*** RMIS View/Print Document Cover Sheet ***

This document was retrieved from the Boeing ISEARCH System.

Accession #: D196057134

Document #: SD-WM-TI-719

Title/Desc:
PRELIMINARY ENGINEERING EVALUATION OF HEAT & DIGEST TREATMENT FOR IN TANK REMOVAL OF RADIONUCLIDES FROM COMPLEXED HANFORD WASTE

SEP 29 1995 (20) ENGINEERING DATA TRANSMITTAL (20) 1. EDT 609542

Page 1 of 1

2. To: (Receiving Organization) Distribution	3. From: (Originating Organization) TWRS Process Technology	4. Related EDT No.: N/A
5. Proj./Prog./Dept./Div.: TWRS	6. Cog. Engr.: M. J. Klem	7. Purchase Order No.: N/A
8. Originator Remarks: Rev 0 of Document WHC-SD-WM-TI-719 is routed for approval.		9. Equip./Component No.: N/A
		10. System/Bldg./Facility: N/A
11. Receiver Remarks:		12. Major Assm. Dwg. No.: N/A
		13. Permit/Permit Application No.: N/A
		14. Required Response Date: September 27, 1995

15. DATA TRANSMITTED

(A) Item No.	(B) Document/Drawing No.	(C) Sheet No.	(D) Rev. No.	(E) Title or Description of Data Transmitted	(F) Approval Designator	(G) Reason for Transmittal	(H) Originator Disposition	(I) Receiver Disposition
1	WHC-SD-WM-TI-719		0	Preliminary Engineering Evaluation of Heat and Digest Treatment for In-Tank Removal of Radionuclides from Complexed Hanford Tank Waste	N/A	1		-

16. KEY

Approval Designator (F)	Reason for Transmittal (G)		Disposition (H) & (I)	
E, S, Q, D or N/A (see WHC-CM-3-5, Sec.12.7)	1. Approval 2. Release 3. Information	4. Review 5. Post-Review 6. Dist. (Receipt Acknow. Required)	1. Approved 2. Approved w/comment 3. Disapproved w/comment	4. Reviewed no/comment 5. Reviewed w/comment 6. Receipt acknowledged

17. SIGNATURE/DISTRIBUTION (See Approval Designator for required signatures)

(G) Reason	(H) Disp.	(J) Name	(K) Signature	(L) Date	(M) MSIN	(J) Name	(K) Signature	(L) Date	(M) MSIN	(G) Reason	(H) Disp.
1	1	Cog.Eng. M. J. Klem	M J Klem	9/27/95	H5-27						
1	1	Cog. Mgr.	[illegible]	9/27/95	H5-27						
		QA N/A									
		Safety N/A									
		Env. N/A									
1	1	R. A. Kirkbride	Randy A. Kirkbride	9/27/95	H5-27						
1	1	A. J. Schmidt	A J Schmidt	9/27/95	K3-75						

18.	19.	20.	21. DOE APPROVAL (if required)
M J Klem 9/27/95 Signature of EDT Originator Date		[illegible] 9/27/95	Ctrl. No.

THIS PAGE INTENTIONALLY
LEFT BLANK

RELEASE AUTHORIZATION

Document Number:	WHC-SD-WM-TI-719, Rev. 0
Document Title:	Preliminary Engineering Evaluation of Heat and Digest Treatment for In-Tank Removal of Radionuclides from Complexed Hanford Waste
Release Date:	9/29/95

This document was reviewed following the procedures described in WHC-CM-3-4 and is:

APPROVED FOR PUBLIC RELEASE

WHC Information Release Administration Specialist:

J. Bishop — 9/29/95

Janis Bishop

TRADEMARK DISCLAIMER. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof or its contractors or subcontractors.

This report has been reproduced from the best available copy. Available in paper copy. Printed in the United States of America. To obtain copies of this report, contact:

Westinghouse Hanford Company - Document Control Services
P.O. Box 1970, Mailstop H6-08, Richland, WA 99352
Telephone: (509) 372-2420; Fax: (509) 376-4989

THIS PAGE INTENTIONALLY
LEFT BLANK

SUPPORTING DOCUMENT

1. Total Pages 109

2. Title

Preliminary Engineering Evaluation of Heat and Digest Treatment for In-Tank Removal of Radionuclides from Complexed Hanford Waste

3. Number

WHC-SD-~~SD~~-WM-TI-719

4. Rev No.

0

5. Key Words

Complexed Waste
High-Level Waste
Low-Level Waste
^{90}Sr Removal
TRU Element Removal
Pretreatment

6. Author

Name: M. J. Klem

Signature

Organization/Charge Code
73510/D3047&D3041

7. Abstract

This report uses laboratory data from low temperature-ambient pressure digestion of actual complexed supernatant to evaluate digestion as a pretreatment method for waste in double-shell tanks 241-AN-102, 241-AN-107 and 241-AY-101. Digestion time requirements were developed at 100 °C to remove organic and meet NRC Class C criterion for TRU elements and NRC Class B criterion for ^{90}Sr. The incidental waste ruling will establish the need for removal of ^{90}Sr. Digestion pretreatment precipitates non radioactive metal ions and produces additional high-level waste solids and canisters of high level glass. This report estimates the amount of additional high-level waste produced and preliminary capital and operating costs for in-tank digestion of waste. An overview of alternative in-tank treatment methods is included.

8. RELEASE STAMP

OFFICIAL RELEASE BY WHC
DATE SEP 29 1995
Sta. 21

THIS PAGE INTENTIONALLY
LEFT BLANK

WHC-SD-WM-TI-719
Revision 0

PRELIMINARY ENGINEERING EVALUATION OF HEAT AND DIGEST TREATMENT FOR IN-TANK REMOVAL OF RADIONUCLIDES FROM COMPLEXED HANFORD TANK WASTE

September 1995

M. J. Klem

Prepared by
Westinghouse Hanford Company
Richland, Washington

THIS PAGE INTENTIONALLY
LEFT BLANK

ACKNOWLEDGEMENTS

The author gratefully acknowledges the contribution of A. J. Schmidt, M. R. Elmore, R. J. Orth, and A. H. Zacher of Pacific Northwest Laboratory for the technical support on low temperature hydrothermal processing, alternative treatment methods and predictions of organic destruction and corrosion rates. Acknowledgement is given to T. L. Waldo of Kaiser Engineers Hanford for assistance on project cost estimates. Acknowledgement is also given to A. L. Boldt, H. Babad, R. P. Colburn, R. A. Kirkbride, and J. L. Nelson of Westinghouse Hanford Company and to W. W. Schulz for their counsel and guidance during preparation of this report.

THIS PAGE INTENTIONALLY
LEFT BLANK

EXECUTIVE SUMMARY

The removal of transuranic (TRU) elements, and possibly ^{90}Sr, from complexed supernatant liquid waste in three (or five) double-shell tanks is a key element in the present Tank Waste Remediation Technical Strategy for low-level waste disposal. This report is a preliminary evaluation of low temperature-ambient pressure digestion (heat and digest) as a treatment method for removal of TRU elements and ^{90}Sr. The report is based on laboratory tests of actual complexed waste from tanks 241-AN-107 and 241-SY-101.

The evaluation establishes the feasibility of the heat and digest method to remove TRU elements and ^{90}Sr, identifies preliminary process requirements and amount of additional high-level waste (HLW) for vitrification, and estimates preliminary capital and operating costs. The process is applicable to both in-tank and out-of-tank (in-facility) scenarios. A discussion of alternative treatment processes, and their impact on HLW, is included. This report can be used in a future engineering study evaluation on alternative pretreatment methods of complexed waste.

The heat and digest treatment of complexed supernatant liquid in tanks 241-AN-102, 241-AN-107, and 241-AY-101 at 100 °C is a feasible method to meet Nuclear Regulatory Commission (NRC) Class C waste criterion for TRU elements and NRC Class B waste criterion for ^{90}Sr (if needed). The incidental waste ruling will establish the need for removal of ^{90}Sr.

Preliminary data indicate treatment can be completed safely in a reasonable time, meet the current retrieval schedule, but will require

additional equipment at the tanks and tank farms. Heat and digest is a slow process compared to alternative methods. The predicted digest times range from 0.9 - 5.6 years per tank to meet NRC Class C criterion for TRU elements, and 0.7 - 3.6 years per tank to meet NRC Class B criterion for ^{90}Sr based on a low temperature hydrothermal process model. Treatment would produce about 9 additional canisters of HLW glass. Few, if any, colloids of ^{90}Sr and TRU elements were found in treated supernatant of tank 241-AN-107.

Preliminary cost estimates were developed for three operation scenarios (1, 2, and 3 tank digestion of waste) and based on projected digestion times. The estimated costs, which include vitrification of additional HLW solids, are $90 M to $200 M, depending on the scenario and digestion time. The single tank sequential scenario meets the waste retrieval schedule, costs $90M - $120M, requires 4 to 14 years to treat the waste, and is recommended as the preliminary approach for in-tank heat and digest. The two tank scenario is recommended as the alternative digestion scenario. It requires 3 to 9 years to treat the waste and costs $140 M to $170 M, including vitrification of additional HLW solids.

Sodium hydroxide and sodium nitrite additions to waste in tanks 241-AN-102 and 241-AN-107 are needed to meet tank farm operating specifications. Modeling of the corrosion rates predicted $\leq$0.2 mils per year at 100 °C.

Heat and digest product gas contained mostly nitrous oxide and nitrogen. Product gas generation from tank 241-AN-107 waste digestion contained

flammable hydrogen. Flammable hydrogen, ammonia, and methane were observed during digestion of waste from tank 241-SY-101. Product gas dilution by water vapor, sparge air, and/or forced air ventilation will be needed to dilute gas concentrations to less than 25% of the flammable limits.

Lack of more extensive bench scale data from tests with actual waste hindered the evaluation. Important follow-on experiments and tasks include the following:

- *Complete heat and digest tests with waste from tank 241-AN-107 using modified experimental set up. Expand the scope of laboratory experiments to include supernatant liquid from tanks 241-AN-102 and 241-AY-101.*

- *Prepare and issue a preliminary process flowsheet for heat and digest of complexed waste in the three tanks.*

- *Evaluate the risk of primary shell failure of tank 241-AN-107 from heat and digest. Current storage of low free hydroxide waste may impact integrity of the shell during digestion of waste at 100 °C.*

- *Evaluate the impact of near term heat and digest of tank 241-AY-101 supernatant liquid on management of tank waste. Treatment of the supernatant liquid to produce non-TRU waste may provide additional flexibility on storage space prior to startup of HLW vitrification.*

- *Develop a more comprehensive cost estimate of heat and digest and impact on HLW waste.*

- *Continue laboratory testing of hydrated iron oxide precipitation and absorbers as the alternatives to organic destruction for removal of TRU elements.*

1.0 INTRODUCTION 1
1.1 BACKGROUND 1
1.2 SCOPE 2
1.3 PURPOSE AND NEED 3
1.4 APPROACH AND CONSTRAINTS 4
1.4.1 Tank 241-SY-101 7
1.4.2 Tank 241-AN-107 8

2.0 CONCLUSIONS AND RECOMMENDATIONS 9
2.1 CONCLUSIONS 9
2.2 RECOMMENDATIONS 11

3.0 DESCRIPTION AND EVALUATION 13
3.1 WASTE TREATMENT REQUIREMENTS 13
3.2 HEAT AND DIGEST 14
3.2.1 Process Description 14
3.2.2 Test Results 15
3.2.3 Organic Destruction Model 20
3.2.4 Heat and Digest Product Gas 22
3.2.5 Application to Large Scale Tanks 26
3.2.6 Process Technical Risk 33
3.2.7 Safety Considerations and Impacts 34
3.2.8 Economic Considerations 36
3.3 RECOMMENDED FUTURE TESTING 39

4.0 REFERENCES 41

APPENDIXES
A - KNOWN ORGANIC COMPONENTS IN COMPLEX CONCENTRATE WASTE AND RADIONUCLIDE SEPARATION REQUIREMENTS A-1

B - SUMMARY OF ALTERNATE IN-TANK TREATMENT PROCESSES B-1

C - SUMMARY OF PRELIMINARY TEST DATA C-1

D - SUMMARY OF CAPITAL AND OPERATING COST ESTIMATES D-1

LIST OF TABLES

1-1 Summary of Data Sources for Organic Destruction 4

2-1 Summary of Predicted Digestion Time for Complexed Waste at 100°C . 9

2-2 Summary of Preliminary Estimates of Metal Oxide Precipitates by Selected Pretreatment Methods 10

2-3 Summary of Preliminary Cost Estimates for Heat and Digest of Waste in Tanks 241-AN-102, 241-AN-107, and 241-AY-101 11

3-1 Summary of Decontamination Factors to meet NRC Limits for ^{90}Sr and TRU Elements Based on 25% Sodium Oxide Loading in Low-Level Waste Glass 13

3-2 Summary of Tank 241-SY-101 and 241-AN-107 Actual Waste Heat and Digest Laboratory Test Results 16

3-3 Summary of Incremental Effect of TOC Destruction from Heat and Digest of Actual Waste 16

3-4 Summary of Estimated Preliminary Activation Energies 22

3-5 Summary of Preliminary Product Gas Composition from Batch Heat and Digest Tests of Undiluted Actual Tank 241-SY-101 Waste 23

3-6 Summary of Preliminary Product Gas Composition from Batch Heat and Digest Tests with $NaOH/NaAlO_2$ Adjusted Tank 241-AN-107 Actual Waste 23

3-7 Summary of Initial Predicted Waste Digestion Time at 100°C to Meet Low-Level Waste Criteria 26

3-8 Summary of Preliminary Heat and Digest Chemical Requirements Based on Hydrothermal Process Batch Model of Tank 241-SY-101 EDTA Chelated Simulant 31

3-9 Summary of Predicted Corrosion Rates for Double-Shell Tanks from Heat and Digest of Waste 32

3-10 Summary of Estimated Metal Oxide Mass Precipitated By Heat and Digest of Waste 36

3-11 Summary of Estimated High-Level Waste Glass Canisters and Disposal Costs by Heat and Digest of Waste 37

3-12 Summary of Capital and Operating Costs for In-Tank Heat and Digest to Meet NRC Class C Criterion for TRU Elements 38

LIST OF FIGURES

3-1 Effect of TOC Destruction on Strontium Removal 18

3-2 Effect of TOC Destruction on Americium and Plutonium Removal . . . 19

3-3 Actual and Predicted Destruction of TOC in Tank 241-SY-101 Waste As a Function of Digestion Time 21

3-4 Predicted Destruction of TOC in Tank 241-SY-101 Waste at 100 °C and 120°C 25

3-5 Predicted Destruction of TOC in Tank 241-AN-102 Waste at 100 °C and 120 °C 28

3-6 Predicted Destruction of TOC in Tank 241-AN-107 Waste at 100 °C and 120 °C 29

3-7 Predicted Destruction of TOC in Tank 241-AY-101 Waste at 100 °C and 120 °C 30

LIST OF ABBREVIATIONS/ACRONYMS

DST	Double-shell tank
EDTA	Sodium ethylenediaminetetraacetate
HLW	High-level waste
LLW	Low-level waste
NCAW	Neutralized current acid waste
NRC	Nuclear Regulatory Commission
PNL	Pacific Northwest Laboratory
TOC	Total organic carbon
TRU	Transuranic
WHC	Westinghouse Hanford Company

PRELIMINARY ENGINEERING EVALUATION OF HEAT AND DIGEST TREATMENT FOR IN-TANK REMOVAL OF RADIONUCLIDES FROM COMPLEXED HANFORD TANK WASTE

1.0 INTRODUCTION

1.1 BACKGROUND

Complexed wastes were generated in the ^{90}Sr removal operations performed at B Plant in the 1970's and 1980's. The supernatant portion of dilute complexed and complexant concentrate wastes contain up to 15 M sodium salts and include $NaNO_3$, $NaNO_2$, $NaAlO_2$, NaOH, Na_2CO_3, and Na_3PO_4. Principal radionuclides are ^{90}Sr, ^{99}Tc, ^{137}Cs, and transuranic (TRU) elements, mainly plutonium and americium.

Chemical flowsheets employed in ^{90}Sr operations used organic complexants such as glycolic acid, citric acid, sodium ethylenediaminetetraacetate (EDTA), sodium N-hydroxy-ethylenediaminetriacetate and in some cases diethylenetriaminepentaacetate. Over time, a portion of these original complexants has undergone extensive chemical and radiolytic degradation. Present wastes contain a combination of some original organic complexants and several organic degradation products. The chelating agents and some of their degradation products form complexes with Sr and TRU elements and may impact meeting low-level waste (LLW) disposal criterion. Tables A-1, A-2 A-3, and A-4 of Appendix A list some of the organic compounds that have been identified in the complexant concentrate waste of tanks 241-SY-101 and 241-AN-107.

The LLW fraction must comply with Nuclear Regulatory Commission (NRC) regulations (10 CFR 61) that govern the allowable concentrations of radionuclides in waste destined for near surface burial. According to these regulations, wastes are classified as class A, B, or C in order of increasing radionuclide concentration. The maximum permissible concentrations of ^{90}Sr, ^{99}Tc, ^{137}Cs and TRU elements in the LLW glass are based on these limits. The NRC limits are provided in Table A-5.

The revised Tri-Party Agreement (Ecology et al. 1994) requires that radionuclides be separated from the supernatant to meet at least NRC Class C criteria. (The NRC's early understanding was that ^{137}Cs and TRU radionuclides in the residual waste would be less than the concentration limits for Class C LLW, as defined in NRC's requirements in 10 CFR Part 61, and that the concentration of other radionuclides would be less than the concentration limits for Class A or B LLW [Bernero 1993]. This position has not been finalized for single-shell tank waste and will be included in the Westinghouse Hanford Company [WHC] November 1995 petition to NRC.)

Incidental waste[1] limits are based on a petition to the NRC recommending 2-3 percent of the original radionuclide inventory generated from reprocessing spent nuclear fuel (7.0 MCi total radionuclides including daughters [decay date 1999]) be disposed to LLW glass due to mixing of wastes from various sources. The proposed incidental waste allocations are summarized in Table A-6 and are based on recommendations in Garfield (1995). Previous analysis of DST waste on a tank by tank basis shows there is no need to remove soluble ^{90}Sr to meet the NRC Class C or proposed incidental waste requirement (Schulz et al. 1995); however, TRU element removal will be needed from complexant concentrate waste in DSTs 241-102-AN and 241-107-AN and dilute complexed waste in DST 241-101-AY. See Table A-7 for details.

Previous organic destruction work focused on out-of-tank technologies to resolve waste tank safety issues and co-removal of complexed ^{90}Sr and TRU elements. Technology development evaluations were performed for hydrothermal, calcination, ozonization, steam reforming, and electrochemical methods using mostly synthetic waste. The baseline material for laboratory and pilot scale testing was 3:1 diluted tank 241-SY-101 simulated waste (Hohl 1993). The low temperature hydrothermal process was selected as the preferred alternative for out-of-tank destruction of organic complexants in Hanford tank wastes. Technology development work on the other methods was stopped in fiscal year (FY) 1994.

Scouting tests were started in FY 1994 on in-tank pretreatment methods such as low temperature-ambient pressure heat and digest, chemical displacement, and permanganate oxidation (FY 1995) for co-removal of soluble ^{90}Sr and TRU elements. Scouting tests on hydroxide precipitation were started in FY 1990. Screening tests on absorber materials were started in FY 1994 using simulated waste. Recent In-Tank Radionuclide Separation Trade Studies identified that heat and digest is the preferred process for destruction of organic materials and removal of chelated radionuclides from supernatant liquid (Raytheon/BNFL 1995).

The most recent plans for management of tank farm waste include transfer of tank 241-AY-101 supernatant liquid to the AP Tank Farm for storage in early FY 1996 (Bacon 1995). Current plans for tanks 241-AN-102 and 241-AN-107 are to retrieve the wastes in year 2020 (Certa 1995). Near term treatment of tank 241-AY-101 supernatant to meet NRC Class C criterion for TRU elements may provide additional flexibility in management of tank storage space prior to start up of HLW vitrification. The insoluble inventory in the HLW storage and staging waste tanks is a critical factor in avoiding retrieval system bottle necks in the period before year 2010.

1.2 SCOPE

This preliminary engineering evaluation examines removal of complexed soluble TRU elements from actual waste by heat and digest to satisfy NRC Class

[1]Incidental waste is non-HLW as defined in Bernero (1993).

C criterion for LLW and applicability of the technology to large scale in-tank processing. Preliminary process requirements and impacts are identified.

Additional process information has been included on co-removal of ^{90}Sr, if needed to meet NRC Class B criterion (see Section 1.1). The incidental waste ruling will establish the need for removal of ^{90}Sr.

If there is a future need to meet NRC Class A criteria for TRU elements and ^{90}Sr, additional treatment methods will be required. Evaluation of treatment methods to meet NRC Class A criteria is outside the scope of this report.

Results are based on supernatant analyses from preliminary heat and digest tests using actual waste from tanks 241-SY-101 and 241-AN-107, low temperature hydrothermal process tests with actual and simulated waste from tank 241-SY-101 as well as other organic destruction tests. It was desired to use only heat and digest test data and other data as needed to cover the concentration range of components.

1.3 PURPOSE AND NEED

This engineering evaluation examines the applicability of heat and digest method for large scale in-tank processing. This information applies also to smaller scale out-of-tank (in-facility) applications. It contributes towards resolution of waste treatment methods in the Function and Requirements for Project W-236B, Initial Pretreatment Module (Swanson et al. 1994) and may help avoid retrieval system bottle necks in the period before year 2010.

Issue 4.2.2.1.2 01 P2 of Swanson (1994) relates to removal of TRU radionuclides. Liquid wastes that contain too much soluble TRU elements to satisfy LLW specifications will have a pH adjustment, be heat treated to reduce the complexing strength of the solution and/or filtered to remove micro particulates. This treatment may be done in-tank. In-facility processes are also being considered.

The removal of some soluble TRU elements from complexed supernatant liquid in DSTs 241-AN-102, 241-AN-107, and 241-AY-101 is needed to meet NRC Class C criterion for TRU elements in LLW glass. Recent ultracentrifuge membrane tests showed that the TRU elements, ^{137}Cs, and ^{90}Sr of tank 241-AN-107 supernatant were in solution (Herting 1995, O'Rourke 1995).

This evaluation includes preliminary requirements to decomplex Sr and achieve NRC Class B criterion for ^{90}Sr in LLW glass, if needed. The incidental waste ruling will establish the need for ^{90}Sr removal.

This report describes alternative in-tank methods for treatment of complexed waste in the selected DSTs (see Appendix B). These methods include hydroxide precipitation, chemical displacement/precipitation by hydrated iron oxide, chemical oxidation, and ion exchange. An engineering evaluation of the alternative methods will be performed when sufficient experimental data are available.

This document satisfies WHC milestone TDC-94-316 and FY 1995 work breakdown structure task 1.1.1.3.01.04.03.37 to evaluate large scale application of heat and digest technology for removal of strontium and TRU elements from complexed waste. It identifies the need to continue organic destruction as an alternative method for removal of TRU elements and ^{90}Sr (if needed) from complexed waste and also completes work break structure task 1.1.1.3.01.04.03.20.

