RMIS Viewprint Document Cover Sheet

This document was retrieved from the Records Management Information System (RMIS). It is intended for information only and may not be the most recent or updated version.

Accession #: **D8443088**

Document #: **HNF-7031**

Title/Desc:
SALTCAKE DISSOLUTION FY2000 STATUS REPORT

Pages: **61**

SEP 27 2000
STA 4 (S)

ENGINEERING DATA TRANSMITTAL

Page 1 of 1

1. EDT 630453

2. To: (Receiving Organization) Distribution	3. From: (Originating Organization) Technology Project Management	4. Related EDT No.:
5. Proj./Prog./Dept./Div.: TFA	6. Design Authority/Design Agent/Cog. Engr.: D. L. Herting	7. Purchase Order No.: N/A
8. Originator Remarks: ~~FY 2000 Saltcake Dissolution Status Report for TTP No. RLO 8 WT 41, Tanks Focus Area (EM 50)~~ Saltcake Dissolution Status Report - LZ 9-27-00 per telecon F. H.		9. Equip./Component No.: N/A
		10. System/Bldg./Facility: N/A
		12. Major Assm. Dwg. No.: N/A
11. Receiver Remarks:	11A. Design Baseline Document? ☐ Yes ☒ No	13. Permit/Permit Application No.: N/A
		14. Required Response Date: September 30, 2000

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	HNF-7031		0	Saltcake Dissolution	N/A	1	1	
				FY 2000 Status Report				

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	(G) Reason	(H) Disp.	(J) Name	(K) Signature	(L) Date	(M) MSIN
		Design Authority									
		Design Agent									
1	1	Cog. Eng. D. L. Herting	Daniel Herting	9/26/00	T6-07						
1	1	Cog. Mgr. W. I. Winters	W. I. Winters	9/26/00	T6-07						
		QA									
		Safety									
		Env.									

18.	19.	20.	21. DOE APPROVAL (if required)
Daniel Herting D. L. Herting 9/26/00 Signature of EDT Originator / Date	J. R. Jewett 9/26/00 Authorized Representative for Receiving Organization / Date	W. I. Winters 9/26/00 Design Authority/ Cognizant Manager / Date	Ctrl No. ____ ☐ Approved ☐ Approved w/comments ☐ Disapproved w/comments

BD-7400-172-2 (10/97)

BD-7400-172-1

DISTRIBUTION SHEET

To	From	
Distribution	D. L. Herting	Page 1 of 3
Project Title/Work Order		Date 09/30/00
Saltcake Dissolution FY 200 Status Report		EDT No. 630453
		ECN No. N/A

Name	MSIN	Text With All Attach.	Text Only	Attach./ Appendix Only	EDT/ECN Only
Baldwin, J.H.	R3-73	X			
Bechtold, D.B.	T6-07	X			
Brooks, K.P.	K6-24	X			
Brouns, T.M.	K9-91	X			
Certa, P.J.	R3-73	X			
Choho, A.F.	R3-47	X			
Conrads, T.J.	R3-73	X			
Crawford, T.W.	R3-73	X			
Foreman, S.K.	K9-46	X			
Gibbons, P.W.	R3-74	X			
Herting, D.L. (10)	T6-07	X			
Honeyman, J.O.	H6-62	X			
Jewett, J.R.	R3-73	X			
Kirkbride, R.A.	R3-73	X			
Lockrem, L.L.	T6-07	X			
Lumetta, G.J.	P7-25	X			
MacLean, G.T.	G3-10	X			
Person, J.C.	T6-07	X			
Place, D.E.	R3-73	X			
Reynolds, D.A.	R2-11	X			
Tingey, J.M.	P7-25	X			
Williams, B.J. (8)	R2-11	X			
Willis, W.L.	R3-73	X			
Cruz, E.J. (DOE-RL)	H6-60	X			
Pietrok, T. P. (DOE-RL)	K8-50	X			
Richins, C.R. (DOE-RL)	K8-50	X			
Offsite					
Kurt Gerdes, DOE Office of Science		X			
and Technology, 19901 Germantown Rd,					
1154 Cloverleaf Bldg., Germantown, MD					
20874-1290					

A-6000-135 (10/97)

DISTRIBUTION SHEET

To	From	Page 2 of 3
Distribution	D. L. Herting	Date 09/30/00
Project Title/Work Order		EDT No. 630453
Saltcake Dissolution FY 2000 Status Report		ECN No. N/A

Name	MSIN	Text With All Attach.	Text Only	Attach./ Appendix Only	EDT/ECN Only
Dr. Jim Henshaw, AEA Technology		X			
220 Harwell, Didcot, Oxfordshire OX11 ORA					
United Kingdom					
R.D. Hunt,Oak Ridge National Laboratory		X			
P.O. Box 2008, Oak Ridge, TN 37831-6223					
Dr. Jeff Lindner, Mississippi State Univ.		X			
MS-9550, Mississippi State, MS 39726					
Phil McGinnis,Oak Ridge National Laboratory		X			
P.O. Box 2008 Oak Ridge, TN 37821-6273					
T.D. Welch, Oak Ridge National Laboratory,		X			
P.O. Box 2008, Oak Ridge, TN 37831-6223					
Reuben Lopez, Hemispherical Center for		X			
Enviromental Technology					
Florida International University					
10555 Flagler Street, Room 2455					
Miami, FL 33174					
Wally Schulz, W2S Company, Inc.,		X			
5314 Arbutos Court, NE					
Albuquerque, NM 87111					
Major Thompson		X			
Westinghouse Savannah River Company					
Bldg., C-140, Room 773-A					
Savannah River Technology Center					
Aiken, SC 29808					
Sam Fink, Westinghouse Savannah River Co.		X			
Bldg., 773-A, Room B-112					
Aiken, SC 29808					
David Hobbs,Westinghouse Savannah River Co.		X			
Bldg., 773-A, Room B-117					
Aiken, SC 29808					

DISTRIBUTION SHEET

To	From	
Distribution	D. L. Herting	Page 3 of 3
Project Title/Work Order		Date 09/30/00
Saltcake Dissolution FY 2000 Status Report		EDT No. 630453
		ECN No. NA

Name	MSIN	Text With All Attach.	Text Only	Attach./ Appendix Only	EDT/ECN Only
James Rindfleisch,Idaho National Eng		X			
and Environmental Laboratory, MS-5218					
P.O. Box 1625,Idaho Falls, ID 83415					
Terry Todd, Idaho National Engineering		X			
and Environmental Laboratory, MS 5218					
850 Energy Drive					
Idaho Falls, ID 83401					
Jack Collins, Oak Ridge National Laboratory		X			
P.O. Box 2008 Oak Ridge, TN 37821-6273					
George Vandergriff, Argonne National		X			
Laboratory, 9700 South Cass Avenue,					
Building 205, Argonne, IL 60439					

A-6000-135 (10/97)

HNF-7031
Revision 0
EDT-630453

Saltcake Dissolution FY 2000 Status Report

D. L. Herting
Fluor Hanford

Date Published
September 2000

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

Project Hanford Management Contractor for the
U.S. Department of Energy under Contract DE-AC06-96RL13200

Fluor Hanford
P.O. Box 1000
Richland, Washington

Release Approval 9/27/00
Date

SEP 27 2000
DATE:
STA: 4
HANFORD RELEASE
ID: 5

Approved for public release; further dissemination unlimited

HNF-7031
Revision 0

Saltcake Dissolution FY 2000 Status Report

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

Project Hanford Management Contractor for the
U.S. Department of Energy under Contract DE-AC06-96RL13200

Fluor Hanford
P.O. Box 1000
Richland, Washington

Approved for public release; further dissemination unlimited

LEGAL DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or any third party's use or the results of such use of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. 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. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced from the best available copy. Available in paper copy and microfiche.

Available electronically at http://www.doe.gov/bridge. Available for a processing fee to the U.S. Department of Energy and its contractors, in paper, from:
U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831-0062
phone: 865-576-8401
fax: 865-576-5728
email: reports@adonis.osti.gov(423) 576-8401

Available for sale to the public, in paper, from:
U.S. Department of Commerce
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
phone: 800-553-6847
fax: 703-605-6900
email: orders@ ntis.fedworld.gov
online ordering: http://www.ntis.gov/ordering.htm

Printed in the United States of America

CONTENTS

1.0 INTRODUCTION AND EXECUTIVE SUMMARY 1
1.1 RESULTS SUMMARY 1
1.1.1 Dissolution Tests, Tank TX-113 2
1.1.2 Radionuclide Distribution Tests 2
1.1.3 Feed Stability Tests 3
1.2 COMPOSITION OF TANK WASTES 4
1.2.1 Tank TX-113 4
1.2.2 Tanks BY-102, BY-106, A-101, and S-102 4

2.0 DESCRIPTION OF LABORATORY STUDIES 5
2.1 PREPARATION OF COMPOSITE SAMPLE 5
2.2 SEQUENTIAL DISSOLUTION TESTS 6
2.3 SERIES DISSOLUTION TESTS 7
2.4 RADIONUCLIDE DISTRIBUTION TESTS 7
2.5 FEED STABILITY TESTS 8

3.0 RESULTS – RAW DATA 10
3.1 TANK TX-113 10
3.1.1 TX-113 Sequential Dissolution Test 10
3.1.2 TX-113 Series Dissolution Test, Ambient Temperature 10
3.1.3 TX-113 Series Dissolution Test, 50 °C 10
3.2 RADIONUCLIDE DISTRIBUTION TESTS 17
3.3 FEED STABILITY TESTS 21

4.0 DILUTION RESULTS, VOLUME AND WEIGHT MEASUREMENTS 23
4.1 TANK TX-113 SERIES DISSOLUTION TESTS 23
4.2 RADIONUCLIDE DISTRIBUTION TEST 24

5.0 CHEMICAL COMPOSITION TRENDS 26
5.1 SERIES DISSOLUTION TESTS, TANK TX-113 26
5.1.1 Nitrite, Chloride, and Oxalate 26
5.1.2 Nitrate 28
5.1.3 Fluoride, Phosphate, Sulfate, And Carbonate 28
5.2 RADIONUCLIDE DISTRIBUTION STUDIES 30
5.2.1 Nitrite, Chloride, Potassium 34
5.2.2 Nitrate 34
5.2.3 Carbonate, Fluoride, Phosphate, Sulfate, Oxalate 36
5.2.4 Partially Soluble Metals (Al, Cr, Si) 36
5.2.5 Insoluble Metals (Ca, Fe) 37
5.2.6 Radionuclides 37
5.3 COMPARISON OF RADIONUCLIDE ANALYTICAL METHODS 37

6.0 EFFECT OF IONIC STRENGTH ON CRYSTAL HYDRATES 38
6.1 SODIUM SULFATE LITERATURE DATA 38

7.0 PHASE DISTRIBUTION ANALYSIS, TANK TX-113 42
7.1 PHYSICAL SAMPLE DATA 42
7.2 COMPOSITION BY FRACTIONS 43
7.3 SOLID/LIQUID PHASE DISTRIBUTION 45

8.0 COMPARISONS 47
8.1 COMPUTER MODELING 47
8.2 COMPARISONS WITH TCR DATA 47
8.3 COMPARISONS WITH EARLIER ANALYSES (BY-106, S-102, A-101) 48

