in the floating crust.

The floating crusts in two DSTs, SY-103 and AW-101, were sampled specifically to determine whether a crust burn was credible. The SY-103 crust was sampled in three locations. Water concentrations ranged between 8 and 28 wt%, and DSC analyses showed no exothermic energy in any of the crust samples. The AW-101 crust was also sampled in three locations. The water concentrations ranged from 32 to 42 wt%, TOC concentrations ranged from 0.3 to 1.2 wt%, and the DSC analyses showed low exothermic energy (-71 to -220 J/g on a dry basis).

Table 4-7. Double-Shell Tank Waste Moisture and TOC Concentrations. (2 sheets)

Tank	Liquid Samples		Solid Samples	
	Water (wt%)	TOC (wt%)	Water (wt%)	TOC (wt%)
AN-101	65 - 66	0.18 - 0.31	NA	NA
AN-102[1]	45 - 51	2.0 - 2.3	36 - 44	2.0 - 2.7
AN-103	48 - 50	0.25 - 0.26	14[2] - 50	0.21 - 0.28
AN-104	35 - 53	0.21 - 0.33	37 - 51	0.46 - 0.47
AN-105	30 - 54	0.20 - 0.51	36 - 53	0.43 - 0.60
AN-106	27 - 100	0.44	NA	NA
AN-107	49 - 52	4.2 - 5.0	38 - 44	2.7 - 3.3
AP-101	57 - 61	0.010 - 0.30	NA	NA
AP-102	74 - 76	0.25 - 0.47	NA	NA
AP-103	97 - 98	0.0062 - 0.015	NA	NA
AP-104	94 - 99	0.011 - 0.022	NA	NA
AP-105	53 - 70	0.0008 - 0.28	38 - 52	0.38 - 0.74
AP-106	70 - 100	0.0086 - 0.28	NA	NA
AP-107	93 - 96	0.0 - 0.028	NA	NA
AP-108	80 - 93	0.039 - 0.17	NA	NA
AW-101	41 - 51	0.25 - 0.30	24[3] - 52	0.13 - 0.31
AW-102	76	0.33 - 0.52	40	0.28 - 0.31
AW-103	91 - 94	0.093 - 0.094	27 - 76	0.0040 - 1.0[4]
AW-104	47 - 99	0.042 - 0.47	25 - 79	0.40 - 0.77
AW-105	75 - 97	0.0029 - 0.67	37 - 82	0.0040 - 3.5
AW-106	69	0.20 - 0.46	No Sample	No Sample
AY-101	60 - 85	0.0 - 0.76	36 - 48	0.31

Table 4-7. Double-Shell Tank Waste Moisture and TOC Concentrations. (2 sheets)

Tank	Liquid Samples		Solid Samples	
	Water (wt%)	TOC (wt%)	Water (wt%)	TOC (wt%)
AY-102[9]	86 - 88	0.17 - 0.18	54	0.30
AZ-101	71 - 74	0.076 - 0.091	43	1.4
AZ-102	83 - 85	0.12 - 0.13	54	0.64
SY-101	22[5] - 79	0.12 - 1.2	10[6] - 56	1.5 - 2.7
SY-102	72 - 95	0.024 - 0.55	39 - 77	0.67
SY-103	48[7] - 75	0.80 - 0.83	8[8] - 69	0.190 - 1.4

Notes: NA = not applicable, the tank contains little or no solids.

[1] AN-102 and AN-107 are complex concentrate tanks and expected to be high in TOC.

[2] AN-103 had several segments with easy to de-water solids. For instance, Segment 8 of core 167 was a convective layer segment that cooled and precipitated in the sampler. The drainable liquor was 378 g and solids recovered amounted to 45 g. The drainable liquid was about 48 wt% water and the solids were 14 and 16 wt% water.

[3] The lowest value is from segment 13, i.e. deep in the tank. The segment had 377 g of drainable liquid and 31 g of solids. The water wt% was measured three times on this solid sample with the results of 1.5, 24, and 30 wt%. Another segment (segment 4 of core 139) had 378 g of drainable liquid and 29 g of solids. Water concentration was measured twice on the solid sample with results of 2.6 and 12 wt%. Segment 2, core 139 had 153 g of drainable liquid and 133 g solids. The lower quarter of the solids measured 19 wt% water. Segment 15, core 132 had 368 g drainable liquid and 42 g solid. The percent water was run four times on the solids with the following results: 19, 24, 30, and 43 wt%.

[4] Analyses indicated an oxalate concentration of 2.9 wt% which is equivalent to 0.78 wt% of TOC.

[5] This is for drainable liquid from a segment at the bottom of the tank. There were two determinations made: 22 and 41 wt%. A resampling of this segment had liquid samples measurements of about 78 wt% water.

[6] This is a sample from the surface. This tank has a crust and all water measurements that were less than 20 wt% are from the surface except for three. One segment had 18 and 47 wt% water measurements. Another had measurements of 18, 31 and 33 wt% water. The third segment had measurements of 20, 31, and 31 wt% water.

[7] The drainable liquid from segment 8 had five water measurements. One analysis yielded 15 wt% water and four replicate analyses of this material ranged from 48 to 49 wt% water.

[8] Auger samples of the surface crust ranged from 8 to 27 wt% water. The crust samples showed no exothermic energy when tested by DSC. Segment 3 had about 262 g of drainable liquid and 91 g of solids that measured 18 and 21 wt% water. Segment 5 had solids measuring 19 and 21 wt% water with 270 g of drainable liquid and 95 g of solids. Segment 7 had solids measuring 15, 17, and 48 wt% and had 262 g of drainable liquid and 88 g of solids. Segment 8 had solids measuring 14 and 18 wt% water that were in a sample with 295 g of drainable liquid and 98 g of solids.

[9] From the sample event in the tank characterization database that occurred after the transfer of waste from C-106.

4.4.2 Double-Contained Receiver Tank Waste Propagation

A DCRT is a short-term storage facility for liquid waste during waste transfer operations. There are six DCRTs. The 244-A, 244-BX, and 244-CR DCRTs are located in 200 East Area and the 244-S, 244-TX, and 244-U DCRTs are located in 200 West Area. The DCRTs are active facilities (with the exception of 244-U which is yet to be put into service) for collection of liquid waste that does not have a high solids loading. The supernatant waste in SSTs are transferred into the DCRTs and held for a short period of time before transferring to DSTs. Table 4-8 provides moisture and TOC concentration data for the five active DCRTs.

Table 4-8. Double-Contained Receiver Tank Waste Moisture and TOC Concentrations

Tank	Water (wt%)	TOC (wt%)	Notes
244-A	97 - 98	0.196 - 0.20	1995 Sample
244-BX	50 - 69	0.15 - 0.42	Based on liquid samples of BY-103, BY-106, and BY-109
CR-003-Tk	59 - 78	0.041 - 0.21	Based on liquid samples of C-102, C-105, C-110, and C-112
244-S	92	0.02	Based on sample
244-TX	88 - 89	0.011 - 0.018	Based on sample
244-U	NA	NA	Empty; tank not yet used

Notes: NA = not applicable

The DCRT waste streams have a high water content and would have to evaporate to dryness to become a hazard. The minimum volume of liquid left in the DCRTs is typically 11,000 to 15,000 L (3,000 - 4,000 gallons). Combustible waste could only be formed if a waste heel was evaporated to dryness, and this heel contained organic material, oxidizer, and low concentrations of inert diluents. Evaporation of waste heels to dryness is not anticipated during the interim storage mission. However, evaporation rates have been estimated for the active DCRTs using liquid level data, and the time to dry and the effect of drying can be calculated.

Liquid level monitoring in tanks 244-A and 244-BX suggest moisture loss through evaporation is negligible. During inactive periods, the liquid level in these two tanks have actually increased.

Tank CR-003-Tk loses about 4 L (1 gallon) per day through evaporation on a yearly average basis. At this rate, the tank would take over five years to dry. Even if the current waste were evaporated to dryness, the maximum TOC concentration would be low, only 0.95 wt%.

Tanks 244-S and 244-TX lose about 2 L (0.5 gallon) per day through evaporation on a yearly average basis. At this rate, these tanks would take over 19 years to evaporate to dryness. Even if the current wastes were evaporated to dryness, the maximum TOC concentrations would be small, 0.25 and 0.18 wt%, respectively.

Tank 244-U is not active but will be used during interim stabilization of tanks U-105 and U-106. The supernatant and interstitial liquid in tank U-106 is high in complexants and nitrates/nitrites salts. Therefore, an analysis similar to that done for the other DCRTs will be necessary for 244-U after interim stabilization is complete.

4.4.3 Catch Tank Waste Propagation

Catch tanks are underground storage tanks used to collect small amounts of waste drained from waste transfer systems and DST equipment. Catch tanks can be emptied to a DST using a submersible pump or, in some instances, a water or steam jet. There are seven active catch tanks in 200 East Area, four active catch tanks in 200 West Area and one active catch tank in the 600 Area (between the 200 East and West Areas). These waste streams have a high water content and would have to evaporate to dryness to become a hazard. Because the catch tanks are active, this is not anticipated during the interim storage mission. The catch tanks do not pose a hazard for propagation during the interim storage mission. Table 4-9 provides moisture and TOC concentration data for the active catch tanks.

Table 4-9. Catch Tank Waste Water and Total Organic Carbon Concentrations

Tank	Water (wt%)	TOC ($\mu g\ mL^{-1}$)	Notes
A-302-A	99	0.017	1995 Sample
ER-311	98	0.010	1995 Sample
U-301-B	98	0.011	1997 Sample

Table 4-10 shows those catch tanks that have not been sampled. A brief description of their function is included to show that the waste in these catch tanks is predominantly liquid.

Table 4-10. Description of Catch Tank Function and Process Histories

Tank	Function and History
AX-152	Diversion box drain – rain, de-entrainer flush, snow melt
AZ-151	Diversion box drain and AZ loop seal
AZ-154	AZ-102 heating coil steam condensate. Now empty, steam is off.
A-350	Collects drainage from A farm – rain, flush water
AR-204	Receives waste from railroad cars during unloading and transfers the waste to the double shell tanks.
A-417	A-702 process condensate – condensate from the aging waste tanks
TX-302-C	TX-154 diversion box drain – rain, snow melt
U-302-A	Diversion box drain – rain, snow melt
S-304	Diversion box drain – rain, snow melt
Vent Station Catch Tank	Drainage from cross-country transfer line pit.

4.4.4 Single-Shell Tank Waste Propagation

Propagation is not possible if the fuel concentration is low. Fuel concentration in the SSTs was assessed using process history and waste sample data. Tanks were grouped based on historic complexant concentration (Section 4.4.4.1), and the waste samples were screened using differential scanning calorimetry (DSC) (see Section 4.4.4.2) and TOC measurements (see Section 4.4.4.3). Analyses showed that the TOC in some wastes was predominantly organic solvent (see Section 4.4.4.4), which is important because testing indicates that the solvents do not contribute to the organic complexant hazard. Those tank wastes with the highest DSC/TOC results were tested for propagation (see Section 4.4.4.5) using adiabatic calorimetry (RSST) and tube propagation [Propagating Reactive System Screening Tool (PRSST)].

4.4.4.1 Waste Process Histories and Bounding Tanks. Tank wastes fall into five groups: (1) high complexant, (2) medium complexant, (3) low complexant, (4) no complexant (tanks that did not receive incoming waste transfers after 1968), and (5) special case tanks that need to be treated individually because of unique process histories. The tank wastes were further divided into four water groups: (1) saltcake - dry surface, (2) saltcake - wet surface, (3) sludge - dry surface, and (4) sludge - wet surface. These groups are intended to be mutually exclusive groups, and are shown in Table 4-11. Tanks shown in ***italics*** were sampled. More details on tank groupings and process histories are provided in Appendix F.

Table 4-11. Assessment of Single-Shell Tank Wastes From Waste Processing Records.[1]

Fuel and Moisture Group	Tanks[2]
High Complexant Waste Dry Surface -Saltcake	***A-101***, ***AX-101***, ***AX-102***, and ***U-111*** (4 of 4 tanks sampled)
High Complexant Waste Dry Surface -Sludge	***A-106***, ***AX-103***, ***C-104***, ***C-105***, ***C-107***, and ***TX-104*** (6 of 6 tanks sampled)
High Complexant Waste Wet Surface - Saltcake	***A-102***, ***A-103***, ***SX-101***, ***SX-106***, ***U-105***, ***U-106***, and ***U-107*** (7 of 7 tanks sampled)
High Complexant Waste Wet Surface - Sludge	***BX-104***, ***BX-105***, ***C-106***, and ***S-107*** (4 of 4 tanks sampled)
Medium Complexant Waste Dry Surface - Saltcake	***BY-102***, ***S-102***, ***SX-103***, ***TX-102***, and TX-111 (4 of 5 tanks sampled)
Medium Complexant Waste Dry Surface - Sludge	***B-109***, ***BX-112*** (2 of 2 tanks sampled)
Medium Complexant Waste Wet Surface - Saltcake	***S-101***, S-103, ***SX-102***, SX-104, SX-105, ***U-102***, ***U-103***, ***U-108***, and ***U-109*** (6 of 9 tanks sampled)
Medium Complexant Waste Wet Surface - Sludge	***B-111*** (1 of 1 tank sampled)
Low Complexant Waste Dry Surface - Saltcake	***AX-104***, B-105, ***BX-111***, ***BY-101***, ***BY-103***, ***BY-104***, ***BY-105***, ***BY-106***, ***BY-107***, ***BY-109***, ***BY-110***, ***BY-111***, ***BY-112***, ***S-104***, S-105, S-108, ***S-109***, ***S-110***, S-112, SX-110, SX-111, SX-114, ***T-106***, ***T-108***, ***T-109***, TX-103, TX-105, TX-106, ***TX-107***, TX-108, TX-109, TX-110, TX-112, TX-113, TX-114, TX-115, TX-116, TX-117, TX-118, ***TY-102***, and ***TY-103*** (21 of 41 tanks sampled)
Low Complexant Waste Dry Surface - Sludge	A-104,***B-101***, ***B-103***, ***B-106***, ***B-108***, ***BX-101***, BX-102, ***BX-107***, ***BX-108***, ***BX-109***, ***BY-108***, ***C-108***, ***C-111***, ***C-112***, SX-115, T-101, ***T-105***, ***T-201***, ***T-202***, ***T-203***, ***T-204***, TX-101, ***TY-101***, U-104, and ***U-110*** (19 of 25 tanks sampled)
Low Complexant Waste Wet Surface - Saltcake	***B-102***, ***S-106***, and ***S-111*** (3 of 3 tanks sampled)
Low Complexant Waste Wet Surface - Sludge	***B-110***, ***B-112***, ***BX-103***, ***BX-106***, ***BX-110***, ***C-109***, ***C-110***, ***T-102***, T-103, ***T-107***, ***T-110***, ***T-111***, ***T-112***, ***TY-104***, U-101, ***U-112***, ***U-201***, ***U-202***, ***U-203***, and ***U-204*** (18 of 20 tanks sampled)
No Complexant Waste Dry Surface - Saltcake	***SX-108*** and SX-109 (1 of 2 tanks sampled)
No Complexant Waste Dry Surface - Sludge	A-105, ***B-104***, ***B-107***, SX-107, SX-112, ***SX-113***, ***TY-105***, and ***TY-106*** (5 of 8 tanks sampled)
No Complexant Waste Wet Surface - Saltcake	(No Tanks in Group)
No Complexant Waste Wet Surface - Sludge	***T-104*** (1 of 1 tank sampled)

Notes: [1] There are eleven special case tanks: ***B-201***, ***B-202***, ***B-203***, ***B-204***, ***C-101***, ***C-102***, ***C-103***, ***C-201***, ***C-202***, ***C-203***, and ***C-204***. (149 tanks total)

[2] Tanks identified in ***italics*** were sampled.

The first group of tanks (consisting of 21 tanks) contains high concentrations of organic complexant waste. Historical records (Anderson 1990, Agnew et al. 1996) show these tanks received direct transfers of process wastes containing organic complexants. The high complexant tanks represent the greatest concentration that could be found in the SSTs. All other SSTs (excluding the special case tanks described below) would contain no greater concentrations because subsequent tank-to-tank transfers would further dilute the organic. All 21 tanks in this group were sampled. The tanks in this group had the highest complexant TOC concentrations with AX-102 and U-106 having peak concentrations of 3.7 and 4.1 wt%, respectively (see Figure 4-6).

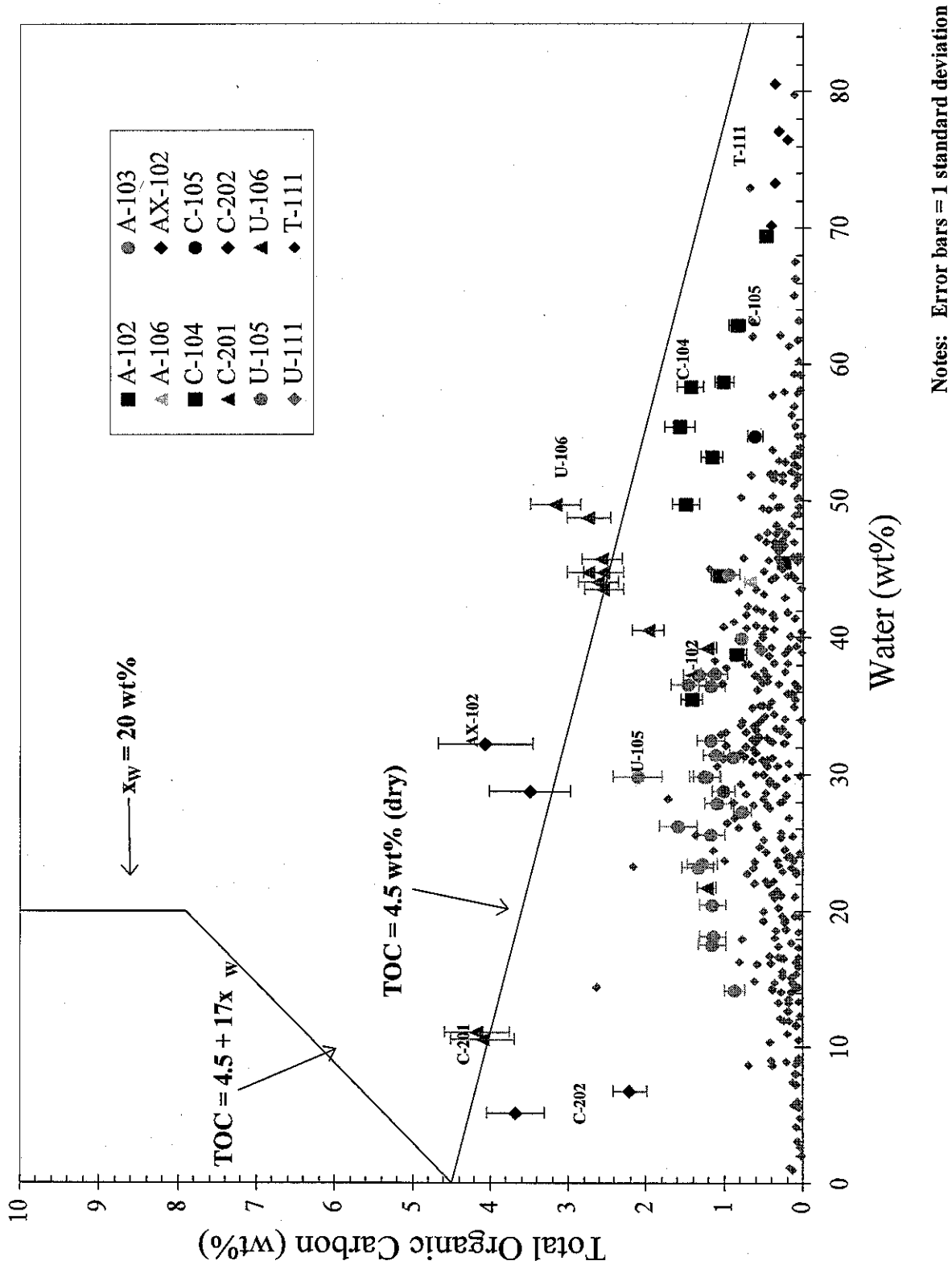
The medium complexant tanks (consisting of 17 tanks) did not receive direct transfers of complexant waste. However, records indicate that these tanks received waste transfers from those tanks with high complexant concentrations. This tank group consists of those tanks identified in Agnew et al. (1996) as containing an average TOC greater than 0.64 wt% but not identified by Anderson (1990) as receiving direct transfers of complexant waste. Thirteen of the 17 tanks were sampled. The measured mean TOC concentrations for this group were about half that of the high group, but about an order of magnitude higher than the TOC mean for the low group.

The low complexant tanks (consisting of 89 tanks) did not receive direct transfers of complexant waste but might have received secondary (dilute) tank-to-tank transfers that contained organic complexants. This tank group contains those tanks identified in Agnew et al. (1996) as containing an average TOC concentration less than 0.64 wt%. Sixty-one of the 89 tanks in this group were sampled.

Organic complexants (i.e., citrate, EDTA, glycolate, and HEDTA) were not used in quantity at the Hanford Site until 1968 (ERDA 1975). Before 1968, any testing or pilot plant operations would have used small quantities of complexants, and these wastes were disposed to the C 200 and B 200 series tanks (see special case tanks below). The records indicate that eleven tanks received no incoming waste transfers after 1968, and it is extremely unlikely that they contain organic complexant waste. These tanks represent the no-complexant tank group, and any TOC in these tanks would most likely be organic solvents or oxalate (a small amount of oxalate waste was disposed in the SSTs). Seven of the eleven tanks in the group were sampled, and all the waste samples from these tanks have shown no exothermic energy by DSC and only trivial (<0.1 wt%) amounts of TOC.

In addition to the four fuel groups, some tanks have unique or hard to track waste transfer histories. These tanks have been grouped together as special case tanks. The C-200 and B-200 series tanks received several small waste transfers from the strontium semiworks at B Plant. The semiworks wastes were often small pilot plant runs that contained unique waste streams. Therefore, it is difficult to assess these tanks on historical records alone, and these tanks were sampled and characterized individually.

Figure 4-6. Total Organic Carbon and Water Concentrations for the Single-Shell Tanks.



Also included in the special case tank group are those tanks that received predominantly organic solvent waste. Solvent wastes (e.g., normal paraffin hydrocarbons and tributyl phosphate) deposited in the tank often contribute a large part of the TOC measured in the tank. Experimentation indicates that these materials do not support and do not contribute to condensed-phase combustion (Cowley et al. 2000, Conner 1996). There are a total of eleven special case tanks and all have been sampled.

The two characteristics used for the tank waste water groupings were (1) the absence or presence of visible liquid on the tank waste surface and (2) whether the waste contains predominantly saltcake or sludge. Visible liquid on the waste surface suggests that the waste is saturated with liquid. The type of waste (saltcake or sludge) is important because waste simulant experiments, theoretical analyses, and actual waste testing indicate that the saltcakes tend to drain liquid more readily than the sludges (Atherton 1974, Handy 1975, Metz 1975a, 1975b, 1976, Kirk 1980, Epstein et al. 1994). Therefore, the saltcake wastes could potentially be drier than the sludge wastes.

The absence or presence of visible liquid on the tank surface was provided from the initial organic-nitrate screening of 149 SSTs. Photographs of the tank waste indicate that fifty tanks have visible liquid on the surface. The type of waste is derived from the waste descriptions in Agnew et al. (1996).

Total organic carbon data from the tanks (Figure 4-6) corroborates the tank groupings and waste histories. One-hundred and thirteen of the 149 SSTs were sampled (see Table 4-11), and the tanks with the greatest TOC measurements all come from the high complexant and special case tank groups. Excluding tanks C-103 and C-204 which have organic solvent (see Section 4.4.4.4), only three tanks (AX-102, C-201, and U-106) had TOC measurements that exceeded the 4.5 wt% (dry) criterion.

4.4.4.2 Differential Scanning Calorimetry Data. For thirty-five tanks, DSC analyses of all the samples show no net exothermic energy (Table 4-12). That is, no exothermic energy was observed from the sample when heated from ambient temperature to 450 °C. Results are consistent with the historical assessment that shows three of these tanks (B-104, SX-108, and SX-113) received no complexants, and that 29 of the tanks would have only received secondary transfers (low complexant). Three of the tanks (B-201, B-204, and C-101) are special case tanks that required separate characterization. Because these tanks were suspected of receiving little organic complexant, and all the DSC screening showed no exothermic energy, TOC analyses were not always performed.

Table 4-12. Tanks With Waste Showing No Exothermic Energy During DSC Analysis and Comparison with Waste Process History Assessment.

Tank	Waste History Assessment	Tank	Waste History Assessment	Tank	Waste History Assessment
B-103	Low Complexant	BX-108	Low Complexant	T-201	Low Complexant
B-104	No Complexant	BX-109	Low Complexant	T-202	Low Complexant
B-106	Low Complexant	C-101	Special Case	T-204	Low Complexant
B-107	Low Complexant	C-110	Low Complexant	TX-107	Low Complexant
B-108	Low Complexant	SX-108	No Complexant	TY-104	Low Complexant
B-111	Low Complexant	SX-113	No Complexant	TY-106	Low Complexant
B-201	Special Case	T-102	Low Complexant	U-112	Low Complexant
B-204	Special Case	T-104	Low Complexant	U-201	Low Complexant
BX-101	Low Complexant	T-106	Low Complexant	U-202	Low Complexant
BX-105	Low Complexant	T-108	Low Complexant	U-203	Low Complexant
BX-106	Low Complexant	T-109	Low Complexant	U-204	Low Complexant
BX-107	Low Complexant	T-112	Low Complexant	-----	----

4.4.4.3 Total Organic Carbon Data. Tanks that contain waste that is too dilute in fuel to support propagation have been identified using TOC data. It is recognized that the concentration of TOC does not provide a consistent, direct correlation with the potential fuel energy that exists in the waste. The organic species associated with the measured TOC concentration include less energetic compounds that result from aging of the original organic complexants. However, assuming that the TOC has the theoretical energy equivalent of sodium acetate allows the TOC concentration to be used as an effective tool for screening tanks. Analytical methods and limitations associated with the TOC measurements are discussed in Appendix F.

The sodium acetate TOC equivalent criterion provides a conservative screen. The magnitude of this conservatism can be easily calculated by examining the detailed organic speciation data presented earlier in Table 4-5, and by using the theoretical heat of reactions for the individual species. The theoretical heats of reaction for acetate, citrate, glycolate, formate, oxalate, EDTA, HEDTA, IDA, and NTA with sodium nitrate are -27.1, -20.3, -20.7, -14.7, -18.6, -27.9, -30.9, -25.4, and -24.3 kJ/g of carbon, respectively (Burger 1993). From the oxalate and organic speciation data in Tables 4-4 and 4-5, the tank wastes showing the least aging (i.e., the most remaining citrate, glycolate, EDTA, HEDTA, and the least oxalate) are tanks AX-102, U-105, and U-106. Acetate has a theoretical heat of reaction of -27.1 kJ/g of carbon. Using the heat of

reactions for the individual species and assuming any unidentified TOC is HEDTA (the organic complexant with the highest heat of reaction), the heats of reaction for TOC in AX-102, U-105, and U-106 are -20.9, -21.6, and -23.1 kJ/g of carbon, respectively. Even the most energetic sample (U-106) has only 85% of the energy of sodium acetate.

The tank groupings shown in Section 4.4.4.1 and TOC characterization data were statistically examined using Analysis of Variance (ANOVA). ANOVA models are used to determine the distributions of TOC in each tank. These distributions are then integrated to determine the portion of waste that might exceed the 4.5 wt% TOC (dry basis) criterion. The distributions produced from the sampling data are imperfect estimates of the actual tank distributions, because the number of samples are typically small. The uncertainty in these distributions is determined by the statistical procedures used to fit ANOVA models to the data and expressed as a confidence bound.

The ANOVA model and associated calculations are described in detail in Appendix I. However, the most important assumptions regarding the calculations are summarized below:

(1) **Distribution** - TOC is assumed to have a logistic-normal distribution. This implies that if a large number of samples were taken from a single waste layer, and the TOC concentrations plotted as a histogram, the histogram would have a logistic-normal shape. Although the assumption of logistic-normality is an approximation, a plot of the ANOVA residuals (see Figure I-3 in Appendix I) demonstrates that the assumption is reasonable.

(2) **Variability** - The variability on the logistic scale of TOC is roughly the same in all tanks and can be pooled together across tanks. In other words, all the TOC distributions have the same standard deviation on the logistic scale. The reasonableness of this assertion can be evaluated by examining Figure I-4 in Appendix I, which displays TOC data residuals from the ANOVA fit on a tank-by-tank basis.

(3) **Tank Groupings** - The tanks in a particular group that have been sampled for TOC and water are representative of that group. The tank grouping employed has a negligible impact on the estimates for sampled tanks, but the assumption is vital for the estimates on unsampled tanks; if the sampled tanks are not representative of the defined groups, the extrapolations will not be legitimate. Appendix F discusses tank groupings in more detail. Section 5.0 in Appendix I discusses a validation test conducted to verify the extrapolations. The TOC data from six recently sampled tanks were compared to the predictions made by the ANOVA model. The TOC values predicted by ANOVA were not significantly different from the data.

(4) **Analytical Error** - The measurement errors present in the TOC and water measurements are assumed to be 10% (more specifically, the relative standard deviation of the measurements is assumed to be 10%). The ANOVA fit actually estimates spatial variability and measurement variability, so measurement variability must be subtracted from the ANOVA estimates to obtain a correct spatial variability. Justification for the

assumption that the measurement variability is roughly 10% comes from laboratory procedure and an examination of replicate measurements in the data set (see Appendix H for additional discussion).

(5) **Representativeness** - It is assumed that the samples taken from each tank are representative of the waste within the tank. The assumption of representativeness is perhaps the most important assumption in this list because its validity impacts upon the general relevance of any measurements taken on the current set of waste samples and any estimates calculated from them.

When assessing tank wastes, it is tempting to ignore statistical uncertainties and require the safety analysis to prove that no waste in a tank is combustible. However, statistical uncertainties cannot be ignored, and acceptable probabilities of making decision errors must be specified. For this evaluation, comparisons were made using one-sided 95% confidence limits on waste fractions that might exceed the 4.5 wt% TOC (dry) criterion. The 95% confidence limit is commonly used in statistical evaluations (Burr 1976, Kreyszig 1988) and this is the confidence limit arrived at in stakeholders discussions during the Data Quality Objective process for the Organic Complexant Safety Issue (Turner et al. 1995).

To pass the TOC screening, there must be 95% confidence that 95% of the waste has a dry concentration less than 4.5 wt%. Note that this 95% - 95% requirement is more conservative than the 95% confidence bound on the tank mean that was used in resolving the Ferrocyanide Safety Issue (Meacham et al. 1996). Tank wastes that pass the double 95% requirement have an acceptably low likelihood of supporting propagation, and required no additional testing.

Results of the TOC screening are shown in Table 4-13 for all 149 SSTs. Details on the TOC screening methodology are provided in Appendix I. For tank wastes that pass the screening, the complexant concentrations are too low to support propagation.

From Table 4-13, only eleven tank wastes failed the TOC screening. These tank wastes warranted additional evaluation. The wastes with the greatest TOC measurements were speciated (see Sections 4.3.2 and 4.3.3) and subjected to direct propagation testing (see Section 4.4.4.5).

Table 4-13. Results From Total Organic Carbon ANOVA Screening for All Single-Shell Tanks.

Tank	Result	Tank	Result	Tank	Result	Tank	Result	Tank	Result	Tank	Result
A-101	Pass	B-204	NA	C-101	NA	S-110	Pass	T-108	Pass	TX-117	Pass
A-102	Fail	BX-101	Pass	C-102	NA	S-111	Pass	T-109	Pass	TX-118	Pass
A-103	Fail	BX-102	Pass	C-103	NA	S-112	Pass	T-110	Pass	TY-101	Pass
A-104	Pass	BX-103	Pass	C-104	Fail	SX-101	Pass	T-111	Fail	TY-102	Pass
A-105	Pass	BX-104	Pass	C-105	Fail	SX-102	Pass	T-112	Pass	TY-103	Pass
A-106	Fail	BX-105	Pass	C-106	Pass	SX-103	Pass	T-201	Pass	TY-104	Pass
AX-101	Pass	BX-106	Pass	C-107	Pass	SX-104	Pass	T-202	Pass	TY-105	Pass
AX-102	Fail	BX-107	Pass	C-108	Pass	SX-105	Pass	T-203	Pass	TY-106	Pass
AX-103	Pass	BX-108	Pass	C-109	Pass	SX-106	Pass	T-204	Pass	U-101	Pass
AX-104	Pass	BX-109	Pass	C-110	Pass	SX-107	Pass	TX-101	Pass	U-102	Pass
B-101	Pass	BX-110	Pass	C-111	Pass	SX-108	Pass	TX-102	Pass	U-103	Pass
B-102	Pass	BX-111	Pass	C-112	Pass	SX-109	Pass	TX-103	Pass	U-104	Pass
B-103	Pass	BX-112	Pass	C-201	NA	SX-110	Pass	TX-104	Pass	U-105	Fail

4.4.4.4 Tanks Containing Organic Solvent Waste. Sampling and analyses show that four* tanks (C-102, C-103, C-104, and C-204) contain a significant quantity of organic solvents. Organic speciation results for the four tanks are shown in Table 4-14. The organic in C-102 waste is comprised of NPH and TBP (Campbell et al. 1995). Tank C-104 contains mostly NPH (Campbell et al. 1996). The organic pool in tank C-103 contains mostly NPH and phosphate esters. The TOC in C-204 was over 99% TBP, with relatively minor amounts of DBP, acetate, and formate (Campbell et al. 1996). These tanks have low free hydroxide concentrations such that hydrolysis of TBP is slow. Furthermore, the immiscibility of TBP with tank waste supernatants places mass transfer limitations on the rates at which aqueous phase oxidizers generated by radiolysis can attack TBP. The long life of immiscible phosphate esters in moderately alkaline wastes is consistent with their chemical properties.

Table 4-14. Tanks Containing Solvent Waste.

Tank	Principal Organic Species (Percent of Total TOC Measured)	Mean TOC (wt%)
C-102	NPH (84%)[1], TBP (16%)[1]	0.70
C-103	TBP (48%)[2], NPH (43%)[2], oxalate (2%)[2]	0.85
C-104	NPH (60%), acetate (12%), formate (5.5%), oxalate (11%), unidentified (11.5%)	0.91
C-204	TBP (99%+)	12

Notes: [1] Percents based on the sum of the individual organic species.
[2] Speciation of the sludge sample; tank C-103 contains a floating pool of organic solvent.

4.4.4.5 Propagation Testing. The best measure of propagation is direct testing (AIChE 1995). Tank waste samples with the highest TOC and DSC measurements were tested for propagation using the RSST and PRSST. Waste samples from ten tanks were air-dried below 100°C until grindable with a mortar and pestle, then tested in the RSST. The samples were selected because the measured TOC concentration exceeded 3.0 wt% (the original Watch List criterion) or DSC analysis showed a heat of reaction greater than 480 J g^{-1}, the safety screening criterion. The

*Tank C-106 sludge samples did contain a small amount of solvent. About 100 mL of sample yielded 2 mL of separable organic when centrifuged. Organic speciation showed that the organic contained 3 wt% TBP, 42 wt% ethylhexyl phosphates, and 54 wt% oxalate (Campbell et al. 1996).

RSST is described in Appendix G, and the results are summarized in Table 4-15. None of the dried waste samples propagated.

Table 4-15. Adiabatic Calorimetry (RSST) Test Results on Tank Waste Samples.

Tank	Waste TOC (wt%, dry)	TOC of Sample (wt%, dry)	DSC Result[1] (J g^{-1}, dry)	Propagate[2]
AN-107	4.5 - 9.8	5.5[3] (0.80)[4]	-1300	No
AW-101	0.8 - 2.0	2.0 (0.11)	-990	No
BY-104	0.2 - 2.6	0.8 (0.02)	-770	No
BY-105	0.1 - 1.1	0.4 (0.03)	-1500[5]	No
BY-108	0.2 - 3.2	3.2 (0.15)	-590	No
C-201	2.8 - 4.6	4.6 (0.40)	-690	No
C-204	6.0 - 13	13[6] (1.1)	>-1200	No
U-102	0.4 - 2.4	2.3 (0.12)	-620	No
U-105	1.2 - 3.3	3.3 (0.10)	-630	No
U-106	1.5 - 7.2	4.9[7] (0.15)	-880	No

Notes:
1 Highest measured exothermic energy measured by DSC for the sample, the negative sign denotes exothermic energy.
2 Propagation behavior measured by the RSST is described in Appendix G.
3 Supernatant samples measured as high as 9.8 wt% TOC on a dry weight basis. The highest TOC measurement on a sample that also contained solids was 5.5 wt%. RSST tests were not performed on purely aqueous samples. Chemical speciation showed that the organic was about 70% low molecular weight acids and 30% chelators/chelator fragments.
4 Standard deviation for sample measurements shown in parentheses.
5 The BY-105 DSC measurements showed high variability. RSST was performed to further assess the sample.
6 Chemical speciation of the organic in tank C-204 showed that the TOC was tributyl phosphate solvent.
7 Supernatant samples measured 4.8 to 7.2 wt% TOC on a dry weight basis, 25 - 36 g L^{-1} in solution. The highest TOC measurement on a sample that also contained solids was 4.9 wt%. RSST tests were not performed on purely aqueous samples.

Waste samples from five of the eleven tanks that failed the TOC screening, and tanks C-201 and C-202 were selected for propagation testing using the PRSST. As shown in Table 4-16, the seven tank waste samples tested (A-102, AX-102, C-104, C-201, C-202, U-105, and U-106) had the highest TOC/DSC measurements concentrations, and were the least aged. Results from the seven tanks tested bound the waste in the six tanks (A-103, A-106, BY-103, C-105, T-111, and U-111) which were not tested. The PRSST is described in Appendix G, and the results are summarized in Table 4-17. None of the dried waste samples propagated.

Table 4-16. Summary of Data from the Tanks That Fail Initial Screening and Selection of Bounding Tanks for Propagation Testing.

Tank	Water (wt%)	TOC (wt%)	DSC (J/g dry)	Percent of TOC as Oxalate
A-102	31 - 37	1.0 - 1.8	-38 to -320	22
A-103	40 - 41	0.77 - 0.80	n/a	n/a[1]
A-106	43 - 45	0.62 - 0.72	n/a	n/a[1]
AX-102	25 - 33	2.0 - 3.7	-150 to -670	10
BY-103	14 - 34	0.22 - 1.7	-5 to -140	99
C-104	39 - 69	0.61 - 1.9	-15 to -720	11
C-105	33 - 77	0.55 - 0.68	-4 to -524	14
C-201	10 - 11	2.1 - 4.3	-57 to -690	30
C-202	6 - 8	2.1 - 3.7	-66 to -580	68
T-111	70 - 85	0.20 - 0.41	-18 to -1890[2]	<5[3]
U-105	18 - 44	0.85 - 2.4	-70 to -880	22
U-106	22 - 50	0.87 - 4.1	-47 to -890	12
U-111	39	0.52 - 0.54	n/a	n/a

Notes: n/a = not available. Waste from tanks A-103, A-106, and U-111 had only TOC analyses. Oxalate analyses were not available for these tanks at the time of this report.

Shaded rows indicate tank wastes selected for RSST/PRSST testing because they had the highest TOC/DSC measurements and were the least aged.

[1] Although oxalate data were not available, examination of the temperature/dose histories (Stauffer 1997) indicate that A-102 was exposed to lower temperatures/dose, and therefore would be less aged than A-103 and A-106.

[2] The T-111 DSC scans were difficult to correct to a dry basis because the samples retained more than 70 wt% water. The DSC results fluctuated an order of magnitude depending on where the analyst interpreted the baseline and the -1890 J/g should be viewed with skepticism since this represented the most conservative interpretation.

[3] Organic speciation of the T-111 samples showed that less than 15 % of the TOC was complexant, or complexant based degradation products. The major complexant constituent was citrate. Ten percent of the TOC was NPH. About 75 % of the TOC was not identified, but the samples were not speciated for other solvents such as TBP and diethylhexyl phosphate.

Table 4-17. PRSST Test Results on Dried Tank Waste Samples.

Tank	TOC of Sample tested (wt%, dry)	Propagate
A-102	2.1 (0.1)[1]	No
AX-102	4.8 (0.8)	No
C-104	2.3 (0.2)	No
C-201	2.8 (0.5)	No
C-202	2.6 (0.1)	No
U-105	1.4 (0.2)	No
U-106	3.6 (0.4)	No

Notes: [1]Standard deviation for sample measurements shown in parentheses.

To assess the safety margin between the waste fuel concentration and that required for propagation, tank wastes with the highest TOC concentrations were spiked with additional fuel (sodium HEDTA) and reanalyzed using the PRSST. About 200 g of waste were required to complete the suite of spike tests for each tank; therefore, the waste samples (segments) with the highest TOC were composited to ensure sufficient material was available for testing. Sodium HEDTA was added to the dried waste samples as a solution (containing 60 to 330 g of sodium HEDTA dihydrate per kilogram solution) and the mixture was dried to constant mass at 105 °C under vacuum. Sodium HEDTA was used because it has the highest theoretical combustion energy of the complexants used at Hanford (Burger 1993), and the simulant mixtures containing HEDTA propagated at the lowest TOC concentrations (see Figure 4-1). Results from the spiked samples are shown in Table 4-18.

From Table 4-18, all of the dried samples required additional fuel to propagate. The AX-102, U-105, and U-106 dried waste samples required 31, 490, and 42 wt% more TOC (as HEDTA) to propagate. The C-202 waste sample failed to propagate even at 7.1 wt% TOC, even though 4.5 wt% TOC (as HEDTA) was added. This was expected because tank C-202 waste had only enough oxidizer to support spiking to 4.3 wt% TOC. As with the simulant test results, propagation only occurred above the theoretical criterion, and the minimum TOC concentration required was more than 4.5 wt%. The TOC and water concentrations in the original samples (Figure 4-6) indicate that there is considerable margin between tank waste conditions and the conditions necessary for propagation. Tank wastes with high TOC concentrations contain considerable water (e.g., AX-102 and U-106 contain about 29 and 49 wt% water, respectively).

Table 4-18. PRSST Test Results on Dried Waste Samples Spike with HEDTA.

Tank	TOC of Dried Composite Sample (wt%, dry)	TOC with HEDTA Added (wt%, dry)	Propagate
AX-102	4.8 (0.8)[1]	5.4 (0.18)	No
AX-102	4.8 (0.8)	5.5 (0.00)	No
AX-102	4.8 (0.8)	6.3 (0.43)	Yes
C-202	2.6 (0.1)	4.3 (0.20)	No
C-202	2.6 (0.1)	7.1 (0.35)	No
U-105	1.4 (0.2)	5.8 (0.51)	No
U-105	1.4 (0.2)	5.8 (0.24)	No
U-105	1.4 (0.2)	6.9 (0.40)	Yes
U-106	3.6 (0.4)	4.3 (0.41)	No
U-106	3.6 (0.4)	4.4 (0.10)	No
U-106	3.6 (0.4)	5.1 (0.40)	Yes
U-106	3.6 (0.4)	5.9 (0.80)	Yes

Notes: [1]Standard deviation for sample measurements shown in parentheses.

4.4.4.6 Special Case Tanks. Eleven tanks have unique or hard to track waste transfer histories, and require individual examination. The C-200 and B-200 series tanks received several small waste transfers from the strontium semiworks at B Plant, and these wastes were often small pilot plant runs that contained unique waste streams. Tanks C-101, C-102, and C-103 received predominantly solvent waste and also need to be characterized separately. The available information for these special case tanks is examined separately below.

Tank B-201. The process history of tank B-201 indicates that while active (1952 to 1975) it received waste from the B Plant 224 facility (Conner et al. 1997). The waste came from a lanthanum fluoride-based separation process (one of the final steps in the bismuth phosphate process) and did not contain complexant waste. Two full-depth core samples were taken in 1991. All the DSC analyses of the wastes samples revealed no exothermic reactions (Conner et al. 1997). Based on the sample data and tank waste history, this tank contains no organic complexant fuel and cannot support propagation. Nitrate/nitrite analyses also show that the waste has a low oxidizer concentration.

Tank B-202. Tank B-202 received mostly non-complexed wastes from B Plant operations. This tank had an active transfer history, but records indicate that it did not receive concentrated

complexant waste (Dougherty 1995). Two full-depth (eight segments) core samples were taken in 1991. Normal paraffin hydrocarbons were used as the hydrostatic head fluid, and some samples might have been slightly contaminated with NPH. All of the subsegment DSC analyses showed a small amount of exothermic energy (-9 to -224 J g^{-1} on a dry basis) relative to the -1200 J g^{-1} energy criterion. The TOC analyses for the samples ranged between 0.2 and 0.4 wt% (Dougherty 1995). Based on the low DSC and TOC analyses for all the waste samples, this tank waste cannot support propagation.

Tank B-203. Tank B-203 received mostly waste from the B Plant 224 facility and also received some B Plant flush (Jo et al. 1996). The B Plant flush would probably contain small amounts of detergent and/or cleaning agents. This waste contains primarily sodium, strontium, hydroxide, nitrate, and fluoride, with trace amounts of iron, lanthanum, carbonate, oxalate, and plutonium. Three full-depth (14 segments) core samples were taken in 1995. All the samples contained considerable water, 63 to 81 wt%. Only two of the 43 half-segment waste samples showed any exothermic reactions by DSC analysis.

The two samples that showed some exothermic energy were from segments ten and thirteen. The lower-half of segment ten had four DSC measurements that showed -170 J g^{-1}, -91 J g^{-1}, no exothermic energy, and no exothermic energy. This sample contained 75 wt% water, and the two energetic results were -700 and -370 J g^{-1} on a dry weight basis. The lower half of segment 13 had duplicate DSC analyses of -72 and -69 J g^{-1} (-290 and -280 J g^{-1} on a dry weight basis). The corresponding TOC analyses for these samples were less than 0.01 wt% (Jo et al. 1996). The small exothermic energy is most likely caused by detergents or other small contaminants from the B Plant flush. Based on the sample data and tank waste history, B-203 waste cannot support propagation.

Tank B-204. Tank B-204 received mostly waste from the B Plant 224 facility and also received some B Plant flush (Sasaki et al. 1996). All the DSC analyses of the wastes samples revealed no exothermic reactions. Based on the sample data and tank waste history, this tank contains no organic complexant fuel and cannot support propagation.

Tank C-101. The waste transfer records of Tank C-101 indicate little complexant waste, but an appreciable amount of organic solvent (Brevick et al. 1994m). An auger was taken from C-101 in 1995 (Sasaki 1995a). DSC analysis of the samples showed no exothermic energy; however, analyses did indicate the presence of TOC (about 0.4 wt%). This is consistent with the presence of organic solvent that can evaporate during DSC analysis before the nitrate/nitrate oxidizer melts. Vapor samples taken in the headspace of C-101 also indicate that this tank contains organic solvent (Huckaby et al. 1997).

Although C-101 does contain TOC, the available evidence indicates that this organic is solvent. Experimentation (Cowley et al. 2000, Conner 1996) shows that the solvents do not support condensed-phase combustion and thus do not contribute to the organic complexant hazard. The organic solvent hazard is covered in a separate topical report (Cowley et al. 2000). Because the TOC in tank C-101 is organic solvent, this tank waste does not pose a organic complexant propagation hazard.

Tank C-102. The waste transfer history of tank C-102 shows an appreciable amount of organic solvent (Brevick et al. 1994m). Two auger samples were taken from C-102, and samples were subjected to detailed chemical speciation (Campbell et al. 1995). Analyses showed that the TOC in this tank waste was comprised of all organic solvent (84% NPH and 16% TBP) and contains a low oxidizer concentration. The organic solvent hazard is covered in a separate topical report (Cowley et al. 2000). Tank C-102 waste cannot support propagation.

Tank C-103. Tank C-103 contains a pool of floating organic solvent. Two full-depth core samples were taken in October through February of 1994/1995 (Winters et al. 1996). The sludge samples, aqueous supernatant, and organic solvent pool were subjected to detailed organic speciation (Campbell et al. 1995). The TOC in the solid sludge samples ranged between 0.8 to 0.9 wt%, and was primarily TBP and NPH (48% and 43%, respectively) with some oxalate (2%). The organic solvent hazard is covered in a separate topical report (Cowley et al. 2000).

Tank C-201. Tank C-201 has a capacity of 55,000 gallon and currently has about thirteen inches of waste (about 2000 gallons) (Sasaki 1995b). Two full-depth auger samples were taken in 1995, but sample recovery was poor and only 16 g of material were recovered. Enough material was available to run DSC, TGA, TOC, and a direct propagation (RSST) test. The DSC scans showed exothermic energy of -57 to -620 J g^{-1}. The TOC concentration ranged from 2.5 to 4.1 wt% (wet), and the water concentration ranged from 9.7 to 11.5 wt%. Direct combustion testing in the RSST (see Appendix G) demonstrated that this waste will not support propagation. The tank was re-sampled in 1997 with good sample recovery (more than 300 g). Speciation showed that the waste had insufficient nitrate/nitrite oxidizer to support 4.5 wt% TOC. An additional propagation test in the PRSST confirmed that the waste cannot support propagation.

Tank C-202. Tank C-202 has a capacity of 55,000 gallons and currently has about eight inches of waste (about 1000 gallons). Transfer histories indicate that the waste in C-202 is similar to that in C-201 (Kelly 1995), and indeed the results from DSC, TGA, and TOC are consistent with the C-201 waste. Two full-depth auger samples were taken in 1995, but sample recovery was poor and only 8.5 g of material were recovered. The tank was re-sampled in 1997 with full sample recovery (over 400 g). Nitrate/nitrite analyses showed that the waste had insufficient oxidizer to support 4.5 wt% TOC. Propagation tests confirmed that the waste will not support propagation. The waste failed to propagate when spiked with sodium HEDTA to 4.3 and 7 wt% TOC. This was expected since the waste only had sufficient oxidizer to support spiking to 4.3 wt% TOC.

Tank C-203. The waste transfers in and out of tank C-203 are not well documented, so most of the judgements about C-203 are based on two full-depth (about 51 cm) auger samples taken in 1995 (Sasaki 1995c). The augers samples were divided into half segments and analyzed by DSC and thermogravimetric analysis (TGA). The DSC showed consistent low exothermic reactions for all the samples ranging from -31 to -97 J g^{-1} (dry basis). The TGA showed 31 to 52 wt% water in the samples. The DSC results indicate that tank C-203 contains organic complexant concentrations too low to support propagation.

Tank C-204. Two full depth auger samples were taken from tank C-204, and the waste samples contained 6 to 13 wt% TOC. The waste samples were subjected to detailed organic speciation and combustion testing in the RSST. Organic speciation showed that the TOC in tank C-204 was almost exclusively TBP (> 99%). An RSST analysis of the waste (see Appendix C) mirrored the RSST test on a TBP waste simulant (Conner 1996, Cowley et al. 2000). Testing and analysis show that C-204 waste cannot propagate.

4.4.5 Inactive Miscellaneous Underground Storage Tank Waste Propagation

Propagation was assessed for each of the IMUSTs individually. Process history, sample analyses, and propagation testing of the source waste were used in the assessments.

Tank 200-W-7. 200-W-7 is a catch tank located northwest of the 242-S Evaporator. The only input to this tank was effluent from personnel decontamination from the Decontamination Trailer MO-0326. This tank contains soap, water, and low levels of contamination rinsed from onsite workers (Stickney et al. 1998). The concentrations of heat generating radionuclides and organic complexants will be lower than SST waste. Based on sample data and tank waste history, 200-W-7 cannot support propagation.

Tank 209-E-TK-111. 209-E-TK-111 is a drain tank located adjacent to the south end of the 209-E Critical Assembly Room (CAR). Process history shows that complexants were not produced or used in the CAR (Caldwell et al. 1993). This tank was sampled routinely, where it was determined that the radionuclide levels were below limits for discharging the contents to a crib. A recent sample of TK-111 identified no detectable flammable gas within the tank (Stickney et al. 1998). Based on sample data and tank waste history, 209-E-TK-111 cannot support propagation.

Tank 216-BY-201. 216-BY-201 is a supernatant disposal flush tank located between the 241-BY Tank Farm and the 216-B Cribs. This tank received waste from the 241-BY tanks and TBP waste line en-route to the 216-B cribs (Stickney et al. 1998). The contents are similar to the contents of the 241-BY tanks. Process history and sampling data show that the 241-BY Tanks received low complexant waste. Propagation tests were also performed on the bounding 241-BY Tanks, further supporting the conclusion that the waste does not propagate (Section 4.4). Based on sample data from the 241-BY Tanks and process history, 216-BY-201 cannot support propagation.

Tank 231-W-151-001 and 231-W-151-002. The 231-W-151 tanks received waste from about 75 floor drains in Building 231-Z. Drainage was received into tank 231-W-151-002, which overflowed into 231-W-151-001. The overflow from 231-W-151-001 emptied to crib 216-Z-7. Solids settled out leaving sludge in each tank. By 1974 the inlet to these tanks had been blanked off. Neutral, dilute waste from plutonium finishing has collected in these tanks (Caldwell et al. 1993). Based on sample data and tank waste history, tanks 231-W-151-001 and 231-W-151-002 contain insufficient complexant to support propagation.

Tank 240-S-302. 240-S-302 is a catch tank that received leakage, spillage, line flushes, and drainage associated with waste transfers through diversion box 240-S-151. These waste transfers were associated with the T and S Tank Farms and Building 202-S (Caldwell et al. 1993). However, the tanks in the T and S tank farms have been shown to contain insufficient complexant for propagation to be a concern (Section 4.4). Based on sample data from the T and S Tank Farms and process history, 240-S-302 cannot support propagation.

Tank 241-A-302B. 241-A-302B is a catch tank that received waste spillage and leakage from the 241-A-151 and 241-A-152 diversion boxes, concrete encasements, and the associated pipe encasements within the A Tank Farm (Caldwell et al. 1993). Waste propagation tests on the bounding tanks in the A Tank Farm have shown that the worst possible waste in 241-A-302B cannot support propagation (Section 4.4).

Tanks 241-AX-151CT, 241-AX-151-TK-D, 241-AX-151-TK-E, 241-AX-TK-151-TK-F, and 241-AX-151-TK-G. 241-AX-151 is a diverter station that contains four small diverter tanks and a catch tank. Since this diversion station routed the waste for the 241-AX Tank Farm, any remaining contents should reflect the waste in the 241-AX tanks (Stickney et al. 1998). Since the 241-AX tanks have been shown to contain insufficient complexant to support propagation (Section 4.4), the waste in the 241-AX-151 diverter station cannot support propagation.

Tanks 241-B-301 and 241-B-302B. 241-B-301 and 241-B-302B are catch tanks that received drainage, primarily flushes and surface water run-off, from drainage boxes 241-B-151, 241-B-152, 241-B-153, and 241-B-252 (Caldwell et al. 1993). The waste in 241-B-301 and 241-B-302B is bound by the waste in the B Tank Farm. The bounding tanks for complexant in B Tank Farm were sampled and analyzed for propagation. Each was found to contain insufficient complexant to support propagation (Section 4.4). Based on sample data and process history, 241-B-301 cannot support propagation.

Tanks 241-BX-302A, 241-BX-302B, and 241-BX-302C. These tanks are catch tanks which received drainage from diversion boxes BR-152, BX-153, BYR-152, BXR-152, BX-154, and BX-155 (Caldwell et al. 1993). These diversion boxes were used to transfer waste around the B, BX, and BY Tank Farms. The waste contained within the catch tanks is bound by the waste stored in the B, BX, and BY Tank Farms. Evaluation of process history and analysis of sample data from B, BX, and BY Tank Farms show that the contained waste cannot support propagation (Section 4.4). Since the bounding waste cannot support propagation, the waste contained in 241-BX-302A, 241-BX-302B, and 241-BX-302C cannot support propagation.

Tank 241-BY-ITS2-TK-1. 241-BY-ITS2-TK-1 is a small vapor condenser that was a component of the ITS-2 In-Tank Solidification (ITS) system. The tank received condensate from the heated in-ground waste tank for return to Tank 241-BY-112. The condensate would have the composition of the tank waste vapors (Stickney et al. 1998). Since organic complexants have very low vapor pressures, the complexant content of 241-BY-ITS2-TK-1 will be bound by Tank 241-BY-112. Process history and sample data have demonstrated that Tank 241-BY-112 has

insufficient complexant to support propagation (Section 4.4), therefore the waste contained in 241-BY-ITS2-TK-1 cannot support propagation.

Tank 241-BY-ITS2-TK-2. 241-BY-ITS2-TK-2 served as a decontamination solution receiver tank for decontamination of the in-tank heater assemblies used in the ITS-2 system (Stickney et al. 1998). Since the waste from the heated tank (241-BY-112) cannot support propagation (Section 4.4), the diluted waste from the heated tank in 241-BY-ITS2-TK-2 cannot support propagation.

Tank 241-C-301. 241-C-301 is a catch tank that received drainage, primarily flushes and surface water run-off, from the diversion boxes 241-C-151, -152, -153, and –252. These diversion boxes were associated with waste transfers to and from the C Tank Farm (Caldwell et al. 1993). The contents of 241-C-301 are bound by the waste contained by the C Tank Farm. Because process history, sample analysis, and propagation testing have shown that the bounding tanks in the C Tank Farm cannot support propagation (Section 4.4), the contents of 241-C-301 cannot support propagation.

Tank 241-ER-311A. 241-ER-311A is a stainless steel catch tank which received waste from the 241-ER-151 Diversion Box due to leaks and decontamination activities. As a catch tank, it also received occasional leaks and surface runoff. 241-ER-311A was taken out of service in 1954 (Stickney et al. 1998). Since process history shows that complexants were not used prior to 1954 (ERDA 1975), this tank cannot support propagation.

Tank 241-S-302A. Tank 241-S-302A is a catch tank that was installed to receive drainage from the 241-S-151 diversion box and concrete encasements. Diversion box drainage consists of jumper connector leakage and precipitation intrusion. Wastes characteristic of the S, SX, and U Tank Farms, and the 222-S Laboratory, mixed with run-off, are expected to be present in 241-S-302A (Caldwell et al. 1993). Waste from the 222-S Laboratory did not contain complexants (Caldwell et al. 1993), and the waste in the S, SX, and U Tank Farms either contained insufficient complexant or was tested and shown to not propagate (Section 4.4). Based on process history, sample analysis and propagation testing, 241-S-302A cannot support propagation.

Tank 241-S–302B. 241-S-302B is a catch tank which received waste from encasement drains for lines connecting the S Tank Farm and diversion box 241-S-151. This tank was approved as interim stabilized on December 4,1984. The stabilization evaluation listed this tank as empty based on measurements taken in September 1984 (Neilsen, 1992). Because the tank contains no waste, it cannot support propagation.

Tank 241-SX-302. Tank 241-SX-302 is a catch tank that was in operation from 1954 to 1983. Drainage to the catch tank originated from the 241-SX-151 and 241-SX-152 diversion boxes, the SX Tank Farm line encasements, and line 456 (Caldwell et al. 1993). Line 456 is the transfer line that connects 241-SX-152 diversion box with the 241-S-151 diversion box and the

241-U-151 diversion box (drawings H-2-71051 and H-2-44511 sheet 38). 241-SX-302 collects run-off, spills, leaks, line flushes, and drainage associated with transfers between the SX Tank Farm and the U and S Tank Farms. The waste in the S, SX, and U Tank Farms either contained insufficient complexant or was tested and shown to not propagate (Section 4.4). Therefore, based on process history, sample analysis and propagation testing, 241-SX-302 cannot support propagation.

Tank 241-T-301B. 241-T-301B is a catch tank that served to collect run-off, spills, leaks, line flushes, and drainage associated with waste transfers in the T Tank Farm. This drainage came from diversion boxes 241-T-151, 241-T-152, 241-T-153, and 241-T-252 (Caldwell et al. 1993). The contents of 241-T-301B are bound by the contents of the T Tank Farm. The waste contained in the T Tank Farm has been shown to contain insufficient complexant to support propagation (Section 4.4), therefore the waste in 241-T-301B cannot support propagation.

Tanks 241-TX-302A and 241-TX–302XB. Tanks 241-TX-302A and 241-TX-302XB are catch tanks that received drainage from a concrete encasement that originated at diversion box 241-TX-153. Diversion box 241-TX-153 was associated with transfers to and from the TX Tank Farm. The drainage included run-off, spills, leaks, and line flushes associated with waste transfers in the TX Tank Farm (Caldwell et al. 1993). The contents of the catch tanks 241-TX-302A and 241-TX-302XB are bound by the contents of the TX Tank Farm. Since the contents of the TX Tank Farm have been shown to contain insufficient complexant to support propagation (Section 4.4), catch tanks 241-TX-302A and 241-TX-302XB cannot support propagation.

Tank 241-TX-302B. 241-TX-302B is a catch tank that was installed to replace 241-TX-302B(R). Tanks 241-TX-302B received drainage from diversion box 241-TX-155. This diversion box was associated with transfers between the TX Tank Farm, Building 221-U, the T Tank Farm, the TY Tank Farm, 202-S, 222-S, and the U Tank Farm. The diversion box received run-off, spills, leaks, and line flushes associated with waste transfers (Caldwell et al. 1993). Process history tells us that waste from 221-U, 202-S, and 222-S did not contain complexants (Caldwell et al. 1993). Process history, sample analysis, and propagation testing has shown that the waste from the T, TX, TY, and U Tank Farms cannot support propagation (Section 4.4). Therefore, 241-TX-302B cannot support propagation.

Tank 241-TX-302B(R). Tank 241-TX-302B(R) is a catch tank that was installed in 1950 to receive drainage from diversion box 241-TX-155. However, the tank sustained acid damage and was isolated in 1954 (Caldwell et al. 1993). Since process history shows that complexants were not used before 241-TX-302B(R) was isolated (ERDA 1975), this tank cannot support propagation.

Tanks 241-TY-302A and 241-TY–302B. 241-TY-302A and 241-302B are catch tanks that received drainage from diversion box 241-TY-153. The diversion box received run-off, spills, leaks, and line flushes associated with waste transfers from the T Plant to the TY Tank Farm (Caldwell et al. 1993). Process history and sample analysis have shown that the waste in the TY

Tank Farm cannot support propagation (Section 4.4). Since the waste in the TY Tank Farm bounds the waste in the catch tanks, 241-TY-302A and 241-TY-302B cannot support propagation.

Tank 241-Z-8. 241-Z-8 is a settling tank that received RECUPLEX process waste before discharge to the 216-Z-8 french drain. The RECUPLEX process did not use or generate complexants. 241-Z-8 was in operation from 1955 to 1962 when it was isolated and stabilized (Caldwell et al. 1993). Process history shows that the RECUPLEX waste cannot support propagation, therefore 241-Z-8 cannot support propagation.

Tank 242-T-135. Tank 242-T-135 is a decontamination liquid storage tank that provided decontamination solutions to the feed tank, evaporator, cyclone separator, and scrubber of the 242-T Evaporator. The expected contents would be acid or caustic decontaminiation solutions. This tank was not used for processing or collecting any wastes (Stickney et al. 1998). Since process history does not suggest the presence of organic salts, 242-T-135 cannot support propagation.

Tank 242-TA-R1. 242-TA-R1 is a receiver tank located at the bottom of the 242-TA receiver vault. Tank 242-TA-R1 was used to neutralize Z-Plant acid waste. The composition of the acid waste is known from design criteria. The acid waste did not contain organics (Stickney et al. 1998). Therefore, process history shows that 242-TA-R1 did not receive complexants. Consequently, 242-TA-R1 contains insufficient complexant to support propagation.

Tanks 244-BXR-001, 244-BXR-002, 244-BXR-003, and 244-BXR–011. Tanks 244-BXR-001, 244-BXR-002, 244-BXR-003, and 244-BXR–011 are individual cells within the BXR Vault. The BXR Vault was in service from 1951 to 1957. The feed material to BXR Vault originated in the BX and BY Tank Farms (Caldwell et al. 1993). Process history shows that the BX and BY Tank Farms did not receive complexant waste until the BXR Vault was out of service (ERDA 1975), consequently tanks 244-BXR-001, 244-BXR-002, 244-BXR-003, and 244-BXR–011 cannot support propagation.

Tanks 244-TXR-001, 244-TXR-002, and 244-TXR–003. Tanks 244-TXR-001, 244-TXR-002, and 244-TXR-003 are individual cells within the TXR Vault. The TXR Vault was in service from 1951 to 1956. The feed material to TXR Vault originated in the T and TX Tank Farms (Caldwell et al. 1993). Process history shows that the T and TX Tank Farms did not receive complexant waste until the TXR Vault was out of service (ERDA 1975), therefore tanks 244-TXR-001, 244-TXR-002, and 244-TXR-003 cannot support propagation.

Tanks 244-UR-001, 244-UR-002, 244-UR-003, and 244-UR-004. Tanks 244-UR-001, 244-UR-002, 244-UR-003, and 244-UR–004 are individual cells within the UR Vault. The UR Vault was in service from 1951 to 1957. The feed material to UR Vault originated in the U Tank Farm (Caldwell et al. 1993). Process history shows that the U Tank Farm did not receive complexant waste until after the UR Vault was taken out of service (ERDA 1975), consequently tanks 244-UR-001, 244-UR-002, 244-UR-003, and 244-UR–004 cannot support propagation.

4.5 PROPAGATION HAZARD POTENTIAL AND ACCIDENT FREQUENCY

4.5.1 Double-Shell Tanks

There is no potential for propagation in DST wastes under current storage conditions. Sample data and process histories show that the wastes contain more than 20 wt% water. Propagation cannot occur when water concentrations exceed 20 wt%.

4.5.2 Double-Contained Receiver Tanks

There is no potential for propagation in DCRT wastes under current storage conditions. Sample data and process histories show that the wastes contain more than 20 wt% water. Propagation cannot occur when water concentrations exceed 20 wt%.

4.5.3 Catch Tanks

There is no potential for propagation in catch tank wastes under current storage conditions. Sample data and process histories show that the wastes contain more than 20 wt% water. Propagation cannot occur when water concentrations exceed 20 wt%.

4.5.4 Single-Shell Tanks

Propagation is not possible in all 149 SSTs. TOC/DSC characterization data, waste process histories, and propagation testing show that the SSTs cannot propagate. A tank-by-tank summary of the analyses that led to this conclusion is presented in Table 4-19.

Table 4-19. Propagation Analysis Summary for All Single-Shell Tanks. (2 sheets)

Tank	Tank	Tank	Tank	Tank	Tank
A-101[5]	B-204[4,9]	C-101[4]	S-110[3,5]	T-108[3,4,6]	TX-117[3,6]
A-102[8,10]	BX-101[3,4,6]	C-102[1,7]	S-111[3,5]	T-109[1,3,4,5]	TX-118[3,5]
A-103[8]	BX-102[13,,6]	C-103[1,7]	S-112[3,6]	T-110[1,3,5]	TY-101[3,5]
A-104[1,3,6]	BX-103[1,3,5]	C-104[1,7,8,10]	SX-101[5]	T-111[3,8,10]	TY-102[3,5]
A-105[1,2,6]	BX-104[1,5]	C-105[1,8]	SX-102[5]	T-112[1,3,4,5]	TY-103[3,5]
A-106[8]	BX-105[4,5]	C-106[5]	SX-103[5]	T-201[1,3,4,5]	TY-104[1,3,4,5]
AX-101[5]	BX-106[1,3,4,5]	C-107[1,5]	SX-104[6]	T-202[3,4,5]	TY-105[2,5]
AX-102[8,10]	BX-107[3,4,5]	C-108[1,3,5]	SX-105[6]	T-203[3,5]	TY-106[2,4,5]
AX-103[5]	BX-108[3,4,6]	C-109[1,3,5]	SX-106[5]	T-204[3,4,5]	U-101[3,6]
AX-104[1,3,6]	BX-109[3,4,5]	C-110[3,4,5]	SX-107[2,6]	TX-101[3,6]	U-102[5,8]
B-101[3,5]	BX-110[3,5]	C-111[1,3,5]	SX-108[2,4,5]	TX-102[5]	U-103[5]
B-102[3,6]	BX-111[3,5]	C-112[3,5]	SX-109[2,6]	TX-103[3,6]	U-104[3,6]
B-103[3,4,5]	BX-112[5]	C-201[1,8,9]	SX-110[3,6]	TX-104[5]	U-105[8,10]
B-104[2,4,5]	BY-101[3,5]	C-202[1,8,9]	SX-111[3,6]	TX-105[3,6]	U-106[8,10]
B-105[3,6]	BY-102[1,5]	C-203[1,9]	SX-112[6]	TX-106[3,6]	U-107[5]
B-106[3,4,5]	BY-103[3,8]	C-204[1,8,9]	SX-113[1,2,4,5]	TX-107[3,4,5]	U-108[5]
B-107[2,4,6]	BY-104[3,5,8]	S-101[5]	SX-114[3,6]	TX-108[3,6]	U-109[5]
B-108[1,3,4,5]	BY-105[3,5,8]	S-102[5]	SX-115[3,6]	TX-109[1,3,6]	U-110[1,3,5]
B-109[1,5]	BY-106[3,5]	S-103[6]	T-101[3,6]	TX-110[3,6]	U-111[8]

Table 4-19. Propagation Analysis Summary for All Single-Shell Tanks. (2 sheets)

Tank	Tank	Tank	Tank	Tank	Tank
B-110[3,5]	BY-107[3,5]	S-104[3,5]	T-102[1,3,4,5]	TX-111[6]	U-112[3,4,6]
B-111[4,5]	BY-108[3,5,8]	S-105[3,6]	T-103[1,3,6]	TX-112[3,6]	U-201[1,3,4,5]
B-112[3,5]	BY-109[3,5]	S-106[3,5]	T-104[2,4,5]	TX-113[3,6]	U-202[1,3,4,5]
B-201[1,4,9]	BY-110[3,5]	S-107[5]	T-105[1,3,5]	TX-114[3,6]	U-203[1,3,4,5]
B-202[9]	BY-111[3,5]	S-108[3,6]	T-106[1,3,4,5]	TX-115[3,6]	U-204[1,3,4,5]
B-203[9]	BY-112[1,3,5]	S-109[3,5]	T-107[1,3,5]	TX-116[3,6]	---

Notes:
1 Waste has low oxidizer concentration (Section 4.3.1).
2 Tank received no incoming transfers after complexants were for first used in 1968 (Section 4.4.4.1).
3 Assessment of waste transfer records and process history indicate that this tank received low complexant concentrations (Section 4.4.4.1).
4 DSC analyses from ambient to 450 °C showed no exothermic chemical reactions (Section 4.4.4.2).
5 Sample data and modeling (ANOVA) show low TOC concentrations (Section 4.4.4.3).
6 ANOVA extrapolation indicates low TOC concentrations (Section 4.4.4.3).
7 Speciation of the TOC shows that almost all the organic is solvent (Section 4.4.4.4).
8 Waste propagation tests on bounding tanks indicates tank waste will not propagate (Section 4.4.4.5).
9 The B 200 and C 200 series tanks were assessed individually (Section 4.4.4.6).
10 Moisture retention studies indicate waste will retain significant water during interim storage. Waste in tanks C-104, T-111, U-105, and U-106 will retain more than 20 wt% water, and 20 wt% water prevents propagation at all TOC concentrations. Tank A-102 and AX-102 wastes will retain about 17 wt% water. This amount of water increases the theoretical requirement for propagation to 7.4 wt% TOC, which is a factor of two higher than the highest measured TOC concentration in AX-102 (3.7 wt%), and about a factor of four higher than the highest measured TOC concentration in A-102 (1.8 wt%).

4.5.5 Inactive Miscellaneous Storage Tanks

Propagation is not possible in any of the 45 RPP "owned" IMUSTs. Process histories, characterization data, and waste propagation testing of the source waste all show that propagation cannot occur in the IMUSTs.

4.6 PROPAGATION CONTROLS

No controls are required to prevent propagation under current waste storage conditions. The SSTs waste is too dilute to sustain propagation. The DST, DCRTs, and catch tanks contain predominantly aqueous wastes and are too wet to support propagation. No operations are currently planned that would result in combustible waste heel during the storage mission.

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APPENDIX A

THE 1957 KYSHTYM ACCIDENT

by

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APPENDIX A

THE 1957 KYSHTYM ACCIDENT

On September 29, 1957, a radioactive waste tank exploded at the Kyshtym Industrial Complex, a Soviet nuclear weapons production site east of the Ural Mountains. The explosion occurred in a 250 m^3 (66,000 gallon) steel-lined concrete vault and resulted in extensive dispersal of fission products to the surrounding environment. The waste, an acidic solution of nitrate and acetate salts, was generated from the separation of uranium and plutonium from fission products by reduction, oxidation and precipitation. In 1989, official reports became available that allowed U.S. DOE personnel to evaluate the Kyshtym accident and assess the likelihood of a similar scenario occurring at a U.S. site. The Hanford assessment was documented by Fisher (1990).

The Kyshtym incident resulted from disruption of a decay heat removal system that resulted in severe overheating and combustion of a sodium acetate - sodium nitrate mixture (Fisher 1990). A layout of a typical Kyshtym tank (1 of 60) is shown in Figure A-1. During normal operation (see Figure A-2), the actively cooled tank contained about 175 m^3 of waste solution with about 100 g L^{-1} of sodium nitrate and about 60 g L^{-1} of sodium acetate. The estimated decay heat of about 200 kW (this is considerably higher than the Hanford Site tank heat loads) was removed at temperatures well below 100 °C. Disruption of the active cooling system, however, led to complete loss of all water leaving behind a solid residue (containing ~10,000 kg of sodium acetate) which continued to overheat and resulted in a severe over-pressurization event when the temperature reached about 300 °C (Figures A-3 and A-4).

Consistent with the above observation, Reactive System Screening Tool (RSST) calorimeter tests with various sodium acetate-sodium nitrate mixtures have demonstrated the onset of combustion at a temperature of about 300 °C when the sodium acetate concentration exceeded about 20 wt% (7 wt% total organic carbon) (Babad and Turner 1993). A simulation of the Kyshtym incident is illustrated in Figure A-5. Extrapolation of the noted RSST pressure (in psi) to the Kyshtym tank suggests a pressure buildup of about 400 psi for the case where the tank does not vent. However, the required overpressure to lift the 160,000 kg tank head plate is only about 4 psi. This plate was found some distance from the incident tank.

