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ENGINEERING CHANGE NOTICE

Page 1 of 2

1. ECN 657296

Proj. ECN

2. ECN Category (mark one)	3. Originator's Name, Organization, MSIN, and Telephone No.	4. USQ Required?	5. Date
Supplemental [] Direct Revision [] Change ECN [] Temporary [] Standby [] Supersedure [X] Cancel/Void []	M. R. Adams, Data Development and Interpretation, R2-12, 373-6167	[] Yes [X] No	09/07/00
	6. Project Title/No./Work Order No.	7. Bldg./Sys./Fac. No.	8. Approval Designator
	Tank 241-AZ-101	241-AZ-101	N/A
	9. Document Numbers Changed by this ECN (includes sheet no. and rev.)	10. Related ECN No(s).	11. Related PO No.
	~~HNF~~ SD-WM-ER-410, Rev. 1 DC WHC fmw 9/7/00	ECNs: 612282, 644480 and 653800	N/A

12a. Modification Work	12b. Work Package No.	12c. Modification Work Complete	12d. Restored to Original Condition (Temp. or Standby ECN only)
[] Yes (fill out Blk. 12b) [X] No (NA Blks. 12b, 12c, 12d)	N/A	N/A Design Authority/Cog. Engineer Signature & Date	N/A Design Authority/Cog. Engineer Signature & Date

13a. Description of Change

13b. Design Baseline Document? [] Yes [X] No

This hard copy document has been released and superseded by an electronic information database and data currently available via hard copy are now available at the HLAN address: http://pctwins.pnl.gov:9397/twinsproto/default.htm.

RECEIVED
SEP 19 2000
EDMC

14a. Justification (mark one)

Criteria Change	[X]	Design Improvement	[]	Environmental	[]	Facility Deactivation	[]
As-Found	[]	Facilitate Const	[]	Const. Error/Omission	[]	Design Error/Omission	[]

14b. Justification Details

Electronic access to information and data is superseding hard copy document.

15. Distribution (include name, MSIN, and no. of copies)

See attached distribution.

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ENGINEERING CHANGE NOTICE	Page 2 of 2	1. ECN (use no. from pg. 1) ECN-657296

16. Design Verification Required	17. Cost Impact						18. Schedule Impact (days)	
	ENGINEERING			CONSTRUCTION				
[] Yes	Additional	[]	$	Additional	[]	$	Improvement	[]
[X] No	Savings	[]	$	Savings	[]	$	Delay	[]

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

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

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

Document Number/Revision	Document Number/Revision	Document Number Revision
N/A		

21. Approvals

	Signature	Date		Signature	Date
Design Authority			Design Agent		
Cog. Eng. M. R. Adams	MRAdams	9/7/00	PE		
Cog. Mgr. J. G. Field	JG Field	9/7/00	QA		
QA			Safety		
Safety			Design		
Environ.			Environ.		
Other			Other		

DEPARTMENT OF ENERGY

Signature or a Control Number that tracks the Approval Signature

ADDITIONAL

Tank Characterization Report for Double-Shell Tank 241-AZ-101

M. R. Adams
CH2M Hill Hanford Group, Inc., Richland, WA 99352
Richland, WA 99352
U.S. Department of Energy Contract DE-AC06-99RL14047

EDT/ECN: ECN-657296 UC: 2070
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Abstract: N/A
http://pctwins.pnl.gov:9397/twinsproto/default.htm

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RECORD OF REVISION	(1) Document Number HNF-~~WHC~~-SD-WM-ER-410	Page 1

(2) Title
Tank Characterization Report for for Double-Shell Tank 241-AZ-101

CHANGE CONTROL RECORD

(3) Revision	(4) Description of Change - Replace, Add, and Delete Pages	Authorized for Release (5) Cog. Engr.	(6) Cog. Mgr. Date
0	(7) Initially released 7/26/95 on EDT 612676.	K. M. Hodgson	J. G. Kristofzski
0A RS	Incorporate per ECN-612282.	M. J. Kupfer MJ Kupfer 7-9-97	K. M. Hodgson K.M. Hodgson 7/21/97
0B RS RS	Incorporate per ECN-644480	M.J. Kupfer 7/22/98	K.M. Hodgson K.M. Hodgson 7/22/98
0-C RS	Incorporate per ECN-653800.	A.M. Templeton A.M. Templeton	K.M. Hallford 6/3/99
RS 1	Incorporate per ECN-657296	M.R. Adams MR Adams	J. G. Field JG Field 9/7/00

A-7320-005 (08/91) WEF168

This report prepared especially for Archive TIR on 9/7/00

Some of the reports herein may contain data that has not been reviewed or edited. The data will have been reviewed or edited as of the date that a Tank Interpretive Report (TIR) is prepared and approved. The TIR for this tank was approved on September 6, 2000.

Tank: 241-AZ-101

Sampling Events:

- 1
- 1AZ-00-1
- 1AZ-00-2
- 1AZ-00-3
- 1AZ-00-4
- 1AZ-00-5
- 1AZ-00-6
- 1AZ-00-7
- 1AZ-00-8
- 1AZ-00-9
- 2
- 266
- 269
- 3
- AZ1011
- AZ1012
- AZ1013

Reports:

- Tank Interpretive Report

Constituent Groups:

- Anions
- Inorganics
- Metals/Nonmetals
- Organics
- PCBs
- Physical Properties
- Radionuclides

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Data Dictionary to Reports in this Document

Report	Field	Description
Tank Interpretive Report		Interprets information about the tank answering a series of seven questions covering areas such as information drivers, tank history, tank comparisons, disposal implications, data quality and quantity, and unique aspects of the tank.

Tank Interpretive Report For 241-AZ-101

Tank Information Drivers

Question 1: What are the information drivers applicable to this tank? What type of information does each driver require from this tank? (Examples of drivers are Data Quality Objectives, Mid-Level Disposal Logic, RPP Operation and Utilization Plan, test plans and Letters of Instruction.) To what extent have the information and data required in the driving document been satisfied to date by the analytical and interpretive work done on this tank?

The information drivers for tank 241-AZ-101 are the Flammable Gas Data Quality Objective (DQO), Tank Safety Screening DQO, Low/High (Low Activity Waste and High Level Waste Feed Processing) DQO, Confirm Tank T is an Appropriate Feed Source for LAW and HLW Feed DQOs (Waste Feed Delivery), Tank 241-AZ-101 Mixer Pump DQO, Interface Control Document-23 (ICD-23) issue, Additional Americium-241 Analysis issue, Retrieval Equipment DQO, Air Emissions DQO, and the Dangerous Waste DQO. As of the date this report was prepared, July 1, 2000, the sampling and analytical results associated with this tank did not address the issues of ICD-23, or the Mixer Pump, Air Emissions and Dangerous Waste DQOs. The analytical results for the Mixer Pump DQO and Air Emissions DQO are not yet available, and the ICD-23 sampling is currently in progress. The issue of the Dangerous Waste DQO is currently being evaluated and will be applied as necessary. The remaining issues are discussed below.

Flammable Gas DQO: Does a possibility exist for releasing flammable gases into the headspace of the tank or releasing chemical or radioactive materials into the environment (Bauer and Jackson, 1998)?

The requirements to support the flammable gas issue are documented in the *Data Quality Objective to Support Resolution of the Flammable Gas Safety Issue* (Bauer and Jackson 1998). The Flammable Gas DQO has been extended to apply to all tanks. Analyses and evaluations will change according to program needs until this issue is resolved. Final resolution of the Flammable Gas issue is expected to be completed by September 30, 2001 (Johnson 1997).

Tank 241-AZ-101 is not on the Watch List for flammable gas (McCain 1999). No H_2 concentration exceeding the 6,250 parts per million (ppm) action level, as set by *Tank Waste Remediation System Final Safety Analysis Report* (CHG 2000a), has been recorded with the Standard Hydrogen Monitoring System (SHMS) installed in this tank. The highest H_2 concentration in a gas release event (GRE) recorded for tank 241-AZ-101 is 750 ppm, on April 18, 1998. McCain (1999) lists an average headspace H_2 concentration of 48 ppm, obtained from 4 grab samples between August 21, 1998 and May 21, 1999. These grab samples were taken from SHMS cabinet, as described in McCain (1999). McCain (1999) reports a baseline H_2 concentration in the tank of 50 ppm in the tank since November 1998, based on a Whittaker cell and in agreement with the grab samples. Based on these measurements, the flammable gas conditions in tank 241-AZ-101 do not exceed the action levels specified in Bauer and Jackson (1998).

The tank headspace was sampled for flammable gases prior to the 1995 and 1999 sampling events and the concentrations were below 25% of the lower flammability limit (LFL) in both cases.

Safety Screening DQO: Does the waste pose or contribute to any recognized safety problems?

Tank Safety Screening Data Quality Objective (Dukelow et al. 1995) identifies the data needed to screen the tank 241-AZ-101 waste for potential safety problems. These potential safety problems are exothermic conditions in the waste, flammable gases in the tank headspaces, and criticality conditions in the waste.

Reynolds et al. (1999) performed a formal review of the sampling data for tank 241-AZ-101 to determine if the safety screening DQO requirements were met. Reynolds et al. (1999) concluded, "An acceptable substitute analysis was performed in lieu of the analysis requirement in the safety screening DQO. Sampling and/or sample recovery was less than optimal. The sampling and analysis for this tank were reviewed and found to be adequate to satisfy the requirements of the safety screening DQO". Therefore, the safety screening DQO was not applied as a driver to the 1999 core sampling event, but the results were assessed against the DQO where available.