9.0 ACKNOWLEDGEMENTS 49

10.0 REFERENCES 50

TABLES

2-1 Segment Samples Used to Create TX-113 Core Composite Sample 6

3-1 Raw Data, Tank TX-113 Sequential Dissolution Test 11
3-2 Analytical Results, Tank TX-113 Sequential Dissolution Test 12
3-3 Raw Data, Tank TX-113 Series Dissolution Test, Ambient Temperature 13
3-4 Analytical Results, Tank TX-113 Series Dissolution Test, Ambient Temp .. 14
3-5 Raw Data, Tank TX-113 Series Dissolution Test, 50 °C 15
3-6 Analytical Results, Tank TX-113 Series Dissolution Test, 50 °C 16
3-7 Raw Data, Radionuclide Distribution Test 17
3-8 Analytical Results, Tank BY-106 Radionuclide Distribution Test 18
3-9 Analytical Results, Tank S-102 Radionuclide Distribution Test 19
3-10 Analytical Results, Tank A-101 Radionuclide Distribution Test 20
3-11 Raw Data, Feed Stability Test 21
3-12 Solid Phases Identified by PLM and SEM/EDS 22

4-1 Percent Centrifuged Solids as a Function of Dilution, Tank TX-113 23
4-2 Percent Centrifuged Solids, Stepwise Dilution 25

5-1 Overall Composition of Composite Saltcake Samples 27
5-2 Distribution by Fraction in Tank BY-106 31
5-3 Distribution by Fraction in Tank S-102 32
5-4 Distribution by Fraction in Tank A-101 33

6-1 Concentrations of Salts at Hydrate Transition Points 40

7-1 Summary of Measurements from TX-113 Sequential Dissolution Test 42
7-2 Tank TX-113 Analysis by Fractions 44
7-3 Tank TX-113 Solid/Liquid Phase Distribution at 100% Dilution 46

8-1 Tank TX-113 Comparison with TCR Data 48

FIGURES

4-1 Tank TX-113 Saltcake Dissolution 24
4-2 Stepwise Dissolution of Saltcakes 25

5-1 Concentrations in Supernatant Liquid 29
5-2 Tank BY-106 Dissolution Profile 35
5-3 Tank S-102 Dissolution Profile 35
5-4 Tank A-101 Dissolution Profile 36

6-1 Sodium Sulfate Transition Temperatures 39
6-2 Na2SO4 Hydrate Transitions in Ternary Systems 41
6-3 Na2SO4 Hydrate Transition vs. Water Activity 41

ACRONYMS AND ABBREVIATIONS

A-101	single-shell tank 241-A-101
AEA	alpha energy analysis
B-106	single-shell tank 241-B-106
BY-102	single-shell tank 241-BY-102
BY-106	single-shell tank 241-BY-106
CSol	centrifuged solids
EDS	energy-dispersive x-ray spectrometer
Extr	extraction (separation method for radionuclide analysis)
ESP	Environmental Simulation Program
FY	fiscal year
GEA	gamma energy analysis
IC	ion chromatography
ICP	inductively coupled plasma spectroscopy
ICP/MS	inductively coupled plasma/mass spectroscopy
PLM	polarized light microscope (or microscopy)
RPP	River Protection Project
S-102	single-shell tank 241-S-102
SEM/EDS	scanning electron microscopy with energy dispersive x-ray spectroscopy
TCR	Tank Characterization Report
TGA	thermogravimetric analysis
TIC	total inorganic carbon
TOC	total organic carbon
TX-113	single-shell tank 241-TX-113
Vol	volume
Wt	weight

1.0 INTRODUCTION AND EXECUTIVE SUMMARY

Laboratory tests were completed on the dissolution characteristics of Hanford saltcake waste from single-shell waste tanks 241-TX-113, 241-BY-102, 241-BY-106, 241-A-101, and 241-S-102 (henceforth referred to as TX-113, BY-102, BY-106, A-101, and S-102, respectively). This work was funded by the Tanks Focus Area (EM-50) under Technical Task Plan Number RL0-8-WT-41, "PHMC Pretreatment – Saltcake Dissolution".

The tests performed on saltcake from tank TX-113 were similar in scope to those completed in previous years on waste from tanks BY-102, BY-106, B-106, A-101, and S-102 (Herting 1998, 1999). In addition to the "standard" dissolution tests, new types of tests were performed this year related to feed stability and radionuclide distribution.

The River Protection Project (RPP) is tasked with retrieving waste from double-shell and single-shell tanks to provide feed for vitrification. The RPP organization needs chemical and physical data to evaluate technologies for retrieving the waste. Little significant laboratory testing has been done to evaluate in-tank dissolution parameters for the various types of saltcake wastes that exist in single-shell tanks.

A computer modeling program known as the Environmental Simulation Program (ESP), produced by OLI Systems, Inc. of Morris Plains, New Jersey, is being used by the RPP organization to predict solubilities during dilution and retrieval of all tank waste types. Data from this task are provided to ESP users to support evaluation, refinement, and validation of the ESP model.

1.1 RESULTS SUMMARY

Sequential dissolution tests (see Section 2.2 for detailed description) were performed on TX-113 saltcake to determine the overall composition of the composite sample. **Series dissolution** tests (Section 2.3) were done on TX-113 saltcake to evaluate solubilities of individual components as a function of the amount of diluent added. **Stepwise dissolution** tests (Section 2.4) were done on saltcake from tanks BY-106, S-102, and A-101 to evaluate the solid/liquid phase distribution of radionuclides during tank waste retrieval operations. **Feed stability** tests were done on saltcake from tanks BY-102, BY-106, S-102, A-101, and TX-113 to evaluate the potential for re-precipitation of solids in the receiver tank during tank waste retrieval.

Weight percent dilution is defined in this report as 100 times the weight of diluent (water or inhibited water for these tests) divided by the weight of undiluted sample. A 50% dilution, for example, would be 50 g of H_2O added to 100 g of undiluted sample.

1.1.1 Dissolution Tests, Tank TX-113

Some of the dissolution data for tank TX-113 are plotted in Figure 4-1 as "Percent Undissolved" vs. weight percent dilution at two temperatures. The Percent Undissolved is defined as 100 times the weight of centrifuged solids after dissolution divided by the initial sample weight before diluent was added. This measurement provides a gross view of the extent of saltcake dissolution at various conditions, and provides a rough measure of the fraction of waste that could be retrieved from the tank by pumping the supernatant liquid. The finding that the Percent Undissolved is greater than 100% at 25 °C and 50% dilution reflects the fact that the weight of centrifuged solids with interstitial liquid under those conditions is greater than the original sample weight before dilution. The undiluted sample had no visible interstitial liquid.

The data in Figure 4-1 show that most of the major salts were dissolved at 150% dilution, and only slightly more solids dissolved at 300% dilution. Dissolution was more extensive at 50 °C than at 25 °C, but not dramatically so.

Data are presented in Section 5 that explain the gross dissolution behavior in terms of solubilities of individual components in the waste. Evidence is provided there of the importance of double salts (sodium nitrate sulfate and others) in controlling the equilibrium concentrations of sulfate, phosphate, fluoride, and carbonate in the dissolved waste solutions. Identification of solid phases in equilibrium with the ions in solution is important for computer modeling of the thermodynamics of the system.

The percentage of sodium that could be retrieved at reasonable dilution levels by pumping liquid from the tank (i.e., the percentage of total sodium that is in the supernatant liquid) is estimated at 90% for tank TX-113 saltcake.

Computer simulations of the saltcake **series dissolution** tests on tank TX-113 were conducted by investigators at Mississippi State University, using ESP. Data from the **sequential dissolution** tests were used as input to the simulation. (See Sections 2.2 and 2.3 for definitions of sequential and series dissolution tests.) For most analytes, major trends in the experimental data were seen in the simulation results. In general, ESP did a good job of predicting the amount of water required to dissolve each of the constituents, and did an excellent job of predicting the concentration of each constituent after it was dissolved. Predictions were less accurate for the concentrations of anions in solution when a solid phase associated with that anion was still present.

1.1.2 Radionuclide Distribution Tests

Stepwise dissolution tests (see Section 2.4) were performed on saltcake composite samples from tanks BY-106, S-102, and A-101 to determine the likely solid/liquid phase distribution of radionuclides during retrieval operations. Radioisotopes of plutonium, americium, strontium, cobalt, and europium remained almost exclusively in

the solid phase throughout the saltcake dissolution. As expected, the ^{137}Cs was found mainly in the liquid phase (2-5% of the total ^{137}Cs remained in the undissolved solids). For ^{99}Tc, the results were different for each tank, ranging from 5% to 48% of the ^{99}Tc remaining in the undissolved solids.

1.1.3 Feed Stability Tests

In-tank dissolution and subsequent retrieval of saltcake is envisioned, in one scenario, to occur by sprinkling inhibited water (0.01 M NaOH / 0.01 M $NaNO_2$) over the saltcake, allowing the water to course through the salt, and retrieving the salt-saturated solution from the tank bottom. The composition of the retrieved solution will vary with time in such a scenario. Components like sodium sulfate and sodium phosphate will not dissolve to any appreciable extent until the sodium nitrate and other more soluble components are removed from the system, because the solubilities of the former are very ionic-strength dependent.

The question arises, then, what would happen if the retrieved solution is pumped into a staging tank where the liquid removed from the source tank late in the retrieval process (which is high in sulfate, phosphate, etc.) is allowed to mix with the early-retrieved solution (which is high in nitrate and has a high ionic strength)? The Feed Stability Tests were designed to evaluate whether the late-retrieved fractions would re-precipitate when mixed with the early-retrieved fractions.

The tests were carried out using composite saltcake samples from tanks BY-102, BY-106, A-101, S-102 and TX-113. The **Stepwise Dissolution** method was used, with a total of ten contacts for each saltcake. All ten of the liquid fractions from each tank were combined in a single jar representing the receiver tank. That jar was monitored for at least 24 hours after each addition to observe whether solids precipitated.

The results of the test found solids precipitating in four out of five of the receiver jars. No solids formed in the S-102 receiver jar. In tanks A-101 and BY-106, the only solids that formed were sodium oxalate, $Na_2C_2O_4$, after the third and fourth fractions were added. Tank TX-113 formed solids after the second, third, and fourth contacts identified as Na_2SO_4, Na_3FSO_4, and $Na_7F(PO_4)_2 \cdot 19H_2O$. Tank BY-102 formed solids after the second, third, fifth, and sixth contacts, and included all of the phases just listed.

The stepwise dissolution and re-combination laboratory test was modeled with ESP by the researchers at Mississippi State University. The ESP correctly predicted virtually all of the solids that formed, but it also predicted the appearance of gibbsite, $Al(OH)_3$, which was not observed experimentally. The kinetics of precipitation of gibbsite are notoriously slow, and might have formed in the laboratory test if enough time had been allowed (weeks instead of 24 hours).

Tank farm operators need to be aware of the potential for solids formation in receiver tanks during saltcake retrieval operations.

1.2 COMPOSITION OF TANK WASTES

1.2.1 Tank TX-113

Core samples were taken from Tank TX-113 in 1998 (core 253) and 1999 (core 258). Core 258 contained nearly pure sodium nitrate. The core composite sample contained 71.5% (w/w) nitrate by analysis, compared to 72.9% for pure $NaNO_3$. Core 253 contained far less nitrate (25.1%) and much more carbonate and sulfate. Both cores contained relatively dry saltcake, with no visible liquid phase.

The composite sample used for the tests reported here was made from segment samples from core 253 only. Archived samples from segments 4, 5, 6, 10, and the archived core composite sample were combined to make the composite for this study.

The chemical compositions of the original core 253 composite sample and the composite sample created for this study are shown in Table 8-1. The major components of the sample used for this study include (approximate weight percent): Na^+ (29%), NO_3^- (18%), CO_3^{2-} (14%), SO_4^{2-} (16%), PO_4^{3-} (4%), F^- (0.3%), H_2O (12.3%).