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Figure A-1. Kyshtym Tank Layout

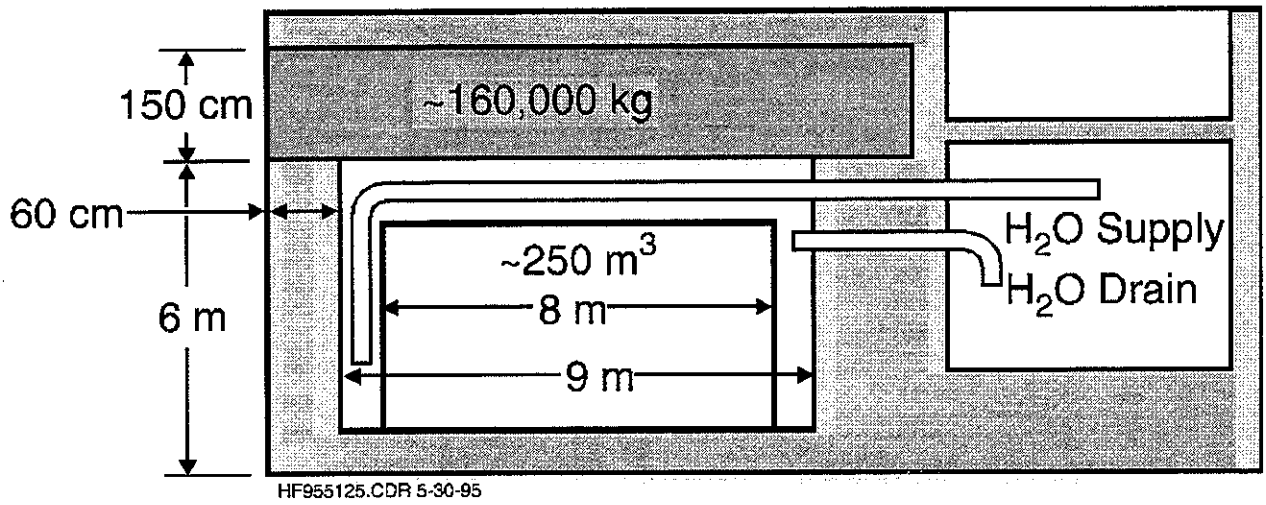


Figure A-2. Kyshtym Normal Operation

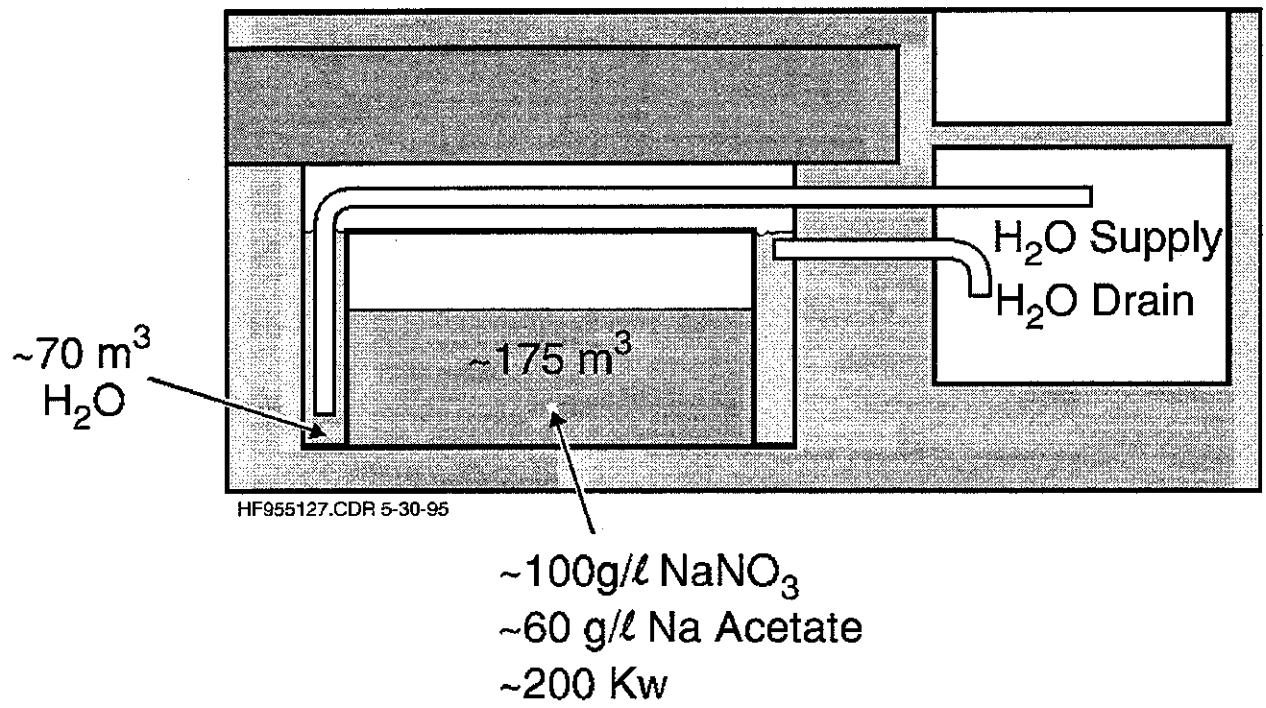


Figure A-3. Kyshtym Incident - Loss of Coolant

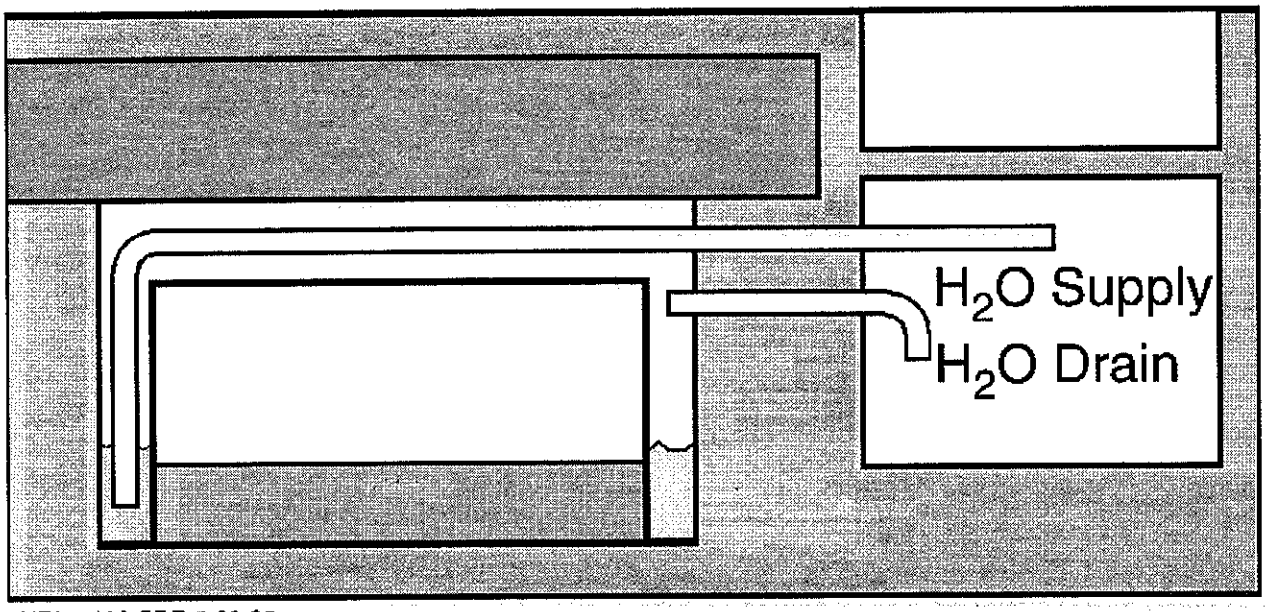


Figure A-4. Kyshtym Incident - Final Stage

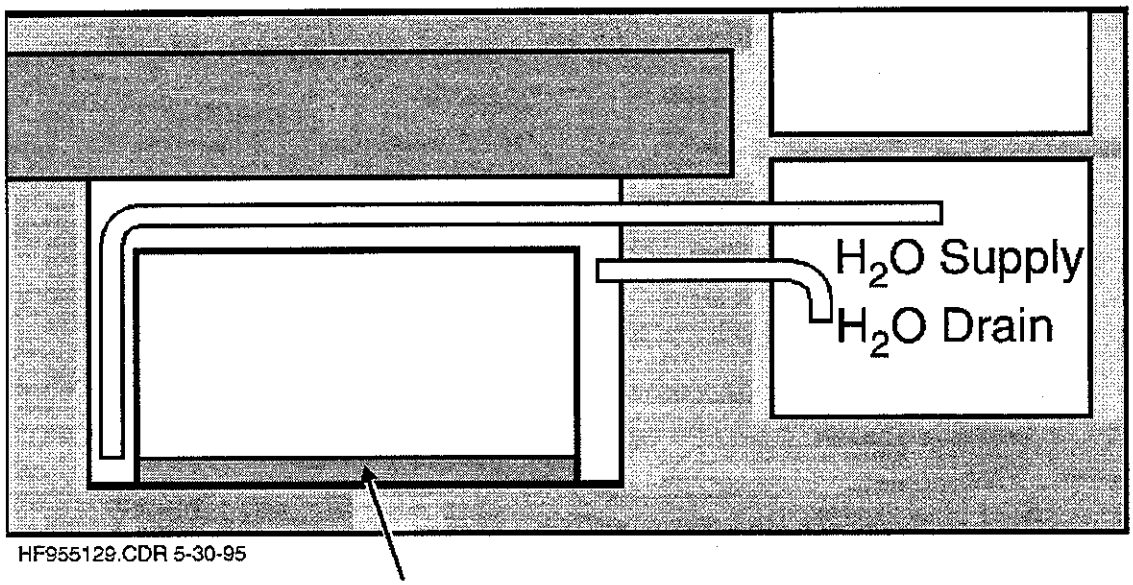
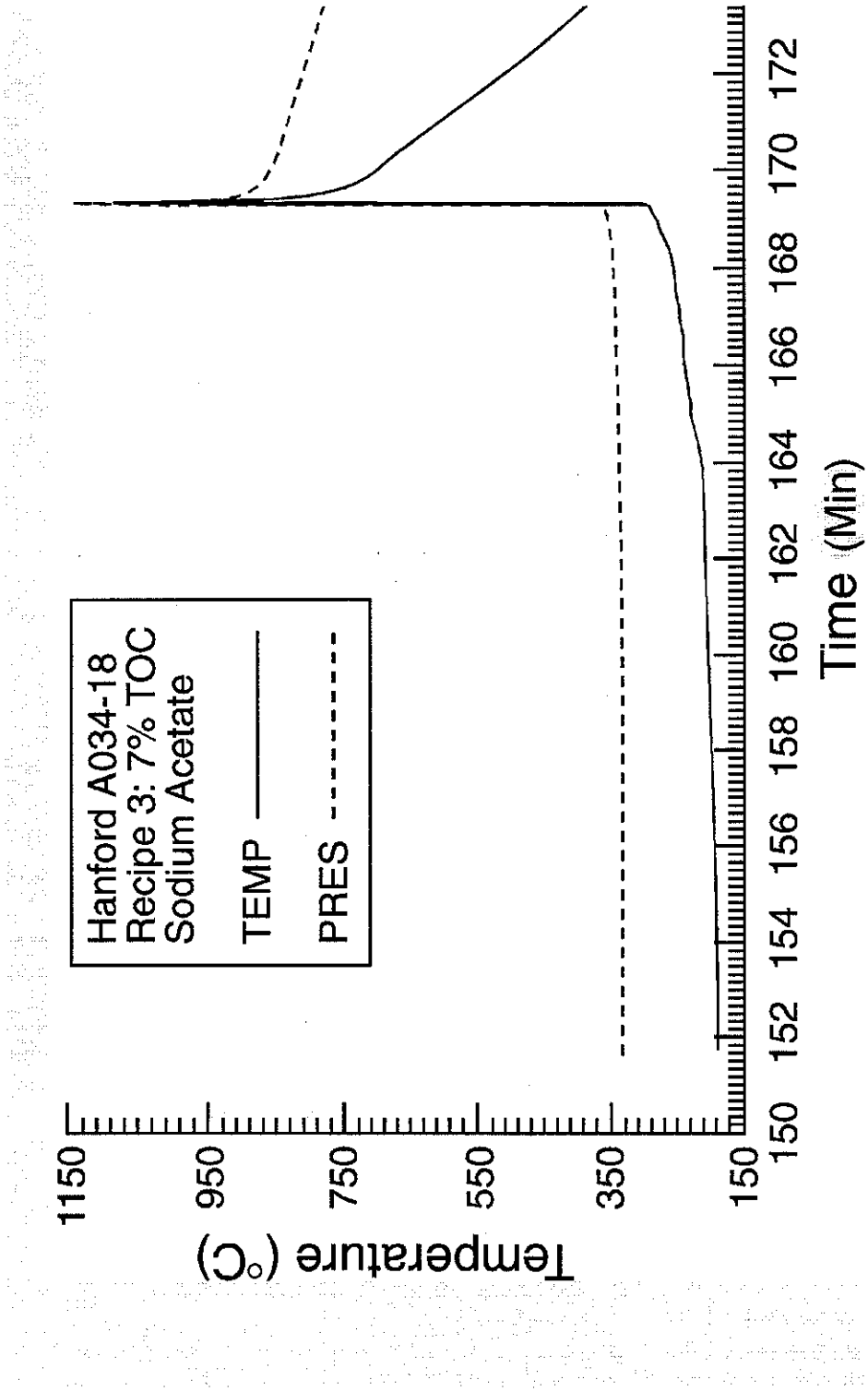


Figure A-5. RSST Simulation of Kyshtym Incident - Following Loss of Water



APPENDIX B

BULK RUNAWAY SCREENING CRITERIA FOR HANFORD HIGH-LEVEL WASTE SINGLE-SHELL TANKS

by

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LIST OF TERMS

A	Pre-exponential constant
A_t	Tank or waste cross-sectional area
c	Specific heat of waste
E	Activation energy
h	Depth of waste region with pore-space formation due to moisture loss
H	Half-thickness of waste slab
k	Thermal conductivity of waste
k_d	Thermal conductivity of dry waste
k_s	Thermal conductivity of soil above tank
k_w	Thermal conductivity of wet waste
L	Waste depth
$\dot{m}$	Moisture loss in one year
q	Ratio of decay heating to chemical heating
Q	Total heat generated in waste (W)
q'''_d	Volumetric decay heat generated in waste (W m^{-3})
$q'''_{ch}(T)$	Volumetric chemical heat generation rate at temperature T (W m^{-3})
R	Ideal gas constant
t	Time
t_c	Characteristic cooling time of waste slab
t_s	Safe storage time of waste
T	Local temperature waste
T_∞	Average ambient temperature
T_0	Temperature at boundaries of waste slab
$T_{v,a}$	Average headspace temperature with active tank ventilation
$T_{w,a}$	Peak waste temperature with active tank ventilation
$T_{w,p}$	Peak waste temperature with passive tank ventilation
x	Distance in waste (Figure B-1)
z	Dimensionless distance in waste

LIST OF TERMS (Continued)

Greek Letters

α	Waste thermal diffusivity
δ	Dimensionless waste slab thickness (Frank-Kamenetskii parameter)
δ_{crit}	Critical value of δ for runaway
ρ	Density of waste
ρ_ℓ	Density of water
τ	Dimensionless time
τ_a	Dimensionless adiabatic runaway time
ϵ	Waste porosity
τ_c	Dimensionless characteristic cooling time of waste slab
τ_s	Dimensionless safe storage time of waste
θ	Dimensionless local temperature in waste
θ_m	Maximum dimensionless temperature in waste

APPENDIX B

BULK RUNAWAY SCREENING CRITERIA FOR HANFORD HIGH-LEVEL WASTE SINGLE-SHELL TANKS

1.0 INTRODUCTION

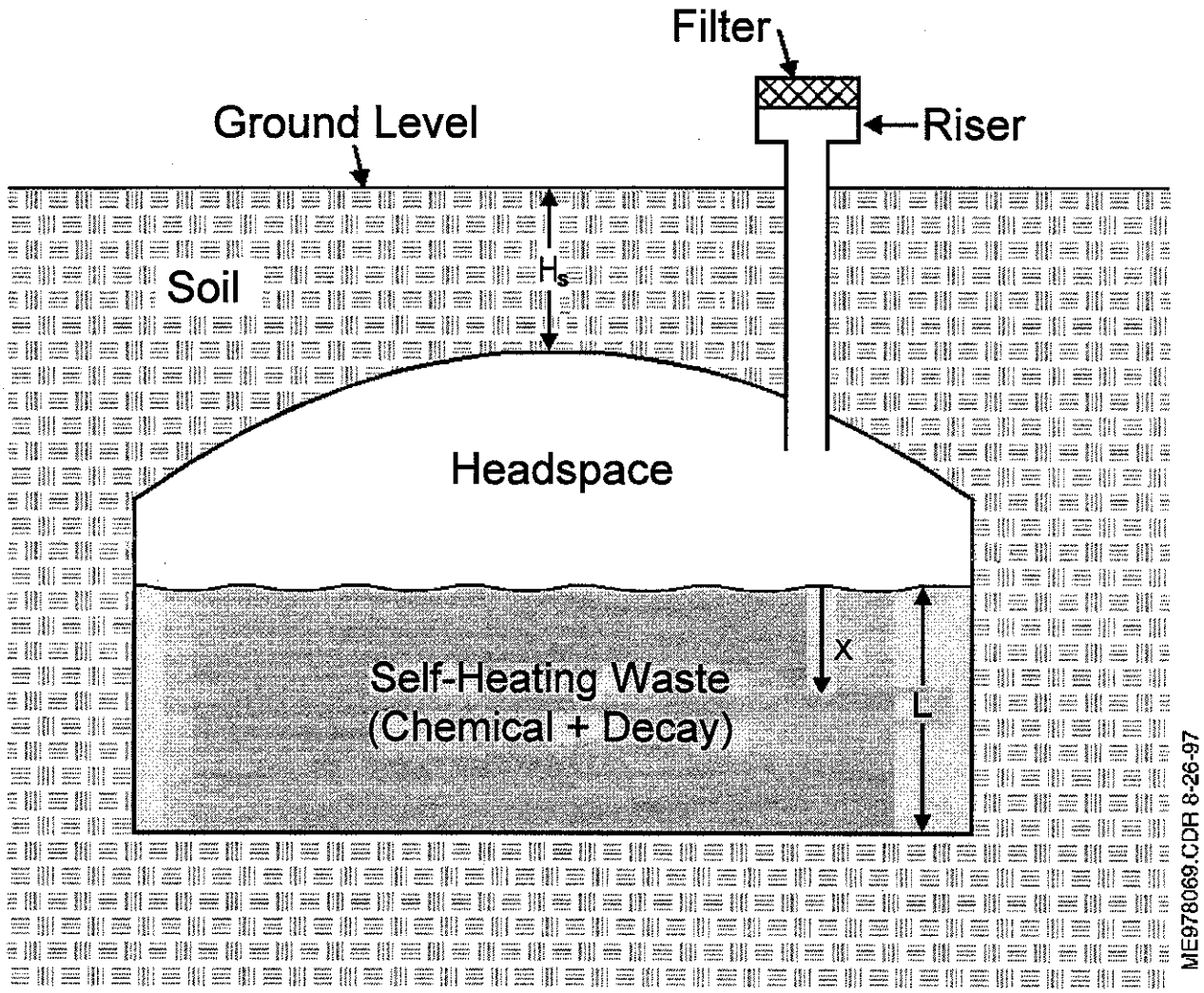
Organic complexants were sent to the waste tanks during operations at the Hanford Site. The principal organic complexants were glycolic acid, citric acid, hydroxyethylethylenediamine-triacetic acid, and ethylenediaminetetraacetic acid. The organic complexants are in waste matrices that include inerts and diluents (e.g., water, sodium carbonate, sodium sulfate, and hydroxy salts of aluminum, iron, and silicon) and potential oxidants (sodium nitrate/nitrite). Since these compounds can react exothermically when combined with nitrate/nitrite oxidizers, the potential exists for bulk runaway chemical reactions similar to the 1957 Kyshtym accident (a brief description of this accident is provided in Appendix A).

The waste tank farm at Hanford consists of 177 tanks including 28 double-shell tanks (DSTs) and 149 single shell tanks (SSTs). The DSTs contain large quantities of supernatants, and bulk runaway is not possible because of high water content. Fifteen of the 149 SSTs are actively ventilated, and 118 SSTs had their supernatants pumped to DSTs (interim stabilization). Interim stabilization operations continue to pump the remaining 31 SSTs. The tanks are located below the ground and the airspace of each tank communicates directly with the atmosphere through a vertical riser pipe. A typical tank with its waste layer is illustrated in Figure B-1.

No SST has received waste since 1980. The SSTs are inactive and no new waste additions will occur. The bulk of the radioactivity in the SSTs is ^{137}Cs and ^{90}Sr, which are also the major heat generating sources in the waste tanks. Volumetric heat generation rates are typically less than 50 W m^{-3} (see Table B-1). The heat generation rates from ongoing chemical reactions are not known, but are generally believed to be much less.

While the waste composition changes with time from both radiolysis and chemical reactions, the waste temperatures are gradually decreasing and no significant adverse physical or chemical events are known to have occurred in these tanks since becoming inactive. This information is used in this appendix to assess the potential for bulk runaway reactions.

Figure B-1. Schematic of Underground Hanford Waste Tank.



2.0 BULK RUNAWAY SAFETY CRITERION

Spontaneous bulk runaway can occur when the chemical plus decay heat production exceeds the rate of heat dissipation from the waste. To derive the requirements for thermal stability, the waste is treated as a non-convective horizontal layer (or slab) of thickness L and of infinite lateral extent. The boundaries of the waste are at a constant and known temperature T_0. The basic equation of the problem is the transient one-dimensional conduction equation:

$$\rho c \frac{\partial T}{\partial t} - k \frac{\partial^2 T}{\partial x^2} = q'''_d + q'''_{ch}(T) \qquad \text{(B-1)}$$

where q'''_d is the constant, volumetric decay heating rate and $q'''_{ch}(T)$ is the temperature dependent volumetric heating rate. The latter quantity is expressed in the usual Arrhenius form

$$q'''_{ch}(T) = A \exp\left(-\frac{E}{RT}\right) \qquad \text{(B-2)}$$

where the pre-exponential A is the product of the rate constant and the heat of reaction. With the origin of the coordinate x at one boundary of the waste slab (see Figure B-1), the boundary and initial conditions for Equation B-1 are

$$T = T_0 \quad \text{at} \quad x = 0 \; ; \; \text{and} \; T = T_0 \quad \text{at} \quad x = L \qquad \text{(B-3)}$$

$$T = T_0 \quad \text{at} \quad t = 0 \qquad \text{(B-4)}$$

Note that as a result of symmetry, the solution of Equations B-1 through B-4 is also the solution to the problem of conduction in a self-heated slab of thickness L/2 with constant temperature T_0 at x = 0 and no flow of heat at x = L/2. In writing the boundary conditions in Equation B-3, constant temperature boundaries are assumed for the surface of the waste and the bottom of the tank.

To simplify the mathematics and display the important parameters that dictate the thermal stability of the waste, the following dimensionless parameters are used from Frank-Kamenetskii (1969) in his now-classical treatment of thermal explosions:

$$\theta = \frac{E}{RT_0^2}(T - T_0) \qquad \text{(dimensionless temperature)} \qquad \text{(B-5)}$$

$$\delta = \frac{q'''_{ch}(T_0)EL^2}{4kRT_0^2} \qquad \text{(Frank-Kamenetskii parameter)} \qquad \text{(B-6)}$$

$$\tau = \frac{4\alpha t}{L^2} \qquad \text{(dimensionless time)} \tag{B-7}$$

$$q = \frac{q'''_d}{q'''_{ch}(T_0)} \qquad \text{(decay-to-chemical heating ratio)} \tag{B-8}$$

$$z = \frac{x}{\left(\frac{L}{2}\right)} \tag{B-9}$$

With this choice of notation, Equations B-1 through B-4 transform to

$$\frac{1}{\delta}\left(\frac{\partial\theta}{\partial\tau} - \frac{\partial^2\theta}{\partial z^2}\right) = q + e^{\theta} \tag{B-10}$$

$$\theta = 0 \quad \text{at} \quad z = 0,1 \quad ; \quad \text{and } \theta = 0 \quad \text{at} \quad \tau = 0 \tag{B-11}$$

In Equation B-10, the Arrhenius term given by Equation B-2 was simplified by making the useful (and crucial) Frank-Kamenetskii approximation that the product $(RT_0/E)\theta << 1$. The argument of the exponential can then be approximated by $-E/RT_0 + \theta$.

Two different ways of examining the thermal stability of the waste slab via Equations B-10 and B-11 are provided below, the time dependent adiabatic approach and the steady-state approach. Both methods give similar critical conditions for chemical runaway.

2.1 TIME DEPENDENT ADIABATIC APPROACH

The time-dependent adiabatic approach is an approximate technique for arriving at the stability condition. Consider a slab at uniform temperature. Heat is applied to the center portion or region of the slab. Early in the thermal transient, the central region of the slab (in the vicinity of z = L/2) is unaffected by the presence of the boundaries at z = 0 and L. Thus the temperature rise in this region occurs in an adiabatic manner and heat conduction is not important. It turns out that there is a finite time for adiabatic heating to drive the central region temperature to infinity.

Considering pure adiabatic heating in the central region of the slab, Equation B-10 becomes

$$\frac{1}{\delta}\frac{d\theta}{d\tau} = q + e^{\theta} \tag{B-12}$$

Integrating Equation B-12. and applying the initial condition $\theta = 0$ at $\tau = 0$ yields

$$\tau = \frac{1}{q\,\delta} \ln\left[\frac{(1+q)\,e^{\theta}}{q + e^{\theta}}\right] \tag{B-13}$$

The finite time that it takes for the central region to reach infinity can be found by taking the limit of Equation B-13 as θ goes to infinity. The adiabatic runaway time, τ_a , is

$$\tau_a = \frac{1}{q\,\delta} \ln(1+q) \tag{B-14}$$

However, as the temperature at the center rises, thermal conduction does take place and starts to influence the temperature of the central portion. Experience with heat conduction problems involving internal heat generation (Carslaw and Jaeger 1959) has shown that regardless of whether the rate of heat production is a function of time or position or both, the time it takes for a thermal conduction wave to reach the center of the slab is always about the same. This time represents a balance between heat conduction out and heat generation. For stability the conduction and generation must balance so in dimensionless notation τ_c must be equal to unity:

$$\tau_c = \frac{4\alpha t_c}{L^2} = 1.0 \tag{B-15}$$

The term τ_c is the characteristic cooling time of the slab; it is the time that elapses before the center of the slab experiences the effects of the relatively low temperatures at its boundaries. Bulk runaway is not possible if the finite time for the "adiabatic" central portion to reach infinity is greater than the time for heat conduction from the edge to influence the center or

$$\tau_a > \tau_c \tag{B-16}$$

Equation B-16, and Equations B-14 and B-15 give the stability criterion

$$\delta < \frac{\ln (1 + q)}{q} = \delta_{crit} \qquad \text{(B-17)}$$

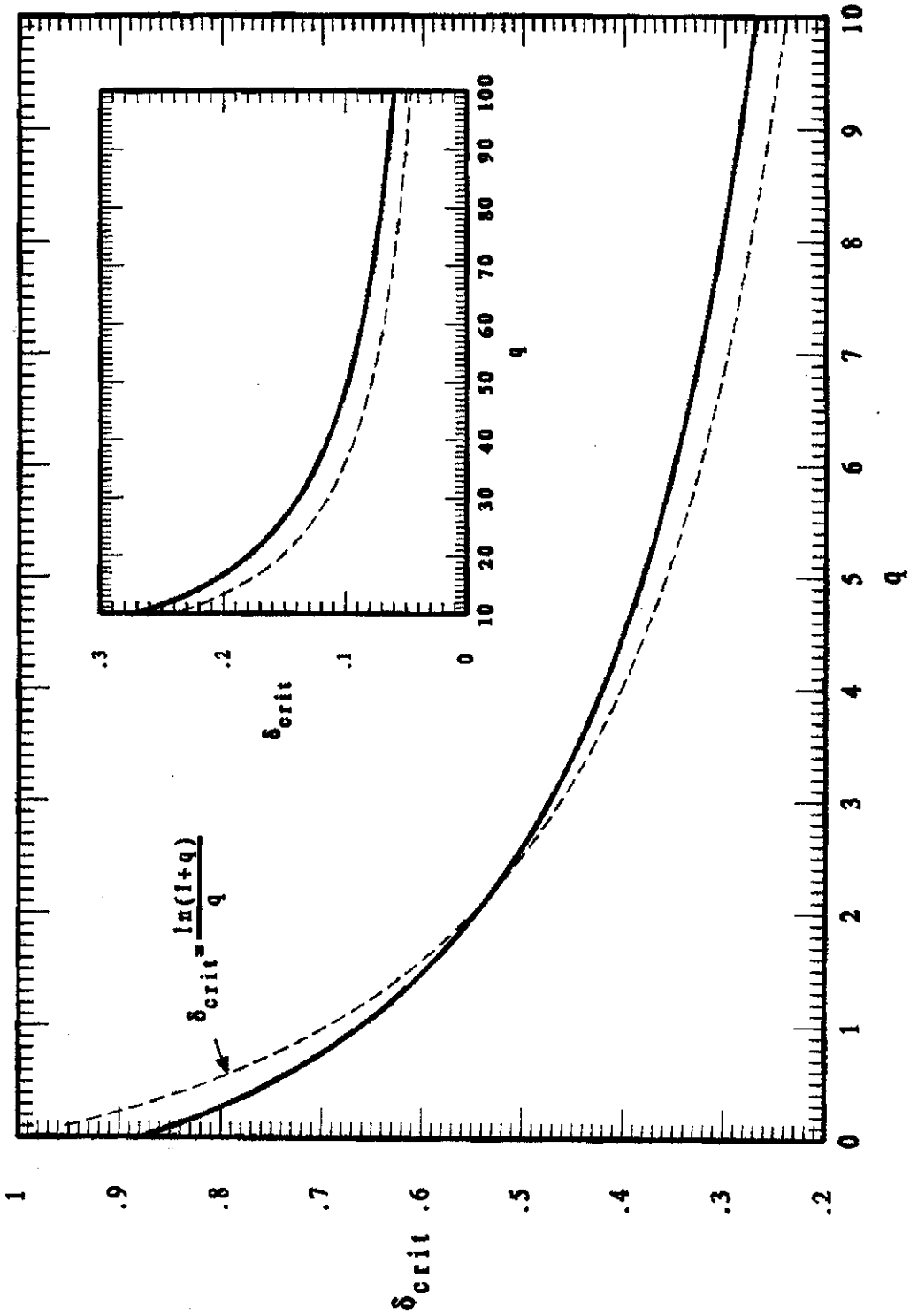
2.2 STEADY STATE APPROACH

With the transient term removed from Equation B-10 the problem is reduced to the solution of an ordinary differential equation. This equation can be integrated once, and can be expressed as a definite integral by using the boundary conditions $\theta = 0$ at $z = 0$, and $\theta = \theta_m$ at $z = 1$:

$$\delta = \frac{1}{2}\left[\int_0^{\theta_m} \frac{d\theta}{\sqrt{q\,(\theta_m - \theta) + e^{\theta_m} - e^{\theta}}}\right]^2 \qquad \text{(B-18)}$$

where θ_m denotes the maximum dimensionless temperature which is achieved at the center of the slab ($z = 1$) where $d\theta/dz = 0$. Equation B-18 can be integrated in closed form for the singular case $q = 0$. For nonzero values of q, it must be integrated numerically. The critical conditions for a runaway may be determined in the following manner. For a particular choice of q, Equation B-18 is integrated many times, each time for a different value of θ_m. A plot of δ versus θ_m is then constructed from which δ is found to pass through a maximum value. The maximum value is the critical value of δ (denoted by δ_{crit}) for a runaway since no steady-state solutions exist for δ values above δ_{crit}. By generating many curves of this type for different values of q, the functional relationship between δ_{crit} and q is arrived at numerically. This relationship is represented by the solid curve shown in Figure B-2. Runaways are to be expected for conditions that result in points (q, δ_{crit}) that lie above this curve. The result $\delta_{crit} = 0.88$ for no decay heat generation ($q = 0$) is well known (Frank-Kamenetskii 1969) and widely used to evaluate the possibility of a runaway in a chemically reactive slab.

Figure B-2. Dimensionless Critical Tank Thickness Versus Decay-to-Chemical Heat Ratio Parameter (Comparison Between Exact Solution and Approximation From Single Time-Dependent Theory).



3.0 APPLICATION TO HANFORD TANKS

The approximate result from Equation B-17 is compared in Figure B-2 with the exact numerical values obtained from Equation B-18 and the agreement is good. For small values of q, Equation B-17 slightly overestimates the exact results, but for large values of q, Figure B-2 shows that Equation B-18 provides slightly conservative estimates of δ_{crit}. For the Hanford wastes q (the ratio of radiolytic heating and chemical heating) is estimated to range between 10 and 100. (Appendix C, page C-14, gives one estimate of the relative values for radiolytic heating and chemical heating.) It follows that Equation B-16 for q values of interest can be said to represent a safe requirement for assessing the absence of chemical runaway in the Hanford waste tanks.

While values for τ_c can be estimated for the waste tanks, values for τ_a are not known. Fortunately, it can be shown that

$$\tau_c \ll \tau_s \tag{B-19}$$

where τ_s is the dimensionless time that the Hanford waste has been demonstrated to be stored safely; it is related to the waste physical safe storage time t_s by the definition (see Equation B-7)

$$\tau_s = \frac{4\alpha t_s}{L^2} \tag{B-20}$$

For any given tank with a given length, L, and thermal diffusivity, α, Equation B-19 becomes:

$$t_c \ll t_s \tag{B-21}$$

Because the tanks have exhibited a downward trend in temperatures since being declared inactive, the waste safe storage time, t_s, is greater than 17 years (from 1980 to present). The maximum characteristic cooling time, t_c, for the passively ventilated SSTs (Tank A-101) is 3.1 years, based on a waste depth L = 8.84 m and waste thermal diffusivity $\alpha = 2 \times 10^{-7}$ m^2 s^{-1}. The minimum cooling time is 14 hrs for the 0.2 m waste depth in tank C-202. Since t_s is well in excess of the characteristic cooling times t_c, and the fact that the wastes have remained stable with gradually decreasing temperatures to date, provides proof that the bulk runaway safety criteria (Equation B-16) is indeed satisfied.

Besides noting the length of time that the waste has been stored safely, with gradually decreasing waste temperatures, it is important to note that some of the tanks are actively ventilated and the question naturally arises as to whether the waste temperature in these tanks would continue to decline following the loss of active ventilation. Long term moisture loss is also a potential concern since the decrease in thermal conductivity of the waste after pore-space formation may

cause the decreasing waste temperature trend to reverse. The loss of active ventilation and the evaporation of interstitial liquid from the waste are the subjects of the next two sections.

3.1 LOSS OF ACTIVE VENTILATION

Of the actively ventilated SSTs only Tanks C-106 and SX-101 through SX-106 are believed to contain amounts of organic materials that may present a bulk runaway reaction threat. Estimates provided by Agnew et al. (1996) in terms of total organic carbon (TOC) are shown in Table B-1. The estimated absence of TOC in the high heat tanks is consistent with the observation that most of these tanks (SX-107, SX-108, SX-109, SX-112 and SX-113) were inactive by 1968 and that organic complexants were not used at Hanford until after 1968. It is noted that Tank C-106 is the only high heat tank that requires periodic water addition along with active ventilation.

Table B-1. Assessment of Actively Ventilated SSTs for Bulk Runaway.

Tank	H (m)	$T_{v,a}$ (°C)	$T_{w,a}$ (°C)	Q (W)	q'''_d (W m^{-3})	TOC[1] (wt%)	t_c
C-105	1.58	28	32	7,300	11	~0	36 days
C-106	2.32	27	68	32,200	34	2.1	78 days
SX-101	4.36	30	53	3,700	2.1	1.3	275 days
SX-102	5.15	33	64	4,400	2.1	1.4	1.1 years
SX-103	6.16	47	79	8,100	3.2	1.5	1.5 years
SX-104	5.79	29	74	3,600	1.5	1.4	1.3 years
SX-105	6.43	30	81	3,700	1.4	1.4	1.6 years
SX-106	5.09	28	42	3,200	1.5	1.3	1.0 years
SX-107	1.10	47	73	16,000	36	~0	18 days
SX-108	1.19	56	88	16,400	34	~0	20 days
SX-109	2.44	51	61	9,100	9.1	~0	86 days
SX-110	0.70	48	75	11,900	42	~0	7.1 days
SX-111	1.28	51	84	17,900	34	~0	24 days
SX-112	0.96	50	68	12,200	31	~0	13 days
SX-114	1.80	57	83	17,200	23	~0	47 days

[1] Estimated average concentration from Agnew et al. 1996 (dry basis).

Waste temperatures under only passive ventilation can be estimated based on work by Kummerer (1994). The fraction of heat lost out the top of a typical passively ventilated SST is about 0.5. Using this value, the peak waste temperature, $T_{w,p}$, under passive ventilation is

$$T_{w,p} \approx \frac{Q H_s}{2 k_s A_t} + T_\infty + (T_{w,a} - T_{v,a}) \qquad \text{(B-22)}$$

where Q (W) is the total heat generated in the waste, k_s is the soil thermal conductivity, A_t (410 m^2) is the tank cross-sectional or net area, H_s (4 m) is the mean soil depth above the tank, T_∞ (13.9°C) is the average ambient temperature, $T_{w,a}$ (°C) is the solid waste temperature with active ventilation, and $T_{v,a}$ (°C) is the average headspace temperature (see Table B-1). The first term on the right-hand-side of Equation B-22 is the temperature drop across the soil layer above the tank. The last term in parenthesis is the temperature drop across the waste layer when the tank is actively ventilated. The resulting estimated values for the organic bearing tanks are shown in Table B-2. Also listed in Table B-2 are actual waste temperatures recorded in 1982 and 1994 (Brevick 1994). The indicated decreases in the recorded waste temperatures are in reasonable agreement with a fractional yearly decrease in decay heat of about 0.023, or about a 25% decrease in the heat load for the 12 year period.

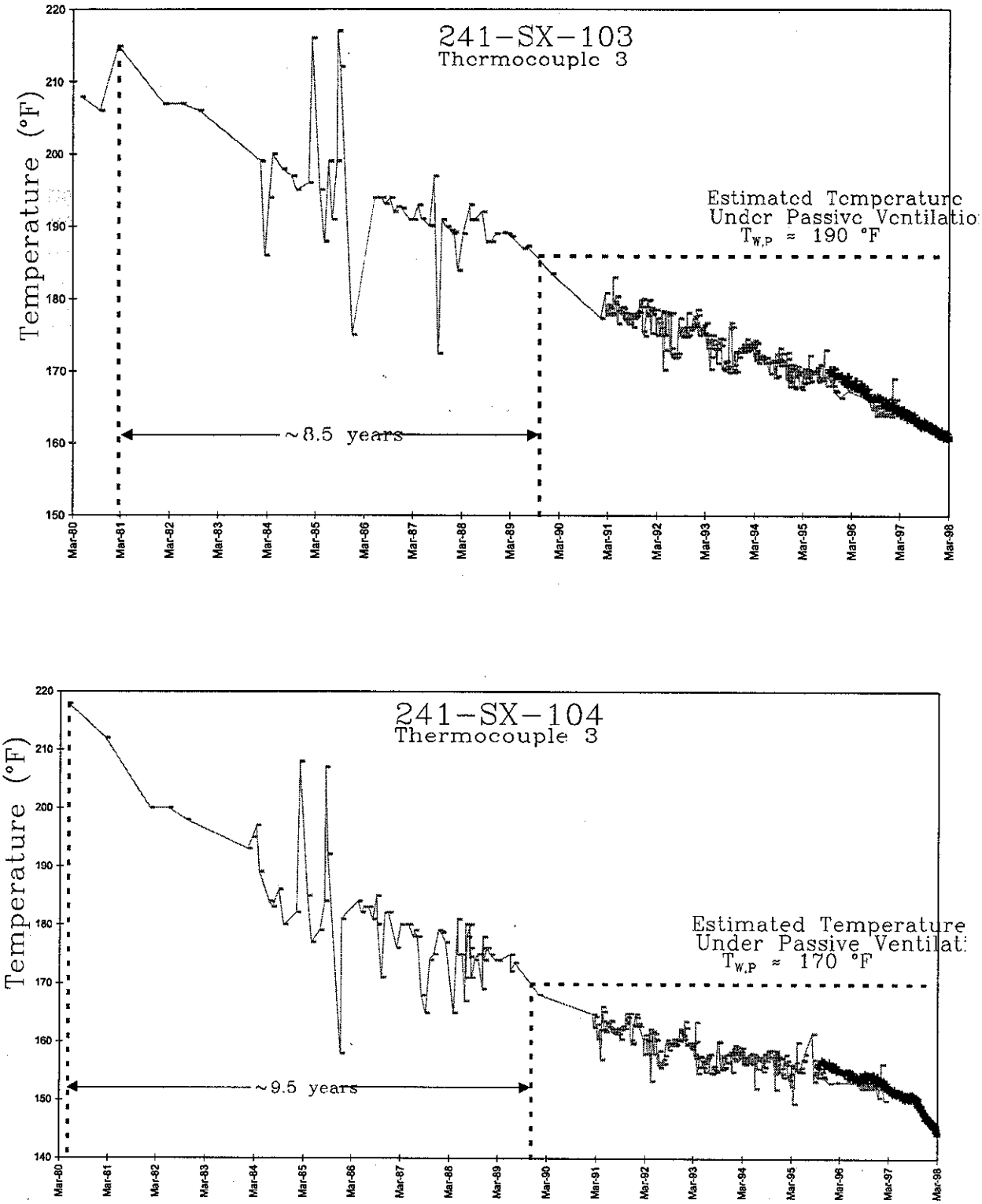
Table B-2. Measured Waste Temperatures Under Active Ventilation and Estimated Waste Temperatures Under Passive Ventilation.

Tank	Active Ventilation		Passive Ventilation Estimated Value $T_{w,p}$, °C
	1982 Reading, °C	1994 Reading, °C	
SX-101	81	53 (64)[1]	54
SX-102	93	64 (73)	67
SX-103	98	79 (77)	86
SX-104	93	74 (74)	76
SX-105	96	81 (76)	84
SX-106	57	42 (46)	44

[1]Anticipated temperature based upon a 25% decrease in decay heat from 1982 to 1994.

While the estimated values corresponding to passive ventilation are somewhat higher than the 1994 measured values (note that the latter values are used with Equation B-21), they are well below the 1982 recorded temperatures. Furthermore, historic waste temperatures were higher than the estimated passively ventilated temperatures for periods greater than 6 to 10 years (Figure B-3 illustrates relevant data for Tanks SX-103 and SX-104).

Figure B-3. Temperature Data for Tanks 241-SX-103 and 241-SX-104 and Comparison With Estimated Temperatures Under Passive Ventilation.



Since these periods are well in excess of the cooling times, t_c, for the solid wastes (see Table B-1), it follows that bulk runaway chemical reactions can also be ruled out for the lower passively ventilated waste temperatures. If such reactions were possible, they would have occurred a long time ago when the waste temperatures were higher and less degraded organic materials were present in the wastes.

3.2 LOSS OF WASTE MOISTURE

The bulk of the radioactivity and heat generating sources in the SSTs is ^{137}Cs and ^{90}Sr. The half-life of both these isotopes is about 30 years. As such, over the last 17 years the decay heats have decreased about 34%.

Historic temperature data show that the time average annual temperature within the solid waste are slowly decreasing with time. Waste temperatures after removal of the pumpable liquid (interim stabilization) have also continued to decline consistent with the principal heat load from radioactive decay rates. Of the 149 SSTs, 118 have been interim stabilized in an on-going program.

An increase in waste temperature from decay heating would only occur if the thermal conductivity of the waste decreases (see discussions of tank A-101 in Appendix C). Thermal conductivity within the waste will decrease as a waste becomes drier (after stabilization); however, the waste temperature would increase only if the solid waste thermal conductivity decreases faster (as the waste becomes drier) than the volumetric heating rate decreases (from radioactive decay).

The temperature difference between the top of the tank and ground level (ambient), ΔT_{soil}, can be estimated by

$$Q = k_s A \frac{\Delta T_{soil}}{H_s} \tag{B-23}$$

In this equation, H_s is the depth of the soil cover, H_s. The total heat transferred, Q, can be expressed on a volumetric basis by dividing by the volume or A*L. Remembering that only half of the heat is transferred out the top and rearranging gives up the following equation:

$$\Delta T_{soil} = q'''_0 \frac{L H_s}{2 k_s} \tag{B-24}$$

where q'''_0 (W m^{-3}) is the solid waste decay heat generation per unit volume at some reference time t = 0, k_s (~ 1 W m^{-1} K^{-1}) is the soil layer thermal conductivity, and H_s (4 m) is the height of the soil layer.

The temperature drop across the waste (ΔT_{waste}) is

$$\Delta T_{waste} = \frac{q'''_0 L^2}{2 k_w} \tag{B-25}$$

where k_w (W m^{-3} K^{-1}) is the waste thermal conductivity, and L (m) is the waste height.

The temperature difference between the waste and soil surface is the sum of Equations B-24 and B-25:

$$\Delta T = q'''_0 \frac{L^2}{2 k_w} + q'''_0 \frac{L H_s}{2 k_s} \tag{B-26}$$

This equation represents the temperature difference as present in the tanks under the current configuration. Note that decreases associated with the heat exchange between the ground and the atmosphere and natural convection within the tank airspace are not accounted for in Equation B-26. These losses are relatively small compared to the conduction losses.

The temperature differential will change over time as waste thermal conductivity decreases from waste dry out, and the volumetric heating decreases from radioactive decay. If moisture loss initiates at the surface of the saturated waste, the position h(t) of the evaporation front below the surface of the waste at time t is

$$h(t) = \frac{\dot{m} t}{A_t \epsilon \rho_\ell} \tag{B-27}$$

where ϵ is the porosity of the "dry" waste between the evaporation front and the waste surface, ρ_ℓ is the density of water, and $\dot{m}$ is the rate at which water (vapor) flows out of the tank.

The volumetric decay heating rate $q'''_d(t)$ decreases over time by the following

$$q'''_d(t) = q'''_0 \exp(-Nt) \tag{B-28}$$

where the constant N is about 2.3 x 10^{-2} $years^{-1}$.

As the waste drys out, the heat conduction changes. The temperature differential changes by the following:

$$\Delta T = q'''_0 \exp(-Nt)\frac{L^2}{2k_d}\left[1-\left(1-\frac{k_d}{k_w}\right)\left(1-\frac{h(t)}{L}\right)^2\right] + q'''_0 \exp(-Nt)\frac{LH_s}{2k_s} \qquad \text{(B-29)}$$

where k_d is the dry waste thermal conductivity which is believed to be less than k_w.

The scenario leading to the greatest temperature rise is dryout of the entire waste layer, h(t) = L, in the shortest time t. Equation B-29 can be simplified as follows:

$$\Delta T = q'''_0 (1 - Nt)\frac{L^2}{2k_d} + q'''_0 (1 - Nt)\frac{LH_s}{2k_s} \qquad \text{(B-30)}$$

Tank waste temperatures will continue to decline if the temperature difference of a future dried out waste is less than the temperature difference of the waste tank in the current configuration. This condition will happen if the following is satisfied:

$$q'''_0\frac{L^2}{2k_w} + q'''_0\frac{LH_s}{2k_s} > q'''_0 (1 - Nt)\frac{L^2}{2k_d} + q'''_0 (1 - Nt)\frac{LH_s}{2k_s} \qquad \text{(B-31)}$$

Complete dry out represents the "worst" case for Equation B-31. Setting h(t) = L, the time required from Equation B-27 is

$$t = \frac{LA_t \epsilon \rho_\ell}{\dot{m}} \qquad \text{(B-32)}$$

Substituting Equation B-32 into B-31, the criterion can be expressed in terms of moisture loss:

$$\dot{m} < \frac{A_t \epsilon \rho_\ell L N}{(1 - k_d/k_w)}\left[1 + \frac{H_s k_d}{L k_s}\right] \qquad \text{(B-33)}$$

Assuming that the waste thermal conductivity decreases linearly with an increase in the porosity value ϵ, i.e., $k_d = k_w (1-\epsilon)$[1], and evaluating the minimum value of $\dot{m}$ by setting L = 0, Equation B-31 simplifies to

$$\dot{m} < \frac{k_w}{k_s} (1 - \epsilon) H_s A_t \rho_\ell N \qquad \text{(B-34)}$$

With $k_w = 1$ W m^{-1} K^{-1}, $k_s = 1$ W m^{-1} K^{-1}, $\epsilon = 0.3$[2], $H_s = 4$ m, $\rho_\ell = 1000$ kg m^{-3} and $A_t = 410$ m^2 (the 1,000,000, 758,000 and 530,000 gallon tanks), $\dot{m}$ is about 26,000 kg year^{-1}. For the 55,000 gallon 200 series tanks, $A_t = 29$ m^2 and $\dot{m}$ is about 2000 kg year^{-1}. Considering that reasonable upper bounds for the yearly moisture losses are well below these values (see Appendix D), the waste temperatures in passively ventilated tanks will continue to decrease for all solid waste inventories, consistent with tank farm observations.

4.0 CONCLUSIONS

The observations rule out bulk runaway reactions or a Kyshtym type accident for the Hanford Tank Farm. This conclusion can be made without requiring knowledge of waste chemical composition or uniformity, and will not be altered by continued interim stabilization or possible long term moisture loss.

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[1]The recommended equation for ϵ shows (Russel 1935) that the relationship between k_ϵ and ϵ is slightly non-linear. For $\epsilon = 0.3$. the reduction in thermal conductivity is 35% rather than 30%.

$$k_\epsilon = k \frac{1 - \epsilon^{2/3}}{1 - \epsilon^{2/3} + \epsilon}$$

[2]For saturated saltcake, a reasonable value of the volume fraction occupied by the interstitial supernatant is about 0.4. Considering that the supernatant is saturated with salts such as $NaNO_3$ etc., the solid salts left behind after drying will result in a porosity value of less than 0.3.

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APPENDIX C

TANK A-101 TEMPERATURE TRENDS

by

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APPENDIX C

TANK A-101 TEMPERATURE TRENDS

1.0 INTRODUCTION

The potential for heat generated during radioactive decay to cause a bulk runaway in the single-shell tanks (SSTs) and double-shell tanks (DSTs) was examined in the main body of this report (Section 3.2). The DSTs and 15 SSTs are actively ventilated and tank C-106 requires the periodic addition of water for cooling. The discussion of the heat transfer characteristics of the 15 actively ventilated SST was extended in Appendix B. The remaining 134 SST are passively ventilated and the historical temperature data show the time averaged annual temperatures within the waste and in the headspace are decreasing. The ongoing monitoring of the temperatures in tank A-101, which was actively ventilated until 1992, suggested its behavior might be exceptional. The temperature trends and the possible explanations for them are examined in this appendix.

An analysis of the time-averaged temperature in the headspace of tank A-101 (Crowe et al. 1993) indicated the temperature in the headspace had increased by 0.5 °F per year from January 1988 to March 1993. Subsequently, Ogden et al. (1996) evaluated the temperature behavior of the entire waste for the interval from January 1993 to January 1996. They found the waste in the bottom 23 feet of the tank was cooling at a rate that was compatible with the changing rate of radioactive decay. But they also found that the waste in the top four to five feet was warming about 0.5 to 1.4 °F per year, and that the waste at the air interface and the air in the headspace was warming 1.3 to 1.4 °F per year.

The finding that a portion of the waste in tank A-101 was warming contrasted with the observations for the other passively ventilated SSTs. Consequently, the finding received special attention and the waste was monitored. The more recent temperature trends in this waste and the special explanations that have been postulated for the unusual temperature behavior (Ogden et al. 1996, Fauske 1997) are discussed in the following sections.

2.0 MORE RECENT OBSERVATIONS

Core sample data (Field et al. 1997), retained gas samples (Shekarriz et al. 1997), temperature profiles, and gamma scans have provided a more complete perspective concerning the distribution of the waste in tank A-101 (Stock and Cash 1998). The more recent, more complete analytical measurements establish that the waste is distributed between a lower, essentially liquid, convective layer (approximately 525,000 gallons) containing only 0.4 % voids and an upper, non-convective layer of wet solids (approximately 410,000 gallons) containing about 15 % voids. The tank temperature profile, the analytical data for the cores, the gas composition, the

gamma scan information and related observations locate the interface between the two layers about 190 inches from the bottom of tank (Stock and Cash 1998).

Tank A-101 was actively ventilated during 1989, and intermittently actively ventilated during 1990 and 1991. The tank has been passively ventilated since 1992. The temperature trends for the tank following the transition from active to passive ventilation are shown in Figures C-1 to C-5.

The temperature measurements for the thermocouples in the convective layer are shown in Figures C-1 and C-2. The observations for the eight thermocouples indicate the waste in this layer cooled from 1991 to 1998. Regression analysis of the data for thermocouple 4, which is located near the center of the convective layer, reveals the temperature at this location changed from 153 °F in 1991 to 146 °F in 1998. This agrees well with the previous conclusion (Ogden et al. 1996) that the waste at this location was cooling by 0.81 °F per year.

The temperature measurements for the thermocouples in the lower portion of the non-convective layer are shown in Figure C-3. The observations for thermocouple 9, which is very near the interface between the two layers, and for thermocouples 10, 11, and 12 show this portion of the waste also cooled from 1991 to 1998. Although there is a large temperature gradient from thermocouple 9 to thermocouple 12, the rate of cooling of the waste in this portion of the non-convective layer is comparable to the rate of cooling of the waste in the convective layer.

The temperature measurements for thermocouples 13, 14, and 15, which are located within the upper five feet of the waste, and the temperature measurements for thermocouples 16, 17 and 18, which are located in air in the headspace, are shown in Figures C-4 and C-5. Seasonal temperature variations influence these temperatures appreciably. The observations shown in the figures indicate the temperatures in the topmost five feet of the waste and in the headspace increased from 1991 to 1994 and then declined from 1994 to 1998.

Ogden et al. (1996) pointed out that changes in the ventilation rate influenced the temperature changes during 1991 and 1992, and attention was focused on the observations from 1993 to 1995. Even though the temperatures measured in 1995 were lower than the temperatures measured in 1994, they concluded that the data for the interval from January 1993 to January 1996 showed that the temperature of the waste in the upper portion of the waste was increasing 1.25 °F per year. Examination of the more recent data indicates the maximum temperatures for thermocouples 14 and 15 were reached in late 1994, and that the waste in the upper portion of the non-convective layer has been cooling, rather than warming since that time.

The changes in the waste temperature for the past ten years are illustrated by the temperature profiles for 1988 and 1998 in Figure C-6. The profile for 1998 indicates the temperature of the convective layer changes from 142 °F (thermocouple 1) at bottom of the tank to 148 °F (thermocouples 8 and 9) near the interface between the convective and non-convective layers.

Figure C-1. Tank A-101 Waste Temperatures (°F) for Thermocouples 1 to 4 in Lower Portion of the Convective Layer from March 1991 to March 1998.

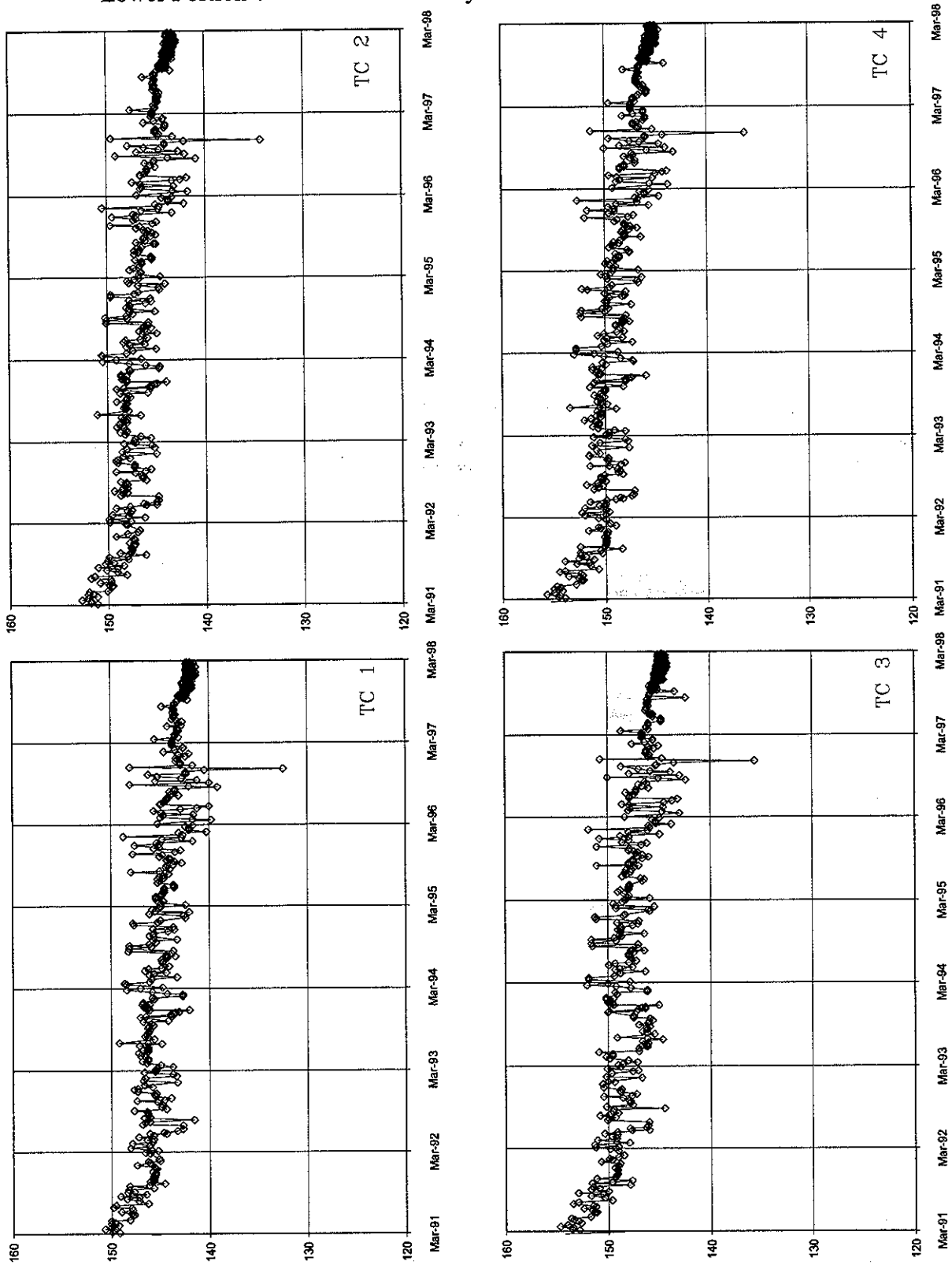


Figure C-2. Tank A-101 Waste Temperatures (°F) for Thermocouples 5 to 8 in Upper Portion of the Convective Layer from March 1991 to March 1998.

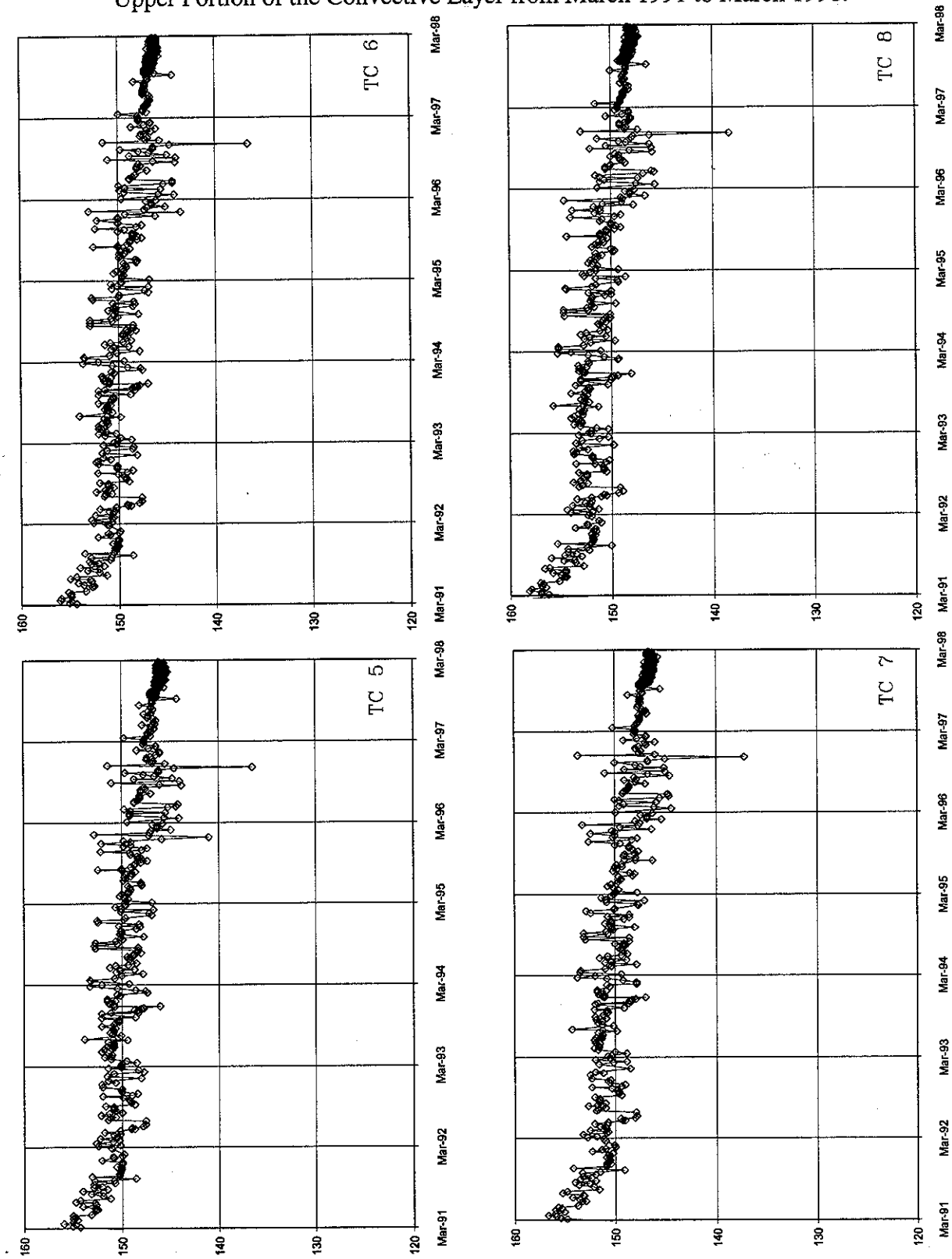


Figure C-3. Tank A-101 Waste Temperatures (°F) for Thermocouples 9 to 12 in Lower Portion of the Non-convective Layer from March 1991 to March 1998.

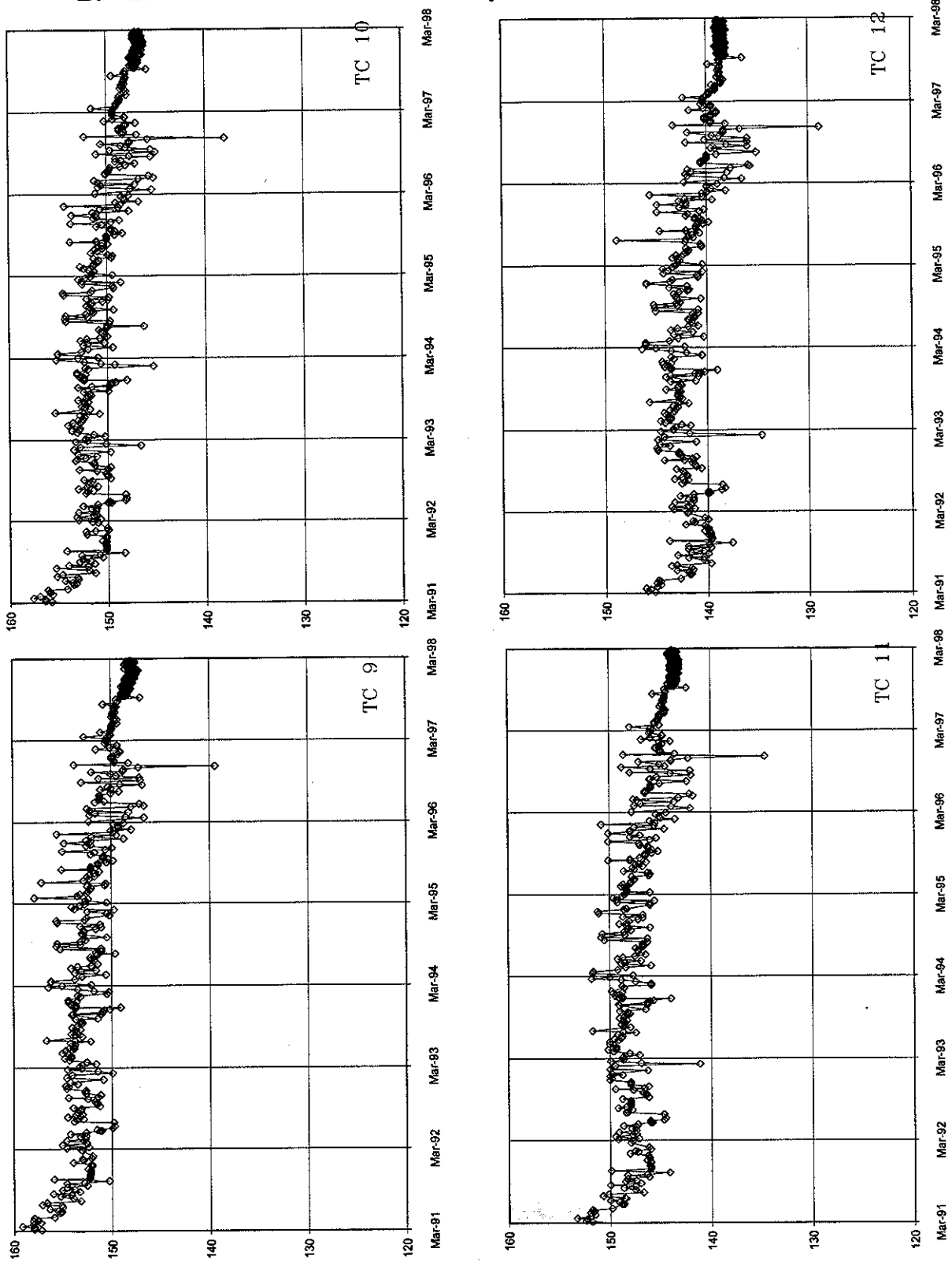


Figure C-4. Tank A-101 Waste Temperatures (°F) for Thermocouples 13 to 15 in Upper Portion of the Non-convective Layer from March 1991 to March 1998.

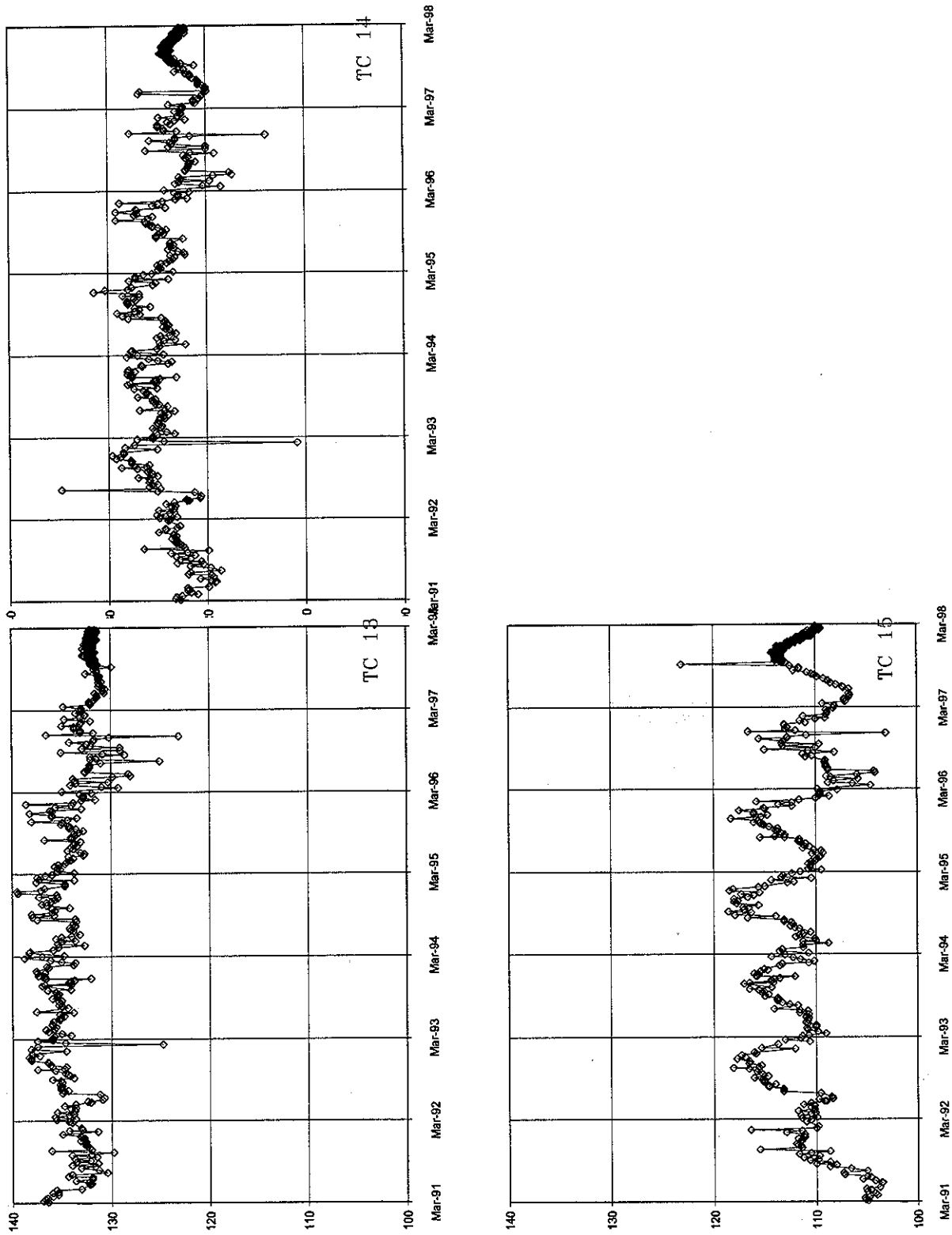


Figure C-5. Tank A-101 Headspace Temperatures (°F) for Thermocouples 16 to 18 from March 1991 to March 1998.

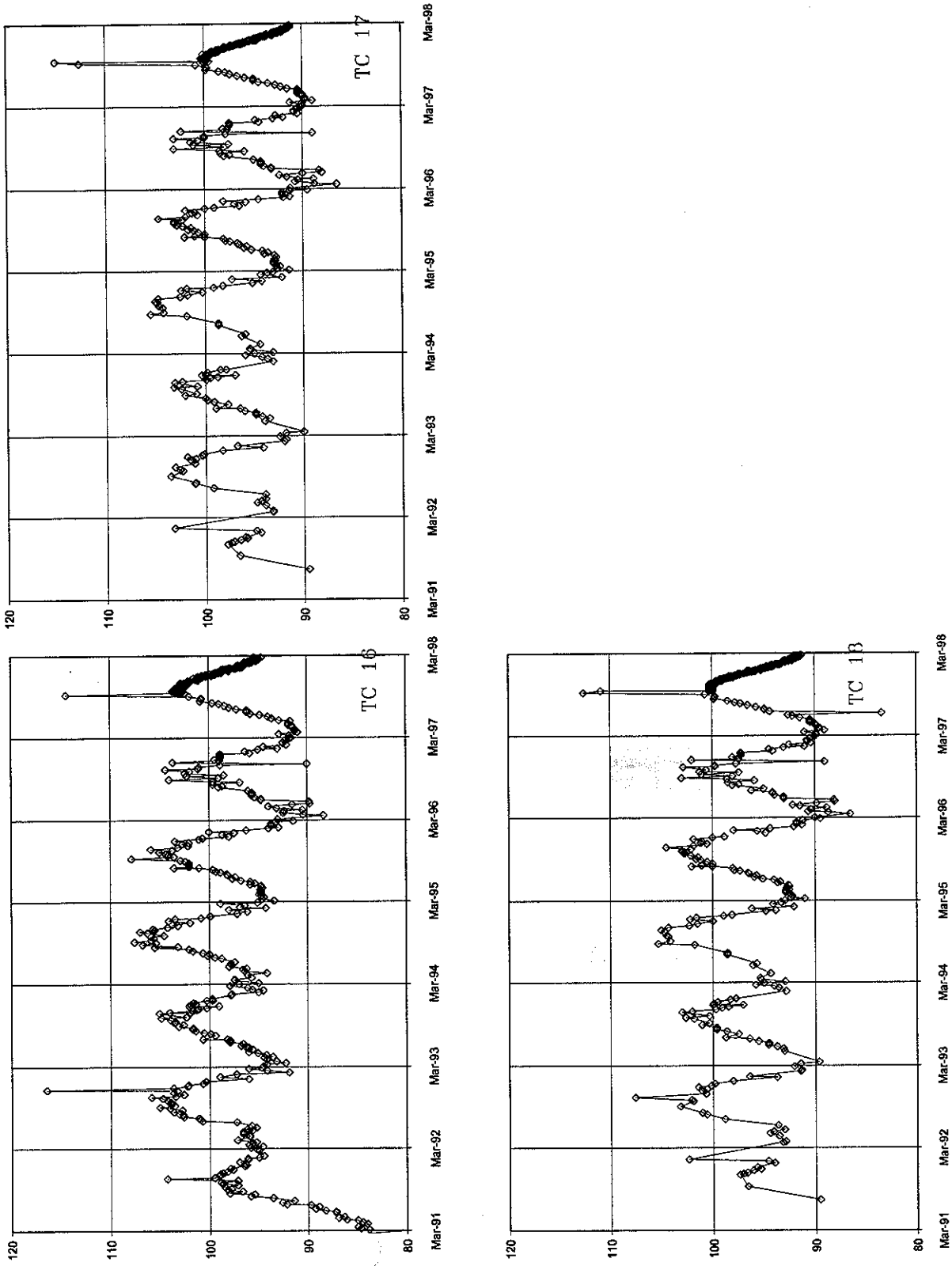
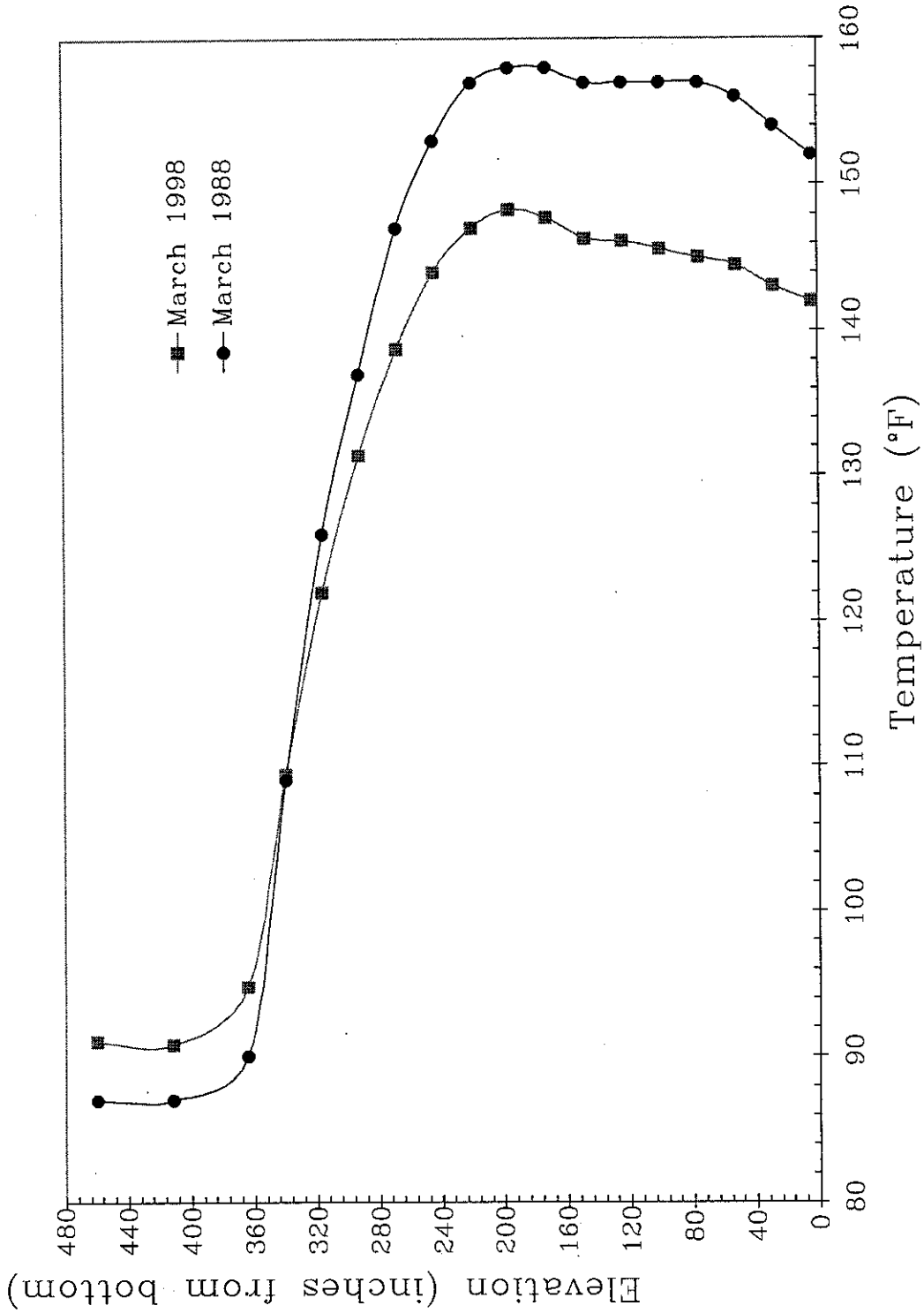


Figure C-6. Tank A-101 Temperature Profiles for Thermocouples 1 to 18 in March 1988 and March 1998.



The non-convective layer has a large temperature gradient from 148 °F near the interface between the condensed layers to approximately 95 °F (thermocouple 15) near the surface. The two profiles also show the waste in the convective layer, thermocouples 1 to 8, and in the lower portion of the non-convective layer, thermocouples 9 to 12, cooled by approximately 10 °F in ten years. The temperature measurements at thermocouples 13 and 14 also imply the waste has cooled at these locations, but the measurement at thermocouple 15 just below the surface is essentially unchanged. The change from active to passive ventilation is manifest in the increase in the headspace temperature from 1988 to 1998.

In summary, the measurements for the remainder of the waste, i.e., the uppermost four or five feet of the waste in the nonconvective layer, indicate this portion of the waste also cooled from 1988 to 1998, but at a much slower rate. Indeed, the wastes in the uppermost portion of the tank apparently warmed from 1991 to 1994 and then cooled from 1995 to 1998.

3.0 INTERPRETATION OF OBSERVATIONS

The novel temperature behavior of the waste in tank A-101 has prompted investigations of the factors governing the temperature changes. Heat changes resulting from the oxidation of organic compounds, the crystallization of salts, and the changes in the efficiency of heat transfer to the surrounding have been considered in previous discussions (Ogden et al. 1996, Fauske 1997). Inasmuch as the work of Ogden and Fauske and their associates was completed before the publication of the tank characterization report (Field et al. 1997), and before it was established that the waste in the upper most portion of the tank was cooling rather than warming, the information and the interpretations were reexamined.

Several recent studies including the characterization report (Field et al. 1997) and the retained gas sample investigation (Shekarriz et al. 1997) provide a more secure basis for the discussion of the chemical and physical properties of the waste in tank A-101. In particular, tank A-101 differs from the other single shell tanks (except AX-101) because the hotter convective layer is located beneath a gas rich and cooler non-convective layer (Shekarriz et al. 1997, Field et al. 1997, Stock and Cash 1998).

Although there is only one thermocouple tree in the waste, the temperature observations for the past ten years appear reliable. As pointed out by Ogden et al. (1996), the measured temperatures, especially the temperatures in the upper portions of the tank, are sensitive to the operation of the ventilation equipment, which was operated essentially continuously in 1988 and 1989 and intermittently in 1990 and 1991. Acknowledging this factor, Ogden et al. (1996) focused attention on the data for the interval from 1993 to 1995 and concluded that the temperature for the upper portion of the non-convective layer was increasing by about 1.3 °F per year. They pointed out that this rate of change is equivalent to a 100 Watt increase in power each year. This change can be realized in several different ways including changes in the rates of heat generation by the precipitation of salts or the oxidation of organic molecules, or the efficiency of heat

transfer between the tank and its surrounding. The merit of each of these explanations is considered in the following sections.

3.1 HEAT FROM SALT CRYSTALLIZATION

The crystallization of sodium nitrate liberates about 21 kJ per mole. Ogden et al. (1996) considered the possibility that water loss and salt crystallization might warm the upper layer and concluded the heat from this source would be insufficient to account for the temperature increase. Their conclusion is based upon the following analysis. A temperature increase of 1.3 °F per year corresponds to the release of 100 Watts per year (Ogden et al. 1996, Fauske 1997). Approximately $1.5 \cdot 10^5$ moles of sodium nitrate would have to crystallize each year, i.e., $1.5 \cdot 10^5$ moles during the first year, $3.00 \cdot 10^5$ moles during the second year, $4.5 \cdot 10^5$ moles during the third year, to liberate the heat necessary to sustain the heat change. Inasmuch as the top three feet of the waste contains only $1.2 \cdot 10^6$ moles of sodium nitrate, most of which is already in the solid state, the suggestion that heat liberated in the phase change could be responsible for a sustained temperature increase is implausible.

3.2 HEAT FROM OXIDATION OF ORGANIC COMPOUNDS

Agnew and his associates suggest the oxidation of the average organic molecule in the Hanford waste produces 509 kJ per mole of carbon (Agnew et al. 1996). The total rate of heat production for tank A-101 from the oxidation of organic compounds predicted to be present by the Hanford Defined Waste model implies that about 15 % of the total heat produced in the tank arises form the oxidation of organic molecules (Agnew et al. 1997). Information of this kind prompted Ogden et al. (1996) to consider the possibility the oxidation of organic compounds might selectively warm the upper layers. They concluded that the oxidation of organic compounds could not be solely responsible for the temperature increase in the upper portions of the waste because the concentrations of the organic compounds were too low and could not supply sufficient heat to warm the upper layer for a prolonged interval. The calculation shown in the next paragraph confirms their suggestion.

The information provided by Ogden and coworkers (Ogden et al. 1996) indicates that the power change corresponding to a temperature increase of 1.3 °F per year for three years is 100 watts per year, a total of 600 watts over three years, i.e., 100 watts the first year, 200 watts the second year, 300 watts the third year. The chemical energy required for this power change is

$$(600\,\mathrm{J\,sec^{-1}})\ (3.145 \cdot 10^7\,\mathrm{sec}) \;=\; 1.89 \cdot 10^{10}\,\mathrm{J}$$

For the organic material in tank A-101, the heat of oxidation is about $5.09 \cdot 10^5$ J per mole of carbon (Agnew 1996). This equates to $3.71 \cdot 10^4$ moles of organic carbon converted to carbonate ion over the three year period. Recent core sample analyses show the upper segments

of the non-convective layer contain about 0.5 wt % organic carbon (Field et al. 1997). The molar quantity of organic carbon in the top three feet is

$$(330\ \mathrm{m^3\ of\ waste})\left(1{,}500\ \frac{\mathrm{kg\ of\ waste}}{\mathrm{m^3\ of\ waste}}\right)\left(0.0050\ \frac{\mathrm{kg\ of\ TOC}}{\mathrm{kg\ of\ waste}}\right)\left(1{,}000\ \frac{\mathrm{g\ of\ TOC}}{\mathrm{kg\ of\ TOC}}\right)$$

$$= \ 2.06 \bullet 10^5\ \mathrm{moles\ TOC}$$

The chemical energy necessary for the heat change requires the oxidation of $3.71 \bullet 10^4$ moles of the available $2.06 \bullet 10^5$ moles of TOC, or 18 % of the available carbon in three years. Several lines of reasoning indicate this rate of oxidation is implausible. Three arguments will be noted here. First, the rate of oxidation of the organic molecules in the waste depends primarily on the dose rate and temperature (Camaioni et al. 1996). The dose rate and temperatures were higher in 1980 than at the present and the implied required rate of oxidation would have consumed all of the organic carbon before 1990. Second, the waste has been stored for 17 years and 50 % of the available carbon is present as oxalate ion (Field et al. 1997). It is unlikely that 18 % of the oxidation occurred in the three year interval from 1993 and 1996. Third, an explanation based on the selective occurrence of organic oxidation in the upper portion of the waste implies there would be significant differences in the oxalate contents of different portions of the non-convective layer. No such variations have been observed. Although chemical oxidation could have a small influence on the temperature trend, it is highly unlikely that it is the primary contributor to the fluctuations in temperature.

3.3 CHANGES IN HEAT TRANSFER

Ogden et al. (1996) examined several alternative explanations related to changes in the rate of heat transfer from the contents of the tank to the surroundings. They noted that changes in the temperature in upper portion of the waste and the headspace could be caused by variations in the breathing rate, the rate of drying of the surface of the waste, and changes in the conductivity of the soil overburden. Fauske (1997) discussed the same features and concluded that relatively small changes in the ambient air temperature, the thermal conductivity of the overburden, the thermal conductivity of the waste from changes in gas content, or alterations in convective heat transfer in headspace could influence the temperature of the waste (Fauske, 1997). A reduction of 2.3 % in the thermal conductivity of the soil would reduce cooling enough to account for the temperature rise in the headspace (Fauske 1997).

Models for the transfer of heat from the waste tanks highlight the dependence of the cooling rate on changes in the thermal conductivity of the waste, the ventilation rate, the thermal conductivity of the overburden, and related parameters. The temperature patterns for tank A-101, especially the contrasting observation that the principal portion of the waste has been continuously cooling while the topmost portion has shown variable behavior, warming from 1991 to 1994 and then

cooling from 1995 to 1998, are most plausibly attributed to small changes in these rates. The susceptibility of the waste in tank A-101 to changes in the rates of heat transfer to the surrounding may be heightened by the lower thermal conductivity of the gas-rich, nonconvective layer.

4.0 CONCLUSION

The entire waste in tank A-101 has cooled during the past ten years. The rate of cooling in the lower 23 feet of the waste is consistent with the changing rate of radioactive decay (Ogden et al. 1996). The small increases and subsequent decreases in the temperature of the topmost four to five feet of the waste do not originate from an increased heat load resulting from salt crystallization or the oxidation of organic molecules. Rather, the variations in the temperature of the topmost portion of the waste are more reasonably attributed to climatic induced changes in heat transfer possibly because of the gas-rich nature of the nonconvective layer.

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APPENDIX D

WASTE DRYOUT

by

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APPENDIX D

WASTE DRYOUT

1.0 INTRODUCTION

Water retention provides an added safety margin for Hanford Site organic-bearing high-level radioactive waste. Water loss from a sound tank occurs primarily by evaporation into the tank headspace, with subsequent removal by the ventilation system. This mechanism for water loss is examined in this Appendix for tank wastes with high total organic carbon concentrations.

The analysis of water loss for specific tanks is based on a simple mathematical model developed in Section 2.0. The model uses empirical data to estimate the rate that water is transported from the waste to the atmosphere. In its complete form, the model considers the diffusion of water vapor from a sub-surface liquid layer upward through a porous waste layer, from the surface of this waste layer through a stagnant boundary layer of air into the tank headspace, and finally the removal of water vapor by ventilation of the headspace. The one-dimensional transport model can be simplified if the waste surface of a tank is wet (i.e., diffusion through the waste layer is eliminated) and when the available data indicate water vapor in the tank headspace is in equilibrium with waste surface moisture.

An important parameter needed to estimate the rate of water evaporation is the equilibrium partial pressure of water above the waste. This equilibrium water partial pressure has been found to vary significantly between wastes from different tanks; therefore, waste samples from tanks of concern have been obtained and tested (Scheele et al. 1996, 1997a, 1997b, 1997c, 1998). Selected results from the experimental waste moisture - water partial pressure equilibria studies are presented in Section 3.0, along with actual tank headspace water partial pressures. Also given in Section 3.0 are a method for adjusting the raw data from the laboratory reference temperature to the estimated temperature of the waste, and a semi-empirical equation used to estimate the waste temperature as a function of time. These are used in concert with the laboratory data to estimate the partial pressure of water in equilibrium with the waste as a function of time. The temperature equation accounts for seasonal variations and the long-term decrease in temperature associated with the decrease in waste radioactivity.

The model for water loss assumes that a quasi-steady state condition exists in the tank headspace, so the net rate at which water is evaporated from the waste is equal to the rate water vapor is removed via the ventilation system. The ventilation rates of the modeled tanks, as deduced from tracer gas measurements, have been incorporated in the model to improve its accuracy. The tracer gas method and the assumptions on which it is based are discussed in Section 4.0, along with a summary of tank ventilation rates measured by the method. Section 4.0 also summarizes available tank headspace humidity data and gives a simple estimate of the water loss rate for each tank with humidity data.

The model is applied to seven tanks to establish a realistic estimate of the maximum amount of water that would be lost by each tank over periods as long as 100 years. The wastes in three of the tanks are classified as high complexant/dry surface waste (tanks A-106, AX-102, and C-104), and the wastes in four of the tanks are classified as high complexant/wet surface waste (tanks A-102, A-103, U-105, and U-106). Equilibrium water partial pressure data are available for A-102, AX-102, C-104, U-105, and U-106. Water losses from tanks U-102 and U-111 are also discussed; however, because of inadequate physical data for these tanks, predictions of their water losses are based on qualitative comparisons to the modeled tanks. The waste in tank U-102 is classified as medium complexant/wet surface waste, and the waste in tank U-111 is classified as high complexant/dry surface waste. These nine tanks were selected for study because their waste has relatively high total organic carbon content; however, they are not intended to be cumulatively characteristic of all tanks.

Because tanks AX-102 and U-106 have the highest total organic carbon concentrations, they are given special attention in this appendix. Though these tanks have markedly different waste characteristics and ventilation rates, the empirical data associated with both tanks indicates the waste moisture and headspace water vapor are essentially at equilibrium. Specifically, the measured tank headspace water vapor concentration is found to be essentially the same as that calculated from measured waste water content (from samples) and the laboratory-determined waste moisture - water partial pressure equilibrium data (corrected to the estimated waste surface temperature). This finding implies water losses from both tanks are currently ventilation rate-limited. Assuming this to remain the case in future years provides a conservative (i.e., maximum) estimate of the water losses, yet neither tank is predicted by the model to dry to a moisture level of concern. Given the assumption of ventilation rate-limiting behavior, the model predicts that tank AX-102 will reach a minimum of ~14 wt% water after about 40 years, and that the upper 48-cm layer (a core segment) of tank U-106 will still be about 45 wt% water after 50 years.

2.0 WATER LOSS MODEL

2.1 MODEL DESCRIPTION

The model is designed to provide estimates for worst-case drying of the waste surface given specified system temperatures and ventilation rates. The model is based on the following simplifying assumptions and limitations:

- The model is one dimensional and neglects horizontal variability of waste properties;
- Assumes waste has initially uniform water content and uniform chemical and physical properties;
- Neglects upward movement of liquid to replace water lost from the surface;
- Assumes tank headspace is mixed, so water vapor concentration is uniform;
- Assumes loss of water is only via ventilation;
- Assumes ventilation rates are constant for all time;
- It uses the water vapor partial pressure measurements of only a few surface waste samples;
- Assumes ambient air temperature and humidity follow the same fixed yearly cycle;
- Assumes ventilation air comes from outside and not from connected tanks; and
- Neglects condensation of water vapor on dome and within ventilation system.

The model has three components: diffusion of water vapor through the subsurface waste layer, across the waste layer surface boundary into the headspace, and removal from the headspace. The net rate at which water evaporates from the waste and enters the headspace is given by

$$\dot{m}_{evap} = k(C_0 - C) \qquad (D-1)$$

where $\dot{m}_{evap}$ is the net mass of water per unit time transported across the waste surface boundary into the headspace per unit time, k is a mass transfer coefficient that addresses diffusion of water vapor through air-filled pores (if present) and the boundary layer for the entire cross-sectional area of the tank, C is the mass concentration of water in the headspace, and C_0 is the mass concentration of water vapor in equilibrium with the waste at some depth at or below the waste surface. The rate at which the mass of water vapor is removed by ventilation, $\dot{m}_{vent}$, is given by

$$\dot{m}_{vent} = v(C - C_{amb}) \qquad (D-2)$$

where v is the volumetric ventilation rate of the tank headspace, and C_{amb} is the mass concentration of water vapor in ambient air.