1.4 APPROACH AND CONSTRAINTS

Actual complexed wastes from tanks 241-SY-101 and 241-AN-107 were used for laboratory heat and digest tests. The results from these tests plus, organic destruction test data from hydrothermal processing, wet air oxidation, ozonization and permanganate oxidation with simulated and actual wastes were considered in this evaluation. Table 1-1 summarizes the sources of data used in this evaluation.

Table 1-1 Summary of Data Sources for Organic Destruction

Organic Destruction Method	Oxidizing Agent	Waste and Dilution	Solid-Liquid Separation Method
Heat and Digest	Nitrite ion	SY-101 Actual None	Centrifuge
	Nitrite ion	AN-107 Actual[a] 13% w OH/Al	Centrifuge
	Nitrite ion	AN-107 Actual None	Centrifuge
Ozonization	Ozone	SY-101 Actual 3:1 w H_2O	Centrifuge
	Ozone	SY-101 Simulant[b] 3:1 w H_2O	Centrifuge
Hydrothermal	Nitrite ion	SY-101 Simulant[c] 3:1 w H_2O	0.45μm filter
	Nitrite ion	SY-101 Simulant[c] None	0.45μm filter
	Nitrite ion	SY-101 Actual 3:1 w H_2O	0.45μm filter
Wet Air Oxidation	Oxygen	SY-101 Simulant[c] 3:1 w H_2	0.45μm filter
	Oxygen	SY-101 Actual 3:1 w H_2O	0.45μm filter
Chemical Oxidation	Permanganate ion	SY-101 Simulant[c] 3:1 w H_2O	0.45μm filter
		SY-101 Actual 3:1 w H_2O	0.45μm filter

a See Appendix C-1 for summary of filtration information.
b Simulant contained EDTA and HEDTA (Hohl 1993).
c Simulant contained EDTA (Hohl 1993).

Heat and digest testing was started on composite samples of undiluted tank 241-SY-101 waste to address waste tank safety issues. Mitigation and resolution of safety issues refocused heat and digest testing to measurement of organic destruction and co-removal of soluble ^{90}Sr and TRU elements in 1994. The revised testing measured gas generation and composition and concentrations of ^{90}Sr, TRU elements, and several non radionuclide constituents in supernatant liquid and slurry during the digestion tests. The

measured organics were total organic carbon and sodium salts of oxalate, formate, and acetate.

Several assumptions and constraints were made on the heat and digest test during the testing and evaluation. They are discussed below.

The assumptions are:

- Lab-scale heat and digest tests with actual composited waste are representative of what would occur in the full scale tanks. Mixing, air addition, higher radiation fields, higher temperatures, and catalyst additions will likely improve organic destruction rates and removal of complexed radionuclides from supernatant.

- TOC reduction coupled with Sr/TRU element removal is the method used to track complexant destruction. Alternate methods include concentration changes of sodium salts of oxalate, formate and/or acetate and hydrogen gas generation rate. Recent work has shown that significant changes in organic species composition and complexant strength can occur without a significant change in the overall system TOC.

- Complexant destruction releases additional metal ions that precipitate and help remove microparticulates. The precipitate permits solid-liquid separation by standard practice methods (e.g. centrifugation).

- A second order kinetic model was developed from extensive continuous low temperature hydrothermal tests with tank 241-SY-101 simulant at temperatures around 350°C and bridged with tests at 175°C to 250°C. It is based on TOC removal and EDTA as surrogate organic. Activation energy for the model is 24.4 Kcal/g mole. The low temperature hydrothermal model is used to predict TOC destruction time requirements from heat and digest processing of actual waste.

- Rate data were also obtained from batch hydrothermal tests with simulated complexed waste. Batch testing represents worst case kinetics due to heat losses and inefficient stirring as compared to continuous testing results. These data were included to bracket what may be occurring under in-tank heat and digest conditions.

- The rate of TRU element removal is equivalent to the rate of ^{90}Sr removal because laboratory data indicated ^{90}Sr removal may be limiting. The log of the stability constant for EDTA complexed Sr^{+2} is 8.73 while for Am^{+3} it is 17.8 (Dean 1992). It is possible that higher levels of TOC destruction or subsequent treatment may be necessary to achieve a given decontamination factor for TRU elements.

- The organic destruction reaction is not surface catalyzed or affected by changes in the trace inorganic chemistry of the waste.

- Heat and digest of waste at tank farm operating specifications for low corrosion of carbon steel (<1 mil/yr) has insufficient oxidation power to oxidize and resolubilize Am, Pu and Cr. Previous ozonization and calcination tests have shown destruction of nitrite and resolubilization of Pu and Cr.

Oxidation and resolubilization information has been developed for actinides in "pure" alkaline solutions (Peretrukhin et al. 1995). Behavior in the presence of large amounts of NO_3^-, CrO_4^{-2}, aluminates, EDTA, and other complexing agents has not been investigated.

Organic destruction by ozonization and calcination (Delegard 1993, 1995) of actual waste have shown that some TRU elements may be oxidized and resolubilized. Hydrothermal tests with actual waste showed >99 % removal of soluble Pu (Am was below detection), about 70% Cr(III) oxidation and about 40% nitrite oxidation. Abundant nitrite and decreased soluble chromium ion in heat and digested actual waste indicate that plutonium remained as the insoluble Pu(III) or Pu(IV) based on ozonization and hydrothermal studies. The possibility of forming stable soluble actinides from heat and digest at tank farm operating specifications appears to be low.

The constraints are:

- The laboratory waste digestion temperature was limited to 65°, 100° and 120° C for tank 241-SY-101 and to 65° and 100°C for tank 241-AN-107. The gas generation was too fast for sustained tests at 120°C in the available equipment for the tank 241-AN-107 waste. Organic destruction under helium cover gas was slow at these temperatures.

- The helium-oxygen cover gas did not arrive in sufficient time to initiate testing with oxygen. Due to radiation exposure from open face hood testing, higher cost of sample analyses, and observation of nitrogen in the product gas, testing with oxygen was deferred.

- The present analytical results from heat and digest testing with actual waste are viewed as tentative and in the direction of general trends because of complex waste matrices and variability of duplicate analyses.

- The laboratory test conditions used a smaller wetted surface area-to-volume ratio reactor (~1 cm^{-1} vs 1.7 cm^{-1}), no mechanical mixing, and stagnant helium cover gas compared to conditions which would prevail during actual in-tank heat and digest.

- Centrifugation was used for solid-liquid separation of the digested waste samples. One sample of digested tank 241-AN-107 waste was ultracentrifuge membrane tested. Results showed that both ^{90}Sr and ^{241}Am remained in solution. The $^{239/240}Pu$ concentrations before and after ultrafiltration were below detection levels. Other sample results may be suspect due to the presence of potential colloidal particles. Support data from ozonization, hydrothermal and chemical oxidation tests used centrifugation or 0.45 μm filtration for solid-liquid separation. Testing with tank 241-SY-101 simulated waste showed that the Sr in supernatant liquid that passes through a 0.45 μm filter also passes through a 0.02 μm filter.

- Analytical costs for organic speciation of waste exceeded budget costs. No speciation analyses were performed in FY 1995.

1.4.1 Tank 241-SY-101 Waste

Two composite samples of undiluted actual supernatant liquid from tank 241-SY-101 were used for laboratory scale heat and digestion testing. After sample results showed a very slow rate of organic destruction at 100°C, near ambient pressure and helium atmosphere, a WHC-PNL review team recommended the digestion temperature be increased to about 120°C. The higher temperature would accelerate chemical reaction kinetics (~4 times faster) and obtain more usable experimental data for application to the hydrothermal process model. During the 120°C digestion test, a few waste boil over events occurred during gas sampling and caused an estimated 20 - 40% loss of supernatant liquid.

The tank 241-SY-101 waste experiment ended in February 1995 after digestion of samples for about 30 days at 65°C, 152 days at 100°C and 213 days at 120°C under helium atmosphere. All planned sample analyses were completed. No actual waste tests were planned to determine the effects of feed dilution, hydroxide or nitrite ion concentration, addition of other chemicals (e.g. displacement, precipitation of hydrated iron oxide or permanganate oxidation), catalyst, and oxygen.

Additional technical support included hydrothermal process tests using simulated and actual wastes. These are described below:

- A cursory nickel catalyst test showed a ~20% better organic destruction at 250 °C than non-catalyzed tests at the same temperature. The catalyst degraded severely and further catalyst testing was abandoned in 1993 (Orth 1993). The test used 3:1 diluted simulated waste.

- Continuous wet air oxidation tests were performed at 280°C using 20% excess oxygen. Results showed the rate of organic destruction increased more than 3 times compared to hydrothermal processing autogenous rates at the same temperature. Batch wet air oxidation tests showed that the concentrations of nitrite and nitrate ions remained essentially unchanged using 3:1 diluted simulated waste.

- A few autogenous batch hydrothermal process tests at 175°C to 350°C were completed using 3:1 diluted actual waste. Test data have been included.

1.4.2 Tank 241-AN-107 Waste

Laboratory scale testing was started on composite samples of actual waste from tank 241-AN-107 with and without addition of NaOH - $NaAlO_2$ solution (Person 1994). Chemical addition was needed to increase corrosion inhibitors to concentrations acceptable for in-tank heat and digest and to obtain gas generation information for a separate safety program. The chemical addition increased the NaOH concentration to 0.5 M and the $NaAlO_2$ concentration to 0.26 M (diluted the actual waste sample about 13 volume percent). Carbon dioxide from air and on-going near ambient temperature organic destruction reactions in the waste tank have reacted with NaOH during waste storage and reduced its concentration to <0.055 M. The lower NaOH concentration has caused precipitation of $NaAlO_2$.

The digestion tests were performed for about 30 days at 65°C and 144 days at 100° - 105°C before the experiment ended in March 1995. Tests were planned, but not performed, using oxygen and secondary processing of digested supernatant by hydrated iron oxide precipitation.

2.0 CONCLUSIONS AND RECOMMENDATIONS

2.1 CONCLUSIONS

Laboratory scale heat and digest treatment of complexed supernatant liquid in tanks 241-AN-102, 241-AN-107, and 241-AY-101 is a feasible alternate process that may be used to meet NRC Class C waste criterion for TRU elements and NRC Class B waste criterion for ^{90}Sr (if needed). Treatment can be done safely in a reasonable time, meet the preliminary retrieval sequence schedule, and requires additional equipment at the tanks and tank farms. Heat and digest is a slow process compared to alternative methods and produces a small mass of additional HLW solids and small number of additional HLW glass canisters.

The digestion time requirements are summarized in Table 2-1 for the three selected waste tanks. The digestion times are calculated based on meeting NRC criteria for TRU elements and ^{90}Sr (target is 50% below criteria to satisfy NRC sum of fraction rule and estimation of preliminary requirements and resources), first order kinetics for destruction of TOC and nitrite ion from low temperature hydrothermal batch reactor tests with tank 241-SY-101 simulant and TOC - Sr percent removal data from simulated and actual waste tests. The projected digestion time requirements for TRU element removal to meet NRC Class C are longer than the time requirements to meet NRC Class B for ^{90}Sr (0.9 - 5.9 yr vs. 0.7 - 3.8 yr per tank). The incidental waste ruling will establish the need for removal of ^{90}Sr.

Ultracentrifuge membrane filtration of digested tank 241-AN-107 waste showed that the ^{90}Sr and ^{241}Am ($^{239/240}Pu$ was below detection level in all samples) remained in solution. Results support earlier findings that very little (if any) ^{90}Sr and TRU element colloids were found in tank 241-AN-107 supernatant. The minor variations between the "before" and "after" ultrafiltration results are negligible compared to the analytical error.

Sodium hydroxide and sodium nitrite additions are needed for waste in tanks 241-AN-102 and 241-AN-107 to meet the tank farm operating specification during organic destruction. Modeling of waste tank corrosion rates predicted $\leq$ 0.2 mil/yr at the tank farm waste operating specification (Harris 1992) and 100°C. Heat and digest treatment of waste and the resulting precipitation do not provide sufficient radio chemical separation capability to meet NRC Class A criteria for ^{90}Sr or TRU elements.

Table 2-1 Summary of Predicted Digestion Time for Complexed Waste at 100°C

Digestion Time to Meet NRC Class B Criterion for ^{90}Sr, Yr			Digestion Time to Meet NRC Class C Criterion for TRU Elements, Yr		
241-AN-102	241-AN-107	241-AY-101	241-AN-102	241-AN-107	241-AY-101
1.1 - 3.8	0.7 - 3.6	0.8 - 2.6	2.0 - 5.6	1.9 - 5.9	0.9 - 2.8

The destruction of organic and chemical displacement treatment methods cause precipitation of several metal ions which increase the mass of HLW solids and number of HLW glass canisters. Table 2-2 summarizes the estimated amounts of additional HLW solids and HLW glass canisters from treatment of complexed supernatant in tanks 241-AN-102, 241-AN-107, and 241-AY-101 and include alternative methods.

Heat and digest treatment of the complexed supernatant liquid produced the least amount of additional HLW solids, number of HLW glass canisters and increased HLW canister disposal costs. Iron and nickel oxides account for 90% of the precipitate from thermal digestion of the waste. The hydroxide precipitation process does not produce supernatant that meets NRC criterion for TRU elements in tanks 241-AN-102 and 241-AN-107.

Table 2-2 Summary of Preliminary Estimates of Metal Oxide Precipitates by Selected Pretreatment Methods

Tank	Metal Oxides and Number HLW Glass Canisters			
	Heat & Digest Metal Oxide	Hydrated Iron Oxide Precip. (0.1 M Fe) Fe_2O_3	$KMnO_4$ Oxidation $MnO_2 + MO_x$ = Total Oxide	3 M Hydroxide Precipitation Metal Oxide
241-AN-102, MT	2.4	30.5	189.7 + 2.4 = 192.1	2.8[d]
241-AN-107, MT	4.5	32.0	226.5 + 4.5 = 231.0	7.0[d]
241-AY-101, MT	1.3	23.5	28.1 + 1.3 = 29.4	0.5
Total, MT (% Increase)	8.2 (0.06)	86.0 (0.6)	444.3 + 8.2 = 452.5 (3.4)	10.3 (0.07)
Added HLW Glass Canisters	9.4[a]	214.0[a,e]	2670[b]	27.8[a,b]
Added HLW Canister Cost $ M[c]	7.0	160.0	1990	20.7

a Based on 12% Fe_2O_3 loading in glass and 3.34 MT glass per canister.
b Based on unconfirmed maximum 5% MnO_2 loading in HLW glass. No experimental basis for loading to this value. Assumes 3.34 MT glass per canister.
c Based on $745,000 incremental cost per canister and includes operation and disposal (Slaagthaug 1995).
d Supernatant does not meet NRC LLW criteria for TRU elements.
e Minimum number of canisters is ~50 based on 50% Fe_2O_3 loading.

The in-tank heat and digest of complexed waste requires up grade of the DST(s) and tank farm support equipment. Three operating scenarios were developed for in-tank heat and digest. They are based on number of tank upgrades and predicted digestion time. The costs and operating times are shown in Table 2-3. See Section 3.2.8 for details.

The sequential scenario is recommended because it minimizes total cost. It requires 4.8 to 14 years of waste digestion, costs $90M to $120M, and meets

completion of waste retrieval by 2020. The combined scenario is recommended as the alternative to sequential digestion. It requires 2.8 to 8.7 years of waste digestion and costs $140M to $170M.

The heat and digest product gas contains mostly nitrous oxide and nitrogen. Product gas from digestion of tank 241-AN-107 waste contained flammable hydrogen. Flammable hydrogen, ammonia and methane were observed from digestion of tank 241-SY-101 waste. Safety considerations require dilution of the product gas to less than 25% of the flammable limit (DOE 1993). Product gas dilution may be accomplished by water vapor, air sparging and/or forced air ventilation. Air sparging is expected to increase the rate of organic oxidation and reduce the digestion time. Insufficient information is available at this time to establish an actual value.

Table 2-3 Summary of Preliminary Cost Estimates for Heat and Digest of Waste in Tanks 241-AN-102, 241-AN-107, and 241-AY-101

	Cost $ M			
Operating Scenario	Project Capital	Expense[a]	Total	Time, yr
Concurrent (3 Tanks)	149.5	31.2 - 48.5	180.7 - 198.0	2.0 - 5.9
Combined (2 Tanks)	118.4	25.9 - 50.4	144.3 - 168.8	2.8 - 8.7
Sequential (1 Tank)	62.0	24.8 - 53.8	86.9 - 115.9	4.8 - 14.3

a Expense cost is based on digestion time, proportioned estimate from Raytheon/BNFL (1995), other information and includes $7.0M for disposal of 9.4 additional HLW glass canisters. See Appendix D.

More data and a revised trade study are needed to determine if organic destruction is needed for removal of TRU elements and ^{90}Sr. Hydrated iron oxide precipitation and absorbers both remove TRU elements but there is insufficient data to say whether the process costs and benefits make them a better process than organic destruction.

2.2 RECOMMENDATIONS

The following activities are needed to complete an evaluation of digesting organic complexants and alternatives.

Revise plans, upgrade equipment, and continue laboratory testing of heat and digest using actual waste. There is need to confirm early predictions of digestion time, product gas generation, chemical consumption, metal ion precipitates, and capability for co-removal of TRU elements and ^{90}Sr to meet NRC LLW criteria. Test parameters should include mixing, air addition, reactor surface area, catalyst additions, temperature, and solid-liquid separation.

Complete heat and digest testing with complexed concentrate waste from tank 241-AN-107. The planned tests included digestion of actual waste using an oxygen-helium cover gas or sparge, quantitative measurements of the rate at which the various complexants and their degradation products are destroyed, ultracentrifuge filtration for potential colloids, and changes in solution concentration of ^{90}Sr, TRU elements, other elements and key anions (eg. carbonate, hydroxide, nitrite, oxalate, etc). Heat and digest tests should be performed with complexed supernatant liquid from tanks 241-AN-102 and 241-AY-101 to confirm preliminary predictions based on extrapolated data from tanks 241-AN-107 and 241-SY-101. Testing with simulated waste should be limited due to uncertainties of the organic components, chelation of cations and solubility.

Prepare and issue a preliminary process flowsheet document for heat and digest of waste in tanks 241-AN-102, 241-AN-107, and 241-AY-101. The flowsheet should be based on available test data and near term laboratory test results.

Revise the In-Tank Radionuclide Separation Trade Studies (Raytheon/BNFL 1995) and reevaluate time-equipment-cost-HLW estimates and safety concerns for heat and digest vs. precipitation of hydrated iron oxide and chemical oxidation methods for co-removal of TRU elements and ^{90}Sr.

Evaluate the safety and risk of in-tank heat and digest treatment for all three tanks especially tank 241-AN-107. The current storage of low hydroxide waste (<0.055 M) at 30 - 40°C and subsequent digestion of adjusted waste at 100°C may lead to early failure of the tank 241-AN-107 primary shell. Digestion of the waste in another waste tank or use of an alternate treatment process may be preferred.

Evaluate the impact of near term heat and digest of tank 241-AY-101 supernatant liquid on management of tank waste. Treatment of the supernatant to produce non-TRU waste may provide additional flexibility on storage space prior to start up of HLW vitrification.

The alternative methods for in-tank treatment are hydrated iron oxide precipitation and absorbers. Precipitation testing would study and evaluate concentrations of hydroxide and iron ions (and use of natural Sr for co-removal of ^{90}Sr if needed), temperature, and time to optimize the method and reduce the amount of additional HLW waste. Testing with actual waste from tanks 241-AN-102, 241-AN-107, and 241-AY-101 is recommended. Absorber testing would be performed with simulated waste to identify the most promising materials and then actual wastes.

The chemical oxidation of organic by potassium permanganate produces the largest large amount of additional HLW precipitate and HLW glass canisters. Hydroxide coprecipitation of TRU elements and Sr produces about three times more additional HLW waste as heat and digest. However, the method does have not sufficient decontamination to meet LLW criteria for tanks 241-AN-102 and 241-AN-107 and has little margin of contingency for tank 241-AY-101. Further work on these methods is not recommmended.

3.0 DESCRIPTION AND EVALUATION

3.1 WASTE TREATMENT REQUIREMENTS

This evaluation is based on meeting LLW specifications for proposed NRC Class C criteria for supernatant liquid in tanks 241-AN-102, 241-AN-107 and 241-AY-101. Included are estimates of preliminary process requirements to meet ^{90}Sr concentrations equivalent to NRC Class B as an additional organic destruction treatment target (Bernero 1993).

The decontamination factors are identified in Table 3-1 for NRC Class A, B, and C wastes (Raytheon/BNFL 1995 and Shelton 1995). They compare the activity within the glass product to the activity in the untreated waste at NRC limits (^{90}Sr and TRU elements). Target concentrations of 50% below these values (2 times higher decontamination factors) were used to satisfy the NRC "sum of fractions" rule and establish a conservative baseline for preliminary predictions of in-tank heat and digest schedule and cost. The NRC "sum of fractions" rule states that the sum of the ratios of each of the radionuclide concentrations to their waste classification limits shall be less than unity.

Estimated process time requirements to achieve target decontamination for NRC Class B criterion for ^{90}Sr and NRC Class C criterion for TRU elements were calculated at a digestion temperature of 100°C. They are based on empirical activation energy from extensive hydrothermal reactor tests, modeling of organic destruction by hydrothermal process, and component removal from actual waste tests with tank 241-SY-101 and 241-AN-107 wastes (Person 1995, 1995a), hydrothermal tests with simulated tank 241-SY-101 waste (Orth et al. 1993, Orth et al. 1995 and Orth et al. 1995a) and other organic destruction test results with actual waste (Delegard 1993).

Table 3-1 Summary of Decontamination Factors to meet NRC Limits for ^{90}Sr and TRU Elements Based on 25% Sodium Oxide Loading in Low-Level Waste Glass

NRC Class	Tank 241-AN-102		Tank 241-AN-107		Tank 241-AY-101		Tank 241-AZ-101[a]		Tank 241-AZ-102[a]	
	^{90}Sr DF	TRU DF	^{90}Sr DF	TRU DF	^{90}Sr DF	TRU DF	^{90}Sr DF	TRU DF	^{90}Sr DF	TRU DF
A	6.0E+03	8.0E+01	5.0E+03	4.5E+01	2.5E+04	1.5E+01	1.8E+03	3.9E+01	1.9E+03	1.8E+01
B	3.4E+00	--	1.4E+00	--	7.0E+00	--	4.8E-01	--	4.8E-01	
C	5.5E-02	8.0E+00	3.0E-02	4.5E+00	1.4E-01	1.5E+00	1.0E-02	3.9E+00	1.0E-02	1.8E+00

a Available analytical data for waste in these tanks indicate that the TRU element concentration in glasses made from supernatant will be below NRC Class C TRU element criterion of 100 nCi/g. Data show that TRU element concentrations of glasses made from combined supernatant and spent solid wastes will exceed NRC Class C criterion by a factor of about 3.

Corrosion rates were predicted by computer model (Divine et al. 1985). The rates were based on waste meeting tank farm operating specifications (Harris 1992) for hydroxide, nitrate and nitrate ions before and after pretreatment and a 1 year digestion time.