1.2.2 Tanks BY-102, BY-106, A-101, and S-102

The compositions of these four tanks were determined in previous years (Herting 1998, 1999), and the same composite samples were used for this year's tests. The compositions are repeated here in Table 5-1.

2.0 DESCRIPTION OF LABORATORY STUDIES

Composite samples of tank waste were prepared in a hotcell. Smaller samples were handled in fume hoods. The procedures, data, and observations are recorded in controlled laboratory notebook HNF-N-70-2. The procedures are described in this section, and the raw data are shown in the following section (3.0).

All dissolution tests were done on composite samples made by combining representative core segment samples from each tank. Two types of dissolution tests were done on saltcake from tank TX-113. The **sequential dissolution tests** were done to establish an overall saltcake waste composition for each tank, as well as to define basic dissolution behavior. The **series dissolution tests** were done to establish dissolution characteristics of individual salts as a function of the amount of diluent added. These tests are described in detail in sections 2.2 and 2.3.

Radionuclide distribution tests were done on saltcake from tanks A-101, BY-106, and S-102 using the **stepwise dissolution** test method. These tests are described in detail in section 2.4.

Feed stability tests were done on saltcake from tanks A-101, BY-102, BY-106, S-102, and TX-113. These tests were meant to evaluate whether solids might form during tank waste retrieval when late-retrieved liquid was mixed with early-retrieved liquid from the same tank. These tests are described in section 2.5.

A literature study and a "cold" (nonradioactive simulant) laboratory study were done to evaluate the **effect of ionic strength on crystal hydrate formation**. These tests are described in section 2.6.

2.1 PREPARATION OF COMPOSITE SAMPLE

The TX-113 composite sample was made by combining archived fractions of individual core segment samples into a single composite jar. The entire contents of each archive jar were transferred to the composite jar. The waste in the completed composite jar was mixed thoroughly before transferring a subsample from the hotcell to the fume hood. Weights of individual core segment samples used for the composite sample are shown in Table 2-1. One aliquot of the composite sample was analyzed for percent water by oven-drying at 120 °C and by thermogravimetric analysis (TGA).

Comparisons between analytical data for the composite sample and the tank core composite sample as reported in the Tank Characterization Report (TCR) are discussed in Section 8.

Table 2-1. Segment Samples Used to Create TX-113 Core Composite Sample

Core	Segment[a]	Jar #	Weight, g
253	Comp[b]	14787	46.4
253	4	14794	111.0
253	5U	14733	108.9
253	5L	14917	45.1
253	6	14919	17.1
	Composite	Total Wt =	328.5

[a] Segment 1 is at top of waste; U = upper half of segment; L = lower half of segment;
[b] Comp = archived core composite sample

For the remaining tanks, the composite samples were the same as those prepared in prior years for this project (Herting 1998, 1999).

2.2 SEQUENTIAL DISSOLUTION TESTS

The following test was performed on portions of the composite sample from tank TX-113. Results for tanks BY-102, BY-106, B-106, A-101, and S-102 were reported previously (Herting 1998, 1999).

Approximately 30 g of tank composite sample were transferred into each of two 50 mL centrifuge cones, and an equal weight of water was added. The cones were mixed with a vortex mixer, then placed on a rocker and tumbled end-over-end for at least 24 hours at ambient temperature (approximately 23 °C). The cones were then centrifuged for one hour at roughly 400 G.

The supernatant liquids from both cones were combined into a sample bottle. The liquid was analyzed by inductively coupled plasma spectroscopy (ICP), ion chromatography (IC), total inorganic carbon (TIC), total organic carbon (TOC), free hydroxide (OH^-), density (SpG), percent water by oven drying at 120 °C, and radionuclides by gamma energy analysis (GEA).

The weight and volume of centrifuged solids in each cone were recorded. Then 30 g of water were added to each cone. The cones were mixed again with a vortex mixer, then tumbled end-over-end for at least 24 hours at ambient temperature. The cones were centrifuged again, and the supernatant liquids combined as before in a new sample bottle. The second wash solution was analyzed for the same components as the first wash solution.

The volume and weight of undissolved centrifuged solids were recorded. Then the solids were transferred from the cones into a sample vial, combining the solids from both cones into a single sample vial. The solids were analyzed for TIC, TOC, and $\%H_2O$ by thermogravimetric analysis (TGA). The solids were also subjected to acid digestion, and the resulting solution was analyzed for metals by ICP.

The analytical results from the sequential dissolution tests were used to determine the overall composition of the composite sample. This overall composition was used as input to the ESP modeling done at Mississippi State University.

2.3 SERIES DISSOLUTION TESTS

The following tests were performed on composite samples from tank TX-113. Results for tanks BY-102, BY-106, B-106, A-101 and S-102 were reported previously (Herting 1998, 1999).

Four to six grams of composite sample were placed into each of six 15 mL centrifuge cones. An amount of water was added to each cone representing 50% to 300% by weight of the composite sample in the cone. Each cone was mixed with a vortex mixer, then tumbled end-over-end for at least 24 hours at ambient temperature. The cones were centrifuged for 30 minutes at roughly 400 G. The total volume and centrifuged solids volume in each cone were recorded. The liquid from each cone was decanted into a sample vial to be analyzed for density, TIC/TOC, IC, and ICP. The cones were re-weighed to determine the weight of undissolved centrifuged solids.

The series dissolution test just described was repeated, except that the 24-hour tumbling was done in an oven maintained at 50 °C, and the centrifuge was heated to approximately the same temperature. The decanted supernatant liquid samples were held at ambient temperature for 24 hours to watch for signs of precipitation that might be caused by cooling. If solids formed, the samples were diluted 1:1 by weight with water to re-dissolve the crystals before the samples were analyzed. This dilution was required for all samples except the 300% dilution sample.

2.4 RADIONUCLIDE DISTRIBUTION TESTS

Radionuclide distribution tests were done on saltcake composite samples from tanks BY-106, S-102, and A-101. These tests were done by the **Stepwise Dissolution** method used in FY99 for BY-102 saltcake (Herting 1999), in which a single saltcake sample is contacted multiple times with inhibited water (0.01 M NaOH/0.01 M $NaNO_2$). The process is similar to the Sequential Dissolution tests, but with more contacts and smaller contact volumes.

For each tank, a 40-gram aliquot of saltcake composite sample was placed into a tare-weighed 50-mL graduated centrifuge cone. The cone plus saltcake was weighed,

then 20 g of inhibited water was added, and the cone was re-weighed. Then the cone was vortex-mixed or agitated manually at least three times over a one-hour period, after which the cone was centrifuged for 30 minutes. Total volume and centrifuged solids volume were recorded, and the liquid was decanted into a sample vial for analysis. The cone with residual solids was weighed to determine the weight of centrifuged solids and (by difference) the weight of solution decanted. Then a fresh 20 g portion of inhibited water was added and the cycle of mixing/centrifuging/decanting was repeated until the weight of centrifuged solids was less than 4 g. For all three tanks, that endpoint was reached after three inhibited water contacts.

The liquid samples were analyzed by ICP, IC, TIC/TOC, OH^-, $\%H_2O$ by oven drying at 120°C, density, and radionuclide concentrations. Radionuclides were analyzed by GEA (^{60}Co, ^{125}Sb, ^{137}Cs, ^{154}Eu, ^{155}Eu, and ^{241}Am), extraction ($^{89/90}Sr$, ^{99}Tc, ^{241}Am), and ICP/Mass Spectroscopy (^{117}Sn, ^{126}Sn, ^{133}Cs, ^{135}Cs, ^{137}Cs, ^{238}Pu, and $^{239/240}Pu$). Residual solids were analyzed for TIC/TOC and $\%H_2O$ by TGA. Fusion digest preparations of the residual solids were analyzed for metals by ICP and radionuclides by the same methods listed for the liquid samples. No IC analyses were performed on residual solids because any reasonable digestion method (acid or fusion) following what was essentially an extensive water digest in the stepwise dissolution would have destroyed or obscured the anion analytes of interest.

2.5 FEED STABILITY TESTS

The objective of this test series was to determine if salt precipitation occurs by mixing clear tank waste solutions from the beginning of the tank waste retrieval with solutions from later fractions retrieved from the same tank. Composite samples from five tanks were used. Dissolution was performed using the **Stepwise dissolution** method.

For each tank, a 30-gram aliquot of saltcake composite sample was placed into a tared 50-mL graduated centrifuge cone. The cone plus saltcake was weighed, then 15 g of inhibited water was added, and the cone was re-weighed. Then the cone was vortex-mixed or agitated manually at least three times over a one-hour period, after which the cone was centrifuged for 30 minutes. Total volume and centrifuged solids volume were recorded, and the liquid was decanted into a 250 mL glass jar representing the receiver tank. The cone with residual solids was weighed to determine the weight of centrifuged solids and (by difference) the weight of solution decanted. The liquid in the receiver jar was monitored for at least 24 hours for signs of precipitation.

After the monitoring period, a fresh 15 g portion of inhibited water was added to each cone, and the cycle of mixing/centrifuging/decanting was repeated. The liquid from this second contact was decanted into the same jar that contained the liquid decanted from the first contact. The liquid in the jar was again monitored for at least 24 hours before going on to the third contact, and so on, until a total of ten contacts had been made for each tank. The amount of inhibited water was increased to 30 g each of the last three contacts.

If solids did form in the 250 mL jar, the solids were collected for analysis by decanting the bulk of the clear liquid into a clean jar, leaving a small amount of slurry behind in the original jar. The new jar became the receiver for subsequent contacts, and the slurry in the original jar was transferred to a sample vial for analysis by polarized light microscopy (PLM) and scanning electron microscopy with energy dispersive x-ray spectroscopy (SEM/EDS).

3.0 RESULTS – RAW DATA

"Raw data" include values of net weight, volume, and chemical and physical analyses of the samples. Visual observations of the test materials are also presented in this section. The raw data provide a reference record of the tests. However, sample-to-sample comparisons of raw data generally should not be made because of variations in initial sample weights and volumes. Comparisons based on normalized data, accounting for initial volume and weight differences, are presented in later sections of the report.

3.1 TANK TX-113

The aliquot of the composite sample taken for %H_2O analysis was labeled TX3Comp2, and was assigned Labcore number S99R000202. Analytical results were 12.3% H_2O by TGA and 12.5% H_2O by oven-drying.

3.1.1 TX-113 Sequential Dissolution Test

Two 50 mL centrifuge cones were labeled SEQA and SEQB. The procedure was described in Section 2.2. Weights, volumes, and analytical sample identification numbers of the various fractions are shown in Table 3-1. Analytical results are shown in Table 3-2.

3.1.2 TX-113 Series Dissolution Test, Ambient Temperature

Six 15 mL centrifuge cones were labeled A through F. The procedure was described in Section 2.3. Weights, volumes, and analytical sample identification numbers of the various fractions are shown in Table 3-3. Sample analytical results are shown in Table 3-4.

3.1.3 TX-113 Series Dissolution Test, 50 °C

Six 15 mL centrifuge cones were labeled G through L. The procedure was described in Section 2.3. Weights, volumes, and analytical sample identification numbers of the various fractions are shown in Table 3-5. The supernatant liquid from samples G-K (50-250% dilution) were diluted to dissolve crystals that formed when the samples cooled from 50 °C to ambient temperature. Sample analytical results for the liquid samples, including the dilution-corrected results for samples G-K, are shown in Table 3-6.