At steady state, the rate at which water is evaporated and diffuses into the headspace is equal to the rate at which it is removed by ventilation:

$$\dot{m}_{vent} = \dot{m}_{evap} \qquad (D-3)$$

Combining Equations D-1 through D-3 yields the following expression for the headspace water vapor concentration,

$$C = \frac{vC_{amb} + kC_0}{v + k} \qquad (D-4)$$

and the following expression for the change in waste water mass,

$$\dot{m} = \frac{-kv}{k + v}(C_0 - C_{amb}) \qquad (D-5)$$

The water mass transfer coefficient, k, can be obtained theoretically by using an equation of the type

$$\frac{1}{k} = \frac{1}{k_e} + \frac{Z}{AD} \qquad (D-6)$$

where D is the effective diffusion coefficient for air in a drained porous material, and k_e is an eddy transfer coefficient for passage of water vapor through a boundary layer of air over the waste surface area, A. From soil physics, D is often taken as drained porosity multiplied by the diffusion coefficient of water vapor in air for a particular temperature. A diffusion distance is defined as depth Z. The eddy transfer coefficient k_e was employed by Heard (1993) to model the drying of an actively ventilated tank. The same formula used by Heard for estimating k_e was used here.

Alternatively, the transfer coefficient k can be estimated using Equation D-4, measured waste wt% water, ventilation rate, and measured headspace water partial pressure. This approach was applied to tank AX-102, for instance, to describe the likely behavior that a crust would form in shallow waste as drying occurs.

For the passively ventilated tanks with wet waste surfaces it was found that the mass transfer coefficient, k, was large compared to the ventilation rate, v, and Equation D-5 can be simplified to

$$\dot{m} = v_l(C_0 - C_{amb}) \qquad (D-7)$$

Similarly, for passively ventilated tanks having a liquid surface below the waste surface, the eddy transfer coefficient, k_e, was found to be large compared to the product AD, and Equation D-6 can be reduced to

$$\frac{1}{k} \approx \frac{Z}{AD} \qquad (D-8)$$

Not enough is currently known about the development of a surface crust as drying occurs to model its diffusion limiting behavior on moisture loss over a long time. Heard (1993) employed a diffusion coefficient for water vapor similar to that for water diffusing through concrete to explain the low rate of water loss in an actively ventilated tank.

Equation D-5 represents the model for waste dryout. For purposes of performing the dryout calculations, the water loss rate Equation D-5 is solved in different ways, depending on the type of waste and how it is expected to dryout. The water lost by the waste is assumed to come from some as yet unspecified waste depth. Note that Equation D-5 does not include a term to describe the possible replenishment of water (as interstitial liquid) by conduction from below the surface. This formulation always leads to greater water loss from the surface than if the model did account for replenishment. The neglect of water replenishment is intended to yield a more conservative evaluation of possible surface drying.

2.2 MODEL EVALUATION

Waste is generally either a saltcake or sludge type. Saltcake waste, which is typically crystalline with significant amounts of sodium nitrate and nitrite, can be drained leaving a solid matrix of liquid-emptied interstices behind. Air and water vapor can diffuse through the emptied interstices (pores) of saltcake when it is drained. By contrast, sludge, which is typically consists of amorphous metal hydroxides, is consolidated by draining, and its volume shrinks without allowing interstices to empty. The chemical compositions characteristic of saltcake and sludge waste types are not of direct use to the physical modeling discussed here. Interpretation of chemical characterization information and observations of physical appearance generally are used to decide if a waste is sludge or saltcake, and no special physical tests are performed on waste to determine if it is best classified as saltcake or sludge. The classification of waste based on

processing history (e.g., as listed in Table 4-11) is not used to classify a waste for purposes of modeling water loss.

For the modeling, it is assumed that evaporation removes liquid from the waste just as draining does. The precipitated porous matrix that would be formed by evaporation rather than by drainage is disregarded, although it may alter the physical structure of the matrix from that formed by drainage. Because the liquid transport properties are not being modeled, this difference in the waste's matrix structure caused by the two distinct processes of water loss is not important here.

The only transport property for the waste needed by the analysis is the apparent diffusion coefficient (transfer coefficient) for water vapor in the dried waste material (i.e., crust). Even in sludge waste tanks, a dry crust is often observed to cover the surface. Just below such crust, core samples of sludge generally show high moisture content.

For tanks with the sludge waste type, a crust layer of fixed depth, Z, is presumed to control evaporation from the waste below it. Below this crust, the wt% water decreases as water is lost, and this in turn changes C_o over time. When no crust is present, the loss of moisture from the waste is not limited by diffusion.

For tanks with saltcake waste type, water loss results in the formation of a dry waste layer of depth Z. The depth Z is continually increasing as water is removed. At and below the interstitial liquid level the wt% water is constant. Above the interstitial liquid level the wt% water of the waste is assumed to be in equilibrium with the water vapor concentration of the headspace. In this model, C decreases as the interstitial liquid level recedes deeper. C is determined from C_0 and C_{amb} by assuming steady loss of vapor.

Using the approximation that the mass of water, m, changes little during each year, and assuming that the mass transfer coefficient and ventilation rates are constant, Equation D-5 can be integrated to obtain the change in m in terms of yearly averages:

$$\Delta m = \frac{-V}{1 + \frac{V}{k}} \left(\hat{C}_0 - \hat{C}_{amb} \right) \Delta t \qquad \text{(D-9)}$$

where $\hat{C}_0$ and $\hat{C}_{amb}$ are averages of the headspace and ambient air water vapor concentrations over the time period $\Delta t = 1$ yr.

Section 3.0 discusses the experimental determination of water concentration in equilibrium with the waste, C_0, for the waste in each tank of interest as a function of weight percent (wt%) of

water in the waste. The temperature dependence of C_0 is also discussed in Section 3.0, as well as the equations used to describe waste temperatures as functions of time. The combination of these relationships allows C_0 to be specified as a function of time and waste wt% water for each tank considered. Integration of the time-dependent expression for C_0 yields $\hat{C}_0$. Section 4.0 provides a tank-specific average ventilation rate, v, for the tanks of primary interest here. The basis for treating v as a constant is also briefly discussed in Section 4.0.

3.0 WASTE MOISTURE - WATER VAPOR EQUILIBRIA

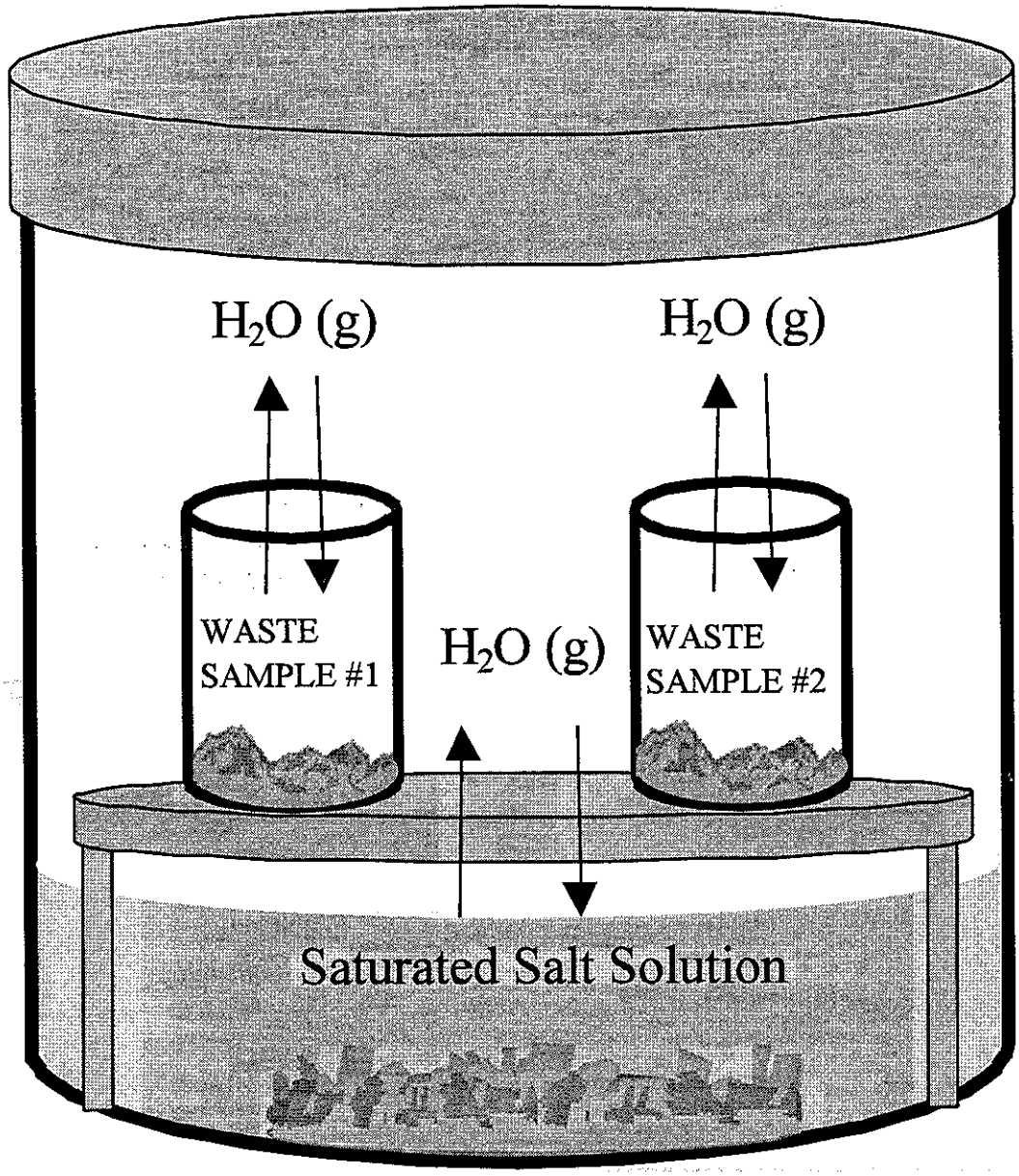
3.1 WATER PARTIAL PRESSURE ISOTHERMS

As discussed earlier, the water partial pressure in the headspace combined with the ventilation rate determines the water loss from the tank/waste system. In turn, the water partial pressure in the tank's headspace depends on the water content in the waste. To obtain information needed to predict whether the water content of specific individual tank wastes is sufficient to allow for safe storage for up to 100 years, laboratory studies were performed to determine the effect of water partial pressure, p, on the waste water content. This section summarizes the results of these studies and provides more detailed results for AX-102 and U-106 because these tanks contained the highest TOC measurements (see Figure 4-5). Samples studied were from tanks A-101, A-102, AX-102, BY-108, BY-110, C-104, SY-102, T-111, U-105, U-106, and U-107; Scheele et al. (1996; 1997a, 1997b, 1997c; 1998) provide more detailed results for these tank waste samples.

The laboratory setup to determine the effect of water partial pressure on a tank waste's water content is illustrated in Figure D-1. Saturated salt solutions at known temperatures were used to control water partial pressures. Duplicate 1 g tank waste samples were exposed to known water partial pressures and allowed to equilibrate at controlled temperatures. The initial sample water contents were determined by drying the samples at 105 °C. The water partial pressures used bounded the ambient water partial pressure at Hanford (p_{amb}) which seasonally varies from a winter average low of 3.8 torr to a summer average high of 7.9 torr (Scheele et al. 1996). The tests were performed at the temperature measured by the uppermost thermocouple located in the solid waste; temperatures ranged from near 20 to 41 °C.

The experimental data were used to estimate (by linear interpolation) the equilibrium water content of the tested waste samples at the average ambient Hanford p_{amb} of 5.5 torr and at the tank's current measured p at the uppermost solid waste's measured temperature T_{ref} (Table D-1). The estimated water content at p_{amb} ranged from 2 wt% to 15 wt%. The estimated water content at a tank's current p ranged from 5 to > 60 wt%. The differences in water content estimates between tank waste samples can be attributed to differences in chemical compositions and temperature in the tanks. Insufficient information is currently available to accurately predict the water content based on the measured chemical constituents in a waste, although initial attempts have been made (Scheele et al. 1996).

Figure D-1. Schematic of constant humidity chamber.



Figures D-2 and D-3 show the effect of p on the equilibrium water contents of waste samples from tanks AX-102 at 26°C and U-106 at 27°C, respectively. In both cases, as p increases the water content increases, although tank AX-102 waste is much less sensitive to increases in p at lower water partial pressures. If allowed to equilibrate with average ambient Hanford p_{amb} conditions of 3.8 to 7.9 torr, the surface waste in tank AX-102 will dry from its current 25 wt% water to between 10 and 12 wt% water (Figure D-2); the three tested tank U-106 samples will dry from their current 40 to 45 wt% water to between 3 and 10 wt% water (Figure D-3).

Table D-1. Estimated Water Contents of Selected Hanford Wastes at Average Ambient Hanford and Tank Headspace Water Partial Pressures.

Tank	Sample[1]	Headspace Water Partial Pressure[2], P_{tank} (torr)	Water Content[3] at T_{ref} (wt %)		Isotherm Reference Temperature T_{ref} (°C)
			$P = P_{amb}$ 5.5 torr	$P = P_{tank}$	
A-101	Core 154 Segment 1UH	24.0	8	19	40
	Core 154 Segment 1LH		9	26	40
	Core 156 Segment 14 DL		8	19	40
A-102	1996 Auger Sample 33	24.5	14	46	32
AX-102	Feb 1998 Auger Sample	21.7	11	>60	27
BY-108	Core 99 Segment 1	24.8	10	32	30
	Core 99 Segment 2D		30	45	30
BY-110	Core 113 Segment 1	26.7	11	30	35
	Core 103 Segment 1UH		8	30	35
C-104	Core 162 Segment 1UH	13.4	3	6	35
	Core 162 Segment 1LH		2	6	35
	Core 162 Segment 4 DL		3	6	35
	Core 165 Segment 2UH		3	6	35
S-102	Core 125 Segment 3	13.2	4	6	41
	Core 130 Segment 3		4	6	41
T-111	Core 33 Segment 2	12.4	14	30	20
U-105	Core 131 Segment 2 IH	13.0	10	18	33
	Core 131 Segment 3 UH		6	13	33
	Core 133 Segment 3		7	14	33
	Core 136 Segment 3 UH		10	20	33
U-106	Core 147 Segment 2 UH	13.2	7	22	27
	Core 147 Segment 3 UH		7	25	27
	Core 147 Segment 2 DL		6	27	27
U-107	Core 129 Segment 1 (Supernatant)	11.6	15	36	26
	Core 134 Segment 2		2	5	26

Notes: [1] UH = Upper Half Sample; LH = Lower Half Sample; DL = Drainable Liquid
[2] Headspace water partial pressures are from the Tank Characterization Database (PNNL 1997).
[3] Water content estimated by linear interpolation of data in Scheele et al. (1996, 1997a, 1997b, 1997c, 1998).

Figure D-2. Water partial pressure isotherm for tank AX-102 waste sample.

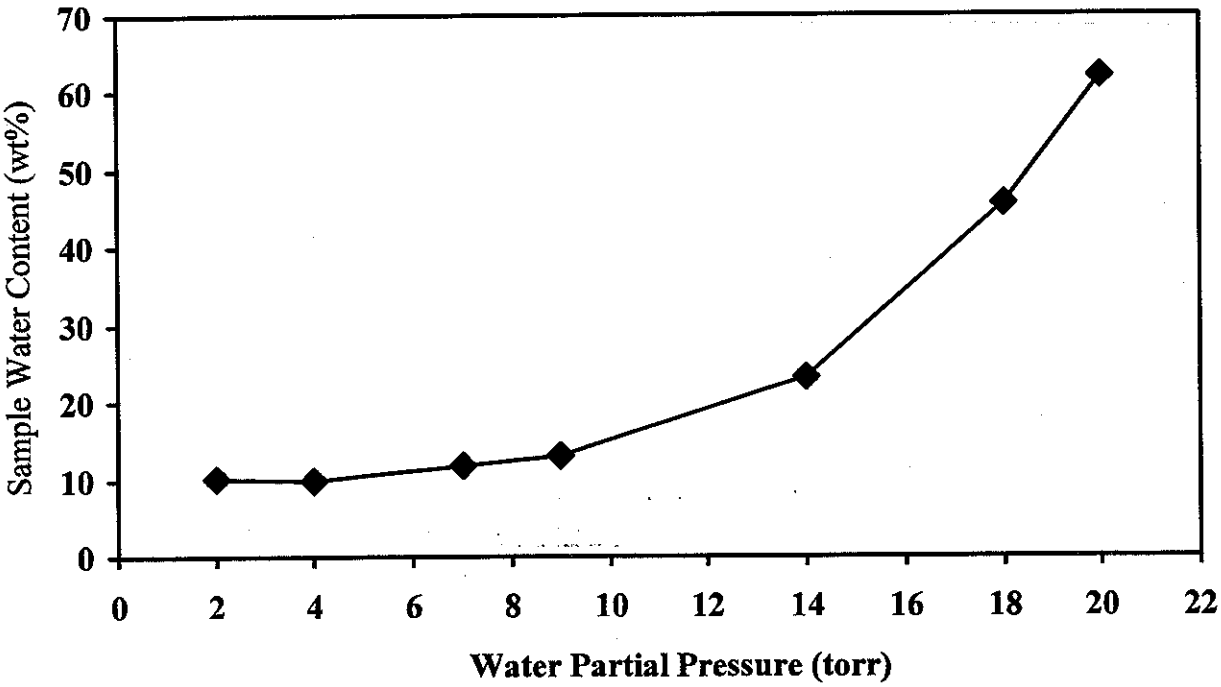
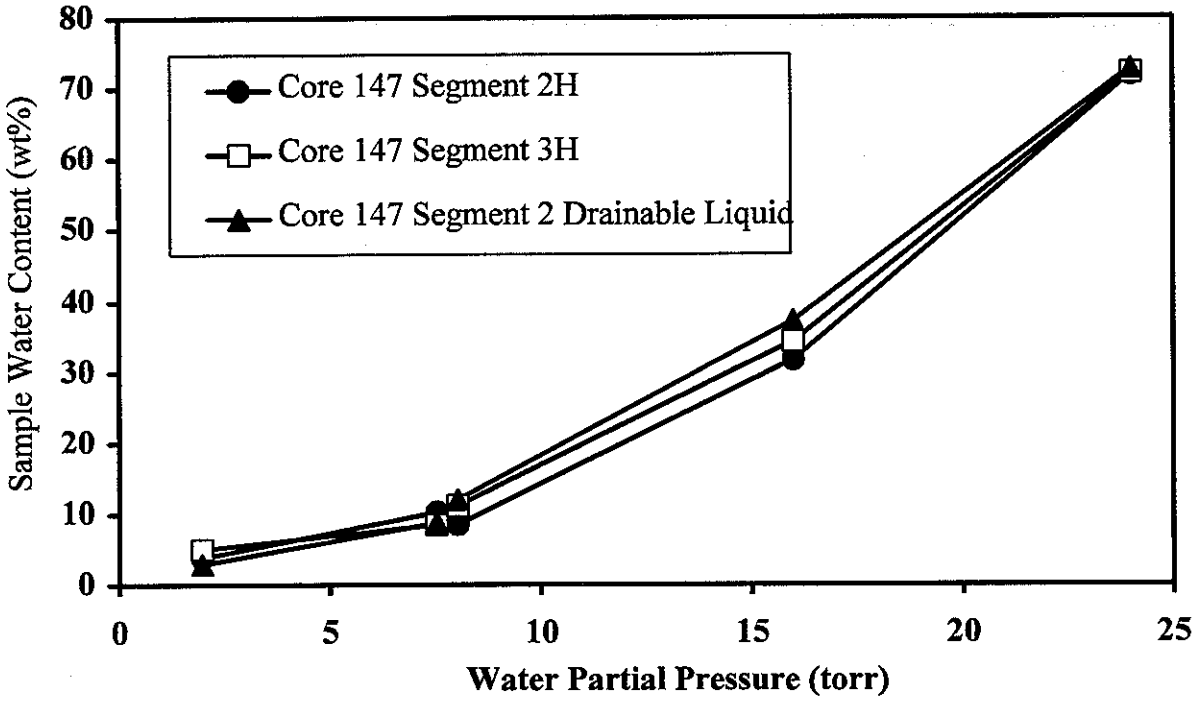


Figure D-3. Water partial pressure isotherm for three tank U-106 waste samples.



3.2 TEMPERATURE DEPENDENCE OF WATER PARTIAL PRESSURE

As discussed in the previous section, waste samples held at a constant reference temperature were allowed to come to equilibrium with various concentrations of water vapor. The resulting partial pressure isotherms (e.g., Figures D-2 and D-3) are only valid at the reference temperature, T_{ref}, which was close to, but not necessarily identical to, temperatures at the solid waste-headspace interface of the tank. To adjust the isotherm from the reference temperature to a different temperature, a relationship was developed based on the assumption that the potential energy of water associated with a given waste type is constant over the temperature range that the wastes may experience during future storage. The potential energy, ψ, may be expressed as

$$\psi = \frac{RT}{M}\ln\left(\frac{p}{p^0}\right) \qquad (D-10)$$

where R is the gas law constant, M is the molecular weight of water, p is the partial pressure of water above the waste, and p^0 is the vapor pressure of pure water at the absolute temperature T. The potential energy, as expressed by Equation D-10, includes all factors (e.g., solution ionic strength, adsorption of water by solid matrix) that affect the partial pressure of water above a waste sample. The concept of water potential energy for porous material with osmotic effects is discussed by Marshall and Holmes (1979). Applying the assumption that the potential energy is constant over a small temperature range gives

$$T\ln\left(\frac{p}{p^0}\right) = T_{ref}\ln\left(\frac{p_{ref}}{p^0_{ref}}\right) \qquad (D-11)$$

or

$$\frac{p}{p^0} = \left(\frac{p_{ref}}{p^0_{ref}}\right)^{\frac{T_{ref}}{T}} \qquad (D-12)$$

In the model, the vapor pressure of water, in torr, was calculated from the following empirical relation adapted from Hammel et al. (1981):

$$p^0 = 4.5848\exp\left(\frac{17.27(T - 273.16)}{T - 35.86}\right) \qquad (D-13)$$

The non-linear character of the adjustment of p is evident in Figure D-4, where the partial pressure isotherm for tank U-105 waste at the reference temperature of 33 °C has been plotted, along with the isotherm adjusted by Equation D-12 to the new temperature of 22.3 °C.

To avoid the selection and justification of a variety of empirical or semi-empirical equations, the model uses linear interpolation to evaluate the isotherms at points between the measured values. The equal potential energy assumption used in Equation D-12 could be incorrect if the solubility of chemical species in the waste is substantially different at the reference and new temperatures.

Confirmation of this adjustment procedure based on Equation D-12 is shown in Figure D-5, which is the measured partial pressure isotherm for waste from tank A-102. Two sets of vapor pressures were measured corresponding to 24 and 32°C. The isotherms are widely separated as a result of the temperature difference. The partial pressures for 24°C adjusted to 32°C are nearly coincident with the actual measurements for the higher temperature, indicating the adjustment method is appropriate.

Figure D-4. Water Partial Pressure Isotherm of Tank U-105 Waste.

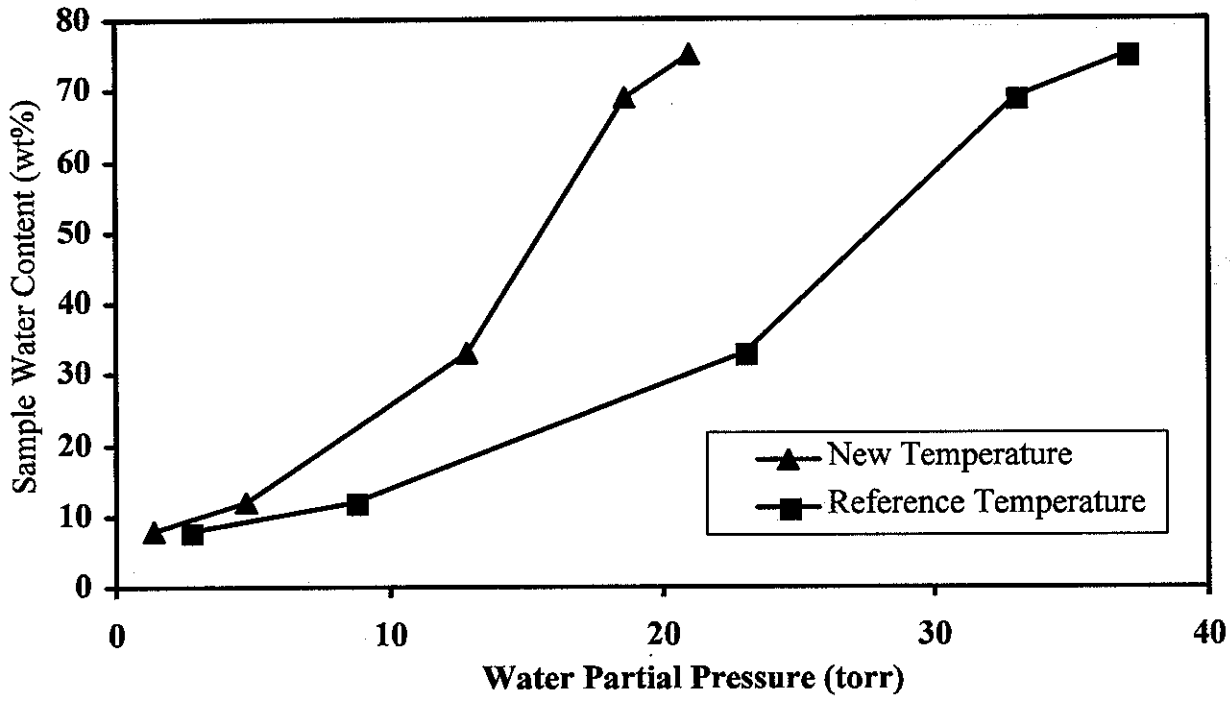
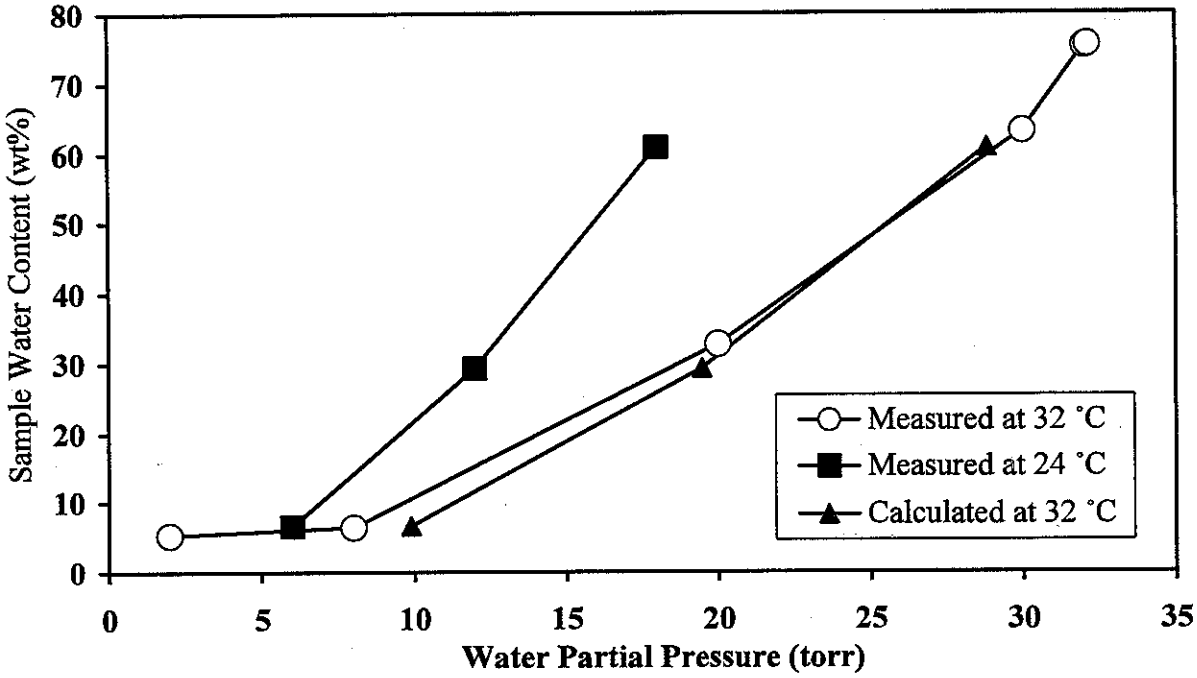


Figure D-5. Comparison of Water Partial Pressure Isotherm at 32 °C with Isotherm Calculated at 24 °C.



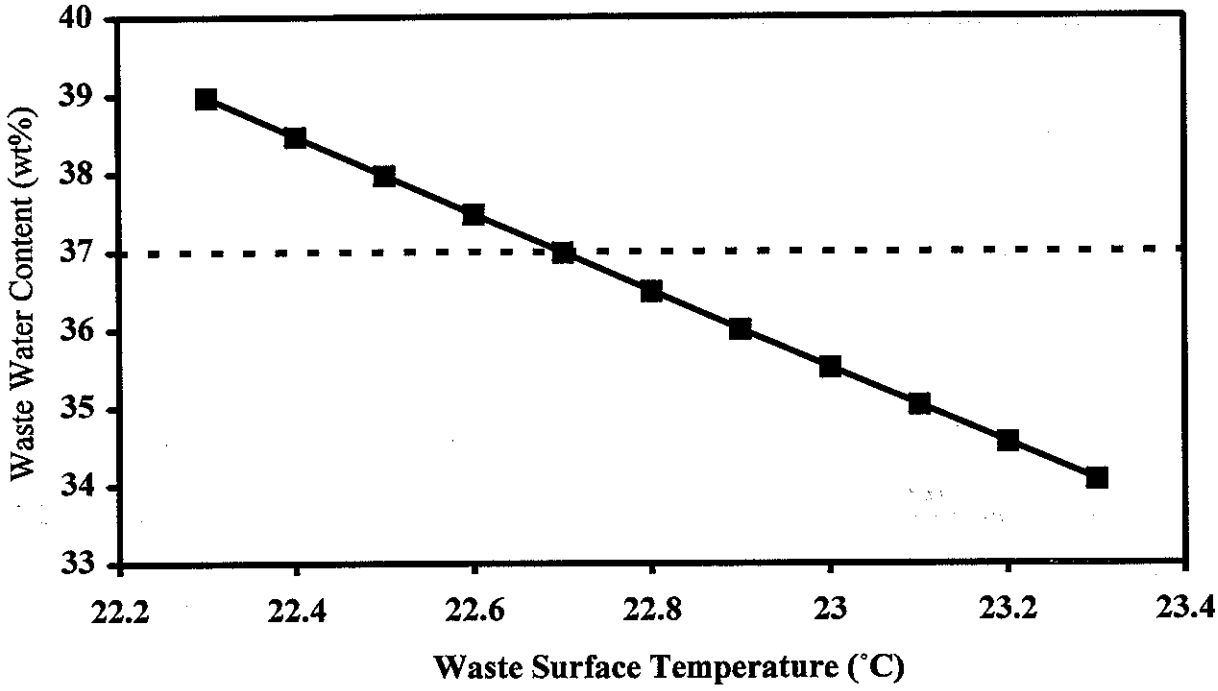
The water partial pressure isotherm and the method for adjusting it to a different temperature can also be shown to be consistent with tank headspace humidity measurements and tank temperatures. In tank U-105, for example, the partial pressure of water in the tank headspace is expected to be essentially the equilibrium partial pressure of water over the waste surface, because the waste surface is covered with supernatant and the ventilation rate is relatively low. The water partial pressure isotherm for the core 131 segment 2 waste sample from tank U-105 (plotted in Figure D-4), has been evaluated at the measured tank headspace water partial pressure of 13 torr (PNNL 1997), and converted with the help of Equation D-11 to an isobar. This is plotted in Figure D-6.

A horizontal line has been drawn in Figure D-6 at 37 wt% water, corresponding to the actual water content measured in the core 131 segment 2 waste sample. The isobar and horizontal line intersect at about 22.7 °C. This is the calculated value for the waste surface temperature when waste having 37 wt% water exhibits a water partial pressure of 13 torr. This calculated value is slightly greater than (as would be expected) the 22.3 °C temperature of the headspace measured at the time the headspace humidity was determined (PNNL 1997). This comparison indicates that the measured quantities and the isotherm adjustment method are consistent with the premise

that the tank U-105 headspace humidity and waste moisture content are essentially in equilibrium[1].

[1] It is also presumed here that the supernatant is saturated, water in the headspace, supernatant and waste phases are essentia

Figure D-6. Predicted Tank U-105 Waste Surface Water Concentration as a Function of Temperature at Constant Water Partial Pressure of 13 torr.



3.3 TANK TEMPERATURE TRENDS

Temperatures of the waste, headspace, and ambient air were each assumed to cycle with seasonal meteorological changes. Also, the waste and headspace temperatures were assumed to decrease with time as the heat produced by radioactive decay diminishes with time. An equation was derived that relates the temperature to these cycles:

$$T = \hat{T}_{final} + (\hat{T}_{initial} - \hat{T}_{final}) e^{-at} + (G + (E - G) e^{-at}) \cos(2\pi (t + h)) \quad (D-14)$$

Here $\hat{T}_{initial}$ is the initial mean temperature, $\hat{T}_{final}$ is the final mean temperature, t is time in years, E and G are initial and final amplitudes of the temperature cycle, h is a phase for synchronizing the equation with the seasonal cycle, and a is the decay constant for decline of the yearly mean temperature.

The decay constant a is approximately the decay constant for ^{137}Cs radioactive decay, since the heat load and temperature are directly related to the amount of ^{137}Cs present. Constants E, G, and h were determined by fitting the available data to Equation D-14. In the atmosphere, $\hat{T}_{initial}$ is equal to $\hat{T}_{final}$, and E is equal to G, so Equation D-14 reduces to

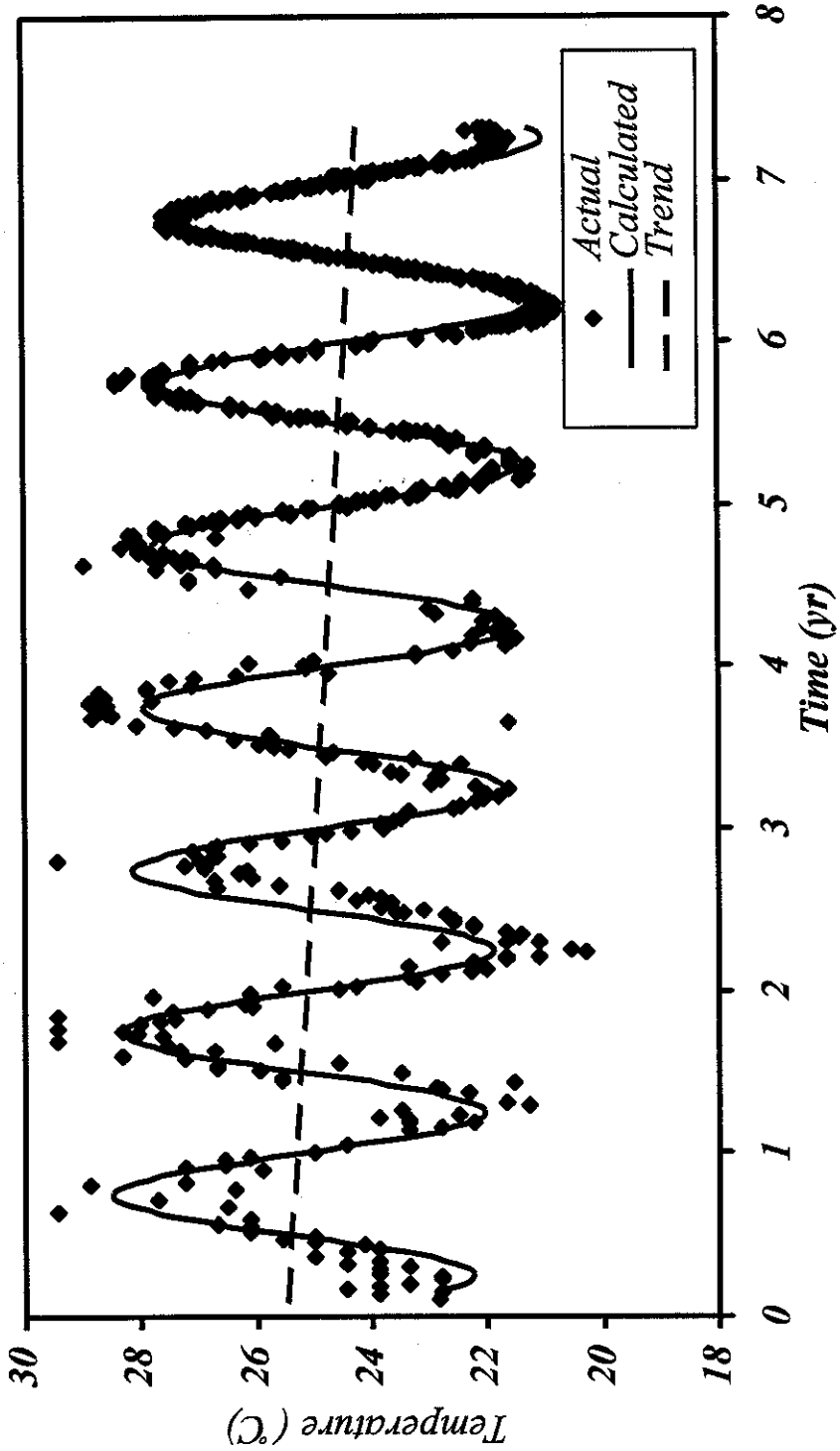
$$T = \hat{T} + G\cos(2\pi(t + h)) \qquad (D-15)$$

This model was found to fit waste, headspace, and atmospheric temperature data quite well. Table D-2 lists parameter values obtained for ambient air and several selected tanks. Figure D-7 demonstrates the fit of the temperature correlation to the thermocouple measurements made in the headspace of tank U-105.

Table D-2. Temperature Correlation Parameters for Ambient Air and Selected Tanks.

Tank	Date of $t = 0$	$\hat{T}_{initial}$ (°F)	$\hat{T}_{final}$ (°F)	a (yr^{-1})	E (°F)	G (°F)	h (yr)
Ambient		56.3	56.3	0	0	0	0.541
AX-102 Headspace	9/14/94	75	56.3	0.023	3.1	1	0.26
AX-102 Waste	9/14/94	75	55	0.023	3.1	1	0.23
U-105 Headspace	1/3/91	78	60	0.021	5.2	1	0.24
U-105 Waste	1/3/91	80.2	60	0.021	5.2	1	0.23
U-106 Headspace	1/3/91	74.9	60	0.023	4.7	1	0.238
U-106 Waste	1/3/91	76.4	60	0.023	4.7	1	0.228

Figure D-7. Tank U-105 Headspace Temperature and Fit With Equation D-14.



4.0 TANK VENTILATION RATES

4.1 VENTILATION RATES FROM TRACER GAS MEASUREMENTS

The ventilation rates of selected passively ventilated waste tanks have been measured using a tracer gas method (Huckaby et al. 1997). This method involves injecting an inert tracer gas, i.e., helium or sulfur hexafluoride, into the tank headspace and periodically measuring the tracer gas concentration in the headspace. Provided the tracer gas mixes quickly and remains well mixed in the headspace, the average ventilation rate, v, is given by

$$v = \frac{V}{(t_j - t_i)} \ln\left(\frac{C_j}{C_i}\right) \qquad (D-16)$$

where V is the headspace volume, and C_i and C_j are the tracer concentrations at times t_i and t_j, respectively (Huckaby et al. 1997).

Average ventilation rates measured for selected tanks and the periods for which the measurements apply are listed in Table D-3. Detailed data are available in Huckaby et al. (1997, 1998). The tracer method was also applied unsuccessfully to one tank, AX-101. Huckaby et al. (1998) concluded that an influx of air from a ventilation riser near the sampling point adversely affected the study of tank AX-101. The ventilation rate of tank U-103 during the January 8 - March 24, 1998 period is given as a range because it received an indeterminate amount of the tracer from tank U-102.

The highest ventilation rate was observed for tank C-104. The measured rate for tank C-104 is reasonable given that it is connected via a 7.6-cm (3-in.) cascade pipe to the actively ventilated tank C-105. At the time the tank C-104 ventilation rate was measured, the ventilation rate of tank C-105 was determined to be 885 m^3/h (521 ft^3/min).

The passive ventilation rate of the waste tanks appears to depend most heavily on the number and size of pathways available for air exchange. For example, high ventilation rates were measured in AX-farm, where an underground ventilation system of 51-cm and 61-cm (20-in. and 24-in.) pipes connects the headspaces of the four AX-farm tanks, allowing relatively free exchange of air between these tanks. A similar ventilation system exists in A-farm. The relatively low ventilation rates measured in S-, TX-, and U-farms are consistent with the lack of large inter-tank connections (the only inter-tank connections are 7.6-cm cascade pipes), and the observation that the risers and pit covers of these tanks would not allow significant fugitive air flow. The 27-m^3/h (16-ft^3/min) ventilation rate of tank BY-105 was the highest observed average ventilation rate among tanks that do not have large inter-tank connections. Based on the apparent relationship between high ventilation rates and large inter-tank connections, and on the moderate variability

of individual tank ventilation rates, it appears that significant increases in the average ventilation rate of a tank are unlikely in the absence of tank configuration modifications.

Table D-3. Average Ventilation Rates for Selected Tanks.

Tank	Tracer Gas	Time Period	Average Ventilation Rate, v	
			ft^3/min	m^3/h
A-101	He	Jul 9 - Jul 15, 1997	10	17
AX-102	He	Aug 28 - Sep 8, 1997	16	28
AX-103	He	Feb 28 - Mar 3, 1997	25	42
BY-105	He	Apr 17 - May 8, 1997	16	27
C-104	He	Apr 14 - Apr 17, 1998	67	114
C-107	He	Feb 21 - Mar 21, 1997	1.1	1.9
S-102	He	Sep 24, 1996 - Feb 11, 1997	2.2	3.8
TX-104	He	Jan 14 - Feb 12, 1997	3.5	5.9
U-102	He	Jan 9 - Mar 24, 1998	2.1	3.5
U-103	SF_6 and He	Feb 27 - Oct 22, 1997	1.7	3.0
	He	Nov 18, 1997 - Jan 8, 1998	2.3	4.0
	He	Jan 8 - Mar 24, 1998	$0.9 < v < 6.6$	$1.5 < v < 11$
U-105	He	Jul 15 - Aug 13, 1997	5.0	8.5
U-106	He	Jan 9 - Mar 24, 1998	1.3	2.2
U-111	He	Jan 9 - Mar 24, 1998	1.9	3.2

Though local meteorology is thought to have a strong influence on variations in the ventilation rates of the passively ventilated tanks, no definitive correlations between the average ventilation rates measured with tracer studies and data from the Hanford Meteorological Station were established. Furthermore, a year-long study of tank U-103 indicated only a moderate correlation between measured ventilation rates and seasonal effects (Huckaby et al. 1998). The correlation suggests that temperature differences between the headspace and atmosphere do play a role in passive ventilation (higher rates are correlated with larger temperature differences), but apparently their role in this tank is weak. For lack of evidence to the contrary and in lieu of a more complete data set, the average ventilation rates of individual tanks were assumed to not vary with seasonal changes.

It is expected that in future years the passive ventilation rates will decrease with efforts to decrease fugitive air emissions (e.g., replacement of riser gaskets, sealing pit covers), and as the

waste itself cools (i.e., thermal buoyancy forces that enhance ventilation diminish). If this expectation is correct, use of the current ventilation rates in the model would tend to result in over-estimating the rate of waste dryout.

4.2 HEADSPACE HUMIDITIES AND SIMPLE WATER LOSS ESTIMATES

In addition to passive ventilation rate studies, many of the single-shell waste tank headspaces have been characterized chemically by the Tank Characterization Program. In particular, water vapor concentrations in 107 different tanks have been measured at least once, and in some cases multiple times. As an adjunct of this appendix, the measured headspace relative humidities obtained from 141 vapor sampling events were used to derive simple estimates of current annual water losses due to evaporation and ventilation.

The annual rate at which water vapor is removed by ventilation, Δm, can be estimated from an integrated form of Equation D-2,

$$\Delta m = v(\hat{C} - \hat{C}_{amb})\Delta t \qquad (D-17)$$

where $\hat{C}$ and $\hat{C}_{amb}$ are the annual average water vapor mass concentrations in the tank headspace and ambient air, respectively, and Δt is the time period of 1 year.

Average tank headspace water vapor concentrations were calculated by assuming the relative humidity of the headspace is approximately constant throughout the year, and equal to that measured during the vapor sampling event. Relative humidities were converted to mass concentrations using the ideal gas law, standard psychrometric relationships, and annual average headspace temperatures (Huckaby et al. 1998). Hanford Site meteorological data for calendar years 1994, 1995, 1996, and 1997 were used to compute an average ambient air water vapor concentration of 5.76 mg/L, at the reference temperature of 25 °C. Table D-4 lists, by tank and sampling date, tank headspace temperatures obtained from thermocouple tree readings on or near the sampling date, headspace relative humidities, average headspace temperatures for calendar year 1995, and the headspace water mass concentrations.

Nominal ventilation rates, based on results discussed in Section 4.1, are also listed in Table D-4. Because ventilation rates have been measured for only a few tanks, the majority of listed ventilation rates are only rough estimates. Generally the 100-series single-shell tanks were assumed to have a ventilation rate of 8.5-m^3/h (5-ft^3/min), unless higher ventilation rates had been observed for other tanks in the same farm. All BX-farm tanks, for example, were assumed to have a 8.5-m^3/h ventilation rate, but all A-farm tanks were assumed to be the same as tank A-101, which had a reported 17-m^3/h average ventilation rate. The 200-series single-shell tanks were universally assumed to have a ventilation rate of 1.7-m^3/h (1-ft^3/min), in lieu of any ventilation measurements for these much smaller tanks.

The last column of Table D-4 lists the estimated current annual water loss. Variations in the results associated with the different sampling events of a single tank are generally reasonable, but do indicate there are occasional problems with the reported data. The headspace water vapor measurement for tank BX-104 obtained on 12/30/94, for example, is apparently a bad measurement. Only tanks C-104, SX-103, and SX-106 were calculated to have water losses greater than 5,000 kg/yr, and each of these are actively ventilated.

Table D-4. Measured Tank Headspace Humidities and 1995 Water Loss Estimates.

Tank	Date Sampled	Headspace Temperature[1] (°C)	Headspace Relative Humidity (%)	Annual Average Headspace Temperature[1] (°C)	Annual Average Headspace Water Concentration (mg/L)	Vent Rate[1] (m^3/h)	Annual Water Loss[2] (kg/yr)
A-101	6/8/95	35.4	55.7	36.4	25.4	17	2957
A-102	11/10/95	32.8	65.6	32.4	24.0	*17*	2732
A-103	11/9/95	30.0	74.5	29.9	23.5	*17*	2661
A-106	1/16/97	40.4	52.9	42.1	32.7	*17*	4059
AX-101	6/15/95	30.4	37.2	30.7	12.3	*34*	1979
AX-102	6/27/95	23.5	56.6	23.9	12.6	27	1619
AX-103	6/21/95	32.2	38.4	32.5	14.1	42	3142
AX-104	1/23/97	31.7	16.2	32.9	6.1	*34*	144
B-102	4/18/96	*16*	86.5	16.8	12.4	*8.5*	479
B-103	2/8/95	13.7	84.5	16.3	11.8	*8.5*	433
B-103	10/16/96	19.5	70.2	16.3	9.8	*8.5*	284
B-105	7/30/96	17.8	64.6	*19*	10.6	*8.5*	355
B-107	7/23/96	15.8	91.4	16.5	12.8	*8.5*	512
B-202	7/18/96	16.0	91.7	15.2	11.9	*1.7*	88
BX-102	7/31/96	18.5	93.7	19.2	15.6	*8.5*	724
BX-103	8/1/96	19.6	83.2	20.3	14.8	*8.5*	669
BX-104	12/30/94	27.7	21.9	26.6	5.7	*8.5*	-3
	8/22/96	22.5	77.8	26.6	20.3		1081
	12/12/96	22.3	72.3	26.6	18.8		975
	2/6/97	19.6	71.7	26.6	18.7		964
	4/7/97	19.1	75.2	26.6	19.6		1031
	6/10/97	20.0	70.3	26.6	18.3		935
BX-105	4/24/96	18.3	63.6	20.6	11.6	*8.5*	427
BX-106	8/15/96	19.4	55.8	19.4	9.4	*8.5*	262
BX-107	11/17/95	21.0	81.5	19.2	13.6	*8.5*	575
BX-110	4/30/96	16.8	56.8	19.1	9.4	*8.5*	262
BX-111	8/27/96	19.1	32.9	19.9	5.7	*8.5*	-8

Table D-4. Measured Tank Headspace Humidities and 1995 Water Loss Estimates.

Tank	Date Sampled	Headspace Temperature[1] (°C)	Headspace Relative Humidity (%)	Annual Average Headspace Temperature[1] (°C)	Annual Average Headspace Water Concentration (mg/L)	Vent Rate[1] (m^3/h)	Annual Water Loss[2] (kg/yr)
BY-101	8/29/96	19.5	52.9	20.4	9.5	*27*	870
BY-102	11/21/95	23.4	64.6	31.1	21.9	*27*	3872
BY-103	11/1/94	25.3	49.5	22.1	9.8	*27*	960
BY-104	6/24/94	26.8	55.1	26.8	14.5	*27*	2096
BY-105	7/7/94	25.8	62.1	27.3	16.9	27	2654
BY-106	7/8/94	29.0	49.3	28.3	14.2	*27*	2031
BY-107	10/26/94	28.0	47.3	24.8	11.1	*27*	1278
BY-108	10/27/94	30.5	42.3	28.0	12.0	*27*	1495
	1/23/96	26.6	50.1	28.0	14.2		2018
	1/23/96	26.6	49.0	28.0	13.9		1945
	1/23/96	26.6	47.6	28.0	13.5		1853
	3/28/96	25.0	52.4	28.0	14.8		2173
	3/28/96	25.0	54.4	28.0	15.4		2310
	9/10/96	27.9	52.0	28.0	14.7		2149
	11/14/96	28.0	57.6	28.0	16.3		2526
	1/30/97	28.0	46.2	28.0	13.1		1757
BY-110	11/11/94	28.4	30.4	26.0	7.7	*27*	456
BY-111	11/16/94	25.0	29.2	21.8	5.7	*27*	-22
BY-112	11/18/94	25.3	47.3	22.4	9.6	*27*	909
C-101	9/1/94	35.1	75.4	32.0	26.9	*8.5*	1583
C-102	8/23/94	26.5	81.3	25.2	19.5	*8.5*	1026
C-103	5/12/94	38.8	88.2	39.3	47.0	*8.5*	3091
	5/19/94	38.8	89.9	39.3	48.0		3160
	5/25/94	39	83.3	39.3	44.4		2897
C-104	3/3/94	28.8	45.1	*30*	14.4	114	8669
C-107	9/29/94	46.4	83.9	43.6	56.2	1.9	831
	1/17/96	42.4	67.8	43.6	45.4		595
	1/17/96	42.4	68.5	43.6	45.9		662
	1/17/96	42.4	70.5	43.6	47.2		684
	3/26/96	40.2	46.6	43.6	31.2		422
	3/26/96	40.2	73.4	43.6	49.2		716
	9/5/96	43.1	89.9	43.6	60.2		897
	12/17/96	41.3	80.9	43.6	54.2		798
	2/7/97	38.6	90.3	43.6	60.4		901

Table D-4. Measured Tank Headspace Humidities and 1995 Water Loss Estimates.

Tank	Date Sampled	Headspace Temperature[1] (°C)	Headspace Relative Humidity (%)	Annual Average Headspace Temperature[1] (°C)	Annual Average Headspace Water Concentration (mg/L)	Vent Rate[1] (m^3/h)	Annual Water Loss[2] (kg/yr)
C-108	8/5/94	25.0	75.8	23.7	16.6	*8.5*	808
C-109	8/10/94	27.1	74.8	25.4	18.1	*8.5*	922
C-110	8/18/94	22.7	62.4	20.6	11.3	*8.5*	409
C-111	9/13/94	26.4	47.3	23.3	10.2	*8.5*	325
C-112	8/11/94	28.1	81.9	26.5	21.2	*8.5*	1152
C-201	6/19/96	16.1	64.7	17.1	9.4	*1.7*	52
C-202	6/25/96	16.3	52.2	17.3	7.7	*1.7*	27
C-204	7/2/96	*18*	46.9	*18*	7.3	*1.7*	20
S-101	6/6/96	31	51.2	33.5	19.9	*8.5*	1063
S-102	3/14/95	24	63.9	26.5	16.6	3.7	357
	1/26/96	26	47.7	26.5	12.4		219
	1/26/96	26	51.9	26.5	13.5		255
	1/26/96	26	48.4	26.5	12.6		224
	4/4/96	24	50.2	26.5	13.1		240
	4/4/96	24	52.2	26.5	13.6		257
	9/19/96	29	49.7	26.5	12.9		235
	12/19/96	27	49.6	26.5	12.9		235
	2/11/97	24	54.6	26.5	14.2		278
S-103	6/12/96	24	46.6	25.2	11.2	*8.5*	408
S-105	12/7/95	23.0	46.2	23.5	10.0	*8.5*	315
S-106	6/13/96	19.4	48.0	22.6	9.9	*8.5*	304
S-107	6/18/96	27.8	74.5	29.5	23.1	*8.5*	1294
S-108	12/6/95	22.1	58.6	23.1	12.4	*8.5*	495
S-109	6/4/96	18.8	60.5	22.6	12.5	*8.5*	495
S-110	12/5/95	28	55.1	28.4	16.0	*8.5*	765
S-111	3/21/95	21.4	58.9	23.7	12.9	*8.5*	532
S-112	7/11/95	20.0	68.0	20.6	12.4	*8.5*	487
SX-101[3]	7/21/95	36.6	23.2	*37*	10.7	*170*	7628
SX-102[3]	7/19/95	34.9	17.2	*35*	7.2	*170*	2455
SX-103[3]	3/23/95	36.6	27.7	*37*	12.7	*170*	10712
SX-104[3]	7/25/95	33	21.5	*33*	8.2	*170*	3937
SX-105[3]	7/26/95	34.7	27.3	*35*	11.3	*170*	8561
SX-106[3]	3/24/95	29.8	47.6	*30*	15.0	*170*	13876
SX-107[3,4]	5/19/97	42.2	8.6	*42*	5.3	*170*	-142

Table D-4. Measured Tank Headspace Humidities and 1995 Water Loss Estimates.

Tank	Date Sampled	Headspace Temperature[1] (°C)	Headspace Relative Humidity (%)	Annual Average Headspace Temperature[1] (°C)	Annual Average Headspace Water Concentration (mg/L)	Vent Rate[1] (m^3/h)	Annual Water Loss[2] (kg/yr)
SX-108[3,4]	7/16/97	52	5.3	*52*	5.4	*170*	165
SX-109[3]	8/1/95	56	5.6	*56*	7.0	*170*	2626
SX-110[3]	7/30/97	43	11.7	*43*	7.6	*170*	3180
SX-111[3,4]	5/22/97	51	5.6	*51*	5.4	*170*	120
SX-112[3,4]	6/18/97	46.4	7.0	*46*	5.4	*170*	36
SX-114[3,4]	6/25/97	51.1	5.5	*51*	5.4	*170*	133
T-101	12/1/97	19.2	90.9	19.2	15.1	*8.5*	690
T-104	2/7/96	15.1	85.0	17.4	12.7	*8.5*	503
T-107	1/18/95	17.4	81.5	18.3	12.8	*8.5*	517
T-110	8/31/95	19.9	87.9	17.5	13.2	*8.5*	543
T-111	1/20/95	16.1	85.9	17.6	13.0	*8.5*	528
TX-101	10/28/97	22	72.0	48.9	63.0	*8.5*	4294
TX-102	10/13/97	22	64.3	*24*	14.4	*8.5*	641
TX-103	10/24/97	21	67.0	19.8	11.6	*8.5*	424
TX-104	5/5/97	16.7	54.6	18.4	8.6	5.9	143
TX-105	12/20/94	25.7	54.8	23.5	11.9	*8.5*	457
TX-106	3/5/97	19.9	54.6	20.1	9.6	*8.5*	281
TX-108	12/5/97	17.1	90.1	19.2	15.0	*8.5*	677
TX-110	9/23/97	23	71.7	*22*	14.2	*8.5*	624
TX-111	10/12/95	19.6	72.4	20.2	12.9	*8.5*	521
TX-112	12/9/97	19	61.0	18.3	9.6	*8.5*	278
TX-113	8/6/97	18	67.5	20.6	12.2	*8.5*	475
TX-114	3/25/97	16.4	53.8	*17*	7.8	*8.5*	142
TX-115	11/20/97	19.7	62.0	19.9	10.8	*8.5*	367
TX-116	9/18/97	21	68.7	*21*	12.8	*8.5*	519
TX-117	12/11/97	20	68.2	20.0	12.0	*8.5*	454
TX-118	12/16/94	22	40.8	20.8	7.5	*8.5*	123
TY-101	4/6/95	16.6	72.8	18.1	11.3	*8.5*	403
TY-102	4/12/96	14.6	71.9	16.4	10.0	*8.5*	305
TY-103	4/11/95	16.4	83.1	18.6	13.3	*8.5*	554
	11/22/96	19.1	81.0	18.6	13.0	*8.5*	530
TY-104	4/27/95	16.3	84.9	17.9	13.1	*8.5*	534

Table D-4. Measured Tank Headspace Humidities and 1995 Water Loss Estimates.

Tank	Date Sampled	Headspace Temperature[1] (°C)	Headspace Relative Humidity (%)	Annual Average Headspace Temperature[1] (°C)	Annual Average Headspace Water Concentration (mg/L)	Vent Rate[3] (m^3/h)	Annual Water Loss[2] (kg/yr)
TY-105	10/20/97	22	82.1	20.4	14.8	*8.5*	663
U-102	12/18/97	*27*	58.7	*27*	15.6	4.6	398
U-103	2/15/95	21.8	65.0	25.1	15.6	4.4	379
U-104	7/16/96	18.7	97.3	17.8	14.9	*8.5*	667
U-105	2/24/95	22.3	64.4	26.0	16.3	8.5	783
U-106	3/7/95	20.3	73.9	24.1	16.6	2.2	209
U-107	2/17/95	20.5	64.4	24.8	15.2	*8.5*	699
U-108	8/29/95	27.7	50.5	23.9	11.2	*8.5*	406
U-109	8/10/95	28.8	42.3	23.0	8.9	*8.5*	233
U-111	2/28/95	20.2	64.4	23.8	14.2	3.7	276
U-112	7/9/96	18.4	77.3	19.3	13.0	*8.5*	529
	12/6/96	18.5	80.0	19.3	13.4		563
U-203	8/9/95	17.8	85.0	16.5	11.9	*1.7*	90
U-204	8/8/95	13.8	122.2	15.7	16.4	*1.7*	155

Notes: [1] Estimated values are in italics.

[2] Annual water loss rate assumes constant vent rate, uses calculated annual average headspace water vapor concentration, and the 1994-1997 average Hanford Site ambient air water vapor concentration of 5.76 mg/L at 25 °C.

[3] All listed SX-farm tanks are actively ventilated.

[4] Concentration of water vapor was reported as <5.89 mg/L; 5.89 mg/L for calculations.

5.0 MODEL RESULTS

The model described in Section 4.0 was applied to estimate the water loss of nine tanks. The tanks studied and results are listed in Table D-5. Table D-6 lists selected characteristics of tanks AX-102, U-105, and U-106. The application of the model to each of the nine tanks is discussed briefly in the following subsections.

Table D-5. Modeling Results.

Tank	Time to reach 20 wt% water	50 year wt% water	10 year wt% water	Initial wt% water
A-102	30 yr	16	28	34
A-103	>> 50 yr	22	34	40
A-106	>> 50 yr	30	40	45
AX-102	15 yr	15	21	25
C-104	>>100 yr	42	48	50
T-111	>>100 yr	78		80
U-102	>> 100 yr			40
U-105	>> 50 yr	29	32.7	34
U-106	>> 100 yr	45	49	50
U-111	>> 50 yr			40

Table D-6. Waste Characteristics for Tanks AX-102, U-105, and U-106.

Characteristic	Tank AX-102	Tank U-105	Tank U-106
Waste type	saltcake	saltcake	sludge
Waste volume (kgal)	39	418	226
Waste depth (m)	0.254 (10 in)	3.96 (156 in)	2.29 (90 in)
Interstitial liquid volume (kgal)	17	170	87
Supernatant volume (kgal)	3	37	15
Ventilation rate (m^3/h)	28	8.5	2.2
Current wt% water (%)	25	34	50
Headspace RH and measure date	57% on 6/27/95	64% on 2/24/95	74% on 3/7/95
Waste surface temperature (°C)	23.5	23.3	21.5

5.1 TANK U-106 WATER LOSS

Core segment samples from tank U-106 indicate the waste is covered by supernatant and that the solid waste is essentially saturated with interstitial liquid. Measurements indicate 15-kgal of supernatant (an average surface liquid depth of 14-cm, PNNL 1997). Although the waste is classified as being mainly saltcake (Hanlon 1998), the relatively low nitrate anion content of samples suggests it may be more like sludge than saltcake. The waste cores were also sludge-like in appearance. The distinction is important because sludge is not easily drained by pumping and tends to shrink as water is removed by evaporation. Saltcake waste is, by comparison, rigid and can be drained to leave interstices (empty pores). It is expected that waste in this tank would dry as a typical sludge and not as saltcake.

The model was first applied with the restriction that relative humidity in the headspace remained constant over time. In this analysis the loss of water was calculated from the expression

$$\Delta m = - v(\hat{C} - \hat{C}_{amb})\Delta t \qquad (D-18)$$

where $\hat{C}$ and $\hat{C}_{amb}$ are averages of the headspace and ambient air water vapor over the time period Δt. The average water vapor concentrations were obtained by integrating the calculated water vapor concentrations over a 1-year period (Δt = 1 yr). The headspace water vapor concentration for constant relative humidity decreases as the waste temperature decreases, because by definition of relative humidity,

$$C = C^0(T)RH \qquad (D-19)$$

where C^0 is the saturation concentration of water vapor at temperature T, and RH is the relative humidity. Here T is a function of time, as determined from the declining cyclic temperature model fit to the previous 7-year record of tank headspace temperatures. This cycle was very regular and similar to that shown for tank U-105. The average water vapor concentration in ambient air was obtained by integrating

$$C_{amb}(t) = C^0(T_{amb})RH_{amb} \qquad (D-20)$$

where RH_{amb} is relative humidity of ambient air. T_{amb}, as a function of time, was based on a model fit of a three-year Hanford Site climate record (Kummerer 1994), and RH_{amb} was based on ambient water partial pressures reported by Scheele et al. (1997).

The cumulative water loss obtained from the constant relative humidity model is shown in Figure D-8. The water loss, even after 100 years, is substantially less than the total water available in the surface supernatant, and waste dryout given the current scenario is not a problem. Figure D-9 graphs the depth of supernatant for this model. The depth of supernatant was calculated with the assumption that the wt% water of the supernatant is a constant, and salt is precipitated as water evaporates. Higher ventilation rates would increase the rate of water removal, but even when the ventilation rate is assumed to be twice the measured average (4.4 m^3/h), the constant relative humidity model predicts the layer of supernatant on top of other wastes is still about 3.15 inches (8-cm) after 50 years.

Note that the constant headspace relative humidity model does not involve the water partial pressure isotherm, and consequently does not take credit for the decrease in water vapor concentration associated with the cooling waste.

The water loss from tank U-106 was also modeled under the supposition that the headspace humidity is in equilibrium with the supernatant on the surface of the waste. In this case the measured water partial pressure isotherm was employed to determine what the water vapor concentration is in the headspace as the temperature declines over time. The likely re-wetting of the drying surface, by movement of water from the 2.3-m waste depth below the supernatant, is neglected. This approach tends to maximize estimated surface drying.

The water partial pressure isotherms at the reference temperature of 27 °C and at the assumed initial waste surface temperature of 21.5 °C are depicted in Figure D-10. The reference temperature isotherm in Figure D-10 is the average of nearly identical results obtained from segment 3 upper half and drainable liquid of core 147. The headspace humidity measured in March 1995 corresponds to a water partial pressure of 13.2 torr (PNNL 1997). From Figure D-10 (or reference isotherm data and Equation D-12), 13.2 torr is the equilibrium partial pressure above the waste at 21.5 °C for waste having 49 wt% water. This agrees very well with the measured 50 wt% of water in the tank U-106 supernatant (see Table D-6). This result indicates the headspace water vapor concentration appears to be in equilibrium with the supernatant, and justifies this modeling assumption.

The waste wt% water calculated by the model is given in Figure D-11 as a function of time. Here it is assumed that dissolved salts will be precipitated from the supernatant as the water wt% is diminished from its initial value of 50%. As indicated by Figure D-11, the decrease in wt% water at the waste surface is predicted to occur very slowly, and the waste remains very wet. The slow water loss rate predicted by the model is consistent with the observation that the surface level and interstitial liquid level have remained about the same over the past ten years.

Figure D-8. Cumulative Water Lost from Tank U-106 Assuming 74% Relative Humidity.

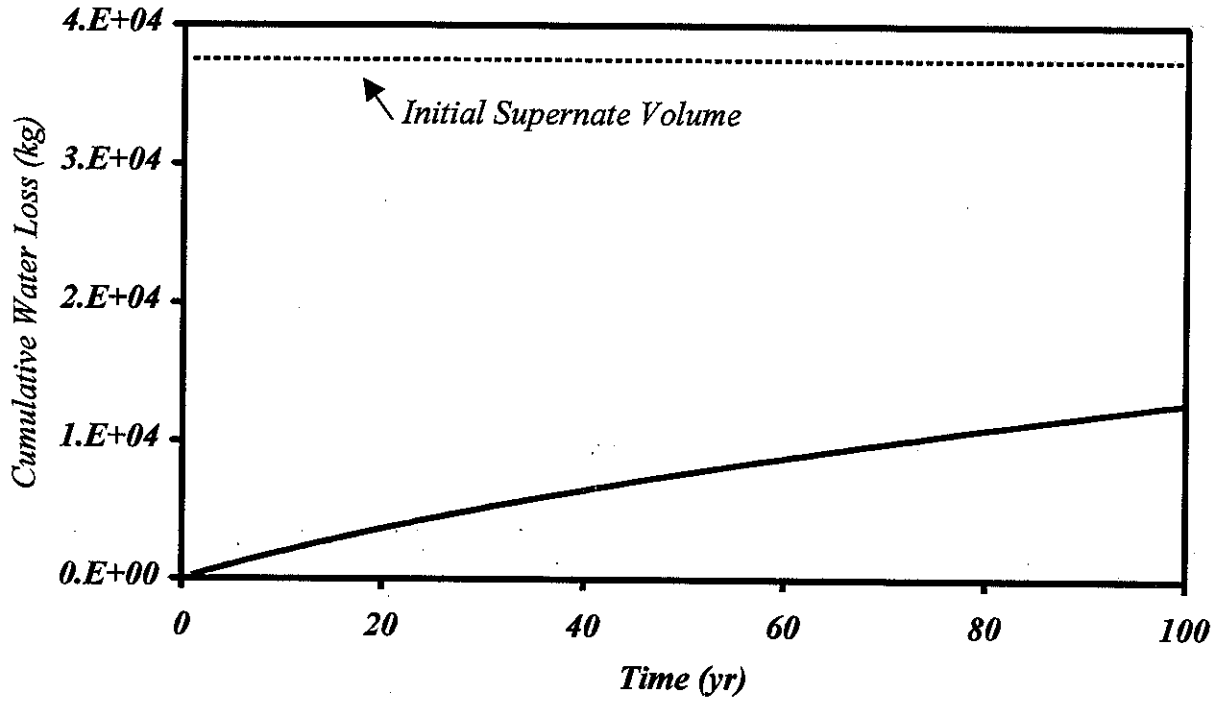


Figure D-9. Depth of Supernatant in Tank U-106 Assuming 74% Relative Humidity.

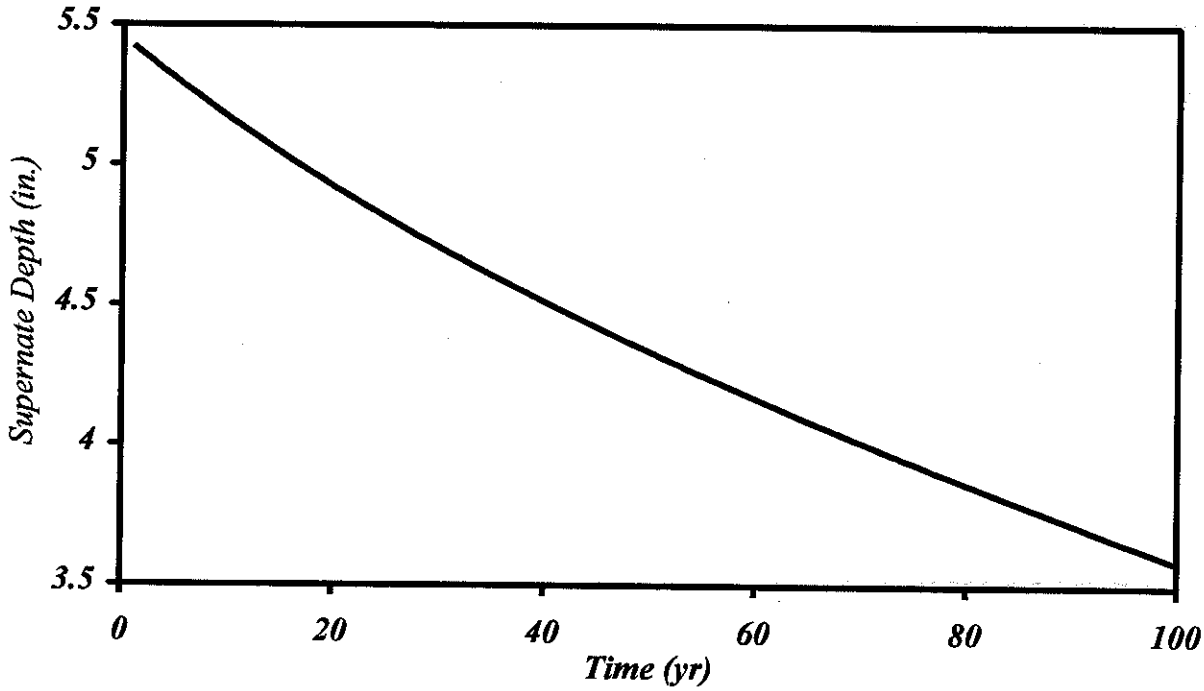


Figure D-10. Water Partial Pressure of Waste Sample from Tank U-106.

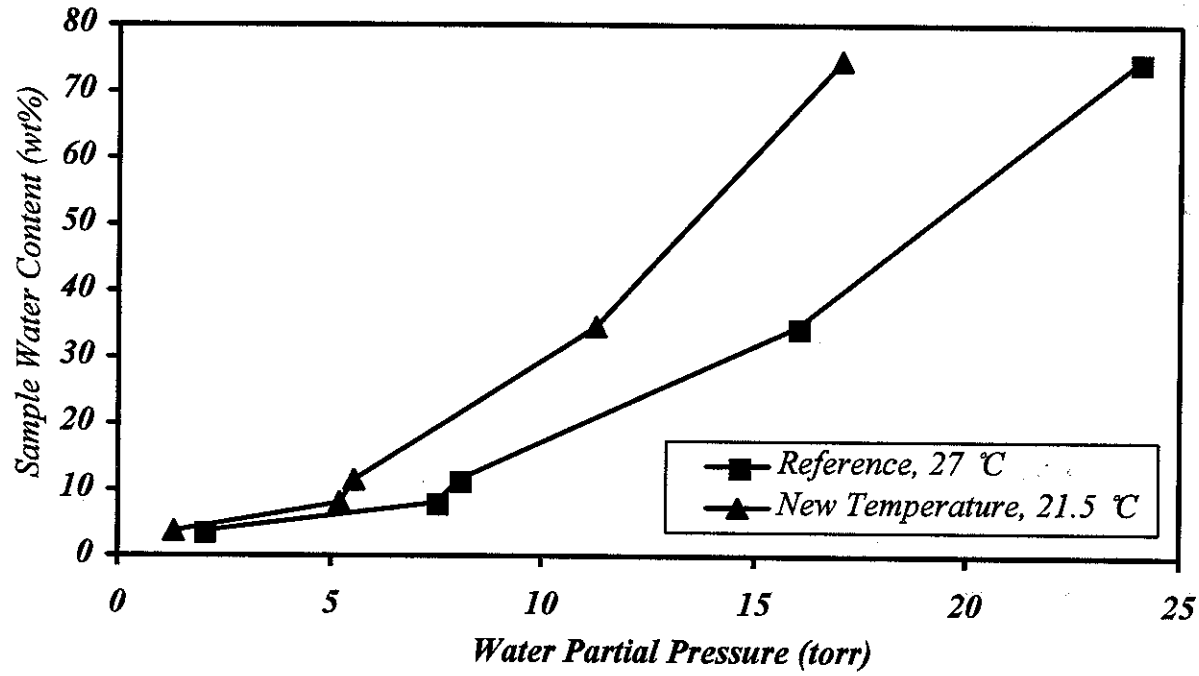
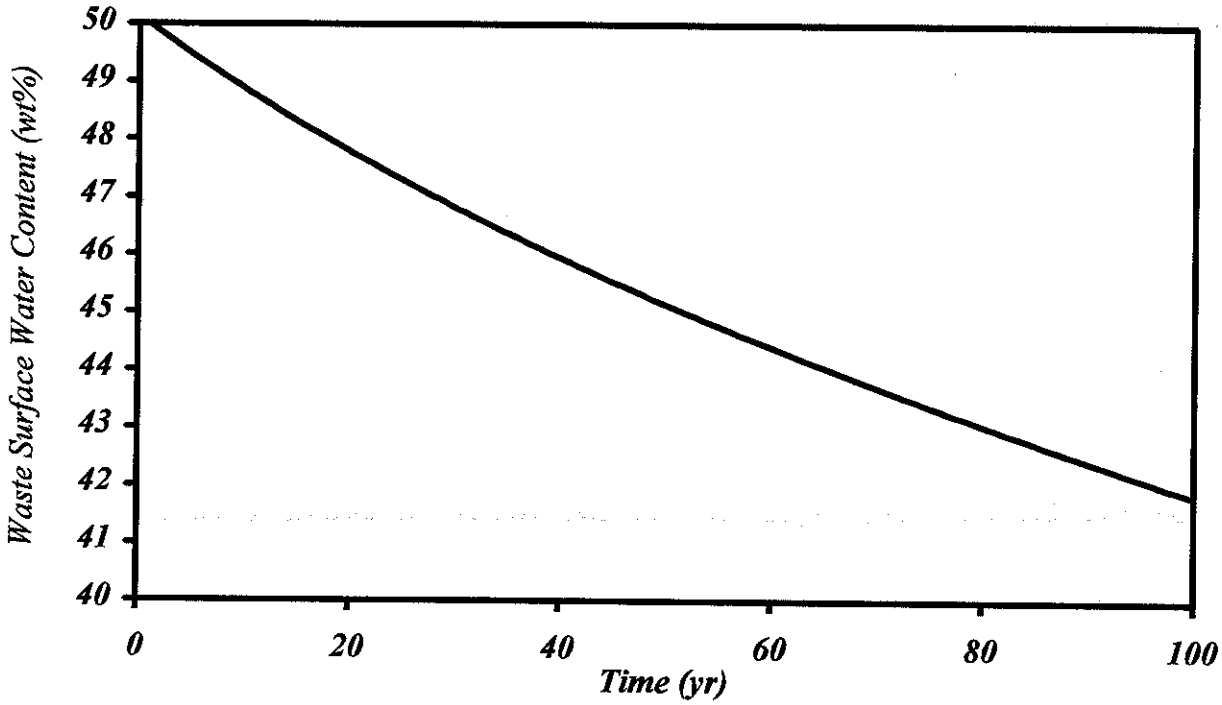


Figure D-11. Waste Surface Water Concentration in Tank U-106.



5.2 TANK AX-102 WATER LOSS

Tank AX-102 is a shallow sludge waste tank that has been interim stabilized (i.e., drainable liquids have been removed). The tank was found to have a high ventilation rate (Huckaby et al. 1997), which may account for the 0.27 in./yr drop in liquid level observed between 1981 and 1988. Two waste samples analyzed for water content gave significantly different results; an auger sample collected in 1995 was reported to be 30.5 wt% water (Sederburg et al. 1995), but a sample collected in 1998 was found to have only 25 wt% water (Scheele et al. 1998). It was assumed in the model that the waste currently has 25 wt% water.

The water content of waste in equilibrium with the measured headspace humidity was calculated to be 25 wt% using the partial pressure isotherm. This agrees very well with the water content of the second sample. It suggests that, despite the relatively high ventilation rate, water vapor in the headspace is nearly in equilibrium with waste moisture. Resistances to transport of water from the waste into the headspace are relatively small, and loss of water from the waste is determined primarily by the ventilation rate. The presence of a diffusion limitation (dry surface crust) is inconsistent with the measured headspace humidity, water partial pressure isotherm, and measured water content of the waste.

When the temperature trends both inside and outside this tank are taken into account, the waste is predicted to reach a minimum water content of about 14.5% in 40 years, then increase gradually as the waste continues to cool and begins to reabsorb water vapor. The predicted wt% water of the waste is shown by the solid curve in Figure D-12 for 100 years. Figure D-13 shows how the vapor concentration in the headspace behaves over time. Note that during the simulated drying period, the headspace relative humidity begins at about 56% and drops to about 37% before increasing again to about 42% at 100 years.

The model for tank AX-102 assumes all incoming air has the water vapor concentration of ambient air, but much of the air introduced to tank AX-102 may actually come from the other humid tanks in AX farm. This is may be true of many tanks but is of particular importance in AX farm where large underground vent pipes connect the tank headspaces and are associated with the relatively high ventilation rates observed in AX farm.

If a crust does form on the surface of the waste that significantly impedes water transport, then water loss from tank AX-102 would occur more slowly. This situation has been modeled by assuming a 5.1-mm (2-in.) thick porous crust forms. Assuming the air-filled pore structure to have a porosity of 10%, the diffusion coefficient for transport through the crust, D, becomes

$$D = 0.1 D_{H2O} \qquad \text{(D-21)}$$

Where D_{H2O} is the coefficient for water in air. Including the eddy transfer coefficient, this gave a transfer coefficient of about $k = 70$ m^3/h. The waste water content predicted by the model under these assumptions is given by the dotted curve in Figure D-12. As is expected, the waste water content decreases less slowly and does not become as dry as when no crust is assumed by the model.

Figure D-12. Water Concentration in Tank AX-102 Waste.

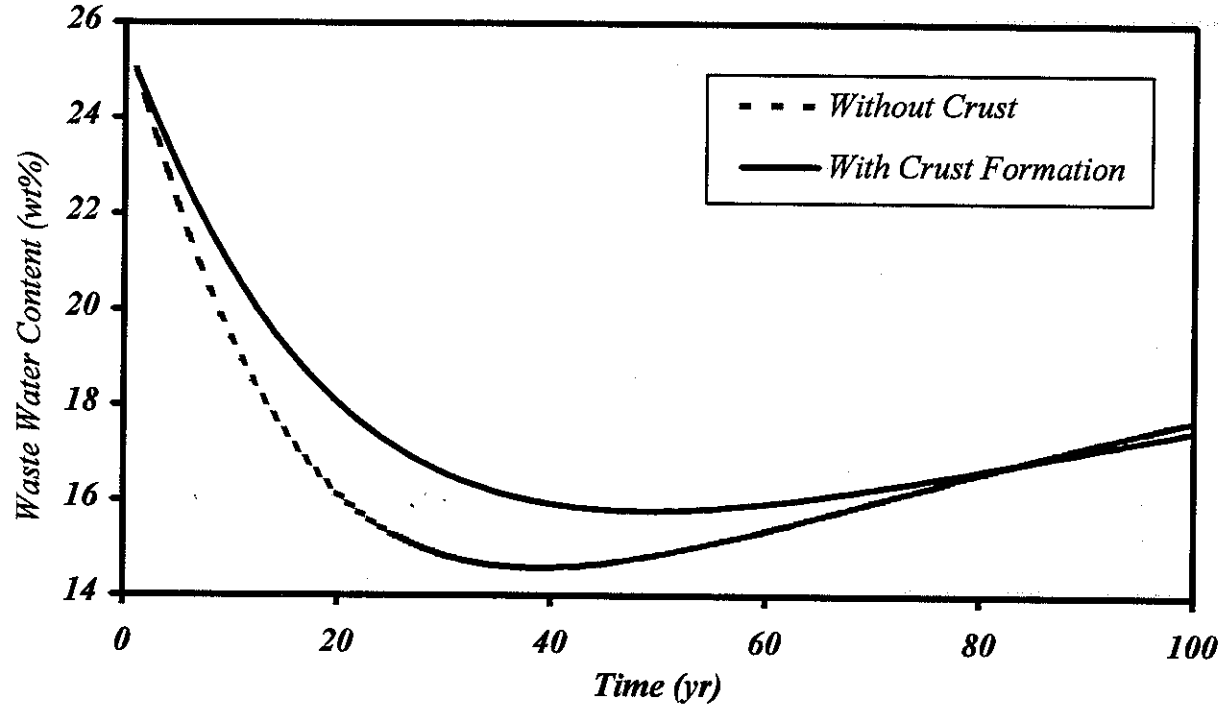
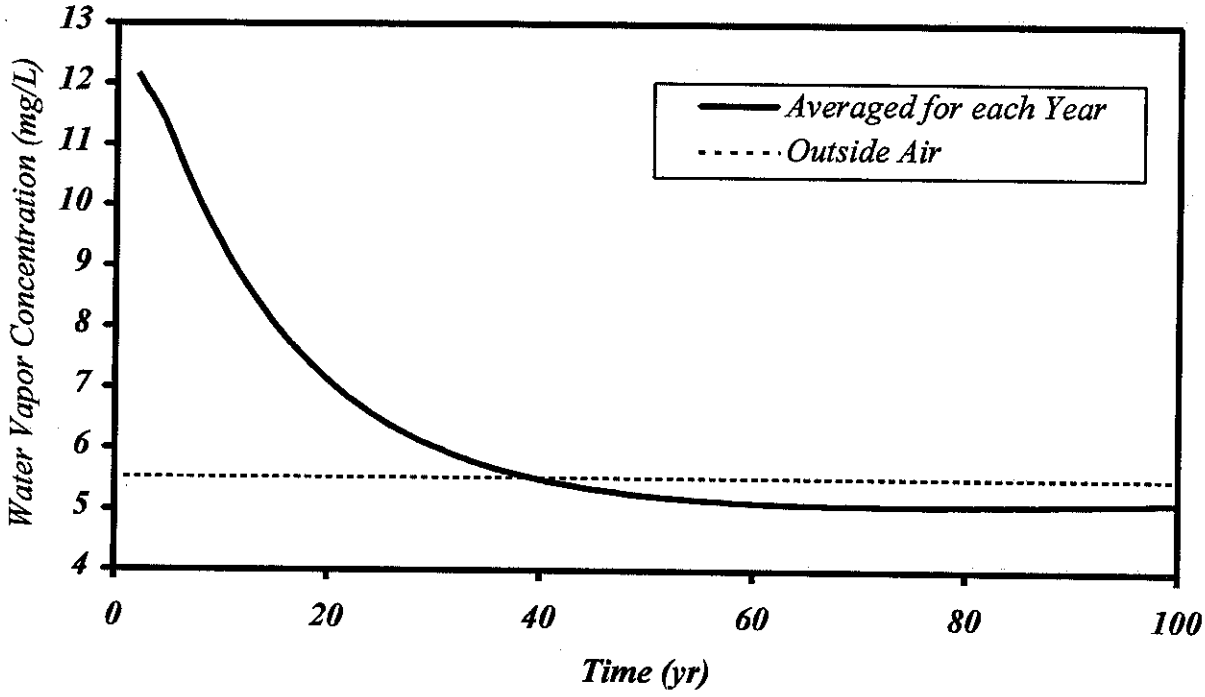


Figure D-13. Predicted Headspace Water Vapor Concentration in Tank AX-102.