Exothermic reactions were not observed during the differential scanning calorimetry (DSC) analysis of the 1995 grab samples (Rollison 1995) from the supernatant. No DSC analyses were performed on the 1999 core samples. An alternative way to determine the energetic potential of a waste is to evaluate the total organic carbon (TOC) content. The decision threshold limit for total organic carbon listed by Dukelow et al. (1995) is 30,000 μg/g, dry-weight. The highest TOC measurement from the 1999 core sampling event was 9,850 μg/g wet weight in sample S00T000806W, from core 266. Water content was not measured on these samples, so dry weights could not be determined. However, water content can be estimated from mean solids content (62.5%) of the core 266 sludge composites. Using this value, the highest TOC value is converted to 15,750 μg/g on a dry weight basis, a quantity below 30,000 μg/g. There were no duplicate analyses for individual subsamples for TOC, so a 95% confidence interval could not be determined.

Flammable gas issues are addressed in the Flammable Gas DQO section above. Measurements of headspace for LFL prior to the 1995 grab and 1999 core sampling events were zero percent of the LFL. The highest H_2 concentration recorded for the tank was 750 ppm, well below 25% of the lower flammability limit. The lower flammability limit is conservatively set at 6,250 ppm by CHG (2000a). The baseline H_2 concentration in the tank is 50 ppm based on a Whittaker cell. Therefore, flammable gas is not an issue for this tank.

The safety screening DQO threshold value for the Criticality Prevention Specification is 1 g/L of plutonium (Dukelow et al. 1995). Assuming that all plutonium alpha activity is from plutonium-239, the 1 g/L threshold value is 61.5 μCi/mL for liquid. For liquids, gross alpha was not detected above a detection limit of 0.0625 μCi/mL. Resolution of high gross alpha values reported for tank 241-AZ-101 solids is reported by Fort (2000), and summarized here. Most of the gross alpha in the solids is from americium-241. For the solids, the sum of the plutonium isotopes in core 266 and core 269 was used. The highest plutonium concentration for the core 266 composite solids is 78.5 μg/g and for core 269 composite solids is 63.8 μg/g. Using the highest bulk density reported for this tank (1.74 g/mL), this comes to 0.121 g/L of plutonium in the core 266 solid composite and 0.164 g/L plutonium in the core 269 solid composite. Therefore, Fort (2000) concluded, "Both core

plutonium sampling results are less than the maximum plutonium Criticality Prevention Specification notification limit of 1 g/L".

Low/High (Low Activity Waste and High Level Waste Feed Processing) DQO: Do the samples taken from tank 241-AZ-101 and the subsequent laboratory analysis meet the needs of the *Low-Activity Waste and High-Level Waste Feed Processing Data Quality Objectives* (Low/High DQO) (Patello et al. 1999)?

Solubility screening, a requirement of the Low/High DQO (Patello et al. 1999), has not been performed on the core samples at the time this report was prepared. A test plan has been written (Person 1999), and these solubility screening tests are planned for the near future.

The Low/High DQO requires that tank composite liquid results for Group-One-analytes from tank 241-AZ-101 be compared against the LAW Envelope B Limits stated in that DQO (Patello et al. 1999). Group-One analytes are those analytes that have specific Envelope limits. The liquid results used are the 1999 core 269 drainable liquid composite data from the *Means and Confidence Interval* Standard Report, as required by the DQO. This comparison shown in Table 1-1 demonstrates that the non-radionuclide Group One analytes met the Envelope B limits. Cobalt-60 (270% of limit) and europium-154+155 (607% of limit) did exceed the limit, but the results for these analytes were below detection limits. These detection limits exceeded the minimum reportable quantities (MRQs) stated in Patello et al. (1999). Europium-154 had a much lower detection limit than europium-155. In the 1999 composite solids, where the europium isotope concentrations were above the detection limit, the europium-154 to -155 ratio was 1.38. If we assume the same isotopic ratio in the supernate, and apply this ratio to the europium-154 detection limit, then the europium-154+155 maximum mean is 0.164 μCi/L, which comes to 106% of the Envelope limits. Both europium isotopes have short half-lives, so the europium concentration would be expected to meet the Envelope limits by the time the tank is retrieved for feed.

Table 1-1. Comparison of Tank 241-AZ-101 Liquids to Envelope B Limits (2 pages)

Analyte	Mean (μg/mL)	Mean (moles/L)	Ratio to Na (mole/mole Na)	Envelope B Limits	Percent Envelope B Limits (%)
Al	8110	0.300576	0.0628	0.250	25.1
Ba	0.0839	6.11E-07	1.277E-07	1.00E-04	0.128
Ca	40.1[1]	0.001	2.09E-04	0.0400	0.523
Cd	4.14	3.68E-05	7.697E-06	0.004	0.192
Cl	172	0.00485	0.001	0.0890	1.14
Cr	742	0.0143	0.00298	0.020	14.9
F	2290	0.121	0.0252	0.20	12.6
Fe	24.9	4.46E-4	9.318E-05	0.010	0.932
Hg	0.0152	7.58E-08	1.584E-08	1.40E-05	0.113
K	4860	0.124	0.0260	0.180	14.4
La	0.0636[1]	4.58E-07	9.569E-08	8.30E-05	0.15
Na	1.10E+05	4.78	1	N/A[2]	N/A[2]
Ni	8.02[1]	1.37E-04	2.855E-05	0.003	0.952
NO_2	73400	1.59	0.333	0.380	87.7

Table 1-1. Comparison of Tank 241-AZ-101 Liquids to Envelope B Limits (2 pages)

Analyte	Mean (μg/mL)	Mean (moles/L)	Ratio to Na (mole/mole Na)	Envelope B Limits	Percent Envelope B Limits (%)
NO_3	5.90E+04	0.951	0.199	0.800	24.9
Pb	40.1[1]	1.94E-04	4.045E-05	6.80E-04	5.95
PO_4	1391	0.0146	0.0031	0.130	2.35
SO_4	15450	0.161	0.0336	0.070	48.0
TIC	6840	0.569	0.119	0.300	39.7
TOC	362	0.0301	0.00630	0.500	1.26
U	201[1]	8.45E-04	1.77E-04	0.00120	14.7
Analyte	Mean (μCi/mL)	Mean (Bq/L)	Bq analyte/ Mole Na	Envelope B Limits	Percent Envelope B Limits
TRU	0.0518[1]	1.917E+06	4.00E+05	4.80E+05	83.5
^{137}Cs	1900	7.03E+10	1.469E+10	2.00E+10	73.5
^{90}Sr	1.02	3.77E+07	7.99E+06	4.40E+07	17.9
^{99}Tc	0.439	1.62E+07	3.90E+06	7.10E+06	47.8
^{60}Co	0.0213[1]	7.88E+05	1.65E+05	6.10E+04	270
$^{154+155}Eu$	0.9416[1]	3.48E+07	7.28E+06	1.20E+06	607

Notes :

[1]Maximum value, based on a detection limit.

[2]No envelope limit on Na.

Patello et al. (1999) also requires that the tank solids be compared against the HLW Envelope D limits. The Envelope D requirements are in the form of grams of constituent in the oxide form per 100 grams of oxide in the waste. A measurement of weight percent oxides was made on the solids to assist in this comparison, but the samples dried before they were analyzed. As requested by Waste Processing Development (WPD) (Burgeson 2000), the envelope limits were compared on a dry weight basis; therefore, each concentration was divided by the weight fraction of solids prior to calculating the weight percent oxides. In addition, WPD has clarified that the sample results be compared against the Envelope D limits separately for core 266 and core 269, because of heterogeneity of the waste (Burgeson 2000). The analytically determined weight percent oxides were reported by Steen (2000b) to be 0.804 g oxide/ g dry waste for core 266 and 0.752 g oxide/ g dry waste for core 269. Tables 1-2 through 1-7 show the sample results in comparison to the Envelope D limits for the sludge in cores 266 and 269.

Table 1-2. Non-Volatile Elements From Core 269 in Comparison to Envelope D Limits (2 Pages)

Non-Volatile Element	g /100 g Waste Oxide	Envelope D Limit	% Envelope Limit
As	0.0132[1]	0.16	8.27
B	0.0598	1.3	4.60
Be	2.10E-09	0.065	3.23E-06
Ce	0.176	0.81	21.7
Co	0.0940	0.45	20.9

Table 1-2. Non-Volatile Elements From Core 269 in Comparison to Envelope D Limits (2 Pages)

Non-Volatile Element	g /100 g Waste Oxide	Envelope D Limit	% Envelope Limit
Cs	0.00949[2]	0.58	1.64
Cu	0.0487	0.48	10.1
Hg	4.27E-04	0.1	0.427
La	0.753	2.6	29.0
Li	0.130	0.14	92.9
Mn	0.229	6.5	3.52
Mo	.00936	0.65	1.44
Nd	0.458	1.7	26.9
Pr	0.0978	0.35	27.9
Pu	0.0143[3]	0.054	26.5
Rb	0.0360	0.19	18.9
Sb	0.00164[1]	0.84	0.196
Se	0.005[1]	0.52	1.05
Sr	0.0702	0.52	13.5
Ta	0.00164[1]	0.03	5.48
Tc	0.00289	0.26	1.11
Te	0.0181	0.13	13.9
Th	0.0596	0.52	11.4
Tl	0.00164[1]	0.45	0.365
V	6.62E-03[1]	0.032	20.7
W	0.00171	0.24	0.711
Y	0.0476	0.26	18.3
Zn	0.0196	0.42	4.66