Table 3-1. Raw Data, Tank TX-113 Sequential Dissolution Test.
(weights in grams, volumes in mL)

	SEQA	SEQB
Sample Wt, g	30.371	29.984
Wt H_2O Added (1st wash)	29.931	30.180
Total Vol, mL	41.5	42.0
1st Water Wash Sample ID[a]	TX3SEQAB1 / S99R000203	
CSol[b] Vol	10.0	11.0
CSol Wt	16.942	18.179
Wt H_2O Added (2nd wash)	30.249	30.061
Total Vol	39.5	40.0
2nd Water Wash Sample ID	TX3SEQAB2 / S99R000204	
CSol Vol[c]	4.2	3.8
CSol Wt	5.393	5.161
CSol Sample ID	TX3SEQABS / S99R000205 and 206	

[a] decanted supernatant liquid; customer ID number / Labcore ID number
[b] CSol = centrifuged solids
[c] volumes below 5 mL are estimates only.

Table 3-2 Analytical Results, Tank TX-113 Sequential Dissolution Test.

Analyte	1st Water Wash TX3SEQAB1 S99R000203 (μg/mL)	2nd Water Wash TX3SEQAB2 S99R000204 (μg/mL)	CSol TX3SEQABS S99R000205-6 (μg/g)
Al	913	134	10900
Ca	< 40	< 40	1280
Cr	293	51	186
Fe	< 20	< 20	1380
K	306	< 200	< 300
Mn	< 4	< 4	18
Na	172000	74100	145000
Ni	< 8	< 8	135
P	1410	2470	41600
Pb	< 40	< 40	< 60
S	30000	17400	7340
Si	194	87	639
U	< 200	< 200	7930
F^-	307	2020	n.a.
Cl	498	60	n.a.
NO_2^-	2060	322	n.a.
NO_3^-	152000	21000	n.a.
PO_4^{3-}	4470	7510	n.a.
SO_4^{2-}	91600	55100	n.a.
$C_2O_4^{2-}$	753	354	n.a.
TIC	17900	8610	4320
TOC	268	414	61
OH	2760	< 1250	n.a.
^{137}Cs (μCi/mL)	5.2	0.7	n.a.
Density (g/mL)	1.431	1.169	n.a.
$\%H_2O$	61.0	82.4	66.5
Mass Balance[b]	97.2	99.8	102.9
Charge Balance[b]	0.96	0.98	--

[a] na = not analyzed
[b] see Section 7.2

Table 3-3. Raw Data, Tank TX-113 Series Dissolution Test, Ambient Temperature
(weights in grams, volumes in mL)

Wt% Dilution:	50	100	150	200	249	299
Cone ID:	A	B	C	D	E	F
Sample Wt	9.970	8.209	7.585	5.687	5.021	4.071
Wt H_2O Added	5.032	8.235	11.372	11.392	12.523	12.186
Total Vol	9.0	11.4	14.1	13.5	14.5	13.5
CSol Vol	6.2	2.1	1.2	0.9	0.5	0.4
CSol Wt	11.075	4.188	2.135	1.376	0.946	0.726
Supernate ID	TX3AMA	TX3AMB	TX3AMC	TX3AMD	TX3AME	TX3AMF
S99R000...	207	208	209	210	211	212

Table 3-4. Analytical Results, Tank TX-113 Series Dissolution Test, Ambient Temp. (μg/mL except as noted)

Wt% Dilution:	50	100	150	200	249	299
Supernate ID	TX3AMA	TX3AMB	TX3AMC	TX3AMD	TX3AME	TX3AMF
S99R000...	207	208	209	210	211	212
Density (g/mL)	1.423	1.381	1.325	1.262	1.219	1.177
Al	1800	750	610	483	369	321
Ca	< 60	< 60	< 60	< 60	< 60	< 20
Cr	571	245	208	159	127	108
Fe	< 30	< 30	< 30	< 30	< 30	< 10
K	597	449	417	< 300	< 300	109
Mn	< 6	< 6	< 6	< 6	< 6	< 2
Na	186000	156000	148000	117000	95900	79100
Ni	< 12	< 12	< 12	< 12	< 12	< 4
P	886	1130	1680	1530	1910	2410
Pb	< 60	< 60	< 60	< 60	< 60	< 20
S	12100	25800	28900	22500	18300	15600
Si	455	232	189	156	138	121
U	< 300	< 300	< 300	< 300	< 300	< 100
F^-	230	290	460	1060	1150	1200
Cl^-	1010	370	330	280	310	200
NO_2^-	3810	1720	1510	1330	1090	1070
NO_3^-	294000	132000	105000	84500	66900	55200
PO_4^{3-}	2070	2880	4200	4830	4470	5750
SO_4^{2}	33900	79600	86400	69700	57800	47400
$C_2O_4^{2}$	< 540	< 540	800	960	< 540	910
TIC	12900	20800	18500	14100	12200	9170
TOC	71	316	322	270	232	328
OH (calc)[a]	6110	2760	2420	2130	1750	1720
Charge Balance	0.99	0.89	0.93	0.91	0.89	0.90

Table 3-5. Raw Data, Tank TX-113 Series Dissolution Test, 50 °C
(weights in grams, volumes in mL)

Wt% Dilution:	50	100	149	200	250	299
Cone ID:	G	H	I	J	K	L
Sample Wt	10.118	8.016	6.552	5.051	5.010	4.318
Wt H2O Added	5.030	8.019	9.776	10.099	12.510	12.895
Total Vol	8.0	10.9	7.8	11.8	14.0	9.4
CSol Vol	4.4	1.5	0.5	0.3	0.1	0.1
CSol Wt	8.490	3.582	0.978	0.620	0.304	0.296
Supernate ID	TX350G	TX350H	TX350I	TX350J	TX350K	TX350L
S99R000...	213	214	215	216	217	218
Sup Sample Wt	5.125	12.414	10.030	14.485	17.164	
Wt H_2O Added	5.175	24.997	10.065	27.969	8.532	
Density Diluted	1.182	1.092	1.146	1.084	1.147	
Vol Diluted	8.71	34.26	17.53	39.16	22.40	
Vol Undiluted	3.54	9.26	7.47	11.20	13.87	
Density Undil	1.45	1.34	1.34	1.29	1.24	
Diln Factor (v/v)	2.46	3.70	2.35	3.50	1.62	

Table 3-6. Analytical Results, Tank TX-113 Series Dissolution Test, 50 °C
(μg/mL except as noted)

Wt% Dilution	50	100	149	200	250	299
Supernate ID	TX350G	TX350H	TX350I	TX350J	TX350K	TX350L
S99R000...	213[a]	214[a]	215[a]	216[a]	217[a]	218
Density (g/mL)	1.45	1.34	1.34	1.29	1.24	1.192
Al	1435	832	599	493	384	343
Ca	< 50	< 75	< 50	< 70	< 32	< 20
Cr	460	266	200	140	126	112
Fe	< 25	< 40	< 25	< 35	< 16	< 10
K	492	492	261	< 350	249	128
Mn	< 5	< 7	< 5	< 7	< 3	< 2
Na	194000	164000	149000	112000	101000	84200
Ni	< 10	< 15	< 10	< 15	< 6	< 4
P	5150	7990	6925	4970	4600	2730
Pb	< 50	< 75	< 50	< 70	< 32	< 20
S	5690	18900	25400	19600	18700	16000
Si	372	233	174	164	160	146
U	< 250	< 370	< 250	< 350	< 160	< 100
F	394	448	568	1040	1860	1160
Cl	702	470	298	409	181	176
NO_2	3640	1940	1430	1530	950	761
NO_3	318000	142000	101000	79800	64300	60500
PO_4^{3-}	15900	22200	19200	14700	13100	7320
SO_4^{2-}	17500	55100	75100	63000	55700	47900
$C_2O_4^{2-}$	< 1300	2420	< 500	< 800	964	< 250
TIC	18900	19300	17700	14000	11400	9310
TOC	259	237	188	203	128	179
OH (calc)	5180	2760	2040	2170	1350	1080
Charge Balance	0.88	0.94	0.92	0.86	0.93	0.93

[a] corrected for dilution of analytical sample to prevent precipitation on cooling

3.2 RADIONUCLIDE DISTRIBUTION TESTS

The **Stepwise Dissolution** test procedure was described in Section 2.4. Weights, volumes, and sample identification numbers are shown in Table 3-7. Sample analytical results are presented in Tables 3-8, 3-9, and 3-10.

Table 3-7. Raw Data, Radionuclide Distribution Test.
(weights in grams, volumes in mL)

Tank	BY-106	S-102	A-101
Composite jar label	BY-106 Comp	17513	17511
Weight composite sample	40.154	39.933	39.551
	First Contact		
Weight inhibited water added	19.137	20.725	21.862
Volume supernatant liquid	25.0	21.5	37.0
Volume centrifuged solids	13.5	16.0	7.0
Weight centrifuged solids	24.129	28.848	11.433
Liquid sample Labcore no. S00R000...	117	119	121
	Second Contact		
Weight inhibited water added	20.466	20.202	21.181
Volume supernatant liquid	29.0	30.0	24.5
Volume centrifuged solids	4.5	4.5	3.0
Weight centrifuged solids	5.352	5.605	4.034
Liquid sample Labcore no. S00R000...	118	120	122
	Third Contact		
Weight inhibited water added	21.250	20.810	20.712
Volume supernatant liquid	23.0	21.5	21.0
Volume centrifuged solids	< 2	3.0	< 2
Weight centrifuged solids	1.636	3.190	1.937
Liquid sample Labcore no. S00R000...	124	126	128
CSol[a] sample Labcore no. S00R000...	152/155	153/156	154/157

[a] CSol = centrifuged solids

Table 3-8. Analytical Results, Tank BY-106 Radionuclide Distribution Test.
[units in μg/mL (μg/g solid) except as noted; radionuclides in μCi/mL (μCi/g solid)]

	1st Contact	2nd Contact	3rd Contact	Undissolved Solids
S00R000...	117	118	124	152/155
Density, g/mL	1.464	1.366	1.097	n.a.
%H_2O (wt%0	52.4	59.4	89.7	i.s.[2]
F^-	1300	3920	5100	n.a.
Cl^-	1650	260	50	n.a.
NO_2^-	29700	7320	770	n.a.
NO_3^-	323000	339000	45000	n.a.
PO_4^{3-}	< 1220	< 1220	3150	n.a.
SO_4^{2-}	2545	4590	8020	n.a.
$C_2O_4^{2-}$	< 1070	< 1070	6640	n.a.
CO_3^{2-}	59500	25500	4200	i.s.
"acetate"[2]	2600	1020	0	n.a.
OH^-	9770	2170	1330	n.a.
Al	18100	3680	456	22200
Ca	< 40	< 40	< 10	3330
Cr	783	167	28	11700
Fe	< 20	< 20	< 5	4060
K	2730	620	59	--
Na	195000	140000	32400	130000
P	276	282	1070	14700
S	688	1430	2850	1880
Si	162	52	48	8040
^{60}Co (GEA)	< 0.002	< 0.0003	< 0.0001	0.038
$^{89/90}Sr$ (Extr)	0.15	0.0067	0.025	135
^{99}Tc (Extr/LS)	0.076	0.015	0.0023	0.323
^{99}Tc (ICP/MS)	0.080	0.018	0.0025	0.412
^{137}Cs (GEA)	80	14.9	2.4	78.5
^{137}Cs (ICP/MS)	68.3	12.1	4.2	2020
^{154}Eu (GEA)	< 0.01	< 0.002	< 0.0003	0.103
^{155}Eu (GEA)	< 0.06	< 0.008	< 0.002	< 0.06
^{238}Pu (AEA)[1]	< 0.00002	< 0.00001	< 0.00001	< 0.016
$^{239/40}Pu$ (AEA)	0.00009	0.00001	< 0.00001	0.092
^{241}Am (GEA)	< 0.15	< 0.02	< 0.006	0.116
^{241}Am (AEA)	0.00008	< 0.00002	< 0.00001	0.108
Mass Balance	98.0	98.3	99.5	i.s.
Charge Balance	0.92	0.86	0.93	i.s.