5.3 TANK U-105 WATER LOSS

The waste in tank U-105 is relatively deep and wet saltcake. Though records indicate the presence of about 37-kgal of supernatant (equivalent to a 34-cm thick layer across the surface), two of the three core samples from this tank did not contain supernatant. It is assumed here that core 131 segment 2 upper-half (which did not contain supernatant) is representative of the waste near the surface. This core was the most central of the three (Brown 1996). The waste has not been stabilized by pumping, and is likely to undergo consolidation (i.e., shrink like sludge) as water is removed by evaporation (Simmons et al. 1997). Only after being partially drained, and the rigid saltcake matrix has formed, would evaporation be expected to occur via a porous saltcake crust. Thus, the waste was treated as a sludge type at this stage of the drying analysis.

Because the waste profile is about 4-m deep and believed to be saturated with interstitial liquids, applying the water loss calculation to the entire volume of waste would result in a negligible decrease in average water content. It is therefore assumed that drying affects only the upper 48-cm (corresponding to the first 19-in. core segment) layer of waste, without replenishment of water from below. The assumption that drying only affects the upper 48-cm is intended to provide a bounding estimate of the surface moisture loss.

The average water content of the waste near the surface was taken to be 34 wt%. Calculations indicate the water vapor concentration of tank U-105 waste agrees very well with the measured headspace humidity. This indicates that, as in the case of tank AX-102, the rate of water loss is determined by the ventilation rate of the tank and not by the rate water is transported from the waste into the headspace. It was therefore assumed that diffusion resistance associated with the waste and headspace boundary layer was negligible.

The calculated water content of the uppermost 48-cm layer of waste in tank U-105 is plotted in Figure D-14 as a function of time. As indicated in the figure, the water content of this thin layer of waste decreases only to about 29 wt% after 50 years. Figure D-15 shows the predicted yearly average headspace relative humidity in tank U-105. The simulation begins in 1991 and roughly agrees with the single measurement of 64% relative humidity made in early 1995.

Another way of expressing the model results is to consider the depth of waste that dries to a particular wt% water. Assuming no replenishment of water from below and neglecting diffusional resistance associated with the formation of a porous layer, the model predicts that the top 10-cm of waste could be dried to about 10 wt% water. Assuming the average ventilation rate were doubled in the model (i.e., $v = 17$ m^3/h), the model predicts that a 19-cm top layer could be dried to 10 wt% water in 25 years.

Figure D-14. Predicted Water Concentration in 48-cm Surface Waste Layer of Tank U-105.

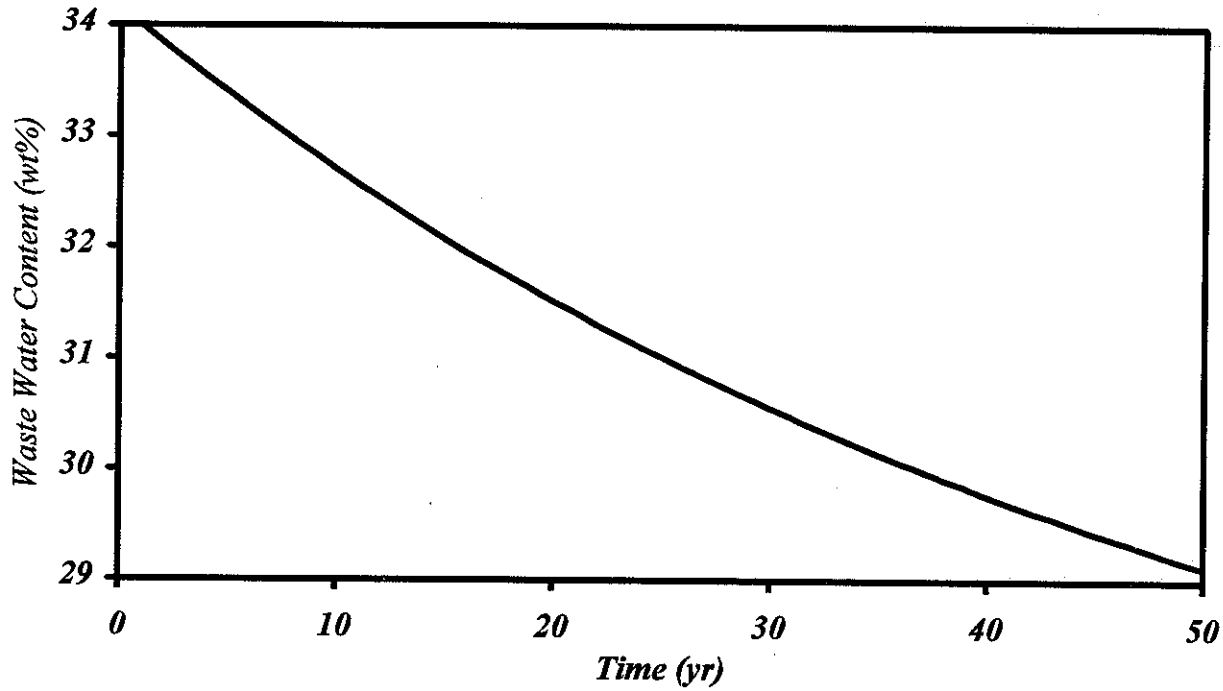
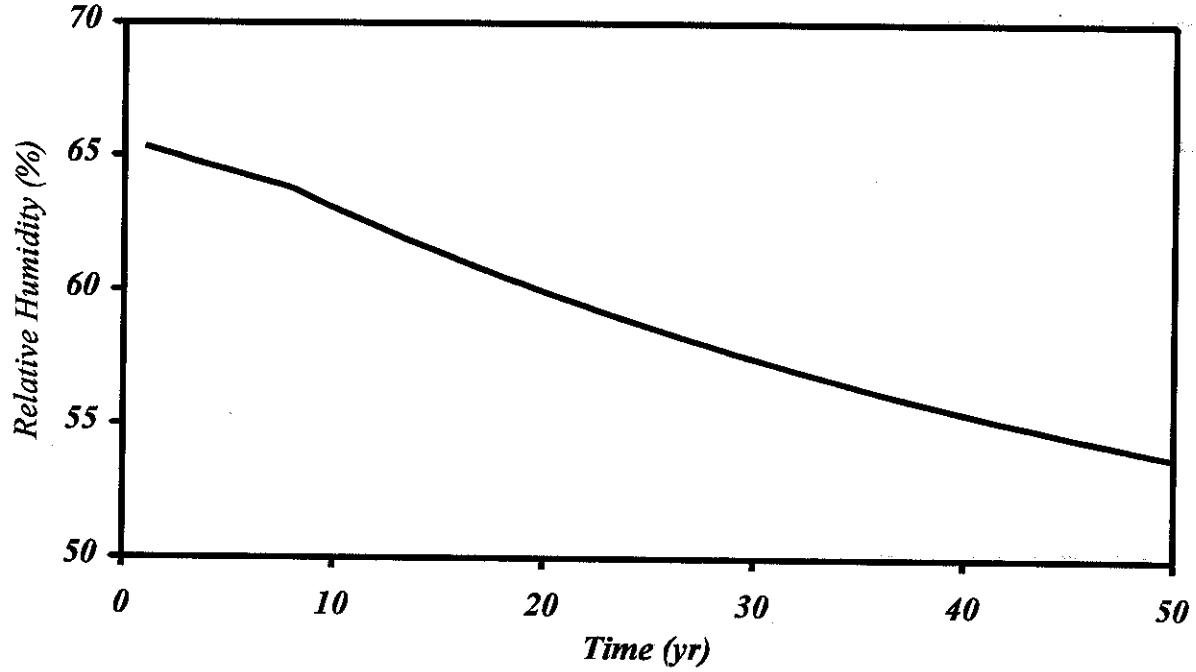


Figure D-15. Predicted Tank U-105 Headspace Relative Humidity.



5.4 TANK A-103 WATER LOSS

Tank A-103 was modeled assuming the water partial pressure versus wt% water curve is similar to that for A-102 waste. It was assumed the waste in this tank was 40 wt% water, and that the breathing rate was 25.5-m^3/h (15-ft^3/min). The model was applied to estimate the drying in a 48-cm (19-in) deep surface layer of waste. For the scenario that the surface dries to 10 wt% water, the drying depth is 15, 28, and 37-cm (6, 11.2, and 14.7-in.) after 10, 25, and 50-yr, respectively.

5.5 TANKS A-102 AND A-106 WATER LOSSES

The wastes stored in tanks A-102 and A-106 are 36 and 76-cm (14 and 30-in.) deep, respectively. Modeling of these tanks included the formation of a crust at the waste surface, the depth of which is assumed to increase as water is lost from the waste. Because the crust presents a resistance to water transport, the water vapor concentration in the headspace decreases as the crust thickness increases. In the absence of a measured ventilation rate, it was assumed that the ventilation rate of both tanks was that calculated for tank A-101, 17 m^3/h (10 ft^3/min); the waste and headspace remain at a constant temperature during the period modeled; and the concentration of water in the waste below the crust remains at its initial concentration.

The constant temperature assumption tends to cause an over-estimation of the water loss rate, because if waste cooling were included in the model the water partial pressure below the crust and in the headspace would be lowered. The constant temperature assumption was adopted because neither tank has exhibited a significant decline in temperature in recent years.

Although the drying of a shallow waste is exaggerated by imposing constant temperatures, the formation of a crust tends to counter the moisture loss. The formation of a crust causes the relative humidity in the headspace to decline substantially with time. Table D-5 lists the average waste water concentration predicted by the modeling of these two tanks. The lower initial waste water concentration and total waste volume of tank A-102 result in the waste in this tank drying faster than in tank A-106, despite the fact that tank A-106 is about 5°C warmer.

5.6 TANKS U-102 AND U-111 WATER LOSSES

The waste water partial pressure isotherms (water partial pressure versus wt% water curves) were not available for tanks U-102 or U-111. Available waste characterization suggests that these waste tanks would behave similar to U-105 and would not dryout any more than this tank over 50 years. Comparison of these tanks to tank U-105, which has a higher average ventilation rate and lower initial waste wt% water than either tank U-102 or U-111, suggests these tanks would require more time to reach 20 wt% water in their wastes.

5.7 TANK C-104 WATER LOSS

The sludge type waste in tank C-104 is about 2.9-m deep (Baldwin 1997). An extensively cracked crust covering the surface is seen in photos. The liquid level decline over an 8-yr period in the past was used to calculate that this tank had a breathing rate of about 102-m^3/h (60-ft^3/min), if the possibility of liquid leaking is discounted. This breathing estimate is obtained by calculating the water loss due to ventilation using the current water vapor concentration measured in the headspace.

The water vapor partial pressure measured in the headspace indicates that a crust is limiting the evaporation and is not in equilibrium with the surface waste. To obtain the measured 45% relative humidity of the headspace at 27.3 °C, while the waste is 33.7 °C, a crust of about 10-cm (4-in.) thickness with 15% empty porosity was imposed. This yielded a transfer coefficient of about 57-m^3/h for the diffusion limited evaporation.

The results of the drying are given in Table D-4. In 50 years, the bulk waste below the crust would dry to 42 wt% water, with a starting concentration of 50 wt% water. In the crust, which remains equilibrated with the headspace water vapor concentration, there would be about 10 wt% water.

5.8 TANK T-111 WATER LOSS

Waste in tank T-111 is deep (4.3-m) and extremely wet (80 wt% water) sludge (Field 1997). The surface appeared as dried mud in a 1994 photo. The moisture distribution is nearly uniform with depth in the waste; however, it does decrease to around 75 wt% by the ninth segment of the two core samples.

The breathing rate of tank T-111 has not been measured, but was assumed to be similar to other passively ventilated tanks and taken to be 5.1-m^3/h (3-ft^3/min). According to the water vapor isotherm, the relative humidity in the headspace in equilibrium with the waste moisture should be about 94% given a headspace temperature of 14.6 °C, which was measured by thermocouple in the headspace (near the top) on January 20, 1995. Given a surface temperature of 17.6 °C and a measured water partial pressure of 11.7 torr (PNNL 1997), the isotherm indicates that the surface waste moisture is between 39 and 46 wt% water. This dried crust, however, does not make up a substantial portion of the first core segment, which is about 80 wt% water.

Under present conditions, a 5-cm (2-in.) deep crust starting with 80 wt% water could not dry down to less that 65 wt% water in less than 50 years. Water loss from the depth of a homogenized, standard core segment leaves 79 wt% water over 50 years, and 78 wt% by doubling the ventilation rate (Table D-4).

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APPENDIX E

DOUBLE-SHELL TANK WASTE COMPOSITIONS

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APPENDIX E

DOUBLE-SHELL TANK WASTE COMPOSITIONS

A database was created to track chemical constituents found in the Operating Specification Documents (OSD) for double-shell tanks. The OSDs in which these limits are located are OSD-T-151-00007, *Operating Specifications for the 241-AN, AP, AW, AY, AZ and SY Tank Farms*; OSD-T-151-00017, *Operating Specifications for Aging-Waste Operations in 241-AY and 241-AZ*; and OSD-T-151-00030, *Operating Specifications for Watch List Tanks*. The tank compositions in the tables were baselined according to the most recent sampling information available. The composition was determined by incorporating the volume and composition of waste that was added to or transferred out of each tank. This composition is based on characterization information and transfer data sheets obtained from the Technical Data Service Centers in single-shell tanks and double-shell tanks.

Table E-1 shows the composition and volume of waste in each DST. The total volumes presented for the sludge and supernatant are slightly different than volumes reported in the Monthly Waste Tank Summary Reports (Hanlon 1997). The summary report uses rounded off surface level values which are used to calculate the volumes.

The compositions in columns two through ten of Table E-1 are as of August 15, 1997. The ^{137}Cs and ^{90}Sr inventories are from the best basis inventories (Kupfer and Leclair 1997) which are derived from the available sampled data. The heatloads are calculated from the ^{137}Cs and ^{90}Sr inventories.

Table E-1. Double-Shell Tank Characterization Data.

Tank	Volume (kgal)	Water (wt%)	pH	SpG	TOC ($gC\ L^{-1}$)	OH (M)	NO_2 (M)	NO_3 (M)	Na (M)	Sr^{90} (Ci)	Cs^{137} (Ci)	Heat Load (W)
AN-101	85 (L)	67.2	13.58	1.23	2.53	1.76	1.01	1.56	-	174	56,800	269
	33 (S)	No sludge characterization information available.										
AN-102	985 (L)	48.7	13.32	1.39	26.0	0.19	1.79	3.60	10.51	368,000	1,490,000	9,495
	89 (S)	42.6	-	1.58	37.6	0.13	1.89	3.50	10.70			
AN-103	548 (L)	51.1	-	1.46	3.06	5.80	3.51	2.58	12.62	8,030	2,310,000	10,957
	410(S)	31.8	-	1.62	4.01	3.18	2.42	4.53	18.43			
AN-104	606(SL)	51.1	-	1.40	3.11	4.17	2.72	2.74	11.13	93,800	2,320,000	11,578
	449(S)	45.6	-	1.60	7.41	2.29	2.18	2.89	16.42			
AN-105	639 (L)	50.2	13.50	1.43	6.1	3.45	2.72	2.56	10.00	33,600	2,060,000	9,948
	489 (S)	45.7	-	1.56	8.46	2.20	2.34	2.94	12.77			
AN-106	23 (L)	76.7	-	1.18	4.38	0.78	0.49	1.34	3.84	137	20,500	98
	17 (S)	No sludge characterization information available.										
AN-107	807 (L)	50.0	11.29	1.37	40.6	0.00	1.33	3.71	8.50	554,000	1,290,000	9,795
	247 (S)	40.3	-	1.48	42.9	-	1.35	3.49	8.97	706	749,000	
AP-101	1114 (L)	61.1	13.97	1.28	3.40	2.48	0.88	2.03	5.99	5,880	931,000	3,540
AP-102	1095 (L)	74.7	13.71	1.20	3.32	0.55	0.84	1.28	4.49			4,434
AP-103	27 (L)	97.7	9.82	1.00	0.20	0.12	0.02	0.04	0.26	<1	577	3
	1 (S)	No sludge characterization information available.										
AP-104	24 (L)	96.0	12.69	1.02	0.17	0.13	0.04	0.21	0.43	8	372	2
AP-105	450 (L)	59.4	13.18	1.34	1.99	2.44	2.88	4.65	7.91	13,600	621,000	3,022
	154 (S)	No sludge characterization information available.										
AP-106	337 (L)	86.0	13.41	1.06	1.42	0.63	0.29	0.73	-	33	43,500	206
AP-107	31 (L)	84.6	13.41	1.01	0.29	0.32	0.04	0.10	0.49	16	16	<1
AP-108	257 (L)	80.6	12.65	1.15	3.76	0.66	0.40	1.08	3.08	32	61,100	289
AW-101	819 (L)	47.1	-	1.45	2.40	4.93	3.13	3.75	-	31,300	1,830,000	8,847
	306 (S)	45.3	-	1.60	-	-	2.33	3.10	-			
AW-102	308 (L)	75.9	12.66	1.19	3.05	1.10	1.00	1.92	4.27	119,000	15,500	869
	33 (S)	-	-	1.42	-	-	-	-	-			
AW-103	151 (L)	94.2	12.93	1.01	0.94	0.15	0.02	0.06	0.87	19,600	132,000	754
	363 (S)	39.2	-	1.43	-	0.90	-	2.33	8.58			
AW-104	829 (L)	97.8	12.40	0.99	0.46	0.10	0.05	0.18	0.44	1,170	272,000	1,292
	290 (S)	-	13.00	-	-	0.52	0.26	0.39	-			
AW-105	152 (L)	94.8	13.47	1.02	2.40	0.22	0.03	0.41	0.61	263,000	53,700	2,013
	286 (S)	75.5	12.92	1.19	2.10	0.09	0.06	0.46	3.56			
AW-106	184 (L)	58.7	13.17	1.34	2.02	2.47	2.97	4.80	8.08	89,400	52,400	845
	224 (S)	-	-	1.95	-	-	-	-	-			

Table E-1. Double-Shell Tank Characterization Data.

Tank	Volume (kgal)	Water (wt%)	pH	SpG	TOC ($gC\ L^{-1}$)	OH (M)	NO_2 (M)	NO_3 (M)	Na (M)	Sr^{90} (Ci)	Cs^{137} (Ci)	Heat Load (W)
AY-101	808 (L)	83.5	9.79	1.08	7.11	0.00	0.80	0.43	2.34	3,750,000	442,000	15,500
	94 (S)	55.8	9.44	1.30	3.73	0.00	0.71	0.21	4.99			
AY-102	806 (L)	97.8	13.30	0.99	0.21	0.15	0.02	0.01	0.29	4,090,000	43,800	13,500
	30 (S)	72.5	10.40	1.12	0.35	0.15	0.02	0.01	0.66			
AZ-101	860 (L)	70.7	13.60	1.21	1.13	0.75	1.35	1.16	4.52	6,360,000	7,430,000	77,618
	35 (S)	43.1	13.60	1.48	13.50	-	1.39	1.09	5.07			
AZ-102	799 (L)	82.9	12.96	1.11	1.62	0.12	0.65	0.41	0.25	3,700,000	4,320,000	45,143
	95 (S)	53.8	-	1.41	6.35	0.13	0.59	0.32	2.34			
SY-101	1117(BK)	37.5	-	1.62	1.99	2.31	3.63	3.00	14.43	125,000	2,210,000	11,267
SY-102	566 (L)	87.8	11.95	1.07	0.62	0.25	0.20	0.68	1.62	38,900	51,000	501
	123 (S)	39.5	-	1.56	6.69	-	0.72	1.92	8.07			
SY-103	384 (L)	48.2	-	1.47	9.69	1.69	3.13	2.90	9.22	79,000	1,130,000	5,862
	362 (S)	33.0	-	1.57	16.6	1.70	2.80	2.48	12.77			

Note: BK = Bulk
DSS = Double Shell Slurry
L = Liquid
S = Solids
SL = Slurry

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APPENDIX F

WASTE TRANSFER HISTORIES AND SINGLE-SHELL TANK GROUPINGS

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APPENDIX F

WASTE TRANSFER HISTORIES AND SST TANK GROUPINGS

1.0 INTRODUCTION

All of the single-shell tanks (SSTs), 100- and 200- series, were evaluated for the organic complexant hazard. The double-shell tanks (DSTs) have been evaluated qualitatively and it has been concluded that as long as moisture is maintained high in the DSTs that there is no hazard of an organic complexant combustion event.

Single-shell tanks have been arranged into groups for screening based on common waste types and waste transfer histories. Grouping helps to support general safety evaluations and the analysis discussed in Appendix I by using information on similar waste conditions within a tank grouping to augment data areas on some tanks having little or no information. For example, these tank groups permit total organic carbon (TOC) and moisture predictions for unmeasured tanks. Some of the SSTs have not been sufficiently characterized at this time to determine total organic carbon concentrations. The hazard, if it exists in a particular tank, will only occur if the waste is dryer than the 20 weight percent moisture criterion. Therefore, the grouping focuses on selecting waste types, processing, and history which could leave a solid residue of dry reactive waste. A glossary of terms used in both tables and text is provided as Section 11 of this appendix.

Five SST groups have been developed to address the potential fuel concentration in the tanks: (1) high complexant, (2) medium complexant, (3) low complexant (precipitation wastes), (4) no complexant (tanks that did not receive incoming waste transfers after 1968), and (5) special case tanks (tanks that need to be treated individually because they do not fit the above groups). These groups are intended to be mutually exclusive groups and are discussed in turn in the following sections. These groups are based on historical process records as evaluated by Agnew et al. (1997), Anderson (1990), and Brevick et al. (1996, 1997a, 1997b). Appendix I of this report provides an evaluation of these SST tank groups based on data from actual characterization of the tank wastes. The Appendix I evaluation confirms that trends in actual TOC concentrations follow the groupings above, with TOC mean values generally declining with declining complexant concentrations. However, because some TOC contributors can be non-complexants (as, for example, solvent wastes), there are individual tanks where TOC is not proportional to the complexant concentration.

Waste moisture is also key to whether tanks might be hazardous. As a secondary parameter, following fuel concentrations in the waste, the current moisture content and expected drainability of the waste were evaluated and these results provide key inputs to the analysis of variance (ANOVA) modeling, as described in Appendix I.

2.0 SINGLE-SHELL TANKS WITH HIGH ORGANIC COMPLEXANT WASTE

The first group of tanks (consisting of 21 tanks) is suspected of containing the highest concentrations of organic complexant waste and are listed in Table F-1. These tanks were identified from historical records (Anderson 1990, Agnew et al. 1997) and were defined as any tanks which received direct transfers of organic complexants waste from B Plant. These tanks are identified in Anderson (1990) by the following waste types: CC, CPLX, CCPLX, HS, and SRR (see glossary for a definition of each of these waste types). In some cases the actual waste type did not change but the terminology for it changed in the quarterly reports over the years.

Table F-1. Single-Shell Tanks With High Complexant Waste (21 Tanks)

Tank	Principal Waste Type	Notes
A-101	P,OWW1,P1,OWW2,P2,OWW3,P2, B,PL1,SRR, EVAP, DSSF, HDRL, RESID, CPLX, NCLPX	Last incoming waste transfer in 1982.
A-102	P,OWW1,P1,OWW2,PSS,B,EVAP, AR, SRR, NCPLX, DSSF, CPLX	Last incoming waste transfer in 1980
A-103	P,OWW1,P1,DW,OWW2,IX,AR,B, CSR, SRR, EVAP, PSS, CPLX, DSSF, HDRL, NCPLX, RESID	Last incoming waste transfer in 1980
A-106	P,OWW1,P1,P2,OWW2,AR,OWW3, SRR, B, EVAP, CCPLX, NCPLX, CCW	Last incoming waste transfer in 1980
AX-101	P,OWW,FP,OWW2,B,P2,PL1,PSS, SRR, EVAP, RESID, DSSF, NCPLX, CPLX	Last incoming waste transfer in 1980
AX-102	P,OWW,OWW2,B,PL1,AR,EVAP, RESID, HDRL, CCPLX, CPLX	Last incoming waste transfer in 1980
AX-103	P,P2,OWW2,OWW3,BL,PL1,B,PSS,AR,EVAP,CC,NCPLX, CPLX,DSSF	Last incoming waste transfer in 1980
BX-104	MW,MW1,TBP,CW,CWP2,CW,IX, EB, CSR, R, BL, EVAP, BYSLTCK, NCPLX, DSSF, CPLX	Last incoming waste transfer in 1980
BX-105	MW, TBP, CW, I X, EB, EVAP, BYSLTCK, NCPLX, DSSF, CPLX	Last incoming waste transfer in 1980
C-104	MW,MW1,TBP,CW,CWP1,DW, OWW,IWW,P,CWP2, OWW3, DW, PL1,TH2,N,BNW,EB,R,IX,LW,LW, PL, B, PSS, NCPLX, BL, FD, CPLX	Last incoming waste transfer in 1980
C-105	MW,TBP,CW,UR,CWP1,P,BL,R, RSN, UNK, PSS, AR, NCPLX, CPLX, CF	Last incoming waste transfer in 1979
C-106	MW,TBP,P,UR,CW,CWP1,DW,PSS,BL,SRS,CPLX, NCPLX	Last incoming waste transfer in 1978
C-107	1C, 1C1, TBP, UR, CW, CWP2, HS, DW, HLO, HS, SSW, BNW, IX, EB, LW, N, SRS, NCPLX	Last incoming waste transfer in 1978
S-107	R,CWR1,R1,CW,CWR2,RSLTCK, EB, B, BL, BNW, DW, IX, LW, N, PL, EVAP, RESID, TL, CC, DSSF, NDRL, PNF	Last incoming waste transfer in 1980
SX-101	R,R1,RSLTCK,EB,RIX,PNF,RESID,TL,CPLX,NCPLX	Last incoming waste transfer in 1980

Table F-1. Single-Shell Tanks With High Complexant Waste (21 Tanks)

Tank	Principal Waste Type	Notes
SX-106	R, HLO, RSLTCK, EB, RIX, B, BL, BNW, CW, DIL, EVAP, IX, LW, N, OWW, PL, PSS, RESID, TBP, CCPLX, CPLX, DSSF, NCPLX, PNF, NIT	Last incoming waste transfer in 1980
TX-104	MW, R, BL, OWW, R, RIX, TBP, CPLX, EB, EVAP	Last incoming waste transfer in 1976
U-105	MW, R, CW, R, CW, EB, EVAP, R, RESID, CCPLX, HDRL	Last incoming waste transfer in 1978
U-106	MW, R, BL, EB, EVAP, PL, RESID, CCPLX, HDRL	Last incoming waste transfer in 1976
U-107	MW,MW1,MW2,CW,EB,BL,BNW, CW, DW, N, IX, LW, R, EVAP, NCPLX, CPLX, DSSF, NIT	Last incoming waste transfer in 1980
U-111	1C,R,BNW,DW,EB,EVAP,RESID, HDRL, LW, N, PNF, CPLX, DSSF, PNF	Last incoming waste transfer in 1980

3.0 SINGLE-SHELL TANKS WITH MEDIUM COMPLEXANT WASTE

This second group of tanks, medium complexant tanks (consisting of 17 tanks), did not receive direct transfers of complexant waste (Table F-2). However, the tanks might have received secondary transfers of waste that contained organic complexants. This tank group contains those tanks identified in Agnew et al. (1996) as containing an average TOC greater than or equal to 0.64 wt%, but were not identified by Anderson (1990) as receiving direct transfers of complexant waste.

Table F-2. Single-Shell Tanks With Medium Complexant Waste (17 Tanks).

Tank	Primary Waste Types	Notes
B-109	1C,EB,BSLTCK,CW,CWP2,IX, 224,NCPLX,BYSLTCK	Last incoming waste transfer in 1976
B-111	2C, 1C, 5-6, EB, DW, FP, P, IX, CSR	Last incoming waste transfer in 1970
BX-112	1C,EB,BSLTCK,CW,,IX,224, BYSLTCK, EVAP, CSR	Last incoming waste transfer in 1974
BY-102	MW, TBP, CW, TBP, EB, EVAP, BYSLTCK	Last incoming waste transfer in 1977
S-101	R,CWR1,R1,RSLTCK,B,BNW, CW, DW, EB, IX, LW, N, PL, TL, EVAP, HDRL, PNF, RESID, DSSF, PNF, (CCPLX in transit)	Last incoming waste transfer in 1979. S-evaporator slurry receiver tank. Received concentrated product but passed to other tanks.
S-102	R,R1,EB,EVAP,DSSF,NCPLX, PNF, NIT (CCPLX in transit)	Last incoming waste transfer in 1980. Feed tank to S evaporator, but was flushed out by other wastes.

Table F-2. Single-Shell Tanks With Medium Complexant Waste (17 Tanks).

Tank	Primary Waste Types	Notes
S-103	R, EB, EVAP, PNF, DSSF, NCPLX, NIT.	Last incoming waste transfer in 1980
SX-102	R, EB, EVAP, PNF, DSSF, RESID	Last incoming waste transfer in 1980
SX-103	R,R1,CW,OWW,EB,EVAP,PNF, RESID ,RSLTCK, DSSF	Last incoming waste transfer in 1978
SX-104	R,R1,RIX,EB,EVAP,PNF, RESID.,RSLTCK, DSSF	Last incoming waste transfer in 1980
SX-105	R,R1,R2,RSLTCK,EB,HLO,RIX, EVAP, PNF, REDID, DSSF	Last incoming waste transfer in 1980
TX-102	MW,MW2,R,CW,EB,OWW,RIX,	Last incoming waste transfer in 1976
TX-111	1C,TBP,EB,EVAP,NCPLX	Last incoming waste transfer in 1977
U-102	MW,MW2,R,EB,EVAP,R,RESID,NIT,HDRL,NCPLX	Last incoming waste transfer in 1977
U-103	MW,R,224,BL,BNW,CW,DW,EB, IX, RIX, NIT, DSSF, HDRL, PNF	Last incoming waste transfer in 1977
U-108	MW,CW,CWR2,EB,BNW,DW,N, EVAP, HDRL, LW, N, RESID, NCPLX, PNF	Last incoming waste transfer in 1976
U-109	MW, CW, R, EB, EVAP, RESID, HDRL, NCPLX, PNF	Last incoming waste transfer in 1977

4.0 SINGLE-SHELL TANKS WITH LOW COMPLEXANT CONCENTRATIONS

This third group of tanks, low complexant tanks (consisting of 89 tanks), did not receive direct transfers of complexant waste (Table F-3). This tank group contains those tanks identified in Agnew et al. (1996) as containing an average TOC less than 0.64 wt%.

Table F-3. Single-Shell Tanks With Low Complexant Waste (89 Tanks)

Tank	Principal Waste Types	Notes
A-104	P, P1, OWW1, OWW2,OWW3, B, PSS, AR, CSR	Last incoming waste transfer in 1974, lot of waste sluiced out in 1975.
AX-104	P, 1WW, OWW, PSS, EF, B, AR	Last incoming waste transfer in 1978
B-101	MW,MW1,EB,BSLTCK,CW,BL,EB	Last incoming waste transfer in 1973
B-102	MW,EB,BSLTCK,CW,CWP2,BL,IX,EF, NCPLX	Last incoming waste transfer in 1978
B-103	MWBSLTCK,EB,CW,CWP2,OWW,IX,BL, IX,BNW,N,LW,R,DW,TBP,224,NCPLX	Last incoming waste transfer in 1975
B-105	2C,1C,BSLTCK,	Last incoming waste transfer in 1955
B-106	2C,1C,EB,TBP,BSLTCK,HLO,BNW,224, EB, IX, NCPLX	Last incoming waste transfer in 1975
B-108	1C,1C1,EB,BSLTCK,CW,CWP2	Last incoming waste transfer in 1967
B-110	2C, 1C, EB, FP, DW, P, BL, IX, BYSltCk, B, CSR	Last incoming waste transfer in 1968. Agnew et al. (1997) indicates CSR in 69
B-112	2C,5-6, 1C,DW,FP,EB,BL,IX,P2, BYSLTCK, NCPLX	Last incoming waste transfer in 1977
BX-101	MW,MW1,TBP,CW,BL,OWW,IWW,RIX, CSR, SIX, IX,,BYSLTCK	Last incoming waste transfer in 1974
BX-102	MW, TBP, CW, EB, BL, OWW, DE	Last incoming waste transfer in 1970
BX-103	MW, TBP, CW, OWW, BL, IWW, RIX, EB, SIX, P, DW, IC, BWW, LW, PL, N, EVA	Last incoming waste transfer in 1977
BX-106	MW, TBP, CW, EB, IX, SIX, BL, OWW, RIX, IX, EVAP, BYSLTCK, NCPLX	Last incoming waste transfer in 1977
BX-107	1C, TBP, IX, EF, NCPLX	Last incoming waste transfer in 1970
BX-108	1C, TBP, CW, IX, NCPLX	Last incoming waste transfer in 1970
BX-109	1C,TBP,UR,CW,CSR,IX	Last incoming waste transfer in 1970
BX-110	1C,1C1,EB,CW,CSR,EB,IX,EVAP, BYSLTCK	Last incoming waste transfer in 1977
BX-111	1C,EB,CW,IX,EVAP,NCPLX,BYSLTCK	Last incoming waste transfer in 1975
BY-101	MW,TBP,CW,1C,EB,EVAP,NCPLX, BYSLTCK	Last incoming waste transfer in 1977
BY-103	MW,TBP,P,CW,CWP2,OWW,EB, BYSLTCK	Last incoming waste transfer in 1973
BY-104	MW, TBP, CW, IX, EB, EVAP, NCPLX	Last incoming waste transfer in 1975
BY-105	MW, TBP, CW, EB, BYSLTCK, CEM, EVAP	Last incoming waste transfer in 1974
BY-106	MW,1C,TBP,PFeCN1,PFeCN2,CW,EB, EVAP, BYSLTCK	Last incoming waste transfer in 1977

Table F-3. Single-Shell Tanks With Low Complexant Waste (89 Tanks)

Tank	Principal Waste Types	Notes
BY-107	1C,TBP,1C1,UR,PFeCN1,PFeCN2,CW, TBP, EB, BYSLTCK, EVAP	Last incoming waste transfer in 1977
BY-108	1C,TBP,PFeCN1,PFeCN2,CW,EB, BYSLTCK, EVAP	Last incoming waste transfer in 1977
BY-109	TBP, MW, CW, OWW, EB, BYSLTCK, EVAP, NCPLX	Last incoming waste transfer in 1977
BY-110	1C,TBP,1C1,1C2,DW,CW,EB,BYSLTCK, EVAP	Last incoming waste transfer in 1979
BY-111	MW1,MW2,MW,TBP,OWW,CW,EB, CWP2,EVAP,BYSLTCK	Last incoming waste transfer in 1978
BY-112	MW1,MW2,MW,TBP,OWW,CW,EB, CWP2,EVAP,BYSLTCK	Last incoming waste transfer in 1975
C-108	1C,TBP,UR,EB,TFeCN,CWP2,HS,SSW, OWW, IX, BNW, N, LW, DW, R	Last incoming waste transfer in 1974
C-109	1C,TBP,1C,TBP,EB,CW,FP,HS, SSW, IX, NCPLX	Last incoming waste transfer in 1970
C-110	1C,1C1,TBP,UR,OWW,OWW1,IX,EB,RIX, NCPLX	Last incoming waste transfer in 1972
C-111	1C, UR, TBP, FeCN, OWW, CWP, CW, EB, FP, HS, SSW, NCPLX	Last incoming waste transfer in 1972
C-112	1C,TBP,UR,TFeCN,EB,CWP1, CW,P2,HS,CW,HS,FP,IX,SWW, OWW, RIX	Last incoming waste transfer in 1975
S-104	R,CWR1,R1,RSLTCK,NCPLX,PNF	Last incoming waste transfer in 1968 Agnew et al. indicates unknown gain in 1975
S-105	R, EB, NCPLX, PNF	Last incoming waste transfer in 1978
S-106	R, EB, EVAP, HDRL, PNF, RESID, NCPLX	Last incoming waste transfer in 1977
S-108	R, EB, EVAP, TL, HDRL, PNF, RESID, NCPLX	Last incoming waste transfer in 1979
S-109	R, EB, EVAP, TL, HDRL, PNF, RESID, NCPLX	Last incoming waste transfer in 1977
S-110	R,CWR1,R1,BL,CW,DW,EB,IX,OWW, RIX,224,EVAP,HDRL,PNF,RESID,NCPLX	Last incoming waste transfer in 1976
S-111	R, EB, EVAP, PNF, NCPLX	Last incoming waste transfer in 1976
S-112	R,EB,EVAP,HDRL, PNF, RESID, NCPLX	Last incoming waste transfer in 1976
SX-110	R,R2,RSLTCK,RIX,224,BL,BNW,EB, EVAP, IX	Last incoming waste transfer in 1976
SX-111	R,R1,R2,RSLTCK,EB,RIX	Last incoming waste transfer in 1972
SX-114	R,R1,R2,RSLTCK,EB,RIX,	Last incoming waste transfer in 1972

Table F-3. Single-Shell Tanks With Low Complexant Waste (89 Tanks)

Tank	Principal Waste Types	Notes
SX-115	R,R1,RSLTCK	Last incoming waste transfer in 1964
T-101	MW,MW1,TBP,MW2,PFeCN1,CW,BL, DW,EB,IX,R,RIX,CWR2,BL,BNW,CW, DW,EB,EVAP,IX,224,NCPLX	Last incoming waste transfer in 1978
T-102	MW, CW, BL, CW, EB, IX, R, RIX	Last incoming waste transfer in 1972
T-103	MW, CW, BL, EB, IX, R, RIX	Last incoming waste transfer in 1972
T-105	1C,2C,2C1,CW,CWR1,HLO,DW, BL,IX	Last incoming waste transfer in 1973
T-106	1C,2C,CW,BL,CW,DW,IX	Last incoming waste transfer in 1973
T-107	1C,1C1,TBP,UR,CW,BL,IX,EVAP,NCPLX	Last incoming waste transfer in 1976
T-108	1C,EB,TBP,T1SLTCK,HLO,BNW,BL,IX	Last incoming waste transfer in 1973
T-109	1C,EB,TBP,T1SLTCK,BL,BNW,IX	Last incoming waste transfer in 1973
T-110	2C,2C1,224,2C2	Last incoming waste transfer in 1966
T-111	2C, 224	Last incoming waste transfer in 1967
T-112	2C2, DW, 2C, BNW, 224, DW, CW, BL, IX, EVAP, NCPLX	Last incoming waste transfer in 1975
T-201	224,EVAP	Last incoming waste transfer in 1975
T-202	224	Last incoming waste transfer in 1953
T-203	224,EVAP	Last incoming waste transfer in 1975
T-204	224	Last incoming waste transfer in 1957
TX-101	MW,MW1,MW2,R,1C,BL,CW,EB,IX, OWW,RIX,SIX,TBP,B,BL, BNW,EVAP, LW,N, OWW,PL, NCPLX,PNF	Last incoming waste transfer in 1978
TX-103	MW,TBP,T1SLTCK,EB,EVAP, NCPLX, PNF	Last incoming waste transfer in 1979
TX-105	MW,MW1,MW2,UR,DW,R,CW,EB,OWW,R, RIX,EVAP	Last incoming waste transfer in 1975
TX-106	MW,R,CW,EB,OWW,RIX,EVAP	Last incoming waste transfer in 1976
TX-107	MW1,MW2,MW,R,EB,EVAP	Last incoming waste transfer in 1976
TX-108	MW,R,TBP,DW,EB,EVAP	Last incoming waste transfer in 1975
TX-109	1C,TBP,1C2,EB,EVAP	Last incoming waste transfer in 1974
TX-110	1C,TBP,EB,EVAP	Last incoming waste transfer in 1976
TX-112	1C,EB,T1SLTCK,EVAP,NCPLX	Last incoming waste transfer in 1975
TX-113	1C1,EB,T1SLTCK,1C	Last incoming waste transfer in 1970
TX-114	1C,MW,EB,T1SLTCK	Last incoming waste transfer in 1973
TX-115	TBP,MW,UR,R,DW,CW,EB,EVAP	Last incoming waste transfer in 1975

Table F-3. Single-Shell Tanks With Low Complexant Waste (89 Tanks)

Tank	Principal Waste Types	Notes
TX-116	EB,T1SLTCK,DE	Last incoming waste transfer in 1969. DE is diatomaceous earth added in 1970
TX-117	1C,EB,T1SLTCK,DE	Last incoming waste transfer in 1956. DE is diatomaceous earth added in 1971
TX-118	1C,TBP,1CEB,DW,EB,T2SLTCK,Z,EVAP,NCPLX,PNF	Last incoming waste transfer in 1979
TY-101	1C,EB,1CFeCN,T1SLTCK,TBP,R	Last incoming waste transfer in 1967
TY-102	1C,EB,T1SLTCK,BL,OWW,R,RIX,TBP, EVAP,FD,NCPLX	Last incoming waste transfer in 1975
TY-103	1C,TBP,1CFeCN,UR,DW,BL,CW,OWW,R,RIX & MISCELLANEOUS UNLABELED TRANSFERS FROM BX & T -SEE ER-351	Last incoming waste transfer in 1973
TY-104	1C,TBP,1C,DW,TBP,BL,OWW,R,RIX, EVAP,NCPLX	Last incoming waste transfer in 1970
U-101	MW,MW1,MW2,R,EVAP,NCPLX	Last incoming waste transfer in 1979
U-104	MW,MW1,MW2,R,DE	Last incoming waste transfer in 1957. 60 tons diatomaceous earth added 1972
U-110	1C,MW1,R,CWR1,R1,CW,BNW, LW	Last incoming waste transfer in 1973
U-112	1C, R, EVAP	Last incoming waste transfer in 1976
U-201	CW,R,EVAP,NCPLX	Last incoming waste transfer in 1970
U-202	CW,R,EVAP,NCPLX	Last incoming waste transfer in 1958
U-203	CW,R,EVAP,NCPLX	Last incoming waste transfer in 1970
U-204	2C,R,CW,EVAP,NCPLX	Last incoming waste transfer in 1965

5.0 SINGLE-SHELL TANKS WITH NO COMPLEXANT WASTE

A fourth group of tanks (consisting of 11 tanks) consisted of those tanks which received no incoming waste transfers after 1968 (Table F-4). Organic complexants were not used at the Hanford Site until 1969 and it is extremely unlikely that these tanks received complexant waste.

Table F-4. Single-Shell Tanks With No Complexant Waste. (11 Tanks)

Tank	Principal Waste Types	Notes
A-105	P,P1,P2,CSR,IX,EVAP,NCPLX	Last incoming waste transfer in 1967. Agnew et al. (1997) indicates 1978.
B-104	2C, 1C, EB, B1SltCk	Last incoming waste transfer in 1953. Agnew et al. (1997) indicates 1957
B-107	1C, EB, TBP, CW, NCPLX	Last incoming waste transfer in 1967. Agnew et al. (1997) indicates 1963
SX-107	R,R1,CWR1,R2,RSLTCK	Last incoming waste transfer in 1968. Agnew et al. (1997) indicates 1968
SX-108	R,R1,R2,RSLTCK	Last incoming waste transfer in 1968. Agrew et al. (1997) indicates 1968
SX-109	R,R1,R2,RSLTCK	Last incoming waste transfer in 1967. Agnew et al. (1997) indicates 1967
SX-112	R,R1,R2,RSLTCK	Last incoming waste transfer was from SX-107 (which contained no complexants) in 1969. The last incoming waste transfer other than SX-107 occurred in 1968. Agnew et al. (1997) indicates gain in 74 which may be measurement error
SX-113	R,R1,DE	Last incoming waste transfer in 1967. Agnew et al. (1997) indicates diatomaceous earth added 1972
T-104	1C,1C2	Last incoming waste transfer in 1957. Agnew et al. (1997) indicates 1954
TY-105	TBP, UR, EVAP	Last incoming waste transfer in 1958. Agnew et al. (1997) indicates 1965
TY-106	TBP, DE	Last incoming waste transfer in 1959. Agnew et al. (1997) indicates diatomaceous earth added 1972

6.0 SPECIAL CASE SINGLE-SHELL TANKS

Some tanks have unique or unusual waste transfer histories. These tanks have been grouped together as special case tanks (consisting of 11 tanks). The C-200 and B-200 series tanks received several small waste transfers from the strontium semiworks at B Plant. These wastes were often small pilot plant runs that contained unique waste streams. Therefore, these tanks must be sampled and characterized individually and do not fit into the other four waste groups.

Also included in the unique tank group are those tanks that received predominantly organic solvent waste. Solvent wastes (i.e., normal paraffin hydrocarbons, tributyl phosphate and their

degradation products) deposited in the tank often contribute a large part of the TOC measured in the tank. While these materials are apparently energetic in other circumstances they do not participate in condensed-phase reactions with nitrates/nitrites. Experimentation indicates that these materials either volatilize or decompose below propagation temperatures and neither support nor contribute to condensed phase combustion (Fauske et al. 1996). Additionally, methods of measuring TOC do not account well for the organic carbon within these solvent wastes. Therefore, TOC measurements from this group of tanks are not included in the general ANOVA model. The tanks that are treated individually are summarized in Table F-5.

Table F-5. Special Case Single-Shell Tanks. (11 Tanks)

Tank	Primary Waste Types	Notes
B-201	224, MW, NCPLX	Strontium semiworks waste. Last incoming waste transfer in 1960.
B-202	224, MW, B, NCPLX	Strontium semiworks waste. Last incoming waste transfer in 1963.
B-203	224, MW, NCPLX	Strontium semiworks waste. Last incoming waste transfer in 1965.
B-204	224, MW, NCPLX	Strontium semiworks waste. Last incoming waste transfer in 1965.
C-101	MW,MW1,TBP,UR,EB,CWP1, CWP2,CW,P,CW,P	Predominantly solvent waste tank. Last incoming waste transfer in 1970
C-102	MW, TBP, OWW, UR, CW, TH66	Tank formerly contained organic solvent pool; TOC predominantly solvent waste. Last incoming waste transfer in 1973.
C-103	MW, TBP, P, CW, CWP, BNW, LW, B, DW, IX, EB, R, BL, PL, OWW, N, PSS, RIX, NCPLX	Tank contains organic solvent pool; TOC predominantly solvent waste. Last incoming waste transfer in 1978.
C-201	(MW before 1954), SSW, HS, SSW, NCPLX	Strontium semiworks waste. Last incoming waste transfer in 1980.
C-202	(MW before 1953), SSW, HS, NCPLX	Strontium semiworks waste. Last incoming waste transfer in 1973.
C-203	(MW before 1953), SSW, HS, SSW, NCPLX	Strontium semiworks waste. Last incoming waste transfer in 1980.
C-204	(MW before 1954), SSW, HS, SSW, NCPLX	Strontium semiworks waste. Last incoming waste transfer in 1974.

GENERAL NOTES FOR TABLES F-1 THROUGH F-5:

- Primary Waste Type data in the second columns are taken directly from Hanford Tank Contents Estimates (HTCE) (Brevick, et al. 1996 and 1997) as the Anderson (1990) and Agnew et al. (1996) timelines on the Waste and Level History diagrams for each tank. The waste types from both timelines are repeated here in sequence but without water and without repeating a waste type that had already appeared earlier in the listings. In general, this relates qualitatively that this type of waste was deposited at some time in the tank. No allowance is made for removals, so some waste types may have been effectively removed by pumpout and sluicing. Refer to Agnew et al. (1996) for actual history of waste deposition and removal. In general, the most recent waste types are found later in

the listing. Definitions of the waste types can be found in the HTCE references as detailed on the level diagrams used for the source.

- The date of latest transfer of waste appears in Column 3 of the tables. This date was inferred from upward level inflections on the HTCE level history diagrams discussed above. This is provided as a convenience for the reader but the HTCE and or Anderson (1990) and Agnew et al. (1996, 1997) should be consulted for more precise dating.

- HTCE for the North East Quadrant of 200 East (Brevick et al. 1996a):
  A Tank Farm
  AX
  B
  BX
  BY
  C

- HTCE for the South West Quadrant of 200 West (Brevick et al. 1997b):
  S Tank Farm
  SX
  U

- HTCE for the North West Quadrant of 200 West (Brevick, 1997a):
  T Tank Farm
  TX
  TY

7.0 MOISTURE GROUPING OF THE SINGLE-SHELL TANKS

This section describes how the tank wastes were grouped according to moisture conditions. While fuel grouping of wastes is the primary key to evaluating the hazard potentials of tanks, the amount of moisture that the waste now contains or is expected to retain in the future is also important. As a secondary key to tank safety, the tanks are assigned subgroups within each primary group. These subgroups are based on whether a tank is currently demonstrated to have a wet surface or a dry surface, and whether the waste contains saltcakes or sludges.

If the waste surface contains aqueous liquid (as determined by visual means, samples, and/or liquid level measurements), then the waste cannot support propagation. Therefore, there is a distinction between tanks that have supernatant, and those that do not. Tanks containing liquid at or above the waste surface are termed wet in Table F-6.

Liquid retention properties of wastes are generally related to whether the wastes are saltcakes or sludges. In general, large crystals were formed as precipitates from early passes through the evaporator. These crystals constitute what is termed saltcake. Large crystal wastes allow their

liquids to drain out comparatively rapidly. Thus, these wastes are expected to loose moisture easily if the tank is saltwell pumped or if the tank leaks. As waste became more concentrated during later evaporator runs and contained higher concentrations of sodium nitrate and nitrite, evpaporation led to precipitation of small crystals which drain poorly. These may be termed "non-draining" saltcakes. By contrast with saltcake production, many of the metal wastes formed sludges by settling when they were deposited. These sludges typically have very fine structures or small particles. These sludges do not drain easily and therefore are expected to retain considerable moisture even if pumped or if the tank leaks. The tank groupings are listed in Table F-6. Tanks are classified in the table as saltcake if Agnew et al. (1997) indicates that 30% or more by volume of the waste is saltcake. (In this classification as listed in the table, no attempt was made to determine whether the saltcakes drained well or not.) Tanks having more than 70% sludge are classified as sludge tanks.

Table F-6. Moisture Groups for the Single-Shell Tanks. (149 Tanks)

Moisture Group	Tanks
Dry Surface - Saltcake	A-101, AX-101, AX-102, AX-104, B-105, BX-111, BY-101, BY-102, BY-103, BY-104, BY-105, BY-106, BY-107, BY-109, BY-110, BY-111, BY-112, S-102, S-104, S-105, S-108, S-109, S-110, S-112, SX-103, SX-108, SX-109, SX-110, SX-111, SX-114, T-106, T-108, T-109, TX-102, TX-103, TX-105, TX-106, TX-107, TX-108, TX-109, TX-110, TX-111, TX-112, TX-113, TX-114, TX-115, TX-116, TX-117, TX-118, TY-102, TY-103, and U-111. (52 tanks)
Dry Surface - Sludge	A-104, A-105, A-106, AX-103, B-101, B-103, B-104, B-106, B-107, B-108, B-109, BX-101, BX-102, BX-107, BX-108, BX-109, BX-112, BY-108, C-101, C-102, C-104, C-105, C-107, C-108, C-111, C-112, C-201, C-202, C-203, C-204, SX-107, SX-112, SX-113, SX-115, T-101, T-105, T-201, T-202, T-203, T-204, TX-101, TX-104, TY-101, TY-105, TY-106, U-104, and U-110. (47 tanks)
Wet Surface - Saltcake	A-102, A-103, B-102, S-101, S-103, S-106, S-111, SX-101, SX-102, SX-104, SX-105, SX-106, U-102, U-103, U-105, U-106, U-107, U-108, and U-109. (19 tanks)
Wet Surface - Sludge	B-110, B-111, B-112, B-201, B-202, B-203, B-204, BX-103, BX-104, BX-105, BX-106, BX-110, C-103, C-106, C-109, C-110, S-107, T-102, T-103, T-104, T-107, T-110, T-111, T-112, TY-104, U-101, U-112, U-201, U-202, U-203, and U-204. (31 tanks)

8.0 FUEL AND MOISTURE GROUPINGS FOR SINGLE-SHELL TANKS

This section shows which tank wastes comprise each of the fuel and moisture groups. When combining the fuel and moisture groups together, each SST waste belongs to one of sixteen possible groups (one of the four moisture groups, and one of the four fuel groups; special case tanks are not included). The fuel moisture groups are shown in Table F-7. The analysis of waste sample data as presented in Appendix I generally confirms the fuel groupings as presented in Table F-7.

Table F-7. Assessment of Single-Shell Tank Wastes From Waste Processing Records.[1]

Fuel and Moisture Group	Tanks[2]
High Complexant Waste Dry Surface -Saltcake	***A-101***, ***AX-101***, ***AX-102***, and ***U-111*** (4 of 4 tanks sampled)
High Complexant Waste Dry Surface -Sludge	***A-106***, ***AX-103***, ***C-104***, ***C-105***, ***C-107***, and ***TX-104*** (6 of 6 tanks sampled)
High Complexant Waste Wet Surface - Saltcake	***A-102***, ***A-103***, ***SX-101***, ***SX-106***, ***U-105***, ***U-106***, and ***U-107*** (7 of 7 tanks sampled)
High Complexant Waste Wet Surface - Sludge	***BX-104***, ***BX-105***, ***C-106***, and ***S-107*** (4 of 4 tanks sampled)
Medium Complexant Waste Dry Surface - Saltcake	***BY-102***, ***S-102***, ***SX-103***, ***TX-102***, and TX-111 (4 of 5 tanks sampled)
Medium Complexant Waste Dry Surface - Sludge	***B-109***, ***BX-112*** (2 of 2 tanks sampled)
Medium Complexant Waste Wet Surface - Saltcake	***S-101***, S-103, ***SX-102***, SX-104, SX-105, ***U-102***, ***U-103***, ***U-108***, and ***U-109*** (6 of 9 tanks sampled)
Medium Complexant Waste Wet Surface - Sludge	***B-111*** (1 of 1 tank sampled)
Low Complexant Waste Dry Surface - Saltcake	***AX-104***, B-105, ***BX-111***, ***BY-101***, ***BY-103***, ***BY-104***, ***BY-105***, ***BY-106***, ***BY-107***, ***BY-109***, ***BY-110***, ***BY-111***, ***BY-112***, ***S-104***, S-105, S-108, ***S-109***, ***S-110***, S-112, SX-110, SX-111, SX-114, ***T-106***, ***T-108***, ***T-109***, TX-103, TX-105, TX-106, ***TX-107***, TX-108, TX-109, TX-110, TX-112, TX-113, TX-114, TX-115, TX-116, TX-117, TX-118, ***TY-102***, and ***TY-103*** (21 of 41 tanks sampled)
Low Complexant Waste Dry Surface - Sludge	A-104,***B-101***, ***B-103***, ***B-106***, ***B-108***, ***BX-101***, BX-102, ***BX-107***, ***BX-108***, ***BX-109***, ***BY-108***, ***C-108***, ***C-111***, ***C-112***, SX-115, T-101, ***T-105***, ***T-201***, ***T-202***, ***T-203***, ***T-204***, TX-101, ***TY-101***, U-104, and ***U-110*** (19 of 25 tanks sampled)
Low Complexant Waste Wet Surface - Saltcake	***B-102***, ***S-106***, and ***S-111*** (3 of 3 tanks sampled)
Low Complexant Waste Wet Surface - Sludge	***B-110***, ***B-112***, ***BX-103***, ***BX-106***, ***BX-110***, ***C-109***, ***C-110***, ***T-102***, T-103, ***T-107***, ***T-110***, ***T-111***, ***T-112***, ***TY-104***, U-101, ***U-112***, ***U-201***, ***U-202***, ***U-203***, and ***U-204*** (18 of 20 tanks sampled)
No Complexant Waste Dry Surface - Saltcake	***SX-108*** and SX-109 (1 of 2 tanks sampled)
No Complexant Waste Dry Surface - Sludge	A-105, ***B-104***, ***B-107***, SX-107, SX-112, ***SX-113***, ***TY-105***, and ***TY-106*** (5 of 8 tanks sampled)
No Complexant Waste Wet Surface - Saltcake	(No Tanks in Group)
No Complexant Waste Wet Surface - Sludge	***T-104*** (1 of 1 tank sampled)

Notes: [1] There are eleven special case tanks: ***B-201***, ***B-202***, ***B-203***, ***B-204***, ***C-101***, ***C-102***, ***C-103***, ***C-201***, ***C-202***, ***C-203***, and ***C-204***. (149 tanks total)

[2] Tanks identified in ***italics*** were sampled.

9.0 SINGLE-SHELL TANK GROUPING DATA BY INDIVIDUAL TANKS

Tanks were grouped by the amount of fuel they contain (in terms of TOC or DSC energy), their surface wetness (whether or not there is liquid near the surface), and their waste type (saltcake or sludge). If Agnew et al. (1997) indicates that at least 30% of the waste is saltcake, then the tank is grouped as a "saltcake" tank. Where sludge makes up 70% or more of the waste, the tank is grouped as a "sludge" tank. Table F-8 compiles the information in Tables F-1 through F-7. The SSTs are listed serially in Column 1, the tank grouping is shown in Columns 2 to 4 and the bases for tank grouping are listed in Columns 5 and 6. Detailed notes explaining Columns 5 and 6 entries follow the table. The analysis of variance (ANOVA) results as presented in Appendix I generally confirm the fuel groupings as presented in Table F-8.

Table F-8. Single-Shell Tank Grouping Data by Individual Tanks (149 Tanks).

Tanks 1	Fuel Group 2	Surface 3	Waste Type 4	Fuel Group Basis 5	Waste Type 6
A-101	H	DRY	SALTCAKE	Anderson ,Agnew-3	A1 saltcake
A-102	H	WET	SALTCAKE	Anderson, Agnew-3, Agnew-6, Agnew-7	A1 saltcake
A-103	H	WET	SALTCAKE	Anderson, Agnew-3	A1 saltcake
A-104	L	DRY	SLUDGE	Agnew-5(1962.8)	Sludge
A-105	N	DRY	SLUDGE	Reynolds	Sludge
A-106	H	DRY	SLUDGE	Anderson , Agnew-3, Agnew-6	A1 saltcake
AX-101	H	DRY	SALTCAKE	Anderson ,Agnew-3, Agnew-6	A1 saltcake
AX-102	H	DRY	SALTCAKE	Anderson ,Agnew-3	A1 saltcake
AX-103	H	DRY	SALTCAKE	Anderson ,Agnew-3	A1 saltcake
AX-104	L	DRY	SALTCAKE	Agnew-5(1978.5), Agnew-7	Sludge
B-101	L	DRY	SLUDGE		B saltcake
B-102	L	WET	SLUDGE		B saltcake
B-103	L	DRY	SLUDGE	Agnew-4	B saltcake
B-104	N	DRY	SLUDGE	And53, Agn57	Sludge
B-105	L	DRY	SALTCAKE		B saltcake
B-106	L	DRY	SLUDGE		B saltcake
B-107	N	DRY	SLUDGE	And67, Agn63	Sludge
B-108	L	DRY	SLUDGE		B saltcake
B-109	M	DRY	SLUDGE	Agnew-3	B saltcake
B-110	L	WET	SLUDGE	And68,Agn69(2kgal CSR)	Sludge
B-111	M	WET	SLUDGE	Agnew-3	Sludge
B-112	L	WET	SLUDGE		BY saltcake

Table F-8. Single-Shell Tank Grouping Data by Individual Tanks (149 Tanks).

Tanks 1	Fuel Group 2	Surface 3	Waste Type 4	Fuel Group Basis 5	Waste Type 6
B-201	S	WET	SLUDGE	Agnew-6, Unique: SrSemiWorks	Sludge
B-202	S	WET	SLUDGE	Agnew-6, Unique: SrSemiWorks	Sludge
B-203	S	WET	SLUDGE	Agnew-6, Unique: SrSemiWorks	Sludge
B-204	S	WET	SLUDGE	Agnew-6, Unique: SrSemiWorks	Sludge
BX-101	L	DRY	SLUDGE		Sludge
BX-102	L	DRY	SLUDGE		Sludge
BX-103	L	WET	SLUDGE		Sludge
BX-104	H	WET	SLUDGE	Anderson ,Agnew-3	Sludge
BX-105	H	WET	SLUDGE	Anderson ,Agnew-3	Sludge
BX-106	L	WET	SLUDGE		BY saltcake
BX-107	L	DRY	SLUDGE		Sludge
BX-108	L	DRY	SLUDGE		Sludge
BX-109	L	DRY	SLUDGE		Sludge
BX-110	L	WET	SLUDGE		Sludge
BX-111	L	DRY	SALTCAKE		BY saltcake
BX-112	M	DRY	SLUDGE	Agnew-3, Agnew-7	Sludge
BY-101	L	DRY	SALTCAKE		BY saltcake
BY-102	M	DRY	SALTCAKE	Agnew-3, Agnew-7	BY saltcake
BY-103	L	DRY	SALTCAKE		BY saltcake
BY-104	L	DRY	SALTCAKE		BY saltcake
BY-105	L	DRY	SALTCAKE		BY saltcake
BY-106	L	DRY	SALTCAKE	Agnew-5, Agnew-7	BY saltcake
BY-107	L	DRY	SALTCAKE		BY saltcake
BY-108	L	DRY	SLUDGE		Sludge
BY-109	L	DRY	SALTCAKE		BY saltcake
BY-110	L	DRY	SALTCAKE	Agnew-5(1978.6)	BY saltcake
BY-111	L	DRY	SALTCAKE		BY saltcake
BY-112	L	DRY	SALTCAKE	Agnew-5(1972.4)	BY saltcake
C-101	S	DRY	SLUDGE	Agnew-7, Solvent waste	Sludge
C-102	S	DRY	SLUDGE	Agnew-4, Solvent waste	Sludge

Table F-8. Single-Shell Tank Grouping Data by Individual Tanks (149 Tanks).

Tanks 1	Fuel Group 2	Surface 3	Waste Type 4	Fuel Group Basis 5	Waste Type 6
C-103	S	WET	SLUDGE	Agnew-3, Solvent waste	Sludge
C-104	H	DRY	SLUDGE	Anderson ,Agnew-3, Agnew-6, Agnew-7	Sludge
C-105	H	DRY	SLUDGE	Anderson, Agnew-7	Sludge
C-106	H	WET	SLUDGE	Anderson	Sludge
C-107	H	DRY	SLUDGE	Anderson, Agnew-5 (1984.0), Agnew-6, Agnew-7	Sludge
C-108	L	DRY	SLUDGE		Sludge
C-109	L	WET	SLUDGE	Agnew-6	Sludge
C-110	L	WET	SLUDGE		Sludge
C-111	L	DRY	SLUDGE	Agnew-5(1970.5), Agnew-7	Sludge
C-112	L	DRY	SLUDGE	Agnew-6	Sludge
C-201	S	DRY	SLUDGE	Agnew-5(1966.0), Agnew-6, Agnew-7, Unique: SrSemiWorks	Sludge
C-202	S	DRY	SLUDGE	Agnew-5(1956.5), Agnew-6, Agnew-7, Unique: SrSemiWorks	Sludge
C-203	S	DRY	SLUDGE	Agnew-5(1956.0), Agnew-6, Agnew-7, Unique: SrSemiWorks	Sludge
C-204	S	DRY	SLUDGE	Agnew-5(1956.0), Agnew-6, Agnew-7, Unique: SrSemiWorks	Sludge
S-101	M	WET	SLUDGE	Complexant only in Transit, Anderson Listed, Agnew-3	S1 saltcake
S-102	M	DRY	SALTCAKE	Complexant only in Transit, Anderson Listed, Agnew-3	S2 saltcake
S-103	M	WET	SLUDGE	Agnew-3	S2 saltcake
S-104	L	DRY	SALTCAKE	And68,Agn75(161kg SLTCK)	R saltcake

Table F-8. Single-Shell Tank Grouping Data by Individual Tanks (149 Tanks).

Tanks 1	Fuel Group 2	Surface 3	Waste Type 4	Fuel Group Basis 5	Waste Type 6
S-105	L	DRY	SALTCAKE		S1 saltcake
S-106	L	WET	SALTCAKE		S1 saltcake
S-107	H	WET	SLUDGE	Anderson ,Agnew-3	Sludge
S-108	L	DRY	SALTCAKE		S1 saltcake
S-109	L	DRY	SALTCAKE		S1 saltcake
S-110	L	DRY	SALTCAKE		S1 saltcake
S-111	L	WET	SALTCAKE	Agnew-4	S1 saltcake
S-112	L	DRY	SALTCAKE	Agnew-4	S1 saltcake
SX-101	H	WET	SALTCAKE	Anderson, Agnew-4	S2 saltcake
SX-102	M	WET	SALTCAKE	Agnew-3	S1 saltcake
SX-103	M	DRY	SALTCAKE	Agnew-3	S1 saltcake
SX-104	M	WET	SALTCAKE	Agnew-3	S1 saltcake
SX-105	M	WET	SALTCAKE	Agnew-3	S1 saltcake
SX-106	H	WET	SALTCAKE	Anderson ,Agnew-3	S2 saltcake
SX-107	N	DRY	SLUDGE	And68,Agn68	Sludge
SX-108	N	DRY	SALTCAKE	And68,Agn68	R2 saltcake
SX-109	N	DRY	SALTCAKE	And67, Agn67	R saltcake
SX-110	L	DRY	SALTCAKE		R saltcake
SX-111	L	DRY	SALTCAKE		R saltcake
SX-112	N	DRY	SLUDGE	And68,Agn69(Last Incoming waste from SX-107 not complexant)	R saltcake
SX-113	N	DRY	SLUDGE	And67, Agn72 (diatomaceous earth)	Sludge
SX-114	L	DRY	SALTCAKE		R saltcake
SX-115	L	DRY	SLUDGE		R saltcake
T-101	L	DRY	SLUDGE		Sludge
T-102	L	WET	SLUDGE		Sludge
T-103	L	WET	SLUDGE		Sludge
T-104	N	WET	SLUDGE	And57,Agn54	Sludge
T-105	L	DRY	SLUDGE	Agnew-5(1980.5)	Sludge
T-106	L	DRY	SALTCAKE		Sludge
T-107	L	WET	SLUDGE		Sludge
T-108	L	DRY	SALTCAKE		T1 saltcake

Table F-8. Single-Shell Tank Grouping Data by Individual Tanks (149 Tanks).

Tanks 1	Fuel Group 2	Surface 3	Waste Type 4	Fuel Group Basis 5	Waste Type 6
T-109	L	DRY	SALTCAKE		T1 saltcake
T-110	L	WET	SLUDGE	Agnew-4, Agnew-6	Sludge
T-111	L	WET	SLUDGE	Agnew-4, Agnew-6	Sludge
T-112	L	WET	SLUDGE		Sludge
T-201	L	DRY	SLUDGE	Agnew-6	Sludge
T-202	L	DRY	SLUDGE	Agnew-6	Sludge
T-203	L	DRY	SLUDGE	Agnew-6	Sludge
T-204	L	DRY	SLUDGE	Agnew-6	Sludge
TX-101	L	DRY	SLUDGE	Agnew-5(1975.5)	Sludge
TX-102	M	DRY	SALTCAKE	Agnew-3	T2 saltcake
TX-103	L	DRY	SALTCAKE		T2 saltcake
TX-104	H	DRY	SLUDGE	Anderson ,Agnew-3	T2 saltcake
TX-105	L	DRY	SALTCAKE	Agnew-4	T2 saltcake
TX-106	L	DRY	SALTCAKE		T2 saltcake
TX-107	L	DRY	SALTCAKE		T2 saltcake
TX-108	L	DRY	SALTCAKE		T2 saltcake
TX-109	L	DRY	SALTCAKE	Agnew-5(1977.7), Agnew-7	Sludge
TX-110	L	DRY	SALTCAKE		T2 saltcake
TX-111	M	DRY	SALTCAKE	Agnew-3	T2 saltcake
TX-112	L	DRY	SALTCAKE		T2 saltcake
TX-113	L	DRY	SALTCAKE		T2 saltcake
TX-114	L	DRY	SALTCAKE		T2 saltcake
TX-115	L	DRY	SALTCAKE		T2 saltcake
TX-116	L	DRY	SALTCAKE		T2 saltcake
TX-117	L	DRY	SALTCAKE		T2 saltcake
TX-118	L	DRY	SALTCAKE	Agnew-4	T2 saltcake
TY-101	L	DRY	SLUDGE		Sludge
TY-102	L	DRY	SALTCAKE		T2 saltcake
TY-103	L	DRY	SALTCAKE		T2 saltcake
TY-104	L	WET	SLUDGE	Agnew-4	Sludge
TY-105	N	DRY	SLUDGE	And58,Agn65	Sludge
TY-106	N	DRY	SLUDGE	And59,Agn72 (20 kgal DE)	Sludge
U-101	L	WET	SLUDGE		Sludge

Table F-8. Single-Shell Tank Grouping Data by Individual Tanks (149 Tanks).

Tanks 1	Fuel Group 2	Surface 3	Waste Type 4	Fuel Group Basis 5	Waste Type 6
U-102	M	WET	SALTCAKE	Agnew-3	T2 saltcake
U-103	M	WET	SALTCAKE	Agnew-3	S1 saltcake
U-104	L	DRY	SLUDGE		Sludge
U-105	H	WET	SALTCAKE	Anderson ,Agnew-3	S2 saltcake
U-106	H	WET	SALTCAKE	Anderson ,Agnew-3	S1 saltcake
U-107	H	WET	SALTCAKE	Anderson ,Agnew-3	S2 saltcake
U-108	M	WET	SALTCAKE	Agnew-3	S1 saltcake
U-109	M	WET	SALTCAKE	Agnew-3	S1 saltcake
U-110	L	DRY	SLUDGE		Sludge
U-111	H	DRY	SALTCAKE	Anderson ,Agnew-3	S2 saltcake
U-112	L	WET	SLUDGE		Sludge
U-201	L	WET	SLUDGE		Sludge
U-202	L	WET	SLUDGE		Sludge
U-203	L	WET	SLUDGE	Agnew-4	Sludge
U-204	L	WET	SLUDGE	Agnew-4	Sludge

NOTES TO SUPPORT TABLE F-8 ABOVE:

In Fuel Group Basis: The Groups in Column 2 are justified by explanations in Column 5.

"Anderson" indicates that Anderson (1990) identified that these tanks contained some form of complexant waste type: CC, CPLX, CCPLX, HS, and SRR

"Agnew-#" indicates that Agnew et al. (1996) *History of Organic Carbon in Hanford HLW Tanks* listed this tank in the relevant table(s):

Agnew-3: "Table 3. Tank Concentrates Sorted by Decreasing TOC (no aging or evaporator degradation) with TOC > 0.64 wt%" (Hanford interpretation for this report- Medium to High TOC)

Agnew-4: "Table 4. Watch List Tank Concentrates with TOC < 0.64 wt%" (Hanford interpretation for this report - Low TOC)

Agnew-5: "Table 5. Concentrates in Non-Watch List Tanks with Historical TOCs > 1.0 wt%" [Dates of Maximum TOC for tank are indicated from Agnew Table 5] (Current TOC Residual is predicted to be very low- Hanford interpretation for this report - Low TOC)

Agnew-6: "Table 6. Tank TLM Layers with TOC > 1.0 wt%" (Hanford interpretation for this report - Low TOC)

Agnew-7: "Table 7. Other Tanks with Residual Organic Layers" (Hanford interpretation for this report - Low TOC)

Tank A-105 went into service in May of 1962. In 1963, it began to receive waste from PUREX and became self-concentrating in March 1963. In January 1965, a violent steam release occurred in A-105. The tank continued to be used because there were no other aging waste tanks available. From 1965 on, the surface level stayed constant until self concentrating brought the sodium concentration up to the limit. At that time, new waste was longer added. In 1967, the surface level exhibited unexplained drops. It was decided that these represented steam surges caused by a ripped bottom. To remove the heat without removing the liquid head, the waste was diluted with waste from A-101. At this time, tank A-101 was full of organic wash waste (contains solvent and not complexant). Anderson (1990) also indicates that "cesium depleted supernate" waste was also used. Once the heat was removed by dilution, the tank was pumped and was sluiced in 1968. All of this happened prior to any waste treatment using complexants. The "cesium depleted supernate" waste, if it came from B-Plant, wouldn't have had any organic. The cesium was removed by an inorganic ion exchange process. It is also possible and even probable that, "cesium depleted supernate" waste was waste that had been treated by ferrocyanide.

Last Incoming Date: (Example Entry: And67 equals Anderson (1990) indicated last transfer was 1967, Agn74 equals Agnew et al. (1997) indicates last transfer was 1974 - The waste type that created layer post Anderson layer is identified in parentheses) First Date is from Anderson (1990), Second Date is from Agnew et al. (1997) Where dates are before 1968, the tanks cannot contain complexant wastes because these chemicals were not used at Hanford until after 1968.

Unique History: Unique waste history different from general waste grouping.

Basis for waste type in Column 4 is stated in Column 6.

SaltCakes were identified in Agnew et al. (1997) as being at least 30 % of the waste total. When two major saltcakes are present in a tank, the saltcake at the top of the waste is identified unless the other saltcake is significantly larger.

10.0 REFERENCES

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11.0 GLOSSARY

This glossary of Hanford terminology has been compiled from numerous sources. A lot of the terms have come from Anderson(1991), Jungfleisch(1984) and Agnew(1996). These definitions may conflict with other sources.

1C	First-cycle decontamination waste from the bismuth phosphate($BiPO_4$) process at B and T Plants consisting of by-products co-precipitated from a solution containing plutonium (contains 10% of the original fission product activity and 2% of the products). By-product cake solution was mixed with product waste and neutralized with 50% caustic. Coating waste from removing aluminum fuel element cladding was added and comprised about 24% of the waste.
1C1	First-cycle decontamination waste from the bismuth phosphate($BiPO_4$) process, 1944-49 (LANL defined waste #3)
1C2	First-cycle decontamination waste from the bismuth phosphate($BiPO_4$) process, 1950-56 (LANL defined waste #4)
224	224-U Waste. LaF_3 finishing waste from $BiPO_4$ process and uranium recovery in the 224 buildings by T Plant and B Plant and the Plutonium Finishing Plant (LANL defined waste #7)
2C	Second-cycle decontamination waste from the bismuth phosphate($BiPO_4$) process at B and T Plants (see second-cycle decontamination waste)
2C1	Second-cycle decontamination waste from the bismuth phosphate($BiPO_4$) process, 1944-49 (LANL defined waste #5)
2C2	Second-cycle decontamination waste from the bismuth phosphate($BiPO_4$) process, 1950-56 (LANL defined waste #6)
5-6	Waste from cell 5 tank 6 in B Plant; the hot waste collected in the bottom of cell 5 when the liquid boiled over during dissolving and neutralizing phases of the $BiPO_4$ process.
Active Drywell	Drywell in which radiation readings of greater than 50 counts per second are detected. The readings must be consistent as to depth and radiation level for repeated readings to be considered active.
Airlift Circulator	A device installed in aging waste tanks to promote mixing of the supernate. By maintaing motion within the body of the liquid, the circulators minimize superheat buildup and, consequently, minimize burping.
AR	Washed PUREX sludge from the 244-AR Vault (LANL defined waste #31)

Assumed Leaker	A waste storage tank for which past surveillance data has indicated a loss of liquid attributed to a breach of integrity.In 1984, the designations of "suspect leaker," "questionable integrity," "confirmed leaker," "declared leaker," "dormant", and "borderline" were merged into one category called "assumed leaker."
B	High-level waste from PUREX acidified waste processed through B Plant to extract strontium (LANL defined waste #32)
BG	Below grade
BL	B Plant low-level waste beginning 1968 (LANL defined waste #33)
BM	Bench mark
BNW	Battelle Northwest Laboratory waste
BSLTCK	Saltcake waste generated from the 242-B Evaporator, 1951-53 (LANL defined waste #41)
BYSLTCK	Saltcake waste generated from in-tank solidification units 1 and 2 in BY Tank Farm, 1965-74 (LANL defined waste #44)
Cascade	Eleven of the single-shell tank farms (all except the AX Tank Farm) were equipped with overflow lines between tanks. The tanks were connected in series and were placed at different elevations creating a downhill gradient for liquids to flow (cascade) from one tank to another. Thus, multiple tanks could be filled with one pump.
Catch Tanks	Small capacity single-shell tanks associated with diversion boxes and diverter stations. The tanks are designed to receive any transfer line clean out, spills or leakage from the boxes, or leakage from the adjacent pipe encasement.
CC	Complexant concentrate waste or concentrated complexant; concentrated product from evaporating dilute complexed waste which contained high concentrations of organic complexants, such as HEDTA, EDTA, and citric acid.
CCPLX	Complexant concentrate or concentrated complexant waste; see CC.
CCW	Concentrated customer waste; the product of concentrating waste received from 100N or the Fast Flux Test Facility having phosphate and/or sulfate concentrations which, after concentration, exhibit the characteristics of a complexed liquid.
CEM	Cement
CF	Cesium feed; a PUREX sludge supernate.
CP	Concentrated phosphate waste; the product of concentrating waste orginating from the decontamination of the N Reactor in the 100 N Area.

CPLX	Complexed waste; dilute waste containing relatively high concentrations of organic chelating agents such as EDTA and HEDTA form B Plant waste fractionization.
Crib	An underground structure filled with aggregate designed to receive liquid waste, usually through a perforated pipe. The filtration and ion exchange properties of the soil in and around the crib were used to contain the radionuclides.
CSR	Waste (supernate) from cesium recovery of tank supernate at B Plant (LANL defined waste #35)
CW	Coating (cladding) waste produced at PUREX from dissolution of Zircaloy or aluminum fuel cladding.
CWZR1	Coating (cladding) waste (PUREX), Zircaloy cladding; 1968-72 (LANL defined waste #23)
CWZR2	Coating (cladding) waste (PUREX), Zircaloy cladding; 1983-88 (LANL defined waste #47); see NCRW and PD; also known as CWP/ZR2
CWP	Coating (cladding) waste (PUREX)
CWP1	Coating (cladding) waste (PUREX); (LANL defined waste #21, CWP/Al, 1956-60)
CWP2	Cladding (coating) waste (PUREX), (LANL defined waste #22, CWP/Al, 1961-72)
CWP/ZR	Now called PD or NCRW
CWR1	REDOX cladding (coating) waste, (LANL defined waste #15, CWR/Al, 1952-60)
CWR2	Coating (cladding) waste (REDOX), (LANL defined waste #16, CWL/Al with some Zr, 1961-72)
DC	Dilute complexed waste characterized by organic carbon including organic complexants: EDTA, citric acid, HEDTA, and iminodiacetate.
DE	Diatomaceous Earth; Diatomite (SiO_2); a light friable siliceous material derived from diatom (algal) remains; added to some underground waste storage tanks to absorb residual liquids.
Ditch	A linear excavation often used for the temporary diversion or disposal of process waste streams.
Diversion Box	A below grade, concrete enclosure containing the remotely maintained jumpers and spare nozzles for routing waste solution to storage tank farms.

DSSF	Double-shell slurry feed; Waste concentrated in evaporators until the solution is nearly saturated with sodium aluminate without exceeding receiver tank composition limits. This form is not as concentrated as double-shell slurry.
Drywell	A steel casing, generally 6-inch internal diameter, drilled into the ground to various depths (but do not reach the water table) and used to insert monitoring instruments for measuring the presence of radioactivity or moisture content.
DW	Decontamination waste; a wash solution from equipment decontamination at T Plant (LANL defined waste #39)
EB	Evaporator bottoms; a slurry from the evaporators
EF	Evaporator feed; various supernatant liquids whose composition depends on the source
EVAP	Evaporator feed (post 1976 designation)
Evaporator Feed	Any waste liquid that can be concentrated to form saltcake; e.g., aged waste, low heat waste, dilute interstitial liquor, and other radioactive waste solutions.
FD	Feed dilute
Ferrocyanide	An ion composed of iron and cyanide with the chemical formula of $Fe(CN)_6^{-4}$.
H_2O	Water
HDRL	Hanford defense residual liquor; late 1970s designation for terminal liquors remaining after evaporation; includes complexed and noncomplexed waste, partially neutralized waste, and DSSF (see RESID).
HLO	Hanford Laboratory Operations; also, Hanford laboratory operations waste; laboratory waste from the 300 Area
HS	Hot Semiworks (C Plant); a pilot facility with a variety of operations. Also, Hot or Strontium Semiworks waste (LANL defined waste #28); see SSW.
ILL	Interstitial liquid level
Inactive Tank	A tank that has been removed from liquid-processing service, has beenpumped to less than 33,000 gallons of waste, and will be, or is in the process of being, stabilized followed by intrusion prevention. This includes all tanks not in active or active-restricted categories. Also included are inactive spare tanks that would be used if an active tank failed.

Interim Isolation	An administrative designation reflecting the completion of the physical effort required to minimize the addition of liquids into an inactive storage tank, process vault, sump, catch tank, or diversion box. (In June 1993, "interim isolation" was replaced by "intrusion prevention".)
Interim Stabilization	A tank which contains less than 50,000 gallons of drainable interstitial liquid and less than 5,000 gallons of supernate. If a jet pump was used to achieve interim stabilization, then the jet pump flowrate must have been at or below 0.05 gallons per minute before interim stabilization was completed.
Interstitial Liquid (voids)	The interstitial liquid within the tanks is the liquid that fills the interstitial spaces of the solid waste.
Intrusion Prevention	An administrative designation reflecting the completion of the physical effort required to minimize the addition of liquids into an inactive storage tank, process vault, catch tank, sump, or diversion box.
IWW	Inorganic wash waste (i.e., concentrated neutralized high-level waste from PUREX); see NCAW and P. This was also designated as 1WW because it is bottoms waste from the #1 acid concentrator.
IX	Ion exchange waste from the cesium recovery process at B Plant
Knuckle	Point where the side wall and the bottom curved surface of a tank meet.
Level Adjustment	Any update in the waste inventory (or tank level) in a tank. The adjustments usually result from surveillance observations or historical investigations.
Liquid Observation Well (LOW)	A liquid observation well is a fiber glass or tefzel-reinforced epoxy-polyester resin, 89 mm (3.5 inches) diameter pipe that is capped on the bottom end. This end is placed within 25 mm (1 inch) above the bottom portion of the steel tank liner. Three types of probes are used in the LOW to monitor changes in the interstitial liquid level: acoustic, gamma, and neutron.
LW	Laboratory waste from the 222-S Building
Mixed Waste	Waste containing both radioactive and hazardous (dangerous as defined in WAC 173-303) waste.
MW	Waste from the bismuth phosphate process (which extracted plutonium) containing all the uranium, approximately 90% of the original fission product activity, and approximately 1% of the product. This waste was brought to the neutral point with 50% caustic and then treated with an excess of sodium carbonate. This procedure yielded almost completely soluble waste at a minimum total volume. The exact composition of the carbonate compounds was not known, but was assumed to be a uranium phosphate carbonate mixture. The term "metal" was the code word for plutonium.
MW1	Metal waste from $BiPO_4$, 1944-49 (LANL defined waste #1, same as MW)

MW2	Metal waste from $BiPO_4$, 1950-56 (LANL defined waste #2, same as MW)
N	Phosphate decontamination waste from N Reactor (LANL defined waste #40)
NCAW	Neutralized current acid waste, primary high-level waste stream from PUREX process (LANL defined waste #45, formerly P3, 1983-88)
NCPLX	Non-complexed waste; general term for supernates and salt well liquors that did not contain organic complexants.
NCRW	Neutralized cladding removal waste, same as CWP/Zr.
NIT	$HNO_3/KMNO_4$ solution added during evaporator operation
Non-Complexed	General waste term applied to all Hanford Site liquors not identified as complexed (containing organics).
Out-of-Service-Tank	A tank that does not meet the definition of an in-service tank. Before September 1988, these tanks were defined as inactive. (Note: All single-shell tanks are out of service.)
OWW	Organic Wash Waste; The solvent used in PUREX was treated before reuse by washing with potassium permanganate and sodium carbonate, followed by dilute nitric acid.
OWW1	Organic wash waste, 1956-62, also known as CARB (LANL defined waste #24)
OWW2	Organic wash waste, 1963-67 (LANL defined waste #25)
OWW3	Organic wash waste, 1968-72 (LANL defined waste #26)
P	High-level neutralized acid waste from PUREX
P1	PUREX high-level waste, 1956-62 (LANL defined waste #17)
P2	PUREX high-level waste, 1963-67 (LANL defined waste #18)
P2	1968-1972, assigned to P2.
P3	1983-1988, now called PXNAW or NCAW.
Partial Interim Isolation	The administrative designation for completing the physical effort required for interim isolation, except for isolating the risers and piping that will be required for jet pumping or for other methods of stabilization.
PASF	PUREX ammonia scrubber feed (LANL defined waste #48)

PD	PUREX decladding waste
PFeCN1	Ferrocyanide sludge produced by in-plant scavenging (using 0.005 M ferrocyanide) of waste from uranium recovery (LANL defined waste #9)
PFeCN2	Same as PFeCN1 except 0.0025 M ferrocyanide used (LANL defined waste #10)
pH	A measure of the hydrogen ion concentration in solution.
PL	Low-level waste from PUREX
PL1	PUREX low-level waste (LANL defined waste #20)
PL2	1983-88, now called PXMSC, among other things.
Primary Addition	An addition of waste from a specific plant or process vault.
PSS	PUREX sludge supernate; produced by leaching PUREX sludge
PXMSC	Dilute, non-complexed waste from PUREX misc. streams
PXNAW	Aging waste from PUREX high level waste; see NCAW (LANL defined waste #45, formerly P3, 1983-88)
R	High-level waste from REDOX
R1	REDOX waste, 1952-57 (LANL defined waste #13)
R2	REDOX waste, 1958-66 (LANL defined waste #14)
RESID	Hanford defense residual liquor (see HDRL)
Riser	A vertical pipe through a tank dome (access to the tank interior).
RIX	REDOX ion exchange waste produced at B Plant by extractng cesium from REDOX supernate
RSLTCK	Salt-cake waste from the REDOX concentrator (LANL defined waste #43)
RSN	REDOX supernate
SACS	Surveillance analysis computer system
Saltcake	Crystallized nitrate and other salts deposited in waste tanks, usually after the waste is concentrated by evaporation.