Notes :

[1]Maximum value, based on a detection limit

[2]Based on the sum of isotopes 133, 135, and 137

[3]Based on the sum of isotopes 239, 240, 241, and 242

Table 1-3. Volatile Components From Core 269 in Comparison to Envelope D Limits

Volatile Components	g/100 g Waste Oxide	Envelope D Limits	% Envelope Limits
Cl	0.0320[1]	0.33	9.70
CO_3	5.73	30	19.1
NO_2 + NO_3 as NO_3	17.9	36	49.8
TOC	0.0687	11	6.24
Cyanide	0.00108[1]	1.6	0.0672
NH_3	0.0489[1]	1.6	30.6

Notes :

[1]Maximum value, based on a detection limit

Table 1-4. Radionuclides From Core 269 in Comparison to Envelope D Limits

Isotope	Ci/100g Waste Oxide	Envelope D Limits	% Envelope Limit
^{3}H	3.22E-06	6.50E-05	4.96
^{14}C	3.60E-07	6.50E-06	5.54
^{60}Co	9.16E-04	1.00E-02	9.16
^{90}Sr	3.84	1.00E+01	38.4
^{99}Tc	4.67E-05	1.50E-02	0.311
^{125}Sb	0.00565	3.20E-02	17.6
^{126}Sn	4.41E-05[1]	1.50E-04	29.4
^{129}I	1.03E-06[1]	2.90E-07	354
^{137}Cs	0.231	1.00E+00	23.1
^{152}Eu	0.0113[1]	4.80E-04	236
^{154}Eu	0.0109	5.20E-02	20.9
^{155}Eu	0.0147	2.90E-02	50.7
^{233}U	1.20E-06[1]	9.00E-07	134
^{235}U	2.39E-08[1]	2.50E-07	9.54
^{237}Np	1.02E-05	7.40E-05	13.8
^{238}Pu	3.29E-04[1]	3.50E-04	94.0
^{239}Pu	7.51E-04	3.10E-03	24.2
^{241}Pu	0.0749[2]	2.20E-02	340.6
^{241}Am	0.0195	9.00E-02	21.7
$^{243/244}Cm$	0.00256[1]	3.00E-03	85.2

Notes :

[1]Maximum value, based on a detection limit.

[2]Based on atomic mass unit 241, and subtracting the americium-241 contribution.

Table 1-5. Non-Volatile Elements From Core 266 in Comparison to Envelope D Limits (2 pages)

Non-Volatile Element	g/100 g Waste Oxide	Envelope D Limit	% Envelope Limit
As	0.0109[1]	0.16	6.83
B	0.0116	1.3	0.896
Be	1.45E-09	0.065	2.23E-06

Table 1-5. Non-Volatile Elements From Core 266 in Comparison to Envelope D Limits (2 pages)

Non-Volatile Element	g/100 g Waste Oxide	Envelope D Limit	% Envelope Limit
Ce	0.100	0.81	12.36
Co	0.00663	0.45	1.47
Cs	0.00446[2]	0.58	0.767
Cu	0.0333	0.48	6.94
Hg	Not measured	0.1	Not measured
La	0.301	2.6	11.6
Li	0.0746	0.14	53.3
Mn	0.195	6.5	3.01
Mo	0.00842	0.65	1.29
Nd	0.238	1.7	14.0
Pr	0.0549	0.35	15.7
Pu	0.0158[3]	0.054	29.2
Rb	0.0247	0.19	13.0
Sb	0.00145[1]	0.84	0.173
Se	0.00932	0.52	1.79
Sr	0.0721	0.52	13.9
Ta	0.00145[1]	0.03	4.83
Tc	0.00194	0.26	0.747
Te	0.0114[1]	0.13	8.77
Th	0.0225	0.52	4.32
Tl	0.00145[1]	0.45	0.322
V	0.00545[1]	0.032	17.04
W	0.00645	0.24	2.69
Y	0.00354	0.26	13.6
Zn	0.0121	0.42	2.87

Notes :

[1]Maximum value, based on a detection limit

[2]Based on the sum of isotopes 133, 135, and 137

[3]Based on the sum of isotopes 239, 240, 241, and 242

Table 1-6. Volatile Components From Core 266 in Comparison to Envelope D Limits

Volatile Components	g/100 g Waste Oxide	Envelope D Limits	% Envelope Limits
Cl	3.15E-04[1]	0.33	0.095
CO_3	5.18	30	17.2
NO_2 + NO_3 as NO_3	13.7	36	38.0
TOC	1.31	11	11.9
Cyanide	0.00211[1]	1.6	0.132
NH_3	1.39[1]	1.6	87.0

Notes :

[1]Maximum value, based on a detection limit

Table 1-7. Radionuclides From Core 266 in Comparison to Envelope D Limits

Isotope	Ci/100g Waste Oxide	Envelope D Limits	% Envelope Limit
^{3}H	2.89E-06	6.50E-05	4.44
^{14}C	4.48E-07	6.50E-06	6.89
^{60}Co	5.53E-04	1.00E-02	5.53
^{90}Sr	4.28	1.00E+01	42.8
^{99}Tc	2.87E-05	1.50E-02	0.191
^{125}Sb	0.00354	3.20E-02	11.1
^{126}Sn	4.19E-05[1]	1.50E-04	28.0
^{129}I	5.33E-07[1]	2.90E-07	184
^{137}Cs	0.160	1.00E+00	16.0
^{152}Eu	9.73E-04[1]	4.80E-04	203
^{154}Eu	0.00647	5.20E-02	12.4
^{155}Eu	0.00924	2.90E-02	31.8
^{233}U	1.14E-06[1]	9.00E-07	127
^{235}U	1.55E-08[1]	2.50E-07	6.21
^{237}Np	7.90E-06	7.40E-05	10.7
^{238}Pu	2.51E-04[1]	3.50E-04	71.7
^{239}Pu	5.20E-04	3.10E-03	16.8
^{241}Pu	0.0532[2]	2.20E-02	243
^{241}Am	0.00977	9.00E-02	10.9
$^{243/244}Cm$	0.00120[1]	3.00E-03	39.9

Notes :

[1]Maximum value, based on a detection limit.

[2]Based on atomic mass unit 241, and subtracting the americium-241 contribution.

Europium-152, iodine-129, uranium-233, and plutonium-241 exceeded the Envelope D limits in both cores (Tables 1-4 and 1-7). For all but plutonium-241, however, the concentrations were based on a high detection limit that may have over estimated their concentration. These detection limits met the minimum reportable quantities (MRQs) stated in Patello et al. (1999). The plutonium-241 value was determined from the measurement of the atomic mass unit 241 by inductively coupled plasma mass spectroscopy (ICP/MS), where the mass of americium-241, determined by alpha energy analysis, was subtracted out. Therefore, the variability associated with both the americium-241 and atomic mass unit 241 measurement goes into the plutonium-241 value. All non-radionuclide concentrations were within the Envelope D limits.

The Low/High DQO (Patello et al. 1999) state that the Group-Two analytes be measured but give no decision requirements relating to their concentrations. These results are reported in Steen (2000b) and the *Analytical Results* Standard Reports. Patello et al. (1999) state that niobium-93 should be measured by ICP/MS. Mass number 93 was measured by ICP/MS and those values are reported in the *Analytical Results* Standard Reports. These mass number 93 results, however, are not expected to represent the concentration of niobium-93 in tank 241-AZ-101 because the Origen2 model predicts that there is approximately 10,000 times more zirconium-93 than niobium-93 in this tank.

The MRQs asked for in the Low/High DQO (Patello et al. 1999) were not achieved in the liquids for vanadium, cobalt-60, iodine-129, europium-154, and europium-155. The MRQs for mercury, vanadium, ammonia, tantalum, thallium, cyanide, americium-243, curium-243+244, plutonium-238,

and tin-126 were not achieved for the solids fraction from core 266 and 269. The high radioactivity of these samples dictated that large dilutions be used (Steen 2000b), and these large dilutions limited the achievable detection limits.

The Low/High DQO (Patello et al. 1999) has a Percent Relative Standard Deviation (%RSD) requirement of 3.5% for sodium and 15% for all other analytes. These limits are applicable to both LAW and HLW. The %RSD of the analytes are reported in Steen (2000b). All of the analytes that failed the %RSD requirement are shown in Table 1-8. This statistic (% RSD) is not defined for analytes below the detection limit.