3.2 HEAT AND DIGEST

3.2.1 Process Description

The heat and digest process is applicable to both in-tank and in-facility process scenarios. It is considered desirable to conduct organic destruction in-tank using DSTs of 4.12 million liters (1.1 million gallons) waste storage capacity. In-facility processing would require use of many smaller size tanks (e.g. 2.1E+05 to 4.1E+05 L) and a faster rate of organic destruction (accomplished by using higher digestion temperature and air sparging) to treat the 1.08E+07 L (2.9E+06 gal) of complexed supernatant in DSTs 241-AN-102, 241-AN-107, and 241-AY-101.

In the conceptual heat and digest process, a nominal 3.78 E+06 L (1E+06 gal) batch of chemically adjusted waste is slowly heated to the designated temperature by recycling the supernatant liquid through a steam heater and using two in-tank waste mixer pumps. The supernatant liquid heat up rate is maintained within temperature-time gradient operating specifications for the DSTs (Harris 1992). Once heated to the desired temperature, the supernatant pump and steam heater maintain the digestion temperature at about 100°C. The mixer pumps are operated intermittently to stir the waste and prevent formation of stagnant zones. If allowed to form, stagnant zones may develop potentially low hydroxide-nitrite ion concentration from destruction of organics and lead to potentially higher tank corrosion rates.

Based on hydrothermal tests with simulated 241-SY-101 waste (Orth et al. 1993 and Orth et al. 1995) air sparging of the digesting waste is expected to increase the organic destruction rate and dilute combustible off gas. Forced air ventilation provides additional dilution to ensure flammable mixtures of product gases (H_2, CH_4, NH_3) do not occur. The dilution and removal of product gases also minimizes potential acid corrosion of the carbon steel tank wall and dome from the water - NO_2 reaction.

The agitated supernatant liquid at 100°C requires periodic chemical analysis for hydroxide and nitrite ions to maintain waste composition specifications (Harris 1992) and to determine progress on removal of soluble TRU elements, ^{90}Sr and some non radioactive constituents (e.g. organic species and their degradation products, key metal ions). Sodium hydroxide and/or sodium nitrite chemicals are added to the waste as needed to maintain waste composition specification and effective rate of organic destruction. Real time corrosion monitors should be used to check corrosion rates.

After organic destruction, the waste is transferred to another tank for additional pretreatment (Orme 1995). The sludge is washed with dilute sodium hydroxide to remove soluble salts such as sodium aluminate. Digested supernatant and sludge washes are concentrated to 7 M Na, cooled to about

25°C for solids removal and ion exchange processing. Resolubilization and/or entrainment of TRU elements (and ^{90}Sr for NRC Class B if needed) during sludge washing must be minimized to ensure meeting LLW criterion.

Organic destruction after waste retrieval and sludge washing has been proposed by Raytheon/BNFL (1995). The in-tank organic destruction process is applicable to both concepts.

3.2.2 Test Results

The laboratory test results for co-removal of Sr and TRU elements from digestion of actual waste are shown in Table 3-2. The digestion of undiluted tank 241-SY-101 waste removed 66% of the ^{90}Sr (final concentration of 2,800 uCi/L), 87% of the ^{88}Sr (final concentration of 0.12 mg/L) and 35% of the TOC (final concentration of 11.4 g C/L = 7,100 mg TOC/kg waste). A helium cover gas and no mechanical mixing were used during the tests. Concentrations of Pu and ^{241}Am in tank 241-SY-101 waste were too low to accurately measure changes.

The importance of the Sr removal data made it necessary to find an alternate method to confirm ^{90}Sr analytical results for actual and simulated waste of tank 241-SY-101. As a part of the hydrothermal processing testing at PNL, inductively coupled plasma - atomic emission spectroscopy and graphite furnace atomic absorption were investigated as methods to measure natural Sr in tank 241-SY-101 simulated waste. Due to the high Na concentrations, significant sample dilution was necessary, and the above two methods were determined to lack the desired sensitivity and consistency. After extensive ^{88}Sr analyses had been successfully performed via inductively coupled plasma-mass spectroscopy, this method was used to perform confirmation testing of actual tank 241-SY-101 samples from heat and digest testing. Based on the consistency of the total body of results obtained with inductively coupled plasma-mass spectroscopy, the ^{88}Sr values are believed to be more reliable than the ^{90}Sr analyses.

Digestion of $NaOH$-$NaAlO_2$ adjusted tank 241-AN-107 waste at 100° - 105°C for 144 days (0.4 yr) removed 19% of ^{90}Sr, (average concentration of 64,500 uCi/L), >88% of the Pu (maximum concentration of <4.7 uCi/L), 71% of ^{241}Am (average concentration of 151 uCi/L) and 1.2% of TOC (concentration of 36.9 g TOC/L = 27,300 mg TOC/kg). Recent ultracentrifuge membrane filtration of 144 day digested supernatant showed that the ^{90}Sr and ^{241}Am were in solution. The $^{239/240}Pu$ concentrations were all below detection level (O'Rourke 1995).

Remaining radionuclide concentrations of the 144 day digested waste do not meet criteria for NRC Class B waste for ^{90}Sr and NRC Class C waste for TRU elements. Additional heat and digest or other treatment is required to complete demonstration of the method.

An additional heat and digest test was performed using the "as is" supernatant liquid of tank 241-AN-107. Digestion removed about four times more ^{90}Sr (16,900 vs. 64,500 μci/L) and destroyed 29% of the TOC (28.1 g TOC/L = 20,800 mg TOC/kg). ^{241}Am removal was slightly better (79% vs. 71%). Pu

removal was comparable at >72%. No mechanical mixing and helium cover gas were used during the tests (Person 1995).

Table 3-2 Summary of Tank 241-SY-101 and 241-AN-107 Actual Waste Heat and Digest Laboratory Test Results

		TOC and Radionuclide Concentrations of Waste				Percent Removed			
Tank	Days @ 100 °C	TOC g C/L	^{90}Sr uCi/mL	Pu uCi/mL	^{241}Am uCi/mL	$^{90}Sr/^{88}Sr$	Pu	^{241}Am	TOC
101-SY[c]	>961[a]	17.4	8.33	NA[b]	NA[b]	66/87	NA[b]	NA[2]	35
107-AN[d]	144	37.7	79.8	0.035	0.53	19/NA	>88	71	1.2
107-AN[e]	144	39.6	77.4	0.034	0.67	78/NA	>72	79	29

a Equivalent days based on activation energy of 19.3 kcal/g mole and normalized for 213 days at 120°C + 152 days at 100°C.
b NA - Not Available or below detection limits.
c Diluted waste composite contained 2.26 M OH^-, 1.71 M AlO_2^-, and 3.91 M NO_2^-.
d Waste adjusted to 0.49 M OH^-, 0.26 M AlO_2^-, and 0.93 M NO_2^-.
e No chemical adjustment to waste <0.055 M OH^-, 1.15 M NO^{2-}.

Table 3-3 Summarizes the incremental effect of TOC destruction on removal of strontium (^{88}Sr and ^{90}Sr) and TRU elements from the heat and digest tests (Person 1995, 1995a). This information was used to relate TOC destruction and removal of Sr and TRU elements from complexed supernatant liquid.

Table 3-3 Summary of Incremental Effect of TOC Destruction from Heat and Digest of Actual Waste

Tank	Digest Time, Days	TOC Destroyed, %	^{88}Sr Removed, %	^{90}Sr Removed, %	^{241}Am Removed, %	Pu Removed, %
241-SY-101	73	24.5	21.1	0	NA	NA
241-SY-101	152	35.3	19.2	0	NA	NA
241-SY-101	365	34.3	87.5	65.9	NA	NA
241-AN-107[a]	32	16.7	NA	4.0	87.1	NA
241-AN-107[a]	96	0	NA	22.3	75.2	>73.1
241-AN-107[a]	144	1.2	NA	19.0	71.2	>88
241-AN-107[b]	96	0	NA	82.7	73.2	50.0
241-AN-107[b]	144	29.1	NA	78.2	79.2	>71.8

a Chemically adjusted supernatant.
b "As is" supernatant.

Figure 3-1 is a compilation of strontium removal test results from heat and digest, low temperature hydrothermal process (Orth et al. 1995), ozonization (Delegard 1993) and permanganate treatment (Orth et al. 1995a). Diluted (3:1) simulant or actual waste of tank 241-SY-101 was used in Delegard's ozonization test and most of the low temperature hydrothermal and permanganate oxidation tests. Heat and digest results are shown by solid symbols.

Figure 3-2 is a compilation of TRU element removal data from heat and digest (Person 1995), low temperature hydrothermal (Orth et al. 1995), potassium permanganate oxidation (Orth et al. 1995a) and Delegard (1993) tests with actual waste. The ^{241}Am data given in the figure was taken from heat and digest (Person 1995) and supplemented with Delegard (1993) test results. The Pu data given in the figure was taken from Person (1995) and supplemented with data from tests with actual waste from Orth (1995, 1995a). Pu data was also available from the ozone testing (Delegard 1993), but was not used. In the ozone testing, Pu was observed to "solubilize" as a result of the treatment, whereas in the hydrothermal, chemical oxidation, and heat and digest testing, Pu solubility decreased. These observations indicate that Pu may be oxidized to the more soluble Pu(VI) form when treated with a strong oxidizer such as ozone. The Pu during heat and digest or low temperature hydrothermal treatment appears to decomplex and precipitate as Pu(III) or Pu(IV). Because of solubility, Pu test results from ozonization treatment were not included. The Sr removal lines were added for comparison. Heat and digest results are shown by solid symbols.

The data of Figures 3-1 and 3-2 appear to divide into two categories. Except for a few data points, significant removal of Sr, Am, and Pu was achieved with very little organic destruction. This separation is used to establish preliminary bounding conditions for estimating organic destruction requirements of complexed waste. Some of this data are suspect but are adequate for initial estimates. The upper and lower bounding categories are represented by a straight line fit of the data (See Table A-8 and Section A-1 for a further discussion of compiled test results). A lower limit equation is to identify minimum organic destruction requirements and an upper limit equation identifies maximum organic destruction requirements. Estimated digestion times and operating costs were developed for both parameters.

Figure 3-1 Effect of TOC Destruction on Strontium Removal

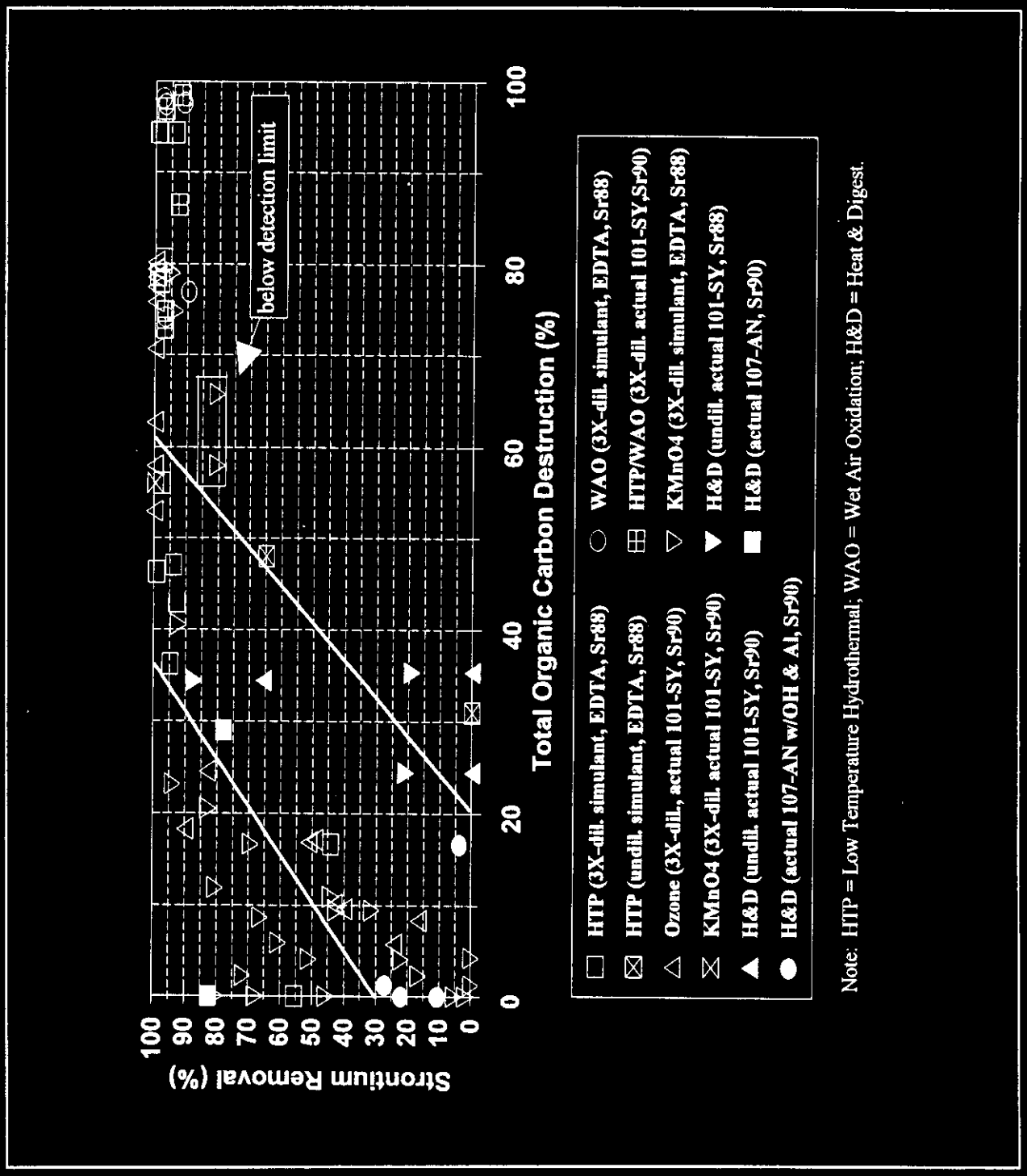
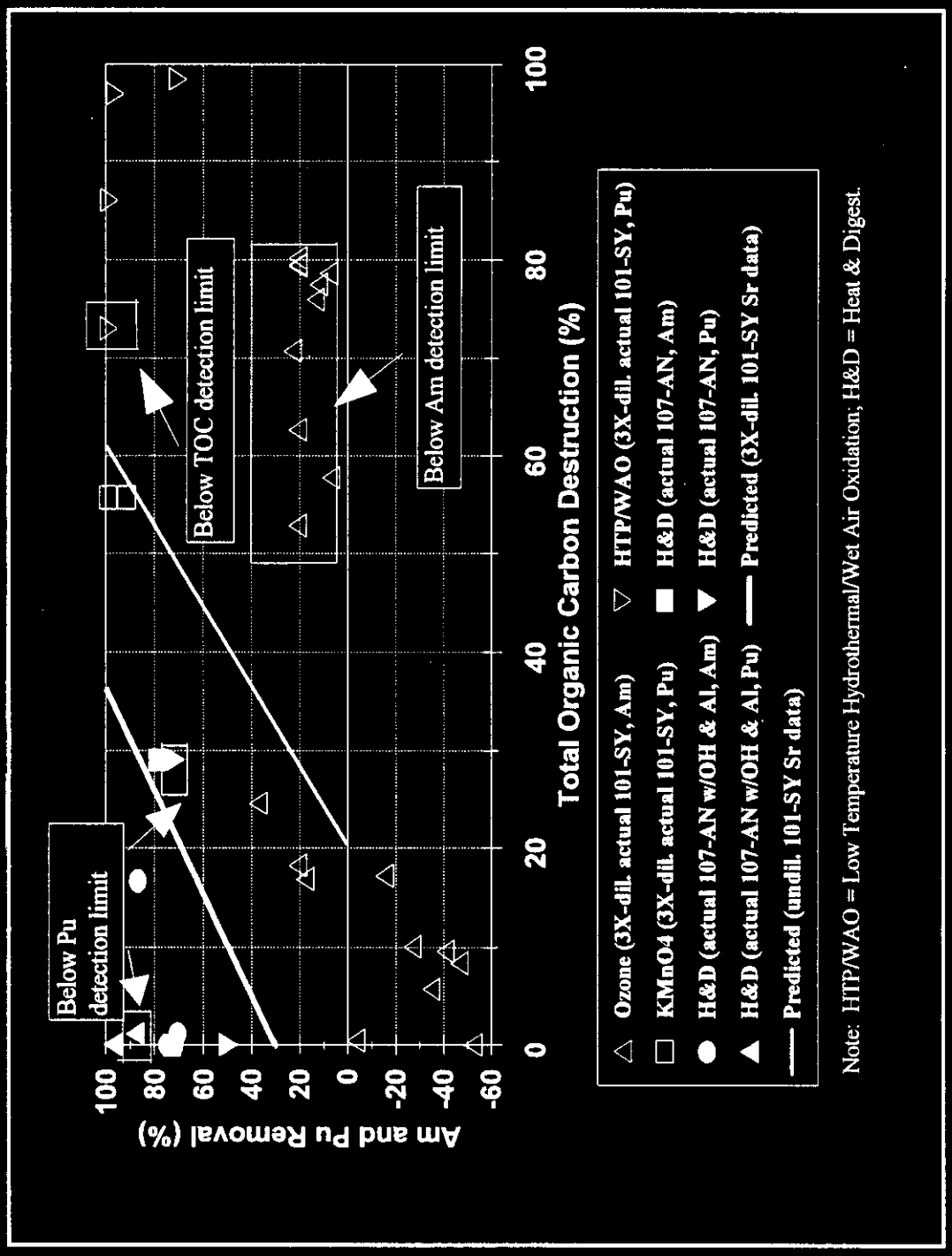


Figure 3-2 Effect of TOC Destruction on Americium and Plutonium Removal



3.2.3 Organic Destruction Model

Organic complexants, such as EDTA react with hydroxide, nitrite and nitrate in the waste to yield carbonate, ammonia, nitrogen, nitrous oxide, water and hydrogen. The organic destruction reaction based on low temperature hydrothermal stoichiometry is:

$$C_{10}O_8N_2H_{12}^{-4} + 7.3OH^- + 7.5NO_2^- + 1.2NO_3^- = 10CO_3^{-2} + 3.5NH_3 + N_2 + 3.1H_2 + 2.6N_2O + 1.3H_2O \quad (3\text{-}1)$$

A comprehensive discussion of the thermal destruction reaction of glycolate, sodium N-hydroxy-ethylenediaminetriacetate (HEDTA) and other organic compounds in DST supernatant liquid is given by McDuffie et al. (1994).

The estimated time to destroy organic materials may be predicted from the chemical reaction, activation energy and assumed chemical reaction order. The proposed low temperature hydrothermal rate equation is:

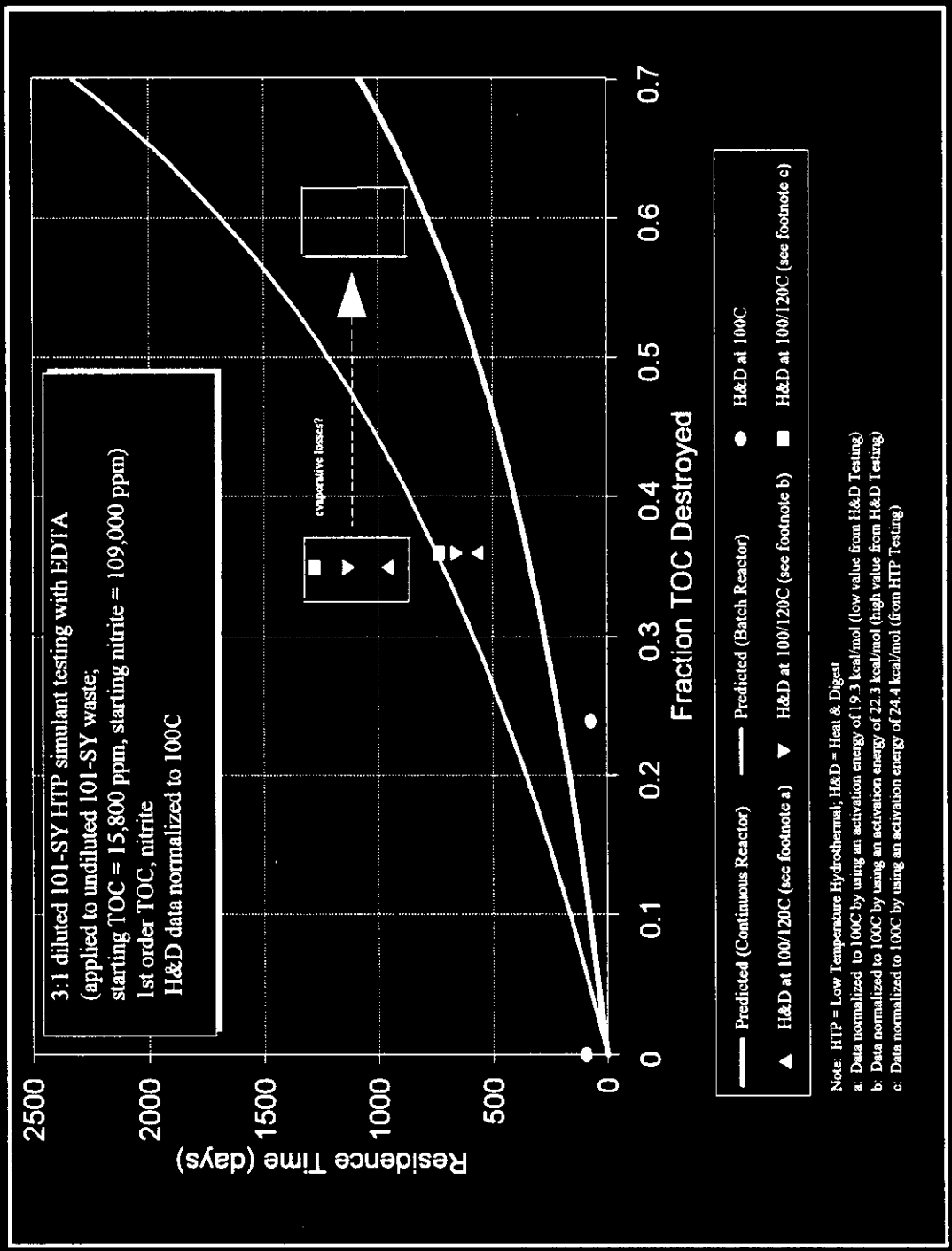
$$d[TOC]/dt = K[NO_2^-][TOC] \quad (3\text{-}2)$$

$$K = Ae^{-E/RT} \quad (3\text{-}3)$$

where: [TOC] = concentration of TOC (ppm) based on EDTA
$[NO_2^-]$ = concentration of NO_2 ion (ppm)
A = 1855 $min^{-1}ppm^{-1}$
E = 24.4 kcal/ g mole Activation Energy
T = Temperature (°K)
R = Gas constant, 1.98 cal/g mole °K
t = Time (minutes)

The activation energy and pre-exponent values are based on continuous, plug flow reactor test results with simulated waste. Based on equation 3-2, predicted residence time and temperature-ambient pressure curves were developed for heat and digest assuming the destruction reaction for the actual waste chelators and degradation products is similar to low temperature hydrothermal processing of simulated waste containing EDTA [irreversible first order reaction TOC, NO_2^- ion (Figure 3-3). This assumption is supported by data that show low temperature hydrothermal test results are in agreement for simulant and actual waste from tank 241-SY-101. FY 1995 hydrothermal results at 175°, 200° and 250°C were consistent with the hydrothermal kinetic model developed from results at temperatures of 300°C to 400°C.