[1] Extr = extraction; Extr/LS = extraction/liquid scintillation; AEA = alpha energy analysis
[2] i.s. = insufficient solids to perform analysis
[3] "acetate" calculated as difference between TOC and carbon found in oxalate, adjusted to acetate speciation

Table 3-9. Analytical Results, Tank S-102 Radionuclide Distribution Test.
[units in μg/mL (μg/g solid) except as noted; radionuclides in μCi/mL (μCi/g solid)]

Analyte	1st Contact	2nd Contact	3rd Contact	Undissolved Solids
S00R000...	119	120	126	153/156
Density (g/mL)	1.461	1.415	1.074	n.a.
%H_2O (Wt%)	52.6	52.6	90.0	71.2
F^-	< 120	< 120	< 25	n.a.
Cl^-	2000	817	99	n.a.
NO_2^-	22000	9400	1330	n.a.
NO_3^-	389000	434000	68200	n.a.
PO_4^{3-}	3620	3010	649	n.a.
SO_4^{2-}	5210	1630	494	n.a.
$C_2O_4^{2-}$	< 1070	< 1070	3070	3700
CO_3^{2-}	36800	18600	3220	1040
"acetate"	1940	964	0	n.a.
OH^-	492	411	317	n.a.
Al	2190	1060	162	79100
Ca	< 40	< 40	< 10	< 2000
Cr	1120	405	54	12600
Fe	< 20	< 20	< 5	1200
K	863	308	< 50	--
Na	195000	173000	26700	31200
P	1650	1110	173	< 4000
S	1550	812	122	< 2000
Si	127	106	22	3530
^{60}Co (GEA)	< 0.0013	< 0.0003	< 0.0001	0.033
$^{89/90}Sr$ (Extr)	0.13	0.062	0.006	35.5
^{99}Tc (Extr/LS)	0.064	0.031	0.004	0.042
^{99}Tc (ICP/MS)	0.070	0.029	0.004	0.24
^{137}Cs (GEA)	66.5	20.0	2.8	33.5
^{137}Cs (ICP/MS)	58.0	18.2	2.4	1140
^{154}Eu (GEA)	< 0.008	< 0.002	< 0.0003	0.25
^{155}Eu (GEA)	< 0.034	< 0.009	< 0.0015	0.16
^{238}Pu (AEA)	< 0.00001	< 0.00001	< 0.00002	< 0.015
$^{239/40}Pu$ (AEA)	0.00005	0.00002	< 0.00001	0.041
^{241}Am (GEA)	< 0.08	< 0.02	< 0.004	0.27
^{241}Am (AEA)	0.0003	0.00004	< 0.00001	0.27
Mass Balance	98.0	98.2	99.7	101.1
Charge Balance	1.01	0.93	0.85	--

Table 3-10. Analytical Results, Tank A-101 Radionuclide Distribution Test.
[units in μg/mL (μg/g solid)except as noted; radionuclides in μCi/mL (μCi/g solid)]

Analyte	1st Contact	2nd Contact	3rd Contact	Undissolved Solids
S00R000...	121	122	128	154/157
Density (g/mL)	1.413	1.153	1.036	n.a.
$\%H_2O$ (Wt%)	49.9	82.2	95.3	52.6
F^-	449	512	46	n.a.
Cl^-	3830	876	73	n.a.
NO_2^-	63850	18500	1620	n.a.
NO_3^-	109000	42300	4425	n.a.
PO_4^{3-}	1320	3700	380	n.a.
SO_4^{2-}	18900	10200	971	n.a.
$C_2O_4^{2-}$	< 1070	2610	16200	46200
CO_3^{2-}	79500	34000	4100	7800
"acetate"	5680	1760	0	n.a.
OH^-	26300	4110	467	n.a.
Al	27700	4750	478	26500
Ca	< 40	< 20	< 4	7770
Cr	450	86	10	78400
Fe	< 20	< 10	< 2	9540
K	3910	679	78	--
Na	208000	62000	14700	44500
P	877	1170	114	< 4000
S	8120	3350	353	< 2000
Si	167	264	6	8170
^{60}Co (GEA)	< 0.004	< 0.0008	< 0.0001	0.37
$^{89/90}Sr$ (Extr)	0.21	0.062	0.014	930
^{99}Tc (Extr/LS)	0.11	0.027	0.0035	2.31
^{99}Tc (ICP/MS)	0.14	0.030	0.0044	2.53
^{137}Cs (GEA)	204	38.7	4.5	97.4
^{137}Cs (ICP/MS)	174	33.7	3.4	6245
^{154}Eu (GEA)	< 0.025	< 0.005	< 0.0005	2.4
^{155}Eu (GEA)	< 0.14	< 0.012	< 0.002	1.5
^{238}Pu (AEA)	0.00003	0.00002	< 0.00001	0.32
$^{239/40}Pu$ (AEA)	0.00007	0.00006	< 0.00001	0.79
^{241}Am (GEA)	< 0.34	< 0.029	< 0.0044	2.2
^{241}Am (AEA)	0.00006	< 0.00002	< 0.00002	2.3
Mass Balance	91.2	98.7	99.6	88.3
Charge Balance	1.01	0.88	0.92	undef

3.3 FEED STABILITY TESTS

The **Feed Stability** test procedure was described in Section 2.5. Weights of diluent added and residual solids after each contact are shown in Table 3-11. Sample analytical results are presented in Table 3-12.

Table 3-11. Raw Data, Feed Stability Test. (weights in grams)

Contact	BY-102	BY-106	A-101	S-102	TX-113
Weight inhibited water added (0.01 M NaOH, 0.01 M $NaNO_2$)					
1	15.6	15.3	14.6	14.4	15.4
2	14.4	15.6	14.7	14.2	14.3
3	14.1	14.0	14.8	16.1	14.8
4	14.5	15.6	15.6	14.6	16.0
5	19.7	19.7	19.7	19.7	20.2
6	15.0	15.5	14.5	16.1	15.9
7	15.9	15.3	14.9	15.6	15.9
8	30.6	29.6	29.9	30.8	30.5
9	29.4	31.0	29.9	31.1	31.3
10	30.4	30.2	29.5	30.5	31.2
Weight centrifuged solids remaining after contact (0th contact = original sample weight)					
0	30.58	30.22	29.73	29.19	24.74
1	23.68	16.34	9.86	19.18	19.33
2	15.12	4.39	3.28	3.32	7.30
3	10.84	2.14	1.77	0.90	4.14
4	7.82	0.60	1.32	0.76	1.77
5	4.49	0.56	1.36	0.68	0.95
6	2.96	0.61	1.35	0.68	0.84
7	2.72	0.59	1.30	0.62	0.69
8	2.62	0.58	1.31	0.59	0.59
9	2.52	0.58	1.26	0.59	0.59
10	2.32	0.64	1.30	0.64	0.61

Table 3-12. Solid Phases Identified by PLM and SEM/EDS[1].
(major phases in boldface)

Contact	BY-102	BY-106	A-101	TX-113
2	**Na_3FSO_4** Na_2SO_4 $Na_7F(PO_4)_2 \cdot 19H_2O$	no solids	no solids	Na_3FSO_4 Na_2SO_4
3	**Na_3FSO_4** Na_2SO_4 $Na_7F(PO_4)_2 \cdot 19H_2O$	**$Na_2C_2O_4$**	**$Na_2C_2O_4$**	**$Na_7F(PO_4)_2 \cdot 19H_2O$** Na_2SO_4
4	no solids	**$Na_2C_2O_4$**	no solids	**$Na_7F(PO_4)_2 \cdot 19H_2O$**
5	**$Na_7F(PO_4)_2 \cdot 19H_2O$** $Na_2C_2O_4$	no solids	no solids	no solids
6	**$Na_7F(PO_4)_2 \cdot 19H_2O$** $Na_2C_2O_4$	no solids	no solids	no solids

[1] No solids formed in the S-102 receiver jar at all, nor in any jar after the 6th contact.

No attempt was made to determine the weight or volume of solids precipitated, but the amount was small in all cases. Weights of precipitated solids were predicted by the ESP runs, and agreed at least qualitatively with the laboratory observations. Those numbers will be included in the pending report from Mississippi State University.

4.0 DILUTION RESULTS, VOLUME AND WEIGHT MEASUREMENTS

All results quoted in this section have been "normalized" to a common basis for comparison. The common basis is defined in each sub-section as appropriate.

4.1 TANK TX-113 SERIES DISSOLUTION TESTS

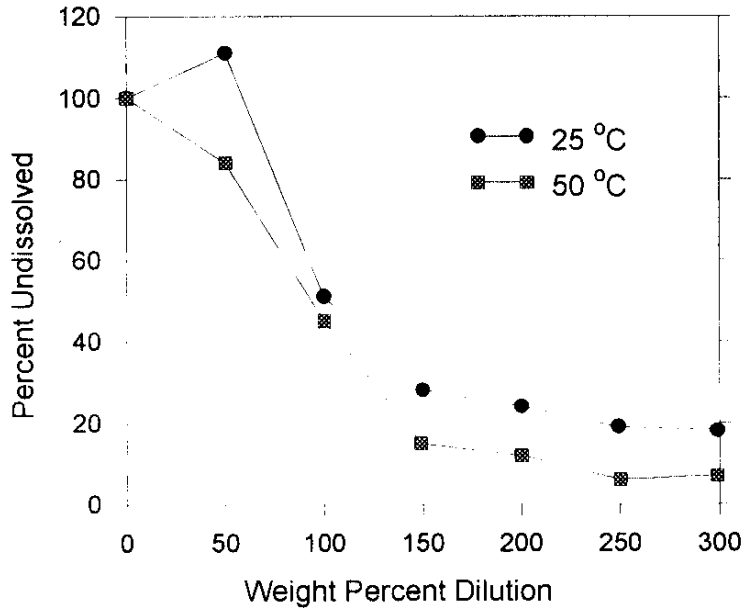
The obvious, direct way to determine how much saltcake dissolved upon dilution is to measure the volume percent and/or weight percent centrifuged solids remaining after the dissolution. These values as measured during the series dilution tests are shown in Table 4-1. Entries for volume percent centrifuged solids (Vol% CSol) and weight percent centrifuged solids (Wt% CSol) are measured relative to the total volume and weight, respectively, of the diluted samples. Entries for "Wt% CSol relative to undiluted sample" are self-explanatory, and provide a more consistent way of visualizing the amount of sample remaining undissolved. The latter data are plotted in Figure 4-1, where the same values are expressed as "percent undissolved".

Table 4-1. Percent Centrifuged Solids as a Function of Dilution, Tank TX-113.

at 25 °C						
Wt% Dilution→	50	100	150	200	249	299
Vol% CSol	69	18	9	7	3	3
Wt% CSol	74	25	11	8	5	4
Wt% CSol relative to undiluted sample	111	51	28	24	19	18
50 °C						
Wt% Dilution→	50	100	149	200	250	299
Vol% CSol	55	14	6	3	1	1
Wt% CSol	62	22	9	4	2	3
Wt% CSol relative to undiluted sample	94	45	15	12	6	7

It is clear from the data that most of dissolution occurred between 50% and 150% dilution, and only a small amount of dissolution took place at higher dilution. It is also clear that raising the temperature from 25 °C to 50 °C had a small but measurable impact on the overall solubility of the saltcake.