Table 1-8. Analytes that Failed the %RSD(2 pages)

Constituent	Method	Phase	% RSD
Cadmium	ICP	Liquid	43.1
Chloride	Ion Chromatography	Liquid	18.0
Cyanide[1]	Distillation	Liquid	57.5
Fluoride	Ion Chromatography	Liquid	16.3
Iron	ICP	Liquid	16.2
Nitrate	Ion Chromatography	Liquid	36.4
Oxalate[1]	Ion Chromatography	Liquid	22.9
Palladium[1]	ICP/MS	Liquid	122.6
Phosphate	Ion Chromatography	Liquid	27.0
Potassium	ICP	Liquid	16.6
Silicon[1]	ICP	Liquid	55.1
Sulfate	Ion Chromatography	Liquid	19.6
Technetium-99	Radiochemical	Liquid	21.9
Total organic carbon	Persulfate	Liquid	34.5
Uranium-238[1]	ICP/MS	Liquid	37.6
Zirconium[1]	ICP	Liquid	56.4
Aluminum	ICP-Acid Digest	sludge, core 266	33.7
Ammonia	Ion Selective Electrode-Water	sludge, core 266	27.3
Boron	ICP-Acid Digest	sludge, core 266	25.1
Nitrate	Ion Chromatography - Water	sludge, core 266	18.7
Nitrite	Ion Chromatography - Water	sludge, core 266	18.3
Oxalate[1]	Ion Chromatography - Water	sludge, core 266	26.5
Phosphorus	ICP-Acid Digest	sludge, core 266	26.5
Plutonium-238	Alpha Energy Analysis-Fusion	sludge, core 266	40.4
Plutonium-239/240	Alpha Energy Analysis-Fusion	sludge, core 266	18.2
Rubidium	ICP/MS-Acid Digest	sludge, core 266	43.8
Selenium	ICP/MS-Acid Digest	sludge, core 266	37.3
Technetium-99	Radiochemical-Fusion	sludge, core 266	16.3

Table 1-8. Analytes that Failed the %RSD(2 pages)

Constituent	Method	Phase	% RSD
Total organic carbon	Persulfate-Water	sludge, core 266	82.7
Total organic carbon	Coulometry-Water	sludge, core 266	22.2
Sodium	ICP-Acid Digest	sludge, core 266	9.55
Americium-241	AEA-Fusion	sludge, core 269	58.2
Bismuth[1]	ICP-Acid Digest	sludge, core 269	22.2
Boron	ICP-Acid Digest	sludge, core 269	24.6
C-14	Radiochemical-Water	sludge, core 269	28.8
Hydroxide[1]	Titration-Water	sludge, core 269	30.4
Potassium	ICP-Acid Digest	sludge, core 269	42.7
Ruthenium[1]	ICP-Acid Digest	sludge, core 269	133
Ruthenium[1]	ICP/MS-Acid Digest	sludge, core 269	17.6
Sodium	ICP-Acid Digest	sludge, core 269	10.7
Sodium	ICP-Fusion	sludge, core 269	6.35

Notes :

[1]Relative standard deviation exceeds Tables 7.1 and 7.2 (Patello et al. 1999) acceptance criteria but reanalysis is not required because analyte is not included in the Envelope limit.

LAW, Waste Feed Delivery (WFD) DQO: Does the liquid waste meet specifications as a LAW feed source for waste treatment?

The current data required to support waste feed delivery for Phase I low-activity waste are documented in *Data Quality Objectives for TWRS Privatization Phase I: Confirm Tank T is an Appropriate Feed Source for Low-Activity Waste Feed Batch X* (LAW WFD DQO) (Nguyen 1999a).

This DQO requires comparison of the supernate composition to the Envelope B limits stated in the DQO. These are identical to the limits in the Patello et al. (1999) DQO above, and are presented there. As stated above, cobalt-60 and europium-154+155 exceeded the Envelope limits because of high detection limits.

Nguyen (1999a) does not give a decision limit on the quantity of Envelope B waste this tank provides, but does require that the quantity be reported. Nguyen (1999a) states that 1 metric ton of Na = 2.6 units for Envelope B waste. At the time the core samples were taken, the supernatant was 3,018 kL (797 kgal), where the volume was determined from an ENRAF reading while subtracting the sludge volume (197 kL; 52 kgal). The sodium concentration was 110,000 μg/mL. From this data, 332 metric tons of Na is calculated for the tank 241-AZ-101 supernatant, which translates into 863 units.

This DQO requires that an appropriate dilution ratio be determined to give the waste a viscosity below 10 centiPoise, a specific gravity below 1.5, and a volume percent solids below 30%. Dilution studies are currently being performed on the tank slurry per Herting (1999).

For tanks with less than 1 M nitrate (such as tank 241-AZ-101), the DQO states that hydroxide concentration must be between 0.10 M and 5.0 M, the nitrite concentration must be between

0.011 M and 5.5 M, and nitrate/(hydroxide + nitrite) must be less than 2.5. The supernatant in tank 241-AZ-101 has a hydroxide concentration of 0.68 M, a nitrite concentration of 1.60 M, and nitrate/(hydroxide + nitrite) = 2.99. Thus, the nitrate/(hydroxide + nitrite) quantity is out of specifications.

The MRQs asked for in the DQO (Nguyen 1999a) were not achieved for 6 analytes: nickel, copper, titanium, zinc, cobalt-60, and uranium-234. Nickel and cobalt-60 are Group-One-analytes.

HLW, Waste Feed Delivery DQO: Does the solid waste meet specifications as a HLW feed source for waste treatment?

The current data required to support waste feed delivery for Phase I low-activity waste are documented in *Data Quality Objectives for RPP Privatization Phase I: Confirm Tank T is an Appropriate Feed Source for High-Level Waste Feed Batch X* (HLW WFD DQO) (Nguyen 1999b).

Dissolution tests, required by the DQO (Nguyen, 1999a) have not yet been performed. These tests are planned for the near future (Herting 1999).

The HLW WFD DQO (Nguyen 1999b) requires that the tank solids be compared against the Envelope D Requirements listed in the DQO. The HLW WFD DQO requires that the two cores be averaged and compared against the Envelope limits. The Envelope D requirements are in the form of grams of constituent in the oxide form per 100 grams of oxide in the waste. Each constituent concentration, in μg/g, was converted to grams of oxide using the stoichiometry presented in Nguyen (1999b). The total grams of oxide per gram of waste were determined by summing up the individual oxides. An attempt was made to measure the grams of oxides per gram of waste directly, but the samples dried before analysis (Steen 2000b). The comparisons required by Nguyen (1999b) are shown below in Tables 1-9 through 1-11. All non-radionuclides were within the Envelope D limits, but iodine-129 (234 %), europium-152 (193 %), uranium-233 (115 %), and plutonium-241 (254 %) exceeded the Envelope limits. The iodine-129, europium-152, and uranium-233 values were based on detection limits, and if better detection limits are achieved for these analytes in the future, it may be shown that they are within the envelope limits. Incidentally, the iodine-129 and uranium-233 detection limits were within the MRQs requested by Nguyen (1999b), so having a detection limit below the MRQs does not assure a detection limit that is within the envelope limits for these analytes. The plutonium-241 value was determined from the measurement of the atomic mass unit 241 by ICP/MS, where the mass of americium-241, determined by alpha energy analysis, was subtracted out. Thus, the variability associated with both the americium-241 and atomic mass unit-241 go into the plutonium-241 value. Americium-241 represents most of the mass unit-241 in the waste, and therefore, small errors in these measurements result in large errors in the plutonium-241 value.

Table 1-9. Non-Volatile Elements in Comparison to Envelope D Limits (2 pages)

Non-Volatile Element	g /100 g Waste Oxide	Envelope D Limit	% Envelope Limit
As	0.0106[1]	0.16	6.63
B	0.0315	1.3	2.42
Be	0.00153	0.065	2.35
Ce	0.119	0.81	14.7
Co	0.00693	0.45	1.54

Table 1-9. Non-Volatile Elements in Comparison to Envelope D Limits (2 pages)

Non-Volatile Element	g /100 g Waste Oxide	Envelope D Limit	% Envelope Limit
Cs	0.00749[2]	0.58	1.29
Cu	0.0349	0.48	7.26
Hg	3.56E-04	0.1	0.355
La	0.447	2.6	17.2
Li	0.090	0.14	64.6
Mn	0.168	6.5	2.58
Mo	0.00784	0.65	1.21
Nd	0.298	1.7	17.6
Pr	0.0664	0.35	18.9
Pu	0.0106[3]	0.054	19.6
Rb	0.0265	0.19	13.9
Sb	0.00136[1]	0.84	0.162
Se	0.00662[1]	0.52	1.27
Sr	0.0630	0.52	12.1
Ta	0.00136[1]	0.03	4.53
Tc	0.00211	0.26	0.813
Te	0.0128	0.13	9.88
Th	0.0348	0.52	6.70
Tl	0.00136[1]	0.45	0.302
V	0.00530[1]	0.032	16.6
W	0.00371	0.24	1.54
Y	0.0363	0.26	13.9
Zn	0.0137	0.42	3.26

Notes :

[1]Maximum value, based on a detection limit

[2]Based on the sum of isotopes 233, 235, and 137

[3]Based on the sum of isotopes 239, 240, 241, and 242

Table 1-10. Volatile Components in Comparison to Envelope D Limits

Volatile Components	g/100 g Waste Oxide	Envelope D Limits	% Envelope Limits
Cl	0.0280[1]	0.33	8.48
CO_3	4.79	30	15.9
NO_2 + NO_3 as NO_3	13.8	36	38.4
TOC	0.895	11	8.14
Cyanide	0.00143[1]	1.6	0.089
NH_3	0.853[1]	1.6	53.3

Notes :

[1]Maximum value, based on a detection limit

Table 1-11. Radionuclides in Comparison to Envelope D Limits (2 pages)

Isotope	Ci/100g Waste Oxide	Envelope D Limits	% Envelope Limit
^{3}H	2.69E-06	6.50E-05	4.13
^{14}C	3.60E-07	6.50E-06	5.53

Table 1-11. Radionuclides in Comparison to Envelope D Limits (2 pages)

Isotope	Ci/100g Waste Oxide	Envelope D Limits	% Envelope Limit
^{60}Co	6.39E-04	1.00E-02	6.39
^{90}Sr	3.60	1.00E+01	35.9
^{99}Tc	3.28E-05	1.50E-02	0.219
^{125}Sb	0.00400	3.20E-02	12.5
^{126}Sn	3.80E-05[1]	1.50E-04	25.3
^{129}I	6.78E-07[1]	2.90E-07	234
^{137}Cs	0.171	1.00E+00	17.1
^{152}Eu	9.25E-04[1]	4.80E-04	193
^{154}Eu	0.00756	5.20E-02	14.5
^{155}Eu	0.0104	2.90E-02	36.0
^{233}U	1.04E-06[1]	9.00E-07	115
^{235}U	1.72E-08[1]	2.50E-07	6.87
^{237}Np	1.92E-05	7.40E-05	25.9
^{238}Pu	2.54E-04[1]	3.50E-04	72.5
^{239}Pu	5.56E-04	3.10E-03	17.9
^{241}Pu	0.0560[2]	2.20E-02	254
^{241}Am	0.0127	9.00E-02	14.1
$^{243/244}Cm$	0.00162[1]	3.00E-03	54.0

Notes :

[1]Maximum value, based on a detection limit.