Salt Well	A hole drilled or sluiced into saltcake and lined with a cylindrical screen to permit drainage and jet pumping of interstitial liquids.
Scavenged Waste	Waste which has been treated with ferrocyanide to remove cesium from the supernate by precipitating it into a sludge.
Self-Concentrating Waste	Liquid, high-level radioactive waste whose decaying radionuclides heat the solution sufficiently to boil off (i.e., evaporate) the water, thus concentrating the waste.
SIX	Waste from removing cesium from PUREX sludge supernate by ion exchange at B Plant
Sluicing or Sluiced	To wash with water. At Hanford, this has meant to dissolve or suspend waste in solution using a high pressure water stream.
Slurry	Insoluble material suspended in water or aqueous solution.
SMM	Supernatant Mixing Model (created at LANL) that calculates the composition of tank liquids and concentrates as linear combinations of supernates from the Agnew et al. (1997).
SMP	Sludge measuring port
SMMA1	Solids from concentrate calculated by SMM. Waste type is tank dependent.
SMMA2	Solids from concentrate calculated by SMM. Waste type is tank dependent.
Sound	The integrity classification of a waste storage tank for which surveillance data indicate no loss of liquid attributed to a breach of integrity.
SRR	Sluiced PUREX sludge from A and AX Tank Farms sent to B Plant to recover strontium from 1967-76 (LANL defined waste #34). The sludge returned from B Plant was sent to the AR Vault and the supernate was sent to 241-C-105.
SRS	Strontium sludge; PUREX sludges sluiced for strontium recovery at B Plant were washed in the AR Vault with supernate from 241-C-105, and the resulting supernates were sent to CSR.
SST	Single-shell tank
SSW	Strontium Semiworks waste; produced from the strontium extraction process at the Strontium Semiworks after 1961
Stabilization	The removal or immobilization, as completely as possible, of the liquid contained in a radioactive waste storage tank by pumping via a salt well, adding diatomaceous earth, etc.
Supernatant	Liquid floating above the solids in the waste storage tanks. Supernate is

or Supernate	usually derived by subtracting the solids level measurement from the liquid level measurement.
T1SLTCK	Salt-cake waste generated from the 242-T Evaporator, 1951-56 (LANL defined waste #42)
T2SLTCK	Salt-cake waste generated from the 242-T Evaporator, 1965-76
Tank Farm	An area containing underground storage tanks for storing waste.
TBP	Tributyl phosphate, a solvent used in the uranium extraction process at U Plant; also, a waste which is sometimes called uranium recovery waste (UR).
Terminal Liquor	The concentrated supernatant liquid decanted from the evaporator bottoms (produced by the evaporators), which may not be concentrated further without forming solids that was unacceptable for storage in single-shell tanks (see HDRL). Terminal liquor is characterized by a caustic concentration of approximately 5.5 M (the caustic molarity was lower if the aluminum salt saturation was reached first).
TFeCN	Ferrocyanide sludge produced by in-tank or in-farm scavenging (LANL defined waste #11)
TH1	Thoria high-level or cladding waste, 1966 (LANL defined waste #29, formerly TH66)
TH2	Thoria high-level or cladding waste, 1970 (LANL defined waste #30, formerly TH70)
TH66	See TH1.
TH70	Thoria 1970.
Thermocouple	Thermocouples are simple devices that develop a millivoltage when parts of the thermocouple are exposed to temperature differentials. The millivoltage can be converted to a temperature reading based on a specific voltage versus temperature curve inherent to the type of thermocouple being used. Thermocouples are attached to a fabricated assembly called a thermocouple tree.
Thermocouple Tree	Thermocouples are attached to a fabricated assembly called a thermocouple tree. The number of thermocouples attached to the tree varies as a function of the depth of the tank as well as the thermocouple tree design. The thermocouples are spaced at intervals, along trees that have many thermocouples, so that a vertical temperature profile of the tank contents can be developed. The thermocouple tree is installed in a riser and left in place inside the tank.
Thorium	A chemical element which is fertile material. Fertile means that when it is subjected to radiation in a nuclear reactor, it will be converted, in this case, to ^{233}U, a potential fuel.

TLM	Tank Layer Model (created at LANL and derived from *Waste Status and Transaction Record Summary* database) models the volumes of wastes in the tanks.
Trench	A linear excavation used for the disposal of solid waste.
TRUEX	Transuranic extraction process
UNK	Unknown waste type (LANL defined waste)
UR	Uranium recovery operation in U Plant, 1952-57. Created uranium recovery waste (UR) (LANL defined waste #8), also known as tributyl phosphate (TBP) waste, and FeCN (scavenging wastes). See TFeCN and PFeCN.
Watch List Tank	An underground storage tank requiring special safety precautions because the tank potentially could release high-level radioactive waste if uncontrolled increases in pressure or temperature occur. Special restrictions have been placed on the tanks by "Safety Measures for Waste Tanks at Hanford Nuclear Reservation," Section 3137, National Defense Authorization Act for Fiscal Year 1991, November 5, 1990, Public Law 101-501 (also called the Wyden Amendment).
WC	Weather cover
WESF	Waste Encapsulation and Storage Facility
WTR	Water; flush water from miscellaneous sources.
Wyden Amendment	See watch list tank.
Z	Waste discharged from Z Plant (PFP) (LANL defined waste #27)

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APPENDIX G

THEORETICAL PROPAGATION CRITERIA AND COMPARISON WITH TEST RESULTS ON ORGANIC WASTE SIMULANTS AND WASTE SAMPLES

by

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EXECUTIVE SUMMARY

Propagation experiments were performed on waste simulants and waste samples. Direct propagation testing of tank wastes with the highest TOC/DSC indicate that Hanford Site High-Level waste will not support condensed-phase propagation under tank waste conditions, or even when dried to almost no water. Propagation was only possible when additional fuel was added to the dried waste. Tank C-201 waste had a low oxidizer concentration and the waste became oxidizer limited when spiked above 4.3 wt% TOC. This sample did not propagate even when fuel was added to the samples.

Theoretical examination of the fuel-moisture conditions that support propagation indicate that a minimum fuel concentration of 4.5 wt% total organic carbon is necessary. The minimum fuel concentration increases linearly to 7.9 wt% at 20 wt% water. Propagation is not possible at water concentrations greater than 20 wt% water, irrespective of the fuel concentration.

The theoretical criterion was corroborated with propagation tests on simulants and waste samples. All simulant and spiked-waste samples that propagated exceeded the theoretical criterion, and the criterion is conservative when compared to the empirical results. The minimum TOC concentration required was more than 4.5 wt%.

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LIST OF TERMS

DSC	Differential Scanning Calorimetry
EDTA	ethylenediaminetetraacetic acid
HEDTA	hydroxyethylethylenediaminetriacetic acid
NPH	normal paraffin hydrocarbon
NTA	nitrilotriacetic acid
PRSST	Propagating Reactive System Screening Tool
RSST	Reactive System Screening Tool
TBP	tributyl phosphate
TOC	Total Organic Carbon
wt%	weight percent

LIST OF SYMBOLS

α	thermal diffusivity
λ	latent heat of vaporization for water
ΔH_{min}	lower bound theoretical chemical energy release that sustains propagation
ΔH_{rx}	heat of reaction
°C	degrees centigrade
$\bar{c}$	effective average specific heat
g	gram
k	thermal conductivity
kg	kilogram
m	meter
MJ	Megajoule
mL	milliliter
s	second
T_{ad}	adiabatic reaction temperature
T_i	interfacial temperature
T_{ig}	ignition temperature
T_0	initial temperature
W	Watt
x_w	weight fraction of water

APPENDIX G

PROPAGATION THEORETICAL CRITERIA AND TEST RESULTS ON ORGANIC WASTE SIMULANTS AND WASTE SAMPLES

1.0 BACKGROUND

Several waste generating processes were operated at the Hanford Site, and radioactive wastes from these processes are stored in underground tanks in alkaline slurries (Anderson 1990). Organic complexant salts were used during waste processing and were subsequently disposed to the tanks as dilute aqueous waste streams. The principal organic complexants were glycolic acid, citric acid, hydroxyethylethylenediaminetriacetic acid (HEDTA), and ethylenediaminetetraacetic acid (EDTA). Besides these complexants, organic salts such as nitrilotriacetic acid (NTA) and oxalic acid were also used, but the quantities were relatively small and were not well quantified.

The organic complexants are in waste matrices that include inerts and diluents (e.g., water, sodium carbonate, sodium sulfate, and hydroxy salts of aluminum, iron, and silicon) and potential oxidants (sodium nitrate/nitrite). In the presence of oxidizing material such as sodium nitrate/nitrite, the complexant salts can be made to react exothermically by heating to high temperatures or by applying an electrical spark of sufficient energy.

There are two common hazards associated with the safe storage and handling of chemically reactive material (AIChE 1995); spontaneous self-accelerating decomposition reactions in the bulk material (bulk runaway), and deflagration after being initiated by an ignition source (propagation). The bulk runaway hazard is described in Appendix B, and the propagation hazard is described in this appendix.

In contrast to bulk runaway, a deflagration propagates by thermal energy transfer (AIChE 1995). Given the presence of an adequate amount of oxidizer ($NaNO_3$/$NaNO_2$) and an ignition source, sustained propagation depends on the fuel concentration and the absence of diluents such as water. Conditions that could support combustion were examined theoretically (Section 2.0), and experimentally on waste simulants (Section 3.0) and waste samples (Section 4.0).

The purpose of this appendix is to summarize the derivation of the theoretical screening criteria and to present the results of propagation experiments on waste simulants and waste samples. The appendix also compares the empirical results to the theoretical criteria.

2.0 FUEL-MOISTURE THEORETICAL CRITERION FOR PROPAGATION

Suppose a region of combustible material combusts and is instantaneously and uniformly chemically heated to its adiabatic reaction temperature (T_{ad}). To sustain a propagation, the chemical energy release must raise the contact or interface temperature (T_i) above the ignition temperature (T_{ig}) :

$$T_i > T_{ig} \qquad \text{(G-1)}$$

If Equation G-1 is not satisfied, the reaction will slow and be quenched by the much colder unreacted material.

The conduction problem that arises immediately following the local, instantaneous chemical heating of the reactive medium resembles the classical thermal contact problem that results from suddenly bringing together two semi-infinite slabs with different initial temperatures, namely the initial temperature (T_0) and the adiabatic reaction temperature (T_{ad}). The temperature at the plane of separation (T_i) of the reacted and unreacted regions are

$$\frac{T_i - T_o}{T_{ad} - T_o} = \frac{1}{1 + \sigma} \qquad \text{(G-2)}$$

and

$$\sigma = \frac{k_u}{k_r}\left(\frac{\alpha_r}{\alpha_u}\right)^{1/2} \qquad \text{(G-3)}$$

where k (W m^{-3} K^{-1}) is the thermal conductivity, α (m^2 s^{-1}) is the thermal diffusivity, and subscripts r and u represent reacted and unreacted materials, respectively. The value of T_i is reached instantaneously, or when the two regions contact one another. If the products of the physical properties (i.e., ρck) are assumed to be the same for both regions, then $\sigma \approx 1$. The contact temperature is simply the arithmetic mean of the adiabatic reaction temperature and the initial temperature:

$$T_i = \frac{T_{ad} + T_0}{2} \qquad \text{(G-4)}$$

In writing Equation G-4, it is assumed that no heat is transmitted from the reacting region to the surrounding unreacted region before the reacted region is chemically heated to T_{ad}. In most applications of interest, some heat transfer from the reacting region to the surroundings will occur before the reaction is complete. The energy supplied to locally raise the combustible material temperature to its ignition temperature will also result in a reacted-region peak temperature that exceeds T_{ad}. If these departures from the ideal situation of an adiabatically and purely chemically heated region up to T_{ad} are treated in full detail, then the conduction theory for the prediction of T_i becomes complicated and would be difficult to calculate. Separate computer solutions would be needed for each case considered. To avoid this complexity, Equation G-4 is selected for calculating T_i. The fidelity of this approximation must be judged by comparison of the derived criterion with experimental results (see Sections 3.0 and 4.0).

To sustain a propagation, T_i must be greater than T_{ig}. Substituting Equation G-1 into Equation G-4 and rearranging for T_{ad} results in the following:

$$T_{ad} > 2\ T_{ig} - T_0 \qquad \text{(G-5)}$$

Accounting for water by subtracting the effective temperature difference taken up by evaporation of the water (i.e., $x_w\ \lambda\ \bar{c}^{-1}$), the criterion for propagation becomes

$$T_{ad} > 2\ T_{ig} - T_0 + \frac{x_w\ \lambda}{\bar{c}} \qquad \text{(G-6)}$$

where x_w is the water mass fraction, λ is the latent heat of evaporation, and $\bar{c}$ is the effective average specific heat value of the reacting mixture and its products over the temperature range of interest that also accounts for heat of melting and sensible heats of water and its vapor. [For further details on equation development see Fauske et al. (1996).]

A lower bound theoretical value for the chemical energy release (ΔH_{min}) to sustain propagation can now be obtained by assessing the reaction enthalpy required to raise the temperature of a unit mass of reacting mixture from T_0 to T_{ad} (note that exothermic reactions have a negative enthalpy thus the $-\Delta H_{min}$):

$$-\Delta H_{min} = (T_{ad} - T_0)\ \bar{c} + x_w\ \lambda \qquad \text{(G-7)}$$

By combining Equations G-6 and G-7, the following is obtained:

$$-\Delta H_{min} > 2\left[T_{ig} - T_0 + \frac{x_w\ \lambda}{\bar{c}}\right]\bar{c} \qquad \text{(G-8)}$$

Equation G-8 can be further simplified by treating T_0 as negligible (i.e., equal to 273 K) with little loss of accuracy. The claim of lower bound values is still well justified by comparison to experimental data (see Sections 3.0 and 4.0).

$$-\Delta H_{min} > 2\left[(T_{ig} - T_0)\,\bar{c} + x_w\,\lambda\right] \qquad (G\text{-}9)$$

Using the ignition temperature for sodium acetate (T_{ig} = 573 K), $\bar{c} \approx 2000$ J kg^{-1} K^{-1}, and λ = 2265 kJ kg^{-1} (Fauske et al. 1997), the minimum chemical energy release (in MJ kg^{-1}) to sustain propagation is

$$-\Delta H_{min} > 1.2 + 4.5\,x_w \qquad (G\text{-}10)$$

For dry material, the x_w term drops out and the minimum chemical energy is simply 1.2 MJ kg^{-1}. This criterion is consistent with the 0.71 to 1.25 MJ kg^{-1} (170 to 300 cal g^{-1}) range found in the literature for materials susceptible to propagation (AIChE 1995).

The criterion for propagation or point source ignition can also be expressed in terms of TOC concentration. The equivalent TOC (fuel) concentration is simply the minimum energy requirement ($-\Delta H_{min}$) divided by the heat of reaction ($-\Delta H_{rx}$) for sodium acetate combustion with sodium nitrate [about 27.1 MJ kg^{-1} from Burger (1993)]. It is also important to note that the above Equations become non-physical for values of x_w greater than about 0.2, since the liquid phase now becomes the continuous phase (Fauske et al. 1997). For such conditions the contact temperature T_i will not exceed the boiling point of the salt solution (about 120 °C) which is well below T_{ig} values of interest. Therefore, the criterion for propagation in terms of wt% TOC (as sodium acetate) becomes

$$\text{wt\% TOC (as Sodium Acetate)} > (4.5 + 17\,x_w)\,; \quad \text{where } x_w < 0.2 \qquad (G\text{-}11)$$

Equation G-11 gives a theoretical criterion for propagation, but the criterion ignores effects which can inhibit propagation, and the actual propagation threshold can be substantially higher. Direct testing of the materials is recommended to determine a more accurate threshold for propagation (AIChE 1995). Results from direct testing on waste simulants and waste samples are compared to the theoretical criterion in Sections 3.0 and 4.0, respectively.

3.0 PROPAGATION TESTS ON WASTE SIMULANTS

Organic complexant waste simulants were tested for propagation using the Reactive System Screening Tool (RSST), and tube propagation test cells. Samples ranging from 10 (RSST tests) up to 50 g (tube propagation) were made up of reagent grade chemicals. The chemicals were ground using a mortar and pestle to sizes generally less than 100 μm and mixed in a small beaker, which is vigorously stirred prior to loading the samples into appropriate test cells. Measured quantities of key interest included ignition and combustion temperatures, the fuel concentration required to support propagating reactions, and moisture concentration that would inhibit such reactions. The apparatuses and test results are described in this Section.

3.1 THE REACTIVE SYSTEM SCREENING TOOL (RSST)

3.1.1 Description of RSST Apparatus

The RSST (Figure G-1) consists of a spherical glass reaction vessel, its surrounding jacket heater and insulation, a thermocouple (imbedded in sample), a pressure transducer, a stainless steel containment vessel, and, not shown, a magnetic stirrer base, a control box containing the heater power supply, temperature/pressure amplifiers, and a data acquisition and control panel. The sample cell volume is 10 mL and the containment volume is 350 mL. A key feature of the apparatus is its low effective heat capacity relative to that of the sample whose value, expressed as the capacity ratio, is ~1.04 (i.e., quite adiabatic).

A test sample (~10 g) was heated at a constant rate of approximately 1°C per minute and the sample self-heat rate (dT/dt) was found as a function of sample temperature under an essentially zero heat loss conditions. Figure G-2 is an example of the reaction kinetics for an initially solid waste simulant of sodium acetate, sodium nitrate, and sodium hydroxide, with a sodium acetate concentration of 24 wt% [or 7 wt% total organic carbon (TOC) content]. For this test, significant exothermic activity was noted at about 200°C which led to a runaway reaction exhibiting an Arrhenius type dependence on temperature up to approximately 300°C; at this temperature, a dramatic step change in the rate of temperature rise was observed. This is interpreted as a threshold for rapid wave-like reaction propagation, and the temperature of 300°C is referred to as the ignition temperature.

It is important to note that the onset of propagating reactions in the RSST tests occurs when the entire sample has essentially reached the ignition temperature. This is in contrast to the tube propagation tests in which propagation can occur at ambient waste temperature given an adequate ignition source.

Figure G-1. Illustration of Reactive System Screening Tool Test Cell.

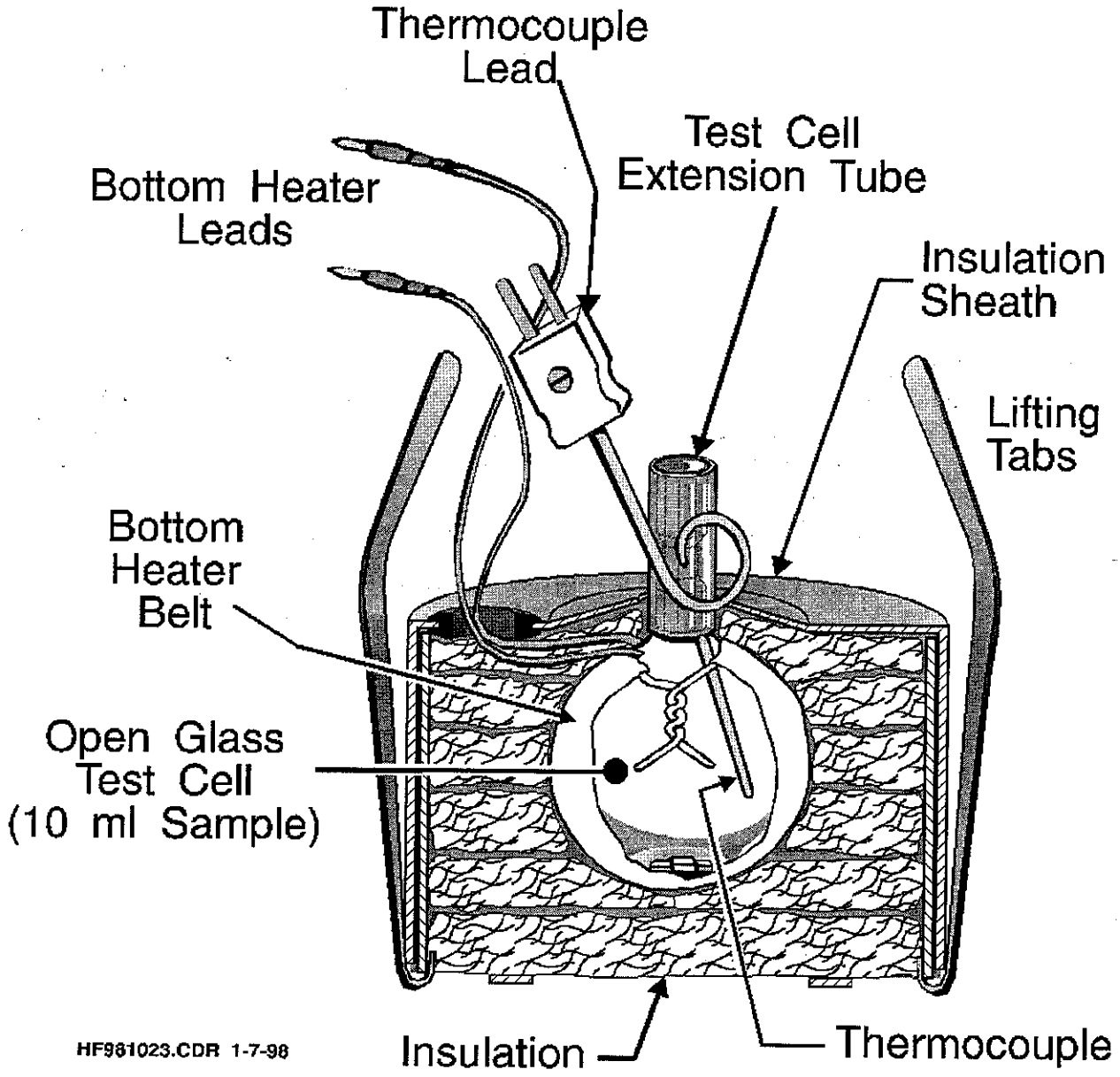
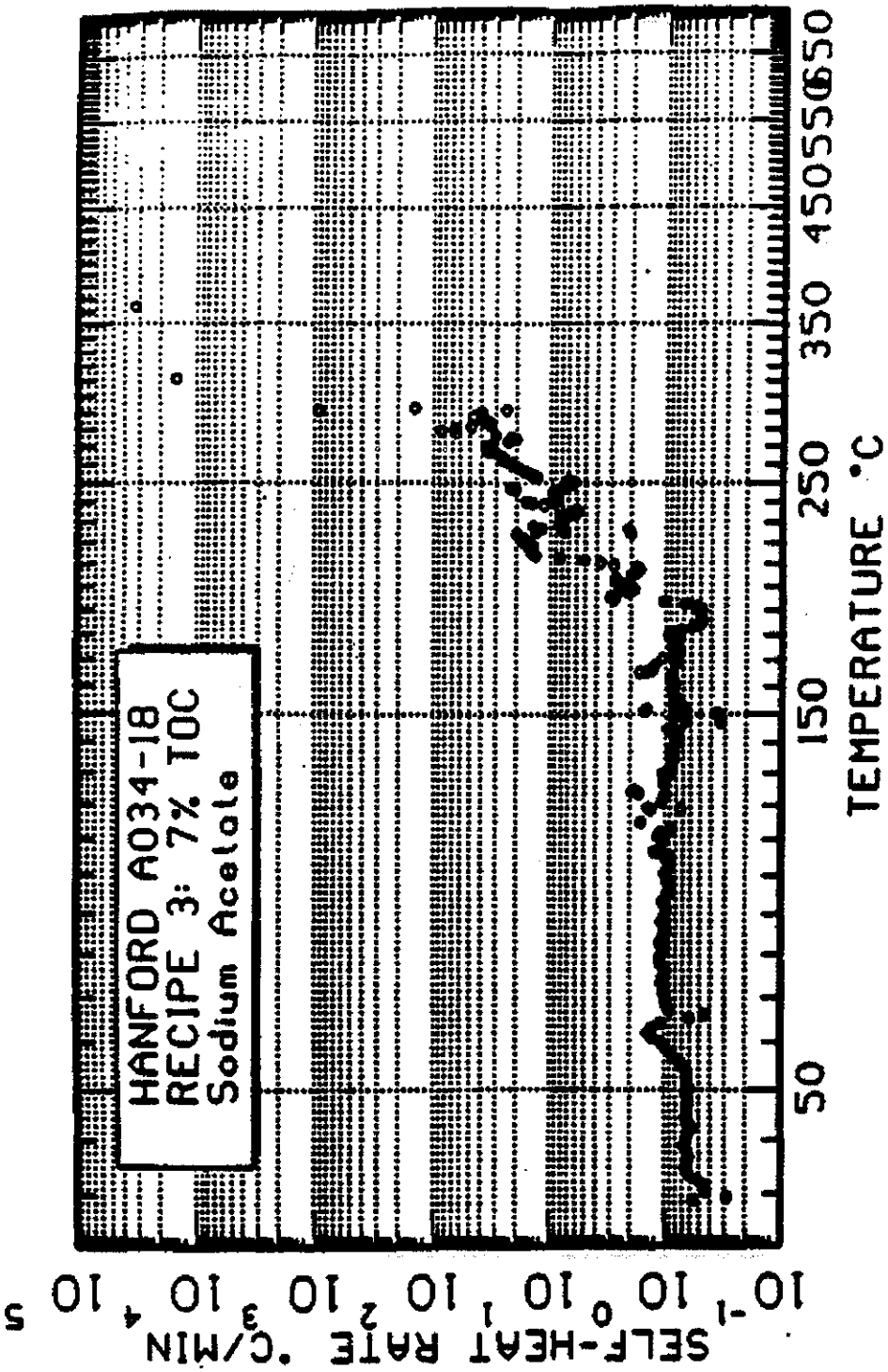


Figure G-2. Transition From a Homogeneous Runaway Reaction to a Propagating Reaction Occurring at About 300°C.



3.1.2 RSST Test Results on Waste Simulants

The simulant mixtures tested in the RSST are reviewed in Table G-1. Examples of measured ignition temperatures are listed in Table G-2. Table G-2 shows that the lowest ignition temperature of about 220°C, and that the ignition temperatures are not significantly affected by the presence of transition metals (Fauske 1996).

Table G-1. Simulant Mixtures Tested by RSST and Propagation Results.

Organic Fuel	TOC (wt%)	$NaNO_3$ (wt%)	$NaNO_2$ (wt%)	NaOH (wt%)	Propagate
Na Acetate	3.0	65.8	16.8	7.2	No
Na Acetate	3.5	62.9	16.8	8.5	No
Na Acetate	5.0	59.7	14.6	8.5	No
Na Acetate	5.0	59.7	14.6	8.5	No
Na Acetate	5.0	59.7	14.6	8.5	No
Na Acetate	5.0	59.7	14.6	8.5	No
Na Acetate	5.0	66.4	16.6	0.0	No
Na Acetate	5.0	61.6	15.5	5.8	No
Na Acetate	5.0	56.2	14.1	12.6	No
Na Acetate	6.0	85	0.0	0.0	Yes
Na Acetate	7.0	51.4	12.6	12.0	Yes
Na Oxalate	11.0	16.4	4.1	18.4	No
Nitrododecanoic Acid	5.0	66.5	16.7	8.5	Yes
Na Dodecanate	5.0	67.2	17.2	7.8	Yes
Na Stearate	4.0	70.9	17.6	5.8	No
Na Stearate	6.0	66.4	16.5	8.6	Yes
Na Stearate	6.0	73.2	18.2	0.0	Yes
Na Stearate	6.0	45.9	11.4	34.2	No
Na Stearate	8.0	61.9	15.5	11.3	Yes
NaEDTA	5.0	55.1	14.0	15.5	No
Tributyl Phosphate	11	79.7	0.0	0.0	No
Al Dibutyl Phosphate	7.9	77.1	0.0	0.0	No
Na Dibutyl Phosphate	9.3	80.9	0.0	0.0	No

Table G-2. Measured Combustion Data for Organic Complexants.

Organic Complexant	Fuel[1] (wt%)	$NaNO_3$ (wt%)	$NaNO_2$ (wt%)	NaOH (wt%)	Inert[2] (wt%)	H_2O[3] (wt%)	T_{ig} (°C)	T_c (°C)	U_b ($m\ s^{-1}$)
NaAcetate	20.5 (6)	47.2	11.8	20.5	--	--	~300	~800	$\sim 3.3 \cdot 10^{-4}$
$Na_3Citrate \cdot 2H_2O$	32.7 (8)	41.7	10.4	15.2	--	4.0	230	~800	$\sim 3.0 \cdot 10^{-4}$
$Na_3HEDTA \cdot 2H_2O$	19.0 (6)	49.6	12.4	19.0	--	1.8	220	~800	$\sim 2.5 \cdot 10^{-4}$
47.5% Na_3 $HEDTA \cdot 2H_2O$/ 52.5% $Na_3Citrate \cdot 2H_2O$	21.0 (6)	29.7	13.8	22.5	12.5[2]	6.8	~230	~730	$\sim 2.0 \cdot 10^{-4}$
31.6% NaGlycolate/ 30.6% $Na_3Citrate \cdot 2H_2O$/ 29.8% $Na_3HEDTA \cdot 2H_2O$/ 7.9% $Na_4EDTA \cdot 2H_2O$	22.3 (6)	29.4	13.7	22.3	12.3[2]	6.0	~230	~700	$\sim 1.7 \cdot 10^{-4}$

Notes: LPL = Lower propagation limit at 30°C.
T_{ig} = Ignition temperature.
T_c = Combustion temperature.
U_b = Burn Velocity.

[1] Total organic carbon equivalent concentration given in parentheses.

[2] The inert was a mixture of (40.7% $A\ell(NO_3)_3 \cdot 9H_2O$, 1.1% $Na_2SiO_3 \cdot 9H_2O$, 5.5% NaF, 1.5% Na_2SO_4, 3.9% $Na_3PO_4 \cdot 12H_2O$, 37.1% $Fe(NO_3)_3 \cdot 9H_2O$, 0.7% $Cr(NO_3)_3 \cdot 9H_2O$, 1% $Ni(NO_3)_2 \cdot 6H_2O$, 0.4% $Mn(NO_3)_2$, 0.5% KNO_3, 0.01% $Pd(NO_3)_2$, 0.02% $RuCl_4 \cdot 5H_2O$, 0.02% $Rh(NO_3)_3 \cdot 2H_2O$, 2.3% $Ce(NO_3)_3 \cdot 6H_2O$, 1.9 $Bi(NO_3)_3 \cdot 5H_2O$, 3.3% $Pb(NO_3)_2$

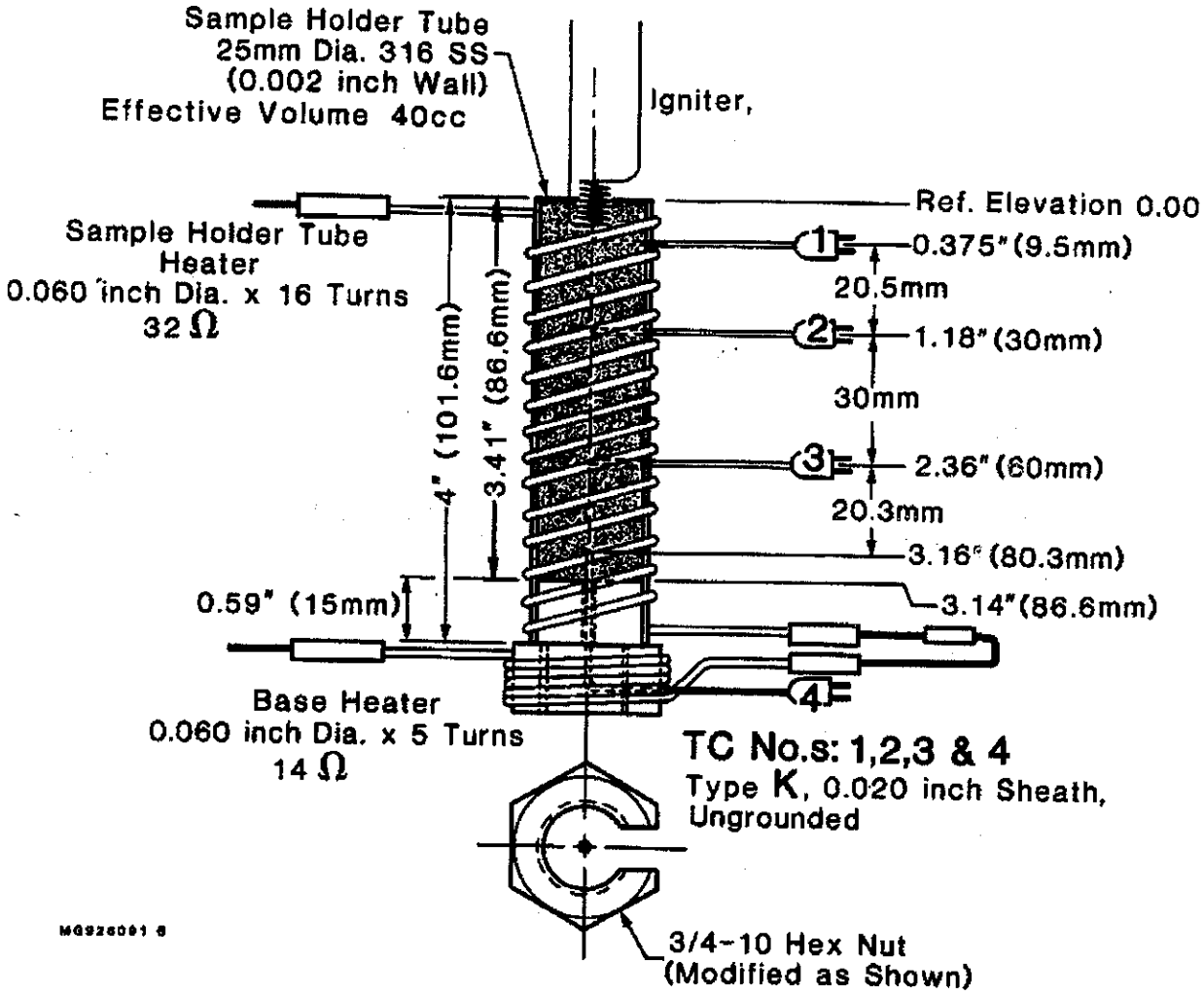
[3] Hydrates contained in fuel and inerts.

3.2 TUBE PROPAGATION

3.2.1 Description of Tube Propagation Apparatus

In the tube propagation tests (see Figure G-3), a confined low heat capacity stainless steel cylinder containing simulated waste (50-70 g) was ignited at the open upper end and the rate of propagation (if any) was measured by noting the time when the reaction front passed imbedded thermocouples. The ignition power was about 20 W and the ignitor was left on until sustained propagation was observed (~15-20 s). In case of no propagation, the ignitor was usually left on for at least 1 minute. These data also provided the necessary fuel concentration to sustain propagating reactions, corresponding burn velocities, and the moisture content that will inhibit propagation including stoichiometric fuel-oxidizer mixtures at ambient waste temperature.

Figure G-3. Illustration of Tube Propagation Test Cell.



3.2.2 Tube Propagation Test Results on Waste Simulants

Tube propagation tests were performed to evaluate the fuel-moisture conditions that support propagation. Simulant waste composition and test results are shown in Table G-3. The samples were ground and well-mixed to maximize fuel-oxidizer contact and the potential for propagation.

Table G-3. Tube Propagation Results for Organic Waste Simulant Mixtures.

Organic Fuel	TOC (wt%)	$NaNO_3$ (wt%)	$NaNO_2$ (wt%)	NaOH (wt%)	Inert (wt%)	Total Water (wt%)	Propagate	Notes
Na Acetate	5.0	83.0	0.0	0.0	0.0	0.0	No	
Na Acetate	5.0	83.0	0.0	0.0	0.0	0.0	No	Replicate of above
Na Acetate	5.5	49.9	12.5	18.8	0.0	0.0	No	
Na Acetate	5.5	31.2	0.0	0.0	50.0	0.0	No	
Na Acetate	6.0	47.2	11.8	20.5	0.0	0.0	Yes	
Na Acetate	6.0	63.6	15.9	0.0	0.0	0.0	No	
Na Acetate	6.0	59.0	20.5	0.0	0.0	0.0	No	
Na Acetate	6.0	0.0	79.5	0.0	0.0	0.0	Yes	
Na Acetate	6.0	34.0	0.0	0.0	45.5	0.0	Yes	Stoichiometric mixture
Na Acetate	7.0	76.1	0.0	0.0	0.0	0.0	No	
Na Acetate	7.5	74.4	0.0	0.0	0.0	0.0	Yes	
Na Acetate	5.9	69.8	0.0	0.0	0.0	10.0	No	
Na Acetate	6.7	35.2	8.8	23.0	0.0	10.0	Yes	
Na Acetate	7.0	33.0	8.2	20.0	0.0	15.0	No	
Na Acetate	8.7	44.2	11.0	0.0	0.0	15.0	Yes	
Na Acetate	9.1	51.8	0.0	0.0	0.0	17.0	Yes	Stoichiometric mixture
Na Acetate	8.8	49.9	0.0	0.0	0.0	20.0	No	Stoichiometric mixture
Na Butyrate	5.0	62.8	15.8	10.0	0.0	0.0	No	
Na Butyrate	6.0	61.0	15.2	10.0	0.0	0.0	No	
Na Citrate	7.0	45.0	11.2	15.2	0.0	3.5	No	
Na Citrate	8.0	53.9	13.5	0.0	0.0	4.0	No	
Na Citrate	8.0	41.7	10.4	15.2	0.0	4.0	Yes	
Na Citrate	9.0	50.6	12.7	0.0	0.0	4.5	Yes	
Na Citrate	10.6	45.0	0.0	0.0	0.0	17.0	Yes	Stoichiometric mixture
Na Citrate	10.3	43.8	0.0	0.0	0.0	19.0	No	Stoichiometric mixture

Table G-3. Tube Propagation Results for Organic Waste Simulant Mixtures.

Organic Fuel	TOC (wt%)	$NaNO_3$ (wt%)	$NaNO_2$ (wt%)	NaOH (wt%)	Inert (wt%)	Total Water (wt%)	Propagate	Notes
Na EDTA	5.5	49.4	12.4	19.1	0.0	1.7	No	
Na EDTA	6.0	46.7	11.7	20.8	0.0	1.6	Yes	
Na Formate	11.8	33.0	0.0	0.0	0.0	0.0	No	Stoichiometric mixture
Na Formate	11.8	33.0	0.0	0.0	0.0	0.0	No	Replicate of above
Na Glycolate	7.6	45.0	11.3	12.7	0.0	0.0	No	
Na Glycolate	8.0	43.2	10.8	13.3	0.0	0.0	Yes	
Na HEDTA	4.5	57.2	14.3	14.2	0.0	0.4	No	Large scale test (Fauske 1996)
Na HEDTA	5.3	53.2	13.3	16.8	0.0	1.6	No	
Na HEDTA	5.8	35.8	0.0	0.0	46.0	1.7	No	Stoichiometric mixture
Na HEDTA	6.0	49.6	12.4	19.0	0.0	1.8	Yes	
Na HEDTA	6.0	37.4	0.0	0.0	43.6	1.8	Yes	Stoichiometric mixture
Na HEDTA	8.0	74.7	0.0	0.0	0.0	2.4	No	
Na HEDTA	8.5	73.1	0.0	0.0	0.0	2.6	Yes	
Na HEDTA	10.3	54.0	13.5	0.0	0.0	3.1	Yes	Large scale test (Fauske 1996)
Na HEDTA	6.6	41.1	0.0	0.0	33.0	7.0	Yes	Stoichiometric mixture
Na HEDTA	7.2	44.9	0.0	0.0	22.3	12.2	No	Stoichiometric mixture
Na HEDTA	8.7	62.4	0.0	0.0	0.0	12.6	No	
Na HEDTA	8.9	49.4	12.4	0.0	0.0	12.7	Yes	
Na HEDTA	9.3	56.2	0.0	0.0	0.0	17.8	No	Stoichiometric mixture
Na HEDTA	9.6	59.6	0.0	0.0	0.0	15.0	Yes	Stoichiometric mixture
Na HEDTA	8.5	44.6	11.1	0.0	0.0	20.0	No	Large scale test (Fauske 1996)
Na IDA	6.0	55.1	13.8	0.0	0.0	9.0	No	
Na IDA	8.0	46.8	11.7	0.0	0.0	12.0	Yes	
Na NTA	7.0	46.4	11.6	15.2	0.0	1.8	No	
Na NTA	8.0	43.4	10.9	15.2	2.0	2.0	Yes	
Na Oxalate	14.3	20.0	0.0	0.0	0.0	0.0	No	Stoichiometric mixture
Na Oxalate	14.3	20.0	0.0	0.0	0.0	0.0	No	Replicate of above
Na Dodecanate	6.0	65.2	16.3	9.1	0.0	0.0	No	
Nitrododecanoic Acid	5.0	66.6	16.5	8.5	0.0	0.0	No	
Nitrododecanoic Acid	6.0	63.6	15.7	10.3	0.0	0.0	Yes	
HEDTA + Citrate	5.0	30.3	14.2	23.0	12.8	6.7	No	47.5% HEDTA, 52.5% Citrate

Table G-3. Tube Propagation Results for Organic Waste Simulant Mixtures.

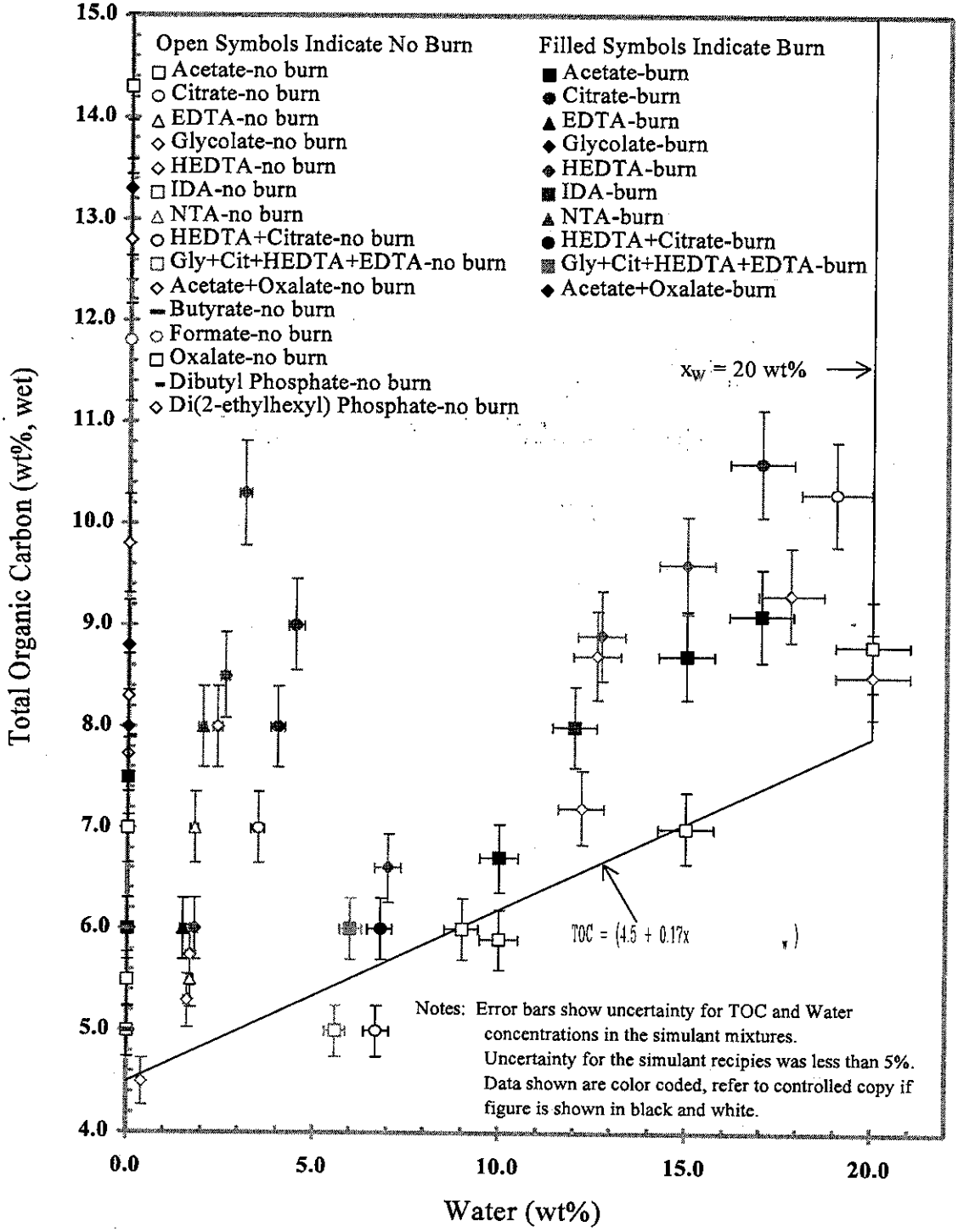
Organic Fuel	TOC (wt%)	$NaNO_3$ (wt%)	$NaNO_2$ (wt%)	NaOH (wt%)	Inert (wt%)	Total Water (wt%)	Propagate	Notes
HEDTA + Citrate	6.0	29.7	13.8	22.5	12.5	6.8	Yes	47.5% HEDTA, 52.5% Citrate
Glycolate + Citrate +HEDTA+EDTA	5.0	30.1	14.1	22.8	12.6	5.6	No	31.6% Glycolate, 30.6% Citrate, 29.8% HEDTA, 7.9% EDTA
Glycolate + Citrate +HEDTA+EDTA	6.0	29.4	13.7	22.3	12.3	6.0	Yes	31.6% Glycolate, 30.6% Citrate, 29.8% HEDTA, 7.9% EDTA
Acetate + Oxalate	8.3	32.9	0.0	0.0	31.7	0.0	No	48% Acetate, 52% Oxalate
Acetate + Oxalate	8.8	34.8	0.0	0.0	72.5	0.0	Yes	48% Acetate, 52% Oxalate
Acetate + Oxalate	12.8	32.3	0.0	0.0	3.4	0.0	No	18% Acetate, 82% Oxalate
Acetate + Oxalate	13.3	33.2	0.0	0.0	0.0	0.0	Yes	18% Acetate, 82% Oxalate
Al Dibutyl Phosphate	7.9	57.9	14.5	10.0	0.0	0.0	No	
Citrate + DBP	6.0	56.8	14.2	10.0	0.0	0.0	No	63.5% Citrate, 36.5% DBP
Na di(2-ethylhexyl) Phosphate	9.8	82.4	0.0	0.0	0.0	0.0	No	Stoichiometric mixture
TBP + NPH	11.3	85.0	0.0	0.0	0.0	0.0	No	30% TBP, 70% NPH
Mineral Oil	ND (12)	88.0	0.0	0.0	0.0	0.0	No	Mixture contained 12 wt% Mineral Oil
Roofing Asphalt	ND (30)	69.9	0.0	0.0	0.0	ND	No	Mixture contained 30 wt% Roofing Asphalt

Notes: ND = Not Determined.

3.3 COMPARISON OF WASTE SIMULANT PROPAGATION TEST RESULTS WITH THEORETICAL CRITERION

The propagation results shown in Table G-3 are compared to the theoretical fuel-moisture requirements in Figure G-4. All the empirical results fall above the theoretical criterion for propagation, and the minimum TOC concentration required was more than 4.5 wt%. Several compounds tested failed to propagate even at stoichiometric fuel-oxidizer conditions with no water present. Compounds which could not sustain propagation included solvents [di(2-ethylhexyl) phosphate, NPH, and TBP] and their degradation products (butyrate and dibutyl phosphate), and complexant degradation products (formate and oxalate).

Figure G-4. Comparison of Tube Propagation Test Results on Organic Waste Simulants with Theoretical Propagation Criterion.



4.0 PROPAGATION TESTS ON WASTE SAMPLES

4.1 RSST TEST RESULTS ON WASTE SAMPLES

Waste samples from ten tanks were tested by RSST. The samples were selected because the measured TOC concentration exceeded 3.0 wt% or differential scanning calorimetry (DSC) analysis showed a heat of reaction greater than 480 J g^{-1}. The TOC concentration for the waste samples tested and the results are summarized in Table G-4. Plots of dT/dt versus temperature are shown in Figures G-5 through G-14.

Table G-4. Adiabatic Calorimetry (RSST) Test Results on Tank Waste Samples.

Tank	Waste TOC (wt%, dry)	TOC of Sample (wt%, dry)	DSC Result[1] (J g^{-1}, dry)	Propagate	Notes
AN-107	4.5 - 9.8	5.5[2] (0.80)[3]	-1300	No	Figure G-5
AW-101	0.8 - 2.0	2.0 (0.11)	-990	No	Figure G-6
BY-104	0.2 - 2.6	0.8 (0.02)	-770	No	Figure G-7
BY-105	0.1 - 1.1	0.4 (0.03)	-1500[4]	No	Figure G-8
BY-108	0.2 - 3.2	3.2 (0.15)	-590	No	Figure G-9
C-201	2.8 - 4.6	4.6 (0.40)	-690	No	Figure G-10
C-204	6.0 - 13	13[5] (1.1)	>-1200	No	Figure G-11
U-102	0.4 - 2.4	2.3 (0.12)	-620	No	Figure G-12
U-105	1.2 - 3.3	3.3 (0.10)	-630	No	Figure G-13
U-106	1.5 - 7.2	4.9[6] (0.15)	-880	No	Figure G-14

Notes: [1] Highest measured exothermic energy measured by DSC for the sample.

[2] Supernatant samples measured as high as 9.8 wt% TOC on a dry weight basis. The highest TOC measurement on a sample that also contained solids was 5.5 wt%. RSST tests were not performed on purely aqueous samples. Chemical speciation showed that the organic was about 70% low molecular weight acids and 30% chelators/chelator fragments.

[3] Standard deviation for sample measurements shown in parentheses.

[4] There was high variability in the DSC measurements for BY-105 waste. RSST was performed to further access the sample.

[5] Chemical speciation of the organic in tank C-204 showed that the TOC was tributyl phosphate solvent.

[6] Supernatant samples measured 4.8 to 7.2 wt% TOC on a dry weight basis, 25 - 36 g L^{-1} in solution. The highest TOC measurement on a sample that also contained solids was 4.9 wt%. RSST tests were not performed on purely aqueous samples.

Figure G-5. Change in Self-Heating Rate (dT/dt) as a Function of Temperature for AN-107 Tank Waste.

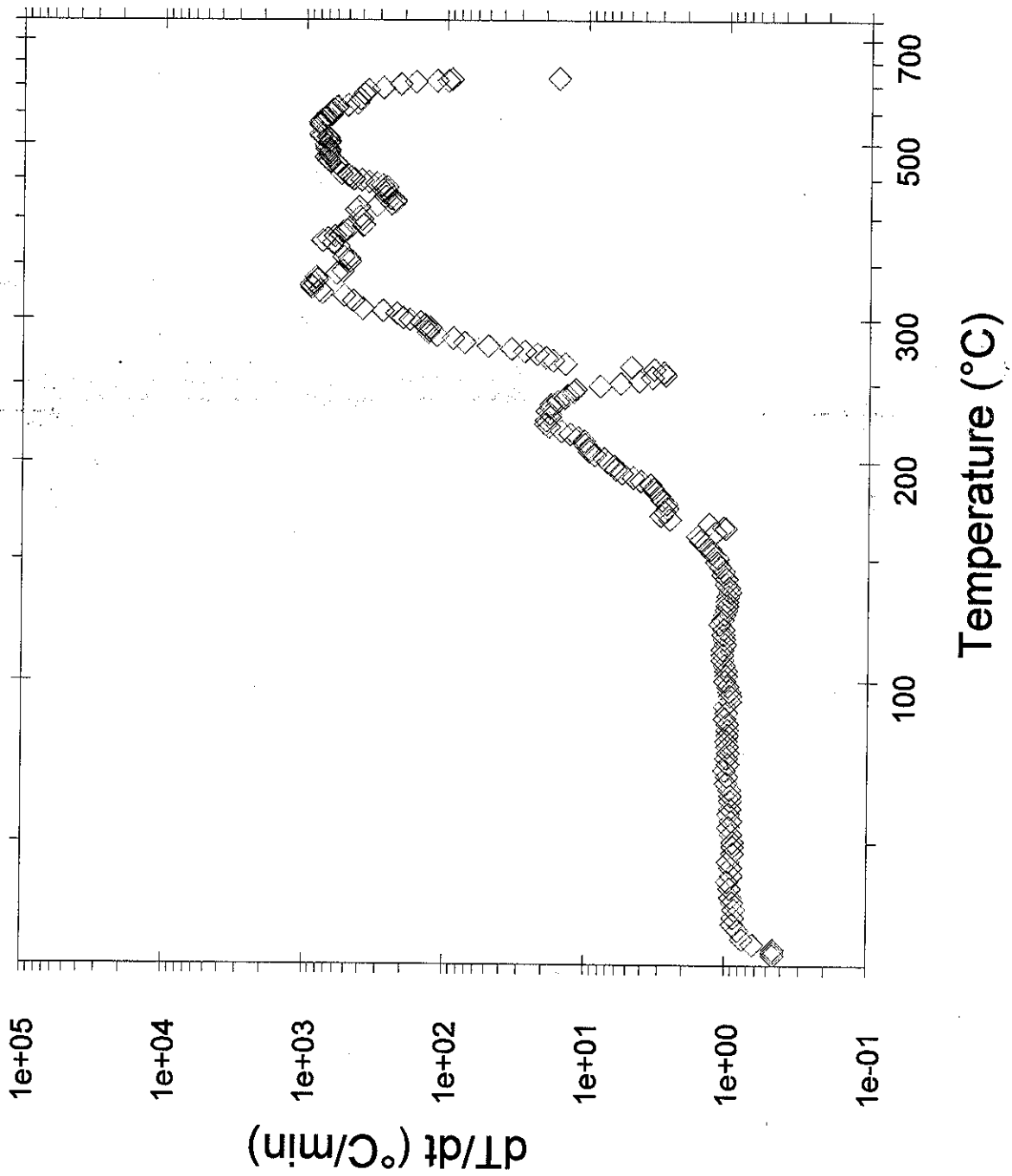


Figure G-6. Change in Self-Heating Rate (dT/dt) as a Function of Temperature for AW-101 Tank Waste.

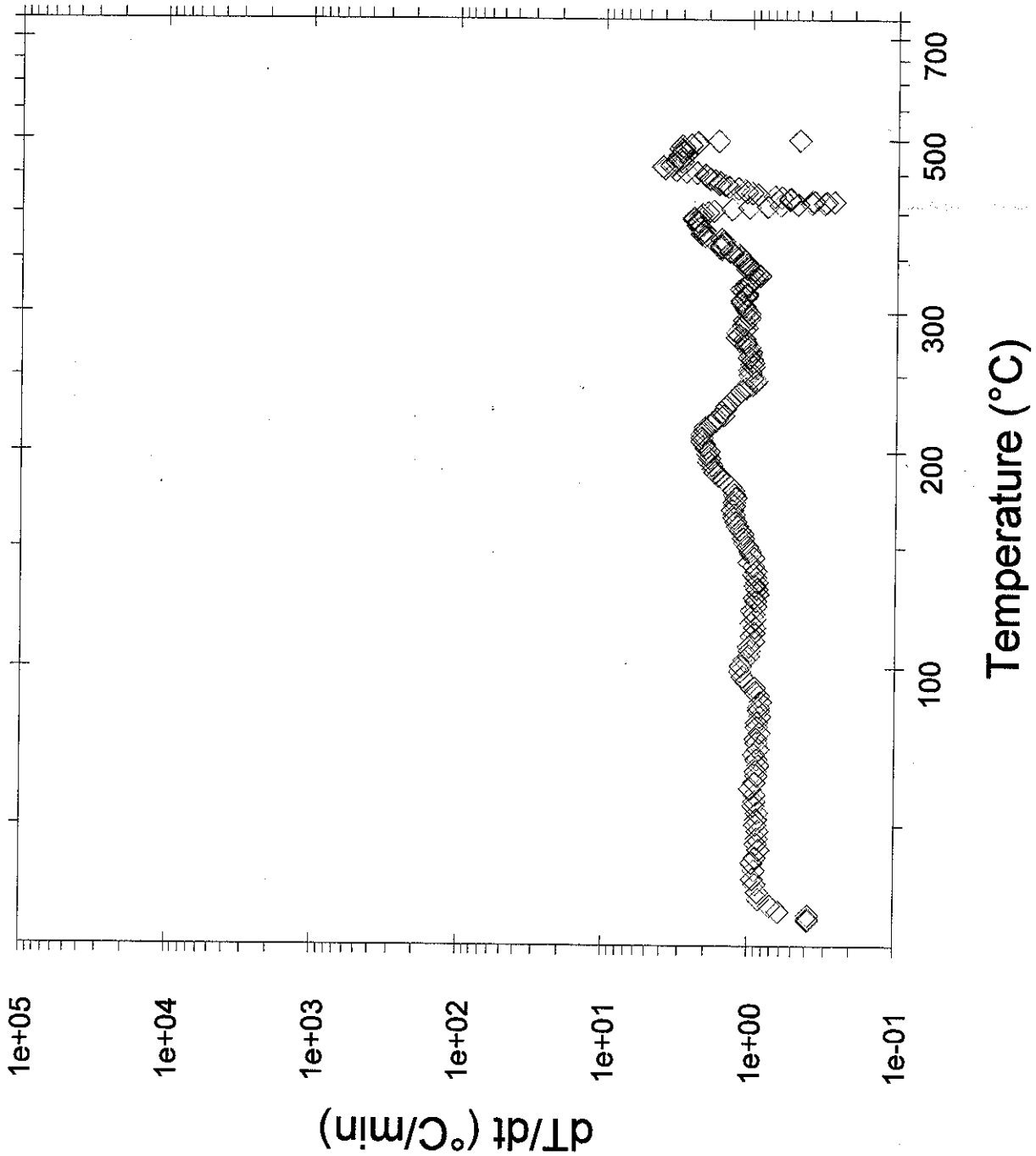


Figure G-7. Change in Self-Heating Rate (dT/dt) as a Function of Temperature for BY-104 Tank Waste.

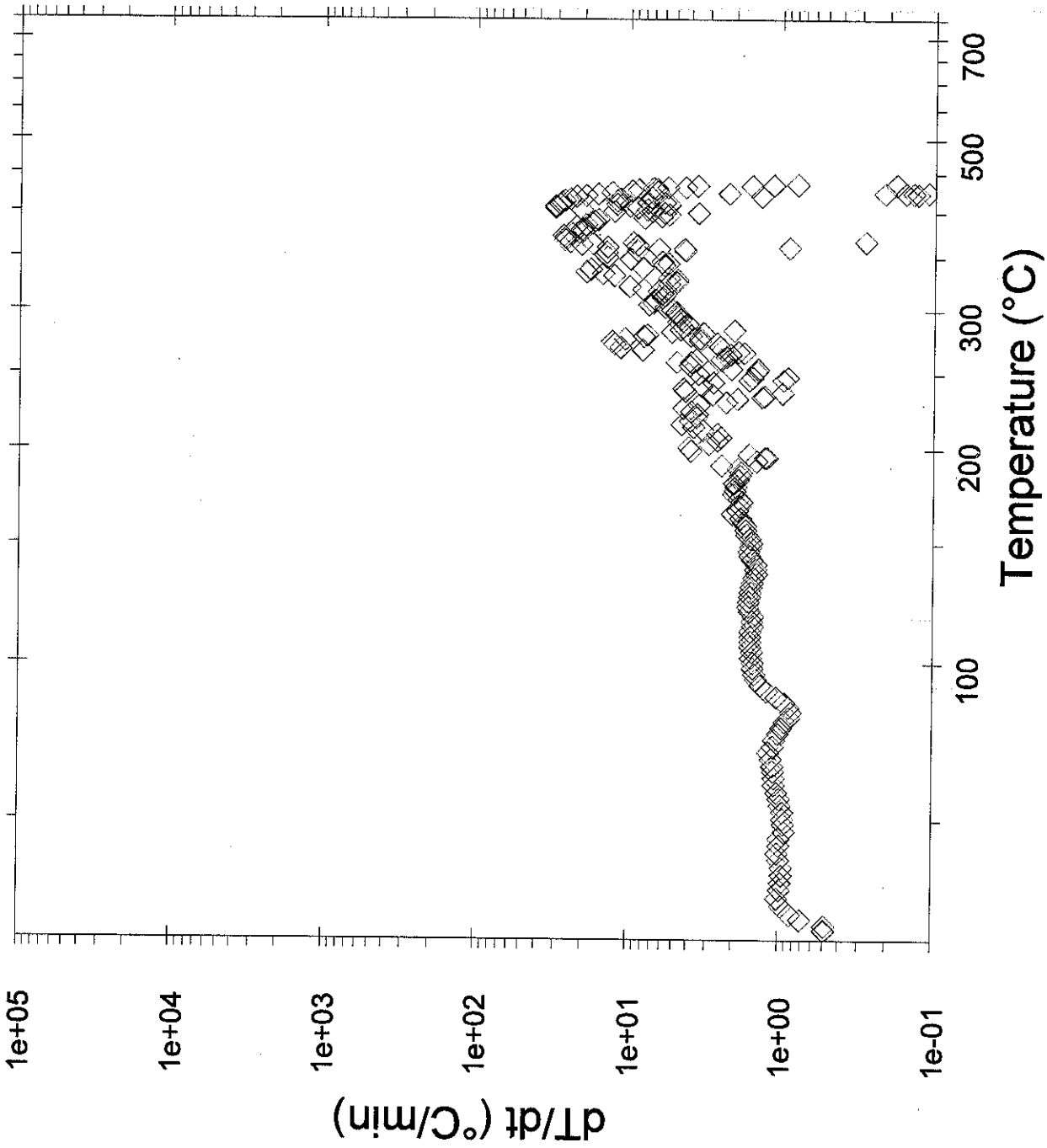


Figure G-8. Change in Self-Heating Rate (dT/dt) as a Function of Temperature for BY-105 Tank Waste.

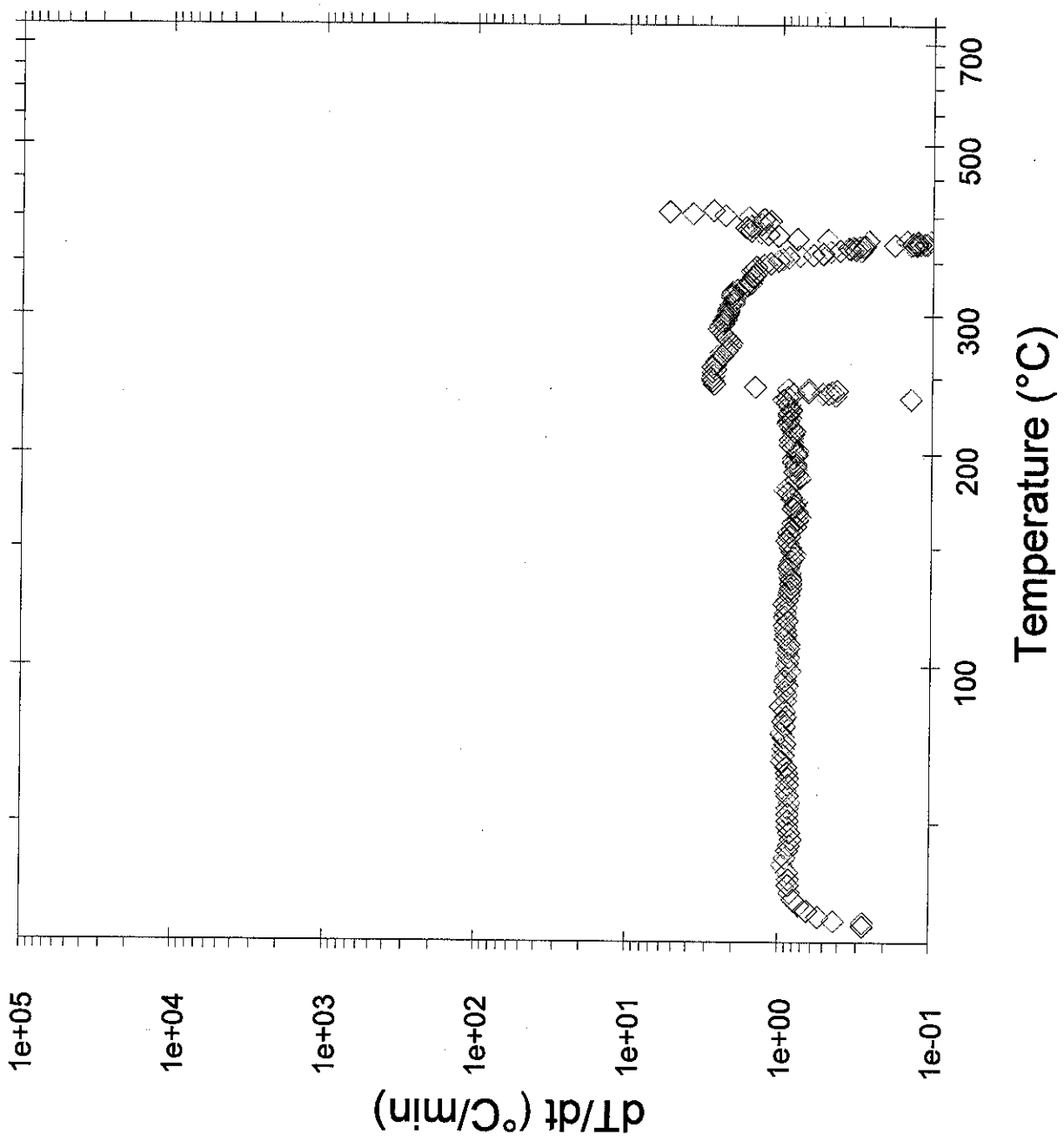


Figure G-9. Change in Self-Heating Rate (dT/dt) as a Function of Temperature for BY-108 Tank Waste.

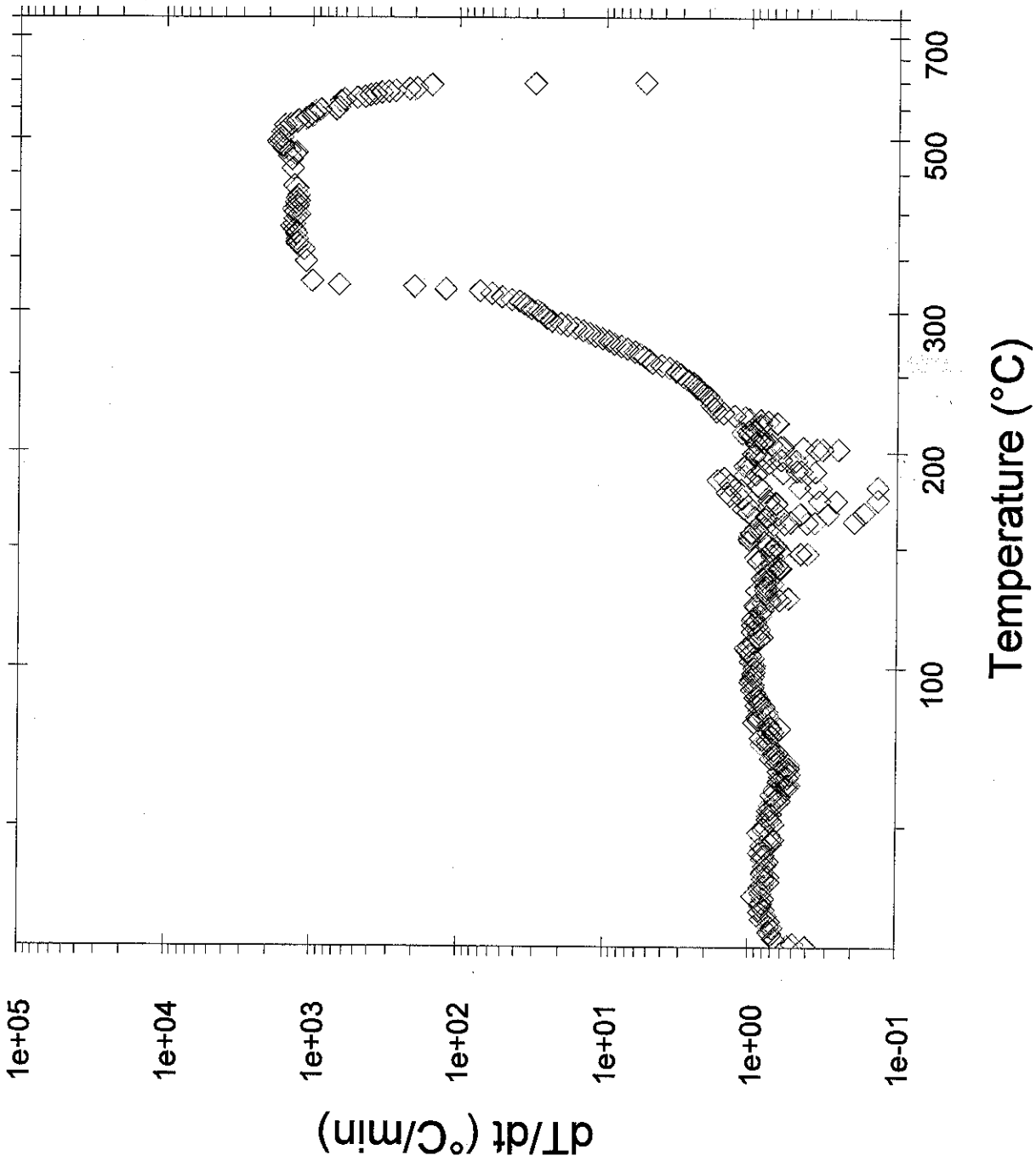


Figure G-10. Change in Self-Heating Rate (dT/dt) as a Function of Temperature for C-201 Tank Waste.

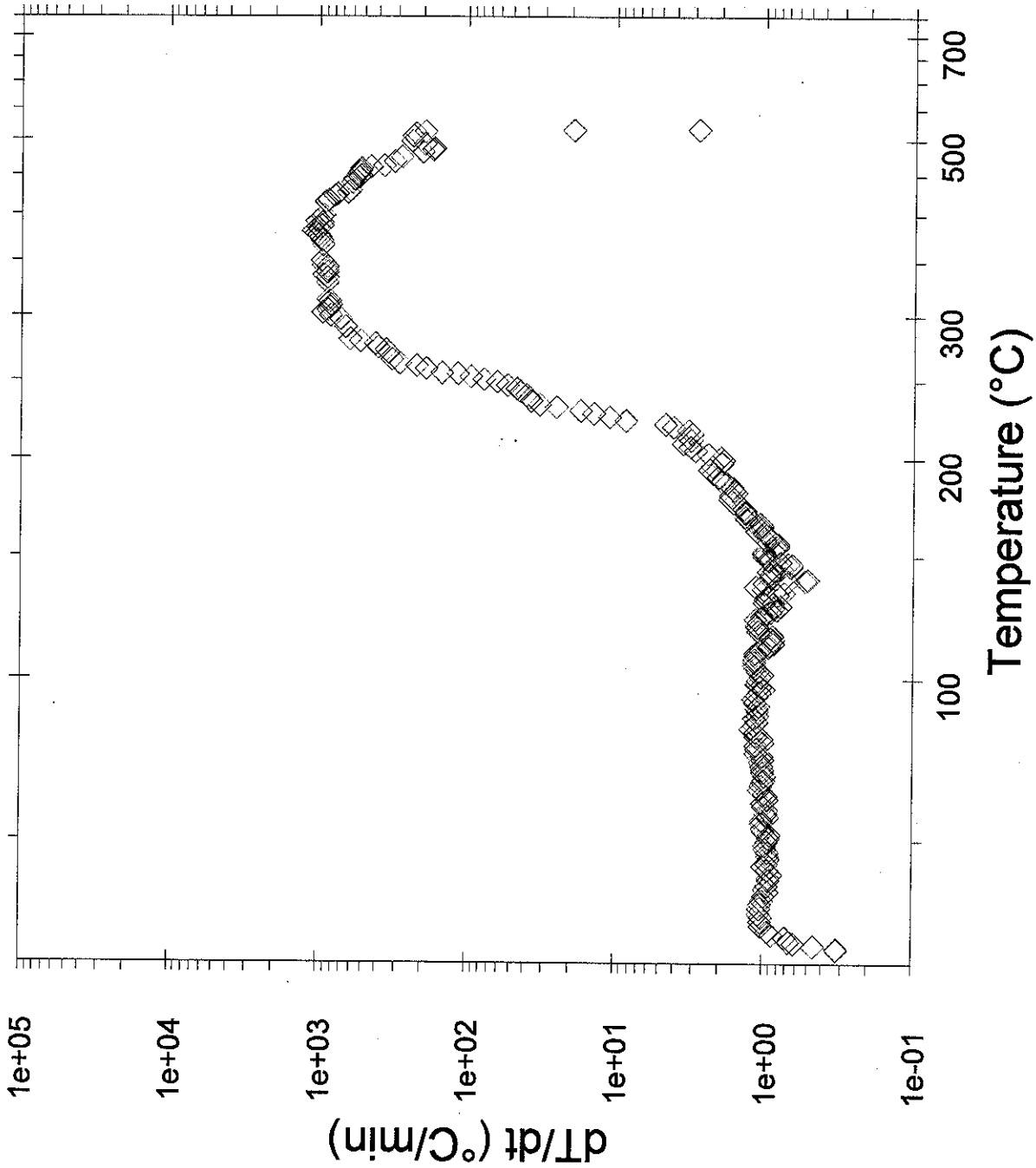


Figure G-11. Change in Self-Heating Rate (dT/dt) as a Function of Temperature for Tank C-204 Waste.

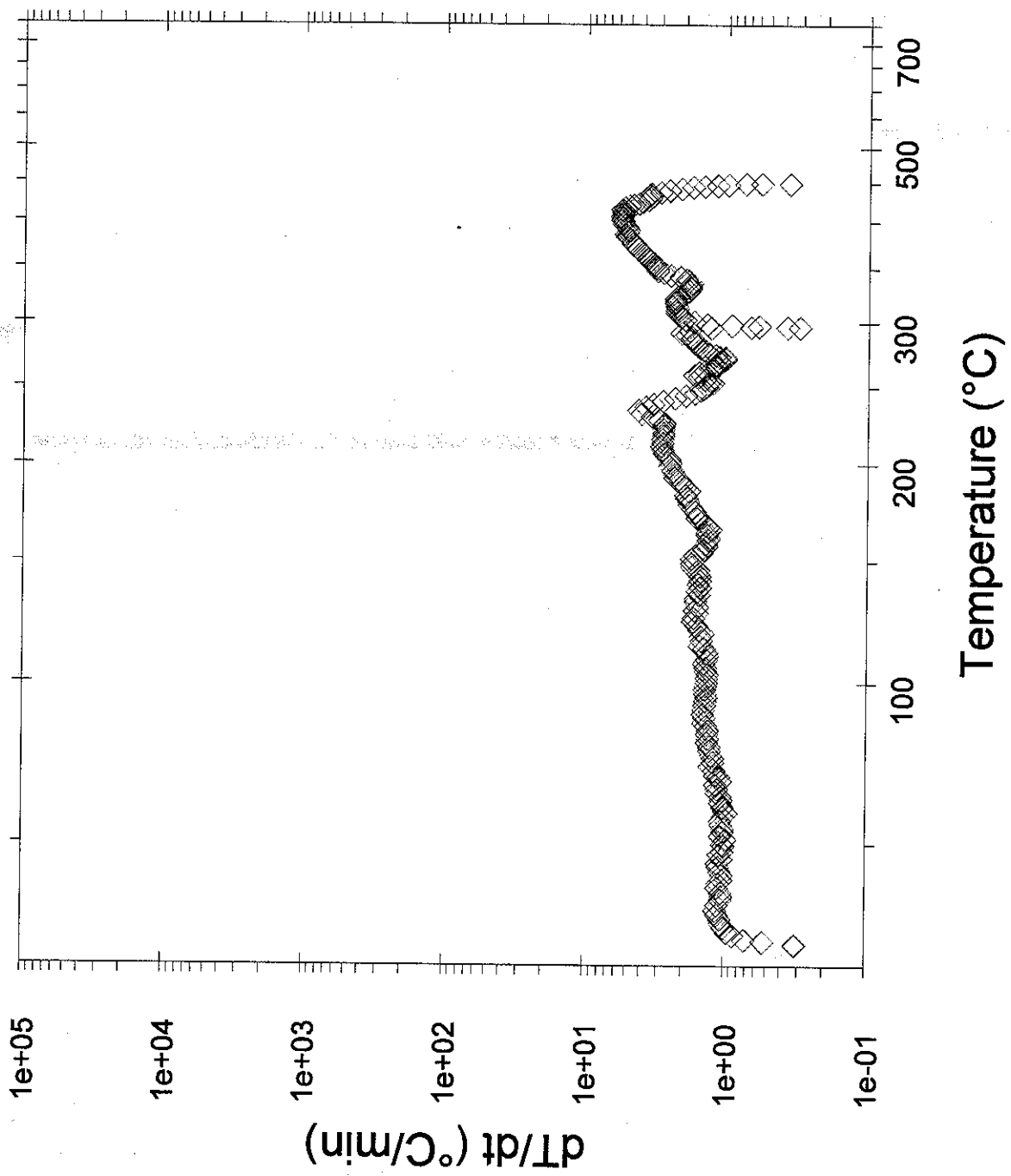


Figure G-12. Change in Self-Heating Rate (dT/dt) as a Function of Temperature for Tank U-102 Waste.

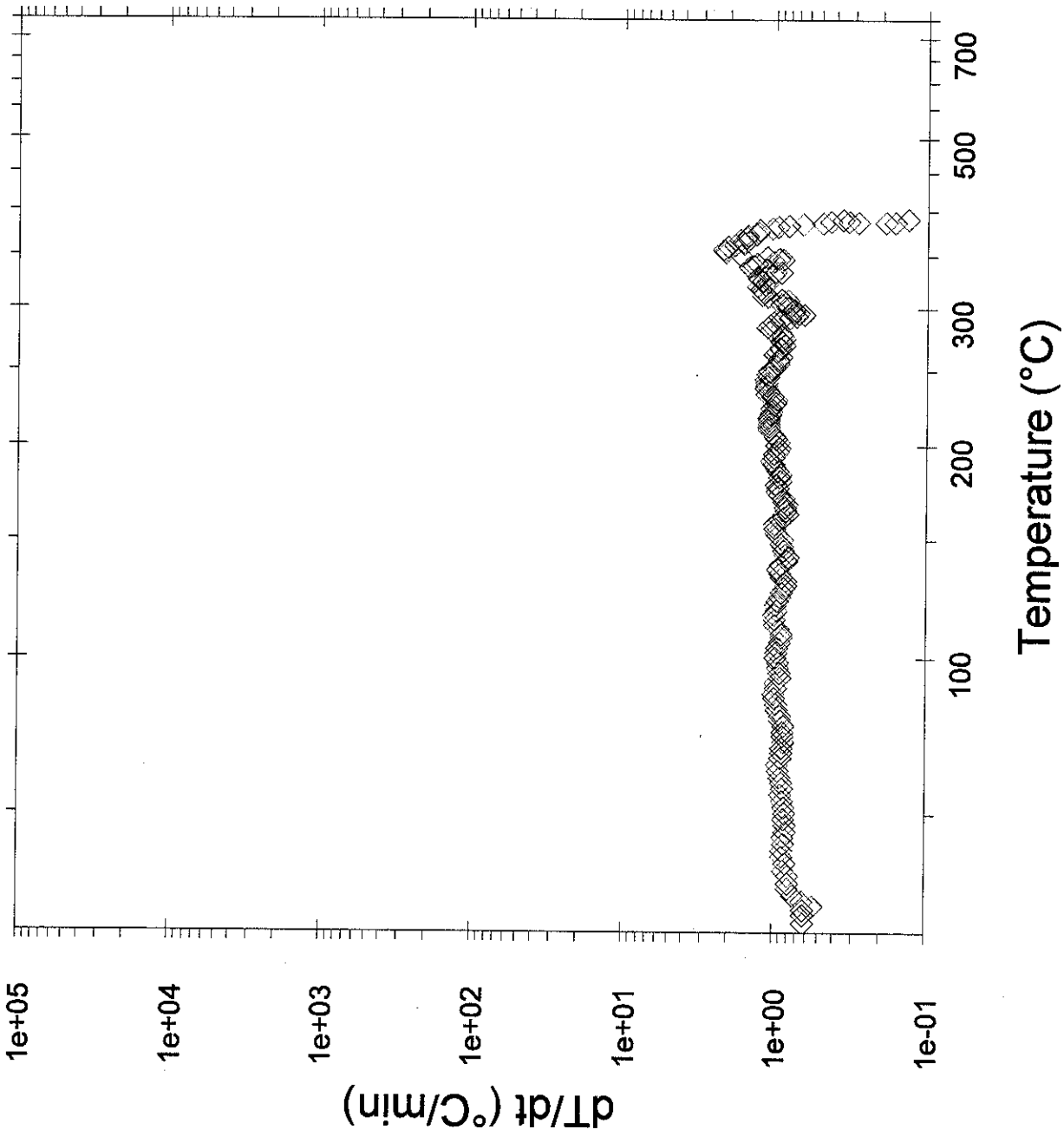


Figure G-13. Change in Self-Heating Rate (dT/dt) as a Function of Temperature for Tank U-105 Waste.