Figure 3-3 Actual and Predicted Destruction of TOC in Tank 241-SY-101 Waste As a Function of Digestion Time



The predicted and actual digestion times as shown on Figure 3-3 are in close agreement at 100°C and to 110 days at 120°C (data normalized to 961 days at 100 °C). Significant deviation between test data and the model predictions is observed after 213 days at 120°C. The deviation may result from any or all of the following conditions:

- Inaccurate material balance from loss of supernatant at 120°C during gas sampling.
- Inaccuracy of the model resulting from extrapolation to lower temperatures.
- Radionuclide solubility change due to changes of some waste components (e.g. OH^-, CO_3^{-2} ions).
- Separable phase (e.g. normal paraffin hydrocarbon) and other organic in the actual waste.

Preliminary activation energy data are compiled in Table 3-4 for heat and digest and low temperature hydrothermal methods. The heat and digest results are based on gas generation from actual waste (Person 1995, 1995a). The low temperature hydrothermal results are based on extensive flow reactor tests with simulated waste (Orth et al. 1993). The results for tank 241-SY-101 show general agreement between the methods.

Table 3-4 Summary of Estimated Preliminary Activation Energies

	Actual Waste		Simulated Waste (EDTA)[a]	
Tank	E Minimum Kcal/g mole	E Maximum Kcal/g mole	E Minimum Kcal/g mole	E Maximum Kcal/g mole
241-SY-101	19[b]	25[b]	24.4	24.6
241-AN-107	19[b]	32[b]	--	--

a Values based on batch (maximum) and continuous (minimum) reactor tests at temperatures around 350°C.
b Based on heat and digest gas generation data and temperature change 65°C to 100°C.

3.2.4 Heat and Digest Product Gas

Heat and digest product gas compositions are shown in Table 3-5 for actual waste of tank 241-SY-101. Results show the gas composition changes with digestion time and temperature. Volatile organic carbon compounds other than methane were observed in the product gas during digestion at both 100° and 120°C.

Table 3-5 Summary of Preliminary Product Gas Composition from Batch Heat and Digest Tests of Undiluted Actual Tank 241-SY-101 Waste

Digest Temp, °C	Digest Days[a]	H_2, vol %	N_2O, vol %	N_2, vol %	NH_3[b], vol %	CH_4, vol %	NO_x[d], vol %	TOC[c], vol%	% TOC Destruction in Waste
100	15	15.3	38.1	17.0	0.0	1.9	6.3	1.9	NA
100	40	20.2	26.9	19.1	27.5	5.1	0.0	8.5	NA
100	96	24.7	27.6	26.1	13.2	7.3	0.9	7.7	24.5
100	152	25.4	27.0	33.3	6.2	6.9	0.9	7.3	35.3
120	20	38.2	24.9	19.1	10.2	5.3	1.9	5.8	NA
120	213	11.7	71.5	12.5	2.4	1.0	0.8	1.3	34.2

a After each gas sample collection the void space of the stainless steel digester was refilled with helium.
b NH_3 values are estimates only. NH_3 is lost to stainless steel of product gas collection system and analytical equipment.
c TOC gas sample value includes methane and larger hydrocarbons.
d NO_x gas sample value includes NO and NO_2 components.

Product gas compositions are shown in Table 3-6 for digestion of tank 241-AN-107 waste. Analyses show that nitrous oxide and nitrogen are the major gaseous products. The hydrogen (4 - 7% vs. 15 - 25% at 100°C) and other minor product gases are lower than observed from digestion of waste from tank 241-SY-101.

Table 3-6 Summary of Preliminary Product Gas Composition from Batch Heat and Digest Tests with $NaOH/NaAlO_2$ Adjusted Tank 241-AN-107 Actual Waste

Digest Temp, °C	Digest Days	H_2, vol %	N_2O, vol %	N_2, vol %	NH_3[a], vol %	CH_4, vol %	NO_x[b], vol%
100	18	3.6	54.4	36.9	4.3	0.2	0.1
100	32	4.7	71.3	22.4	0.7	0.1	0.7
100	44	6.2	73.1	13.3	6.3	0.3	0.7
100	66	7.4	74.8	13.5	3.3	0.2	0.7
100	93	6.5	75.7	12.2	5.1	0.3	0.0
100	144	6.1	79.2	11.4	2.9	0.3	0.0

a NH_3 values are estimates only. NH_3 is lost to the stainless steel of the product gas collection system and analytical equipment.
b NO_x sample value includes NO and NO_2 components.

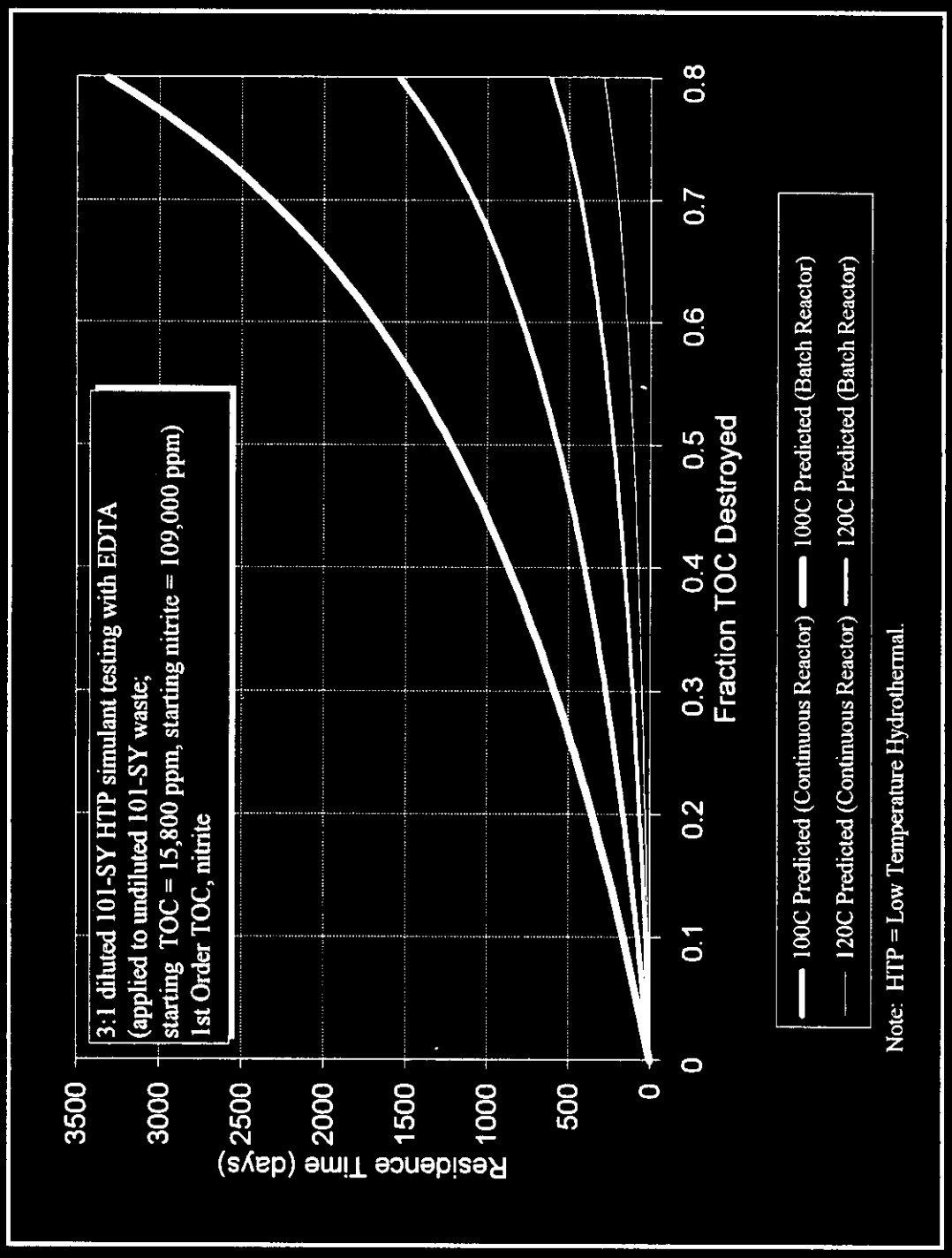
The major flammable gases produced are hydrogen, ammonia and methane. The ammonia measurements were hampered by losses to the walls of the equipment, so that the quoted values are likely to be low. A modest amount of methane is produced by the tank 241-SY-101 material, especially after some heating. This observation is opposite to the trace amounts of methane produced by the tank 241-AN-107 waste. A small amount of NO_x is produced in some samples; analyses of duplicate samples show the most scatter for ammonia and NO_x. The difficulties in analyzing small amounts of NO_x make it difficult to predict a product gas composition and identify off gas clean up measures. Personnel should be aware that heat and digest product gas from tank 241-SY-101 may contain a few percent NO_x.

The hydrogen and other combustible gases must be diluted to less than 25% of the lower flammability limit by water vapor, sparge and/or forced air ventilation (DOE 1993). Forced air ventilation prevents formation of possible trace acid condensate (reaction of water and NO_2 to form nitric acid) in the tank vapor space. Acid condensate would be expected to corrode the dome and upper wall of the carbon steel waste tank.

The rate of gas generation varies with temperature and digestion time. At 100°C, the tank 241-SY-101 average gas generation rate is about 0.96 mmole of gas/liter of waste/day for the first 10 days of heating and decreases to a constant rate of about 0.65 mmole/L/day after 15 days (Person 1995a). At 100°C, the tank 241-AN-107 average gas generation rate is about 3.4 mmole of gas/L/day for the first 10 days of heating and then decreases to about 0.6 mmole/L/day at 144 days (Person 1995).

Figure 3-4 shows the predicted residence time requirements for TOC destruction at both 100° and 120°C from hydrothermal batch and continuous reactor tests with tank 241-SY-101 simulated waste. Increased TOC destruction is expected using higher temperature and a continuous (plug flow) reactor.

Figure 3-4 Predicted Destruction of TOC in Tank 241-SY-101 Waste at 100 °C and 120°C



3.2.5 Application to Large Scale Tanks

The heat and digest treatment of complexed supernatant is a feasible method to achieve the NRC Class C criterion for TRU elements and NRC Class B criterion for ^{90}Sr (if needed). It can be done safely in a reasonable time and requires addition of new equipment to the tanks and tank farms. Heat and digest is a slow process, compared to alternative methods, and adds a small mass of new solids to HLW.

The storage of low hydroxide (<0.055 M) waste in tank 241-AN-107 may impact heat and digest operations in this tank. Some increased general and local corrosion effects on the primary shell may lead to subsequent failure during digestion of the waste. Additional evaluation is necessary to reduce risk of potential primary tank shell failure during waste digestion at 100°C.

The projected corrosion rates for tank 241-AN-107 and the other two tanks during waste digestion are all acceptably low, ranging from zero to 0.2 mils per year. Some additional corrosion testing should be performed at 100° - 120°C with adjusted actual waste to confirm model predictions.

Two approaches were used to predict residence time of organic destruction at 100°C. The results are summarized in Table 3-7 for tanks 241-AN-102, 241-AN-107, and 241-AY-101. They are based on reducing ^{90}Sr and TRU element concentrations to below 50 % of the NRC waste criteria, as initial estimates of time and cost and to satisfy the NRC "sum of fraction" rule. The projected digestion time requirements for removal of TRU elements to meet the NRC Class C criterion are longer than the time requirements for ^{90}Sr removal to meet NRC Class B criterion, with the possible exception of tank 241-AY-101.

Table 3-7 Summary of Initial Predicted Waste Digestion Time at 100°C to Meet Low-Level Waste Criteria

	Digestion Time to Meet NRC Class B Criterion for ^{90}Sr, Yr			Digestion Time to Meet NRC Class C Criterion for TRU, Yr		
Method	241-AN-102	241-AN-107	241-AY-101	241-AN-102	241-AN-107	241-AY-101
Batch Hydrothermal	1.1 - 3.8	0.7 - 3.6	0.8 - 2.6	2.0 - 5.6	1.3 - 5.9	0.9 - 2.8
Heat & Digest	1.8	1.0	1.7	12	3.4	0.2

The recommended approach is based on effects of TOC destruction on radionuclide removal and the low temperature hydrothermal batch and continuous reactor model prediction of residence time from EDTA destruction of tank 241-SY-101 simulated waste. It uses the percentage removal Sr curves (Figures 3-1 and 3-2 or Table A-8 equations) to estimate required amount of organic destruction and the hydrothermal reactor model to estimate residence times. The rate of TRU element removal is assumed to be the same as Sr.

Use the following steps to calculate these values:

- Determine percent radionuclide removal of tank waste to meet or exceed NRC LLW criterion.
- Determine corresponding percents or fractions of TOC destruction to meet criterion (use Figures 3-1 and 3-2 or equations of Table A-8).
- Determine digestion time for tank(s) using the batch reactor curve for required TOC destruction (use Figures 3-5 to 3-7)..

The predictions are that 0.7 to 3.8 yr/tank are needed to remove ^{90}Sr and achieve concentrations 50% below NRC Class B and 0.9 to 5.9 yr/tank of digestion are needed to remove TRU elements and achieve concentrations 50% below NRC Class C for the selected DSTs. Hydrothermal batch reactor results are closer to conditions anticipated in the mixer pump agitated DSTs than the hydrothermal continuous reactor results, which are also shown on Figures 3-5 to 3-7.

The alternate approach estimates digestion time at 100°C by extrapolation of heat and digest digestion time and the remaining concentration of radionuclide(s) in the supernatant liquid. Best fit linear equations (e.g. $y = mx + b$) were developed from regression analysis of tank 241-AN-107 heat and digest data for ^{90}Sr, ^{241}Am and Pu. New constants (b_{Sr}, b_{Am}, b_{Pu}) were developed at or near time zero for starting waste concentrations in Shelton (1995) for tanks 241-AN-102, 241-AN-107, and 241-AY-101. The equations were used to predict digestion times necessary to achieve concentrations 50% below the NRC Class B and C criteria (see Table A-12).

The steps to calculate these values are:

- Determine final concentration of radionuclide(s) in tank waste to meet or exceed NRC LLW criterion.
- Determine digestion time for tank(s) using equations in Table A-12.

The predicted digest times of extrapolated heat and digest data are inside the range predicted by the hydrothermal model for removal of ^{90}Sr from the three tanks and for TRU elements from tank 241-AN-107.

Additional heat and digest testing of actual waste is needed to confirm initial predictions for tank 241-AN-107. Testing with actual waste from tanks 241-AN-102 and 241-AY-101 are also needed to confirm initial projections based on tank 241-AN-107. The validity of the models can not be established at this time since testing of tank 241-AN-107 waste was stopped after 0.4 yr of heating (March 1995) before achieving NRC Class B waste or C waste criteria concentrations for ^{90}Sr and TRU elements. However, the range predicted by the hydrothermal batch testing to achieve target NRC Class B or C criteria should be valid for initial estimate of feasibility, time, and resources.

Figure 3-5 Predicted Destruction of TOC in Tank 241-AN-102 Waste at 100 °C and 120 °C

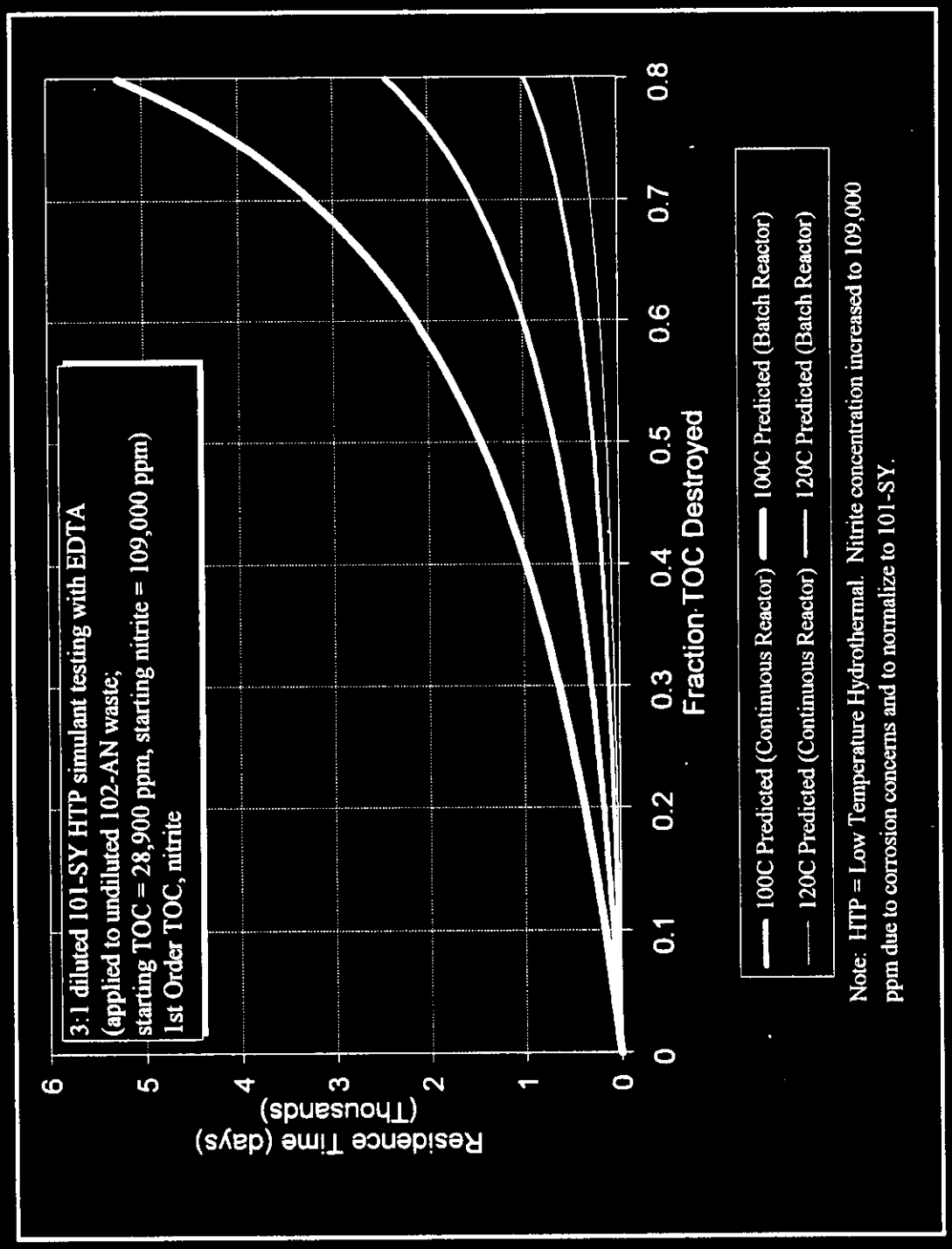


Figure 3-6 Predicted Destruction of TOC in Tank 241-AN-107 Waste at 100 °C and 120 °C

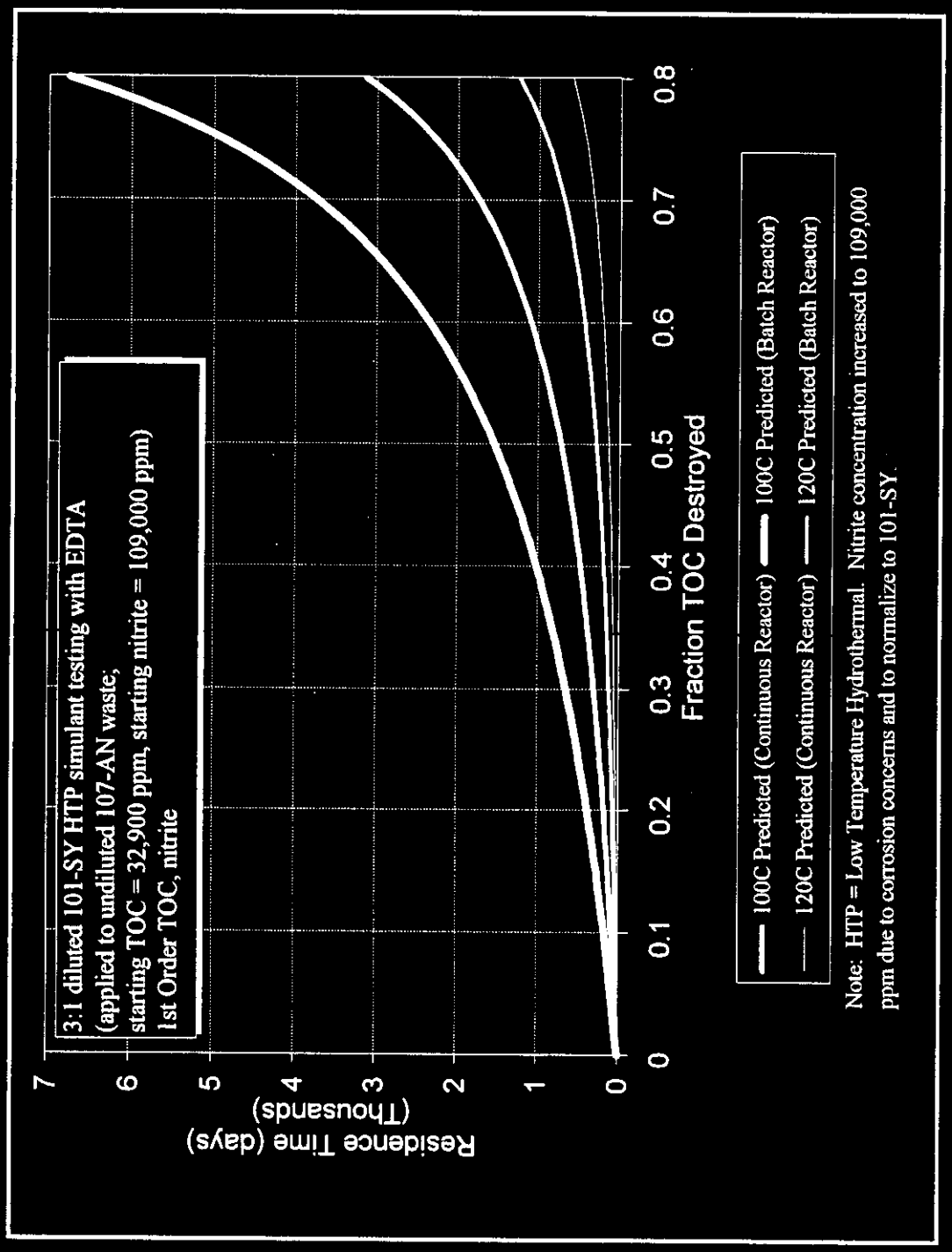
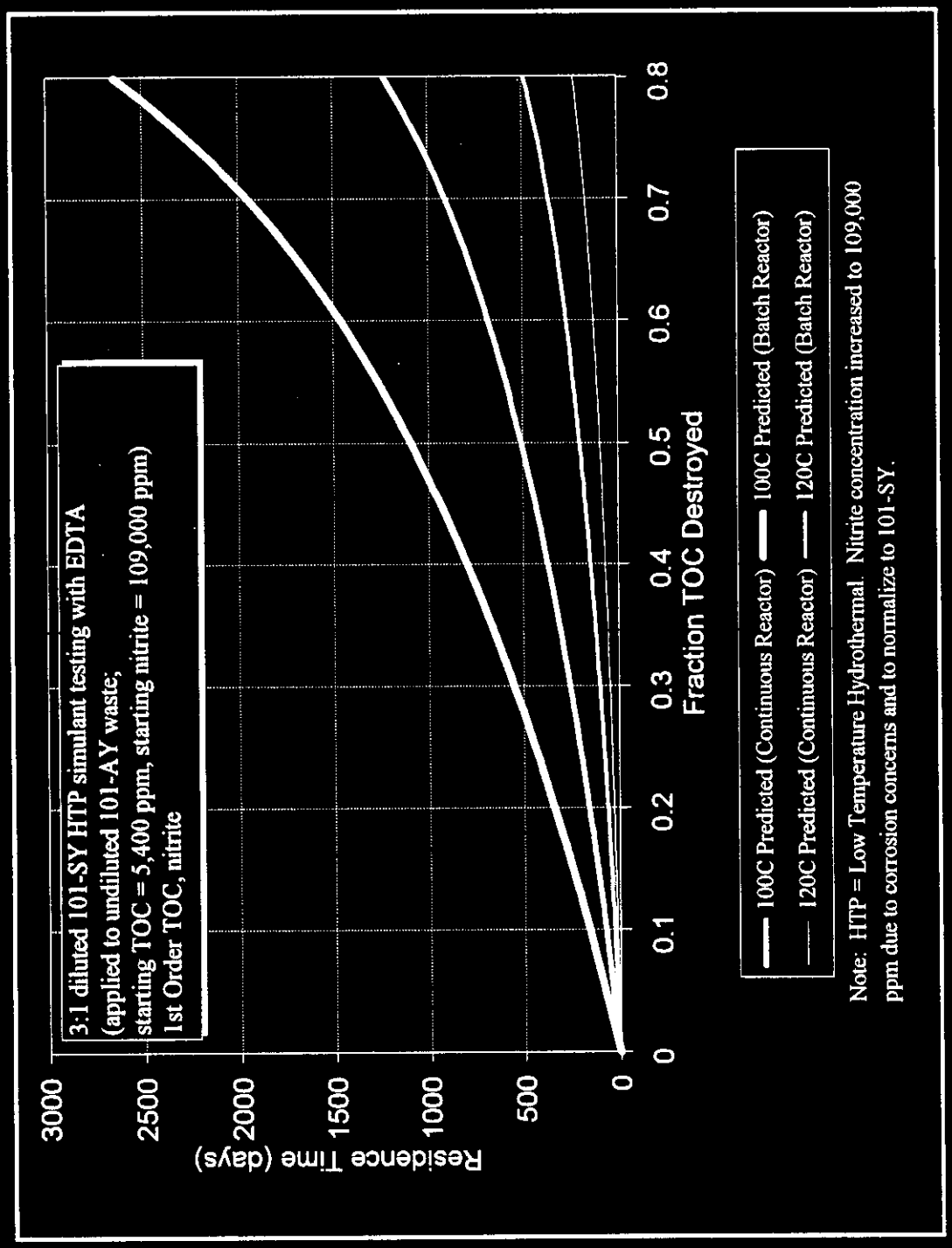