[2]Based on atomic mass unit 241, and subtracting out the americium-241 contribution.

The HLW WFD DQO (Nguyen 1999b), requires that the weight % oxides in the waste be reported and compared with minimum weight percentages required in the glass. This comparison is shown in Table 1-12 below. The purpose of this exercise is to allow the prediction waste loading in the glass and the number of glass canisters each batch of waste will create.

Table 1-12. HLW Glass Components Needed To Estimate The Number of Canisters Per Batch of HLW Feed (2 pages)

Oxide	Weight % Oxide	Minimum Weight % Oxide	Oxide	Weight % Oxide	Minimum Weight % Oxide
Fe_2O_3	18.0	12.5	Bi_2O_3	0.013	4.0
Al_2O_3	19.4	11.0	P_2O_5	0.190	3.0
$Na_2O + K_2O$	30.5	15.0	F	3.39	1.7
Zr_2O	61.8	10.0	$Al_2O_3 + ZrO_2$	25.5	14
UO_2	1.03	8.0	$Al_2O_3 + ZrO_2 + Fe_2O_3$	43.6	21
CaO	0.560	7.0	MgO + CaO	0.721	8.0
MgO	0.160	5.0	Cr_2O_3	0.137	0.5
BaO	0.122	4.0	SO_3	15.3	0.5
CdO	1.18	3.0	Ag_2O_3	0.0315	0.25
NiO	0.906	3.0	Rh_2O_3 +	0.768	0.25

Table 1-12. HLW Glass Components Needed To Estimate The Number of Canisters Per Batch of HLW Feed (2 pages)

Oxide	Weight % Oxide	Minimum Weight % Oxide	Oxide	Weight % Oxide	Minimum Weight % Oxide
			Ru_2O_3 + PdO		
PbO	0.0559	1.0	Total Other[1]	1.96	8.0
TiO_2	0.0094	1.0	Total[2]	37.5	40

Notes :

[1]Total of oxides not on this table

[2]Total of all waste oxides exclusive of Na_2O and SiO_2

ICD-23: Have the required samples been provided to the waste treatment plant contractor (BNFL 2000)?

Tank 241-AZ-101 is currently being sampled for the ICD-23 issue, as indicated in Adams et al. (2000). Per the letter of instruction (Templeton 2000a), 5 L of liquid and the equivalent to 250 grams of centrifuged solids will be obtained for the ICD-23 issue.

Additional Americium-241 Analysis: Has americium-241 analysis been performed in duplicate on three subsamples on each solid segment for the 1999 core sample event (Poppiti, 1999)?

Poppiti (1999) requested additional americium-241 analyses to support design and safety basis development of the vitrification facility. These analyses have been performed and the Americium-241 results, which ranged from 49.3to 116 μCi/g of centrifuged solids, are in the *Analytical Results* Standard Report. The data are also reported in Steen (2000a).

Retrieval Equipment DQO: Were shear strength measurements performed as designated in Bloom (1996)?

The shear strength measurements completed on undisturbed sludge from the 1999 sampling event were 450 Pascals on segment 16R of core 266, and 190 Pascals on segment 16 of core 269 (Steen 2000b).

Bounding Concentration Limits:

Sample results from the 1999 core sampling were screened against current bounding concentration limits used to develop the authorization source term. These bounding concentrations for aging waste tanks are found in Tables 4-1 and 4-2 of Section 18 of *River Protection Project Process Engineering Desk Instruction and Guidance Manual* (Adams 2000). Six solid and two liquid sample results from the cesium-137 analysis exceeded the bounding concentration limits. In addition, one ammonium analysis from the liquids exceeded the bounding concentration for an aging waste tank. Notification to the managers of Nuclear Safety and Licensing and Process Engineering were made (Templeton 2000b) in accordance with Adams (2000).

Air Lift Circulator and Mixer Pump Bump Test: Does running the air lift circulators (ALCs) or the mixer pump release gases above the vapor program required quantification limit (VPRQL) of five parts per billion by volume (ppmv) for organic analytes or 50 parts per million by volume (ppmv) for permanent gases?

An ALC test at four flow rates and a mixer pump bump test, where the mixer pumps were run for approximately five minutes, was performed in 1999. Gases were collected from the tank dome space via riser 24C with SUMMA® canisters, and quantified by gas chromatography mass spectrometry. Table 1-13 summarizes all of the gases that exceeded the VPRQL at each ALC flow rate in cubic feet per minute (cfm) during the ALC test (Bonfoey et al. 2000). Running the ALCs increased the hydrogen concentration above the baseline concentration and the VPRQL, but the concentration decreased with increasing flow rate. Increasing the ALC flow rate generally decreased the concentration of the gases of concern (Bonfoey et al. 2000), presumably because they were diluted.

Table 1-13. Gases Exceeding Vapor Program Required Quantification Limits During Air Lift Circulator Tests

Analyte	Baseline	Three cfm	Five cfm	Seven cfm	Ten cfm
Acetone	13 ppbv	11 ppbv	9.8 ppbv	10 ppbv	6.3 ppbv
Freon 11	86 ppbv	79 ppbv	42 ppbv	43 ppbv	30 ppbv
Tetrachloroethylene	16 ppbv	14 ppbv	5.5 ppbv	6.2 ppbv	7.3 ppbv
H_2	Below VPRQL	490 ppmv	110 ppmv	91 ppmv	Below VPRQL
CO_2	60 ppmv	Below VPRQL	Below VPRQL	Below VPRQL	Below VPRQL

The two mixer pumps in tank 241-AZ-101 were operated for approximately five minutes each on January 5, 2000. SUMMA canisters were used to collect samples from the tank headspace via riser 24C. The samples were collected approximately one hour after the operation of both mixer pumps. Eight analytes exceeded the VPRQLs in these samples, including acetone (13 ppbv), butanol (8.8 ppbv), 1-butanol (14 ppbv), 1,4-dioxane (8.2 ppbv), Freon-11 (71 ppbv), tetrachloroethylene (7.7 ppbv), hydrogen (390 ppmv), and carbon dioxide (86 ppmv) (Bonfoey et al. 2000).

Heat Load Estimate:

Heat generation and temperature are factors affecting tank safety. Radioactive decay generates heat in the tanks. Agnew et al. (1997a) estimated the heat load to be 77,300 W (264,000 Btu/hr) based on process history. The heat load estimate from the best-basis inventory is 72,000 W (245,700 Btu/Hr), as shown in Table 1-14. All of these estimates are less than the 1,172,000 W (4,000,000 Btu/hr) operating specification limit for this tank (Fowler 2000).

Table 1-14. Heat Load Estimate Based on Best Basis Inventory

Radionuclide	Waste Inventory (Ci)	Decay Heat (W/Ci)	Heat Load (W)
^{90}Sr	5.65E+06	0.00669	37,800
^{137}Cs	7.09E+06	0.00472	33,500
^{241}Am	2.47e+04	0.00328	800
Total			72,000

Tank History

Question 2: What is known about the history of this tank as it relates to waste behavior?

The AZ Tank Farm contains two 100-series, double-shell tanks. Tank 241-AZ-101 has a design capacity of 3,790 kL (1,000 kgal), a diameter of 22.9 m (75 ft), and an operating depth of 11 m (35 ft). Additional tank descriptive material is located in Standard Reports *Description of Tank, Tank Plan View, Tank Profile View*, and *Riser Configuration Table*.

Tank 241-AZ-101 went into service in 1976. It soon began to receive a mixture of evaporator feed, double-shell slurry feed, complexed waste, and non-complexed waste totaling 3,610 kL (953 kgal) by 1980 (Agnew et al. 1997b). Tank 241-AZ-101 provided waste feed to the 242A evaporator-crystallizer during three campaigns: 81-1, 82-1, and 83-1 and was emptied in the third quarter of 1983. The tank then received aging waste from the Plutonium Uranium Extraction (PUREX) plant from 1983 to 1986. The remainder of the fill history consists of a series of small additions from tanks 241-AZ-102 and 241-AY-102 as well as transfers of dilute non-complexed waste.

A major ventilation system upgrade was made on the AZ/AY tank farm in 1998. This upgrade included a new stack, ventilation fans, emission control equipment, emission monitoring equipment, and connecting piping (DOE/RL 1998). In addition, this modification allows for an increased air flow rate from 0.4 m^3 per second to 0.5 m^3 per second.

Tank 241-AZ-101 underwent mixer pump tests from April 27 through June 2, 2000. The tests had three main objectives. One objective was to check that the two, 300-horsepower pumps could be operated within operating requirements. Another objective was to determine that the pumps could mobilize the sludge waste in sufficient quantities to provide feed to the waste treatment plant. The third objective was to check that the tank instrumentation was capable of monitoring sludge mobilization and mixer pump operation. Based on a preliminary review of the available data, all the tests were successful (Carlson et al. 2000).