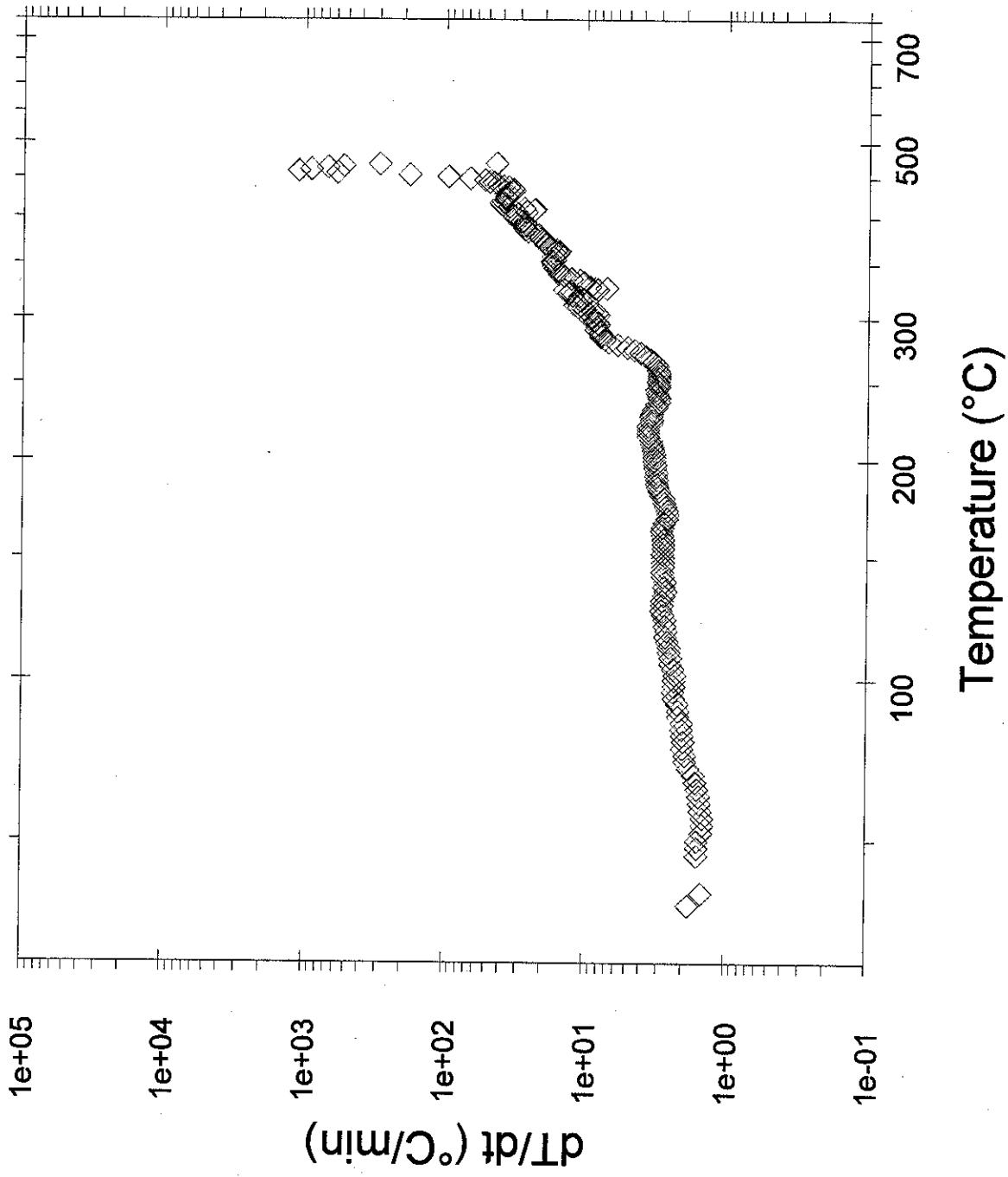
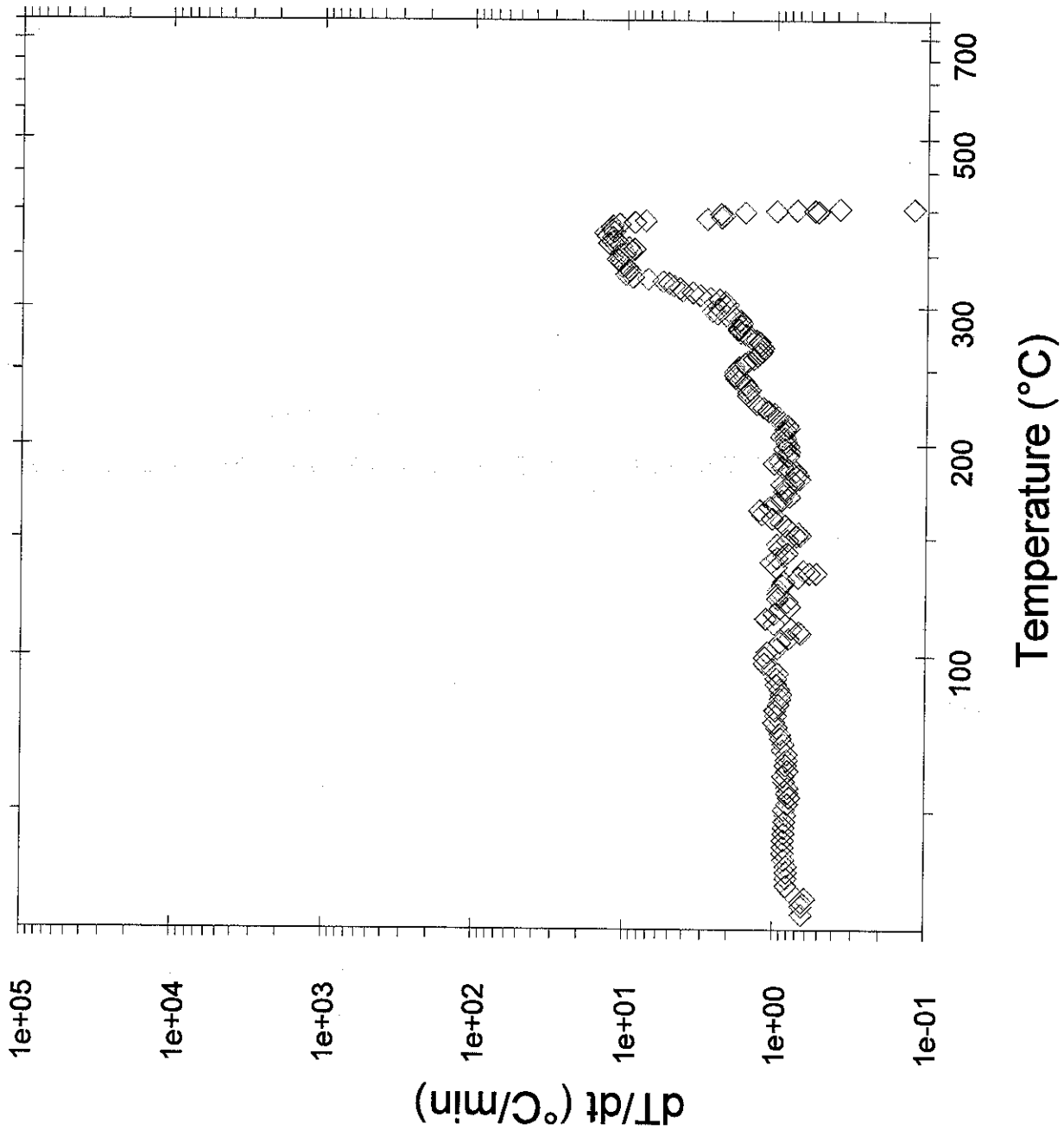


Figure G-14. Change in Self-Heating Rate (dT/dt) as a Function of Temperature for Tank U-106 Waste.



When interpreting the RSST test results, there are two important parameters to examine, the peak reaction rate and any transition from typical Arrhenius or runaway behavior (i.e., a doubling of reaction rate for every 10 °C rise in temperature) to a propagation (i.e., a step increase in reaction rate as the combustion front passes the embedded thermocouple). Figure G-2 shows a propagation in a waste simulant containing 7.0 wt% TOC as sodium acetate. From the figure, at 290 °C the reaction rate was about 105 °C per minute, and at 360 °C the peak reaction rate was about 3 E4 °C per minute. Over this 70 °C temperature increase, a typical Arrhenius reaction would increase by 2^7 (a factor of 128). The observed change was a factor of 300, a clear propagation.

The most energetic RSST results were for waste samples from AN-107 (Figure G-5), BY-108 (Figure G-9), C-201 (Figure G-10), and U-105 (Figure G-13). For AN-107, the peak reaction rate was about 800 °C per minute. The test shows a chemical reaction between 250 – 350 °C. A typical Arrhenius change would be a factor of 2^{10} (1,024) and the observed change was about a factor of 785. For BY-108, the peak rate was about 1 E3 °C per minute (over an order of magnitude less than the 3 E4 °C per minute observed in the simulant propagation experiment). The observed change in reaction rate between 240 – 350 °C was about a factor of 1,000, and a typical Arrhenius would be 2^{11} (2,048). For C-201, the peak reaction rate was 1,000 °C per minute. The observed change in reaction rate between 220 and 320 °C was a factor of about 970, and a typical Arrhenius change would be 2^{10} (1,024).

For U-105, the peak reaction rate was 2 E3. The measured change in reaction rate between 300 and 450 °C was a factor of 970, and a typical Arrhenius would be 2^{15} (32,768). It is interesting to note that there was a distinct transition at 450 °C where the reaction rate increases by an order of magnitude. However, transitions at these high temperatures are not relevant to safe storage because there is no intent to store wastes at 450 °C.

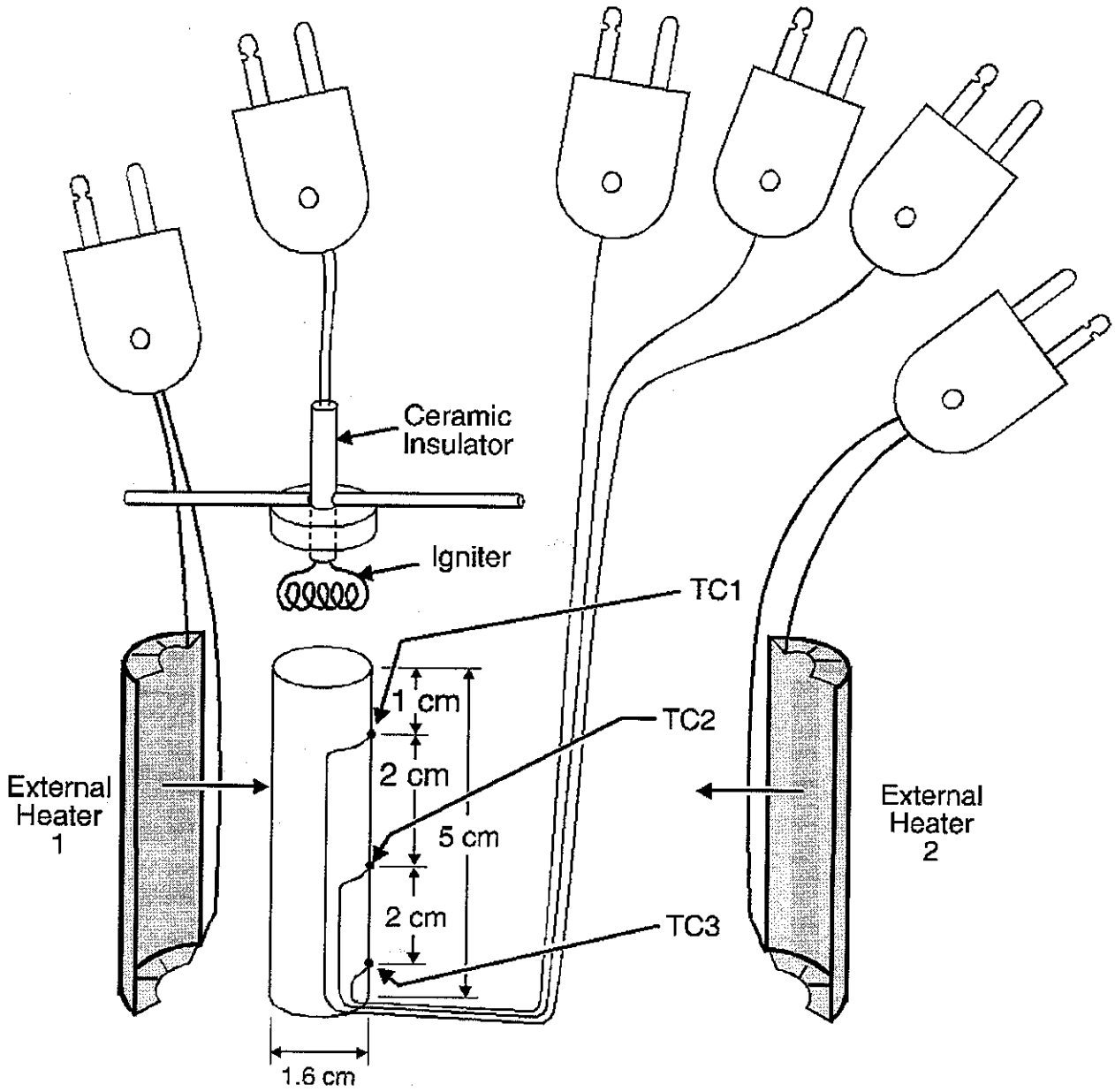
4.2 PROPAGATING REACTIVE SYSTEM SCREENING TOOL (PRSST)

4.2.1 Description of PRSST Apparatus

The PRSST System features a 1.6 cm diameter, 5 cm long cylindrical test cell made out of thin stainless steel (Figure G-15). The sample holder is wrapped in insulation, similar to the RSST sample holder illustrated in Figure G-3. Along the length of this cell are placed three thermocouples. A small wire coil ignitor is immersed in the top of the sample. When the ignitor fires (~ 20 W), if the sample's composition is such that a propagating reaction front can be sustained, the reaction front will proceed down the length of the sample. The thermocouples placed along the length of the cell will indicate the passing of the reaction front. Also, the speed of propagation of the reaction front can be determined by simple distance/time calculations using the thermocouple locations and time temperature histories.

In addition to the ignitor circuit, the PRSST is equipped with a standard type RSST heater element for performing typical RSST constant heat-up rate tests. This heater is also capable of holding constant sample temperature.

Figure G-15. Illustration of Propagating Reactive System Screening Tool Test Cell.



The test cell is contained in a one liter pressure sealed containment vessel. The vessels were specifically equipped to facilitate remote operation using manipulators (necessary for handling radioactive samples).

4.2.2 PRSST Test Results on Waste Samples

Tank wastes that had the highest TOC concentrations (Figure G-16) were tested for propagation in the PRSST. As shown in Figure G-16, the waste samples contained considerable water. The waste samples were dried to constant mass at 105 °C under vacuum, to maximize the potential for propagation. The samples were pulverized to ensure intimate mixing of fuel and oxidizer, and placed in the test cell. Before the ignitor was fired, the sample was heated to the tank ambient temperature and held there for one-half hour to ensure uniform temperature. Thermocouple 1 is close to the ignitor and can verify that the ignitor worked. Thermocouples 2 and 3 measure a rapid increase in temperature as a propagation front passes. The increased temperatures are accompanied by a pressure increase. An example of propagation is shown in Figure G-17 for a simulant mixture containing 7.0 wt% TOC (as sodium HEDTA).

A split of each dried waste sample tested in the PRSST was analyzed for water and TOC concentration. Waste sample propagation test results are reviewed in Table G-5 and Figures G-18 through G-23.

Table G-5. PRSST Test Results on Dried Tank Waste Samples.

Tank	TOC of Sample tested (wt%, dry)	Propagate	Notes
A-102	2.1 (0.1)*	No	Figure G-18
AX-102	4.8 (0.8)	No	Figure G-19
C-104	2.3 (0.2)	No	Figure G-20
C-201	2.8 (0.5)	No	Figure G-21
C-202	2.6 (0.1)	No	Figure G-22
SX-101	1.6 (0.05)	No	Figure G-23
U-105	1.4 (0.2)	No	Figure G-24
U-106	3.6 (0.4)	No	Figure G-25

Notes: *Standard deviation for sample measurements shown in parentheses.

Figure G-16. Total Organic Carbon and Water Concentrations for the Single-Shell Tanks.

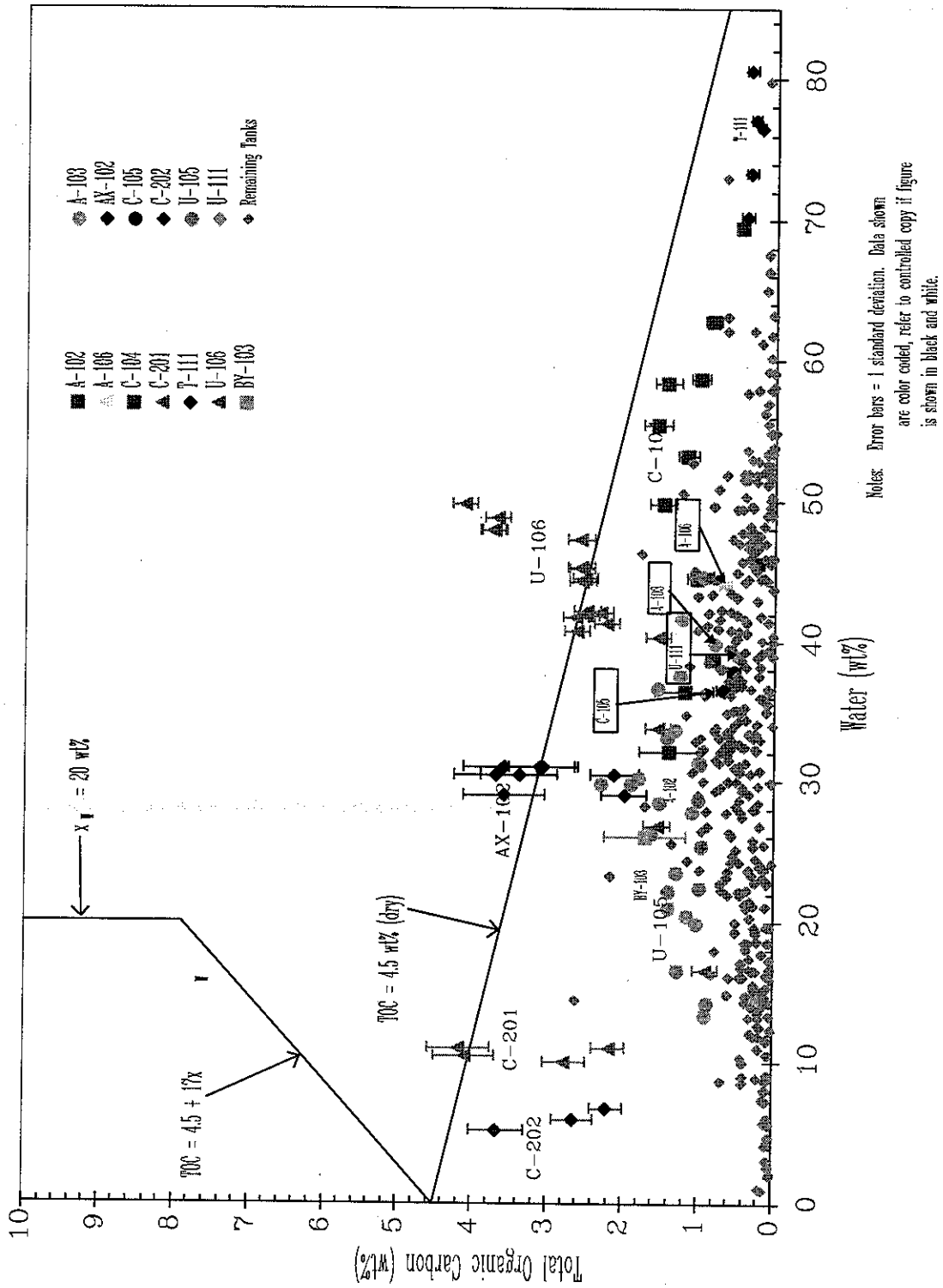


Figure G-17. PRSST Results Showing Propagation in a Waste Simulant Containing 7.0 wt% Total Organic Carbon (HEDTA).

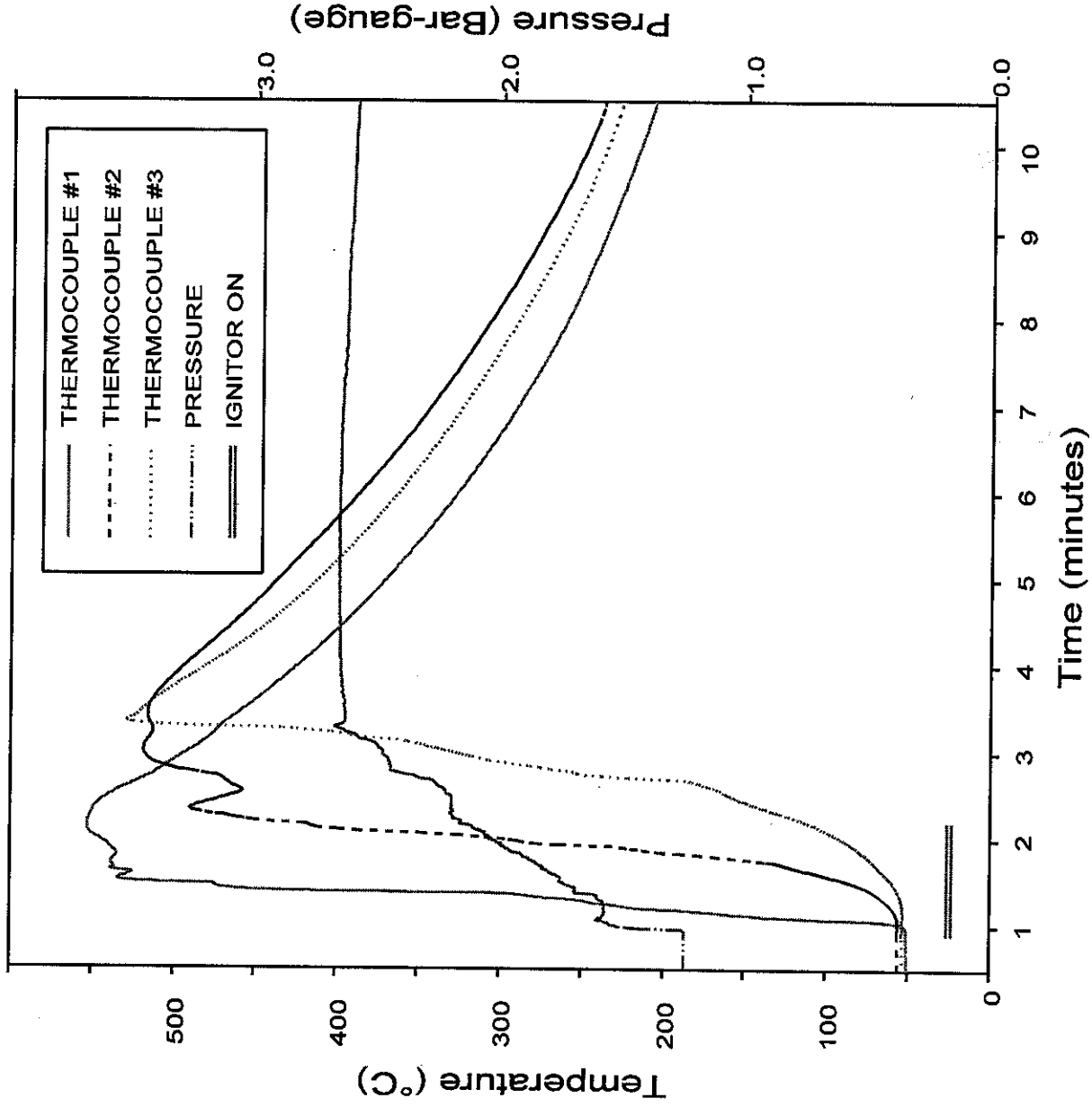


Figure G-18. Temperature Verses Time Plot Showing No Propagation for Dried A-102 Waste Sample.

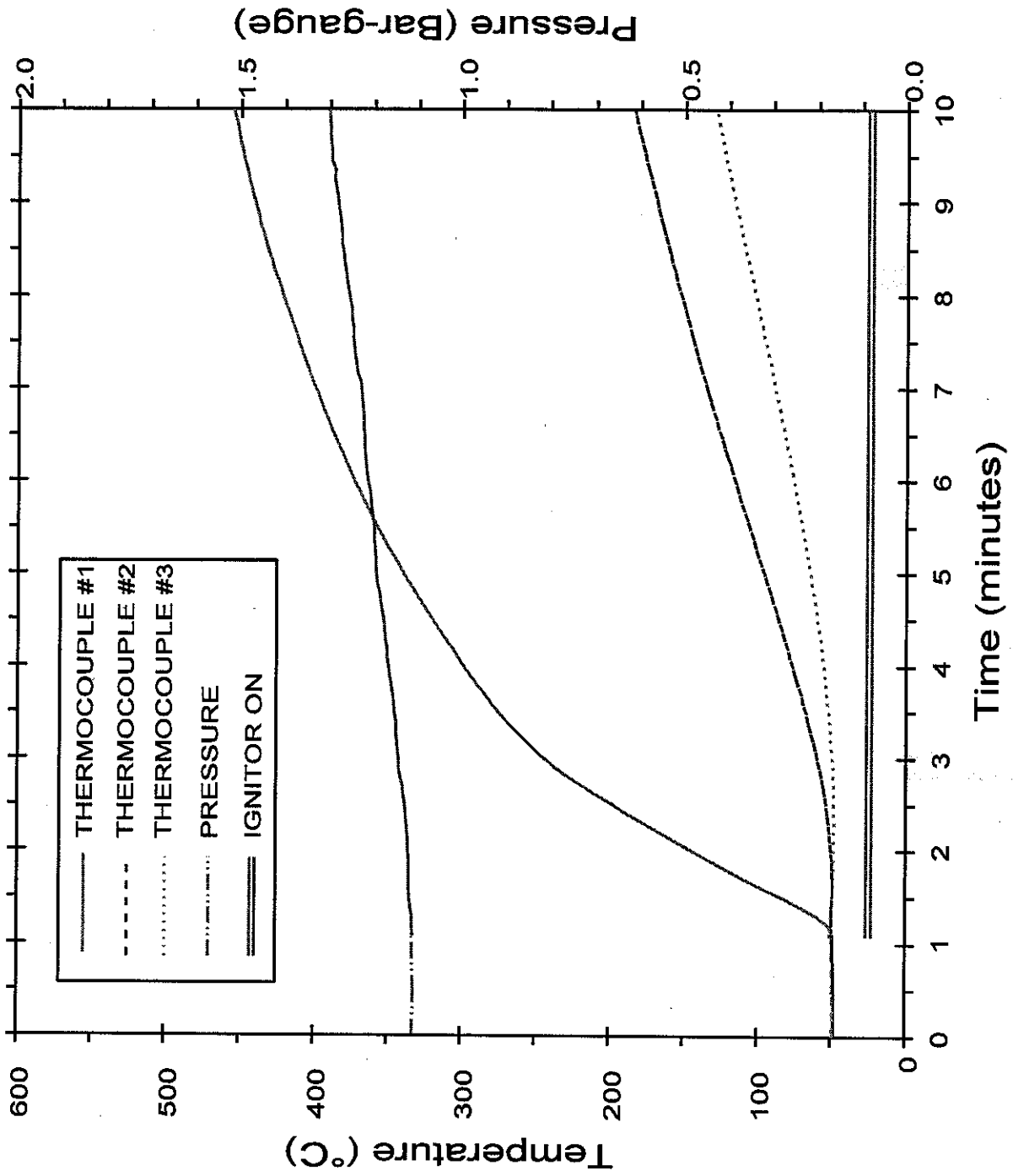


Figure G-19. Temperature Verses Time Plot Showing No Propagation for Dried AX-102 Waste Sample.

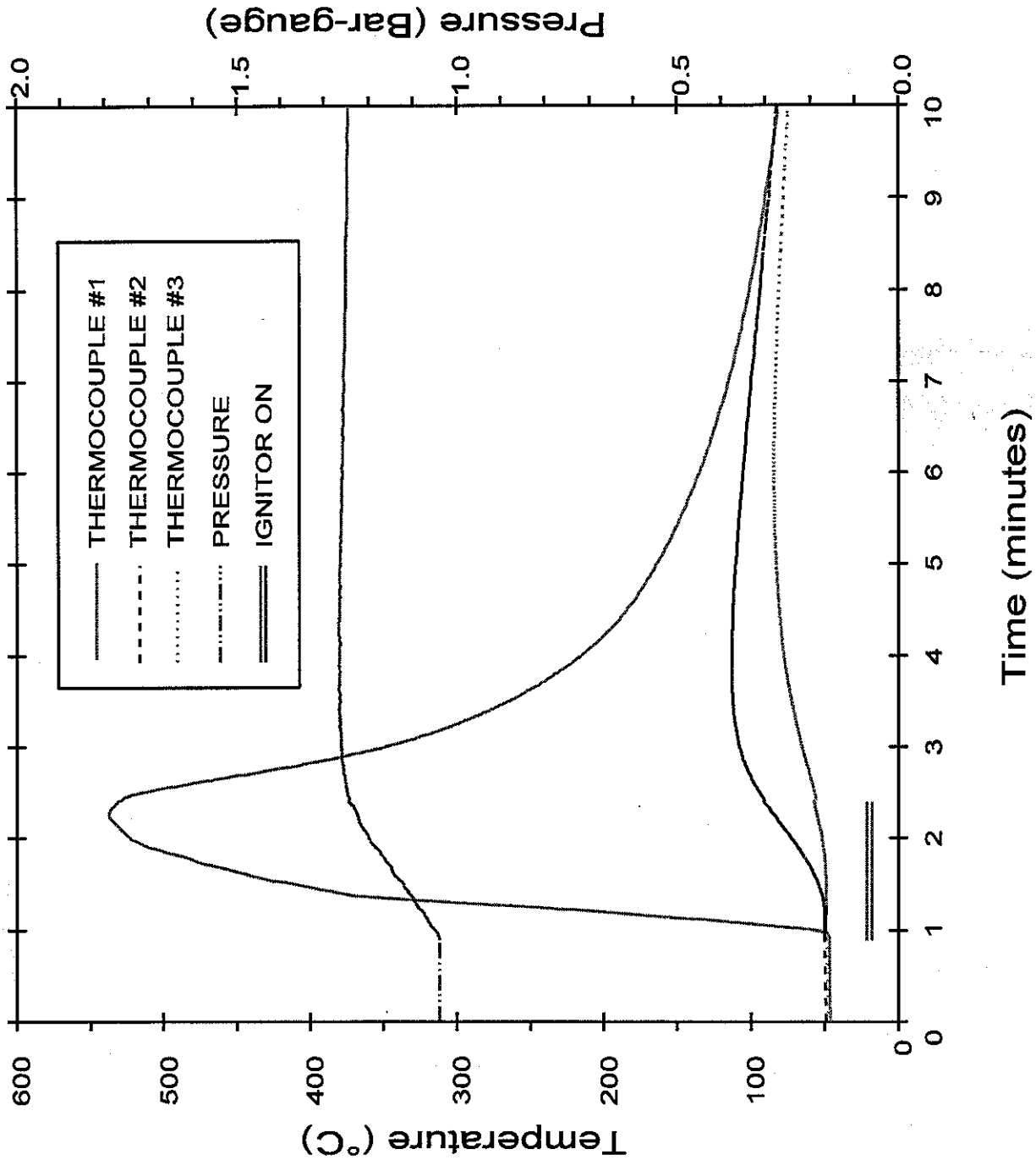


Figure G-20. Temperature Verses Time Plot Showing No Propagation for Dried C-104 Waste Sample.

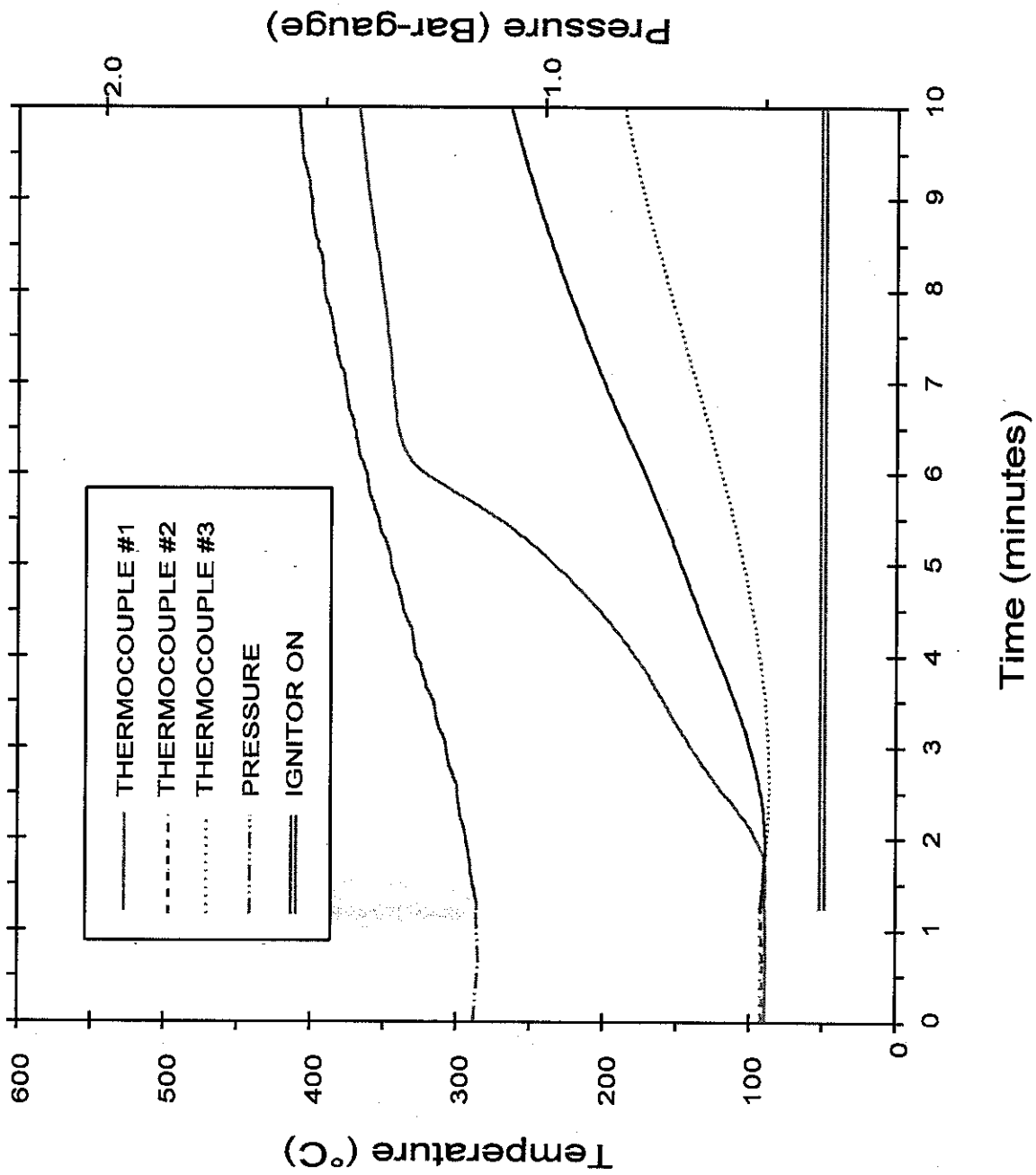


Figure G-21. Temperature Verses Time Plot Showing No Propagation for Dried C-201 Waste Sample.

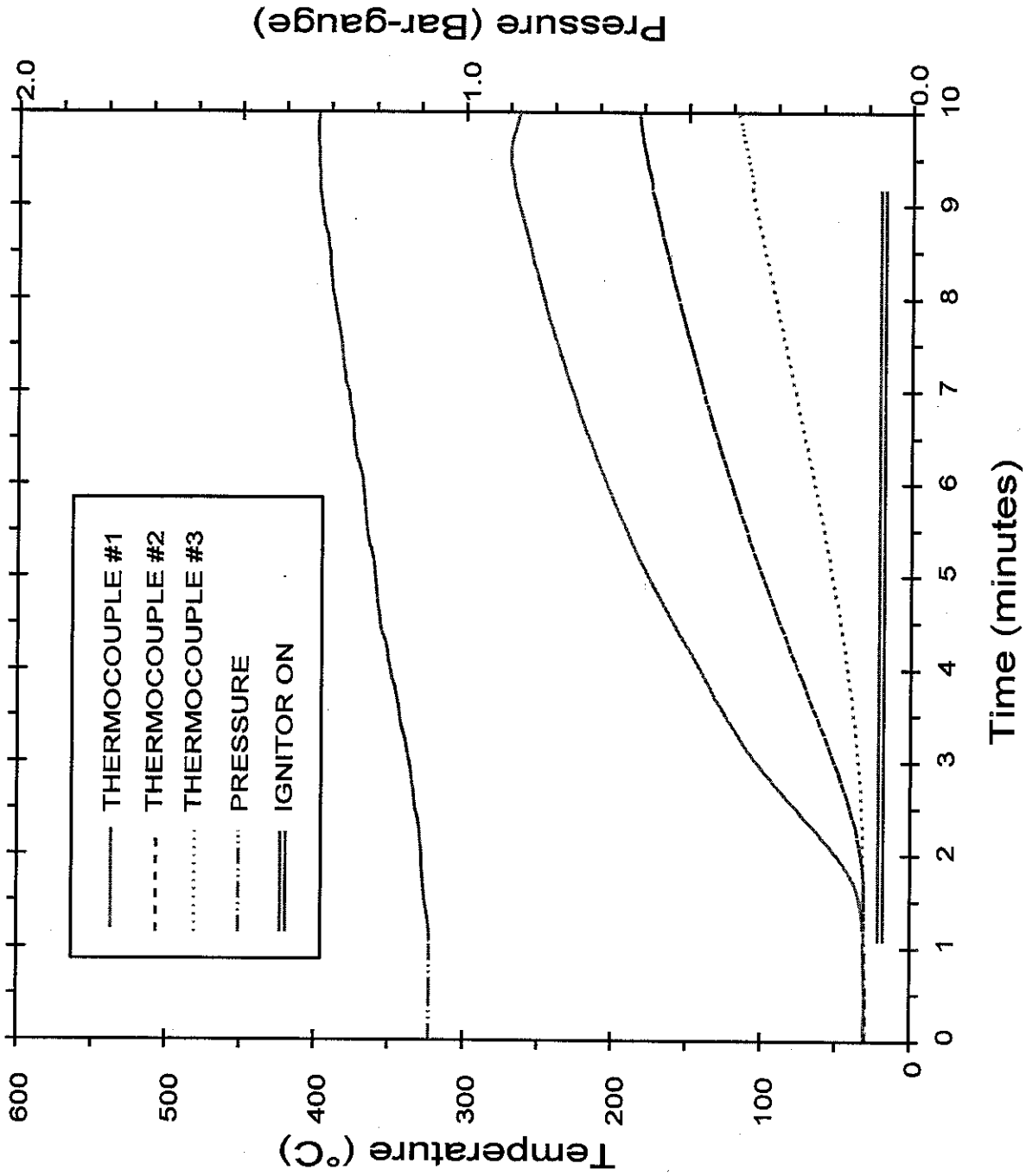


Figure G-22. Temperature Verses Time Plot Showing No Propagation for Dried SX-101 Waste Sample.

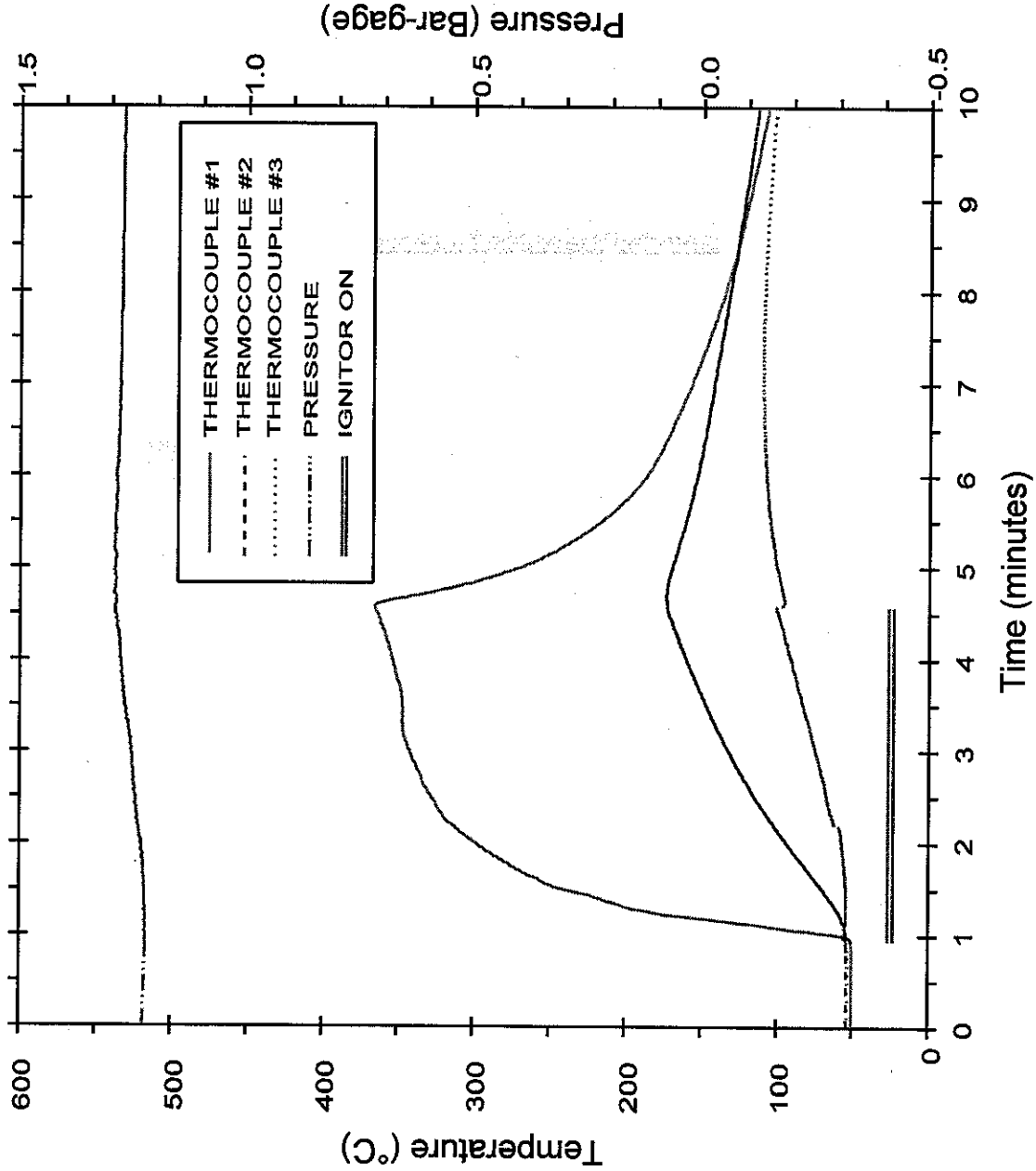


Figure G-23. Temperature Verses Time Plot Showing No Propagation for Dried C-202 Waste Sample.

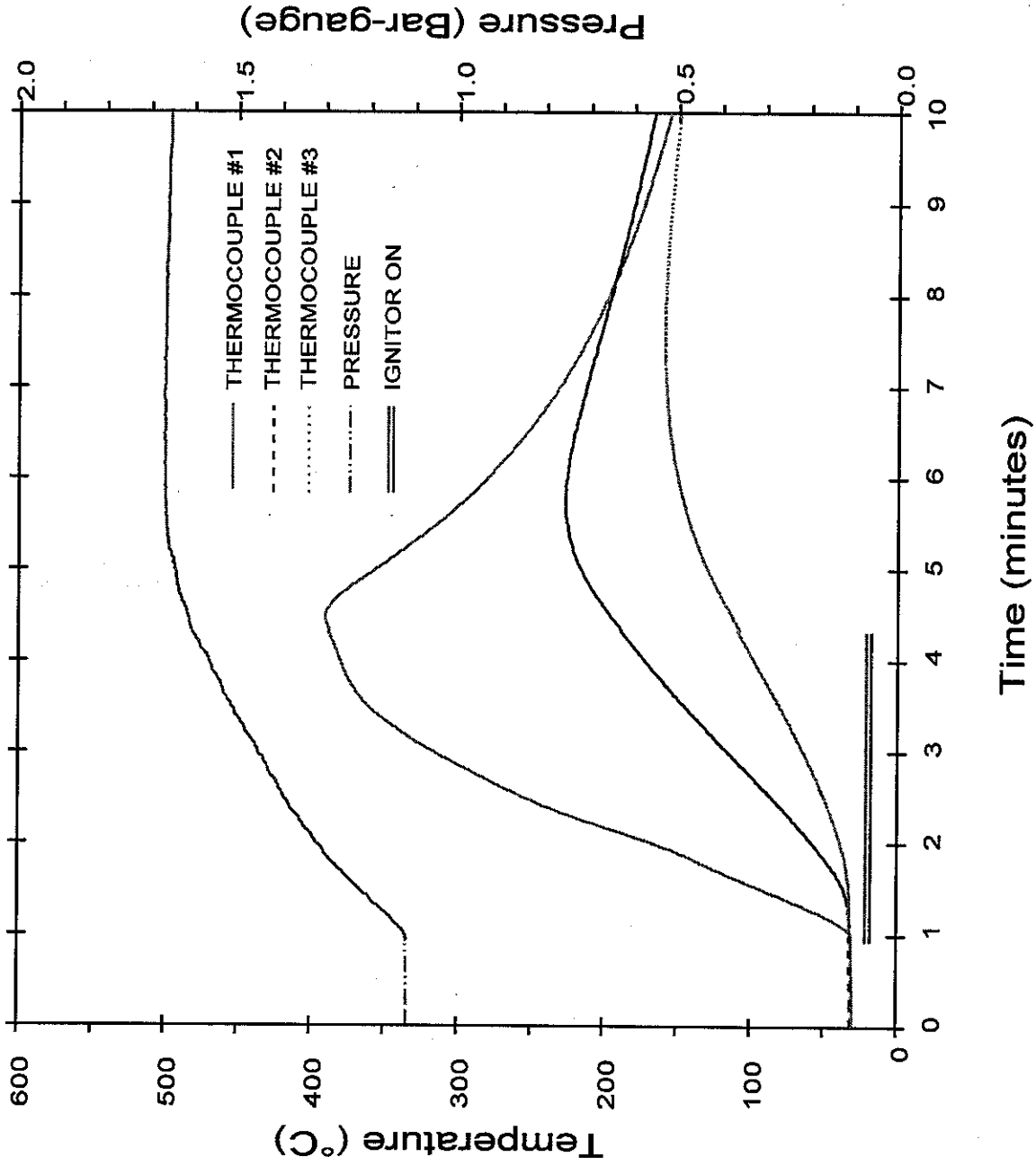


Figure G-24. Temperature Verses Time Plot Showing No Propagation for Dried U-105 Waste Sample.

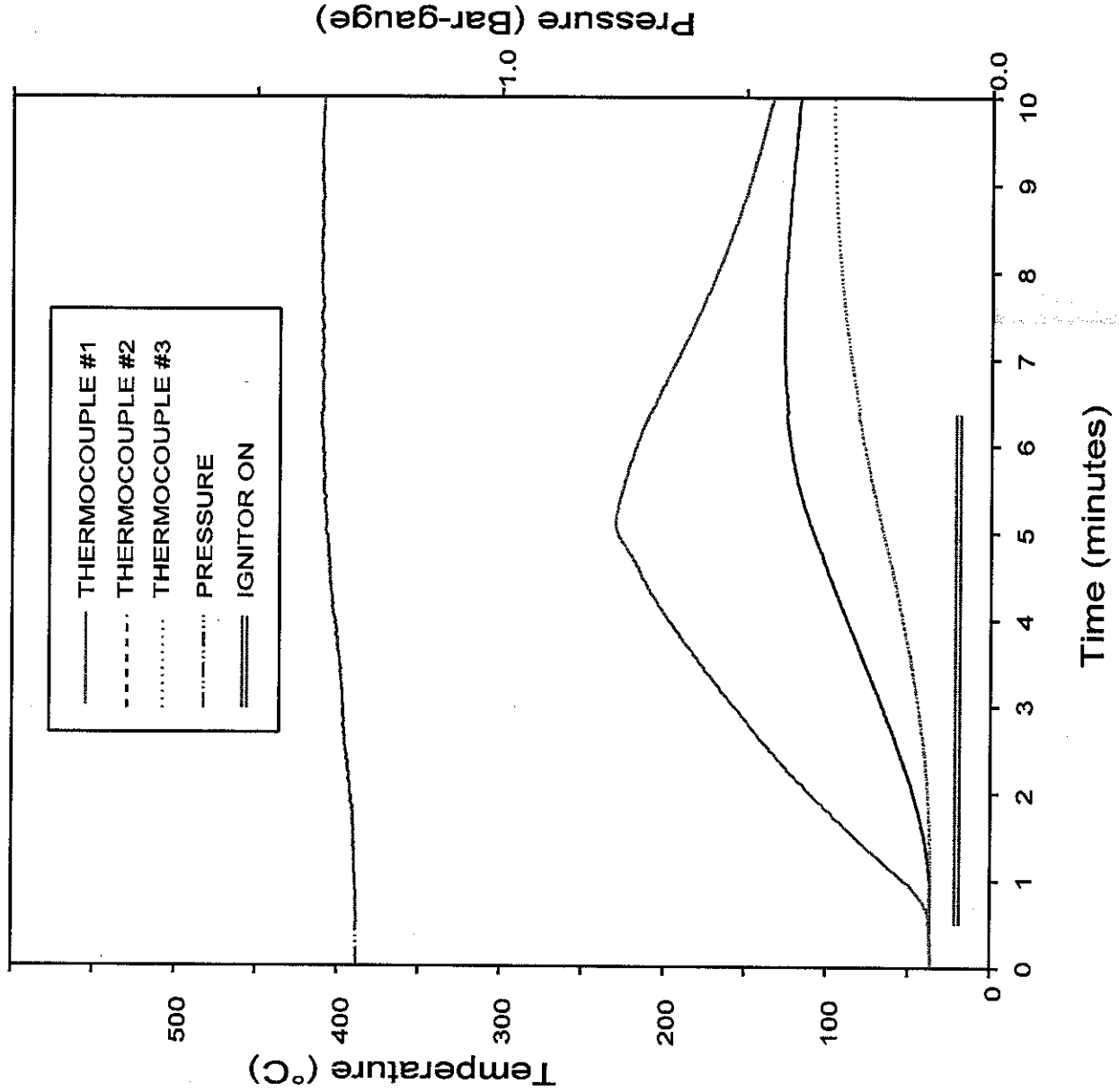
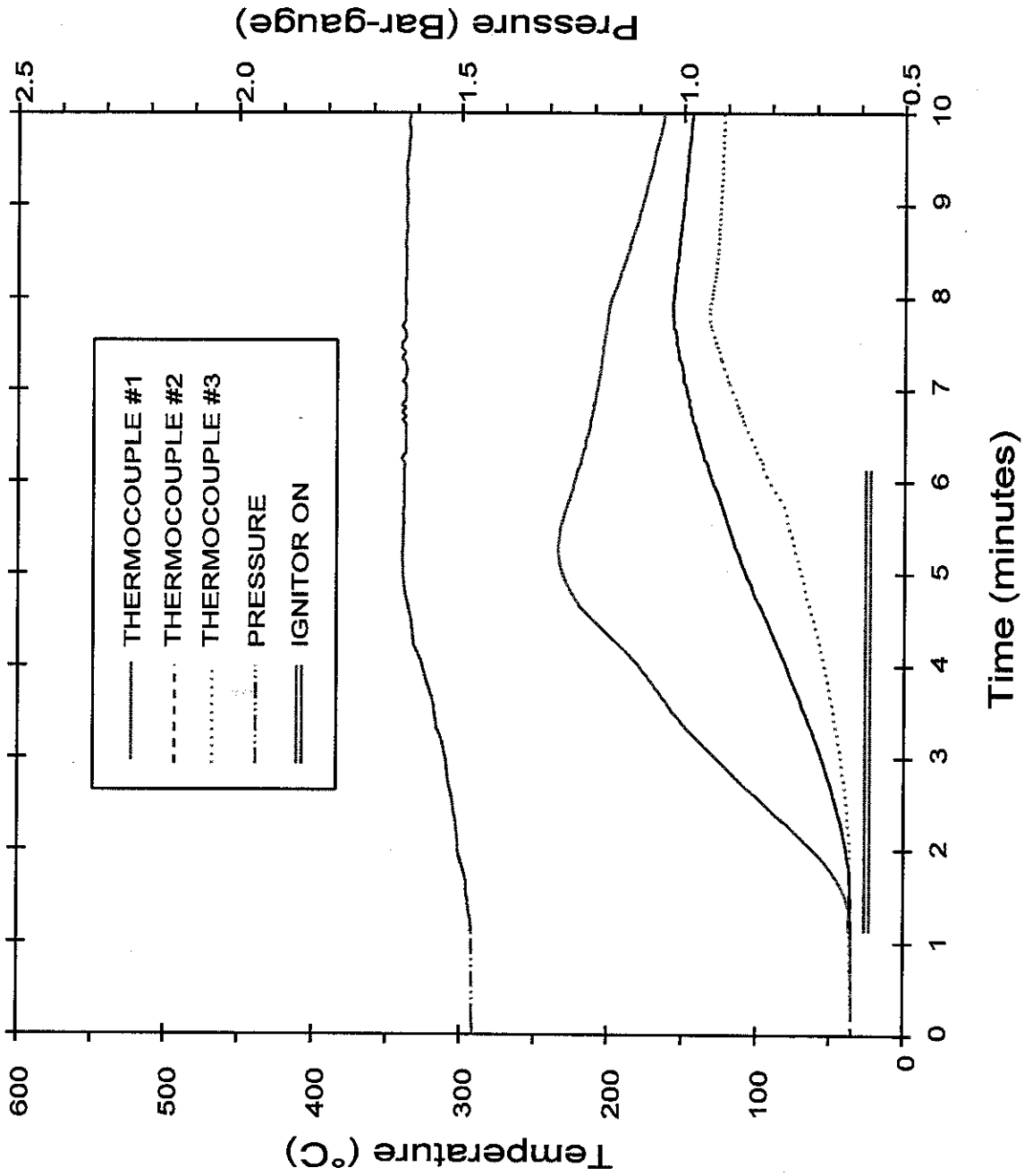


Figure G-25. Temperature Verses Time Plot Showing No Propagation for Dried U-106 Waste Sample.



From Table G-5 and Figures 18 through 23, none of the tank waste samples exhibited propagation. Some samples were spiked with sodium HEDTA to quantify how much more fuel would be required to sustain propagation, and results are discussed in Section 4.2.3.

4.2.3 PRSST Test Results on Spiked Waste Samples

As shown in Tables G-4 and G-5, none of the dried waste samples propagated. To access the safety margin between the waste fuel concentration and that required for propagation, tank wastes with the highest TOC concentrations were spiked with additional fuel (sodium HEDTA) and reanalyzed using the PRSST. About 200 g of waste were required to complete the suite of spike tests for each tank, therefore, the waste samples (segments) with the highest TOC were composited to ensure sufficient material was available for testing. Sodium HEDTA was added to the dried waste samples as a solution (containing 60 or 330 grams of HEDTA per liter) and the mixture was dried to constant mass at 105 °C under vacuum. HEDTA was used because it has the highest theoretical combustion energy of the complexants used at Hanford (Burger 1993), and the simulant mixtures containing HEDTA propagated at the lowest TOC concentrations (see Figure G-4). Results are shown in Table G-6 and Figures G-26 through G-34.

Table G-6. PRSST Test Results on Dried Waste Samples Spike with HEDTA.

Tank	TOC of Dried Composite Sample (wt%, dry)	TOC with HEDTA Added (wt%, dry)	Propagate	Notes
AX-102	4.8 (0.8)*	5.4 (0.18)	No	-----
AX-102	4.8 (0.8)	5.5 (0.00)	No	Figure G-26
AX-102	4.8 (0.8)	6.3 (0.43)	Yes	Figure G-27
C-202	2.6 (0.1)	4.3 (0.20)	No	Figure G-28
C-202	2.6 (0.1)	7.1 (0.35)	No	Figure G-29
U-105	1.4 (0.2)	5.8 (0.51)	No	-----
U-105	1.4 (0.2)	5.8 (0.24)	No	Figure G-30
U-105	1.4 (0.2)	6.9 (0.40)	Yes	Figure G-31
U-106	3.6 (0.4)	4.3 (0.41)	No	-----
U-106	3.6 (0.4)	4.4 (0.10)	No	Figure G-32
U-106	3.6 (0.4)	5.1 (0.40)	Yes	Figure G-33
U-106	3.6 (0.4)	5.9 (0.80)	Yes	Figure G-34

Notes: *Standard deviation for sample measurements shown in parentheses.

Figure G-26. Temperature Verses Time Plot Showing No Propagation for Dried AX-102 Waste Spiked to 5 wt% Total Organic Carbon.

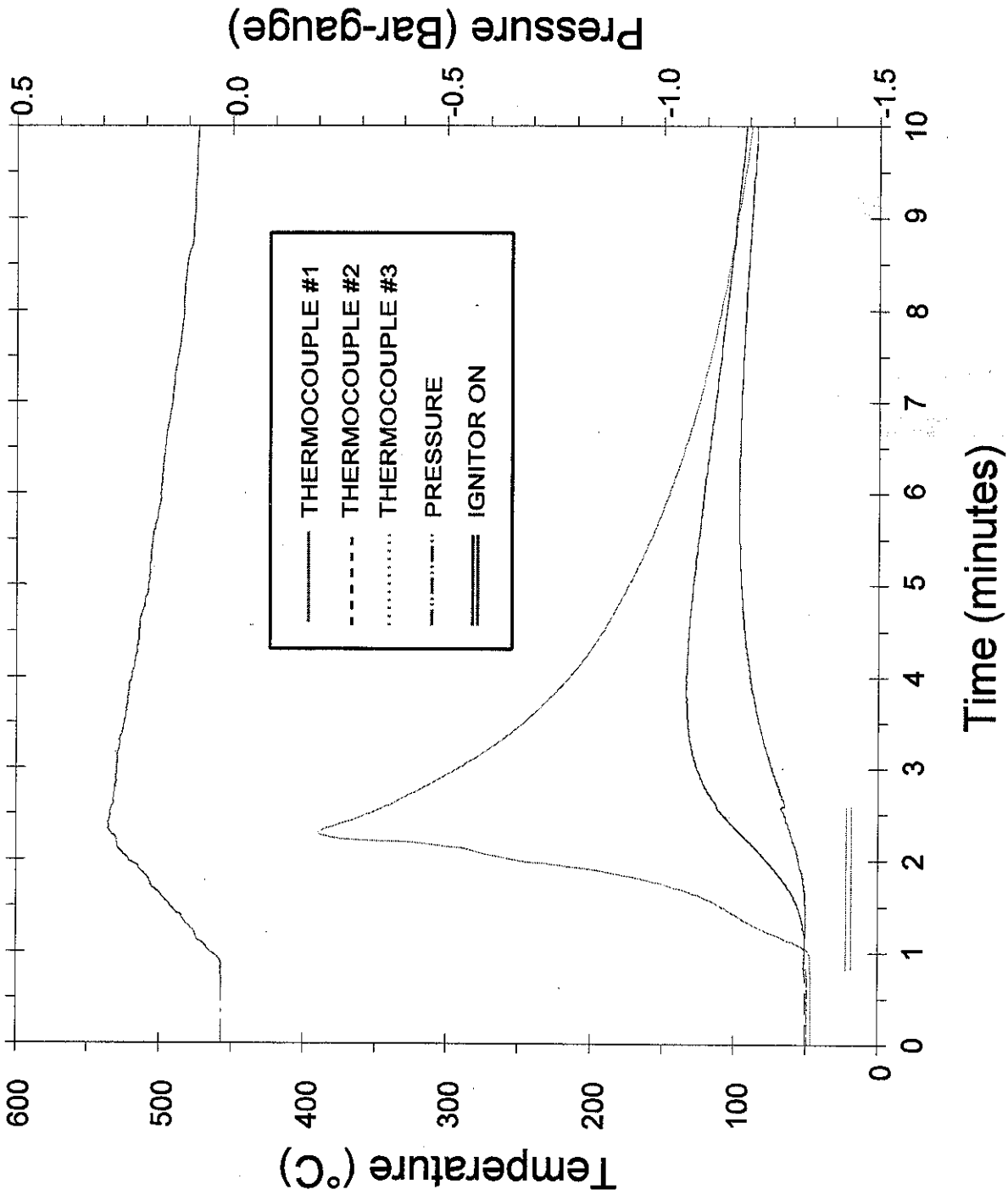

Pressure (Bar-gauge)
0.5
0.0
-0.5
-1.0
-1.5
THERMOCOUPLE #1
THERMOCOUPLE #2
THERMOCOUPLE #3
PRESSURE
IGNITOR ON
Temperature (°C)
600
500
400
300
200
100
0
1
2
3
4
5
6
7
8
9
10
Time (minutes)

Figure G-27. Temperature Verses Time Plot Showing Propagation for Dried AX-102 Waste Spiked to 6 wt% Total Organic Carbon.

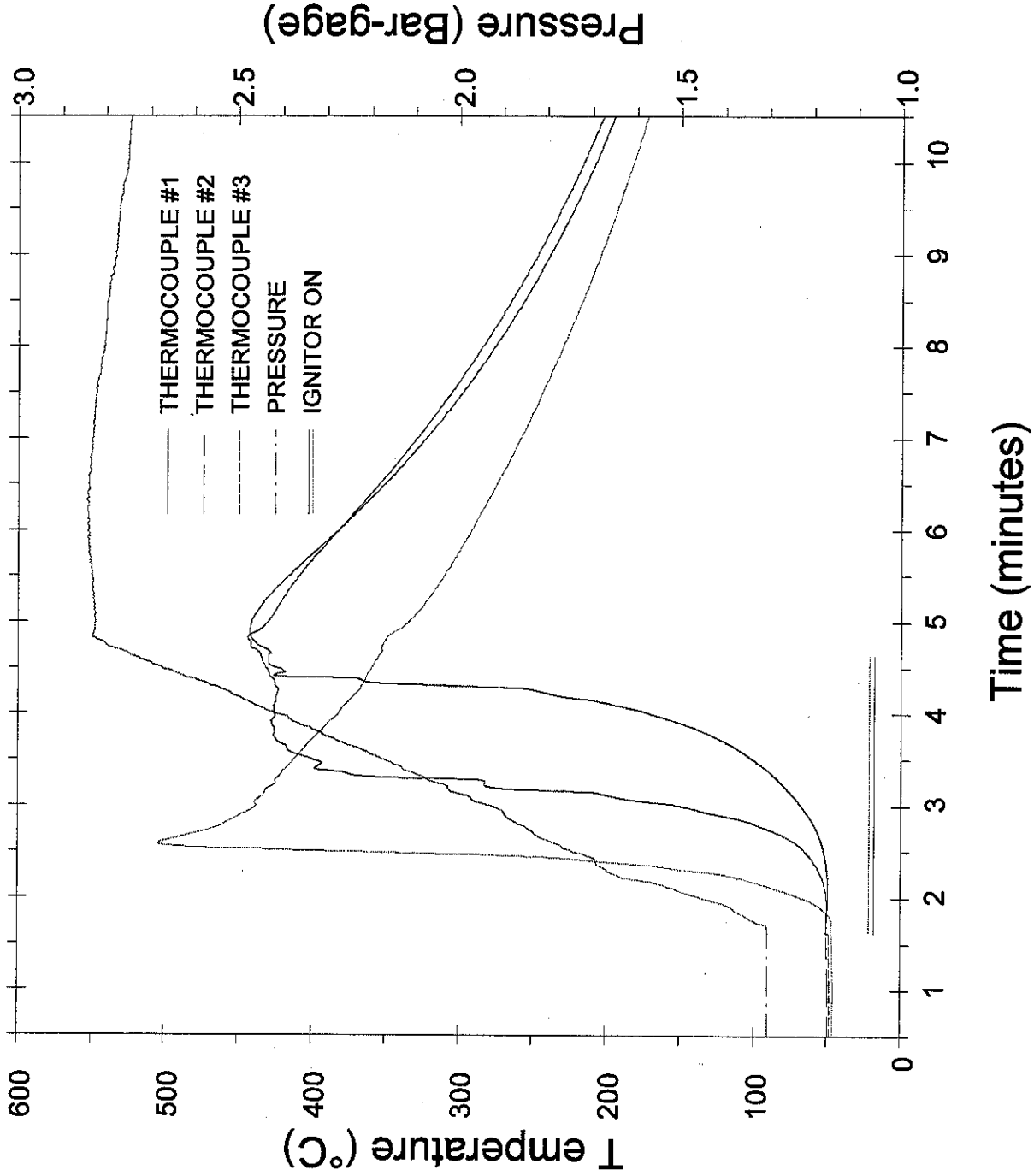


Figure G-28. Temperature Verses Time Plot Showing No Propagation for Dried C-202 Waste Spiked to 4.3 wt% Total Organic Carbon.

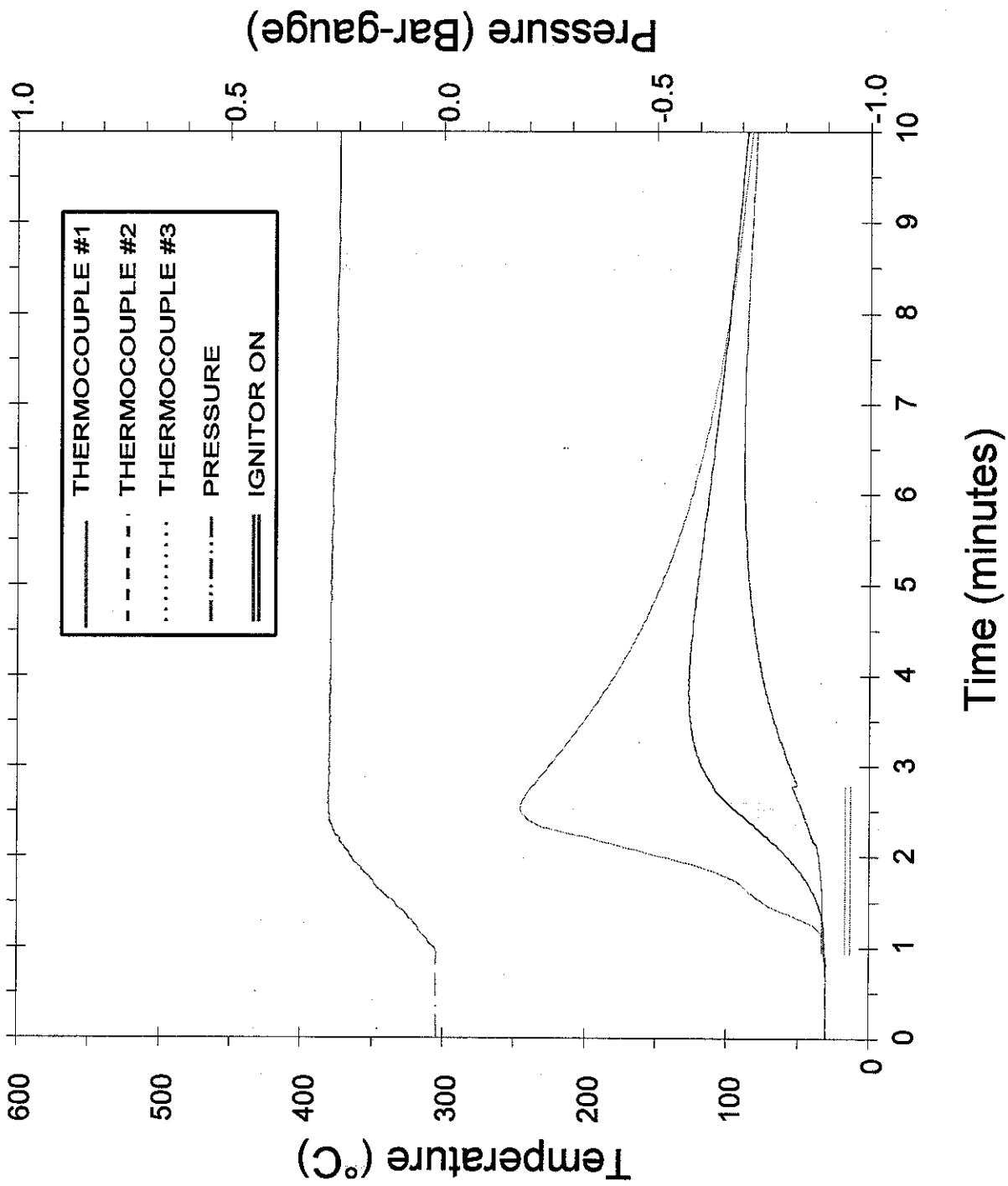


Figure G-29. Temperature Verses Time Plot Showing No Propagation for Dried C-202 Waste Spiked to 7.1 wt% Total Organic Carbon.

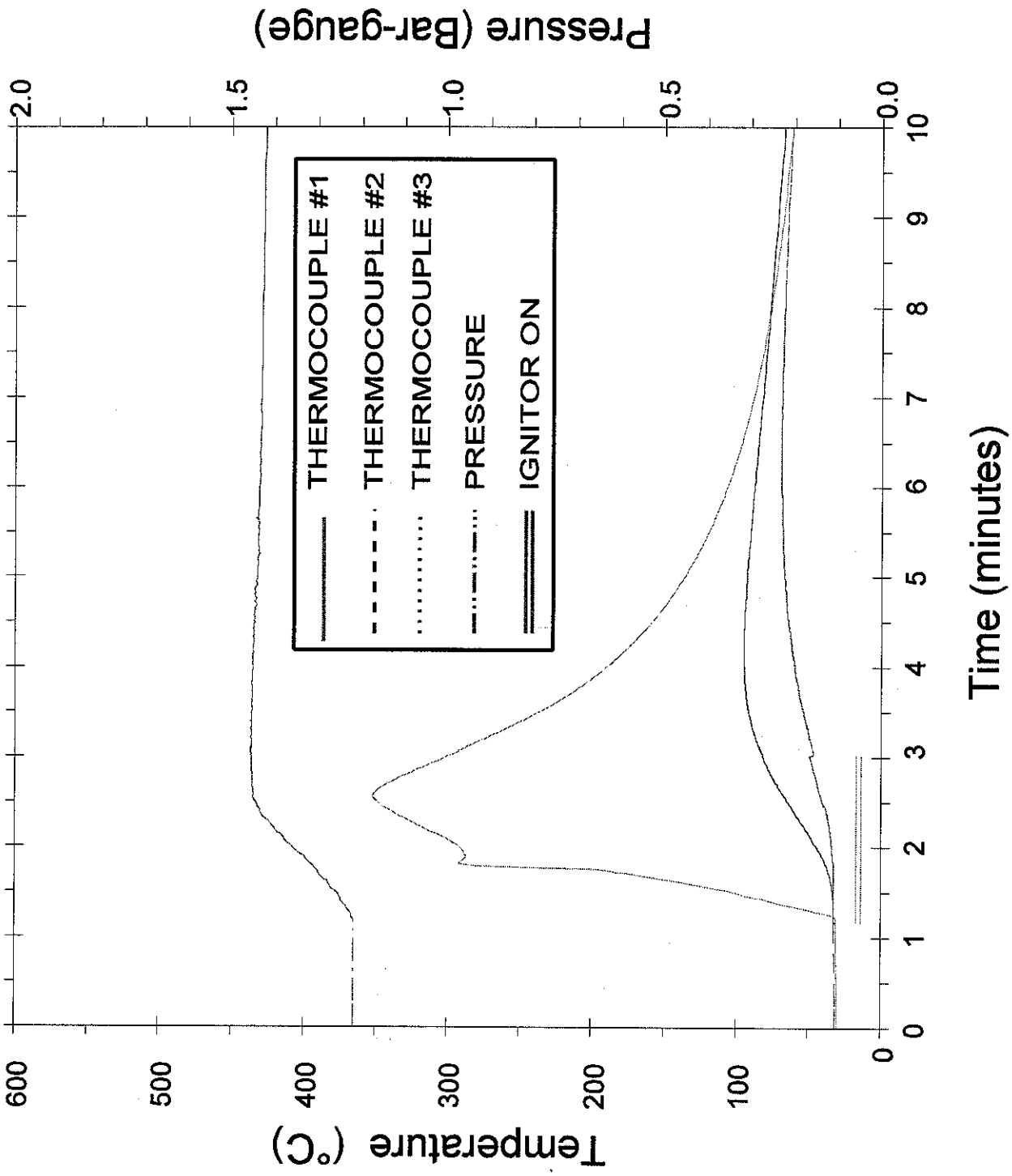


Figure G-30. Temperature Verses Time Plot Showing No Propagation for Dried U-105 Waste Spiked to 5.8 wt% Total Organic Carbon.

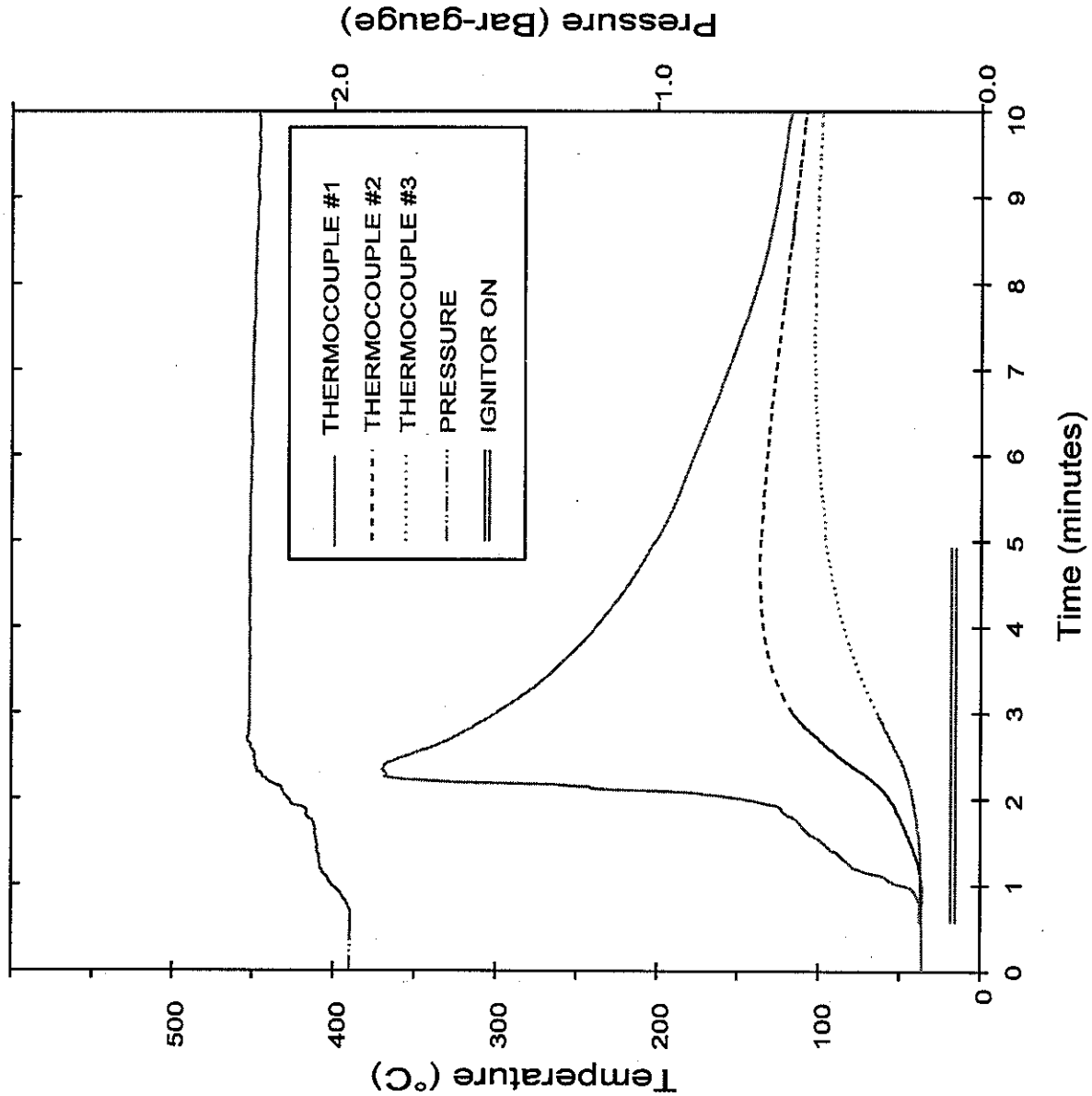


Figure G-31. Temperature Verses Time Plot Showing Propagation for Dried U-105 Waste Spiked to 6.9 wt% Total Organic Carbon.

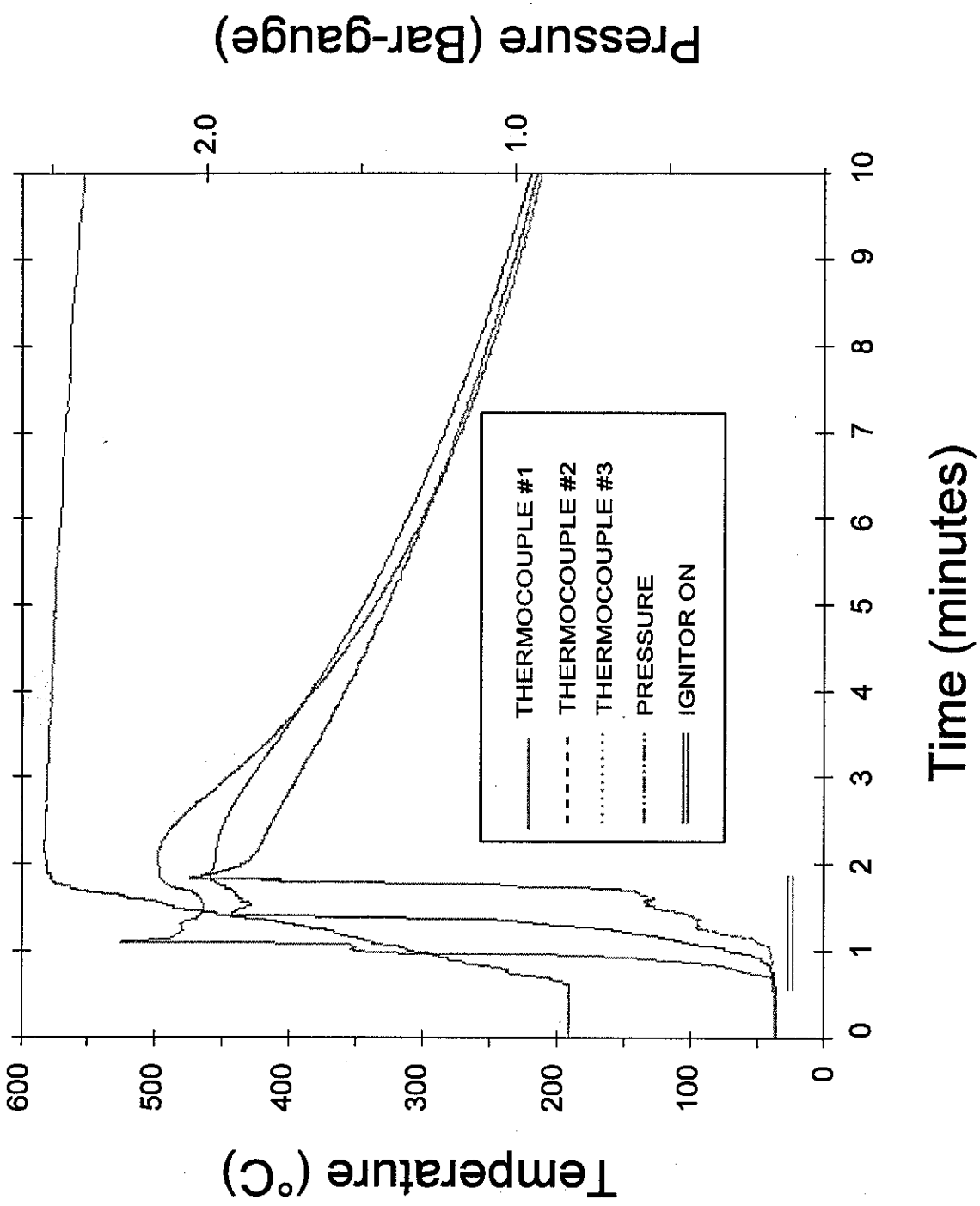


Figure G-32. Temperature Verses Time Plot Showing No Propagation for Dried U-106 Waste Spiked to 4.4 wt% Total Organic Carbon.

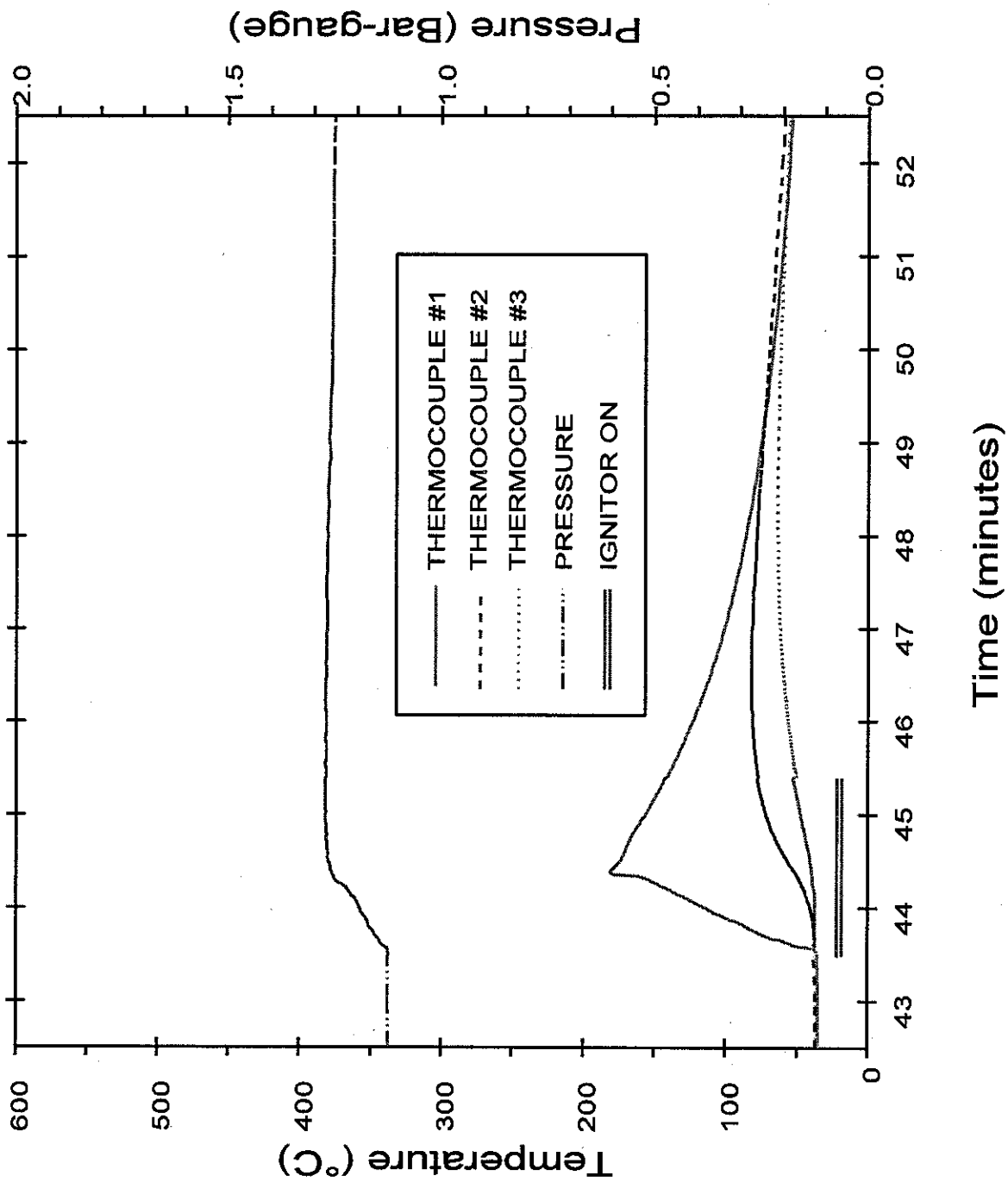


Figure G-33. Temperature Verses Time Plot Showing Propagation for Dried U-106 Waste Spiked to 5.1 wt% Total Organic Carbon.