Figure 3-7 Predicted Destruction of TOC in Tank 241-AY-101 Waste at 100 °C and 120 °C



Destruction of organic in tank wastes by the heat and digest method consumes hydroxide, nitrite and nitrate ions (Equation 3-1). However, the hydroxide and nitrite ion concentrations in tank wastes are specified by the tank farm operating specifications to minimize corrosion of the tank primary shell by the wastes. The limits for hydroxide and nitrite ions are dependent on temperature and nitrate ion concentration. For temperatures at or below 100°C the concentration ranges are established by the nitrate ion concentration.

Table 3-8 summarizes the chemical requirements for heat and digest of waste in tanks 241-AN-102, 241-AN-107, and 241-AY-101. They are based on the hydrothermal batch/continuous model of tank 241-SY-101 EDTA chelated simulant. They include chemical additions to meet waste compositions specification (Harris 1992). The chemical consumptions of hydroxide, nitrite and nitrate ions could not be confirmed during heat and digest tests (see Table C-5).

Table 3-8 Summary of Preliminary Heat and Digest Chemical Requirements Based on Hydrothermal Process Batch Model of Tank 241-SY-101 EDTA Chelated Simulant

		Chemical Additions to Achieve Target of 50% Below NRC Class B Criterion for ^{90}Sr			Chemical Additions to Achieve Target of 50 % Below NRC Class C Criterion for TRU		
Parameter	Consumption G mole/G mole Carbon Oxidized[a]	Tank 241-AN-102	Tank 241-AN-107	Tank 241-AY-101	Tank 241-AN-102	Tank 241-AN-107	Tank 241-AY-101
NaOH, MT	0.70	114 - 213	163 - 298	0	158 - 247	240 - 358	0
$NaNO_3$, MT	0.10	0	0	0	0	0	0
$NaNO_2$, MT	0.75	0	0	0	44 - 209	190 - 409	0

a These consumption values could not be confirmed during heat and digest tests. Values are assumed to be applicable. NaOH addition to tank 241-AN-107 is scheduled for FY 1996.

Based on several laboratory corrosion studies, including Divine (1985), the corrosion rate of carbon steel in Hanford alkaline wastes is acceptably low when the when the waste composition is maintained within the tank farm operating specifications (Harris 1992). Before and during heat and digest processing, the tank waste would be adjusted with additional NaOH and $NaNO_2$ to maintain their compositions within operating specifications.

Corrosion testing has evaluated methods other than general corrosion. Results have showed that when the waste composition and rate of temperature change are within operating specifications not only is the general corrosion rate believed to be acceptable low but localized corrosion effects such as stress corrosion cracking, pitting crevice corrosion, etc. are effectively

inhibited. The current specifications were developed to avoid conditions that would promote stress cracking or pitting.

A temperature of 100°C was used for most of the calculations, although temperatures were varied for some experiments from 75°C to 125°C. Temperature effects were negligible for these calculations. An exposure time of 1 year was used for the majority of the corrosion rate calculations. In general, the corrosion rates measured in coupon tests (starting with clean surface coupons) is highest initially, decreasing with time as passivating films of corrosion products accumulate on the metal surface. Measured corrosion rates on test coupons after 1-year exposure should be conservative but approaching the actual long-term corrosion rate expected in the tanks.

The corrosion rates calculated for tanks 241-AN-102, 241-AN-107, and 241-AY-101 were made using waste compositions taken from the integrated data base (Shelton 1995). Two of these tanks (102-AN and 107-AN) apparently have hydroxide ion concentrations below the operating specifications. Plans are to add sodium hydroxide to tank 241-AN-107 in FY 1996 to meet the tank farm specification.

Assuming that the hydroxide and nitrite ion concentrations will be adjusted to be within the operating specifications, adjusted compositions for these tanks were used in the calculations. This set of predicted corrosion rates represents the corrosion rates at heat and digest times and temperatures but at the starting waste compositions. A second set of calculations was then performed with the waste compositions adjusted for the consumption of hydroxide and nitrite ions occurring during organic destruction, yet maintained within the operating specifications.

Corrosion rates predicted by this model for the given waste compositions and conditions were all acceptably low, ranging from zero to 0.2 mils per year, significantly less than the assumed design basis corrosion allowance of ~1 mil per year. Table 3-9 summarizes the predicted corrosion rates of the tank shell.

Table 3-9 Summary of Predicted Corrosion Rates for Double-Shell Tanks from Heat and Digest of Waste

Corrosion[a] Rate, mils/yr		
Tank 241-AN-102	Tank 241-AN-107	Tank 241-AY-101
<0.2	<0.1	<0.2

a Ranges of corrosion rate are based on digesting adjusted waste at 100°C using compositions before and after digestion and for 1 yr exposure time. Addition of sparge air during digestion may change these rates due to potential oxidation of polyvalent metal ions (e.g. Cr(III) to Cr(VI)).

Addition of air to the 100°C supernatant liquid is expected to increase the rate of organic destruction. There is insufficient information available from higher temperature wet air oxidation tests to accurately predict rate increases at 100°C. Perry's Chemical Engineer's Handbook (Perry 1963) suggests that up to 18% excess air is required to obtain complete combustion in air/liquid fuel systems.

Air addition will have the following beneficial results:

- Increases the rate of organic destruction based on wet air oxidation tests with simulated waste.
- Adds oxygen and changes mechanism of organic destruction by reducing formation of chemical reaction combustible gas components (eg H_2 and nitrous oxide).
- Ensures dilution of chemical reaction product gas (via nitrogen addition from air) for safety purposes.
- Oxidizes some Cr(III) to Cr(VI) during digestion at 100°C; the oxidation would help reduce the mass of HLW waste; no significant impact on tank shell corrosion rates is anticipated.

The negative impacts of air addition are:

- Increases hydroxide consumption by reaction with carbon dioxide in air; forms additional carbonate ion and increases mass of tank solids (using CO_2 free sparge air would reduce this impact).
- Increases hydroxide consumption by reaction with trace nitric acid; (e.g. oxygen reacts with nitric oxide product gas to form additional nitrogen dioxide and then water reacts with nitrogen dioxide to form nitric acid).

Forced air ventilation of the tank vapor space is needed to prevent accumulation of potential combustible gas and formation of acid condensate (reaction of water and NO_2 gas; see Tables 3-5 and 3-6 for summary of NO_x product gas from digestion of actual waste; see Person (1995, 1995a) for additional information). Acid condensate is expected to corrode the dome and upper wall of the carbon steel waste tank if NO_2 gas is not adequately removed by the ventilation system.

3.2.6 Process Technical Risk

Preliminary heat and digest tests were performed with actual waste from tank 241-AN-107 and 241-SY-101. The data have been used to estimate treatment requirements to meet NRC Class B criterion for ^{90}Sr and the NRC Class C criterion for TRU elements. Applicability of this data to treatment of any of the three tanks has risk.

The digestion time required to achieve the needed levels of organic destruction is based on simple first order kinetics for TOC (EDTA as the organic) and nitrite ion. There are numerous organics in the waste and the actual digestion times should be within the predicted ranges. Continued heat and digest testing with actual waste is needed to confirm preliminary predictions of organic destruction as shown in Figures 3-5 to 3-7 for removal of ^{90}Sr and TRU elements. The testing should include actual waste from tanks 241-AN-102, 241-AN-107, and 241-AY-101, methods such carrier precipitation and ion exchange co-removal of ^{90}Sr and TRU elements.

3.2.7 Safety Considerations and Impacts

The heat and digest product gases (Tables 3-5 and 3-6) are potentially flammable because their of hydrogen, ammonia and/or methane content. Cashdollar et al. (1992) report that the lower flammability limit for 1:1 H_2:N_2O in nitrogen is 14% H_2, 14% N_2O, and 72% nitrogen. In one test reported by Cashdollar et al. (1992), apparent detonation of a 50% N_2O - 50% H_2 gas mixture occurred. No data were reported in the range of 20% H_2 to 50% H_2, making it impossible to determine where detonation takes place. A maximum 0.9 H_2:N_2O mole ratio was realized during digestion tests of tank 241-SY-101 waste at 100°C. Therefore heat and digest product gas should be considered as flammable/detonable in the absence of water vapor and/or air dilution.

Heat and digest tests at 100°C show a maximum gas generation rate of 61.5 liter/min (standard conditions) would be produced during the first few days of digesting undiluted waste in tank 241-SY-101 under inert cover gas (0.96 mmole of gas/L of waste/day x 1,099,000 gal waste x 3.78 L/gal x 22.4 L/g mole x 0.001 mole/mmole x day/1440 min = 61.5 L/min). Air addition is needed to increase the rate of organic destruction and ensure dilution of the product gas to less than 25% of the lower flammability limit (DOE 1993). A forced air ventilation system would further dilute the product gas and prevent accumulation of potentially flammable, corrosive or toxic components especially in the vapor space of the tank. The tank ventilation system must include methods to control releases of toxic gases to the environment and should return condensate to the tank.

Heat and digest tests at 100°C show a maximum gas generation rate of 195 liter/min (standard conditions) would be produced during the first few days of digesting adjusted waste in tank 241-AN-107 under inert cover gas (3.4 mmole of gas/L of waste/day x 990,000 gal waste x 3.78 L/gal x 22.4 L/g mole x 0.001 mole/mmole x day/1440 min = 195 L/min). Digestion of tank 241-AN-107 waste at 100°C generated product gas containing mostly nitrous oxide and nitrogen. The flammable gas component concentrations are 3.6 to 7.4% hydrogen, <0.3% methane and 0.7 to 6.3% ammonia. Dilution to less than 25% of lower flammability limit for hydrogen is required.

Determination of product gas generation and composition from heat and digest treatment of waste in DSTs 241-AN-102 and 241-AY-101 are needed. Until data are available on these tanks, the gas generation rate of tank 241-AN-107 should be used for tank 241-AN-102 and the generation of tank 241-SY-101 should be used for tank 241-AY-101 based on TOC. The slow heating of waste to

100°C would reduce gas generation below the projected rates from any of the tanks.

There are 217,000 to 386,000 L (58,000 to 103,000 gal) of available space in the 3 DSTs for management of water/hydroxide/nitrite additions, supernatant expansion (heating, mixing and air sparging) and supernatant decrease by water evaporation. Preliminary information shows a volume increase of up to 375,000 L (100,000 gal) from liquid chemical additions and 75,000 to 131,000 L (20,000 to 35,000 gal) increase from thermal expansion of waste at 100°C. Further evaluation of these parameters and water balance is needed because they impact in-tank heat and digest treatment of waste. Concentration of some the waste and/or addition of some solid sodium hydroxide and/or sodium nitrite may be required. These impacts would be evaluated in the preliminary process engineering flowsheet.

Raytheon/BNFL (1995) have identified additional safety concerns. Those concerns which require further evaluation include:

- Chemical spills and leaks.
- Chemical reaction(s) in tank.
- Release of radioactive material.
- Worker exposure during installation and replacement of equipment.
- Thermal stresses on tank.
- Tank dome load limits and seismic qualification with mixer pumps installed.
- Condensation in the ventilation system.

The heat and digest process is not capable of achieving the decontamination to meet NRC Class A waste criteria for ^{90}Sr and TRU elements based on initial projections of preliminary test data. Additional treatment such as ion exchange will be needed.

The in-tank heat and digest of waste may impact the sequence of DST processing and/or rate of single-shell tank waste retrieval due to the long digestion time requirements and waste storage availability. Transfer of supernatant from tank 241-AY-101 to AP Tank Farm is planned for early FY 1996 (Bacon 1995) and waste of tanks 241-AN-102 and 241-AN-107 is scheduled to be retrieved in calendar year 2020 (Certa 1995).

Near term treatment of tank 241-AY-101 supernatant to meet NRC Class C criterion for TRU elements may provide additional flexibility in management of tank storage space prior to start up of HLW vitrification. The insoluble inventory in the HLW storage and staging waste tanks is a critical factor in avoiding retrieval system bottle necks in the period before year 2010. The following section evaluates three operating scenarios for in-tank heat and digest of waste.

3.2.8 Economic Considerations

The destruction of organic components will result in precipitation of several non radioactive metal ions and increase the amount of HLW solid waste for vitrification. Table 3-10 summarizes the projected mass of iron, nickel and other metal ion oxides that would be added to the HLW glass from heat and digest of waste in tanks 241-AN-102, 241-AN-107, and 241-AY-101. Table 3-11 summarizes the estimated number of HLW glass canisters that would be produced by the additional metal oxide waste.

The heat and digest precipitation information was developed by soluble metal ion concentration difference using information in Shelton (1995) at initial and projected final TOC values (Tables A-9, A-10, and A-11). Metal ion concentrations of tank 241-SY-101 were used to represent final conditions of tanks 241-AN-102 and 241-AN-107 after organic destruction. Average metal ion concentrations of tanks 241-AP-102, 241-AP-105, and 241-AN-106 were used for waste of tank 241-AY-101 after organic destruction.

About 8170 Kg of metal oxides (~0.06% increase of HLW mass for vitrification) and ~9 HLW canisters would result from heat and digest of waste in the 3 tanks. The operating and disposal cost of the additional HLW canisters is estimated at $7.0 M. Precipitate from tank 241-AN-107 produces most of the additional HLW solids. The 12 % loading limit of Fe_2O_3 in glass impact the number of HLW glass canisters. Iron and nickel oxides account for about 90% of the precipitated solids.

Appendix sections B-2 and B-3 contain information on estimated masses of metal oxide from precipitation of hydrated iron oxide and permanganate oxidation treatment methods (see Table 2-2 for overall summary of estimated metal oxide precipitates).

Table 3-10 Summary of Estimated Metal Oxide Mass Precipitated By Heat and Digest of Waste

Tank	BaO, Kg	CaO, Kg	Fe_2O_3, Kg	MgO, Kg	MnO_2, Kg	NiO, Kg	Total Kg
241-AN-102	NA	NA	800	NA	NA	1630	2430
241-AN-107	NA	NA	2650	NA	NA	1830	4480
241-AY-101	20	NA	20	40	1000	180	1260
Total	20	NA	3470	40	1000	3640	8170

Table 3-11 Summary of Estimated High-Level Waste Glass Canisters and Disposal Costs by Heat and Digest of Waste

Tank	Number of Added HLW Glass Canisters	HLW Canister Added Costs[c] $ M	Predicted Number HLW Canisters[d]
241-AN-102	2.0[a]	1.5	24.2
241-AN-107	6.6[a]	4.9	22.6
241-AY-101	0.8[b]	0.6	262.0
Total	9.4	7.0	308.8

a Number of canisters is based 12% iron oxide limit in HLW glass and 3.34 MT per canister.
b Number of canisters is based on 45 % total oxide limit in glass and 3.34 MT per canister.
c Based on $745,000 incremental cost per HLW glass canister and includes operating and disposal costs (Slaathaug 1995).
d Number of predicted HLW glass canisters (3.34 MT) based on ASPEN.

Three operating scenarios were developed for in-tank heat and digest of waste. They are:

(1) Perform concurrent batch digestion of waste in the 3 tanks to minimize operating time (digestion time is 2.0 - 5.9 years).

(2) Perform concurrent digestion in 2 tanks and then sequential digestion in 1 tank (combined scenario - digestion time is 2.8 - 8.7 years) as a balance of cost and schedule; the proposed operations are:

- Perform concurrent batch digestion of waste in tanks 241-AN-102 and 241-AN-107 or AP Farm tank (supernatant from tank 241-AY-101) and one AN Farm tank.
- Retrieve and transfer treated waste from 1 of the 2 tanks to available DSTs for interim storage and subsequent pretreatment.
- Transfer untreated waste to the empty tank for heat and digest treatment.

(3) Perform sequential digestion of waste in one tank to minimize initial resources and distribute operating cost over a digestion time of 4.8 - 14 years. The proposed operations are:

- Start sequential digestion of the waste in AP Farm tank (241-AY-101 supernatant).
- Retrieve and transfer treated waste from the first batch of digested waste to an available DST for interim storage and subsequent pretreatment.
- Transfer untreated waste from the second DST to the empty AP Farm tank for heat and digest treatment.
- Retrieve and transfer treated waste from the second batch to an available DST for interim storage and subsequent pretreatment.
- Transfer untreated waste from the third tank to the empty AP Farm tank for heat and digest treatment.

Table 3-12 summarizes estimated costs for the three scenarios. The costs include TRU element removal back up support equipment (e.g. precipitation hydrated iron oxide). They are based on modified cost estimates of Raytheon/BNFL (1995) and other information. See Appendix D for information.

Table 3-12 Summary of Capital and Operating Costs for In-Tank Heat and Digest to Meet NRC Class C Criterion for TRU Elements

	Cost[a] $M			
Operating Scenario	Project Capital	Expense	Total	Time, yr
Concurrent (3 Tanks)	149.5	31.2 - 48.5	180.7 - 198.0	2.0 - 5.9
Combined (2 Tanks)	118.4	25.9 - 50.4	144.3 - 168.8	2.8 - 8.7
Sequential (1 Tank)	62.1	24.8 - 53.8	86.9 - 115.9	4.2 - 14.3

a Expense costs include $ 7.0M for disposal of 9.4 additional HLW glass canisters.

The Raytheon/BNFL estimates were for a larger in-tank treatment system and did not include up grade of the ventilation system for heat and digest pretreatment. Ventilation up grade cost was based on Project W-30.

Expense costs were based on predicted organic destruction times, proportioned Raytheon/BNFL estimates, and estimated equipment replacement (e. g. a mixer pump replacement each 2 years [mixer pump life is 5000 hrs operation] assuming a need for periodic mixing of the waste). Additional cost was included for safety and permitting issues.

The sequential operating scenario minimizes capital cost, requires 4.8 to 14 years of waste digestion at 100°C and meets the preliminary waste transfer/retrieval sequence. The combined scenario is recommended as the alternative to sequential operation. Further evaluation of both scenarios is needed.

3.3 RECOMMENDED FUTURE TESTING

The heat and digest testing with complexed waste from tank 241-AN-107 should be completed. Planned testing includes digestion of the waste at 120°C (accelerate kinetics), using a oxygen-helium cover gas or sparge, quantitative measurements of the rate at which the various complexants and their degradation products are destroyed (including limited organic speciation analyses), ultracentrifuge filtration of digested supernatant, and changes in solution concentration of ^{90}Sr, TRU elements, other elements and key anions (eg. carbonate, hydroxide, nitrite, nitrate).

Testing would complete demonstration of co-removal of TRU elements and ^{90}Sr to meet NRC Class C criterion (and NRC Class B criterion for ^{90}Sr if needed) by heat and digest or alternate methods. Similar heat and digest and subsequent behavior tests should be performed with complexed supernatant from DSTs 241-AN-102 and 241-AY-101. The testing should include low temperature hydrothermal processing of actual waste from these tanks at 175° to 250°C in existing pressurized reactors. The reaction rate at 175°C is about 250 times faster than at 100°C.

Testing with simulants should be limited because of uncertainties of the organic components, chelation of cations and solubility of sludge components. Simulant testing should focus on tanks 241-AN-102, 241-AN-107, and 241-AY-101, and include testing with a matrix of different organic components that have been identified in the waste (Table A-4). Results from simulant testing would be used to identify the most promising test conditions and most efficient testing methodology for testing with actual waste.

Future testing needs to include radiation field effect and integrated dose received by waste in the tanks, reactor surface area to volume ratio, agitation, solids concentration, added trace amounts of transition metal and nobel metals, ultracentrifuge filtration, some organic speciation and addition of hydrated iron oxide to treated waste (measure remaining complexion of TRU elements and ^{90}Sr).

Some additional corrosion testing should be performed at 100° - 120°C with adjusted actual waste from tanks 241-AN-102, 241-AN-107, and 241-AY-101 to confirm model predictions.