Figure 4-1. Tank TX-113 Saltcake Dissolution



4.2 RADIONUCLIDE DISTRIBUTION TEST

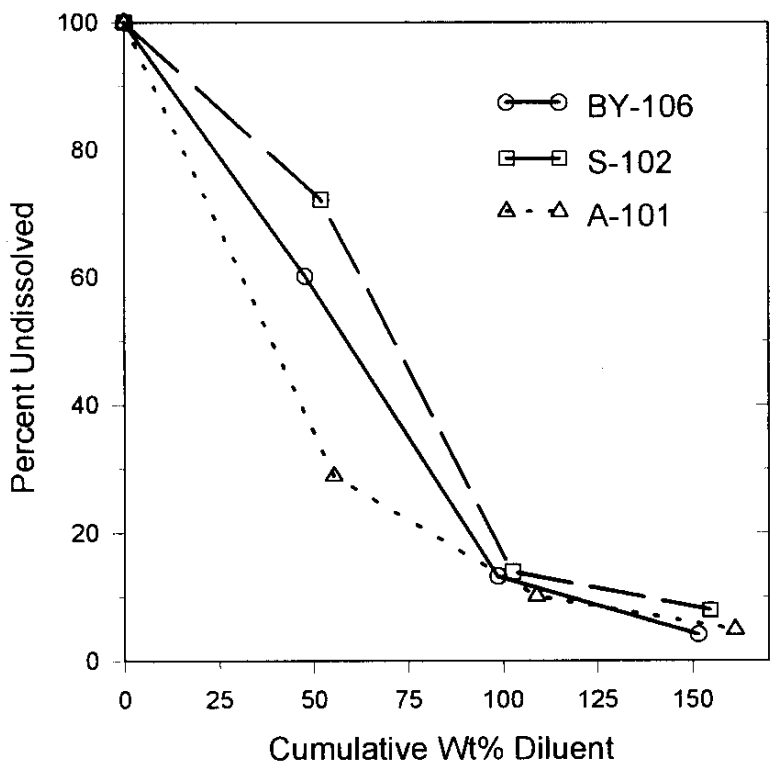
One way to measure the effectiveness of the dissolution brought about by stepwise addition of inhibited water is to measure the weight percent of centrifuged solids remaining after each dissolution contact. The weight of these solids relative to the original sample weight gives the "Wt% CSol" values presented in Table 4-2. The "Cum Wt% Diluent" is the sum of the weights of inhibited water added relative to the original sample weight. These data are plotted in Figure 4-2.

The largest differences among the samples occur at about 50% diluent. The differences here are correlated with the percent water in the undiluted saltcake. The more moisture present in the original saltcake, the more solids are dissolved at 50% diluent. (See Table 5-1 for the percent water values for each saltcake.)

Table 4-2. Percent Centrifuged Solids, Stepwise Dissolution
(Radionuclide Distribution Test)

Contact	Cum Wt% Diluent (avg)	BY-106	S-102	A-101
1st	52	60.1	72.2	28.9
2nd	104	13.3	14.0	10.2
3rd	156	4.1	8.0	4.9

Figure 4-2. Stepwise Dissolution of Saltcakes



5.0 CHEMICAL COMPOSITION TRENDS

Sequential and series dissolution tests have now been performed on saltcake samples from five single-shell tanks: BY-102 and BY-106 in FY 1998 (Herting 1998), A-101 and S-102 in FY 1999 (Herting 1999), and TX-113 in FY 2000. The gross sample behavior explored in the previous section (i.e., volume and weight of centrifuged solids as a function of dilution) can be understood in terms of what happens to individual saltcake components. These trends are discussed in Section 5.1.

The overall composition of the composite sample from each tank was determined by the sequential dissolution tests. The results are summarized in Table 5-1. Saltcakes from BY-106 and S-102 are similar in that they are both relatively high in $NaNO_3$. Tank A-101 saltcake is higher in moisture than the others, and is therefore higher in all of the components that are normally not saturated in waste liquors, including nitrite, aluminate, hydroxide, acetate, chloride, potassium, and ^{137}Cs. Saltcakes from BY-102 and TX-113 are similar in that they are much higher than the others in carbonate, phosphate, sulfate, and fluoride. TX-113 is significantly lower than BY-102, though, in both the relatively insoluble components like Cr, Fe, and oxalate, and the completely soluble components like nitrite, chloride, and potassium.

5.1 SERIES DISSOLUTION TESTS, TANK TX-113

5.1.1 Nitrite, Chloride, and Oxalate

The amount of nitrite in TX-113 saltcake was roughly an order of magnitude smaller than in the other four tanks previously studied. Its concentration in the liquid phase during the series dissolution tests (Tables 3-4 and 3-6) fit the standard dilution pattern of a soluble salt that is completely dissolved at the lowest dilution. Therefore, no new information about nitrite is learned from tank TX-113, and no figures are shown.

The amounts of chloride and oxalate in TX-113 saltcake are also much smaller than in the other four tanks. Chloride is very near the detection limits of the ion chromatography analytical method, and oxalate is below the detection limit in most samples.

Table 5-1. Overall Composition (in wt%) of Composite Saltcake Samples

	BY-102	BY-106	A-101	S-102	TX-113
Al	1.65	1.59	2.39	0.67	0.30
Cr	0.20	0.11	0.17	0.12	0.04
Fe	0.05	0.02	0.02	0.03	0.02
K	0.10	0.24	0.31	0.07	0.03
Na	27.8	25.0	21.2	23.0	29.1
P	1.00	0.08	0.14	0.18	1.17
S	2.04	0.45	0.80	0.13	5.30
Si	0.07	0.02	0.03	0.03	0.04
U	0.06	0.02	0.03	< 0.01	0.14
F^-	1.17	0.62	0.07	< 0.02	0.27
Cl^-	0.11	0.16	0.41	0.16	0.06
NO_2^-	1.85	2.71	7.43	2.04	0.25
NO_3^-	10.9	40.5	12.6	53.7	18.2
PO_4^{3-} by IC	0.60	0.34	0.39	0.52	1.35
PO_4^{3-} by ICP	3.06	0.24	0.44	0.56	3.57
SO_4^{2-} by IC	5.12	1.16	2.44	0.32	16.0
SO_4^{2-} by ICP	6.11	1.34	2.41	0.38	15.9
$C_2O_4^{2-}$	1.99	1.26	1.35	0.17	0.12
CO_3^{2-}	20.6[a]	7.15	9.04	2.95	14.4
"acetate"[c]	0.21	0.16	0.75	0.39	0.02
OH^-	1.09	1.14	2.10	0.42	0.29
^{137}Cs (μCi/g)	44	78	197	61	6.2
H_2O	26.5	14.7	31.2	5.0[b]	12.3
Mass Bal[c]	105.5	98.9	94.8	90.5	95.8
Chg Bal (+/-)[c]	0.89	0.92	0.93	0.91	0.99

[a] probably erroneously high due to analytical error; should be closer to 15% (Table 8-1)
[b] probably erroneously low due to analytical error; should be closer to 11%
[c] see Section 7.2 for definitions of "acetate", Mass Bal, and Chg Bal (+/-)

5.1.2 Nitrate

There are no obvious surprises in the nitrate analytical data (Tables 3-4 and 3-6), which follow a simple dilution pattern. Nitrate is below the saturation point at 50% dilution and all greater dilutions.

What isn't observable in the analytical data is the nature of the nitrate solid that is present in the undiluted saltcake. Examination of the TX-113 composite sample with the polarized light microscope shows that the dominant solid phase in the sample is the nitrate-sulfate double salt $Na_3NO_3SO_4 \cdot xH_2O$ [where x = either 1 (Winchell 1964) or 2 (Linke 1958)]. This salt was identified during tests with simulated saltcake samples (Herting 1999). The statement was made then that "It will take some time to evaluate whether this is a significant species in saltcake waste." Now, one year later, it is clear that the double salt is the major solid phase in the TX-113 saltcake from core 253.

This salt is a good example of an incongruent double salt, which is defined as a double salt that cannot exist in equilibrium with a solution in which the two salts are present in the molecular ratio of the solid (Mason 1983). When placed in water, the solid appears to undergo decomposition with appearance of a new phase, e.g.:

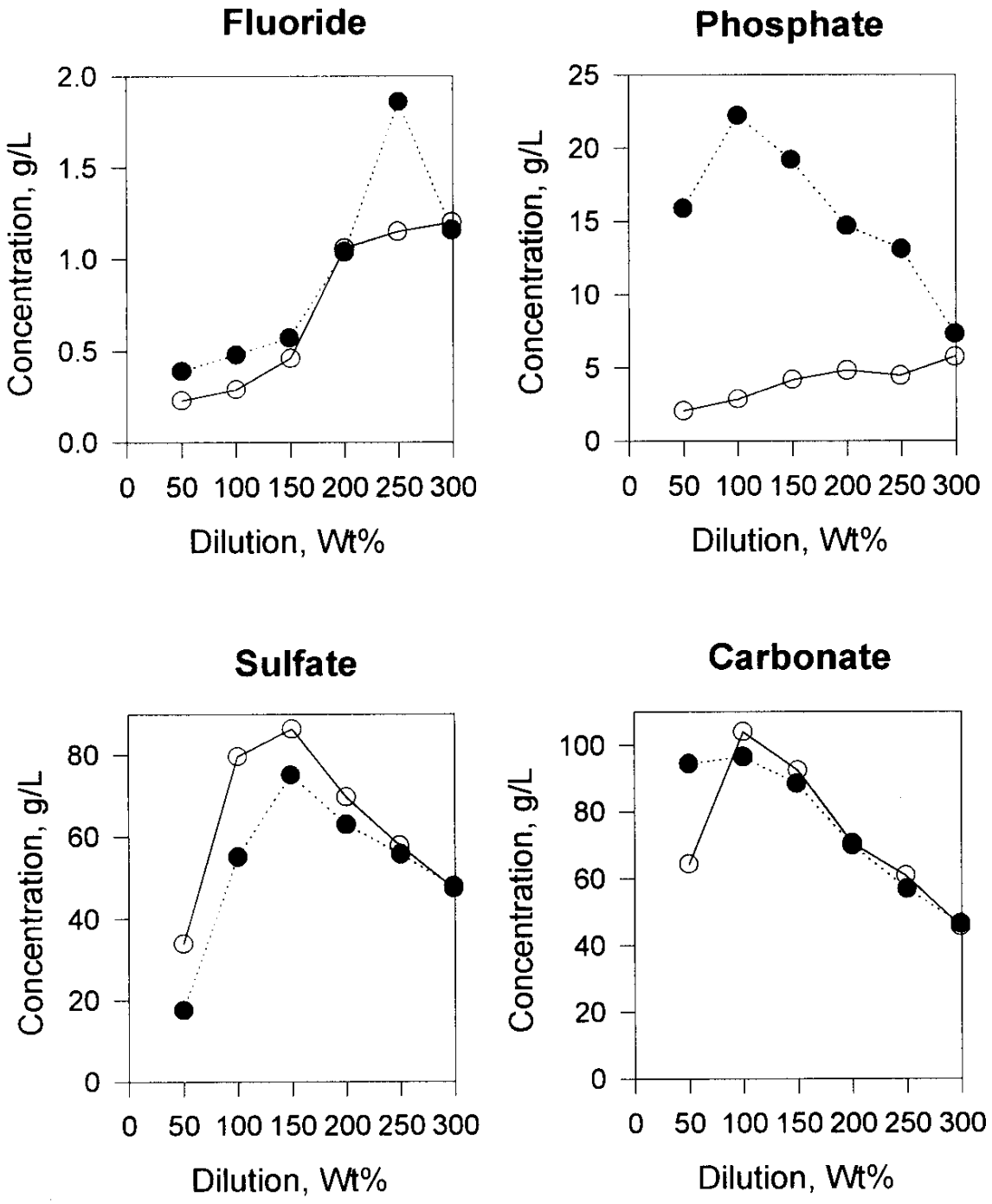
$$Na_3NO_3SO_4 \cdot xH_2O\ (s) + H_2O \rightarrow Na_2SO_4 \cdot 10H_2O\ (s) + NaNO_3\ (aq)$$

Apparently, the solubility of the double salt can be fully described in terms of the solubilities of the individual component salts, sodium sulfate and sodium nitrate. Computer modeling of the system with ESP appears to bear this out, as ESP does not have data for the double salt, but still does a reasonable job of predicting the nitrate and sulfate concentrations in solution at various dilutions (see Section 8.1).