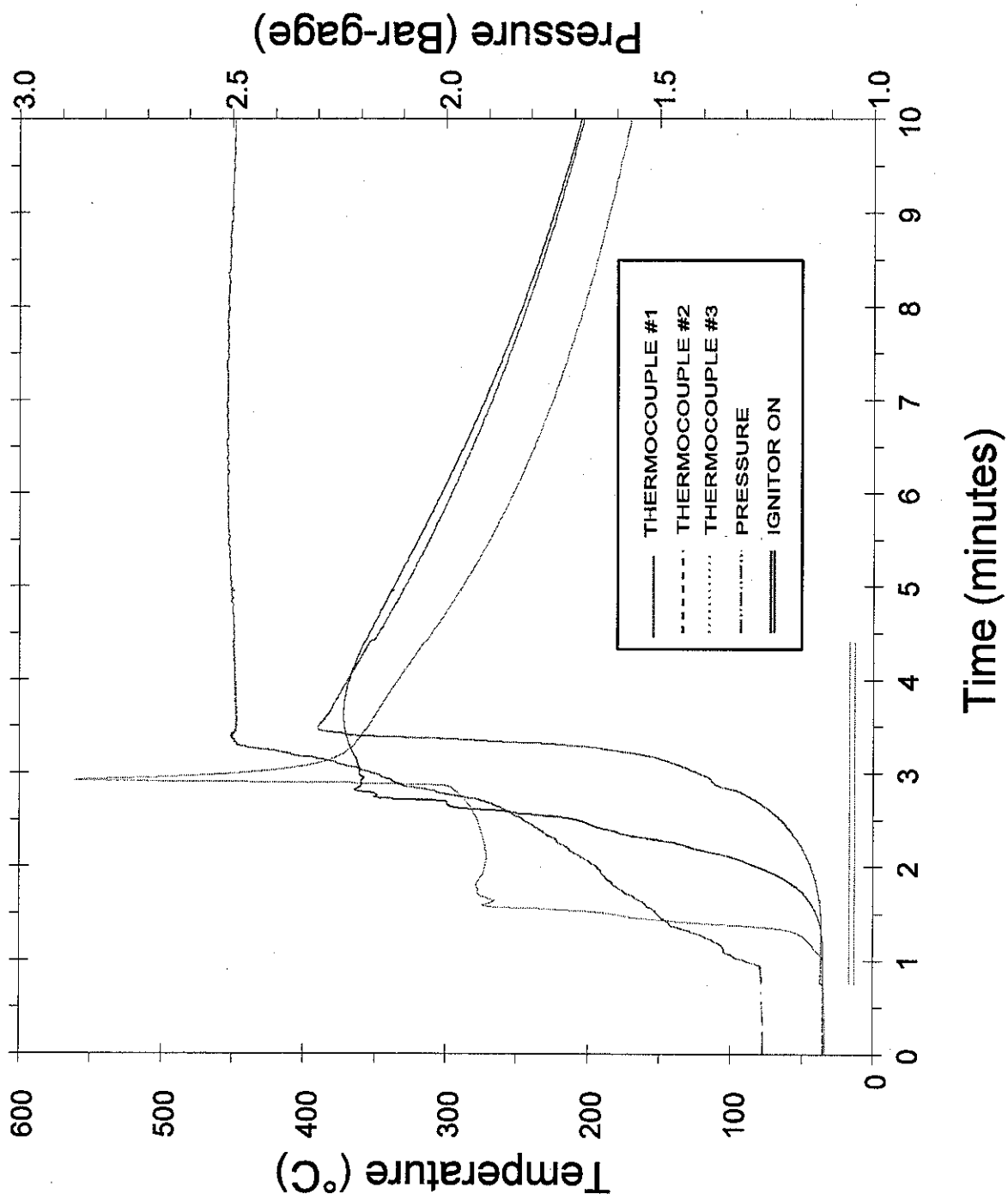
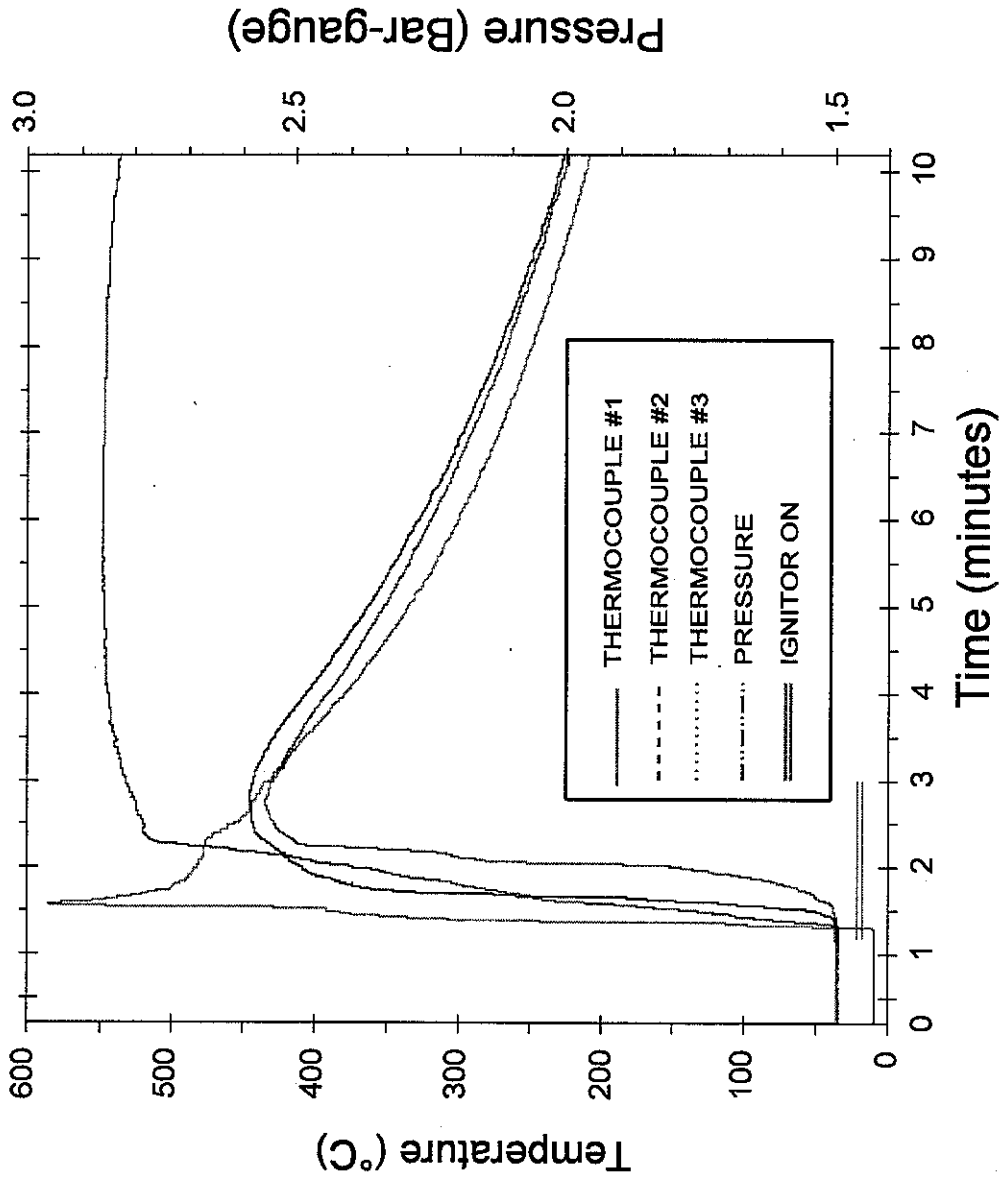


Figure G-34. Temperature Verses Time Plot Showing Propagation for Dried U-106 Waste Spiked to 5.9 wt% Total Organic Carbon.



From Table G-6 and Figures G-25 through G-34, all of the dried samples required a significant amount of additional fuel to propagate. The dried tank AX-102 and U-106 waste samples required 31 and 42% more fuel to propagate. Tank U-105 waste fuel concentration was increased by over a factor of four before the sampled propagated. The C-202 waste sample failed to propagate even at 7.1 wt% TOC, when 4.5 wt% TOC (as HEDTA) was added. This was expected because tank C-202 waste had only enough oxidizer to support spiking to 4.3 wt% TOC. Waste test results are consistent with the simulant test results. The waste propagation test results are compared to the theoretical criterion in Section 4.3.

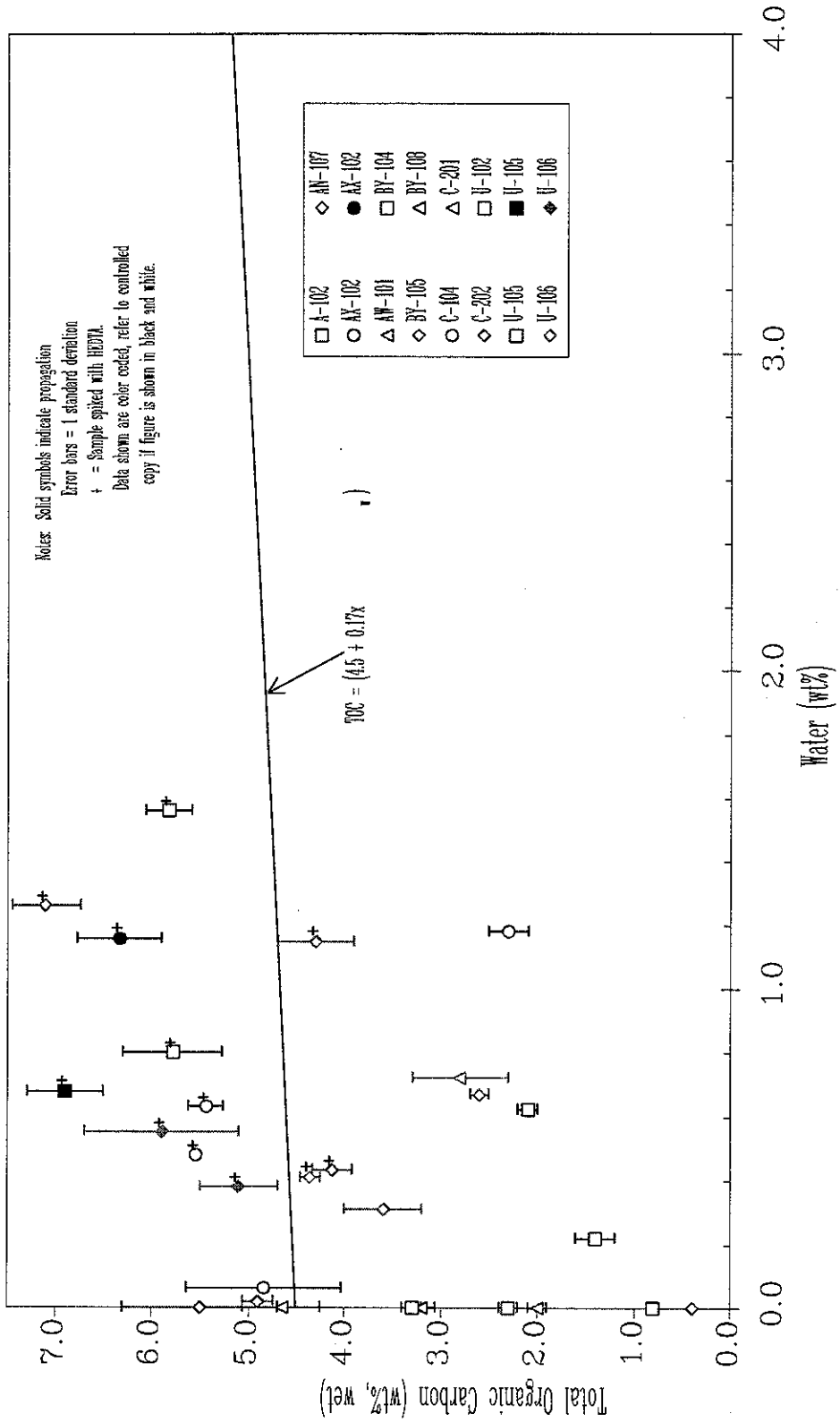
4.3 COMPARISON OF WASTE SAMPLE PROPAGATION TEST RESULTS WITH THE THEORETICAL CRITERION

The propagation test results (RSST and PRSST) on waste samples (Tables G-4 and G-5) and waste samples spiked with HEDTA (Table G-6) are compared to the theoretical fuel-moisture requirements in Figure G-33. As with the simulant test results, propagation only occurred above the theoretical criterion, and the minimum TOC concentration required was more than 4.5 wt%. Figure G-34 shows that there is a considerable margin between tank waste conditions and the conditions necessary for propagation. Tank wastes with high TOC concentrations contain considerable water (e.g., AX-102 and U-106 wastes contain about 29 and 49 wt% water, respectively). Even when dried to almost no water, none of the waste samples propagated when tested. Dried waste samples would only propagate after fuel was added to the mixture.

5.0 CONCLUSIONS

Many experiments including RSST, tube propagation, and PRSST tests were performed on waste simulants and waste samples. Direct propagation testing of tank wastes with the highest TOC/DSC indicate that Hanford Site high-level waste will not support condensed-phase propagation under tank waste conditions. Furthermore, tank waste samples failed to propagate even when dried to almost no moisture, and propagation was only possible when additional fuel (>1 wt% TOC as HEDTA) was added to the dried waste. All simulant and spiked waste samples that propagated exceeded the theoretical criterion, and the criterion is conservative when compared to the empirical results.

Figure G-35. Comparison of RSST and PRSST Test Results on Dried Waste Samples and Spiked Dried Waste Samples with Theoretical Propagation Criterion.



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APPENDIX H

TOTAL ORGANIC CARBON ANALYSES

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APPENDIX H

TOTAL ORGANIC CARBON ANALYSES

1.0 DESCRIPTION OF TOTAL ORGANIC CARBON ANALYSIS METHODS

The basis for screening tanks for the Organic Complexant-Nitrate hazard is the measurement and prediction of total organic carbon (TOC). This appendix will discuss the methods, the quality controls used, and some of the results from measuring TOC in the waste. Much of this work was done in support of the Ferrocyanide Safety Issue but the information is also relevant to the Organic Complexant-Nitrate Safety Issue.

1.1 HOT PERSULFATE METHOD

The Ag(I)-catalyzed, O_2-sparged hot persulfate method, operating in a batch-mode at 92 - 95 °C, is in routine use at Hanford for TOC analysis of tank waste samples. In this method, a 50-milligram sample is loaded into the acid digestion unit for the wet oxidation step. Normally, the sample is initially reacted only with acid, releasing the carbonate for a measure of total inorganic carbon (TIC). Then, potassium persulfate ($K_2S_2O_8$) is added, in solid form to the 50 ml digestion flask to a concentration of 20% in 2 M H_2SO_4. The catalyst (0.2 mmol of 1 M $AgNO_3$) is added directly to the flask. The system is closed, inserted into the preheated heater well, and oxidation and release of CO_2 begins. A coulometric detector system is used for detection of liberated CO_2. Alternatively, all reactants can be added initially for a single measurement of total carbon.

Most tank sludge samples are found to be entirely dissolved by this hot sulfuric acid/persulfate treatment. This method is not used for acid-insoluble silica-based solids, such as soils and sand materials.

1.2 FURNACE OXIDATION METHOD

This method is well described in the literature (literature examples are provided in Baldwin et al. 1994), but the application of this method for the organic content of caustic salt solutions is not discussed in the literature. Furnace oxidation methods may use both liquid and solid samples. The furnace tube at the 222-S laboratory is configured to receive an aqueous sample injected by syringe. Therefore, the sample is typically a water leach of a solid but can also be an aqueous sample. The liquid (typically 200 microliters) is injected into a furnace operating at 800 °C with an oxygen purge. The carbon is reacted and the carbon dioxide is measured with the coulometer. Normally, sparging of the acidified sample is performed prior to the furnace injection so that carbonates are removed.

2.0 EVALUATION OF ANALYTICAL METHODS FOR TOTAL ORGANIC CARBON

The analytical recovery of several organic compounds were evaluated at Hanford (Baldwin et al. 1994) and at Los Alamos National Laboratory (Vance 1994). These studies were performed with 34 compounds representing 12 different categories. This work included several different tests of the methodology including spike tests with pure compounds. Results are shown in Table H-1.

Volatile compounds tend to be a problem for both methods. To drive off the inorganic carbons, the sample is acidified and purged with oxygen. This sweeps the volatile carbons from the solutions prior to the oxidation step. The hot persulfate method may have higher volatile loses than the furnace method because of the higher temperature used during the purge.

It was found that the hot persulfate method was useful for most non-volatile organic compounds, which would be analogous to the complexant and complexant degradation products. The evaluation tests show that the compounds of most concern for the organic- nitrate safety evaluation (i.e., complexants) are oxidized and recovered very well. There was no indication that this class of compounds would be a problem in routine measurements.

3.0 EVALUATION OF RESULTS WITH ACTUAL WASTE

Data from the Tank Characterization Database were examined to assess the accuracy and the precision of the TOC analyses. During 1997, the TOC analyses were reviewed for evidence of systematic quality problems. At the time, there were 6671 data points labeled TOC from all single-shell and double-shell tanks including numerous Quality Assurance observations for the Hanford Site tank waste.

3.1 QUALITY ASSURANCE

Most of the analyses performed for TOC are associated with quality assurance runs rather than actual waste samples. These include tests for standard recovery and minimum detection, plus method blanks, reagent blanks, and spike recovery. The various blank samples (method blank, field blank, hot cell blank, reagent blank, etc.) uniformly showed TOC below minimum detection except for an occasional value above the detection threshold of 40 μg/g.

The minimum detection limit has been measured about 1800 times. The minimum detection level was most commonly reported to be 40 μg/g by the hot persulfate method. The furnace TOC method tended to have higher minimum detection levels. The furnace method for solids frequently reported minimum detection levels in the 400 to 500 μg/g range. However, that is still two orders of magnitude below the limits of concern for organic nitrate reactions and the addition of 0.05 wt% to any value would still not influence the interpretation of the observation.

Table H-1. Tested Carbon Compounds and Recovery (%Rec ± SD) for Each Method[1]

Compound	Name	Hot Persulfate	Furnace method[3]	LANL Persulfate[4]
organic salts	sodium formate	93.2 ±1	102	NT
	sodium oxalate	93.4 ±5	98.8	100
	sodium gluconate	85.1 ±6	101 ±1	NT
	potassium acetate	95.5 ±1	NT	99
	ethyl acetate[2]	17.4 ±2	88.3 ±1	NT
	potassium acid phthalate	90.7 ±4	NT	NT
complexants	EDTA	83.6 ±7	96.6 ±5	98
	HEDTA	82.9 ±5	119 ±1	NT
	NTA	83.2 ±6	97.2 ±2	NT
	DPTA	97.7 ±5	96.8 ±2	49
saccharide	glucose	95.4 ±3	101 ±3	91.5
ketones, alkanes, organic acids	MIBK[2]	22.1 ±4	NT	NT
	dodecane	<1	NT	NT
	succinic acid	97.4 ±1	99.4 ±1	NT
	glycolic acid	102 ±1	111 ±1	NT
	citric acid	NT	NT	102
alcohols, diols	1-butanol[2]	58.2 ±9	103 ±2	28.7
	ethylene glycol	96.0 ±3	99.9 ±1	95.7
	glycerol	94.0 ±9	98.1 ±1	NT
long-chain hydrocarbons	NPH[2]	<1	NT	NT
	Paraffin wax	<1	NT	NT
N-containing organics	hexylamine[2]	56.1 ±12	NT	NT
	urea	84.3 ±2	98.2 ±1	101
P-containing compounds	tributyl phosphate[2]	40.2 ±14	NT	NT
	dibutyl butyl phosphate	74.7 ±2	NT	NT
cyanide compounds	sodium ferrocyanide	10.0 ±5	105 ±1	40
	sodium thiocyanate	35.0 ±5	74.4 ±2	79

Notes: [1] Table extracted from Baldwin et al.1994.

[2] Compound is volatile at 90 °C and is partially lost during sparged oxidation.

[3] Furnace method values shown were obtained with no acid sparging.

[4] Vance (1994).

NT = Not Tested

There were 1074 points from standard recovery tests. All of the standard recoveries were between 85% and 106%. The standard recovery samples use pure potassium acid phthalate and the purpose is to determine the reliability of the analytical information.

Spike recovery tests are done by adding a known amount of organic (potassium acid phthalate) spike to an actual sample and then performing the test. The purpose of a spike recovery is to assure that there is not a matrix interference with the method. There are 484 spike recovery tests reported. The average value 93.55% recovery with a standard deviation of 26.2%. There were 69 tests which had less than 80% recovery and 31 tests with greater than 120% recovery. This would mean that about 1 out of 5 spikes is outside this desired range. However, there were only 9 less than 40% and 8 greater than 160%. Spiked samples are prepared before the actual organic content of the waste has been measured. When the sample contains more organic material than anticipated, and the amount of organic material in the spike is small relative to the analytical observation, and the spike recovery is overshadowed by the TOC in the waste. Because the amount of TOC in the waste is subtracted from the spike and the TOC value comes from a different analytical run, sample inhomogeneity also affects the spike recovery.

A similar analysis of spike recovery for furnace TOC showed slightly better recovery. The average spike recovery was 97.8% with the standard deviation of 25.2%. After examining the QA type analysis, it is clear that both methods are being run in a controlled manner with blanks below detection levels and spike recovery in an acceptable range.

During 1998, it was determined that a spike that more closely represents the type of organic material in the tank waste may be more appropriate. Table H-2 provides the make-up of the organic complexant spike.

Table H-2. Make-up of the Organic Complexant Spike.

Compound	Fraction of Carbon in Spike (g of Carbon/g of sample)	Fraction of TOC (wt%)
sodium EDTA	0.05791	22.8
sodium IDA	0.03927	15.5
sodium HEDTA	0.07054	27.8
sodium citrate	0.04987	19.6
sodium acetate	0.03624	14.3
Total	0.25383	100

The spike material is prepared from sodium salts dissolved in 100 mL of water, making a 2538 ugC/mL spiking solution. For the furnace method this spike is diluted by a factor of 4.

The spike has been analyzed in replicate (n=10) by both the furnace and persulfate methods. The furnace method gave an average recovery of 100.2% with a standard deviation of 0.8%. The persulfate method gave an average recovery of 86.9% with a standard deviation of 5.2%.

The low recovery for the persulfate may not be totally due to the make-up of the spike but may be inherent in the method. It is important to note that the TOC measurement is used for screening of tanks to determine which wastes have the highest likelihood of supporting a propagating organic complexant reaction. A 10 to 20% low bias in the persulfate TOC results would still result in the same set of tanks being identified for propagation testing and organic speciation.

3.2 WASTE SAMPLE CONSIDERATION

A review of the TOC analysis results from 2687 observations of waste samples was performed. There were 1352 primary samples; 1248 duplicate samples; and 76 triplicate samples. Triplicate samples are typically run when there is an unacceptably large variability between primary and duplicate samples. About 5% of the analyses were performed in triplicate.

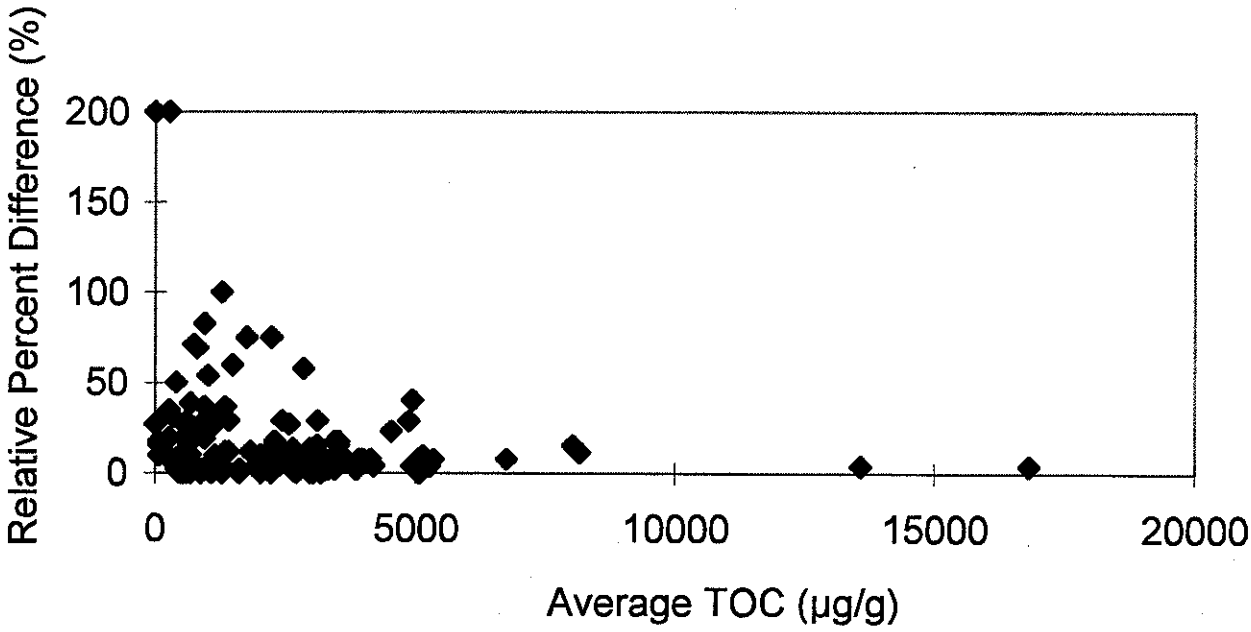
The data were sorted by the units given for the values. There were two units that predominated: µg/g representing solid samples and µg/ml which represents liquid samples. The analytic information reveals that about half of the solids samples and most of the liquid samples are less than 0.5% TOC.

Inspection of the observations indicates that the tanks thought to contain relatively high concentrations of organic materials on the basis of historical information provide the largest TOC values. For example, all liquid points greater than 50,000 µg/ml were from tank AN-107 which is know to contain complexed concentrate with the highest amount of organics in the tank farms. The remainder of the liquid data points over 30,000 µg/ml are from tanks U-106 or C-106. Tank U-106 is known to contain complexed concentrate in the past. The liquid samples from C-106 represent a separable phase organic, rich in phosphate esters, and is expected to be high in TOC.

Qualitative observations suggested that the results for the samples with low organic content appeared to be less precise than the results for the samples with higher organic content. Herting (1996) investigated this feature of the method by measuring the organic content of a simulant which was spiked with a sodium salts of glycolate, HEDTA, EDTA, and citrate. The simulant was successively diluted and the TOC measured. The results showed that the measured TOC did not deviate from the expected values until TOC was diluted to detection levels (a 1:1000 dilution). This study suggests that the method is more accurate for the samples with higher concentrations of organic carbon than for the samples with barely detectable quantities of organic carbon.

Another measure of the differences in the precision of the method for samples with different amounts of organic carbon is provided by an examination of the difference between the primary and secondary sample. The difference is captured in a term called the relative percent difference (RPD). This is a measure of method repeatability but any sample inhomogeneity will also influence this value. When examining the RPD from several hundred samples, it was found that there was an inverse relationship between the RPD and the quantity of organic carbon in the waste. As shown in Figure H-1, the samples with high TOC values tended to exhibit low RPD values and samples with low TOC tended to exhibit high RPD values. These results indicate that the precision of the TOC analysis is poorer for samples containing small amounts of organic carbon, and higher for samples containing larger amounts of organic carbon. Thus, the sample results with higher organic content are more precise than the results for samples with low organic content. It is pertinent that accurate but imprecise information can be tolerated for the samples with low organic content without compromising conclusions about the safety of the tank. Further, when an RPD is greater than 20%, the analyst performs a third analysis.

Figure H-1. Relative Percent Difference (RPD) Between Replicate Total Organic Carbon (TOC) Measurements as a Function of TOC Concentration.



There have been 24 samples where both persulfate and furnace TOC analyses were performed. Of the 24 samples, 22 showed that the furnace method result is greater than the persulfate method result. The values for these 24 observations are shown in Table H-3.

Table H-3. Comparison of Furnace and Persulfate TOC Results for Waste Samples.

Tank	Sample Type	Furnace Method	Persulfate Method	Units
AN-105	Core 151 composite	6100	2590	µg/g
AW-105	Core 196 segment 4	1110	385	µg/g
AX-101	Grab supernate	3590	3680	µg/ml
AX-101	Grab supernate	3890	4050	µg/ml
AX-101	Grab supernate	4190	4160	µg/ml
C-103	Core 63 drainable liquid	7750	7370	µg/ml
C-103	Core 63 drainable liquid	7600	7450	µg/ml
C-106	Grab 11 interstitial liquid	2070	1630	µg/ml
C-106	Grab 12 supernate	2520	2030	µg/ml
C-106	Grab 4 interstitial liquid	2320	1790	µg/ml
C-106	Grab 5 supernate	3300	2240	µg/ml
C-106	Grab 7 interstitial liquid	2440	2320	µg/ml
S-106	Core 183 segment 1	2375	1110	µg/g
S-106	Core 183 segment 2	2090	805	µg/g
S-106	Core 183 segment 4	2430	1130	µg/g
S-106	Core 183 segment 5	2360	1070	µg/g
S-106	Core 183 segment 7	1640	1440	µg/g
S-106	Core 184 segment 1	1560	1020	µg/g
S-106	Core 184 segment 2	1520	1000	µg/g
SX-103	Grab 1 supernate	3590	3170	µg/ml
SX-103	Grab 2 decanted liquid	4090	2420	µg/ml
SX-103	Grab 3 decanted liquid	2670	2380	µg/ml
U-106	Core 148 segment 1	40,400	33,500	µg/g
U-106	Core 148 segment 2	41,700	33,600	µg/g

4.0 CONCLUSIONS

The technical literature reports that hot persulfate oxidation will oxidize the organic compounds including solvents and complexants that exist in the Hanford Site waste tanks. The hot persulfate method with a silver ion catalyst has been employed at Hanford for many years, with a limited number of analyses performed by the furnace oxidation technique. The implementation of the hot persulfate method for the measurement of the TOC content requires the removal of carbonate ion and this approach removes some low molecular weight organic solvents, but tests at Hanford and LANL indicate that the complexants are retained and accurately determined.

Thousands of analyses have been performed providing a large database for the assessment of the precision and accuracy of the method. Nearly all waste analyses have been performed in duplicate. It has been established that the detection limit for liquid samples is 40 μg/ml and that for solids is 400 to 500 μg/g. The recovery for analyses of pure standards range between 85% and 106%. The average value for about 500 spike recovery tests is 93.5% with a standard deviation of 26.2%. The relatively large standard deviation arises from the use of independent samples in the test and the blind nature of the test, which can result in variability being introduced into the organic content of the original sample and the spike sample.

Tanks that are known to contain high quantities of organic solvents on the basis of historical information or other work provide high TOC values. Other assessments of the accuracy indicate that the precision of the method decreases when the samples contain small amounts of organic carbon. These findings indicate that the method measures the organic carbon content of the wastes with sufficient accuracy to screen tanks for the organic complexant hazard.

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APPENDIX I

CALCULATION NOTES FOR ANALYSIS OF VARIANCE (ANOVA) MODEL

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APPENDIX I

CALCULATION NOTES FOR ANALYSIS OF VARIANCE (ANOVA) MODEL

1.0 PURPOSE

This appendix describes how moisture (H_2O) and total organic carbon (TOC) tank measurements are used to calculate combustible waste fractions (CWF) for Hanford single shell tanks. The combustible waste fraction of a tank is defined as that proportion of waste that is capable of burning. These CWF estimates are used to screen tanks for the organics safety issue. Tanks with a low fraction of combustible waste are classified safe.

The calculation has been organized to determine the combustible waste fraction in the tanks under two different moisture conditions; under current (wet) moisture conditions, and after complete dry out (moisture = 0%). The first fraction is called the **current or wet combustible waste fraction** (wet CWF) and the second is called the **dry combustible waste fraction** (dry CWF). In this appendix, only dry CWF is discussed and estimated. In Heasler et al. (1998) the current (wet) CWF is also estimated and discussed. No wet CWF estimates from that report fail the screening criteria.

Although studies have shown that waste in Hanford tanks is not likely to dry out completely (see Appendix D for details), to be conservative, we will estimate dry waste under the worst possible dry-out scenario. Combustible waste in this report is defined as waste with dry TOC weight percent above 4.5%. For each tank, this analysis will produce not only the best estimate of combustible waste fraction, but also uncertainty distributions associated with it. The current safety criteria uses the upper 95 percentile of this distribution (upper 95% bound) to classify tanks. A combustible waste fraction for a tank is considered acceptable if its upper 95% bound is below 5%. In other words, the tank passes the screening test if there is 95% confidence that the combustible waste fraction is below 5%. It should be noted that this safety criteria could also be expressed in terms of a tolerance bound. The tank is safe if the 95 - 95 tolerance bound for TOC is less than 4.5%.

This screening operation is only the first step in the complete tank assessment strategy that is discussed in this report. Other information may change the initial categorization of a tank. For example, additional measurements might find the TOC in the tank is degraded, or one might determine that the tank can never completely dry out, or one might find that the waste is oxidizer poor.

Although this calculation is capable of estimating the CWF in all tanks and consequently screening all tanks, we have chosen to not apply the screening operation to all tanks. A set of 11 tanks were classified as "special" tanks, with waste streams that were considered much more unpredictable than the other tanks (see Appendix F for a more complete discussion of this). Because of this unpredictability, the CWF methodology was thought not to be applicable to these

tanks and is not applied. Therefore this appendix produces CWF estimates for 149 - 11 = 138 single shell tanks.

Also, tanks that currently have no TOC sampling data are identified and treated differently when evaluating the screening results than those that do. Presently, 98 tanks have sampling data, 40 do not, and 11 are special tanks.

2.0 DESCRIPTION OF THE DATA

This section describes the data used to estimate the combustible waste fractions for tank screening. The data consists of total organic carbon (TOC) and moisture (H_2O) measurements taken on various waste samples.

Nearly 6000 H_2O and TOC measurements have been collected from the Tank Characterization Database (TCD) and various laboratory reports. However, all the collected measurements are not relevant for the estimation of CWF. Furthermore, this initial set of data requires substantial transformation before it is useful for CWF estimation; The measurements must be converted to consistent units (wet weight percent), laboratory replicates must be averaged together, and measurements on the drainable liquid and solid portions of the sample must be combined. The resulting "transformations" produce a single (H_2O,TOC) estimate for each discrete sample location. After these transformations and averages are completed, (H_2O,TOC) measurements are produced for approximately 800 tank locations.

These (H_2O,TOC) measurements are summarized in Section 6 and form the basic input for the calculated CWF. The initial 6000 (H_2O,TOC) measurements that were gathered to produce this data set are recorded in complete detail in Heasler et al. (1998) and the steps required to produce the transformed data used in this report are also documented there.

Most of the data (approximately 80%) has been extracted from the Tank Characterization Database, an electronic database that contains almost all of the recent Hanford sampling measurements. The additional records not from the TCD includes (1) data from the process aids reports and (2) data measured in 1998 that has not yet been entered into TCD. These sample measurements for TOC and H_2O have been reviewed to verify that the sample measurements represent current tank waste. If sample measurements were not representative, they were not used in the screening calculations. For example, if they were known to have been contaminated by liner liquid or are superceded by more recent samples, then they were not used in the screening calculations.

Core composite measurements, although collected in the initial data set, are not generally used in the CWF calculations. The CWF calculation requires that the spatial variability of (H_2O,TOC) concentrations be determined in the tanks. Since a composite measurement averages (H_2O,TOC) over an entire vertical profile, it is not useful for accomplishing this.

However, a few selected measurements of core composite data have been included for tanks that have no core segment measurements. These composite measurements were added to the data base to produce improved TOC average estimates for those tanks. Since relatively few composite measurements have been added, the estimates for spatial variability in the tanks are not noticeably affected. The amount of composite data that is used in this way has been progressively reduced, as more sampling data becomes available.

Table I-1 summarizes the amount of (H_2O,TOC) data available for these calculations. As one can see, approximately one-half of the tanks have been sampled for TOC while about two-thirds of the tanks have been sampled for moisture. This sampling has allowed us to produce (H_2O,TOC) estimates for 795 discrete locations within the tanks. A total of 553 of the 795 locations have both TOC and H_2O measurements associated with them, while the remaining 242 only have moisture measurements. TOC measurements are missing at several sampled location because sampling protocol did not require TOC measurements to be taken on every sample.

Table I-1. Summary of H_20/TOC Data.

Number Tanks Sampled for H_2O or TOC	98
Number Tanks Sampled for H_2O and TOC	81
Number Tanks Sampled for H_2O	98
Number Tanks Sampled for TOC	81
Number of H_2O Measurements Collected	4213
Number of TOC Measurements Collected	2620
Number Locations sampled for TOC or H_2O	795
Number Locations sampled for TOC and H_2O	553
Number Locations sampled for H_2O	795
Number Locations sampled for TOC	553

The number of locations sampled in each tank varies from tank to tank. Since this number determines how well TOC can be estimated in a tank, this number determines what statistical techniques can be applied to the data. Table I-2 shows that 36 tanks were sampled at more than 4 locations, while 19 tanks were sampled at only one location. The most heavily sampled tank, A-101, was sampled for TOC at 28 locations (various vertical locations at three risers).

Table I-2. Amount of TOC Data for Tanks.

Tanks	Locations Sampled in Tank
36	>4
4	4
6	3
16	2
19	1
57	0

2.1 HANFORD SAMPLING METHODOLOGY

Samples at Hanford have been obtained through core sampling, auger sampling, and grab sampling with the majority of measurements in the compiled data originating from core sampling. Core sampling is both push mode and rotary mode. Push-mode sampling is primarily used to sample sludge or soft saltcake. The cylindrical cross section of the tank waste contents below the riser is obtained by pushing or rotating a 2.5 cm x 48 cm (1 inch x 19 inches) stainless steel sampler bit into the waste. The usable volume of each segment sampler is 187 mL. The samples collected from each segment are extruded in the hot cell and the mass of solid sample and drainable liquid recovered from each segment sampler is recorded. The mass recovered from each segment can vary from 0 to 100%. The waste, approximately 7 cm (3 in) from the tank bottom cannot be sampled because of design and safety constraints of the sampling method. However, waste at the tank bottom has the least chance of propagation.

Push-mode core samples represent the majority of the sampling technique. Seventy percent of the water measurements were push-mode core samples, and 65% of the TOC measurements were push-mode core samples. Auger samples collect the first 20 to 30 cm of waste from the surface. This sampling method is used to collect samples for the safety screening program. The ANOVA analysis treats auger samples as surface samples belonging to the same location as cores from segment 1 (surface core samples).

Grab samples are obtained using a special sampling bottle that is contained in a cage and can be used to obtain liquid or suspended slurry samples of the waste. In the sampling procedure, the bottle is stoppered and lowered to the desired level. The bottle is then open and filled with liquid and any suspended solids, and is then retrieved and closed with a lid.

2.2 CHEMICAL ANALYSIS METHODOLOGY

The cores are extruded from the sampler in the hot cell, and separated into drainable liquid and solid phases. The solid waste is then homogenized. The solid waste (and liquid waste if present) is then split into aliquots, and these aliquots are used to perform the desired chemical analyses. A typical waste sample may have six or seven different chemical analysis run on it to produce concentration measurements on 10 to 50 different analyses.

2.2.1 Thermogravimetric and Gravimetric Analyses

To measure moisture in a sample using Thermal Gravimetric Analysis, (TGA) the mass of a sample is measured while it is heated at a constant rate. The mass of the sample is approximately 10 mg. A gas, such as nitrogen or air, is passed over the sample during the heating to remove any sample offgases. Any decrease in the mass of the sample represents a loss of gases from the sample though evaporation or through a reaction that forms gas phase products. Mass loss versus sample temperature is recorded on a graph. Mass loss from ambient temperature to approximately 150 °C (230 °F) is assumed to be water unless the responsible chemist evalutes the graphed data and finds an exception to this rule. The weight percent water by TGA was

performed using procedures LA-560-112, Revision B-1 (Mettler ™) equipment and LA-514-114 (Perkin Elmer™ Equipment).

To measure moisture in a sample using gravimetric analysis, the mass of a sample is measured while being heated at a constant temperature of 110 °C (230 °F) for 18 hours. Any decrease in the mass of the sample represents a loss of gases from the sample though evaporation, and is assumed to be water.

The assay errors of using either the TGA and gravimetric methods were evaluated on the grab sample sludges and are reported C-106 Tank Characterization Report (Schreiber 1996). Samples of the supernatant, centrifuged solids, and filtered centrifuged solids were analyzed and the results are shown in table I-3. For the solids samples the percent water for gravimetric analysis are greater than the TGA method. This is expected because the gravimetric method uses larger samples and a constant drying temperature of 105 °C for 18 hours could potentially drive off more water in solid samples.

Table I-3. Comparison of Percent Water by Thermogravimetric and Gravimetric Analyses.

Laboratory Number[1]	Sample Number	Thermogravimetric Analysis (% water)	Gravimetric Analysis (% water)
Supernatant			
S96T000538	6C-96-5	80.88	81.4
S96T001023	6C-96-12	79.27	79.0
Filtered Centrifuged Solids			
S96T001537/ S96T001539	6C-96-4	24.10	25.1
S96T000567/ S96T000569	6C-96-7	25.74	26.8
S96T000551/ S96T000553	6C-96-10	12.78	19.05
S96T001685/ S96T001687	6C-96-11	31.92	34.1
S96T001559/ S96T001561	6C-96-13	23.7	26.3

Laboratory Number[1]	Sample Number	Thermogravimetric Analysis (% water)	Gravimetric Analysis (% water)
Centrifuged Solids			
S96T001527	6C-96-4	3.58	5.75
S96T000542	6C-96-7	8.28	9.9
S96T000558	6C-96-10	12.86	17.1
S96T001674	6C-96-11	9.03	11.65
S96T001030	6C-96-13	9.36	20.85

2.2.2 Total Organic Carbon

Appendix H discusses the methods, the quality control used, and some of the results from measuring total organic carbon in the waste.

2.3 DATA EDITING AND TRANSFORMATIONS PERFORMED

The following data are excluded from calculation for the analysis of variance model as incorrect measurements:

1. The water or total organic carbon values reported are not consistent with reported values of surrounding samples. The reported values are widely different from duplicate and triplicate results of the same sample.
2. The responsible chemist has indicated the reported values do not represent the waste in the tank because of unusual out-of specification conditioning or heating of the waste sample after being retrieved from the tank.
3. The reported values are from samples that have been contaminated with lithium bromide from hydrostatic head fluid.
4. Reported values are from secondary or tertiary sources of data and cannot be verified. This is especially true with pre-1989 data.

All (H_20,TOC) measurements have been converted to consistent units (wet weight percent concentration) from the original units. Also, sample and duplicate replicates have been averaged together to produce a best estimate of drainable liquid and solid (H_2O,TOC) concentrations.

In the laboratory, drainable liquid is separated from the core and auger samples before analysis. If a sufficient volume of drainable liquid exists, the laboratory will perform TOC and moisture measurements on the liquid, so the measurements reported are unique to the phase of the waste.

The Tank Characterization Database (TCD) identifies the measurements as solid or liquid (liquid analyses are also reported per unit volume).

In the TCD, the measurements on the two phases (solid and liquid) are not combined to form a best estimate of sample contents. To produce correct (H_2O,TOC) measurements for samples that do have recordable amounts of drainable liquid, a weighted average of the two measurements has been formed, with the weights representing the liquid and solid fractions of the sample.

It should be noted that this averaging affects only 15% of the samples. Since the waste in the single-shell tanks is generally dry enough to form a solid with little drainable liquid, no drainable liquid is present, and the solid waste measurements describe the state of the sample. The objective of this data collection effort is to obtain a relatively complete and unbiased description of TOC and moisture in the tanks. We have therefore tried to collect all sample data for the tanks and then selected the most representative measurements from those available. We have attempted to deal with potential biases by grouping the tanks into TOC groups. These groupings are based upon tank process history and should help reduce the biases associated with the current set of sampling data.

3.0 ESTIMATION METHODOLOGY OF DRY COMBUSTIBLE WASTE FRACTIONS

This section describes the statistical calculations that produce the dry combustible waste fractions (dry CWF) from (H_2O,TOC) sampling data. The calculation actually produces more than a single-point estimate for combustible waste fractions. A Bayesian "uncertainty distribution" is produced which describes how close the true CWF is to the estimate.

The calculations can be summarized into four steps:

1. Transform the (H_2O,TOC) data, which describes waste in its present state, to account for dry-out. The result is a dry-TOC measurement.

2. Perform an ANOVA analysis on dry-TOC measurements to determine the TOC distribution in each tank.

3. Transform the TOC distribution into a combustible waste distribution.

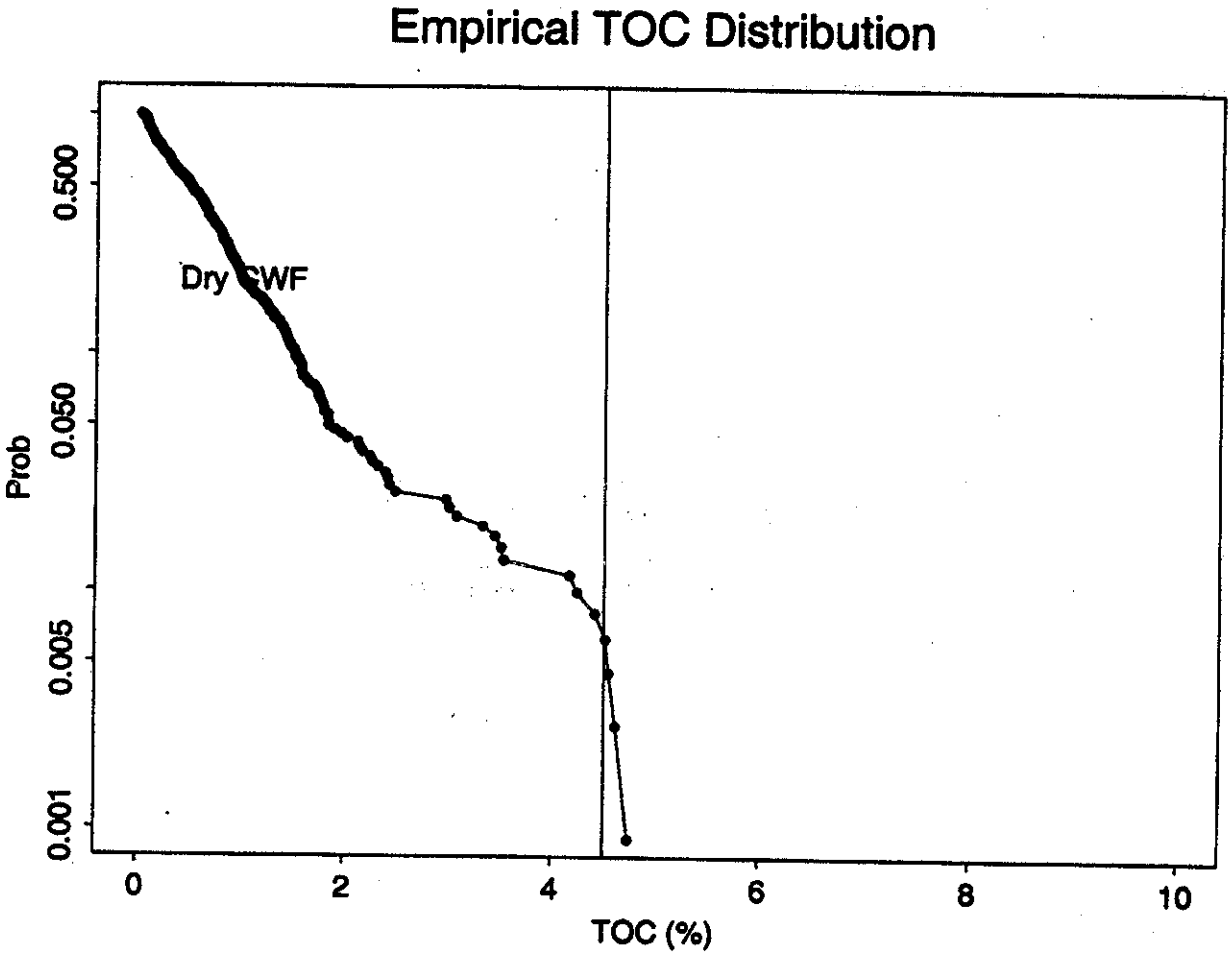
4. Compare the upper 95% quantile on the CWF distribution to the 5% screening threshold to determine whether or not the tank passed the screening calculation

Dry combustible waste is currently defined as waste with a TOC concentration above 4.5%. According to this definition, CWF is then the fraction of waste in a tank that exceeds this threshold. The strategy employed to calculate CWF requires that the sampling data available be used to estimate the TOC distribution in a tank. Such a dry-TOC distribution describes what proportion of the waste has a TOC concentration above any specified threshold, in particular the threshold that defines combustible waste.

The basic components of this strategy can be illustrated with tank data. Figure I-1 presents all the dry-TOC values that can be computed (H_2O,TOC) data (553 points). If these data represented a random sample from the tank farm, this plot would estimate the actual site-wide TOC distribution. One could therefore estimate the site-wide combustible waste fraction by counting the number of points that fall above the 4.5% threshold. In this example, 4 points are above the threshold, so we would estimate the dry combustible waste fraction at 4/553 = 0.7%.

This illustrative estimate has several deficiencies: it produces site-wide estimates, when tank specific estimates are needed; it may be biased because the tanks chosen for sampling are the "problem" TOC tanks; finally, it requires a great deal of data to produce accurate estimates. The methodology developed for tank screening attempts to deal with these difficulties, but it still utilizes the same simple strategy as illustrated.

Figure I-1. Illustration of a Dry Combustible Waste Estimate from Tank Data.



To estimate the distribution of dry-TOC in the tanks, statistical procedures suited to the structure of the available data have been chosen. The TOC distribution has been assumed to have a logistic-normal distribution and the two unknown parameters that define such a distribution (i.e. logistic-mean and logistic-standard deviation) are estimated using ANOVA (Analysis of Variance) procedures. A simple parametric form has been chosen for the distribution because sufficient data do not exist to estimate the distribution empirically for each tank. Although the assumption of logistic-normality is undoubtedly an approximation to reality, the residual plots presented in Section 4 demonstrate that the assumption is reasonable.

A logistic distribution was chosen because it obeys the natural constraints on the measurement (TOC concentration can't be negative or greater than 20%). Also, the distribution is similar to

the log-normal distribution, when the mean is small. TOC concentration has been observed to obey such a relationship between mean and standard deviation.

In previous reports, the TOC and H_2O distributions were assumed to be log-normal. When concentrations are low (as is generally the case for TOC), there is virtually no difference between the log-normal and logistic distributions. However, the log-normal distribution does not have an upper bound, so the distributions differ markedly when concentrations are high (as is frequently the case for H_2O). The logistic distribution was selected over the log-normal because the logistic distribution obeys the natural bounds that exist for TOC concentration and the log-normal does not.

3.1 TRANSFORMING (H_2O,TOC) MEASUREMENTS TO DRY TOC

Dry-out removes moisture from the waste and therefore makes it more likely to burn. We consider a dry-out scenario in which the moisture is reduced from its present concentration of $X_{H2O}(wet)$ to the value $X_{H2O}(dry)$. If $X_{TOC}(wet)$ represents the TOC currently in a unit of waste then after dry-out the result is:

$$X_{toc}(dry) = \frac{1 - X_{h2o}(dry)}{1 - X_{h2o}(wet)} X_{toc}(wet) \qquad (I-1)$$

The above formula is applied by making the most pessimistic assumption for dry-out, that $X_{H2O}(dry) = 0$, or all water is eliminated. Studies have shown that after 50 years, a typical single-shell tank would achieve equilibrium between 15% to 45% moisture (see Table D-4 in Appendix D), so if best estimates for dry-out were used in the screening calculation, much different results might be obtained.

3.2 TANK GROUPING

Tank groups have been introduced into the ANOVA modeling to allow TOC to be predicted in unmeasured tanks. Tanks have been arranged into 5 complexant waste groups to represent the expected concentration of complexants (TOC), and these are described in detail in Appendix F.

Five categorizations cannot perfectly predict TOC. For example, a "non-complexant" tank may still contain TOC because secondary waste streams contain TOC, because the TOC may be solvents or extractants, or because of errors in the historical records. Splitting the tanks into more categories will decrease the within group variations, but also decrease the amount of data available to estimate TOC for each group. Given this constraint (i.e., data must exist to describe TOC in each group), we decided to limit the categories to the following five:

High: Tanks receiving high complexant waste streams

Medium: Tanks receiving indirect transfers of complexant waste.

Low: Tanks receiving very little complexant waste.

Non-TOC: Tanks that should not have received any complexant waste.

Special: Tanks that have unique or unusual waste transfer histories and have been excluded from the screening.

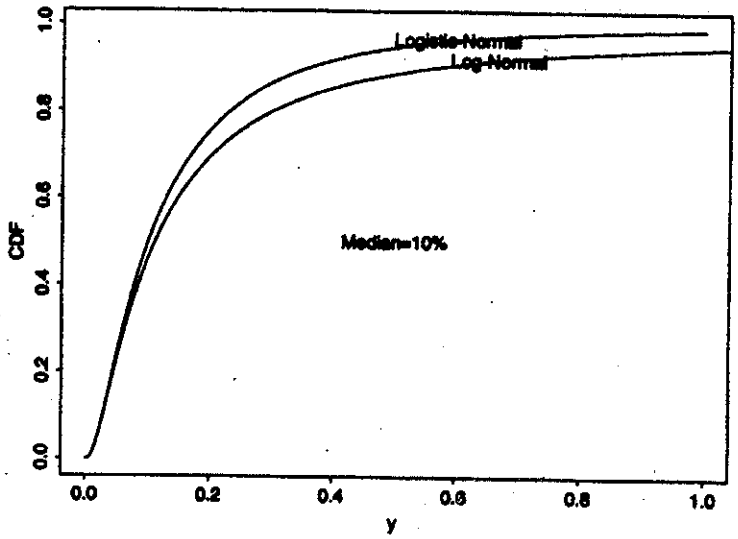
3.3 CONSTRUCTING DISTRIBUTIONS FOR DRY-TOC WITH ANOVA

The distribution of dry-TOC in a tank is assumed to be a *logistic-normal* distribution. The selected distribution is created by applying a logistic transformation to the TOC values and assuming the result is normally distributed. If X_{min} and X_{max} represent the minimum and maximum bounds on a TOC measurement, then the logistic transformation of the TOC value X_{TOC} is defined by:

$$Y = \log\left(\frac{X_{TOC} - X_{\min}}{X_{\max} - X_{TOC}}\right) = logistic(X_{TOC}) \qquad (I-2)$$

The transformed value Y is assumed to be normally distributed with a mean of μ and a standard deviation of σ. This transformation produces a distribution that is very close to a log-normal distribution when the TOCs are small. This distribution is called the logistic-normal distribution and is most frequently utilized in binomial regression modeling. Figure I-2 compares a logistic-normal to a log-normal fit on a data set with relatively small values (i.e. near X_{min}, which for this case is 0). One can see that the logistic-normal distribution is really equivalent to the log-normal for small values.

Figure I-2. Comparison of Logistic and Log-Normal Distributions.



For the screening analysis, the minimum bound on TOC has been set at $X_{min} = 0$ and the maximum bound has been set to $X_{max} = 20\%$. The maximum bound is set to 20%, a value much lower than 100% because the waste cannot consist of 100% *combustible* organic carbon. Oxidizer must be present in the waste and the organic carbon must be chemically combined with a cation. These constraints result in an upper bound on TOC of 20%.

To "fit" a logistic-normal distribution to TOC data, one really needs to estimate the two parameters: the mean, μ, and the standard deviation, σ, of the logistic-transformed data. There are several ways to do this, and what is optimal depends on the amount of data available as well as any relationships that might exist between tanks. An ANOVA model is employed to estimate these two parameters for each tank.

The ANOVA model assumes that (1) the σ parameter is the same for all tanks and that (2) the means, μ are described by a certain random-effects ANOVA formula. Because of these assumptions, the ANOVA model can produce estimates with modest amounts of data, and can in fact produce TOC distributions for tanks that have no data.

Let us identify the transformed TOC data by Y_{ijkl} where the indices describe the conditions that the data were taken under. These are defined as:

i: Describes the layer (surface layer, subsurface layer) the sample was taken from. The model divides the tank into a surface layer (the top 19 inches of waste), and the sub-surface layer (the remaining portion of the waste).

j: Identifies a tank group. There are four tank groups, (High TOC, Medium TOC, Low TOC, and Non-TOC).

k: Represents the tank associated with the sample.

ℓ: Identifies the "replicate" measurements that occur within a layer in a specific tank.

This notation can be used to identify the distribution parameters μ and σ that we desire to estimate, which must be estimated for the surface and subsurface layers of every tank. Thus layer i in tank jk therefore has parameters μ_{ijk} and σ_{ijk} associated with it.

ANOVA estimates are produced by fitting an ANOVA model of the form

$$Y_{ijk\ell} = \mu + D_i + G_j + DG_{ij} + T_{jk} + DT_{ijk} + e_{ijk\ell} \qquad (I-3)$$

with the model terms (parameters) defined as follows (on the logistic scale):

μ: logistic-mean TOC for the site.

D_i: Deviation of layer i from the mean μ.

G_j: Deviation of tank group j from the mean μ.

DG_{ij}: Deviation of layer i from group average.

T_{jk}: Deviation of Tank k from the group average.

DT_{ijk}: Deviation of layer i in tank k from its average.

$e_{ijk\ell}$: Spatial deviations within layer (i, j, k).

σ_T^2: $Var(T_{jk})$, tank to tank variability.

σ_{DT}^2: $Var(DT_{ijk})$, layer to layer variability.

σ_e^2: $Var(e_{ijk\ell})$, within layer variability.

The terms μ, D_i, G_i, and DG_i are fixed effects, while the other terms are random effects. However, because of relatively large degrees of freedom associated with the fixed effects terms,

one can consider the fixed effects terms to be random, and obtain similar results. The ANOVA fitting procedure treats all terms in the above model as random effects so that a simpler ANOVA algorithm can be used.

This model includes the tank groups in the form of G_j and DG_{ij}, which are important in determining estimates of TOC for tanks without any data. The waste within the tanks has been divided into two layers because the surface of the waste was thought to be different than the subsurface. Ideally, one would like to include more layers than this in the model (perhaps a layer for every segment taken) but not enough data are available to do this.

The ANOVA fitting algorithm estimates the model parameters (as well as their uncertainty). These model parameters can be used to estimate the desired distributional parameters as follows:

$$\hat{\mu}_{ijk} = \hat{\mu} + \hat{D}_i + \hat{G}_j + \hat{DG}_{ij} + \hat{T}_{jk} + \hat{DT}_{ijk} \qquad (I-4)$$

and

$$\hat{\sigma}^2_{ijk} = \hat{\sigma}^2_e \qquad (I-5)$$

where the hat over the parameter signifies its estimated value.

Once the parameters μ_{ijk} and σ_{ijk} are estimated, they are used to produce an estimate for the combustible waste fraction. Since the combustible waste fraction is just the amount of waste with TOC concentration above 4.5%, it must be given by

$$R_{ijk} = 1 - F(4.5) \qquad (I-6)$$

where R_{ijk} represents the combustible waste fraction estimate and F(x) represents the cumulative distribution function for TOC in the layer identified by *ijk*. Our analysis assumes that F(x) is logistic normal, with a logistic mean of μ_{ijk} and logistic standard deviation of σ_{ijk}, so the combustible waste fraction can also be written as:

$$R_{ijk} = \Phi\left(\frac{\mu_{ijk} - logistic(4.5\%)}{\sigma_{ijk}}\right) \qquad (I-7)$$

with $\Phi(z)$ representing a standard normal CDF. To obtain a combustible waste fraction for the whole tank, the top and bottom layers are averaged together, using the respective layer volumes as weights:

$$R_{jk} = \frac{V_{surf}}{V_{surf} + V_{bot}} R_{1jk} + \frac{V_{bot}}{V_{surf} + V_{bot}} R_{2jk} \qquad (I-8)$$

As discussed previously, the calculation must produce more than simple point estimates, because there is substantial uncertainty in such an estimate. We actually desire to calculate the posterior (uncertainty) distribution of R_{jk} given the available data. This more complicated problem is discussed in the next section, but the solution is closely related to the point estimation formulas presented above.

3.4 CALCULATION OF UNCERTAINTY DISTRIBUTIONS

The ANOVA estimation method can produce approximate posterior distributions for the parameters μ_{ijk} and σ_{ijk}. To simplify the discussion, we will concentrate on tank *jk*, so that the indices *jk* can be dropped from the parameters. For tank *jk*, we desire the joint posterior distribution on (μ_1, μ_2, σ) (1=surface, 2=subsurface), which can be denoted by:

$$f(\mu_1, \mu_2, \sigma^2 | data) \qquad (I-9)$$

Because the transformed data are normally distributed, the posterior is related to the estimates according to the approximate formula:

$$f(\mu, \sigma^2 | data) = N(\mu : \hat{\mu}, \hat{A}) IG(\sigma^2 : \hat{\sigma}^2, dof) \qquad (I-10)$$

where $N(x : \mu, A)$ represents a multivariate normal distribution with mean μ and a covariance matrix of A. In the above formula, μ represents (μ_1, μ_2), so the normal distribution is two dimensional. The covariance matrix $\hat{A}$ is produced by the ANOVA fitting procedure.

The variance, σ^2, is distributed according to an inverse gamma distribution, which is denoted by $IG(x : z, d)$. The random variable x has an inverse gamma distribution with parameters z and d if 1/x has a gamma distribution with a mean of z and d degrees of freedom.

Equation I-9 describes the uncertainty in the TOC distribution parameters μ and σ^2. Furthermore, Equations I-6 and I-7 relate these parameters to combustible waste R, a relationship that we can express by writing $R(\mu, \sigma^2)$. Thus, the uncertainty distribution of R is given by;

$$F(R_0|Data) = Pr(R < R_0|Data) \quad (I-11)$$

$$F(R_0|Data) = \int_{R(\mu_1,\mu_2,\sigma^2)<R_0} f(\mu_1,\mu_2,\sigma^2|Data)\,d\mu_1\,d\mu_2\,d\sigma^2 \quad (I-12)$$

This distribution describes the combustible waste in tank *jk*, and is the final output of the calculation. An estimate is produced from this distribution by using its median. To classify tanks as pass or fail, the upper 95% quantile from this distribution is used.

3.5 FORMULAS FOR ESTIMATING ANOVA MODEL PARAMETERS

The ANOVA model presented in Equation I-3 is fit to the data using the Restricted Maximum Likelihood Algorithm present in Splus [see Chambers and Hastie (1992), Corbeil and Searle (1976), Searle et al. (1992), and Dempster et al. (1981) for details]. The ANOVA fitting procedure will produce estimates for all the unknown terms present in the above equation. Since all terms in the model are considered to be random variables (with the exception of μ), it also calculates their variances (such as $Var(E_{ijk\ell}) = \sigma_E^2$, $Var(T_{jk}) = \sigma_T^2$, etc.). These variances are used by the ANOVA procedure to calculate uncertainty in the TOC estimates.

This model can produce estimates for all random effects by conditioning on the observed data ($Y_{ijk\ell}$). We explain how this is done by re-specifying the model [see Dempster et al. (1981) and Searle et al. (1992)] in Equation I-3 in matrix form as:

$$Y = X\beta + E \quad (I-13)$$

where Y is a $n \times 1$ response vector, X is the design matrix from the over-parameterized model comprised of zeros and ones denoting absence or presence of effects for a particular response. β is a vector comprised of μ and all of the random effects in the model, and E is the error vector of $E_{ijk\ell}$. Therefore it is assumed;

$$\beta \sim N(0, \Sigma) \quad (I-14)$$

$$E \sim N(0, \sigma^2 I) \quad (I-15)$$

where Σ is a diagonal matrix with the variances of the model effects on the diagonal (i.e., $\Sigma = diag\{\infty, \sigma_D^2, \sigma_D^2, \sigma_G^2, \sigma_G^2, \cdots\}$). The first diagonal element corresponds to μ which is fixed and it

is mathematically equivalent to consider it as a random term with infinite variance [see Dempster et al. (1981)]. The joint density of the random variables Y and β can be written as

$$\begin{bmatrix} Y \\ \beta \end{bmatrix} \sim N\left(\begin{bmatrix} 0 \\ 0 \end{bmatrix}, \begin{bmatrix} X\Sigma X^T + \sigma^2 I & X\Sigma \\ \Sigma X^T & \Sigma \end{bmatrix} \right). \tag{I-16}$$

If Y is observed, then the conditional distribution of β given Y is a multivariate normal with

$$E(\beta|Y) = (X^T X + \sigma^2 \Sigma^{-1})^{-1} X^T Y \text{ and} \tag{I-17}$$

$$Cov(\beta|Y) = \sigma^2 (X^T X + \sigma^2 \Sigma^{-1})^{-1} \tag{I-18}$$

and the Σ inverse matrix having the form

$$\Sigma^{-1} = diag\left\{0, \frac{1}{\sigma_D^2}, \frac{1}{\sigma_D^2}, \frac{1}{\sigma_G^2}, \frac{1}{\sigma_G^2}, \ldots\right\}. \tag{I-19}$$

$E(\beta|Y)$ is the "best estimate" for the random effect vector β and $Cov(\beta|Y)$ represents its associated uncertainty. The ANOVA fitting procedure [Restricted Maximum Likelihood, Dempster et al. (1981)] uses the above formulas to determine all unknown model parameters in an iterative fashion. Given estimates for Σ, an estimate for the random effects parameter β is determined. Given β, the variances in Σ can be determined using sum of squares formulas [see Corbeil and Searle (1976)].

In matrix form, the best estimate for a specific layer [identified by indices (i, j, k)] is given by:

$$\hat{\mu}_{ijk} = V^T E(\beta|Y) \text{ or} \tag{I-20}$$

$$\hat{\mu}_{ijk} = \hat{\mu} + \hat{D}_i + \hat{G}_j + \hat{DG}_{ij} + \hat{T}_{jk} + \hat{DT}_{ijk} \tag{I-21}$$

where V represents a vector of zeros and ones chosen to select the 6 terms listed in the second part of the above equation. The uncertainty of this estimate is given by:

$$Var(\hat{\mu}_{ijk}|Y) = V^T Cov(\beta|Y) V \tag{I-22}$$

Formulas 20 and 22 produce reasonable estimates for tank layers, even when no data actually exist for that layer. To have these estimates produced, one must only include columns in the design matrix, X that represent all layers to be estimated.

For a tank having no data, it can be shown that the best estimate is actually reduced to

$$\hat{\mu}_{ijk} = \hat{\mu} + \hat{G}_j + \hat{D}_i + \hat{DG}_{ij} \qquad (I-23)$$

because T_{jk}, and DT_{ijk} are estimated as zero. In other words, when no data exists for a tank, the ANOVA uses group averages to estimate the layer concentrations, a strategy that makes intuitive sense. Of course, estimates associated with unsampled tanks are much less certain than the previous estimate, and their uncertainties are inflated by the amount *Var(T)+Var(DT)*. The actual estimates for all tank layers are automatically produced by an ANOVA estimation program [see *S-PLUS* (1996) and Corbeil and Searle (1976)] using Equation I-16.

The variance σ_E^2 (specified above as σ^2) represents within-layer variability (contaminated with some measurement error) and is particularly important in the combustible waste calculation because it describes how homogeneous the waste is. If this variance were zero, one measurement from a tank layer would be sufficient to determine whether or not it was safe. This variability is also affected by the physical dimensions of the sample used to produce the data for the ANOVA. Making the samples dramatically larger or smaller than those currently produced by Tank Waste Characterization sampling might produce a significantly different σ_E^2.

Since the measurement $Y_{ijk\ell}$ is typically on a core-segment, the unit of waste being described in the ANOVA model is actually a cylinder 1 inch in diameter and about 20 inches in height. This analysis is therefore evaluating the variability for units of waste that are about 20 inches (or 0.4M) in dimension. A unit of waste of this dimension is approximately the size of concern for safety.

4.0 RESULTS OF THE DRY-CWF CALCULATION

4.1 ANOVA FIT TO DRY TOC

The ANOVA model fit to the dry-TOC data is described by Equation I-3. The variance components of this model (i.e. σ^2_E, σ^2_T, etc.) are summarized in Table I-4. The estimates are produced in logistic-transformed space, but the original estimates have been converted to relative standard deviations (RSD).

Table I-4. ANOVA Results For Dry-TOC

Variance Component	ANOVA Estimate	Approx. RSD(%)
σ^2_D	0	0%
σ^2_G	0.267	52%
σ^2_T	0.557	75%
σ^2_{DG}	0	0%
σ^2_{DT}	0.185	43%
σ^2_e	0.519	72%

One would like the variance components associated with tank grouping to be large because this would result in more effective predictions on unsampled tanks. The within-group correlation, which measures of how well the model predicts TOC in unsampled tanks, is 27%. The within-group correlation is calculated from:

$$\rho = \frac{\sigma^2_D + \sigma^2_G + \sigma^2_{DG}}{\sigma^2_D + \sigma^2_G + \sigma^2_T + \sigma^2_{DG} + \sigma^2_{DT}} \qquad (I-24)$$

The logistic-mean TOC for all sampled tanks, μ, is estimated as μ = -4.06, which translates into a concentration of 0.33%.

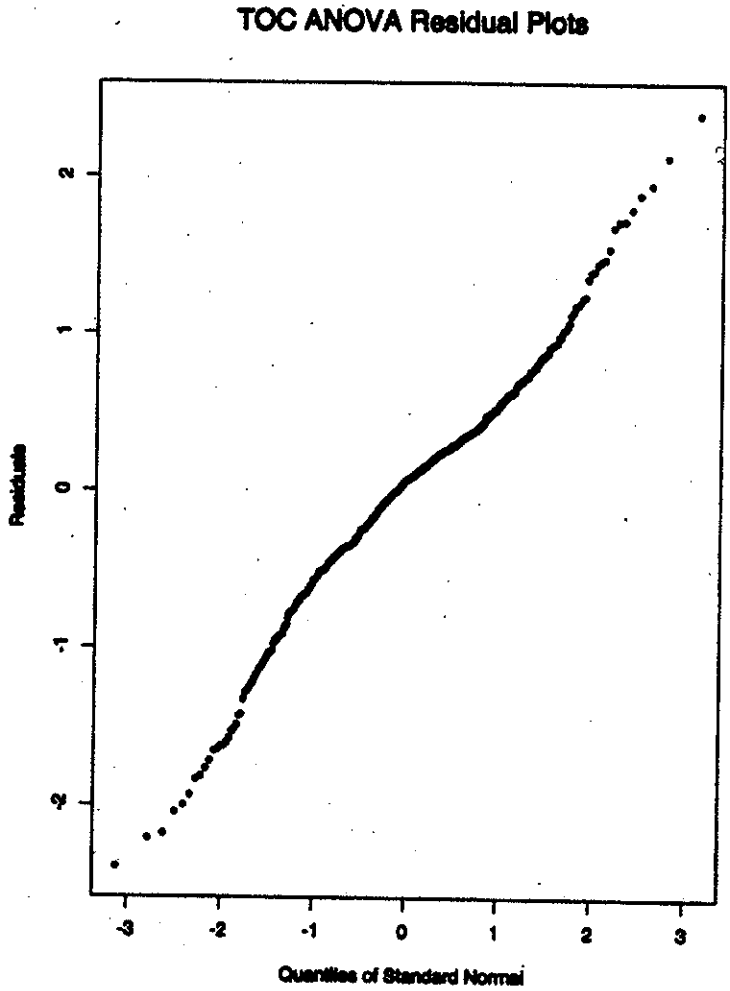
The ANOVA table contains a fairly large tank-to-tank variability of σ^2_T = 0.56. In previous evaluations this number was somewhat lower. The addition of more tanks to the data-base has increased this variability. It is also important to note that the terms involving waste layers (σ^2_D *and* σ^2_{DT}) are zero, indicating that there is no difference between surface and subsurface TOC (dry-basis), an important observation.

The ANOVA model assumes that the data is logistic-normally distributed, and this assumption is quite important when calculating the combustible waste fractions. Figure I-3 presents a "Q-Normal" plot of the ANOVA residuals to check the hypothesis of logistic normality. These residuals are from logistic-transformed data, so they should be normally distributed if the assumption is correct. When the residuals are normally distributed, the Q-normal plot should produce roughly a straight line. As one can see, this is largely the case, particularly the distribution tails.

The fit of logistic-normal distribution to the right-hand tail of the distribution is particularly important because the CWF calculation relies on this portion of the distribution. The fact that there seem to be no "outlier" data-points is important.

The principal deficiency apparent in the Q-normal plot is the bump in the middle of the distribution. This bump provides evidence that the distribution may be a mixture of two

Figure I-3. Q Normal-Plot of Moisture Anova Residuals.



populations with different sigmas. This provides some evidence that the assumption σ_{ijk} = constant is not strictly true.

The ANOVA also predicts the logistic-means for the two layers in each tank. These predictions are presented graphically in Figure I-4. The Figure lists tanks by TOC groups, with the group mean identified by the solid line on each plot. Of course, these predictions have an uncertainty associated with them and this is represented in the plots by square brackets, which identify 95% bounds on the prediction (the prediction is represented by the open circle).

The figures also present the data used in the ANOVA fit; this data is represented on the plots as solid dots. Each data point in this plot is actually the average of all raw data (usually sample/duplicate measurements) from a single location. Thus the scatter of the data points represents the spatial variability of dry TOC within the defined layer. The dry-TOC data used in this fit is also listed in Section 6, for the reader's reference.

As one can see from the plots, the ANOVA basically computed a layer estimate by averaging existing data on the logistic scale. If the layer has only one or two data points, the estimate might deviate from the simple logistic-mean, because the ANOVA includes the group mean in the averaging process. One can also see a substantial difference in confidence bound widths on the plots. Layers that have data can have confidence bounds that are about an order of magnitude smaller than layers without data.