Tank 241-AZ-101 is currently active, receiving small volumes of wash water periodically. The tank contains 3,448 kL (911 kgal) (Table 8-1) of aging waste and is listed as sound (Hanlon 2000).

Tank Comparisons

Question 3: What other tanks have similar waste types and waste behaviors, and how does knowledge of the similar tanks contribute to the understanding of this tank?

The predominant waste type for tank 241-AZ-101 is neutralized current acid waste (NCAW) waste. Tank 241-AZ-102 was also used for aging waste storage. This NCAW waste was added to tank 241-AZ-101 between 1983 and 1986 while tank 241-AZ-102 received NCAW between 1986 and 1990. The exact composition of NCAW varied with each processing run.

Tank 241-AZ-102 contains more sludge than tank 241-AZ-101 (397 kL versus 197 kL in the respective tanks). The sludge volume in tank 241-AZ-102 is larger than in tank 241-AZ-101 for several reasons. First, tank 241-AZ-102 contained a larger initial waste heel at the time PUREX waste was added than tank 241-AZ-101. Second, a larger fraction of the tank aluminum precipitated in tank 241-AZ-102 than tank 241-AZ-101 as a result of a lower hydroxide concentration. Third, more ferrous sulfamate was used to process the reactor fuels associated with the tank 241-AZ-102 waste because of the implementation of neptunium recovery.

A comparison was done on the recent analytical data from tanks 241-AZ-101 and 241-AZ-102 from samples taken in 1998 and 1999. The data from the two tanks agreed closely in many areas including the radionuclide data. Notable exceptions to this agreement include higher plutonium-239/240 concentration in tank 241-AZ-102 liquid layer, higher phosphate and aluminum concentration in tank 241-AZ-101 liquid layer and higher zirconium concentration in tank 241-AZ-101 solid layer. These exceptions were at least 3 times higher in concentration than that of the other tank.

Disposal Implications

Question 4: Given what is known about the waste properties and waste behaviors in this tank, what are the implications of the waste properties and behaviors to the waste retrieval/processing methodologies and equipment selection?

Both the solids and liquids of tank 241-AZ-101 have been selected as feeds sources for Phase I vitrification. According to *Tank Farm Contractor Operation and Utilization Plan* (Kirkbride et al. 2000), the tank supernate will provide LAW feed for Envelope B, and the solids will provide HLW feed for Envelope D.

Tank 241-AZ-101 has passed the Envelope B limits for LAW, except for cobalt-60 and europium-154+155. The nitrate, nitrite, and hydroxide ratios did not meet the requirements set by Nguyen (1999a). Hydroxide may need to be added to this tank to meet the DQO requirements. Uranium-233, iodine-129, europium-152 and plutonium-241 did not meet the Envelope D limits for HLW. All of these constituents in both LAW and HLW except for plutonium-241 were below the analytical detection limits. If better detection limits are achieved than it may be found that these constituents do indeed meet the Envelope requirements.

The MRQs required by Patello et al. (1999) and Nguyen (1999a;b) were, for many analytes, not met. These MRQs were determined by looking at the detection limits achieved for waste from other

tanks. Tank 241-AZ-101 waste is more radioactive than most tanks at Hanford, and, therefore required more dilution to work with in the laboratory than most other tanks. Consequently, the detection limits achieved for waste from other tanks may not be achievable for tank 241-AZ-101.

Additional solubility screening and dissolution studies need to be performed in support of the LAW and HLW WFD DQOs (Nguyen 1999a; b), as well as the Low/High DQO (Patello et al. 1999). Test plans have been written to support these studies (Herting 1999; Person 1999).

One shear strength measurement was made on each of the two cores taken in 1999. Core 266 had a shear strength of 450 Pa, and core 269 had a shear strength of 190 Pa. The purpose of the shear strength measurements is to determine if the sludge can be mobilized with a mixer pump. An in-situ test has already demonstrated that the waste can be successfully mobilized with mixer pumps (Carlson et al. 2000).

Mixer pumps have been installed to suspend the tank solids so that they can be transferred to the waste treatment plant. A mixer pump test was performed between April 27 and June 2, 2000, with two mixer pumps. Carlson et al. (2000) reviewed the mixer pump operation and reports that the mixer pumps were able to clear at least 95% of the tank bottom and uniformly suspend the tank solids. Carlson et al. (2000) suggests that more solids were suspended at higher pump speeds than at lower pump speeds and with both pumps operating than with just one operating. One pump operating at a high speed was more effective than two pumps operating at minimum speed. Significant solids settling occurred within 12 hours of mixer pump shut off (Carlson et al. 2000). Nine sets of grab samples and four vapor samples were collected at various times during the mixer pump test. These results are not yet available. The Notice of Construction limit of 50-ppm organics (Szyszkowski and Wilson 1997) out the 702-AZ stack was not exceeded during the mixer pump test.

No visible organic layer was observed in the 1995 grab sample or 1999 core samples (Rollison 1995; Steen 2000b). Some volatile organics, however, did slightly exceed the VPRQL during the mixer pump bump tests and while running the air-lift circulators (see Question #1).

Scientists Assessment of Data Quality and Quantity

Question 5: Given the current state of understanding of the waste in this tank on the one hand and the information drivers on the other; should additional tank data be sought via sampling/analysis from a strictly technical point-of-view? Can the waste behavior in this tank be adequately understood by other means (eg. archive samples, tank grouping studies, modeling) without additional sampling and analysis? If so, what characteristics of the tank waste lend themselves to a non-sample alternative? Is the quality of the data from this tank adequate from a field sampling and analytical laboratory point-of-view? Are there any clarifications or explanations needed for the data tables and figures?

Sampling and Analysis

The following DQOs and waste issues have been addressed for this tank: Flammable Gas, Safety Screening, Additional Americium-241 Analyses, Low/High DQO, as well as the LAW and HLW WFD DQOs. No additional sampling or analyses are necessary to satisfy the Additional Americium-241 Analysis issue or the flammable gas requirements for this tank. Additional samples

testing is being performed to support the Low/High DQO as well as the LAW and HLW WFD DQOs, but the data is not yet available.

The core sampling events from 1999, performed in support of the Low/High and WFD DQOs, was adequate for the tank liquids. The solids recovery, however, was inadequate and the solids recovered may not accurately reflect the typical solids in the tank. Analytically, the solids from core 266 did not match the expected inventory for the tank based on process estimates. Large concentrations of sulfate were found in the core 266 sludge that diluted out all of the other analytes. Approximately 95% of the two-liter tank composite prepared for core 266 was spilled in the laboratory hot cell while being slurried (Steen 2000b). Consequently, the solids that remained and were analyzed was material that was not suspended during the attempt to slurry the waste. This solid material does not appear to represent the typical tank waste. A homogeneity check was performed using IC and ICP results on the liquid segments, and were concluded to be homogeneous. Therefore, the remaining core 266 tank composite liquids were not analyzed. The sludge in core 269 more closely resembled previous cores and process estimates than core 266, though it appears to be low in iron and aluminum (see question #8). New solid grab samples have been taken (Templeton 2000d), but these results are not yet available.

Data Quality

1989 Core Sample Data

Data from a 1989 grab sample of the tank is available and is somewhat representative of the tank because little waste has been added to the tank since 1989. The sludge data, however, needs to be modified before use because aluminum has precipitated in the sludge since 1989. A discussion of how to modify the data to apply to the current sludge in the tank is discussed in Question # 8. The 1989 core sample data was not sampled for any current issues relevant to the tank, and is discussed in previous tank characterization reports (Lambert 1998; Templeton 1999). Only tank composite results are in the *Analytical Results* Standard Reports, other treatments are reported in Gray et al. (1993) or Peterson et al. (1989). Some of these treatments include washing the solids and flocculating with ferric nitrate. A mass balance between the washed solids and the original core composites was evaluated. For the core from riser 15F, this mass balance showed 20 to 60% more barium, calcium, strontium, zirconium, and iron, and 50% less sulfate in the products than the original core composites (Peterson et al., 1989). For the core from riser 24D, twice as much potassium was recovered in the washing products as found in the core composites, and the recoveries in washing products for nitrite (171 %), nitrate (146 %) and phosphate (406 %) were also high (Gray et al. 1993). It is not clear if these were the result of poor analyses on the original composites or on the treated materials.

1995 Grab Sample Data

Only a limited set of analyses was performed on the 1995 grab samples, and they are reported in Rollison (1995). The %RPDs were less than 15% for all analyses except for sulfate in sample S95T000307, which was 16.8%. The spike recovery for nitrate in sample S95T000305 was 120.3%. This data was not needed for any issue currently applicable to this tank. Issues addressed by this sample were evaluated in a previous tank characterization report for tank 241-AZ-101 (Templeton 1999).

1999 Core Sample

Solid core composites were created as requested by Templeton (2000c). For core 266, the solids from segment 16 and 16R were combined. For core 269 segments 16, 16R, 16R1, and 16R2 were combined.

Whole tank composites were prepared as requested by Templeton (2000c), and liquid and solid materials were combined. The liquid was subsequently separated from the solids for analysis by centrifugation (Steen 2000b).

The composite sample (S00T00748) for core 266 was dropped during hotcell processing. Most of the liquid material was not recovered from the spill and what was recovered was insufficient for the required analysis. Some analyses were performed on the solid material, but insufficient amounts of solids were recovered from core 266 to perform the bulk density, mercury, graphite furnace analysis, and total organic as well as total inorganic carbon analyses (Steen 2000b).