5.1.3 Fluoride, Phosphate, Sulfate, And Carbonate

Concentration data for fluoride, phosphate, sulfate, and carbonate are shown in Figure 5-1. From the PLM analysis of the TX-113 composite sample, it is clear that much of the fluoride in the sample is present as the fluoride phosphate double salt $Na_7F(PO_4)_2 \cdot 19H_2O$. In the series dissolution test at 25 °C, the concentrations of fluoride and phosphate both increase fairly steadily throughout the entire dilution range. At 50 °C, though, the phosphate concentration increases dramatically over the 25 °C concentrations, but the fluoride does not. It is likely that the $Na_7F(PO_4)_2 \cdot 19H_2O$ dissolves as the temperature increases, but the fluoride re-precipitates as the fluoride sulfate double salt Na_3FSO_4.

Figure 5-1. Concentrations in Supernatant Liquid, TX-113
(open symbols 25 °C, filled symbols 50 °C)



Both $Na_7F(PO_4)_2 \cdot 19H_2O$ and Na_3FSO_4 are examples of congruent double salts (Mason 1983, Bowden 1938). These salts dissolve in water to form solutions that have the same mole ratios of anions as the solid salts. Furthermore, the double salt is less soluble than either of the component salts alone. That is, a saturated solution contains far less fluoride when phosphate or sulfate is present than when they are absent, and conversely, the solution contains far less phosphate or sulfate when fluoride is present than when it is absent.

Phosphate, which is present perhaps exclusively as $Na_7F(PO_4)_2 \cdot 19H_2O$, is nearly an order of magnitude more soluble at 50 °C than at 25 °C (see Figure 5-1). At 25 °C, the concentrations increases throughout the dilution range. At 50 °C, the solid phase is completely dissolved at about 100% dilution, and displays a simple dilution pattern beyond that point.

Sulfate is present initially (at zero dilution) as the double salt $Na_3NO_3SO_4 \cdot xH_2O$. When water is added, the incongruent double salt "decomposes", and the solid phase is replaced by Na_2SO_4, with perhaps some Na_3FSO_4. The solubilities of both of these solids have inverse temperature dependence, so the concentration of sulfate in solution is higher at 25 °C than at 50 °C (Figure 5-1).

Carbonate solubility data (Figure 5-1) show that the carbonate is completely dissolved at about 100% dilution. The fact that the carbonate concentration at 50% dilution is slightly higher at 50 °C than at 25 °C implies that the original sodium carbonate solid phase is hydrated (probably $Na_2CO_3 \cdot H_2O$). Similar behavior was observed for tank BY-102 (Herting 1999). While there is no direct evidence here for the existence of the double salt $Na_6CO_3(SO_4)_2$, its existence should not be ruled out.

5.2 RADIONUCLIDE DISTRIBUTION STUDIES

The gross material dissolution behavior explored in Section 4.2 can be understood better by examining the chemical compositions of the individual solutions and the residual solids. The fractional dissolution gives a good initial understanding of the saltcake dissolution process achieved by the stepwise addition of diluent. Chemical as well as radionuclide analyses were done in the hope of being able to correlate radionuclide distribution information with chemical composition data. The data hint at some correlations, but conclusions will have to wait until more data are available.

Table 5-2 shows the amount (grams or μCi) of each component in each fraction from the BY-106 test, based on concentration times volume for the three liquid samples, or concentration times weight for the residual solids. The column labeled "Total" is the sum of the four fractions. The column labeled "Percent Dissolved" is 100 times the sum of the three liquid samples divided by the total. The column labeled "Wt%" is the "Total" divided by the initial saltcake sample weight, and represents the composition of the composite sample in weight percent. Similar data for the other tanks are shown in Tables 5-3 and 5-4.

Table 5-2. Distribution by Fraction in Tank BY-106
(total undiluted sample weight 40.154 g)

(chemicals in grams, radionuclides in μCi)

Analyte	Liquid Samples			Residual Solids	Total	Percent Dissolved	Wt%
	1st Contact	2nd Contact	3rd Contact				
F^-	0.03	0.11	0.12	n.a.	0.26	(100) (assumed)	0.66
Cl^-	0.041	0.008	0.001	n.a.	0.05		0.12
NO_2^-	0.74	0.21	0.02	n.a.	0.97		2.42
NO_3^-	8.08	9.83	1.04	n.a.	18.9		47.2
PO_4^{3-}	0.02	0.03	0.07	0.07[d]	0.19	62	0.48
SO_4^{2-}	0.06	0.13	0.18	0.01[d]	0.39	98	0.97
$C_2O_4^{2-}$	<[a]	<	0.15	i.s.[b]	--[c]	--	i.s.
CO_3^{2-}	1.49	0.74	0.02	i.s.	--	--	i.s.
Al	0.45	0.11	0.01	0.04	0.61	94	1.51
Ca	<	<	<	0.005	0.005	0	0.01
Cr	0.020	0.005	0.001	0.019	0.044	43	0.11
Fe	<	<	<	0.066	0.066	0	0.02
K	0.068	0.018	0.001	n.a.	0.088	(100)	0.22
Na	4.88	4.06	0.75	0.21	9.89	98	24.6
P	0.007	0.008	0.025	0.024	0.064	62	0.16
S	0.017	0.041	0.066	0.003	0.127	98	0.32
Si	0.004	0.002	0.001	0.013	0.020	34	0.05
^{60}Co	<	<	<	0.062	0.062	0	
$^{89/90}Sr$	3.75	0.19	0.58	221	225	2	
^{99}Tc	1.90	0.44	0.05	0.53	2.92	82	
^{137}Cs	2000	432	55	128	2616	95	
^{154}Eu	<	<	<	0.17	0.17	0	
$^{239/40}Pu$	0.002	<	<	0.151	0.153	2	
^{241}Am	0.002	<	<	0.177	0.179	1	

[a] (<) = "less than" analytical result (below detection limit), amount not calculated.
[b] (i.s.) = insufficient solids to perform analysis.
[c] (--) = not calculated because one or more data points missing.
[d] calculated from ICP result for P or S.

Table 5-3. Distribution by Fraction in Tank S-102.
(total undiluted sample weight 39.933 g)

(chemicals in grams, radionuclides in μCi)

Analyte	Liquid Samples			Residual Solids	Total	Percent Dissolved	Wt%
	1st Contact	2nd Contact	3rd Contact				
F^-	< [a]	<	<	n.a.	-- [b]	(100%) (assumed)	--
Cl^-	0.043	0.025	0.002	n.a.	0.070		0.17
NO_2^-	0.47	0.28	0.03	n.a.	0.78		1.96
NO_3^-	8.36	13.02	1.47	n.a.	22.85		57.2
PO_4^{3-}	0.078	0.090	0.014	n.a.	0.182		0.46
SO_4^{2-}	0.112	0.049	0.011	n.a.	0.172		0.43
$C_2O_4^{2-}$	<	<	0.066	0.024	0.090	74	0.22
CO_3^{2-}	0.79	0.56	0.07	0.02	1.43	99	3.60
Al	0.047	0.032	0.003	0.252	0.335	25	0.84
Cr	0.024	0.012	0.001	0.040	0.078	48	0.19
Fe	<	<	<	0.004	0.004	0	0.01
K	0.019	0.009	<	n.a.	0.028	(100)	0.07
Na	4.19	5.19	0.57	0.10	10.05	99	25.2
P	0.035	0.033	0.004	<	0.072	100	0.18
S	0.033	0.024	0.003	<	0.060	100	0.15
Si	0.003	0.003	0.001	0.011	0.018	36	0.04
^{60}Co	<	<	<	0.105	0.105	0	
$^{89/90}Sr$	2.80	1.86	0.13	113	118	4	
^{99}Tc	1.38	0.93	0.08	0.13	2.52	95	
^{137}Cs	1430	600	60	107	2197	95	
^{154}Eu	<	<	<	0.80	0.80	0	
$^{239/40}Pu$	0.0011	0.0007	<	0.131	0.132	1	
^{241}Am	0.007	0.001	<	0.861	0.869	1	

[a] (<) = "less than" analytical result, amount not calculated.
[b] (--) = not calculated because one or more data points missing.

Table 5-4. Distribution by Fraction in Tank A-101.
(total undiluted sample weight 39.551 g)

(chemicals in grams, radionuclides in μCi)

Analyte	Liquid Samples			Residual Solids	Total	Percent Dissolved	Wt%
	1st Contact	2nd Contact	3rd Contact				
F^-	0.017	0.013	0.001	n.a.	0.030	(100) (assumed)	0.08
Cl^-	0.142	0.021	0.002	n.a.	0.165		0.42
NO_2^-	2.36	0.45	0.03	n.a.	2.85		7.21
NO_3^-	4.03	1.04	0.93	n.a.	5.16		13.1
PO_4^{3-}	0.05	0.09	0.01	n.a.	0.15		0.37
SO_4^{2-}	0.70	0.25	0.02	n.a.	0.97		2.45
$C_2O_4^{2-}$	< [a]	0.06	0.34	0.18	0.58	69	1.47
CO_3^{2-}	2.94	0.83	0.09	0.02	3.87	99.5	9.80
Al	1.02	0.12	0.01	0.05	1.20	96	3.04
Ca	<	<	<	0.015	0.015	0	0.04
Cr	0.017	0.002	0.000	0.152	0.171	11	0.43
Fe	<	<	<	0.018	0.018	0	0.05
K	0.145	0.017	0.002	n.a.	0.163	(100)	0.41
Na	7.70	1.52	0.31	0.09	9.61	99	21.2
P	0.032	0.029	0.002	<	0.064	100	0.16
S	0.300	0.082	0.007	<	0.390	100	0.99
Si	0.006	0.006	0.000	0.017	0.029	45	0.07
^{60}Co	<	<	<	0.72	0.72	0	
$^{89/90}Sr$	7.8	1.5	0.3	1800	1810	1	
^{99}Tc	4.2	0.7	0.1	4.5	9.4	52	
^{137}Cs	7548	948	95	189	8779	98	
^{154}Eu	<	<	<	4.6	4.6	0	
$^{239/40}Pu$	0.003	0.001	<	1.530	1.534	0	
^{241}Am	0.002	<	<	4.475	4.477	0	

[a] (<) = "less than" analytical result, amount not calculated.

The stepwise dissolution method used for the radionuclide distribution test was similar to the stepwise dissolution profile test done last fiscal year on tank BY-102 saltcake (Herting 1999). In that case, the only radionuclide that was analyzed was ^{137}Cs. Comparisons of the BY-102 data with the current tanks BY-106, S-102, and A-101 are included here wherever appropriate.

The following set of figures (5-2 through 5-4) are called "dissolution profile" plots. They show the "Fraction Removed" on the y-axis, defined as the cumulative weight of constituent removed in the decanted liquid phase divided by the total amount present (liquid and solid phases) in the undiluted sample. The "Fraction Removed" at the highest dilution point matches the "Percent Dissolved" in the preceding tables. The legend for each figure follows the order of dissolution, with the components with the highest fraction removed listed at the top of the legend.