The recommended alternative treatment methods are hydrated iron oxide precipitation and absorbers. The treated waste must meet NRC Class C criterion for TRU elements and minimize the mass of additional solids and number of additional canisters of HLW glass. Testing should be performed with actual waste from tanks 241-AN-102, 241-AN-107, and 241-AY-101. Precipitation testing would study and evaluate concentrations of hydroxide and iron ion (and natural Sr for co-removal of ^{90}Sr if needed), temperature and time. Absorber testing would identify the most promising materials with simulated waste and then perform tests with actual waste. Selected testing would include physical properties, batch distribution coefficients, loading capacity, break through curves, radiation and chemical degradation, post treatment of heat and digested waste, disposal, and other parameters for an engineering evaluation.

4.0 REFERENCES

10 CRF 61, 1995, *Licensing Requirements for Land Disposal of Radioactive Waste*, U. S. Code of Federal Regulations, U. S. Nuclear Regulatory Commission, Washington, D. C.

Bacon, R. F., 1995, Double-Shell Tank Waste Consolation and Retrieval Planning Base Case, Internal Memo 73510-95-017, Westinghouse Hanford Company, Richland, Washington.

Bernero, R. M. to J. Lytle, Nuclear Regulatory Commission 10 CFR Part 60 Docket No PRM-60-4 Denial of Petition for Rule Making, dated March 2, 1993, Nuclear Regulatory Commission, Washington, D. C.

Cashdollar, K. L., J. Jo, M. Hertzberg, I. A. Zlochower, C. E. Lucci, G. M. Green, R. A. Thomas, 1992, *Laboratory Flammability Studies of Mixtures of Hydrogen, Nitrous Oxide and Air*, WHC-SD-WM-ES-219 Rev 0, Westinghouse Hanford Company, Richland, Washington.

Certa, P. J. 1995, *Preliminary Retrieval Sequence and Blending Strategy*, WHC-SD-WM-RPT-167 Rev 0, Westinghouse Hanford Company, Richland, Washington.

Dean, J. A., 1992, *Lange's Handbook of Chemistry*, 12th edition, McGraw-Hill Book Company, New York, New York.

Delegard, C. H., 1995, *Chemistry of Proposed Calcination/Dissolution Processing of Hanford Site Tank Wastes*, WHC-EP-0832, Westinghouse Hanford Company, Richland, Washington.

Delegard, C. H., A. M. Stubbs, S. D. Bolling, 1993, *Laboratory Testing of Ozone Oxidation of Hanford Waste from Tank 241-SY-101*, WHC-EP-0701, Westinghouse Hanford Company, Richland, Washington.

Devine, J. D., W. M. Bowen, D.B. Mackey, D. J. Bates, K. H. Pool, 1985, *Prediction Equations for Corrosion Rates of A-537 and A-516 Steels in Double Shell Slurry, Future Purex and Hanford Facilities Wastes*, PNL-5488, Pacific Northwest Laboratory, Richland, Washington.

DOE, 1993, *Environmental Protection, Safety, and Health Protection Standards*, DOE Order 5480.4, U.S Department of Energy, Washington, D. C.

Ecology, EPA, and DOE, 1994, *Hanford Federal Facility Agreement and Consent Order*, 2 vols, as amended, Washington State Department of Ecology, U.S. Environmental Protection Agency, and U.S. Department of Energy, Olympia, Washington.

Garfield, J. S., 1995, LLW Classification and Solids Liquid Separation Criteria for IPM, Internal Memo 71220-95-006, Westinghouse Hanford Company, Richland, Washington.

Geeting, J. G. H., D. E. Kurath, 1993, *Preliminary Assessment of Blending Hanford Tank Wastes*, PNL-8589, Pacific Northwest Laboratory, Richland, Washington.

Harris, J. P., 1992, *Unclassified Operating Specifications for the 241-AN, AP, AW, AY, AZ and SY Tank Farms*, OSD-T-151-00007 Rev H-5, Westinghouse Hanford Company, Richland, Washington.

Herting, D. L., 1995, Addendum to Results of Ultracentrifuge Test on Tank 107-AN Waste, Internal Memo 8E110-PCL95-015, Westinghouse Hanford Company, Richland, Washington.

Hohl, T. M., 1993, *Synthetic Waste Formulations for Representing Hanford Tank Waste*, WHC-SD-WM-TI-549 Rev 0, Westinghouse Hanford Company, Richland, Washington.

McDuffie, N. G., E. C. Ashby, A. Annis, E. K. Barefield, D. Boatright, F. Doctorovich, C. L. Liotta, H. M. Neumann, A. Konda, C. F. Yao, K. Zhang, 1994 *Synthetic Waste Chemical Mechanism Studies*, WHC-EP-0823, Westinghouse Hanford Company, Richland, Washington.

Orme, R. M, 1995, *TRWS Process Flowsheet*, WHC-SD-WM-TI-613 Rev 1, Westinghouse Hanford Company, Richland, Washington.

O'Rourke, J. F., 1995, Results of Ultrafiltration Test with Digested Tank 107-AN Waste, Internal letter 75764-PSC95-079, Westinghouse Hanford Company, Richland, Washington.

Orth, R. J., A. J. Schmidt, M. R. Elmore, A. H. Zacher, T. R. Hart, G. G. Neunschwander, S. R. Gano, R. W. Lehmann (Zimpro), J. A. Momont (Zimpro), 1995, *Removal of Strontium and Transuranics from Hanford Tank waste via Hydrothermal Processing - FY 1994/FY 1995 Test Results*, PNL-10765, Pacific Northwest Laboratory, Richland, Washington.

Orth, R. J., A. J. Schmidt, A. H. Zacher, M. R. Elmore, K. R. Elliot, G. G. Neuenschwander, S. R. Gano, 1995a, *Removal of Strontium and Transuranics from Hanford Tank Waste via Addition of Metal Cations and Chemical Oxidant - FY 1995 Test Results*, PNL-10766, Pacific Northwest Laboratory, Richland, Washington.

Orth, R. J., A. J. Schmidt, M. R. Elmore, T. R. Hart, G. G. Neuenschwander, A. H. Zacher, E. O. Jones. J. C. Poshusta, 1993, *Hydrothermal Processing of Hanford Tank Waste Organic Destruction Technology Development Task*, PNL-10108, Pacific Northwest Laboratory, Richland, Washington.

Peretrukhin, V. F., V. P. Shilov, A. K. Pikaev, C. H. Delegard, 1995, *Alkaline Chemistry of Transuranium Elements and Technetium and the Treatment of Alkaline Radioactive Wastes*, WHC-EP-0817, Westinghouse Hanford Company, Richland, Washington.

Perry, J. H., 1963, *Chemical Engineer's Handbook*, ed R. H. Perry, C. H. Chilton, S. D. Kirkpatrick, 4th edition, McGraw-Hill Book Company, New York, New York.

Person, J. C. 1995, *Strontium and TRU Co-Removal and Gas Generation During Low-Temperature Digestion of Waste from Tank 241-AN-107*, WHC-SD-WM-DTR-041, Westinghouse Hanford Company, Richland, Washington.

Person, J. C., 1995a, *Strontium Removal and Gas Generation During Low-Temperature Digestion of Waste from Tank 241-SY-101*, WHC-SD-WM-DTR-042, Westinghouse Hanford Company, Richland, Washington.

Person, J. C., 1994, Informal Test Plan for Studies of Gas Generation and Organic Digestion in Waste from Tank 241-AN-107, Internal Memo 12110-PCL94-027, Westinghouse Hanford Company, Richland, Washington.

Raytheon/British Nuclear Fuels Ltd (BNFL), 1995, *In-Tank Radionuclide Separation*, E/B-SD-W236B-018 Rev 1, Richland, Washington.

Schulz, W. W., M. J. Kupfer, M. M. McKeon, 1995, *In-Tank Processes for Destruction of Organic Complexants and Removal of Selected Radionuclides*, WHC-SD-WM-ES-321 Rev 0, Westinghouse Hanford Company, Richland, Washington.

Shelton, L. W., 1995, Double Shell Inventories, Internal Memo 71320-95-003, Westinghouse Hanford Company, Richland Washington.

Slaathuag, E. J., 1995, *Tri-Party Agreement Alternative Engineering Data Package of the Tank Waste Remediation System Environmental Impact Statement*, WHC-SD-WM-EV-104 Rev 0, Westinghouse Hanford Company, Richland, Washington.

Swanson, L. M., T. W. Crawford, M. E. Johnson. E. C. Norman, 1994, *Functions and Requirements for Project W-236B Initial Pretreatment Module*, WHC-SD-W236B-FRD-002 Rev 1, Westinghouse Hanford Company, Richland, Washington.

This page intentionally left blank

APPENDIX A

KNOWN ORGANIC COMPONENTS IN COMPLEX CONCENTRATE WASTE AND RADIONUCLIDE SEPARATION REQUIREMENTS

This page intentionally left blank.

Table A-1 Results of Derivatization[a] GC/MS Analysis on Tank 241-101-SY Window E Core Segment Samples. Concentrations of Chelators and Chelator Fragments (mg Carbon/g Sample)[2]

Sample Number	NIDA	NTA	CA	ED3A[b]	EDTA	HEDTA[c]	SA	TOC Accounted For[d,f]	% TOC Accounted For
R4258/C	1.30	0.04	0.44	0.19	2.00	-	0.07	4.8	44
R4259/C	0.88	0.32	0.22	0.18	1.30	-	0.05	3.3	33
R4260/C	1.00	0.30	0.38	0.05	1.70	-	0.08	5.0	46
R4261/C	0.97	0.29	0.23	0.34	3.90	-	0.08	6.4	52
R4262/NC	0.24	0.06	0.14	0.32	0.81	-	0.02	2.2	20
R4263/NC	1.40	0.37	0.47	0.24	0.79	-	0.08	3.5	32
R4264/NC[e]	NA	NA	NA	NA	NA	NA	NA	NA	NA

a Derivatization performed in fume hood.
b Assuming response similar to EDTA.
c HEDTA was found in window E composite, but not in segment subsamples.
d Total includes minor components not included in this summary table.
e Sample was lost.
f Sum incremental information in Tables A-1, A-2 and A-3 to obtain total % TOC identified.

C Convective layer
CA citric acid
ED3A ethylenediaminetriacetic acid
EDTA ethylenediaminetetraacetic acid
GC/MS Gas Chromatograph/Mass Spectrometer
HEDTA N-(2-hydroxyethyl)ethylenediaminetriacetic acid
NA Not available
NC Nonconvective layer
NIDA nitrosoiminodiacetic acid
NTA nitrilotriacetic acid
SA succinic acid
TOC Total organic carbon

[2]Source of data is Campbell et al. 1994.

Table A-2 Liquid Chromatography Results for Oxalate, Formic, Glycolic, and Acetic Acids (mg Carbon/g Sample) for 241-SY-101 Window E Core Segment Samples[3]

Sample Number	Oxalic	Glycolic	Acetic	Formic	Total	% TOC Accounted For[b]
R4258/C	1.7	0.6		1.1	3.3	30
R4259/C	2.0	0.43	0.81	1.4	4.5	44
R4260/C	1.8	0.6		1.9	4.4	41
R4261/C	1.6			1.0	2.5	23
R4262/NC	5.0			0.87	5.8	53
R4263/NC	6.4			0.37	6.8	61
R4264/NC[a]	NA	NA	NA	NA	NA	NA

a Sample was lost
b Sum incremental information in Tables A-1, A-2 and A-3 to obtain total % TOC identified.

C Convective layer
NC Nonconvective layer
NA Not Available

Table A-3 Concentration (ppm) of Normal Paraffin Hydrocarbon (NPH) in Tank 241-SY-101 Core Segment Samples[4]

Sample Number	NPH	% TOC Accounted For[b]
R4258	1440	13
R4259[a]		
R4260	410	4
R4261	670	6
R4262	20	<1
R4263[a]		

a Insufficient sample remaining to determine concentration of NPH.
b Sum incremental information in Table A-1, A-2 and A-3 to obtain total % TOC identified.

[3]Source of data is Campbell et al. 1994

[4]Source of information is Campbell et al. 1994a

Table A-4 Organics Identified in Complexed Concentrate Waste of Tank 241-AN-107, Based on 1986 Sample Results[5]

Chelating/Complexing Agents	Concentration mM	Concentration gC/L
Citric Acid	64.39	4.61
HEDTA	37.53	4.53
EDTA	31.41	3.77
Methane Tricarboxylic Acid	17.32	1.45
NTA	7.33	0.53
Chelator Fragments		
Ethylenediaminetriacetic Acid (ED3A)	17.91	1.72
N-(2-Hydroxyethyl)ethylenediamine-N'N'-diacetic Acid (EHDOA)	2.39	0.26
N-(ethylene)ethylenediaminetriacetic Acid (E_2DTA)	2.28	0.23
N-(2-Hydroxyethyl)iminodiacetic Acid (HEIDA)	2.14	0.18
N-(2-Hydroxyethyl)-N'-(methyl)ethylenediamine 'N,N'-diacetic Acid (MeHEDD'A)	1.83	0.20
N-(methyl)ethylenediamine-N,'N-diacetic Acid (MeEDDA)	1.02	0.08
Iminodiacetic Acid (IDA)	187.9	10.92
Molecular Weight (MW) Species		
A: MW 122	0.90	0.04
B: MW 173	0.23	0.02
C: MW 247	0.90	0.08
Carboxylic Acids		
Docos-13-enoic Acid	2.50	0.67
Hexanedioic Acid	2.04	0.15
Hexadecanoic Acid	2.04	0.39
Phthalic Acid	1.10	0.10
Nonanedioic Acid	0.83	0.07
Tetradecanoic Acid	0.68	0.12
Pentanedioic Acid	0.60	0.04
Octadecanoic Acid	0.54	0.11
Hydroxybutanedioic Acid	0.33	0.01
Butanedioic Acid	0.10	0.01
Alkalines		
nC_{23}- nC_{35}	7.77	2.50
Phthalate Esters		
Dibutylphthalate	1.24	0.23
Dioctylphthalate	0.05	0.01
Total Organic Carbon Identified		33.03
Total Organic Carbon	3670	44.00
% TOC Identified		75.1%

[5]Source of information is Lokken et al. 1986

Table A-5 10 CFR 61.55 Limits in Low-Level Waste Glass

Radionuclide	Class A (Ci/m^3)	Class B (Ci/m^3)	Class C (Ci/m^3)
^{137}Cs	1.0	44	4600
^{90}Sr	0.04	150	7000
^{99}Tc	0.3	--	3
TRU	10 nCi/g	--	100 nCi/g

Table A-6 Proposed Incidental Waste Allocation[6]

	Incidental Waste	
Radionuclide	Allocation (MCi)	Equivalent Average Concentration in Glass (Ci/m^3)
^{137}Cs	0.4	2.5
^{137}Ba	0.38	--
^{90}Sr	3.1	20
^{90}Y	3.1	--
^{99}Tc	0.03	0.19
TRU	Insignificant	<100 nCi/g

Table A-7 Concentrations of ^{90}Sr and TRU Elements in Complexed Waste at 50% Below NRC Limits in Low-Level Waste Glass

	50 % NRC Class A		50 % NRC Class B		50 % NRC Class C	
Tank[a]	^{90}Sr µCi/L	TRU µCi/L	^{90}Sr µCi/L	TRU µCi/L	^{90}Sr µCi/L	TRU µCi/L Am/Pu
241-AN-102	9.04	5.92	3.39E+04	-	1.58E+06	39.0/20.2
241-AN-107	8.64	5.46	3.24E+04	-	1.51E+06	40.0/14.6
241-AY-101	11.8	1.57	4.42E+04	-	2.06E+06	11.0/4.6

a Available analytical data for NCAW in tanks 241-AZ-101 and 241-AZ-102 indicate that the TRU element concentration in glasses made from non-complexed supernatant will be below NRC Class C TRU element criterion of 100 nCi/g. Data show that TRU element concentrations of glasses made from combined supernatant and spent solid wastes will exceed NRC Class C criterion by a factor of about 3. No heat and digest treatment of the waste in NCAW tanks is planned.

[6]Source of information is Garfield 1995

Table A-8 Equations for TOC Destruction and Sr Removal For Hydrothermal Model[7]

Applicability	Equation
Upper Limit	% TOC Destruction = 0.521x(% Sr Removal) - 15.76
Lower Limit	% TOC Destruction = 0.409x(% Sr Removal) + 20.20

Table A-9 Summary of Preliminary Requirements for 50% Below NRC Class C for Am Based on Batch Reactor Digestion Model and Percent Method at 100 °C

Tank	Initial TOC, mg/kg	Initial ^{241}Am, µCi/L	Target ^{241}Am, µCi/L	^{241}Am Removal, %	TOC Destruct, %	Final TOC, mg/kg	Estimated Digestion Time, Yr
241-AN-102[a]	28500	655	39	94.0	33.2 - 58.7	11780 - 19030	2.0 - 5.6
241-AN-107[a]	32400	364	40	89.0	30.6 - 56.7	14020 - 22490	1.9 - 5.6
241-AN-107[b]	27600	529	41	92.2	32.3 - 58.0	11590 - 18680	2.0 - 5.9
241-AY-101[a]	5400	33.4	11	67.1	19.2 - 47.6	2730 - 4360	0.9 - 2.8

a Concentrations are based on data from Shelton (1995).
b Concentrations are based on heat and digest data from Person (1995).

[7]Source of information is data of Figure 3-1

Table A-10 Summary of Preliminary Requirements for 50% Below NRC Class C Criteria for Pu Based on Hydrothermal Batch Reactor Digestion Model at 100 °C

Tank	Initial TOC, mg/kg	Initial Pu, µCi/L	Target Pu, µCi/L	Pu Removal, %	TOC Destruct, %	Final TOC, mg/kg	Estimated Digestion Time, Yr
241-AN-102[a]	28500	340	20.2	94.1	33.2 - 58.7	11780 - 19030	2.0 - 5.6
241-AN-107[a]	32400	130.9	14.6	88.8	30.5 - 56.5	14090 - 22520	1.8 - 5.5
241-AN-107[b]	27600	41	9.5	76.8	24.2 - 51.6	13360 - 20910	1.3 - 4.6
241-AY-101[a]	5400	13.9	4.6	66.9	19.1 - 47.6	2830 - 4370	0.9 - 2.8

a Concentrations are based on data from Shelton (1995).
b Concentrations are based on heat and digest data from Person (1995).

Table A-11 Summary of Preliminary Requirements for 50% Below NRC Class B for ^{90}Sr Based on Hydrothermal Batch Reactor Digestion Model at 100 °C

Tank	Initial TOC, mg/kg	Initial ^{90}Sr, µCi/L	Target ^{90}Sr, µCi/L	^{90}Sr Removal, %	TOC Destruct, %	Final TOC, mg/kg	Estimated Digestion Time, Yr
241-AN-102[a]	28500	114000	34000	70.2	20.8 - 48.9	14560 - 22580	1.1 - 3.8
241-AN-107[a]	32400	87000	32400	56.7	13.8 - 43.4	18340 - 27940	0.7 - 3.2
241-AN-107[b]	27600	76600	29000	62.1	16.6 - 45.6	15000 - 23000	0.8 - 3.6
241-AY-101[a]	5400	122000	44200	63.8	17.4 - 46.3	2900 - 4460	0.8 - 2.6

a Concentrations are based on data from Shelton (1995).
b Concentrations are based on heat and digest data w/addition of NaOH and $NaAlO_2$ from Person (1995).

Table A-12 Summary of Extrapolation Equations and Predicted Digest Times Based on Heat and Digest of Complexed Waste at 100 °C

Tank 241-	Radionuclide	Equation	50% NRC Class B or C Limits, µCi/L	Predicted Digestion Time, Days
AN-107	^{241}Am	Ln(Am µci/l) = - 0.289xLn(days) + 6.038	53.6[a] 40.0	1232 3390
AN-107	Pu	Ln(Pu µci/l) = - 0.0155x(days) + 3.439	1.0 14.6	222 48
AN-107	^{90}Sr	Sr(µ ci/l) = - 123.27x(days) + 79132	32400	379
AN-102	^{241}Am	Ln(Am µci/l) = - 0.289xLn(days) + 6.4846	58[a] 39	4394 17350
AN-102	Pu	Ln(Pu µci/l) = - 0.0155x(days) + 5.8290	1.0 182	376 20.2
AN-102	^{90}Sr	Sr(µ ci/l) = - 123.27x(days) + 114000	34000	650
AY-101	^{241}Am	Ln(Am µci/l) = - 0.289xLn(days) + 3.5086	11	47
AY-101	Pu	Ln(Pu µci/l) = - 0.0155x(days) + 2.6348	4.6	72
AY-101	^{90}Sr	Sr(µ ci/l) = - 123.27x(days) + 122000	44000	633

a Assumes Pu removal to $\leq$1.0 µCi/L has been achieved.

A-1 COMPARISON OF TEST RESULTS

The compilation of test data of Figure 3.1 shows about 30% Sr removal was obtained at both 0% and ~35% TOC destruction depending on the complexed waste and/or its dilution. Results of alternative treatment methods (using 3:1 diluted actual waste of tank 241-SY-101) closely resemble results to date from heat and digest treatment of tank 241-AN-107 waste.

At 50% TOC destruction >70% Sr removal is expected from undiluted waste while >95% was demonstrated by all treatment methods using 3:1 diluted tank 241-SY-101 waste. Heat and digest tests removed 66-87% of the Sr at 35% TOC destruction from undiluted tank 241-SY-101 actual waste; 27% of the Sr was removed at ~0% TOC destruction from chemically adjusted tank 241-AN-107 actual waste. Heat and digest testing of the tank 241-AN-107 "as is waste" destroyed 29% of TOC and removed 78% of the ^{90}Sr.

The limited data obtained from hydrothermal tests using undiluted tank 241-SY-101 simulated waste were in fair agreement with the heat and digest results. In both cases greater than 20% TOC destruction (starting TOC ~18 g/L = 10,600 mg TOC/kg for tank 241-SY-101) was required prior to any appreciable change in the Sr supernatant concentration.

REFERENCES

Campbell, J. A., S. A. Clauss, K. E. Grant, F. V. Hoopes, B. D. Lerner, R. B. Lucke, G. M. Mong, J. K. Rau, R. T. Steele, 1994, *Flammable Gas Safety Program Analytical Methods Development: FY 1993 Progress Report*, PNL-9062, Pacific Northwest Laboratory, Richland, Washington.

Campbell, J. A., S. A. Clauss, K. E. Grant, F. V. Hoopes, B. D. Lerner, R. B. Lucke, G. M. Mong, J. K. Rau, L. K. Wahl, R. T. Steele, 1994a, *Flammable Gas Safety Program Analytical Methods Development: FY 1994 Progress Report*, PNL-10127, Pacific Northwest Laboratory, Richland, Washington.

Garfield, J. S., 1995, LLW Classification and Solids Liquid Separation Criteria for IPM, Internal Memo 71220-95-006, Westinghouse Hanford Company, Richland, Washington.

Lokken, R. O., R. D. Steele, D. M. Strachan, A. P. Toste, 1986, *Complex Concentrate Pretreatment FY 1986 Progress Report*, PNL-7687, Pacific Northwest Laboratory, Richland, Washington.

Person, J. C. 1995, *Strontium and TRU Co-Removal and Gas Generation During Low-Temperature Digestion of Waste from Tank 241-AN-107*, WHC-SD-WM-DTR-041, Westinghouse Hanford Company, Richland, Washington.