The detection limits for some analytes did not meet the MRQs required in the Tank Sample Analysis Plan (TSAP) (Steen 2000b). The high concentrations of some analytes required large dilutions, and when these diluted samples were analyzed by multi-elemental techniques, analytes with low concentrations were often diluted out. In addition, the high radioactivity of the samples forced high dilutions and small sample sizes.

Ammonia, Cyanide and Mercury

A relative standard deviation (RSD) of greater than 15% was reported for ammonia and cyanide in the core 269 liquids. Steen (2000b) states that the low ammonia and cyanide concentration in the waste decreased precision. Standard and spike recoveries were within the required limits for these analytes.

A (RSD) of greater than 15% was recorded for mercury in core 269 solids, and is attributed to the low concentration of mercury in the waste (Steen 2000b). Standard and spike recoveries for mercury were within the required limits. The composite for core 266 did not yield enough material for mercury analysis (Steen 2000b).

Ion Chromatography and Inductively Coupled Plasma Atomic Emissions Spectroscopy

One subsample for IC and ICP from segment number seven from core 269 was dropped and no analysis was performed on this segment.

Templeton (2000e) did not specify any quality control (QC) requirements for the IC and ICP analysis done on individual segments because this analysis was only to test for homogeneity in the liquids.

Relative standard deviations of greater than 15% were reported for fluoride, nitrate, nitrite, and oxalate for core 266 solid composite. For the core 269 composite, chloride, fluoride, nitrate, oxalate, phosphate, and sulfate, had RSDs greater than 15%. Steen (2000b) attributed these high RSDs to sample inhomogeneity. The solid digests were performed remotely in the hotcell, making it

difficult to ensure sample homogeneity. The standard and spike recoveries were within the limits required by Templeton (2000e) for all IC analytes.

Steen (2000b) identified a number of QC problems for the ICP analysis of the 1999 cores. Cadmium, iron, phosphorus, and silicon had RSDs greater than 15% for the core 269-core composite liquids. Aluminum, boron, and phosphorus for core 266 and boron, bismuth, potassium, and ruthenium for core 269 solids had RSDs greater than the 15% limit specified in Templeton (2000e). Analysis of sodium by ICP gave a RSD value greater than the required 3.5% limit. Matrix spike recoveries for aluminum, silver, cadmium calcium, iron, sodium, potassium, silicon, sulfur, and zirconium were outside the 75% to 125% limit. Steen (2000b), however, attributes these spike failures to the small amount of spike added relative to the concentration in the sample. When there are high concentrations of analytes, it is difficult to add sufficient spike material for a meaningful analysis. Matrix spikes on diluted samples were acceptable for all analytes except potassium. Standard recoveries for acid digestions were outside the 80% to 120% limit for boron, calcium, sodium, and silicon because it was difficult to weigh samples accurately in the hotcell. A standard recovery of 79.2% was recorded for bismuth in the core 269 liquid composite samples.

Inductively Coupled Plasma Mass Spectrometry

For ICP/MS analysis, RSDs exceeded the limit (15%) for selenium, rubidium, ruthenium, zirconium, and uranium-238, in the tank solids and for palladium in the liquid subsamples (Steen 2000b). Steen (2000b) said that the low precision was the result of the analyses being below the detection limit. Spike and standard recoveries were outside the limit (70 to 130% spike; 90 to 110% standard) for mass unit 90, 93, and 241, as well as, cerium, uranium 235, and praseodymium. The spike recovery failures were attributed to a high sample concentration relative to the spike concentration (Steen 2000b).

Palladium determination by ICP/MS is susceptible to interferences from cadmium isobars and zirconium compounds. The acid digests, which were analyzed by ICP/MS, contained notable concentrations of both zirconium and cadmium (Steen 2000b). Therefore, the palladium result is potentially biased high. Ruthenium, also, may suffer from a high bias from polyatomic ions and isobaric interferences (Steen 2000b). Steen (2000b) noted a 2X difference between two ruthenium isotopes monitored. Inductively coupled plasma mass spectrometry data were not used for palladium or ruthenium in the *Best-Basis Inventory* Standard Report.

The ICP/MS data for cesium-137 in the core 269 solids was 10 to 16 times larger than the cesium-137 results determined by gamma energy analysis (GEA). The tank temperature and solubility of cesium does not support the presence of the cesium-137 determined by ICP/MS, and this data was not used in the *Best-Basis Inventory (Radionuclides)* Standard Report or for any of the issues in question #1.

Total Inorganic Carbon/Total Organic Carbon (TIC/TOC)

Analysis of TIC/TOC by persulfate exceeded the 15% RSD limit in the core composite samples of core 266 and the liquid composites for core 269 (Steen 2000b). The high radioactivity of the waste forced the use of small sample sizes (<0.05 grams), and inhomogeneity was likely the cause of high RSDs. A high RSD (> 15%) was also reported for TOC analysis by combustion for core 266 composites, and attributed to inhomogeneity (Steen 2000b).

Gamma Energy Analysis, and other Radiochemical Analyses

Steen (2000b) reports that all QC parameters required by Templeton (2000e) were met for all analytes measured by GEA, tritium, and iodine-129. There was insufficient sample from segment 14 of core 266 and segment 7 of core 269 to analyze for cesium-137.

A standard recovery for carbon-14 for core 266 solid core composites was outside the required range of 80% to 120% (Steen 2000b). A spike recovery was also outside the required range of 75% to 125% was also reported for core 266 solid composite subsamples. The RSD for carbon 14 was less than 15%. Results below the detection limit lowered the sample precision for carbon-14.
An RSD above 15% was recorded for technicium-99 in the core 266 solid composite subsamples and americium-241/curium243/curium244 in the liquid composite subsamples, but the standard recoveries were adequate. The sample results were near the detection limit, which decreased the precision.

The laboratory does not currently have a procedure for performing the curium-242 analysis (Steen 2000b).

Total beta was not performed on the solid composites. No QC parameters were stated in the TSAP (Templeton 2000e) for total alpha or total beta, but the analyses were within the typical QC limits for the laboratory.

For plutonium-238/239 analysis, the RSD for the core 266 composite solid subsamples was higher than the limit reported by Templeton (2000e). The results were very close to the detection limit, which increased variability (Steen 2000b).

Clarification and Explanation of Data Tables and Figures.

The *241-AZ-101 HTCE Surface Levels* and *241-AZ-101 Average Monthly Tank Surface Level* Standard Reports: These reports show that the surface level has fluctuated substantially since the last PUREX waste transfer into the tank in 1986. These fluctuations are attributed to evaporation and the addition of small quantities of wash water. A record of evaporation and water additions can be found in the *Tank Transfers* standard report. The increase in tank waste level and volume of May 2000 is attributed to a 64 kL (17 kgal) "unknown" increase in waste volume and the addition of 159 kL (42 kgal) of flush water.

The *241-AZ-101 Tank Temperature Profile* Standard Reports: This profile reports the maximum temperature for the thermocouples in the tank waste as a function of time. The increases in waste temperature evident from March through June 2000 are associated with the tank 241-AZ-101 mixer pump tests that occurred during that time. During the test, the mixer pumps redistributed the warm sludge from the bottom of the tank and caused localized heating around the thermocouples near the tank bottom. The operation of the mixer pumps themselves also caused some increase in the bulk waste temperature. After completion of the mixer pump tests, the waste temperature began to decline again as expected.

The *241-AZ-101 Core Profiles* Standard Reports: The sampling dates shown on this report are inclusive of, but may not be identical with, the sample dates reported on the segment chain-of-

custody forms. This report shows that the lowest elevation sampled is nearly 15 cm (6 in.) from the tank bottom. Furthermore, the amount of sludge recovered is much less than expected. These two observations may indicate either a hard sludge layer that the push-mode sampling method could not penetrate, or that the tank bottom elevation is not correct, or that the bottom detector went off prematurely. The sludge layer is scheduled to be core sampled again after the mixer pump tests; the additional core sampling effort may provide information to determine which explanation (or combination of explanations) is correct.

The *Tank 241-AZ-101 Transfers (1994 to present)* Standard Reports: This report ignores individual waste volume transfers of less than 11 kL (3 kgal), and evaporation losses. Consequently, the correct total of flush water transferred into the tank is over the time period shown is 1,836 kL (485 kgal). Over the same period of time, 1,968 kL (520 kgal) of water is estimated to have evaporated from the tank.

Unique Aspects of the Tank

Question 6: What are unique chemical, physical, historical, operational or other characteristics of this tank or its contents?

Tank 241-AZ-101 is uncommon in that it is a double-shell tank designed to provide storage space for high-level aging waste generated at the PUREX Plant. Aging waste tanks have a special support system to allow the tanks to store high-heat generating wastes with minimum probability of loss of integrity. The support system includes a tank preheating system comprised of a steam coil, a waste mixing system comprised of 22 airlift circulators, and an exhaust condenser system to control condensation in the exhaust stream. The only double-shell tanks containing these systems are tanks 241-AY-101, 241-AY-102, 241-AZ-101, and 241-AZ-102.

The current tank 241-AZ-101 contents consist of NCAW and dilute non-complexed waste. The majority of the NCAW waste is limited to tanks 241-AZ-101 and 241-AZ-102. The NCAW waste resulted from the first-cycle solvent extraction step in the PUREX processing of zirconium-clad N Reactor fuel elements. Following the removal of cladding, irradiated nuclear fuel was dissolved in nitric acid. The dissolved nuclear fuel was then fed to a solvent extraction system that removed most of the neptunium, plutonium, and uranium. The waste stream was then concentrated and most of the nitric acid was extracted. The waste was then neutralized with sodium hydroxide before being transferred to the aging-waste tanks.