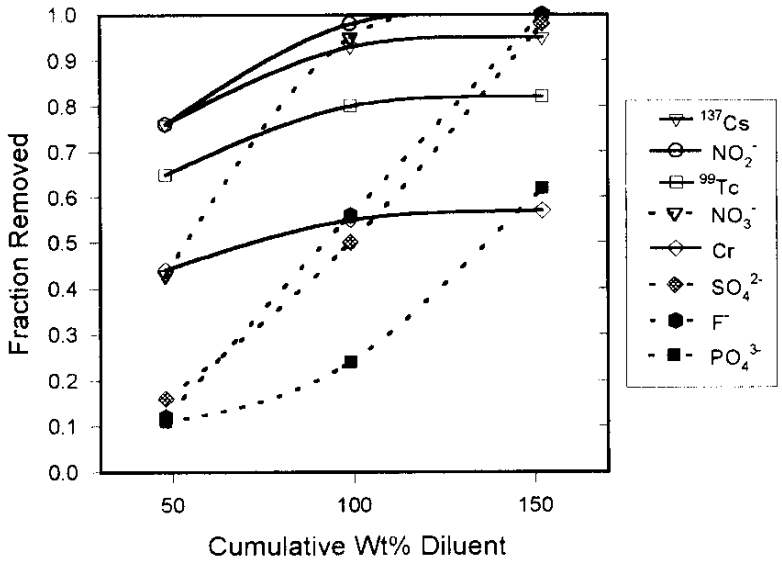
5.2.1 Nitrite, Chloride, Potassium

There is a short list of components that are essentially 100% in the liquid phase at all levels of dilution, namely nitrite, chloride, and potassium. In Tables 5-2 through 5-4, the weights of these components in the liquid phase are seen to drop sharply from one contact to the next in all cases. The Fraction Removed for each of these components depends only on the separation of the liquid phase from the solid phase. Nitrite is the only component from this group displayed in Figures 5-2 through 5-4, and it represents the maximum achievable removal efficiency for each tank. The variation from tank to tank, most notable at about 50% diluent, correlates with the amount of centrifuged solids – the more solids, the lower the fraction of nitrite removed. These findings also hold for the tank BY-102 from last year.

5.2.2 Nitrate

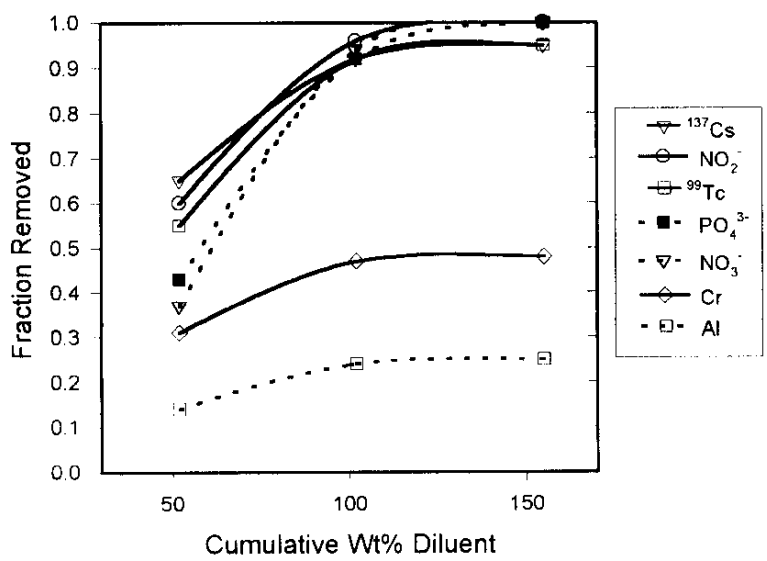
The four saltcakes included in this discussion have a broad range of nitrate concentrations, from 11% to 54% by weight of the undiluted composite samples (see Table 5-1). Note in Tables 5-2 through 5-4 that the weight of nitrate in the liquid phase falls sharply from the first contact to the second contact for tank A-101, but increases for tanks BY-106 and S-102. Thus, after the first contact some of the saltcakes (at least BY-106 and S-102) still contain undissolved sodium nitrate. For nitrate, then, the dissolution profiles depend on more than the separation of the liquid phase from the undissolved solids, but tend to follow the order of sodium nitrate concentration in the undiluted saltcake. In tanks BY-102 and A-101 (with the lower nitrate concentrations), the nitrate dissolution profile nearly matches the nitrite profile, and for tanks BY-106 and S-102 the profile is much lower.

Figure 5-2. Tank BY-106 Dissolution Profile



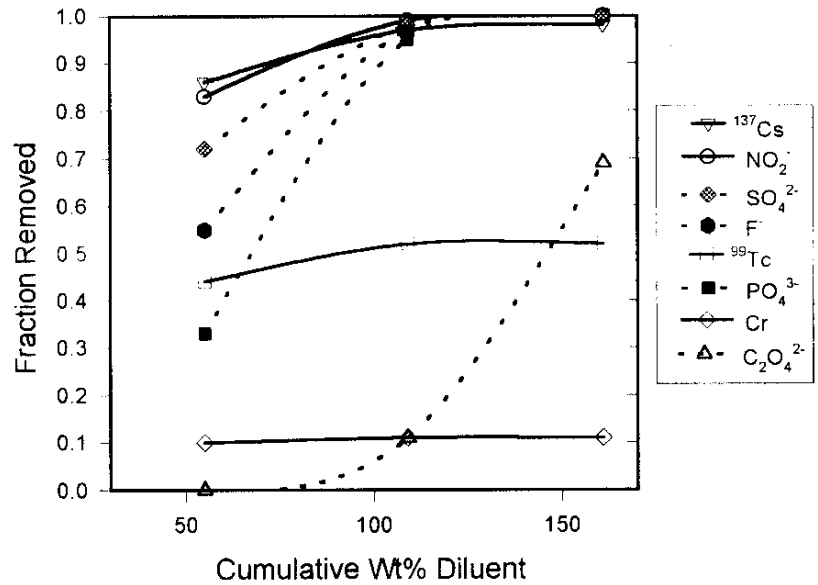
[not shown: Al curve matches ^{137}Cs curve]

Figure 5-3. Tank S-102 Dissolution Profile



[not shown: CO_3^{2-}, SO_4^{2-} similar to NO_2^-]

Figure 5-4. Tank A-101 Dissolution Profile



[not shown: NO_3^-, CO_3^{2-}, Al similar to NO_2^-]

5.2.3 Carbonate, Fluoride, Phosphate, Sulfate, Oxalate

The sodium salts in this group tend to be less soluble than sodium nitrate, but will dissolve if enough water is added. Sodium oxalate is the least soluble. Solubilities of the other salts are complicated by the existence of various double salts (fluoride-phosphate, fluoride-sulfate, carbonate-sulfate).

5.2.4 Partially Soluble Metals (Al, Cr, Si)

The solubilities of Al, Cr, and Si are seen to vary a great deal from tank to tank. In each case, there appear to be at least two distinct species, one of which is very soluble and one of which is virtually insoluble. Thus, the total amount of Al dissolved in the three contacts ranges from 25% for tank S-102 to 96% for tank A-101; Cr varies from 11% for tank A-101 to 60% for tank BY-102; Si varies from 11% for tank BY-102 to 45% for tank A-101.

5.2.5 Insoluble Metals (Ca, Fe)

Calcium and iron are present at low levels in most of the saltcakes, but no detectable amount of either metal was ever found in a liquid phase sample.

5.2.6 Radionuclides

The radionuclides fall into more or less the same classes as the chemicals just discussed. The most soluble is ^{137}Cs, though each tank has a distinct fraction that is insoluble. The percentage of ^{137}Cs dissolved ranged from 67% (tank BY-102) to 98%.

The behavior of ^{99}Tc was similar to ^{137}Cs, though the insoluble fraction tended to be quite a bit higher. The percentage of ^{99}Tc dissolved ranged from 52% to 95%.

The remaining radionuclides were either insoluble or very sparingly soluble. The percentages dissolved ranged from 1 - 4% for $^{89/90}$Sr, 0 - 2% for $^{239/240}$Pu, 0 - 1% for ^{241}Am, and strictly 0% for ^{60}Co and ^{154}Eu.

5.3 COMPARISON OF RADIONUCLIDE ANALYTICAL METHODS

Several radionuclide activities were measured by more than one method, with results shown in Tables 3-8, 3-9, and 3-10: ^{99}Tc by extraction/liquid scintillation ('Extr' in the tables) and ICP/MS; ^{137}Cs by GEA and ICP/MS; and ^{241}Am by GEA and extraction/atomic energy absorption (AEA) spectroscopy.

For ^{99}Tc, the ICP/MS results tended to be about 10% higher than extraction/liquid scintillation results for all samples. For one sample of centrifuged solids (from tank S-102), the ICP/MS result was about six times higher. Except for that one sample, the agreement between the methods is reasonably good. For the trends discussed above (Section 5.2, Tables 5-2 through 5-4), the extraction/liquid scintillation results were used.

For ^{137}Cs, the GEA results were higher than the ICP/MS results for eight of the nine of the liquid samples, averaging about 20% higher. For the ninth sample (tank BY-106, 3rd contact), the ICP/MS result was nearly twice as high as the GEA result. For the three centrifuged solids samples, the ICP/MS results were very much higher than the GEA results, by more than one order of magnitude. These large discrepancies should be investigated in future testing. The GEA results were used in Tables 5-2 through 5-4.

For ^{241}Am, where the GEA results were not less-than values (i.e. the centrifuged solids samples) the agreement between the GEA and AEA results was excellent. In the liquid samples, the less-than values from AEA were much lower than the GEA less-than values, but they were consistent with one another, and some non-less-than AEA values were reported.

6.0 EFFECT OF IONIC STRENGTH ON CRYSTAL HYDRATES

The sodium salts of all of the common multi-valent anions in Hanford waste (carbonate, phosphate, and sulfate) exist in more than one crystal hydrate form. Sodium carbonate, for example, can crystallize from water solution as the decahydrate, heptahydrate, monohydrate, or anhydrous salt, depending on the temperature. The solubility of each hydrated form has a distinctly different temperature dependence. The solubility of sodium carbonate decahydrate, for example, increases sharply with small increases in temperature; the monohydrate solubility is almost temperature-independent; and the solubility of the anhydrous salt decreases with increasing temperature. Accurate computer modeling of the solubility depends on correct identification of the hydrate form of the solid phase.

The hydrate transition temperatures are very well known for the binary systems (i.e., one sodium salt plus water). However, the transition temperature is known to vary with ionic strength, probably due mainly to the change in water activity. No systematic study has been made of the relationship between the hydrate form and ionic strength. The general direction of the change is known – the transition temperature goes down as the ionic strength goes up – but the magnitude of the change isn't known. A laboratory test program is needed to establish the relationship between the crystal hydrate form and the solution ionic strength for multi-hydrate salts like sodium carbonate, sodium phosphate, and sodium sulfate.

6.1 SODIUM SULFATE LITERATURE DATA

Sodium sulfate crystallizes from water as the decahydrate or anhydrous salt. In water, the transition occurs at 32.4 °C. The solubility of the decahydrate increases rapidly with increasing temperature, while the solubility of the anhydrous salt decreases with increasing temperature.

Literature solubility data for the sodium sulfate system (Linke 1958) are shown in Figure 6-1 for the binary system (the curve labeled "in H_2O") and the ternary system $Na_2SO_4/NaNO_3/H_2O$ (curves labeled "in 1.5 m and 5 m $NaNO_3$). The hydrate transition temperature decreases from 32.4 °C in water to 30 °C in 1.5 m $NaNO_3$ to 25 °C in 5 m $NaNO_3$.