Shelton, L. W., 1995, Double Shell Inventories, Internal Memo 71320-95-003, Westinghouse Hanford Company, Richland Washington.

This page intentionally left blank

APPENDIX B

SUMMARY OF ALTERNATE IN-TANK TREATMENT PROCESSES

This page intentionally left blank.

There are several alternate processes available that have potential for achieving decontamination requirements for Sr and TRU elements to meet the NRC waste classifications. A description of these processes is given below.

B-1 PRECIPITATION OF ^{90}Sr AND TRU ELEMENTS BY METAL HYDROXIDE

The analysis of DST radionuclide removal requirements by Schulz (1995) indicates that TRU element removal from actual complexed waste may be achieved by addition of NaOH. Washington (1990) conducted several tests with actual tank 241-AN-107 waste to study the effects of increasing the free hydroxide ion concentration from <0.02 M to a value in the range of 0.48 to 0.65 M.

After hydroxide ion adjustment, Washington let portions of solution stand a) 24 hours at room temperature, b) 30 days at room temperature, and c) 42 hours at 100 °C. In the latter case, Washington observed about a two-fold decrease in the concentration of TRU elements, presumably as a result of precipitation of their metal hydroxides. Washington reported a slight decrease in the TRU element concentration of the solutions which were allowed to stand at room temperature, but upon close inspection Washington's data do not support the latter observation. The behavior of ^{90}Sr in these experiments was not studied.

After Washington's work, Herting (1993) investigated further the effects of adding NaOH to tank 241-AN-107 supernatant liquid. Herting adjusted portions of 241-AN-107 supernatant liquid to free hydroxide concentrations of 0.26 to 1.47 M and let them stand for 24 hours. No precipitates were observed to form in any of the tests and no changes in either TRU element or ^{90}Sr concentrations were noted.

Herting extended his tests (1994, 1994a, 1995) with waste from tank 241-AN-107. Precipitation tests were performed at 22 to 25 °C, with portions of tank 241-AN-107 supernatant liquid adjusted to 1.5 or 3.0 M NaOH. Findings show that increasing the hydroxide concentration from <0.05M to 1.5 or 3.0 M resulted in precipitation of 7 to 20% of the ^{90}Sr, about 25% of the Pu and 14 to 75% of the ^{241}Am (Herting 1995). More ^{90}Sr and ^{241}Am precipitated at the higher hydroxide concentration (See Table B-1). The later behavior is in agreement with Washington's (1990) preliminary observations, and with Ryan's predictions (Ryan 1992).

Table B-1 Analytical Results for Hydroxide Precipitation of Tank 241-AN-107 Waste After 5 Days Mixing

Analyte	^{90}Sr		^{241}Am		$^{239/240}Pu$	
[NaOH] M	1.5 M	3.0 M	1.5 M	3.0 M	1.5 M	3.0 M
Baseline µCi/ml	93.0[a]		0.67		0.037	
Results µCi/ml	86.6	74.3	0.53	0.19	0.027	0.029

a An average of several historical values was used for this value.

The hydroxide precipitation process produces a supernatant liquid that is above or slightly below the 100 nCi TRU/g LLW glass limit, depending on the waste tank. Table B-2 summarizes the estimated mass of calcium, chromium, iron, magnesium, and nickel that are expected to precipitate by addition of NaOH. Table B-3 summarizes the estimated number of HLW glass canisters that would be produced by the additional precipitate. Hydroxide treatment increases the number of canisters by about 28 and costs by $21 M.

The precipitation information is based on laboratory solubility data for tank 241-AN-107 and percentage removal data (from tank 241-AN-107) for tanks 241-AN-102 and 241-AY-101, using Shelton (1995) tank inventories. Chelation of metal ions impacts solubility of the components in these tanks. The percentage removal method provides a conservative initial estimate of precipitate. Laboratory testing with waste from tanks 241-AN-102 and 241-AY-101 is needed to confirm preliminary estimates.

Table B-2 Summary of Estimated Metal Oxide Mass Precipitated by 3 M NaOH Treatment[a]

Tank	CaO, MT	Fe_2O_3, MT	MgO, MT	MnO_2, MT	NiO, MT	Total MT
241-AN-102	0.1	0.4	0.0	1.8	0.5	2.8
241-AN-107	0.1	5.9	0.0	0.9	0.1	7.0
241-AY-101	0.0	0.0	0.0	0.4	0.1	0.5
Total	0.2	6.3	0.0	3.1	0.7	10.3

a Solubilities based on preliminary laboratory test data for tank 241-AN-107 by Herting (1993, 1995), Washington (1990) and Shelton (1995). Tanks 241-AN-102 and 241-AY-101 based on percentage removal of component.

Table B-3 Summary of Estimated HLW Oxide Solids by 3 M NaOH Treatment

Tank	Number Added HLW Canisters	HLW Canister Added Costs[c] $M	Number Predicted HLW Canisters[d]
241-AN-102	10.7[b]	8.0	24.2
241-AN-107	14.7[a]	10.9	22.6
241-AY-101	2.4[b]	1.8	262.0
Total	27.8	20.7	308.8

a Number of canister based on 12% iron oxide loading in HLW glass and 3.34 MT per canister.
b Based on unconfirmed maximum 5% MnO_2 loading in HLW glass. No experimental basis for loading to this value. Assumes 3.34 MT glass per canister.
c Based on $745,000 incremental cost per HLW glass canister and includes operating and disposal costs (Slaathaug 1995).
d Number of predicted HLW glass canisters (3.34 MT) based on ASPEN.

B-2 DISPLACEMENT OF ^{90}Sr AND TRU ELEMENTS BY METALS ADDITION

The displacement of ^{90}Sr and TRU elements from complexing organics via the addition of other metals is a good alternative method for decontamination of complexed waste. The process could involve addition of a metal ion with a comparable or higher affinity for the organic complexants in the tank waste, followed by filtration to remove the displaced and precipitated ^{90}Sr and TRU element components. This process is relatively simple, and could potentially be conducted as an in-tank process. Review of the literature (Dean 1985) indicates that many of the chelators present in complexant concentrate have potentially higher affinities for numerous other metal ions as compared to TRU elements and, in particular, ^{90}Sr.

A number of in-tank processes for the destruction of organic complexants to enhance the removal of selected radionuclides were recently reviewed (Schulz et al. 1995). Metals and hydroxide addition were among the processes reviewed. These included tests conducted by Washington (1990) and Herting (1993, 1994, 1994a, 1995). Washington (1990) conducted several tests, using actual tank 241-AN-107 waste to study the effects of increasing free hydroxide ion concentration on TRU elements. The data indicated that after addition of hydroxide (i.e., from 0.02 M to 0.48-0.65 M), and allowing the solution to stand at elevated temperature for an extended period of time (i.e., 42 hours at 100 °C), a two-fold decrease in the concentration of (soluble) TRU elements was observed. No definite conclusion were drawn when treatment was conducted at lower, ambient, temperatures. Herting (1993) later conducted hydroxide addition tests, using actual 241-AN-107 waste, and observed no changes in either TRU element or ^{90}Sr supernatant concentrations.

Herting (1993) also performed two tests to study the effect of Fe(III) and Sr(II) ions addition in precipitating and scavenging TRU elements at 1.4 M free hydroxide. In these tests waste was adjusted to 0.01 M $Fe(NO_3)_3$ and 0.01 M $Sr(NO_3)_2$ and stirred 24 hours at room temperature. In both tests a two to three fold decrease was observed in the TRU element concentration, but no change in the ^{90}Sr concentration. See Table B-4.

Herting (1994, 1994a, 1995) extended his tests on actual 241-AN-107 waste to include higher Fe(III) concentrations and nonradioactive Sr(II) addition at 1.5 and 3.0 M NaOH. This work indicated that the addition of non-radioactive strontium gave a ^{90}Sr decontamination factor (DF) of approximately 20. The addition of non-radioactive strontium had little effect on TRU element removal. Upon Fe(III) addition, maximum decontamination factors obtained for ^{90}Sr, $^{239/240}Pu$, and ^{241}Am were approximately 6, 4, and 30, respectively. The 0.01 M Fe (III) produced about the same TRU element removal performance as the 0.1 M Fe(III). See Table B-4.

and simulant dilution were investigated. Strontium decontamination factors on the order of 10 to 20 were obtained. Metal ions such as Ca(II), Cu(II) and Ni(II) appear to be effective in removing Sr, primarily via displacement from the chelating organic, whereas Fe(III) ion appeared to act primarily as a flocking agent (i.e., the Fe(III) remains insoluble) to remove Sr from solution. Results shows that addition of Fe(III) ion resulted in a 80% to 500% increase in the amount of solids originally present (final Fe(III) concentrations of 0.04 to 0.21 M). Substantially more solids were produced via Fe(III) addition than by addition of Ca(II), Cu(II) or Cu(II) ions.

From the data presented to date, it appears that metals addition is affective in achieving modest decontamination factors of between approximately 5 to 20 for ^{90}Sr and TRU elements. Fe(III) ion addition is effective in removing both ^{90}Sr and TRU elements, however, due to its apparent flocking action (i.e., insolubility) a relatively large amount of solids are formed as compared to the addition of other metal ions. It is important to continue hydrated iron oxide precipitation tests with actual waste and study the effect of hydroxide and iron concentrations, temperature and time on removal of TRU elements and additional HLW. The additional solids will impact plant operation.

This page intentionally left blank

Table B-4 Common-Basis Analytical Results for Removal of Radionuclides

Analyte	^{90}Sr µCi/mL		^{241}Am µCi/mL		$^{239/240}Pu$ µCi/mL	
[NaOH]	1.5 M	3.0 M	1.5 M	3.0 M	1.5 M	3.0 M
Baseline	93.0[a]		0.67		0.037	
NaOH only	86.6	74.3	0.53	0.19	0.027	0.029
0.1 M Fe	47.0	51.2	0.11	0.028	0.016	0.10[b]
0.3 M Fe	26.4	18.7	0.066	0.030	0.010	0.008
0.1 M Fe (2x)	22.3	18.1	0.030	0.021	0.012	0.015
Fe/Sr/PO_4	5.7	5.0	0.092	0.057	0.015	0.014
0.1 M Sr	4.8	6.1	0.40	0.42	0.033	0.031
0.01 M Fe/Sr[c]	~75.0	-	~0.16	-	~0.014	-

a Historical value (Herting 1993a) used for ^{90}Sr baseline.
b Suspect result, may be factor of 10 high; should be 0.010 µCi/mL.
c Test performed for 24 hr.

Table B-5 shows a summary of the volume percent solids formed in each test relative to the original volume of waste before sodium hydroxide adjustment. Doubling the NaOH concentration to 3 molar produces significantly larger volumes of solid, which impact plant operation. Optimization of Fe(III) and NaOH concentration is needed.

Herting (1994a) also conducted metals displacement testing with a composite sample of tank 241-AW-101 (70 vol%), 241-AP-106 (20 vol%), and 241-AP-102 (10 vol%) waste. The total organic carbon, ^{90}Sr, and TRU contents of this waste composite were considerably less than most of the complexed concentrate wastes. A number of displacement metals/precipitants were tested in this work. It was observed that nonradioactive Sr(II) addition resulted in 99.4% removal of the ^{90}Sr from solution; Ni(II) addition resulted in 98.5% removal of ^{90}Sr from solution; and addition of Mn(II) or Ca(II) resulted in removal of approximately 86% of the ^{90}Sr from solution. The concentration of TRU elements in the supernatant was not affected by the addition of any of the metals/precipitation agents that were tested.

Table B-5 Volume Percent Centrifuged Solids[a]

Reagent Added	1.5 M NaOH	3.0 M NaOH
NaOH only	<3	58
0.1 M Fe	8	34
0.3 M Fe	15	34
0.1 M Fe (2x)	16	41
Fe/Sr/PO_4	33	55
0.1 M Sr	6	31
0.01 M Fe/Sr	Not Available	-

a Relative to volume of tank 241-AN-107 before sodium hydroxide addition.

Table B-6 summarizes the estimated amount of metal oxide solids and HLW glass that would result from addition of 0.1 M Fe(III) to tanks 241-AN-102, 241-AN-107, and 241-AY-101. The resulting Fe_2O_3 solids would increase the number canisters by 215 and cost about $160 M.

Table B-6 Summary of HLW Ferric Oxide Solids and Corresponding HLW Glass Canisters Based on Preliminary Hydrated Iron Oxide Precipitation Tests with Actual Waste of Tank 241-AN-107

Tank	Supernatant, L	Fe_2O_3, MT 0.1 M Fe[c]	Number Added HLW Canisters[a]	HLW Canister Added Costs[b] $ M	Number Predicted HLW Canisters[d]
241-AN-102	3.83E+06	30.5	76.2	56.6	24.2
241-AN-107	4.01E+06	32.0	79.8	59.4	22.6
241-AY-101	2.94E+06	23.5	58.5	43.6	262.0
Total	1.08E+07	86.0	214.5	160.0	308.8

a Number of HLW canisters based on 12% Fe_2O_3 loading in glass and 3.34 MT per canister. Minimum number of canisters is ~50 based on 50% Fe_2O_3 loading.
b Based on $745,000 incremental cost per canister and includes operating and disposal costs (Slaathaug 1995).
c Based on information in Schulz et al. (1995).
d Number of predicted HLW glass canisters from sludge (3.34 MT) based on ASPEN model.

Recent metals displacement work determined the effect of Ca(II), Cu(II), Ni(II), and Fe(III) on Sr removal, using tank 241-SY-101 simulated waste (Orth, et al. 1995a). The effects of metals addition concentration, time, temperature, stage-wise addition, chelating organic (i.e., EDTA, NTA, HEDTA),

B-3 STRONTIUM REMOVAL VIA CHEMICAL OXIDANT TESTING

Experiments were initiated to assess the use of chemical oxidants to remove strontium from tank 241-SY-101 simulated supernatant via low temperature organic destruction. The use of chemical oxidants, such as potassium permanganate and hydrogen peroxide, is widespread in the waste water treatment industry for the removal of organics in an aqueous media. From initial screening tests and literature review, hydrogen peroxide was discarded, and potassium permanganate was selected for initial testing on simulant. Test information on simulant was later used to initiate some batch chemical oxidant tests on actual waste.

The 3:1 diluted 101-SY-SIM simulant recipe, with EDTA as the organic source, was the primary simulant for testing. NTA and HEDTA were also tested. Experiments were conducted in closed flasks in a controlled environment incubator/shaker for 70 hour tests at both 30°C and 65°C and ambient pressure, with nominal sampling intervals at 1, 4, 20, and 70 hours. Samples were filtered through a 0.45μm syringe filter, and the filtrate was analyzed for Sr and TOC. At the conclusion of the test, the simulant was also tested for percent solids. Chemical oxidant dosage was selected by taking a dose range between zero and twice the estimated oxidant requirement to stoichiometrically oxidize only the EDTA in the simulant. The potassium permanganate was added to the simulant in dry, granular form rather than a stock solution to avoid adding extra water to the simulant and unnecessarily increasing the total volume.

Actual waste testing was initiated following the screening experiments on the tank 241-SY-101 simulant using 0.13 M concentration of potassium permanganate (~2.0E-05 g mole/L $KMnO_4$ per ppm TOC). After 1 hr mixing at near ambient temperature, about 99% of ^{90}Sr, 92% of the Pu and 97% of the Am were removed from the supernatant (Orth et al. 1995a).

Testing to date has provided three primary results. Organic complexants are quickly destroyed in the simulant and actual waste; ^{90}Sr and TRU elements removal was achieved to decontamination factors of around 20 (corresponding to an approximate TOC destruction of 50% to 70%). Solids formed in the simulated and actual waste after potassium permanganate addition.

Table B-7 summarizes the amount of metal oxide solids that would result from chemical oxidation of waste in tanks 241-AN-102, 241-AN-107, and 241-AY-101. About 452 MT (444.3 MT of MnO_2 plus about 8.2 MT of metal oxides) are expected to precipitate from permanganate addition. At maximum 5% loading in HLW glass (Geeting et al. 1993), the additional MnO_2 solids would increase the number canisters by 2670 and cost about $1990 M.

There is <u>no</u> experimental basis for the 5% loading of MnO_2. Information on high manganese glass (CVS2-55 2.8% Mn, 7.7% Fe, 0.9% Cr and CVS2-56 4.7% Mn, 7.7% Fe, 0.7% Cr) shows the liquidus temperature is about 1120 °C, which results in the formation of spinel solids in the melter. Further evaluation is needed.

Table B-7 Summary of Estimated HLW Oxide Solids from Chemical Oxidation of Complexed Waste

Tank	Supernatant, L	MnO_2+MO_x, MT[a]	Number Added HLW Canisters[b]	HLW Canister Added Costs[c] $ M	Number Predicted HLW Canisters[d] (Sludge)
241-AN-102	3.83E+06	189.7+2.4	1135.9	846.2	24.2
241-AN-107	4.01E+06	226.5+4.5	1356.3	1010.4	22.6
241-AY-101	2.94E+06	28.1+1.3	174.3	129.8	262.0
Total	1.08E+07	444.3+8.2	2666.5	1986.4	308.8

a Amount MnO_2 based on addition of 2.0E-05 g mole/L $KMnO_4$ per ppm TOC in supernatant. The MO_x is assumed the same as produced by heat and digest of waste (total 8.2 MT).

b Maximum 5% MnO_2 in glass from Geeting et al. (1993) (maximum 20 wt% in HWVP feed x 25% loading = 5%) and 3.34 MT glass per canister. No experimental basis for this loading. Number includes metal oxide (MO_x) from destruction of organic.

c Based on $745,000 incremental cost per canister and includes operating and disposal costs (Slaathaug 1995).

d Number of predicted HLW glass canisters (3.34 MT) based on ASPEN.

3:1 diluted tank 241-SY-101 simulant tests using EDTA, HEDTA, and NTA, control sample solids averaged 1.1%; 0.1 M permanganate addition yielded final total filterable solids at 2.5%; 0.3 M addition yielded 7.1% filterable solids, and at 0.5 M chemical oxidant, the solids averaged 10.3% by weight.

Preferential species oxidation in the sample matrix was observed to follow the relative order of redox potentials of the controlling standard half reactions. By varying the amount of chemical oxidant it was determined that the Cr(III) is oxidized to Cr(VI) first, TOC (EDTA) oxidation is second, and then nitrite oxidation to nitrate. The oxidation of organic appears to start when the Cr(III) oxidation is about 80% complete and significant nitrite oxidation does not occur until the TOC destruction is about 60% complete.

It was observed that the chemical oxidation in actual waste was quickly exothermic, due to the rapid organic oxidation, compared to simulant. The fast rate of heat release experienced with the actual waste tests appeared to be similar to results from destruction of HEDTA and NTA, rather than EDTA.

B-4 USE OF ABSORBERS FOR ENHANCED STRONTIUM AND TRU ELEMENT REMOVAL

A number of investigations have been conducted to examine Sr and TRU element removal from alkaline Hanford tank waste supernatant with absorber materials. Several recent comprehensive studies have been completed at Los Alamos National Laboratory and Sandia National Laboratory in support of the TWRS mission (Marsh et al. 1994; Marsh et al., 1994a; Marsh et al. 1995; Svitra 1994; Marsh et al. 1995). Results from these investigations showed that, in the absence of organic complexants, a significant number of the absorbers (more than 20) provided four-digit or greater K_d values for sorbing strontium. However, upon adding EDTA to a 241-101-SY supernatant simulant, only four of the tested absorbers provided triple digit K_d values.

Additional testing was conducted to determine the effect of degradation and destruction of the complexants prior to adsorbent testing. These tests showed that exposing EDTA-containing simulant to a 34×10^6 Rad of gamma radiation (to simulate the effects of radiation during storage in Hanford Site Tanks) increased the K_ds for the more effective strontium absorbers by a factor of 1.5 to 2.

In another set of experiments, the irradiated simulant was subjected to hydrothermal treatment prior to performing the absorption testing. In the hydrothermal treatment, conducted at 450°C and 15,000 psi, at a residence time of 25 seconds, approximately 70% of the organic carbon was destroyed. Subsequent to the hydrothermal treatment, K_ds for strontium greater than 1000 were obtained for 10 of the tested absorbers (compared to only 4 absorbers given triple digit K_ds prior to treatment).

The LANL/SNL investigations showed that the presence of organic complexants have little effect on the absorption of cesium and technetium for most of the tested adsorbents. However, the sorption of americium was significantly reduced by the presence of organic compounds (only two demonstrated triple digit K_ds). For most absorbers, the americium K_ds decreased by one to two orders of magnitude in the presence of organics. Similar to what was found for Sr, after hydrothermal treatment, 17 of 18 tested adsorbents displayed triple digit K_ds.

In summary, several absorbers demonstrated triple digit K_ds for both Sr and Am in the presence of complexing organics in tank 241-SY-101 simulated waste. Thus, depending upon the final treatment targets, it is potentially feasible that the tank waste supernatant can be treated with existing absorbers for Sr and TRU element removal. Caution should be used with the data from the LANL/SNL investigations, since the test results have not been confirmed with actual tank waste testing.

The LANL/SNL investigations also showed that K_ds can be improved by 1 to 2 orders of magnitude by pretreating the tank waste with a organic destruction process. If NRC Class A criteria must be achieved for Sr, a combination of organic destruction and adsorption will almost certainly be required.

This page intentionally left blank.

REFERENCES

Dean, J. A., 1985, Lange's Handbook of Chemistry, 13th Edition. McGraw-Hill, New York, New York.

Geeting, J. G. H., D. E. Kurath, 1993, *Preliminary Assessment of Blending Hanford Tank Wastes*, PNL-8589, Pacific Northwest Laboratory, Richland,

Herting, D. L., 1995, *Report on Scouting Study on Precipitation of Strontium, Plutonium and Americium from Hanford Complexant Concentrate Waste*, WHC-SD-WM-DTR-040, Rev 0, Westinghouse Hanford Company, Richland, Washington. Washington.

Herting, D. L., 1994, Strontium Removal Study - Feed Characterization. Internal Letter 12110-PCL94-017, Westinghouse Hanford Company, Richland, Washington.

Herting, D. L., 1994a, Strontium Removal by Precipitation. Internal Memo 12110-PCL94-026, Westinghouse Hanford Company, Richland, Washington.

Herting, D. L., 1993, Effect of Tank 107-AN Caustic Addition on Radionuclide Solubilities, Internal Memo 12110-PCL93-043, Westinghouse Hanford Company, Richland, Washington.

Herting, D. L, 1993a, Tank 241-AN-107 Caustic Demand, Internal Memo 12110-PCL-043, Westinghouse Hanford Company, Richland, Washington.

Marsh, S. F., Z. V. Svitra, and S. M. Bowen, 1995, *Effects of Aqueous-Soluble Organic Compounds on the Removal of Selected Radionuclides from High-level Waste, Part I: Distribution of Sr, Cs, and Tc onto 18 Absorbers from an Irradiated Organic-Containing Leachate Simulant for Hanford Tank 101-SY*, LA-12862, Rev, Los Alamos National Laboratory, Los Alamos, New Mexico.

Marsh, S. F., Z. V. Svitra, and S. M. Bowen, 1995a, *Effects of Soluble Organic Complexants and Their Degradation Products on the Removal of Selected Radionuclides from High-level Waste, Part II: Distribution of Sr, Cs, Tc and Am onto 32 Absorbers from four Variations of Hanford Tank 101-SY*, LA-12943, Rev, Los Alamos National Laboratory, Los Alamos, New Mexico.