Figure I-4. Dry-TOC ANOVA Results (Sheet 1 of 11)

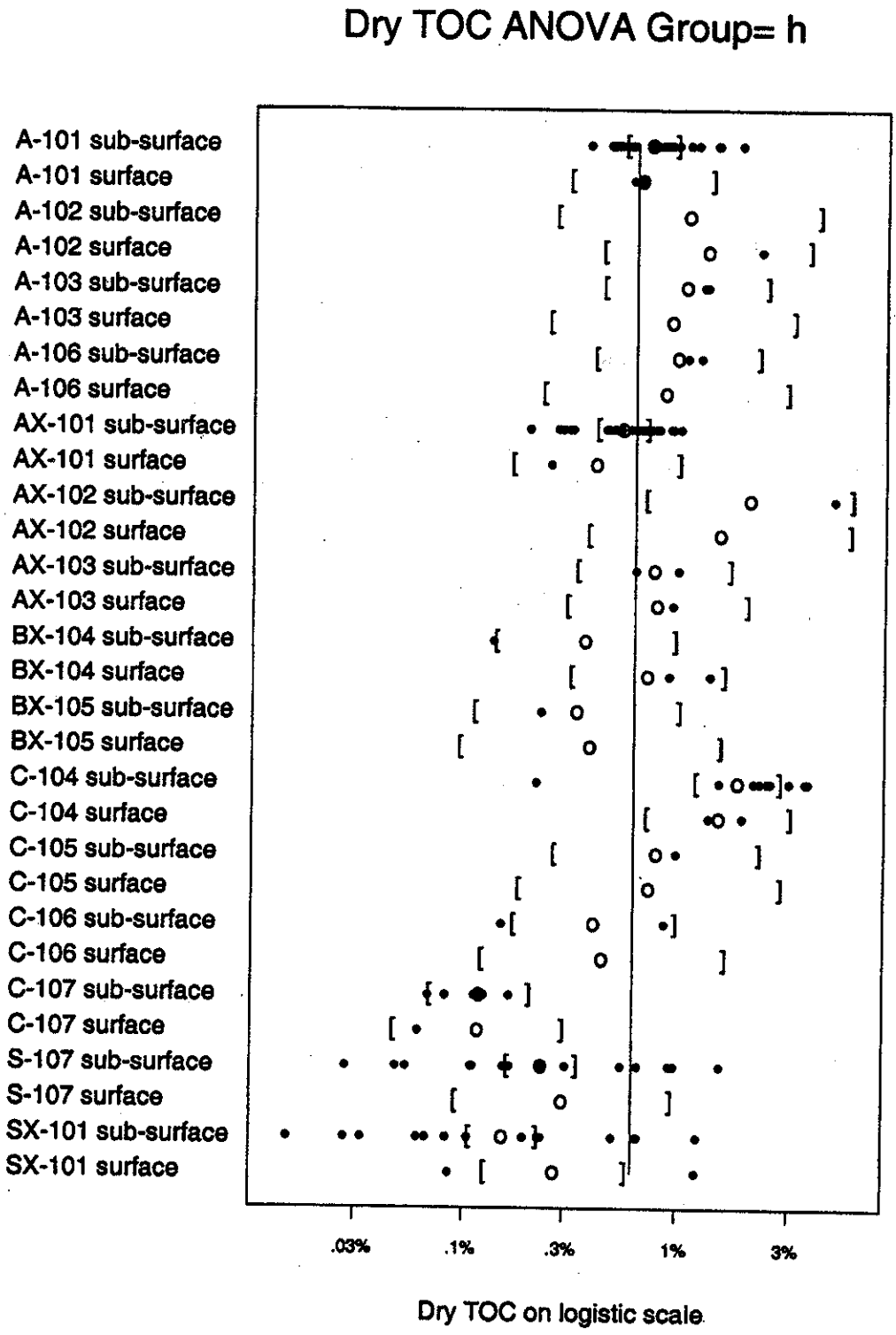


Figure I-4. Dry-TOC ANOVA Results (Sheet 2 of 11)

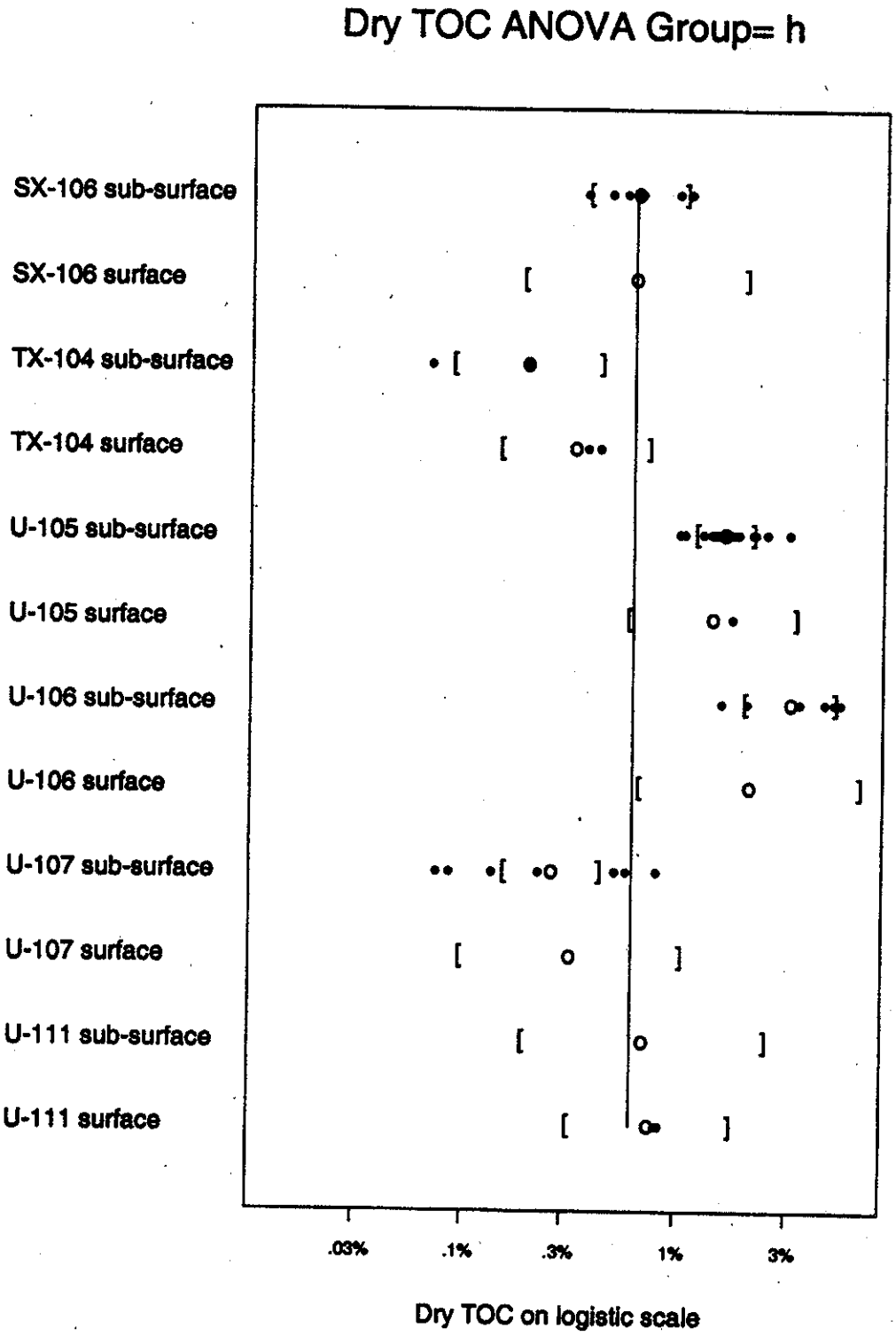


Figure I-4. Dry-TOC ANOVA Results (Sheet 3 of 11)

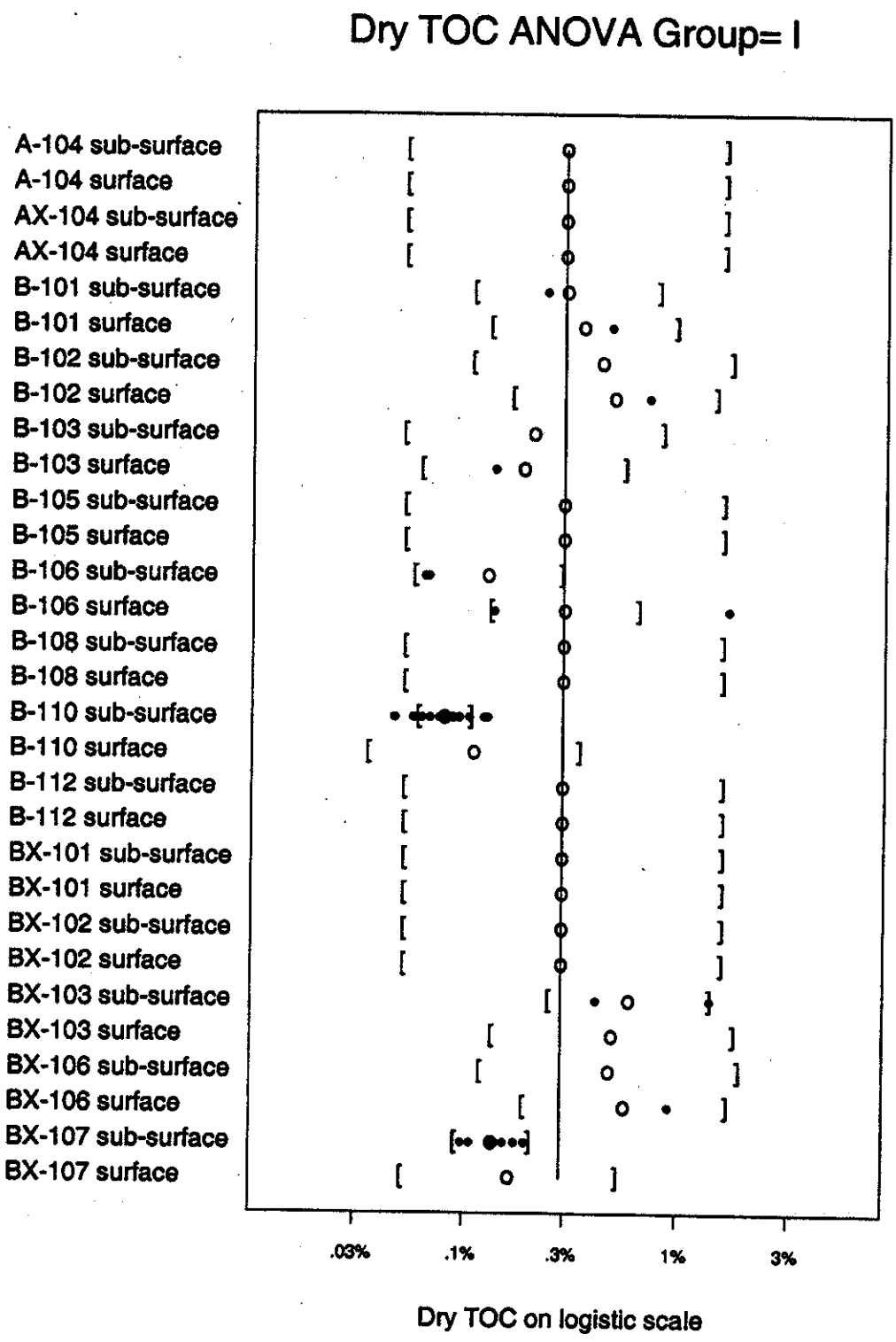


Figure I-4. Dry-TOC ANOVA Results (Sheet 4 of 11)

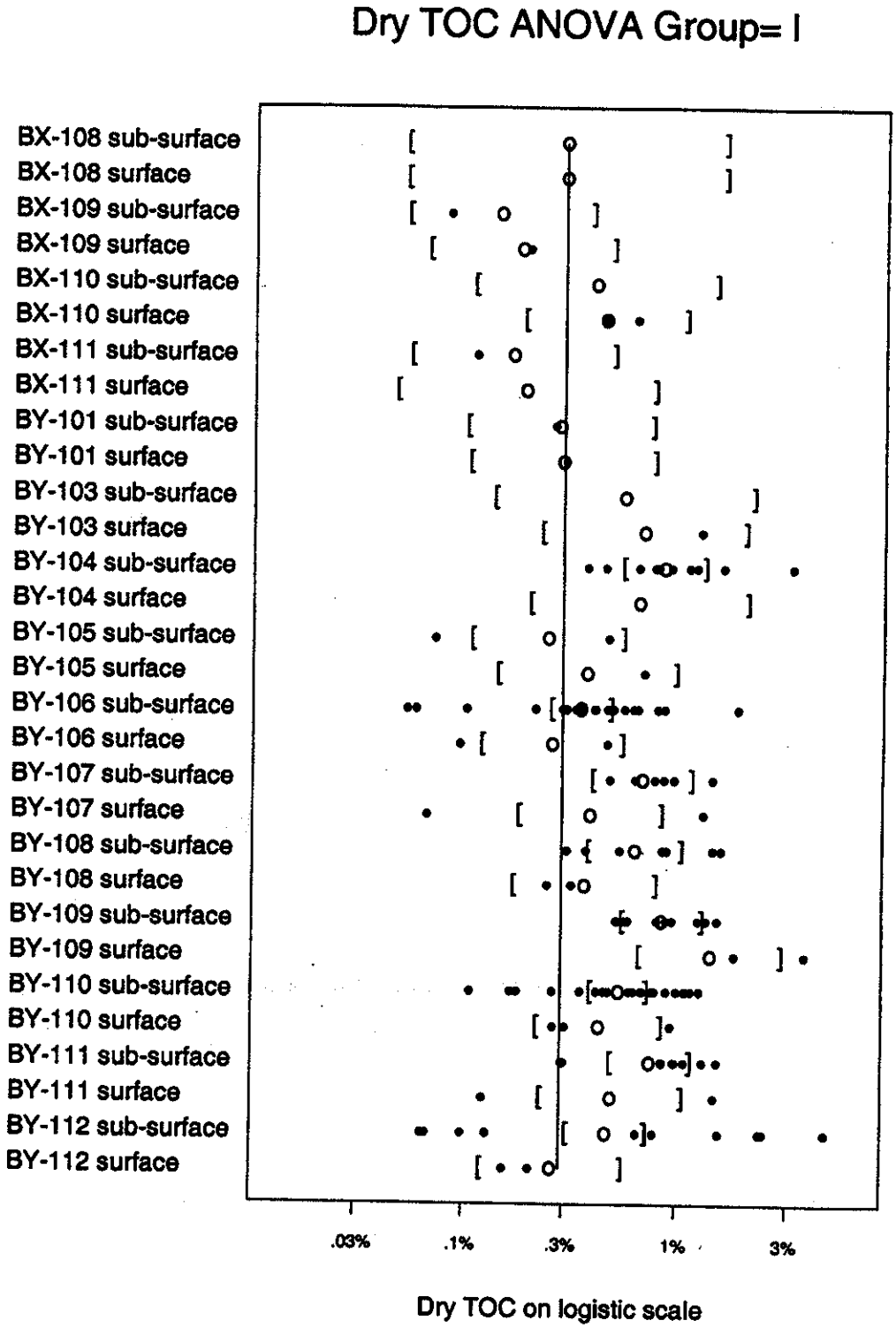


Figure I-4. Dry-TOC ANOVA Results (Sheet 5 of 11)

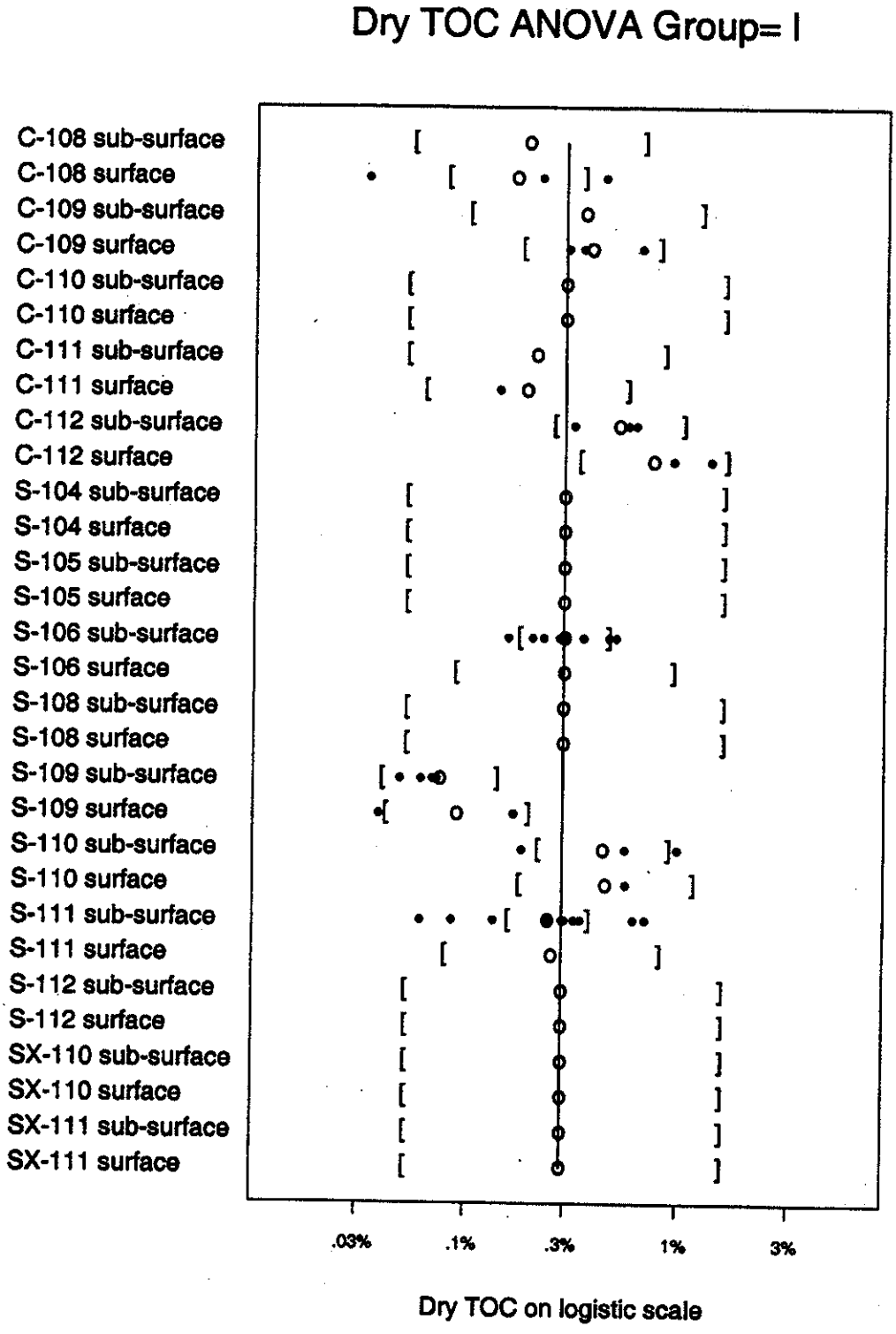


Figure I-4. Dry-TOC ANOVA Results (Sheet 6 of 11)

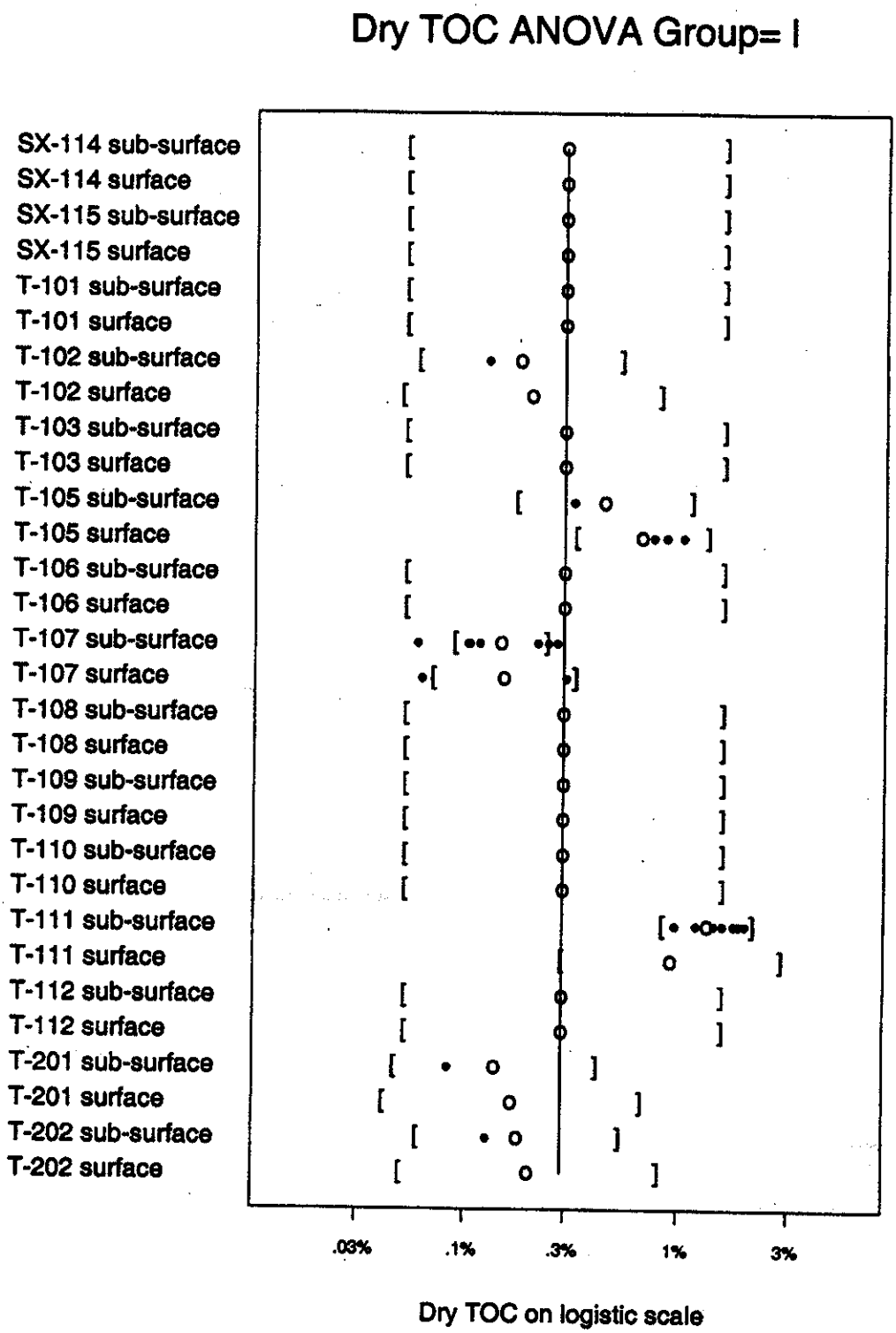


Figure I-4. Dry-TOC ANOVA Results (Sheet 7 of 11)

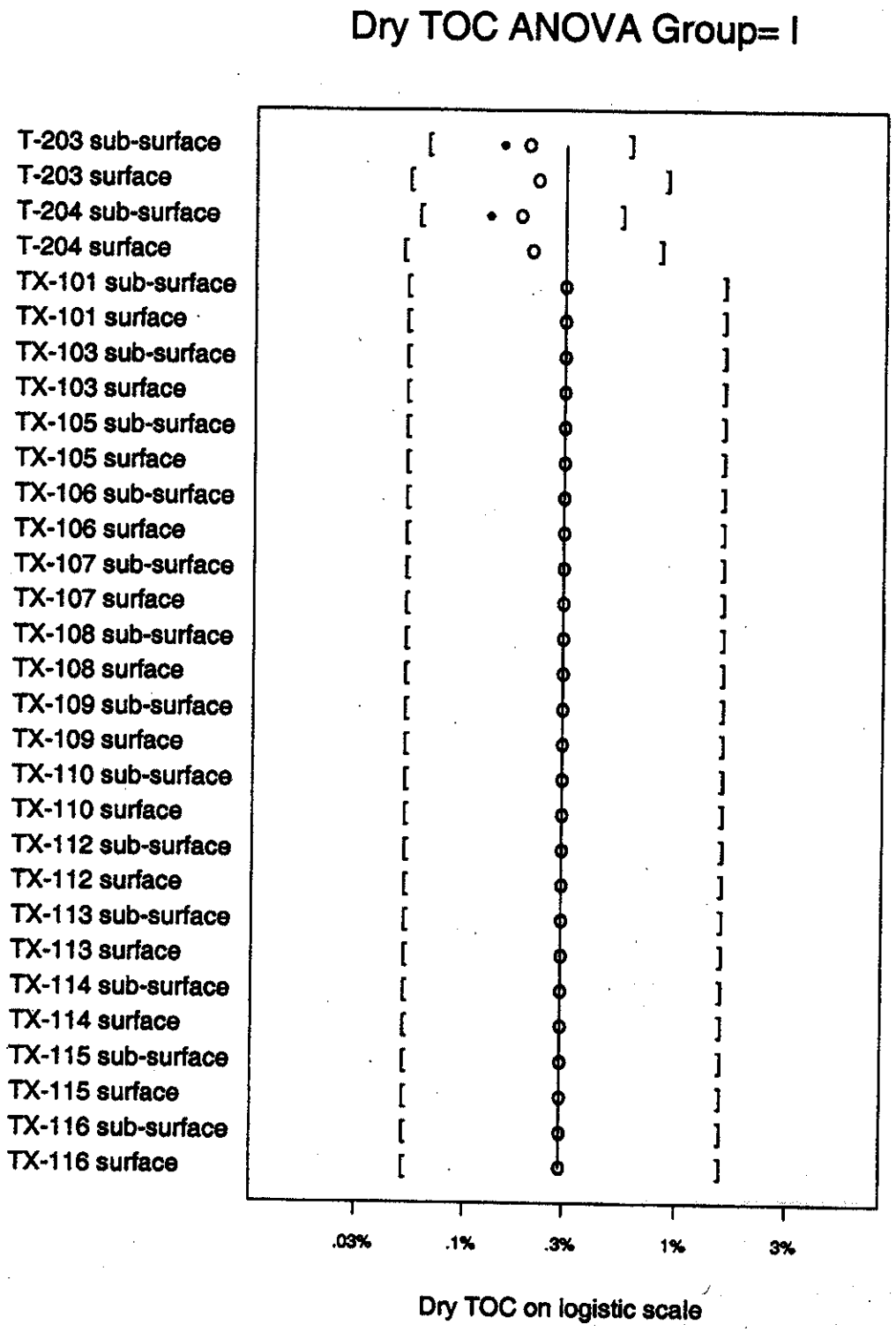


Figure I-4. Dry-TOC ANOVA Results (Sheet 8 of 11)

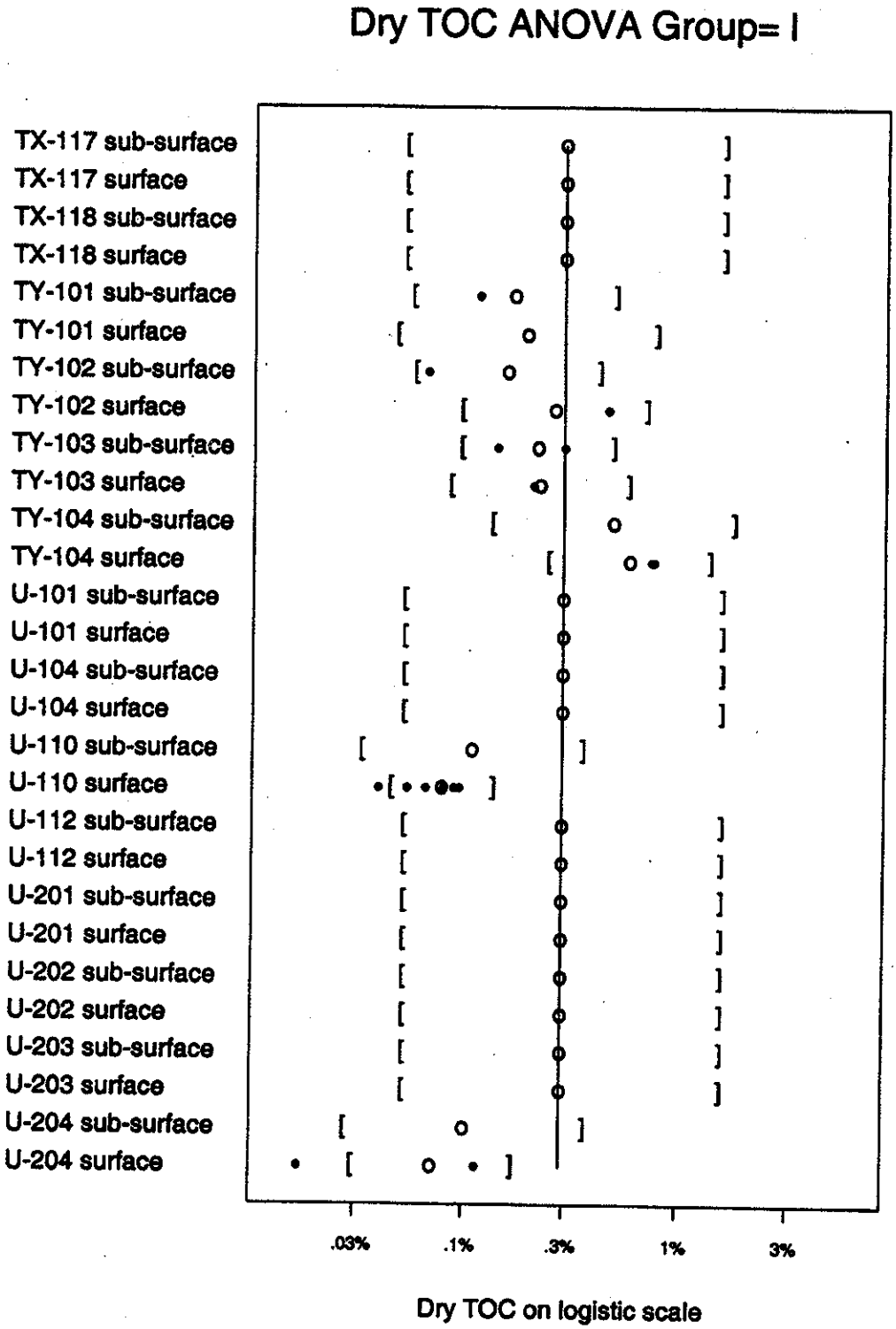


Figure I-4. Dry-TOC ANOVA Results (Sheet 9 of 11)

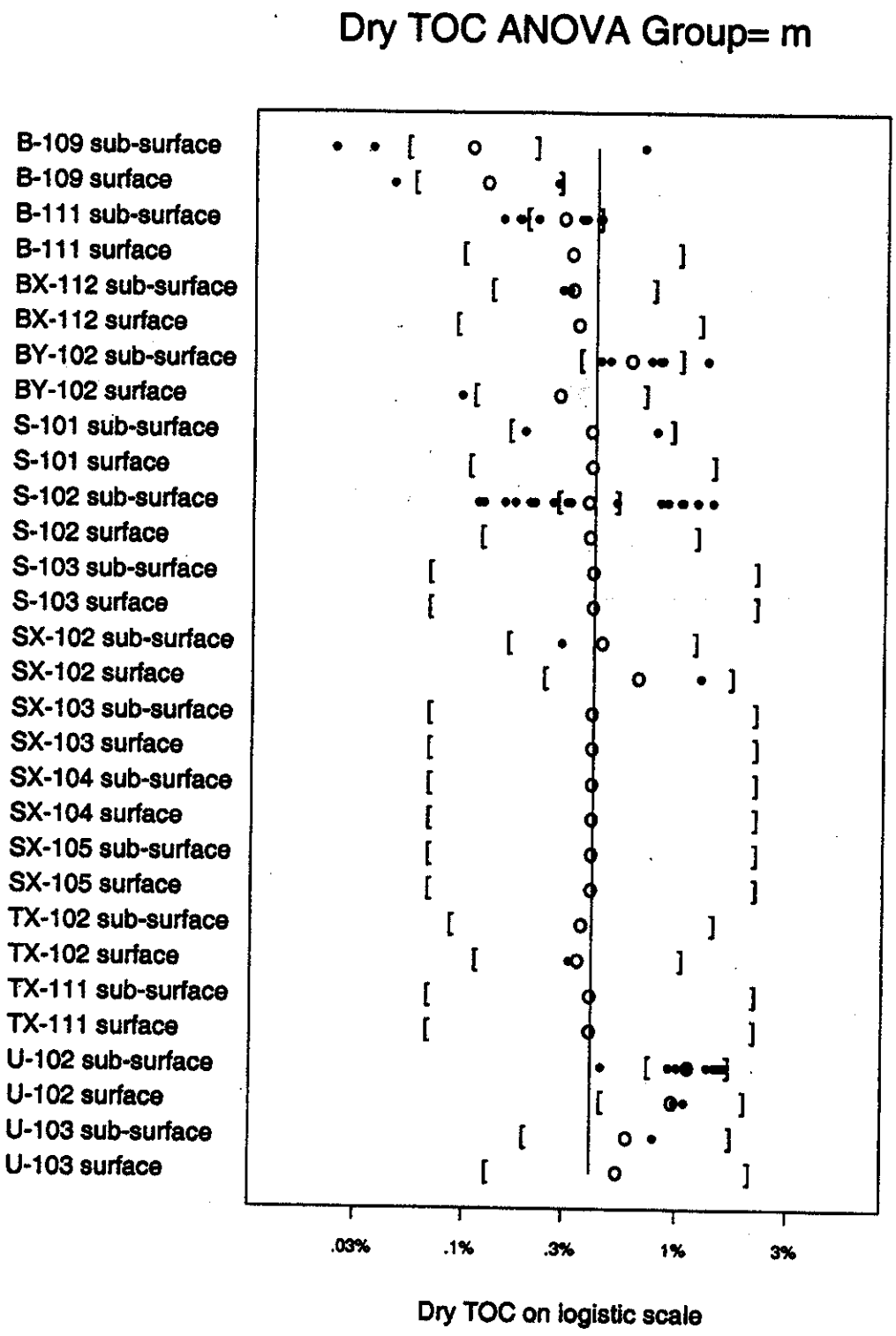


Figure I-4. Dry-TOC ANOVA Results (Sheet 10 of 11)

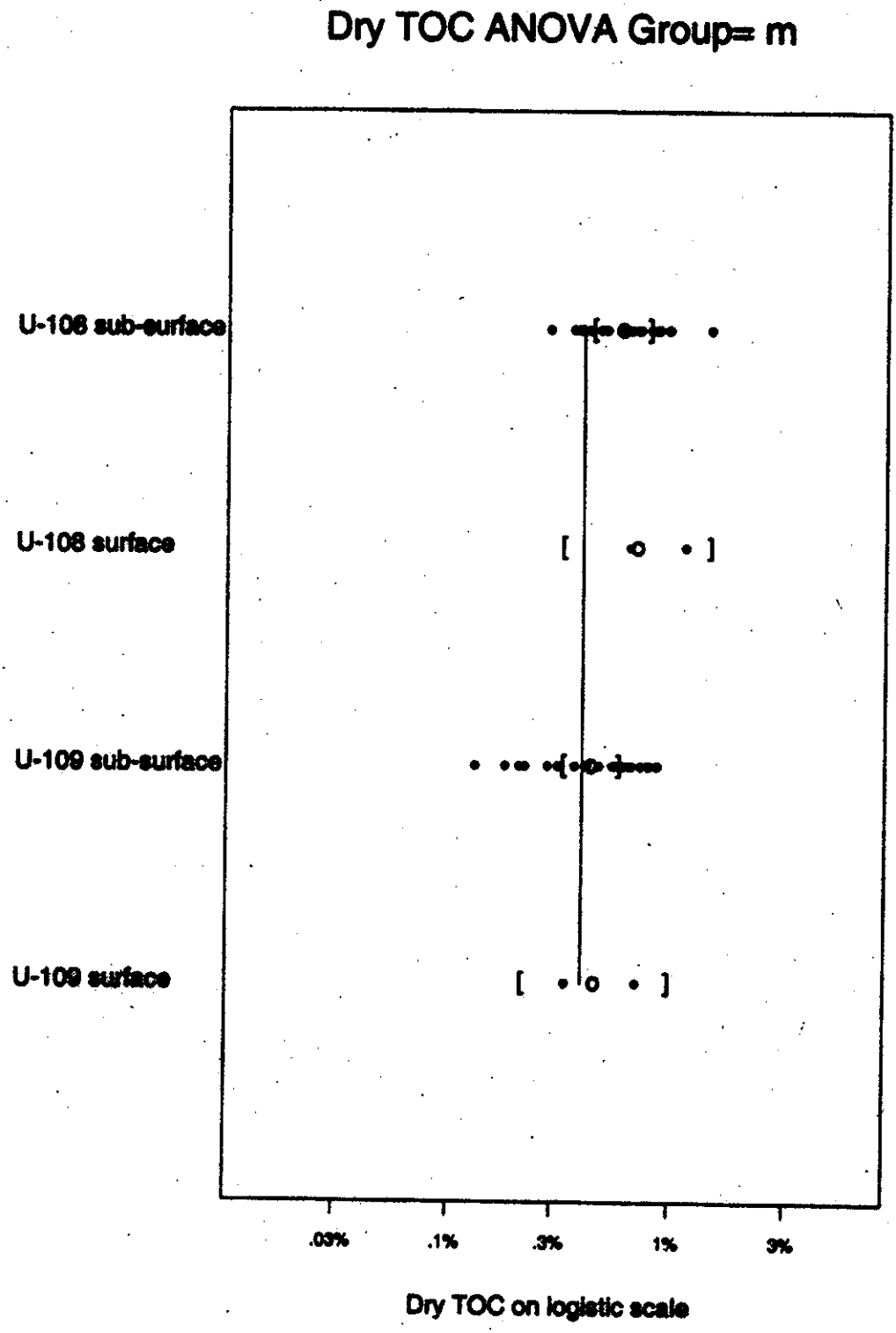
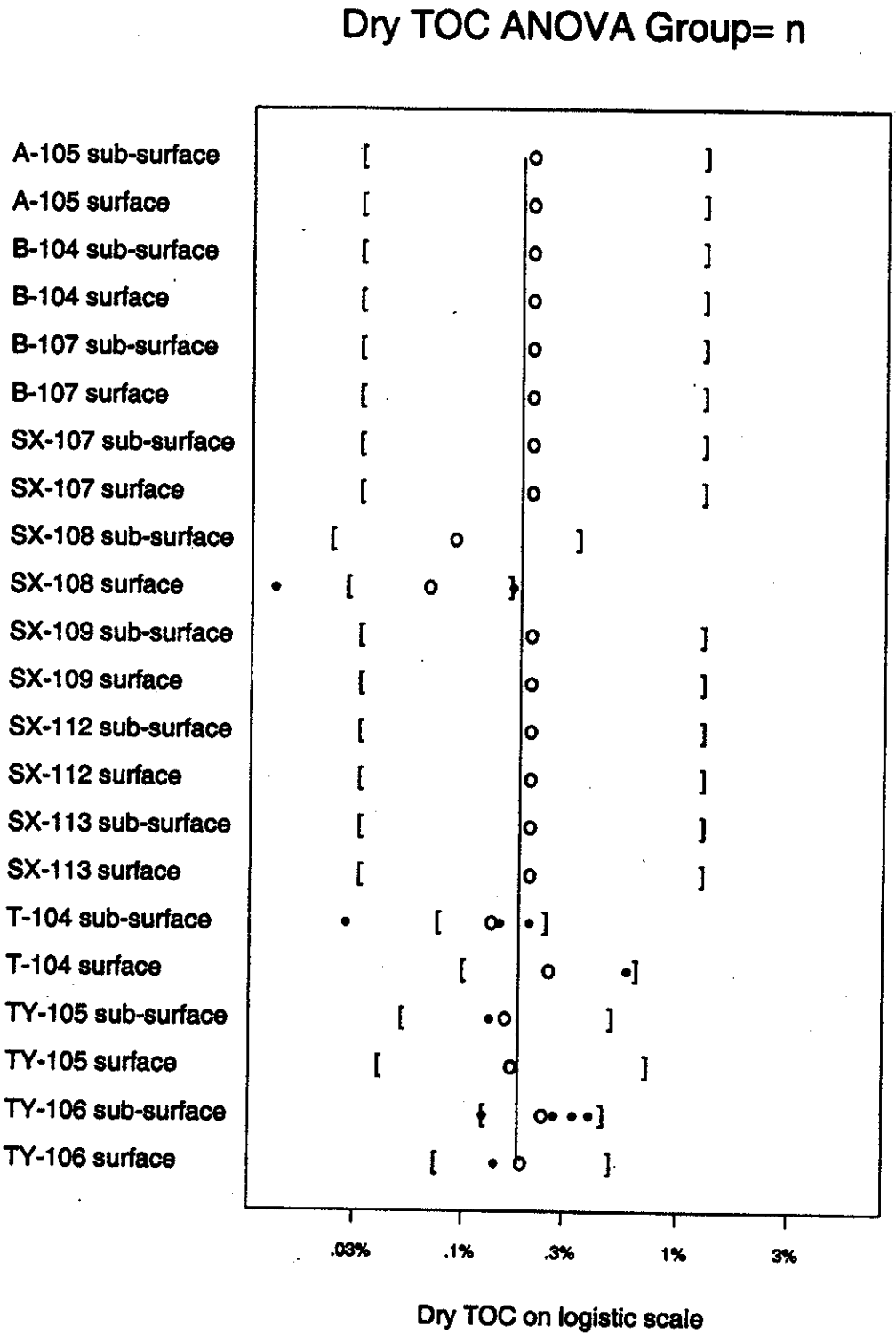


Figure I-4. Dry-TOC ANOVA Results (Sheet 11 of 11)



4.2 CALCULATION OF COMBUSTIBLE WASTE FRACTIONS

The ANOVA results presented in the last section are used to calculate the dry fraction of combustible waste. These fractions are then used to screen tanks into pass/fail categories as described earlier. This section presents best estimates (medians) for these fractions as well as upper 95% bounds.

Table I-5 lists the failing tanks from the dry-CWF calculations. There are 11 such tanks, and they are listed in order of the 95% bound on estimated CWF. Tank U106 has the largest CWF, with a best estimate of 25% and an upper 95% estimate of 44%. A tank as high as this is an obvious failure.

Table I-5. Failing Combustible Waste Fractions

Tank	Grp	# Obs	Dry-TOC Est.		Dry CWF	
			Surf	Sub-Surf	Median	Upper 95
U106	h	8	2.074	3.061	24.6	44.2
AX102	h	1	1.501	2.024	7.3	40.9
A102	h	1	1.306	1.073	2.5	22.6
C104	h	11	1.5	1.816	6.8	16.1
A103	h	2	0.908	1.049	1.1	9.8
U105	h	22	1.426	1.611	4.9	9.6
T111	l	8	0.923	1.34	2.6	8.3
U111	h	2	0.757	0.711	0.2	8.3
A106	h	2	0.853	0.965	0.9	8.3
C105	h	1	0.734	0.791	0.4	7.8
BY103	l	1	0.69	0.557	0.1	5.4

On the other hand, there are several tanks that are "close to" the pass/fail threshold of 5% (BY103, C105, A106, U111, T111), and their categorization is more ambiguous. A small change in assumptions (such as the completeness of dry-out) or a small alteration of input data could change their status. It should be noted that there are also several tanks just below the 5% threshold (see SX103, SX104, and SX105 from Table I-6) that might move onto the list of failures with a slight change in data or assumptions.

In previous evaluations, the list of failed tanks has indeed changed as the data changed, with most alterations occurring with "boundary" tanks. Such ambiguities are unavoidable, when one is required to use a specific pass/fail threshold.

Table I-6 presents the median and upper bounds on the dry combustible waste fractions for all relevant tanks. The fractions are compared to the 5% screening threshold and those that are below are marked with a P (Pass), while those above are marked with an F (Fail). The reader should note that this screening is a first step in final categorization of the tanks. Failing tanks may be judged safe because of other information. One column in the table, "grp," also identifies the TOC group the tank belongs to. The TOC groups are: h-High, l-Low, m-Medium, n-NonTOC, s-Special.

Table I-6. Combustible Waste Fraction Estimates. (4 sheets)

			Dry CWF					Dry CWF	
Tank	Grp	Status	Median	Upper 95	Tank	Grp	Status	Median	Upper 95
A101	h	P	0.2	0.6	A102	h	F	2.5	22.6
A103	h	F	1.1	9.8	A104	l	P	0	1.9
A105	n	P	0	0.7	A106	h	F	0.9	8.3
AX101	h	P	0.1	0.2	AX102	h	F	7.3	40.9
AX103	h	P	0.4	3.6	AX104	l	P	0	1.6
B101	l	P	0	0.2	B102	l	P	0.1	2
B103	l	P	0	0.1	B104	n	P	0	0.7
B105	l	P	0	1.6	B106	l	P	0	0
B107	n	P	0	0.7	B108	l	P	0	1.8
B109	m	P	0	0	B110	l	P	0	0
B111	m	P	0	0	B112	l	P	0	1.8
B201	s	NA	NA	NA	B202	s	NA	NA	NA
B203	s	NA	NA	NA	B204	s	NA	NA	NA
BX101	l	P	0	1.8	BX102	l	P	0	1.8
BX103	l	P	0.1	2.3	BX104	h	P	0.1	0.9
BX105	h	P	0	1.1	BX106	l	P	0.1	3.2
BX107	l	P	0	0	BX108	l	P	0	1.7

Table I-6. Combustible Waste Fraction Estimates. (4 sheets)

			Dry CWF					Dry CWF	
Tank	Grp	Status	Median	Upper 95	Tank	Grp	Status	Median	Upper 95
BX109	l	P	0	0	BX110	l	P	0	1.4
BX111	l	P	0	0	BX112	m	P	0	0.2
BY101	l	P	0	0.1	BY102	m	P	0.1	0.6
BY103	l	F	0.1	5.4	BY104	l	P	0.5	1.9
BY105	l	P	0	0	BY106	l	P	0	0
BY107	l	P	0.2	1	BY108	l	P	0.1	0.7
BY109	l	P	0.7	2.1	BY110	l	P	0.1	0.2
BY111	l	P	0.3	1.1	BY112	l	P	0	0.2
C101	s	NA	NA	NA	C102	s	NA	NA	NA
C103	s	NA	NA	NA	C104	h	F	6.8	16.1
C105	h	F	0.4	7.8	C106	h	P	0	0.6
C107	h	P	0	0	C108	l	P	0	0
C109	l	P	0	0.6	C110	l	P	0	1.7
C111	l	P	0	0.1	C112	l	P	0.1	1
C201	s	NA	NA	NA	C202	s	NA	NA	NA
C203	s	NA	NA	NA	C204	s	NA	NA	NA
S101	m	P	0	0.4	S102	m	P	0	0.1
S103	m	P	0	4.8	S104	l	P	0	1.6
S105	l	P	0	1.6	S106	l	P	0	0
S107	h	P	0	0	S108	l	P	0	1.6
S109	l	P	0	0	S110	l	P	0	0.4
S111	l	P	0	0	S112	l	P	0	1.6
SX101	h	P	0	0	SX102	m	P	0	0.9
SX103	m	P	0	4.9	SX104	m	P	0	4.9
SX105	m	P	0	4.9	SX106	h	P	0.2	0.9

Table I-6. Combustible Waste Fraction Estimates. (4 sheets)

			Dry CWF					Dry CWF	
Tank	Grp	Status	Median	Upper 95	Tank	Grp	Status	Median	Upper 95
SX107	n	P	0	0.8	SX108	n	P	0	0
SX109	n	P	0	0.7	SX110	l	P	0	1.9
SX111	l	P	0	1.7	SX112	n	P	0	0.8
SX113	n	P	0	0.8	SX114	l	P	0	1.7
SX115	l	P	0	1.6	T101	l	P	0	1.8
T102	l	P	0	0.1	T103	l	P	0	1.6
T104	n	P	0	0	T105	l	P	0.1	0.9
T106	l	P	0	1.6	T107	l	P	0	0
T108	l	P	0	1.8	T109	l	P	0	1.
T110	l	P	0	1.6	T111	l	F	2.6	8.3
T112	l	P	0	1.9	T201	l	P	0	0
T202	l	P	0	0	T203	l	P	0	0
T204	l	P	0	0	TX101	l	P	0	1.8
TX102	m	P	0	1.3	TX103	l	P	0	1.7
TX104	h	P	0	0	TX105	l	P	0	1.6
TX106	l	P	0	1.6	TX107	l	P	0	1.8
TX108	l	P	0	1.7	TX109	l	P	0	1.6
TX110	l	P	0	1.6	TX111	m	P	0	4.9
TX112	l	P	0	1.6	TX113	l	P	0	1.6
TX114	l	P	0	1.6	TX115	l	P	0	1.6
TX116	l	P	0	1.6	TX117	l	P	0	1.6
TX118	l	P	0	1.6	TY101	l	P	0	0
TY102	l	P	0	0	TY103	l	P	0	0
TY104	l	P	0.1	2.2	TY105	n	P	0	0
TY106	n	P	0	0	U101	l	P	0	1.6

Table I-6. Combustible Waste Fraction Estimates. (4 sheets)

			Dry CWF					Dry CWF	
Tank	Grp	Status	Median	Upper 95	Tank	Grp	Status	Median	Upper 95
U102	m	P	1.4	4.4	U103	m	P	0.1	3.4
U104	l	P	0	1.7	U105	h	F	4.9	9.6
U106	h	F	24.6	44.2	U107	h	P	0	0
U108	m	P	0.1	0.3	U109	m	P	0	0.1
U110	l	P	0	0	U111	h	F	0.2	8.3
U112	l	P	0	1.8	U201	l	P	0	1.9
U202	l	P	0	1.9	U203	l	P	0	1.9
U204	l	P	0	0					

5.0 VALIDATION OF THE ANOVA MODEL

The ANOVA modeling results presented previously in this appendix should produce reasonable predictions of TOC in unsampled tanks. "Reasonable" in this context means that the predictions and actual values agree within the limits of uncertainty produced by the ANOVA model. In this section, a validation test for the predictive capabilities of this model are discussed and applied.

Data from six recently sampled tanks are compared to the predictions made by the ANOVA model. In order to produce a fair comparison, the ANOVA model has been run without the data from these six tanks and these predictions are then compared to the available data. The tanks being used for this validation are AX103, BX103, BX104, BY109, S106, and S110. In Table I-7, the ANOVA estimates (on the logistic scale) for these tanks are given as well as the logistic-mean averages obtained from sample data.

5.1 A CHI-SQUARED VALIDATION TEST

In mathematical terms, the ANOVA has produced predictions $\hat{\mu}_{ij}$ for each layer j in each of the i tanks listed above, as well as the associated standard errors S_{ij}. The sampling data that is available can be averaged together to form data-derived estimates for each of the layers, which we denote by X_{ij}. Each of these averages will have a standard error given by;

$$Stderr(X_{ij}) = \sigma_E/\sqrt{N_{ij}} \qquad (I-24)$$

where N_{ij} represents the number of sample measurements averaged together to produce X_{ij} and σ_E is the within-layer standard deviation produced by the ANOVA ($\sigma_E^2 = 0.531$).

The most standard test for X_{ij} versus $\hat{\mu}_{ij}$ uses a Chi-squared statistic that compares the distance between the predictions and data to their standard errors. This statistic has the form;

$$\chi^2 = \sum_{i,j} \frac{(X_{ij} - \hat{\mu}_{ij})^2}{S_{ij}^2 + \sigma_E^2/N_{ij}} \qquad (I-25)$$

If the two sets of estimates are the same, we would expect this statistic to have a Chi-squared distribution. On the other hand, if there are significant differences between the ANOVA predictions and data-derived estimates, the statistic will be much larger than a chi-squared variate.

5.2 PREDICTION INTERVAL TEST

The chi-squared statistic compares all predictions with the data-derived estimates in one calculation. One may also desire to individually check each prediction. To accomplish this, we can compare the difference between observed and predicted, $X_{ij} - \hat{\mu}_{ij}$, to its standard error. This produces a test statistic of the form:

$$Z = \frac{X_{ij} - \hat{\mu}_{ij}}{\sqrt{S_{ij}^2 + \sigma_{E/}^2 N_{ij}}} \qquad (I-26)$$

a value that is closely related to the Chi-squared statistic. This statistic is significant at the 95% level when it is above 1.96 or below -1.96. Thus when $|Z| < 1.96$, predicted and observed would be considered in agreement. Since this test is conducted at the 5% level, one would expect about 5% of the tests to fail, even when there is nothing wrong with the predictions. It would not be unusual to see one failure among 11 prediction intervals. However, more that 3 test failures would be considered significant.

5.3 TEST RESULTS

Table I-7 presents the comparisons for the designated tanks. Available data allows one to compare eleven ANOVA estimates to data. For example, the ANOVA estimate for the top layer in AX103 is -3.508, while the sample data produces an estimate of -3.023, a fairly close agreement. The test statistic column in the table describes how many standard deviations the two estimates are from each other, i.e. (-3.508- -3.023)/0.994=-0.514. If the two estimates are more than 1.96 standard deviations from each other, then the ANOVA estimate does not fit the data. Consequently, this test statistic shows the ANOVA estimate and data are in good agreement for this particular example.

An examination of the last column in Table I-6 shows that all the individual TOC test statistics have a magnitude less than 1.96 except for tank BY-109 (surface), which is quite different from its predicted value. This tank is in the low TOC tank group and has measured values that are atypically high for this group. The ANOVA estimates, which are basically the group means are -4.300 (0.27% TOC) while the data derived estimate is 2.5% TOC, a very large difference.

Even including one tank that does not fit, the over-all Chi-squared test (with a value of 13.2) is not significant at the 5% level. The P-value for the test is 21%, which indicates good agreement between ANOVA predictions and sampling data.

Table I-7. Comparison of ANOVA Predictions to Data

Tank	ANOVA Pred.		Data Res.			Pred. Test	
	Est.	SD(Est)	NOBS	Est.	SD(Est)	SD.	Stat.
Surface							
AX103	-3.508	0.887	1	-3.023	0.322	0.944	-0.514
BX103	-4.300	0.876	0	NA	NA	NA	NA
BX104	-3.508	0.887	2	-2.838	0.223	0.915	-0.732
BY109	-4.300	0.876	2	-1.938	0.387	0.958	-2.466
S106	-4.300	0.876	0	NA	NA	NA	NA
S110	-4.300	0.876	1	-3.528	0.322	0.933	-0.827
Sub-Surf							
AX103	-3.508	0.877	2	-3.196	0.234	0.918	-0.370
BX103	-4.300	0.876	2	-3.217	0.624	1.076	-1.007
BX104	-3.508	0.887	1	-4.988	0.322	0.944	1.568
BY109	-4.300	0.876	10	-3.140	0.132	0.886	-1.309
S106	-4.300	0.876	8	-4.215	0.146	0.888	-0.095
S110	-4.300	0.876	3	-3.728	0.506	1.012	-0.565

Chi-Squared Value=13.2 DOF=10 P-value=0.213

6.0 (H_2O,TOC) DATA USED IN THE SCREENING CALCULATION

This section presents the (H_2O,TOC) data used in the screening calculation. The data set presents (H_2O,TOC) estimates at each location sampled in the tanks, which are weighted averages of the laboratory data. The data is organized by tank, riser, and segment id. "Sampled locations" are generally equivalent to core segments. However, data points with missing core or segment information are averaged by layers.

The concentrations presented in the table are in weight percent. The number of observations column identifies how many raw measurements (usually sample and duplicate) were averaged together to produce the result. The acronym "NA" stands for "Not Available" and usually signifies that no useable measurements were available at that location.

Table I-8. Water and Total Organic Carbon Data. (14 sheets)

Tank/Riser Segment	Liq. Frac	Wet		Tank/Riser Segment	Liq. Frac	Wet	
		H2O	TOC			H2O	TOC
A101.15.1	0	31	0.46	A101.15.10	2	38	1.13
A101.15.13	78	47	0.27	A101.15.14	83	51	0.26
A101.15.15	68	45	0.26	A101.15.16	69	47	0.25
A101.15.18	74	38	0.23	A101.15.2	0	32	0.6
A101.15.3	0	33	0.57	A101.15.4	0	33	0.64
A101.15.6	0	31	0.51	A101.15.7	0	37	0.51
A101.15.9	0	29	1.02	A101.15.999	NA	40	0.46
A101.24.1	16	38	0.37	A101.24.10	52	39	0.45
A101.24.11	77	47	0.26	A101.24.12	75	46	0.3
A101.24.13	83	47	0.27	A101.24.14	81	45	0.28
A101.24.15	81	47	0.26	A101.24.17	84	46	0.32
A101.24.18	71	47	0.31	A101.24.3	0	33	0.57
A101.24.4	0	30	0.6	A101.24.5	0	33	0.72
A101.24.6	0	34	0.78	A101.24.7	0	33	0.6
A101.24.8	0	32	0.98	A102.19.1	0	32	NA
A102.5.1	0	36	1.42	A103.nA129.-7037	NA	38	0.77
A103.nA130.7036	NA	38	0.8	A103.nA60.7037.5	NA	40	NA
A103.nA61.7036.5	NA	40	NA	A106.nA131.7035	NA	42	0.72
A106.nA132.7034	NA	42	0.62	A106.nA62.7035.5	NA	43	NA
A106.na63.7034.5	NA	45	NA	AX101.226.1	NA	34	0.16

Table I-8. Water and Total Organic Carbon Data. (14 sheets)

Tank/Riser Segment	Liq. Frac	Wet		Tank/Riser Segment	Liq. Frac	Wet	
		H2O	TOC			H2O	TOC
AX101.226.10	NA	39	0.57	AX101.226.11	NA	39	0.17
AX101.226.12	NA	41	0.17	AX101.226.13	NA	34	0.21
AX101.226.14	NA	22	0.5	AX101.226.15	NA	30	0.47
AX101.226.2	NA	37	0.44	AX101.226.3	NA	36	0.37
AX101.226.4	NA	33	0.49	AX101.226.5	NA	37	0.51
AX101.226.6	NA	35	0.51	AX101.226.7	NA	35	0.5
AX101.226.9	NA	36	0.44	AX101.226.999	NA	25	0.34
AX101.228.10	NA	28	0.36	AX101.228.11	NA	30	0.14
AX101.228.12	NA	46	0.17	AX101.228.13	NA	46	0.15
AX101.228.14	NA	46	0.25	AX101.228.15	NA	44	0.28
AX101.228.2	NA	34	0.5	AX101.228.3	NA	29	0.44
AX101.228.4	NA	36	0.41	AX101.228.5	NA	33	0.4
AX101.228.6	NA	35	0.48	AX101.228.7	NA	39	NA
AX101.228.8	NA	33	0.6	AX101.228.9	NA	34	0.66
AX101.228.999	NA	40	0.42	AX102.3a.999	NA	29	NA
AX102.9e.999	NA	32	NA	AX102.riser.9g.999	NA	30	3.06
AX103.9a.2	NA	45	0.54	AX103.9f.1	NA	42	0.54
AX103.9f.2	NA	44	0.35	B101.2.1	0	33	0.32
B101.2.2	45	37	0.15	B101.7.1	0	39	NA
B101.7.2	18	30	NA	B102.1.1	NA	19	0.58
B103.2.1	0	40	NA	B103.7.1	0	50	0.07
B104.2.1	68	51	NA	B104.2.2	0	46	NA
B104.2.3	0	45	NA	B104.2.4	0	41	NA
B104.2.5	NA	48	NA	B104.2.6	0	46	NA
B104.2.7	0	46	NA	B104.7.1	28	49	NA
B104.7.2	0	48	NA	B104.7.3	0	47	NA
B104.7.4	0	48	NA	B104.7.5	0	48	NA
B104.7.6	0	48	NA	B104.7.7	NA	47	NA
B106.2.1	NA	61	0.64	B106.2.2	NA	58	0.03
B106.7.1	NA	63	0.05	B106.7.2	NA	59	0.03

Table I-8. Water and Total Organic Carbon Data. (14 sheets)

Tank/Riser Segment	Liq. Frac	Wet		Tank/Riser Segment	Liq. Frac	Wet	
		H2O	TOC			H2O	TOC
B108.3.1	NA	31	NA	B108.3.2	NA	32	NA
B109.4.1	NA	40	0.03	B109.4.2	NA	40	0.01
B109.4.3	NA	24	0.03	B109.7.1	NA	45	0.15
B109.7.2	NA	39	0.4	B110.1.2	NA	47	0.06
B110.1.3	NA	47	0.06	B110.1.4	NA	47	0.04
B110.1.5	NA	47	0.05	B110.2.3	NA	47	0.05
B110.2.5	NA	47	0.02	B110.3.2	NA	47	0.05
B110.3.3	NA	47	0.05	B110.3.4	NA	47	0.04
B110.3.5	NA	47	0.02	B110.4.3	NA	47	0.07
B110.4.5	NA	47	0.05	B110.na100.999	NA	47	0.04
B110.na101.999	NA	47	0.04	B110.na102.999	NA	47	0.03
B110.na103.999	NA	47	0.03	B110.na110.999	NA	47	0.04
B110.na111.999	NA	47	0.04	B110.na112.999	NA	47	0.05
B110.na113.999	NA	47	0.05	B110.na114.999	NA	47	0.03
B110.na115.999	NA	47	0.05	B110.na116.999	NA	47	0.03
B110.na97.999	NA	47	0.04	B110.na98.999	NA	47	0.04
B110.na99.999	NA	47	0.03	B111.3.2	68	62	NA
B111.3.3	69	64	NA	B111.3.4	65	58	NA
B111.3.5	63	56	NA	B111.3.999	64	62	0.07
B111.5.2	NA	67	NA	B111.5.3	67	66	NA
B111.5.4	65	60	NA	B111.5.5	68	65	NA
B111.5.999	62	62	0.14	B111.na107.999	NA	62	0.07
B111.na108.999	NA	62	0.07	B111.na109.999	NA	62	0.13
B111.na121.999	NA	62	0.13	B111.na122.999	NA	62	0.13
B111.na123.999	NA	62	0.16	B111.na124.999	NA	62	0.16
B111.na93.999	NA	62	0.06	B111.na94.999	NA	62	0.16
B111.na95.999	NA	62	0.08	B111.na96.999	NA	62	0.13
B112.3.1	0	46	NA	B112.7.1	38	37	NA
BX101.1.1	NA	17	NA	BX101.7.1	NA	14	NA
BX103.2.2	5	27	0.31	BX103.7.2	5	52	0.66

Table I-8. Water and Total Organic Carbon Data. (14 sheets)

Tank/Riser Segment	Liq Frac	Wet		Tank/Riser Segment	Liq. Frac	Wet	
		H2O	TOC			H2O	TOC
BX104.1.1	NA	52	0.66	BX104.7.1	NA	25	0.68
BX104.7.2	NA	37	0.09	BX105.2.1	NA	12	NA
BX105.6.1	NA	13	NA	BX105.na133.999	NA	21	0.18
BX106.2.1	0	41	NA	BX106.6.1	0	36	0.59
BX107.3.2	NA	44	NA	BX107.3.3	NA	55	NA
BX107.3.5	NA	35	NA	BX107.3.6	NA	45	NA
BX107.3.7	NA	42	NA	BX107.3.999	NA	49	0.1
BX107.7.2	55	50	NA	BX107.7.4	54	52	NA
BX107.7.5	NA	55	NA	BX107.7.6	58	51	NA
BX107.7.7	NA	47	NA	BX107.7.999	NA	49	0.07
BX107.na104.999	NA	49	0.06	BX107.na105.999	NA	49	0.07
BX107.na106.999	NA	49	0.08	BX107.na118.7048	NA	49	0.05
BX107.na55.7083.5	NA	54	NA	BX107.na57.999	NA	52	NA
BX107.na58.7	NA	50	NA	BX107.na59.7048.5	NA	56	NA
BX107.na83.7083	NA	49	0.07	BX107.na88.999	NA	49	0.09
BX107.na89.7	NA	49	0.06	BX107.na90.999	NA	49	0.06
BX107.na91.999	NA	49	0.06	BX107.na92.999	NA	49	0.07
BX108.2.1	NA	52	NA	BX108.6.1	NA	5	NA
BX109.2.1	20	54	NA	BX109.2.2	0	49	NA
BX109.2.3	0	51	NA	BX109.2.4	19	59	NA
BX109.6.1	0	49	0.1	BX109.6.2	0	51	NA
BX109.6.3	0	49	0.04	BX109.6.4	0	51	NA
BX110.3.1	NA	9	0.4	BX110.6.1	NA	44	0.35
BX111.na54.7084.5	NA	52	NA	BX111.na82.7084	NA	46	0.06
BX112.2.1	0	64	NA	BX112.2.2	NA	68	0.1
BX112.2.3	NA	68	NA	BX112.3.1	0	63	NA
BX112.3.2	NA	66	0.09	BX112.3.3	NA	68	NA
BY101.10b.2	NA	24	0.2	BY101.10d.1	NA	17	0.24
BY102.5.1	NA	12	0.08	BY102.5.2	NA	23	0.63
BY102.5.3	NA	26	0.96	BY102.5.4	NA	25	0.55

Table I-8. Water and Total Organic Carbon Data. (14 sheets)

Tank/Riser Segment	Liq. Frac	Wet		Tank/Riser Segment	Liq. Frac	Wet	
		H2O	TOC			H2O	TOC
BY102.5.5	NA	22	0.36	BY102.5.6	NA	50	0.39
BY102.5.7	NA	29	0.3	BY103.10b.1	0	21	0.98
BY103.12a.1	0	16	NA	BY104.11.2	0	14	2.63
BY104.11.3	0	10	0.41	BY104.11.4	0	26	0.57
BY104.11.5	0	24	0.61	BY104.11.6	0	22	0.51
BY104.11.7	0	27	0.87	BY104.11.8	0	31	1.09
BY104.11a.1	91	48	NA	BY104.11a.2	31	38	0.69
BY104.11a.3	0	32	0.63	BY104.11a.4	0	14	NA
BY104.11a.5	0	17	0.31	BY105.12a.1	NA	22	0.54
BY105.12a.2	NA	22	0.37	BY105.12a.3	NA	6	0.07
BY106.10b.1	0	47	0.25	BY106.10b.10	58	45	0.16
BY106.10b.11	95	13	0.05	BY106.10b.13	0	26	1.36
BY106.10b.2	0	47	0.26	BY106.10b.3	79	61	0.18
BY106.10b.4	0	17	0.28	BY106.10b.5	0	14	0.09
BY106.10b.6	86	50	0.28	BY106.10b.8	0	24	0.16
BY106.10b.9	0	17	0.04	BY106.5.1	0	16	0.08
BY106.5.10	0	33	0.2	BY106.5.2	0	31	0.45
BY106.5.3	0	21	0.32	BY106.5.4	0	13	0.31
BY106.5.5	0	20	0.5	BY106.5.6	0	15	0.35
BY106.5.7	0	17	0.42	BY106.5.8	0	34	0.57
BY106.5.9	0	26	0.59	BY107.8.1	NA	20	0.05
BY107.8.2	NA	41	0.51	BY107.8.3	NA	48	0.33
BY107.8.4	NA	34	0.63	BY107.9b.1	NA	43	0.74
BY107.9b.2	NA	32	0.33	BY107.9b.3	NA	45	0.43
BY107.9b.4	NA	42	0.83	BY108.12a.1	NA	29	0.23
BY108.12a.2	NA	29	0.63	BY108.12a.3	NA	32	0.37
BY108.12a.4	NA	33	1.04	BY108.7.1	NA	27	0.18
BY108.7.2	NA	20	0.24	BY108.7.3	NA	17	0.31
BY108.7.4	NA	33	0.57	BY108.7.5	NA	29	1.01
BY109.10b.1	NA	39	1.09	BY109.10b.2	NA	28	1.07

Table I-8. Water and Total Organic Carbon Data. (14 sheets)

Tank/Riser Segment	Liq. Frac	Wet		Tank/Riser Segment	Liq. Frac	Wet	
		H2O	TOC			H2O	TOC
BY109.10b.3	NA	33	0.59	BY109.10b.4	NA	36	0.78
BY109.10b.5	NA	48	0.3	BY109.10b.6	NA	44	0.3
BY109.10b.7	NA	33	0.64	BY109.12c.1	NA	38	2.18
BY109.12c.2	NA	39	0.81	BY109.12c.3	NA	42	0.3
BY109.12c.4	NA	48	0.31	BY109.12c.5	NA	48	0.42
BY110.12b.1	NA	5	0.29	BY110.12b.2	NA	9	0.39
BY110.12b.3	NA	30	0.55	BY110.12b.4	NA	12	0.31
BY110.12b.5	NA	16	0.22	BY110.12b.6	NA	15	0.09
BY110.12b.7	NA	18	0.14	BY110.4.1	NA	18	0.76
BY110.4.2	NA	26	0.12	BY110.4.3	NA	16	0.4
BY110.4.4	NA	22	0.47	BY110.4.5	NA	37	0.56
BY110.4.6	NA	35	0.4	BY110.4.7	NA	35	0.45
BY110.4.8	NA	32	0.78	BY110.7.1	NA	16	0.22
BY110.7.2	NA	17	0.38	BY110.7.3	NA	16	0.58
BY110.7.4	NA	21	0.78	BY110.7.5	NA	22	0.6
BY110.7.6	NA	29	0.54	BY110.7.7	NA	32	0.73
BY110.7.8	NA	31	0.74	BY110.7.9	NA	29	0.89
BY111.12a.1	NA	1	0.12	BY111.12a.3	NA	24	0.99
BY111.12a.4	NA	49	0.43	BY111.12a.5	NA	52	0.51
BY111.12a.6	NA	46	0.16	BY111.12a.7	NA	48	0.44
BY111.15.1	NA	33	0.98	BY111.15.2	NA	24	1.14
BY111.15.3	NA	15	0.92	BY111.15.4	NA	16	0.81
BY111.15.5	NA	35	0.64	BY111.15.6	NA	33	0.2
BY112.18.1	NA	24	0.12	BY112.18.2	NA	14	0.05
BY112.18.3	NA	15	0.11	BY112.18.4	NA	23	3.25
BY112.18.5	NA	38	0.95	BY112.18.6	NA	35	0.51
BY112.21.1	NA	36	0.13	BY112.21.2	NA	15	0.08
BY112.21.3	NA	19	0.05	BY112.21.4	NA	28	1.71
BY112.21.5	NA	37	1.46	BY112.21.6	NA	29	0.47
C104.14.1	NA	39	0.83	C104.14.2	NA	53	1.16

Table I-8. Water and Total Organic Carbon Data. (14 sheets)

Tank/Riser Segment	Liq. Frac	Wet		Tank/Riser Segment	Liq. Frac	Wet	
		H2O	TOC			H2O	TOC
C104.14.3	NA	63	0.84	C104.14.4	NA	55	1.57
C104.14.5	NA	58	1.43	C104.14.6	NA	69	0.46
C104.165.999	NA	14	1.83	C104.3.1	NA	45	1.05
C104.3.2	NA	50	1.49	C104.3.3	NA	48	1.25
C104.3.4	NA	34	0.14	C105.2.1	NA	35	NA
C105.2.2	NA	37	0.61	C105.2.3	0	17	NA
C105.8.1	NA	42	NA	C105.8.2	NA	16	NA
C105.8.3	NA	21	NA	C106.na117.999	NA	47	0.46
C106.na87.7079	NA	47	0.08	C107.3.1	NA	61	0.02
C107.3.2	NA	54	NA	C107.3.3	NA	37	0.04
C107.3.4	NA	58	0.05	C107.3.5	NA	55	0.05
C107.7.1	NA	63	NA	C107.7.2	NA	50	NA
C107.7.3	NA	43	0.05	C107.7.4	NA	57	0.07
C107.7.5	NA	68	0.04	C108.3.1	NA	21	0.35
C108.4.1	2	47	0.12	C108.7.1	0	12	0.03
C109.2.1	33	38	0.22	C109.6.1	29	29	0.21
C109.7.1	52	48	0.34	C109.8.1	NA	20	NA
C110.2.2	NA	57	NA	C110.2.3	NA	58	NA
C110.2.4	NA	55	NA	C110.5.2	60	57	NA
C1105.4	72	56	NA	C110.7.1	NA	59	NA
C110.7.4	NA	60	NA	C111.2.1	NA	28	NA
C111.6.1	NA	37	0.09	C112.2.1	45	47	0.49
C112.2.2	54	46	0.34	C112.7.2	34	42	0.18
C112.8.1	53	52	0.65	C112.8.2	55	48	0.3
S101.11.4	NA	41	NA	S101.11.5	NA	44	NA
S101.11.6	NA	38	NA	S101.11.7	NA	36	NA
S101.11.8	NA	31	NA	S101.11.999	NA	41	0.45
S101.6.5	NA	44	NA	S101.6.6	NA	40	NA
S101.6.7	NA	35	NA	S101.6.8	NA	34	NA
S101.6.9	NA	33	NA	S101.6.999	NA	35	0.12

Table I-8. Water and Total Organic Carbon Data. (14 sheets)

Tank/Riser Segment	Liq. Frac	Wet		Tank/Riser Segment	Liq. Frac	Wet	
		H2O	TOC			H2O	TOC
S102.11.10	NA	42	0.59	S102.11.11	NA	18	0.21
S102.11.2	NA	15	0.13	S102.11.3	NA	8	0.1
S102.11.4	NA	14	0.18	S102.11.5	NA	13	0.18
S102.11.6	NA	13	0.18	S102.11.7	NA	32	0.35
S102.11.8	NA	38	0.73	S102.11.9	NA	41	0.59
S102.14.10	NA	43	0.46	S102.14.11	NA	31	0.95
S102.14.2	NA	14	0.15	S102.14.3	NA	6	0.11
S102.14.4	NA	13	0.17	S102.14.5	NA	22	0.24
S102.14.6	NA	18	0.21	S102.14.7	NA	16	0.25
S102.14.8	NA	34	0.79	S102.14.9	NA	42	0.51
S104.2.1	NA	35	NA	S104.2.2	NA	40	NA
S104.2.3	NA	44	NA	S104.2.4	NA	46	NA
S104.2.5	NA	28	NA	S104.2.6	NA	24	NA
S104.3.1	NA	42	NA	S104.3.2	38	42	NA
S104.3.3	NA	43	NA	S104.3.4	32	31	NA
S104.3.5	NA	30	NA	S104.3.6	NA	27	NA
S104.7.1	NA	40	NA	S104.7.2	NA	37	NA
S104.7.3	NA	48	NA	S104.7.4	NA	33	NA
S104.7.5	NA	30	NA	S104.7.6	NA	23	NA
S106.7.2	NA	33	0.19	S106.7.4	NA	34	0.24
S106.7.6	NA	31	0.14	S106.8.4	NA	51	0.13
S106.8.5	NA	32	0.16	S106.8.7	NA	29	0.11
S106.8.8	NA	27	0.34	S106.8.9	NA	31	0.35
S107.11.2	49	52	0.46	S107.11.3	0	23	0.71
S107.11.4	0	41	0.09	S107.11.5	0	38	0.19
S107.11.6	0	24	NA	S107.11.7	0	33	NA
S107.11.8	0	30	0.03	S107.16.2	33	58	0.64
S107.16.3	0	31	0.38	S107.16.4	0	29	0.08
S107.16.5	0	23	0.09	S107.16.6	0	37	NA
S107.16.7	0	33	NA	S107.16.8	0	29	0.04

Table I-8. Water and Total Organic Carbon Data. (14 sheets)

Tank/Riser Segment	Liq. Frac	Wet		Tank/Riser Segment	Liq. Frac	Wet	
		H2O	TOC			H2O	TOC
S107.2.2	23	42	0.38	S107.2.3	0	46	NA
S107.2.4	0	36	0.15	S107.2.5	0	35	0.11
S107.2.6	0	26	NA	S107.2.7	0	33	NA
S107.2.8	0	34	0.02	S109.14.1	NA	15	0.14
S109.14.2	NA	9	0.06	S109.14.3	NA	9	0.05
S109.14.4	NA	6	0.07	S109.16.1	NA	3	0.04
S109.16.2	NA	9	0.04	S110.140.1	NA	39	0.35
S110.140.2	NA	27	0.41	S110.140.3	NA	29	0.7
S110.140.4	NA	18	0.15	S111.8.10	NA	12	0.08
S111.8.11	NA	11	0.05	S111.8.3	NA	51	0.35
S111.8.4	NA	41	0.37	S111.8.5	NA	32	0.22
S111.8.6	NA	28	0.25	S111.8.7	NA	25	0.22
S111.8.8	NA	24	0.19	S111.8.9	NA	33	0.19
S111.na18.4263	NA	11	NA	S111.na19.4264	NA	25	0.1
SX101.225.1	NA	51	0.04	SX101.225.2	NA	43	0.38
SX101.225.3	NA	47	0.27	SX101.225.4	NA	2	0.01
SX101.225.5	NA	48	0.34	SX101.225.6	NA	8	0.21
SX101.225.7	NA	20	0.08	SX101.225.8	NA	47	0.03
SX101.225.999	NA	39	0.12	SX101.227.1	NA	39	0.75
SX101.227.2	NA	40	0.74	SX101.227.4	NA	34	0.05
SX101.227.5	NA	15	0.03	SX101.227.6	NA	5	0.06
SX101.227.7	NA	11	0.02	SX101.227.999	NA	23	0.18
SX102.na73.7903	NA	34	0.82	SX102.na86.7080	NA	30	0.2
SX106.223.10	NA	23	0.37	SX106.223.7	NA	42	0.57
SX106.223.8	NA	42	0.3	SX106.224.11	NA	38	0.35
SX106.224.6	NA	43	0.63	SX106.224.8	NA	33	0.43
SX106.224.9	NA	30	0.26	SX108.16.1	0	2	0.01
SX108.7.1	0	1	0.17	SX113.6.1	NA	43	NA
SX113.7.1	NA	49	NA	T102.2.999	13	47	0.07
T104.3.1	NA	29	NA	T104.3.2	57	52	NA

Table I-8. Water and Total Organic Carbon Data. (14 sheets)

Tank/Riser Segment	Liq. Frac	Wet		Tank/Riser Segment	Liq. Frac	Wet	
		H2O	TOC			H2O	TOC
T104.3.3	NA	68	NA	T104.3.4	72	55	NA
T104.3.5	NA	60	NA	T104.3.6	71	64	NA
T104.3.7	NA	64	NA	T104.3.8	71	63	NA
T104.3.9	NA	67	NA	T104.3.999	NA	63	0.08
T104.6.2	NA	61	NA	T104.6.3	NA	66	NA
T104.6.4	NA	69	NA	T104.6.5	NA	71	NA
T104.6.6	NA	64	NA	T104.6.7	NA	66	NA
T104.6.8	NA	69	NA	T104.6.9	NA	67	NA
T104.na139.999	NA	63	0.06	T104.na140.999	NA	63	0.06
T104.na141.999	NA	63	0.06	T104.na53.7085.5	NA	62	NA
T104.na81.7085	NA	51	0.29	T104.na85.7081	NA	63	0.01
T105.2.1	27	49	0.39	T105.5.1	48	49	0.53
T105.5.2	25	49	0.16	T105.8.1	NA	52	0.41
T106.3.1	NA	17	NA	T106.5.1	NA	17	NA
T107.2.4273	NA	18	NA	T107.2.4274	NA	43	0.07
T107.2.1	18	16	0.05	T107.2.2	45	36	0.07
T107.2.3	NA	43	NA	T107.2.4	NA	58	NA
T107.3.4271	NA	17	NA	T107.3.1	17	15	0.25
T107.3.2	48	56	0.1	T107.3.3	52	53	0.05
T107.3.4	NA	58	NA	T107.5.2	60	59	0.11
T107.5.3	54	57	0.1	T107.5.4	52	54	0.03
T108.2.1	0	27	NA	T108.5.1	0	2	NA
T109.2.1	NA	47	NA	T109.6.1	NA	32	NA
T110.2.1	NA	79	NA	T110.2.2	NA	76	NA
T110.2.3	NA	79	NA	T110.2.4	NA	76	NA
T110.2.5	NA	75	NA	T110.2.6	NA	73	NA
T110.2.7	NA	73	NA	T110.2.8	NA	73	NA
T110.6.1	NA	77	NA	T110.6.2	A	76	NA
T110.6.3	NA	76	NA	T110.6.4	NA	76	NA
T110.6.6	NA	73	NA	T110.6.7	NA	74	NA

Table I-8. Water and Total Organic Carbon Data. (14 sheets)

Tank/Riser Segment	Liq. Frac	Wet		Tank/Riser Segment	Liq. Frac	Wet	
		H2O	TOC			H2O	TOC
T110.6.8	NA	74	NA	T111.3.1	NA	80	NA
T111.3.2	NA	83	NA	T111.3.3	NA	57	NA
T111.3.4	NA	83	NA	T111.3.5	NA	82	NA
T111.3.6	NA	81	NA	T111.3.7	NA	76	NA
T111.3.8	NA	80	NA	T111.3.9	NA	79	NA
T111.3.999	72	79	0.25	T111.6.1	NA	84	NA
T111.6.2	78	74	NA	T111.6.3	NA	90	NA
T111.6.4	NA	72	NA	T111.6.5	NA	85	NA
T111.6.7	NA	81	NA	T111.6.8	71	80	NA
T111.6.9	NA	72	NA	T111.6.999	68	79	0.37
T111.na119.999	NA	79	0.3	T111.na120.999	NA	79	0.2
T111.na125.999	NA	79	0.41	T111.na126.999	NA	79	0.38
T111.na127.999	NA	79	0.33	T111.na128.999	NA	79	0.37
T112.2.2	NA	77	NA	T112.7.2	NA	71	NA
T201.3.6	NA	68	NA	T201.3.7	NA	64	NA
T201.3.8	NA	71	NA	T201.3.999	NA	74	0.02
T202.3.1	NA	78	NA	T202.3.2	NA	77	NA
T202.3.3	NA	74	NA	T202.3.4	NA	76	NA
T202.3.5	NA	74	NA	T202.3.999	NA	73	0.03
T203.3.1	NA	79	NA	T203.3.2	NA	76	NA
T203.3.3	NA	75	NA	T203.3.4	NA	75	NA
T203.3.5	NA	77	NA	T203.3.6	NA	76	NA
T203.3.7	NA	74	NA	T203.3.8	NA	76	NA
T203.3.9	NA	75	NA	T203.3.999	NA	71	0.04
T204.3.1	NA	82	NA	T204.3.10	NA	69	NA
T204.3.2	NA	77	NA	T204.3.3	NA	80	NA
T204.3.4	NA	73	NA	T204.3.5	NA	76	NA
T204.3.6	NA	77	NA	T204.3.7	NA	74	NA
T204.3.8	NA	72	NA	T204.3.9	NA	74	NA
T204.3.999	NA	75	0.03	TX102.na52.7086.5	NA	45	NA

Table I-8. Water and Total Organic Carbon Data. (14 sheets)

Tank/Riser Segment	Liq. Frac	Wet		Tank/Riser Segment	Liq. Frac	Wet	
		H2O	TOC			H2O	TOC
TX102.na80.7086	NA	40	0.19	TX104.230.1	NA	39	0.26
TX104.230.2	NA	3	0.04	TX104.231.1	NA	51	0.18
TX104.231.2	NA	49	0.1	TX107.9a.1	0	22	NA
TY101.na135.999	NA	42	0.07	TY102.na136.999	NA	50	0.03
TY102.na51.7088.5	NA	58	NA	TY102.na78.7088	NA	49	0.24
TY103.na137.999	NA	49	0.15	TY103.na138.999	NA	49	0.07
TY103.na50.7089.5	NA	53	NA	TY103.na65.999	NA	51	NA
TY103.na77.7089	NA	47	0.11	TY104.15.1	NA	52	0.36
TY104.18.1	NA	52	0.37	TY105.na134.999	NA	40	0.08
TY105.na64.999	NA	39	NA	TY106.6.1	NA	37	NA
TY106.7.1	NA	31	NA	TY106.na142.999	NA	38	0.21
TY106.na143.999	NA	38	0.17	TY106.na144.999	NA	38	0.08
TY106.na145.999	NA	38	0.25	TY106.na49.7090.5	NA	36	NA
TY106.na67.999	NA	39	NA	TY106.na76.7090	NA	35	0.09
U102.19.1	NA	46	0.58	U102.19.2	NA	50	0.78
U102.19.3	NA	38	0.98	U102.19.4	NA	31	1.01
U102.19.5	NA	29	0.72	U102.19.6	NA	41	0.89
U102.9.1	NA	39	0.6	U102.9.2	NA	31	0.64
U102.9.3	NA	14	0.39	U102.9.4	NA	26	0.81
U102.9.5	NA	37	1.03	U102.9.6	NA	41	0.81
U103.na56.7082.5	NA	9	NA	U103.na84.7082	NA	13	0.69
U105.2.2	NA	29	1.01	U105.2.3	NA	36	1.16
U105.2.4	NA	28	1.08	U105.2.5	NA	24	1.29
U105.2.6	NA	37	1.54	U105.2.8	NA	18	1.15
U105.2.9	NA	18	1.15	U105.20.1	NA	30	1.22
U105.20.2	NA	37	1.12	U105.20.3	NA	31	0.88
U105.20.4	NA	26	1.17	U105.20.5	NA	27	0.77
U105.20.6	NA	14	0.87	U105.20.7	NA	31	1.1
U105.20.8	NA	30	1.26	U105.20.9	NA	26	1.6
U105.7.3	NA	45	0.95	U105.7.4	NA	32	1.17

Table I-8. Water and Total Organic Carbon Data. (14 sheets)

Tank/Riser Segment	Liq. Frac	Wet		Tank/Riser Segment	Liq. Frac	Wet	
		H2O	TOC			H2O	TOC
U105.7.5	NA	37	1.33	U105.7.6	NA	20	1.15
U105.7.7	NA	30	2.11	U105.7.9	NA	23	1.34
U106.19.2	NA	42	2.65	U106.19.3	NA	41	1.98
U106.19.4	NA	44	2.54	U106.19.5	NA	39	1.22
U106.2.2	NA	42	2.41	U106.2.3	NA	46	2.57
U106.2.4	NA	45	2.55	U106.2.5	NA	22	1.22
U107.2.1	NA	26	NA	U107.2.2	NA	18	0.06
U107.7.2	NA	7	0.08	U107.7.3	NA	13	0.2
U107.7.4	NA	29	0.41	U107.7.5	NA	33	0.54
U107.9.1	NA	19	NA	U107.9.2	NA	34	0.34
U107.9.3	NA	15	0.12	U108.2.1	NA	40	0.4
U108.2.2	NA	19	0.23	U108.2.3	NA	25	0.27
U108.2.4	NA	29	0.34	U108.2.5	NA	37	0.45
U108.2.6	NA	39	0.43	U108.2.7	NA	37	0.61
U108.2.8	NA	41	0.48	U108.2.9	NA	43	0.83
U108.7.1	NA	46	0.63	U108.7.2	NA	24	0.33
U108.7.3	NA	28	0.28	U108.7.4	NA	34	0.43
U108.7.5	NA	30	0.42	U108.7.6	NA	20	0.31
U108.7.7	NA	40	0.58	U108.7.8	NA	40	0.51
U108.7.9	NA	32	0.25	U108.9.2	NA	33	0.27
U108.9.3	NA	46	0.33	U108.9.4	NA	33	0.34
U108.9.5	NA	24	0.46	U108.9.6	NA	31	0.45
U108.9.7	NA	43	0.5	U108.9.8	NA	41	0.37
U108.9.9	NA	44	0.4	U109.19.2	NA	18	0.15
U109.19.3	NA	42	0.25	U109.19.4	NA	11	0.19
U109.19.5	NA	22	0.43	U109.19.6	NA	32	0.59
U109.19.7	NA	17	0.31	U109.19.8	NA	34	0.48
U109.19.9	NA	40	0.52	U109.2.1	NA	21	0.27
U109.2.2	NA	17	0.24	U109.2.3	NA	7	0.12
U109.2.4	NA	9	0.2	U109.2.5	NA	12	0.25

Table I-8. Water and Total Organic Carbon Data. (14 sheets)

Tank/Riser Segment	Liq. Frac	Wet		Tank/Riser Segment	Liq. Frac	Wet	
		H2O	TOC			H2O	TOC
U109.2.6	NA	28	0.45	U109.2.7	NA	19	0.34
U109.2.8	NA	21	0.38	U109.2.9	NA	25	0.49
U109.7.1	NA	30	0.5	U109.7.2	NA	20	0.26
U109.7.3	NA	14	0.27	U109.7.4	NA	33	0.45
U109.7.5	NA	35	0.44	U109.7.6	NA	34	.52
U109.7.7	NA	38	0.5	U109.7.8	NA	28	0.42
U109.7.9	NA	34	0.37	U110.na35.1	NA	8	NA
U110.na36.1	NA	6	0.08	U110.na37.1	NA	6	NA
U110.na38.1	NA	6	0.05	U110.na39.1	NA	5	NA
U110.na40.1	NA	6	0.04	U110.na41.1	NA	4	NA
U110.na42.1	NA	6	0.07	U110.na43.1	NA	3	NA
U110.na44.1	NA	6	0.06	U110.na45.1	NA	9	NA
U110.na46.1	NA	6	0.09	U111.na48.7091.5	NA	39	NA
U111.na74.7092	NA	36	0.54	U111.na75.7091	NA	36	0.52
U201.6.1	85	65	NA	U201.6.2	37	49	NA
U202.2.1	46	46	NA	U202.2.2	43	50	NA
U203.6.1	0	28	NA	U204.2.1	NA	29	0.08
U204.6.1	NA	23	0.01				

7.0 REFERENCES

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APPENDIX J

CHECKLIST FOR TECHNICAL PEER REVIEW

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Practice 134 290 1112
Publication Date 01Mar99
Attachment 02 - Sheet 1 of 1

FLUOR DANIEL NORTHWEST

TECHNICAL PEER REVIEWS

CHECKLIST FOR TECHNICAL PEER REVIEW

Document Reviewed: Organic Complexant Topical Report
Title: HNF 3588, Rev 1
Author:
Date: 6/2/00
Scope of Review: Sections 3.2.2, 3.3.5, 4.4.5, Exec. Summary, Section 1, 2, 3.3.1, 3.2.2.5, 3.3.4.2

Yes	No*	NA	
[ ]	[ ]	[X] **	Previous reviews complete and cover analysis, up to scope of this review, with no gaps.
[X]	[ ]	[ ]	Problem completely defined.
[ ]	[ ]	[X]	Accident scenarios developed in a clear and logical manner.
[X]	[ ]	[ ]	Necessary assumptions explicitly stated and supported.
[ ]	[ ]	[X]	Computer codes and data files documented.
[X]	[ ]	[ ]	Data used in calculations explicitly stated in document.
[X]	[ ]	[ ]	Data checked for consistency with original source information as applicable.
[X]	[ ]	[ ]	Mathematical derivations checked including dimensional consistency of results.
[X]	[ ]	[ ]	Models appropriate and used within range of validity or use outside range of established validity justified.
[X]	[ ]	[ ]	Hand calculations checked for errors. Spreadsheet results should be treated exactly the same as hand calculations.
[ ]	[ ]	[X]	Software input correct and consistent with document reviewed.
[ ]	[ ]	[X]	Software output consistent with input and with results reported in document reviewed.
[ ]	[ ]	[X]	Limits/criteria/guidelines applied to analysis results are appropriate and referenced. Limits/criteria/guidelines checked against references.
[ ]	[ ]	[X]	Safety margins consistent with good engineering practices.
[X]	[ ]	[ ]	Conclusions consistent with analytical results and applicable limits.
[X]	[ ]	[ ]	Results and conclusions address all points required in the problem statement.
[X]	[ ]	[ ]	Format consistent with applicable guides or other standards.
[ ]		[X] **	Review calculations, comments, and/or notes are attached.
[ ]	[ ]	[X]	Traceability
[X]	[ ]	[ ]	Document approved (for example, the reviewer affirms the technical accuracy of the document).

Robert Marusich / Robert Marusich — Reviewer (printed name and signature)

6/2/00 — Date

* All "no" responses must be explained below or on an additional sheet.

** Any calculations, comments, or notes generated as part of this review should be signed, dated, and attached to this checklist. Such material should be labeled and recorded in such a manner as to be intelligible to a technically qualified third party.

FLUOR DANIEL NORTHWEST

TECHNICAL PEER REVIEWS

CHECKLIST FOR TECHNICAL PEER REVIEW

Document Reviewed: Organic Complexant Topical Report
Title: HNF-3588, Rev 1
Author:
Date: 2/9/01
Scope of Review: Reviewed "time to dryout", final temperature rise for Tank AY-102

Yes	No*	NA	
[X]	[ ]	[ ]**	Previous reviews complete and cover analysis, up to scope of this review, with no gaps.
[X]	[ ]	[ ]	Problem completely defined.
[ ]	[ ]	[X]	Accident scenarios developed in a clear and logical manner.
[X]	[ ]	[ ]	Necessary assumptions explicitly stated and supported.
[ ]	[ ]	[X]	Computer codes and data files documented.
[X]	[ ]	[ ]	Data used in calculations explicitly stated in document.
[ ]	[ ]	[X]	Data checked for consistency with original source information as applicable.
[X]	[ ]	[ ]	Mathematical derivations checked including dimensional consistency of results.
[X]	[ ]	[ ]	Models appropriate and used within range of validity, or use outside range of established validity justified.
[X]	[ ]	[ ]	Hand calculations checked for errors. Spreadsheet results should be treated exactly the same as hand calculations.
[ ]	[ ]	[X]	Software input correct and consistent with document reviewed.
[ ]	[ ]	[X]	Software output consistent with input and with results reported in document reviewed.
[ ]	[ ]	[X]	Limits/criteria/guidelines applied to analysis results are appropriate and referenced. Limits/criteria/guidelines checked against references.
[ ]	[ ]	[X]	Safety margins consistent with good engineering practices.
[ ]	[ ]	[X]	Conclusions consistent with analytical results and applicable limits.
[X]	[ ]	[ ]	Results and conclusions address all points required in the problem statement.
[ ]	[ ]	[X]	Format consistent with applicable guides or other standards.
[ ]		[X]**	Review calculations, comments, and/or notes are attached.
[X]	[ ]	[ ]	Document approved (for example, the reviewer affirms the technical accuracy of the document).

Robert Marusich / Robert Marusich — Reviewer (printed name and signature)

2/9/01 — Date

* All "no" responses must be explained below or on an additional sheet.

** Any calculations, comments, or notes generated as part of this review should be signed, dated, and attached to this checklist. The material should be labeled and recorded in such a manner as to be intelligible to a technically qualified third party.