Marsh, S. F., Z. V. Svitra, and S. M. Bowen, 1994, *Distribution of 14 Elements of 63 Absorbers from Three Simulant/Solutions(Acid-Dissolved Sludge, Acidified Supernate, and Alkaline Supernate) for Hanford HLW Tank 102-SY*, LA-12654, Rev, Los Alamos National Laboratory, Los Alamos, New Mexico.

Marsh, S. F., Z. V. Svitra, and S. M. Bowen, 1994a, *Distribution of 15 Elements on 58 Absorbers from Hanford Double-Shell Slurry Feed (DFFS)*, LA-12863, Rev Los Alamos National Laboratory, Los Alamos, New Mexico.

Orth, R. J., A. J. Schmidt, M. R. Elmore, A. H. Zacher, T. R. Hart, G. G. Neunschwander, S. R. Gano, R. W. Lehmann (Zimpro), J. A. Momont (Zimpro), 1995, *Removal of strontium And Transuranics from Hanford Tank Waste via Hydrothermal Processing - FY 1994/FY 1995 Test Results*, PNL-10765, Pacific Northwest Laboratory, Richland, Washington.

Orth, R. J., A. J. Schmidt, A. H. Zacher, M. R. Elmore, K. R. Elliot, G. G. Neuenschwander, S. R. Gano, 1995a, *Removal of Strontium and Transuranics from Hanford Tank Waste via Addition of Metal Cations and Chemical Oxidant - FY 1995 Test Results*, PNL-10766, Pacific Northwest Laboratory, Richland, Washington.

Schulz, W. W., M. J. Kupfer, and M. M. McKeon, 1995, *In-Tank Processes for Destruction of Organic Complexants and Removal of Selected Radionuclides.* WHC-SD-WM-ES-321, Rev. 0. Westinghouse Hanford Company, Richland, Washington.

Shelton, L. W., 1995, Double Shell Inventories, Internal Memo 71320-95-003, Westinghouse Hanford Company, Richland Washington.

Slaathuag, E. J., 1995, *Tri-Party Agreement Alternative Engineering Data Package of the Tank Waste Remediation System Environmental Impact Statement*, WHC-SD-WM-EV-104 Rev 0, Westinghouse Hanford Company, Richland, Washington.

Svitra, Z. V., S. F. Marsh, and S. M. Bowen, 1994, *Distribution of 12 Elements on 62 Absorbers from Hanford Neutralized Current Acid Waste (NCAW)*, LA-12889 Rev, Los Alamos National Laboratory, Los Alamos, New Mexico.

Washington, L. O., 1990, Chemical Addition to Tank 107-AN, Internal Memo 16220-PCL90-079, Westinghouse Hanford Company, Richland, Washington.

APPENDIX C

SUMMARY OF PRELIMINARY TEST DATA

This page is intentionally left blank.

Table C-1 Summary of Preliminary Test Data from Heat and Digest of Undiluted Tank 241-SY-101 Actual Waste - Part 1[8]

Days	TOC, M	Al, M	Fe, M	Ca, M	Ni, M	Sr, M	K, M	Na, M	OH, M	Cr, M
0	1.451	1.713	NA	4.88E-03	4.05E-03	1.1E-04	0.128	13.60	2.26	0.0044
73	1.096	0.419	NA	3.57E-03	1.52E-03	8.4E-05	0.120	14.83	3.06	0.0036
96	1.586	0.757	NA	3.90E-03	1.93E-03	7.9E-05	0.144	12.39	3.79	NA
262	0.938	2.040	NA	4.76E-03	5.1E-04	8.8E-05	0.125	12.96	1.93	.00011
365	0.954	2.208	NA	2.26E-03	<2.7E-04	1.4E-05	0.148	12.16	2.37	<.00015

Table C-2 Summary of Preliminary Test Data from Heat and Digest of Undiluted Tank 241-SY-101 Actual Waste - Part 2[9]

Days	TOC, M	Oxalate, M	Acetate, M	Formate, M	^{90}Sr, µci/L	^{241}Am, µci/L	Pu, µci/L
0	1.451	0.063	0.116	0.280	8330	NA	NA
73	1.096	0.014	0.044	0.255	9280	NA	NA
96	1.586	0.067	0.063	0.262	NA	NA	NA
262	0.938	0.054	0.099	0.344	9750	NA	NA
365	0.954	0.028	0.061	0.706	2840	NA	NA

[8]Source of information is Person (1995a)

[9]Source of information is Person (1995a)

Table C-3 Summary of Preliminary Test Data from Heat and Digest of Adjusted Tank 241-AN-107 Actual Waste - Part 1[10]

Digest Days	Al, M	Fe, M	Cr, M	Ca, M	Ni, M	Zr, M	K, M	Na, M	OH, M	TOC, M
0	0.262	0.0231	2.7E-03	0.0124	0.0076	7.0E-04	0.0409	8.18	0.490	3.11
32	0.265	0.0001	5.0E-05	0.0125	0.0078	2.0E-05	0.0404	8.05	0.303	2.59
96	0.339	0.0124	1.43E-03	0.0184	0.0104	3.4E-04	0.0486	9.92	0.247	3.19
144	0.301	NA	NA	0.0143	0.0094	NA	0.0443	8.98	0.189	3.07

Table C-4 Summary of Preliminary Test Data from Heat and Digest of Adjusted Tank 241-AN-107 Actual Waste - Part 2[11]

Days Digest	TOC, M	Oxalate, M	Acetate, M	Formate, M	^{90}Sr, µci/L	^{241}Am, µci/L	Pu, µci/L
0	3.11	<0.035	0.017	0.162	79800	529	41
32	2.59	NA	NA	NA	76600	68.4	NA
96	3.19	NA	0.027	0.189	62000	131	<11
144	3.07	<0.035	0.035	0.191	64500	151	<4.7

[10]Source of information is Person (1995)

[11]Source of information is Person (1995)

Table C-5 Comparison of Preliminary Chemical Consumption Results from Hydrothermal and Heat and Digest Testing[12]

Tank	Days of Digestion	OH/TOC, g mole/g mole	NO_2/TOC, g mole/g mole	NO_3/TOC, g mole/g mole
241-SY-101 Simulant 3:1 Diluted (EDTA)	Based on Hydrothermal Processing	0.70	0.75	0.10
241-SY-101 Actual Undiluted	73	1.11	-0.53	-3.09
	152	0.65	0.34	-1.13
	365	-0.22	1.35	0.10
241-AN-107 Actual w/ Chemical Addition	32	0.35	NA	NA
	96	-2.80	-1.26	10.22
	144	7.92	9.21	-6.05
241-AN-107 Actual w/o Chemical Addition	96	0.092	-3.47	-1.22
	144	0.019	1.07	-0.27

[12]Source of information is Orth et al. (1993) and Person (1995, 1995a)

This page intentionally left blank.

C-1 FILTRATION TEST DATA OF SIMULATED AND ACTUAL WASTE

Filtration tests were conducted to determine 1) what the filtering requirements are for removing strontium from solution after hydrothermal treatment, and 2) whether strontium exists as colloids in untreated or hydrothermally treated tank 241-SY-101 simulated waste. An Amicon®[13] Series 8000 Stirred Ultrafiltration Cell, with 0.04 μm filter, was used in the tests (Orth et al. 1995a).

The filtering was conducted in series, initially passing the solutions through a Whatman™ #4 filter (i.e., 20-25μm pore size), then through a 0.45 μm filter, and finally through a 0.04 μm filter. The 0.04 μm filter was assumed (via conversation with Dr. Bruce Bunker, PNL) to be small enough such that colloidal Sr, if present, would be retained. Thus, if colloidal Sr were present, a decrease in Sr concentration would be expected when comparing the filtrate from the 0.45 μm filtration step with the 0.04 μm filtration step. Untreated and hydrothermally treated tank 241-SY-101 simulant (undiluted and 3X-diluted) solutions were evaluated during this testing. EDTA was the organic carbon source in the simulants; the untreated, undiluted tank 241-SY-101 simulant contained approximately 26,000±2600 μg/Liter total organic carbon, and the untreated, 3X-diluted tank 241-SY-101 simulant contained approximately 5775±580 ug/Liter total organic carbon.

The analytical results from this testing are given in Table C-6. The experimental uncertainties for the Sr concentrations were estimated by the analytical laboratory. The only sample that shows a possible slight decrease (i.e., very close to the estimated experimental error) in Sr concentration when comparing the filtrates from the 0.45 μm and 0.04 μm filtering steps is the undiluted, untreated tank 241-SY-101 simulated waste. In all other cases, the Sr levels are essentially unchanged when comparing the filtrates from these two filtering steps. In fact, all of the other solutions, with the exception of one (undiluted 241-SY-101, 250 °C, 1507 psig, 5 hours) showed no change in Sr concentration in the filtrates from all three filtering steps.

These results indicate that 1) minimal amounts of the Sr <u>may</u> exist as colloidal material in the undiluted, untreated tank 241-SY-101 simulant; numerous repeat analyses would be required to establish a more certain experimental error to determine whether this observation is "real" or not, 2) there was no definitive evidence that Sr was present as colloids in treated undiluted 241-SY-101 simulant, or untreated and treated 3X-diluted 241-SY-101 simulant, 3) the hydrothermal treatment does not appear to lead to the formation of strontium colloids, and 4) in most cases, filtration, using a Whatman #4 filter is sufficient to remove insoluble Sr from solution.

Also, for the undiluted tank 241-SY-101 simulant, 32% total organic carbon destruction resulted in no decrease in strontium concentration in any

---

[13] ® Series 8000 Stirred Cell is a registered trademark of Amicon Corporation

of the filtrates, whereas 48% total organic destruction, lead to approximately 78% strontium removal from solution (based on Whatman #4 filtrate). For the 3X-diluted simulant, 17% total organic destruction lead to approximately 48% removal of Sr via filtration with a Whatman #4 filter, and 43% total organic destruction lead to between 80 and >97% removal of Sr upon filtration.

Table C-6 Strontium Filtration Results

			Strontium Concentration (µg/Liter)		
Simulant Description	Hydrothermal Conditions[a]	Total Organic Carbon Destruction (%)	Whatman #4 Filtrate	0.45 µm Filtrate	0.04 µm Filtrate
Undiluted 101-SY	None	---	2250±225	2805±561	1695±339
Undiluted 101-SY	250°C, 1519 psig, 5 hour hold	32[b]	2495±499	2270±454	2182±436
Undiluted 101-SY	200°C, 1507 psig, 48 hour hold	48	496±99	303±30	299±60
3X-diluted 101-SY	None	---	352±35	379±38	381±38
3X-diluted 101-SY	250°C, 2940 psig, 1 hour	17	170±17	171±17	152±15
3X-diluted 101-SY	250°C, 1830 psig, 5 hours	43	<10 40±30	<10 18±2	<10 13±5

a The hydrothermal testing was conducted using a 1-liter batch reactor.
b The % total organic destruction values given in the table are accurate to approximately ±10% of the reported value (e.g., 32±3).

In an earlier study (Herting 1995) a supernatant sample from tank 241-AN-107 was passed through an ultracentrifuge membrane to evaluate the presence of colloidal ^{90}Sr and alpha-emitting radionuclide solids. It was observed that most, but not all, of the ^{90}Sr and alpha isotopes passed through the membrane, and thus were present mainly as true solute species, rather than colloidal particles. It was conceivable that dilution, caused by the pretreatment of the membrane, may have been responsible for the lower ^{90}Sr and alpha isotope concentrations in the filtrate, therefore, it was impossible to say without doubt that a fraction of the these species were present as suspended solids.

Another earlier study Herting (1994) used a composite supernatant sample from three tanks -- 70% (by volume) 241-AW-101, 20% 241-AP-106, and 10% 241-AP-102 and measured concentration changes after centrifugation, filtration through a 0.45 µm filter and after 10 minutes of boiling. The differences

among the analytical results were no larger than the expected analytical uncertainty. These physical treatment had no effect on the concentration of ^{90}Sr, total alpha, ^{137}Cs and ^{99}Tc.

In a recent study (O'Rourke 1995), a 5 month old sample of $NaOH-NaAlO_2$ adjusted, 144 day digested supernatant of tank 241-AN-107 was passed through an ultracentrifuge membrane to evaluate presence of colloids. The ultracentrifuge membrane (Amicon Centriflo® Type CF25)[14] is capable of removing particulates with diameters larger than 15 angstroms or molecular weights above 25,000. Results show that the ^{90}Sr and ^{241}Am of the digested supernatant passed through the membrane and were truly in solution (Table C-7). The $^{239/240}Pu$ concentrations were below detection level in all samples. The results support earlier findings that very little (if any) ^{90}Sr and TRU element colloids were found in treated supernatant of tank 241-107-AN.

Table C-7 Analyses of Digested Tank 241-AN-107 Supernatant Before and After Ultrafiltration

Analyte	Before Ultrafiltration (μCi/mL)	After Ultrafiltration (μCi/mL)
^{60}Co	0.194	0.206
^{90}Sr	69.6	69.7
^{137}Cs	350	352
$^{239/240}Pu$	$<3.88 \times 10^{-4}$	$<4.41 \times 10^{-4}$
^{241}Am	0.144	0.154

[14]Centriflo is a registered trademark of the Amicon Corporation

This page intentionally left blank.

REFERENCES

Herting, D. L., 1994, Strontium Removal By Precipitation, Internal Memo 12110-PCL94-026, Westinghouse Hanford Company, Richland, Washington.

Herting, D. L., 1995, Addendum to Results of Ultracentrifuge Test on Tank 107-AN Waste, Internal Letter 8E110-PCL95-015, Westinghouse Hanford Company, Richland, Washington.

O'Rourke, J. F., 1995, Results of Ultrafiltration Test with Digested Tank 107-AN Waste, Internal letter 75764-PSC95-079, Westinghouse Hanford Company, Richland, Washington.

Orth, R. J., A. J. Schmidt, M. R. Elmore, A. H. Zacher, T. R. Hart, G. G. Neunschwander, S. R. Gano, R. W. Lehmann (Zimpro), J. A. Momont (Zimpro), 1995, *Removal of strontium And Transuranics from Hanford Tank Waste via Hydrothermal Processing - FY 1994/FY 1995 Test Results*, PNL-10765, Pacific Northwest Laboratory, Richland, Washington.

Orth, R. J., A. J. Schmidt, A. H. Zacher, M. R. Elmore, K. R. Elliot, G. G. Neuenschwander, S. R. Gano, 1995a, *Removal of Strontium and Transuranics from Hanford Tank Waste via Addition of Metal Cations and Chemical Oxidant - FY 1995 Test Results*, PNL-10766, Pacific Northwest Laboratory, Richland, Washington.

Orth, R. J., A. J. Schmidt, M. R. Elmore, T. R. Hart, G. G. Neuenschwander, A. H. Zacher, E. O. Jones. J. C. Poshusta, 1993, *Hydrothermal Processing of Hanford Tank Waste Organic Destruction Technology Development Task*, PNL-10108, Pacific Northwest Laboratory, Richland, Washington.

Person, J. C. 1995, *Strontium and TRU Co-Removal and Gas Generation During Low-Temperature Digestion of Waste from Tank 241-AN-107*, WHC-SD-WM-DTR-041, Westinghouse Hanford Company, Richland, Washington.

Person, J. C., 1995a, *Strontium Removal and Gas Generation During Low-Temperature Digestion of Waste from Tank 241-SY-101*, WHC-SD-WM-DTR-042, Westinghouse Hanford Company, Richland, Washington.

This page intentionally left blank.

APPENDIX D

SUMMARY OF CAPITAL AND OPERATING COST ESTIMATES

This page intentionally left blank.

Table D-1 Summary of Preliminary Project Cost Estimates for One Tank Configuration (Sequential Scenario)

Description	Cost $	Contingency		Total Cost $
		%	$	
Engineering	7,920,000	40	3,170,000	11,090,000
Engineering/ HVAC Upgrades	3,410,000	40	1,360,000	4,770,000
Other Structures	3,720,000	40	1,490,000	5,210,000
Tank HVAC Upgrades	5,720,000	40	2,290,000	8,010,000
Utilities	870,000	40	350,000	1,220,000
Special Equip/ Process Systems	16,810,000	40	6,720,000	23,530,000
Demolition (Adjusted to Meet DOE 5100.4)	430,000	40	170,000	600,000
Total Estimated Cost	38,880,000	40	15,550,000	54,430,000
Other Project Costs				7,620,000
Total Project Cost				62,050,000

a Based on modified BNFL Trade Study and Project W-030 cost estimates by T. L. Waldo of Kaiser Engineers Hanford Company.

Table D-2 Summary of Preliminary Project Cost Estimates for Two Tank Configuration (Combined Scenario)

Description	Cost $	Contingency		Total $
		%	$	
Engineering	13,000,000	40	5,200,000	18,200,000
Engineering/ HVAC Upgrades	10,000,000	40	4,000,000	14,000,000
Other Structures	5,170,000	40	2,070,000	7,240,000
Tank HVAC Upgrades	15,230,000	40	6,090,000	21,320,000
Utilities	870,000	40	350,000	1,220,000
Special Equip/ Process Systems	29,030,000	40	11,610,000	40,640,000
Demolition (Adjusted to Meet DOE 5100.4)	860,000	40	350,000	1,210,000
Total Estimated Cost	74,160,000	40	29,670,000	103,830,000
Other Project Costs				14,530,000
Total Project Cost				118,360,000

a Based on modified BNFL Trade Study and Project W-030 cost estimates by T. L. Waldo of Kaiser Engineers Hanford Company.

Table D-3 Summary of Preliminary Project Cost Estimates for Three Tank Configuration (Concurrent Scenario)[a]

Description	Cost $	Contingency		Total $
		%	$	
Engineering	18,260,000	40	7,300,000	25,560,000
Engineering/ HVAC Upgrades	10,000,000	40	4,000,000	14,000,000
Other Structures	6,610,000	40	2,640,000	9,250,000
Tank HVAC Upgrades	15,230,000	40	6,090,000	21,320,000
Utilities	870,000	40	350,000	1,220,000
Special Equip/ Process Systems	41,420,000	40	16,570,000	57,990,000
Demolition (Adjusted to Meet DOE 5100.4)	1,128,000	40	510,000	1,790,000
Total Estimated Cost	93,670,000	40	37,460,000	131,130,000
Other Project Costs				18,370,000
Total Project Cost				149,450,000

[a] Based on modified BNFL Trade Study and Project W-030 cost estimates by T. L. Waldo of Kaiser Engineers Hanford Company.

Table D-4 Summary of Preliminary Operating and Maintenance Costs Based on Maximum Predicted Digestion Times

Description	Incremental Cost[a], $K	Scenario and Cost ($M)		
		Sequential (14 Yr)	Combined (8.7 yr)	Concurrent (5.9 yr)
Operating Persons	80	16.8	17.1	17.1
Maintenance	90	2.5	2.1	2.1
Cog Engineer	120	0.8	0.5	0.4
Laboratory	260	3.6	2.3	1.5
PNL Support	150	2.1	1.3	0.8
RR, OTP, SOP	1200	1.2	1.2	1.2
Prelim Safety Eval	250	0.3	0.3	0.3
Safety Analysis	1100	1.1	1.1	1.1
NEPA	100	0.1	0.1	0.1
Permitting	400	0.4	0.4	0.4
Working Space	50	0.7	0.4	0.3
Misc Supplies	6	1.2	1.0	0.8
$NaNO_2$	1.0/MT	0.6	0.6	0.6
NaOH	0.5/MT	0.3	0.3	0.3
NaOH (3M Option)[b]	0.5/MT	(2.4)	(2.4)	(2.4)
$Fe(NO_3)_3$ (Option)[b]	4.8/MT	(1.3)	(1.3)	(1.3)
LLW Waste	700	2.1	2.1	2.1
Procure New Mixer Pumps	900	5.4	4.5	4.5
Replace Pumps	300	0.9	0.8	0.8
Procure New Supernatant Pumps	230	2.6	2.6	2.6
Replace Pumps	150	1.8	1.8	1.8
Procure Slurry Pumps	230	0.7	0.7	0.7
Replace Pumps	150	0.5	0.5	0.5
Misc Pumps & Equip	870	0.9	0.6	0.4
Total	-	46.6	42.3	40.4

a Based on modified BNFL Trade Study and Project W-211 cost estimates.
b Cost for 3 M NaOH & 0.1 M Fe was not included in total. Some tanks may require less than these concentrations for removal of TRU elements.

Table D-5 Summary of Preliminary Operating and Maintenance Costs Based on Minimum Predicted Digestion Times

Description	Incremental Cost[a], $K	Scenario and Cost ($M)		
		Sequential (4.8 Yr)	Combined (2.8 yr)	Concurrent (2.0 yr)
Operating Persons	80	5.8	5.9	5.8
Maintenance	90	0.9	0.9	0.7
Cog Engineer	120	0.3	0.2	0.1
Laboratory	260	1.2	0.7	0.5
PNL Support	150	0.7	0.4	0.3
RR, OTP, SOP	1200	1.2	1.2	1.2
Prelim Safety Eval	250	0.3	0.3	0.3
Safety Analysis	1100	1.1	1.1	1.1
NEPA	100	0.1	0.1	0.1
Permitting	400	0.4	0.4	0.4
Working Space	50	0.2	0.1	0.1
Misc Supplies	6	0.4	1.0	0.8
$NaNO_2$	1.0/MT	0.6	0.6	0.6
NaOH	0.5/MT	0.3	0.3	0.3
NaOH (3M Option)[b]	0.5/MT	(2.4)	(2.4)	(2.4)
$Fe(NO_3)_3$ (Option)[b]	4.8/MT	(1.3)	(1.3)	(1.3)
LLW Waste	700	2.1	2.1	2.1
Procure New Mixer Pumps	900	3.6	0.0	0.0
Replace Pumps	300	0.6	0.0	0.0
Procure New Supernatant Pumps	230	0.9	0.8	0.5
Replace Pumps	150	0.6	0.5	0.5
Procure Slurry Pumps	230	0.7	0.7	0.7
Replace Pumps	150	0.5	0.5	0.5
Misc Pumps & Equip	870	0.6	0.4	0.1
Total	-	23.1	17.8	16.7

a Based on revised BNFL Trade Study and Project W-211 cost estimates.
b Cost for 3 M NaOH & 0.1 M Fe was not included in total. Some tanks may require less than these concentrations for removal of TRU elements.

This page intentionally left blank.

REFERENCES

Raytheon/British Nuclear Fuels Ltd (BNFL), 1995, *In-Tank Radionuclide Separation*, E/B-SD-W236B-018 Rev 1, Richland, Washington.

Rieck, C. A. 1994, *Conceptual Design Report, Initial Tank Retrieval Systems for Project W-211*, WHC-SD-W211-CDR-002 Rev 0, Westinghouse Hanford Company, Richland, Washington.

Rieck, C. A. 1993, *Conceptual Design Report, Initial Tank Retrieval Systems for Project W-211*, WHC-SD-W211-CDR-001 Rev 0, Westinghouse Hanford Company, Richland, Washington.

This page intentionally left blank.