During the additions of the NCAW waste between 1983 and 1986, solids from the waste additions settled to the bottom of the tank, creating a sludge waste layer below the supernatant. The aluminum concentration in the sludge layer increased, and the supernate has decreased between the 1989 and 1999 core sampling events. Presumably, aluminum precipitated during this period.

Means and Confidence Intervals

Question 7: What statistical model was used to generate the means and confidence intervals? What data was included in the calculations?

A nested analysis of variance (ANOVA) model was fit to the laboratory sample data. Mean analyte concentrations, and 95% confidence intervals on the mean, were estimated using results from the

ANOVA. Two variance components were estimated and used in the computations. The variance components represent concentration differences between laboratory samples and between analytical replicates.

The model is:

$$Y_{ij} = \mu + L_i + A_{ij},$$

$$i=1,2,\ldots,a;\ j=1,2,\ldots,n_i;$$

where

Y_{ij} = concentration from the jth analytical result from the ith riser

μ = the mean

L_i = the effect of the ith laboratory sample

A_{ij} = the analytical error

a = the number of laboratory samples

n_i = the number of analytical results from the ith laboratory sample.

The variable L_i is a random effect. This variable and A_{ij} are assumed to be uncorrelated and normally distributed with means zero and variances $\sigma^2(L)$, and $\sigma^2(A)$, respectively.

The restricted maximum likelihood method (REML) was used to estimate the mean concentration and standard deviation of the mean for all analytes that had 50% or more of their reported values greater than the detection limit. The mean concentrations and standard deviations of the mean were used to calculate the 95% confidence intervals.

Some analytes had results that were below the detection limit. In these cases the value of the detection limit was used for non-detected results. For analytes with a majority of results below the detection limit, a simple average is reported.

The lower and upper limits, LL(95%) and UL(95%), of a two-sided 95% confidence interval on the mean were calculated using:

$$\text{LL}(95\%): \hat{\mu} - t_{(df,\ 0.025)} \times \hat{\sigma}(\hat{\mu})$$

$$\text{UL}(95\%): \hat{\mu} + t_{(df,\ 0.025)} \times \hat{\sigma}(\hat{\mu}).$$

In these equations, $\hat{\mu}$ is the REML estimate of the mean concentration, $\hat{\sigma}(\hat{\mu})$ is the REML estimate of the standard deviation of the mean, and $t_{(df,\ 0.025)}$ is the quantile from Student's t distribution with *df* degrees of freedom. The degrees of freedom are the number of laboratory samples with data minus one. In cases where the lower limit of the confidence interval was negative, it was reported as zero.

The means reported for americium-241, gross alpha, and bulk density in the *Means and Confidence Interval* Standard Report are the means of the centrifuged solids and do not include the analysis on the uncentrifuged material available. For a description of the sample compositing, see Templeton (2000c)

Best-Basis Inventory Derivation

Question 8: What is the source data used to derive this tank's Best-Basis inventories by mass (kg) and activity (Ci) for the standard list of 25 chemicals and 46 radionuclides?

The Best-Basis Inventory (BBI) effort involves developing and maintaining waste tank inventories comprising 25 chemical and 46 radionuclide components in the 177 Hanford Site underground storage tanks. These best-basis inventories provide waste composition data necessary as part of the River Protection Project (RPP) process flow sheet modeling work, safety analyses, risk assessments, and system design for waste retrieval, treatment, and disposal operations.

Development and maintenance of the best-basis inventory is an on-going effort. New sample data were recently made available for double-shell tank 241-AZ-101, so a re-evaluation of the best-basis inventories was performed and is documented in the following text. The following information was used in this evaluation:

- Average analytical results for supernatant segments from the 1999 core sampling event (see *Means and Confidence Interval* Standard Report).

- Average analytical results for the composite liquids and solids data for core 269, from the 1999 core sampling event (see *Means and Confidence Interval* Standard Report).

- Average analytical results from 1989 core sampling events (Peterson et al. 1989; Gray et al. 1993).

- Data for the Tank 241-AZ-101 supernatant mixing model (SMM) and the Tank Layer Model (TLM) from the Hanford Defined Waste (HDW) model document (Agnew et al. 1997a).

- Data from the Origen2 Model for Tank 241-AZ-101.

Table 8-1. Tank 241-AZ-101 Best-Basis Inventory Source Data(2 pages).

Waste Phase	Waste Type	Applicable Concentration Data	Associated Density	Associated Volume
Supernatant	Dilute non-complexed	1999 Core Supernate Segment Means	1.22	3,251 kL (859 kgal)
		1999 Liquid Core 269 Composite means	1.22	
		SMM HDW model for tank 241-AZ-101	1.10	

Table 8-1. Tank 241-AZ-101 Best-Basis Inventory Source Data(2 pages).

Waste Phase	Waste Type	Applicable Concentration Data	Associated Density	Associated Volume
Sludge	NCAW	1989 sludge sample concentration	1.67	197 kL (52 kgal)
		TLM HDW for AZ-101	1.50	
		Core 269 reconstituted solids means	1.62	
		Combined Process Knowledge: Origen2, Iodine129, and Al.	1.62	
Total				3,448 kL (911 kgal)

The total tank volume was taken from a July 1, 2000 manual ENRAF reading of 331.32 inches. The sludge volume is calculated from the average sludge level measurement from February 3, 2000. Included in this average is a 23.9 inch measurement from riser 24D taken in 1989. This 1989 measurement was included in the average because there is known to be a mound below riser 24D (Lambert 1998), and more recent measurements were not available for that riser. Since February 3, 2000, mixer pumps have been run in the tank, which changed the physical properties of the sludge (Carlson et al. 2000). Running the mixer pumps may have altered the sludge volume and bulk density, but the total inventory should not change. Therefore, the sludge was assumed to have the same volume and bulk density after the mixer pumps were run as before. Laboratory sample results from the grab samples collected during the mixer pump test are not yet available.

A separate drainable interstitial liquid inventory was not determined for this tank because the core segments containing the sludge also contained supernatant, making drainable liquid measurements impossible. Assuming an average in-tank sludge drainable porosity of 0.15 (Field and Vladimiroff 1999), the volume of drainable interstitial liquid (DIL) present in the sludge was estimated to be 30 kL (8 kgal). A capillary height was not included in the DIL calculation. The supernatant volume was determined by subtracting the sludge volume from the total volume.

The sample data available to describe the supernatant in this tank are data from supernate segments and liquid composites made from the 1999 core sample. Data from a 1995 grab sample are available, but were not needed because all of the analytes in this vector are available in the 1999 core vectors. The 1999 liquid core composite data are from an analysis of a mixture of supernate and sludge interstitial liquid, mixed at the ratio that they occur in the tank. This vector is assumed to represent the supernatant because the interstitial liquid volume is a small fraction of the supernatant volume. The 1999 core segment data set is the preferred vector because it is the mean of more analyses. The cesium-137 mean from the composite vector is used instead of the segment data because the composite cesium-137 mean is more consistent with other analysis and process estimates for the tank, and because there were only four replicates for this analyte in the segment means vector. The 1999 core composite data had a high detection limit for europium-155. A more accurate estimate for europium-155 was made by assuming that the supernatant had the same europium isotope ratio as the sludge (1.38), where both europium-154 and europium-155 were

measured. This ratio was applied to the europium-154 detection limit in order to calculate a more accurate inventory for europium-155. The sample data were supplemented by the Supernate Mixing Model (SMM) (Agnew et al. 1997a) for minor radionuclides that were not measured or had inadequate detection limits.

The core 269 composite solids vector is the means from the solids composite samples for core 269, taken in 1999. This vector is the preferred vector because it is the most recent, and the sludge samples were taken concurrently with the supernatant. The acid data were used instead of the fusion data for Ni, Si, and B, because the fusion data were considerably higher than the acid data. Most likely, the Ni in the fusions came from the nickel crucible, and the B and Si came from the leaching of borosilicate glassware. The cesium-137 value determined by gamma energy analysis (GEA) was used instead of the ICP/MS data because the ICP/MS data are a factor of 16 larger than the GEA data. The tank temperature and evaporation rate does not support the presence of the cesium-137 inventory calculated from the ICP/MS data. The 1989 Core Solids vector is derived from the means from two cores taken at that time period. These data are not included in the *Analytical Results* Standard Report, but can be found in Peterson et al. (1989) and Gray et al. (1993) and in the TWINS historical database (CHG 2000b). The HDW tank 241-AZ-101 Tank Layer Model (TLM)(Agnew et al. 1997a) is used for minor radionuclides that were not measured in the 1989 or 1999 sampling events. The 1989 core solids vector was used over the 1999 core for iron, because the iron inventory predicted by the core 269 data is not very close to the iron inventory that is known to be in the tank. The 1989 core gives an iron inventory consistent with process knowledge (Lambert 1998).

Data on the solids from Core 266 were available but not used. The solids recovery from core 266 was very poor (Steen 2000b). In addition, the laboratory spilled the composite made from core 266 and most of the composite was lost (Steen 2000b). The solids that were not spilled and subsequently analyzed, did not appear to represent the typical tank solids. The solids from core 266 were much higher in sulfur and fluoride than any other sampling event from this tank. In addition, the inventory calculated from the core 266 solids poorly matched the inventory predicted by the PUREX flow sheets or the inventory predicted by core 269 and the cores taken in 1989.

The net volume of the supernatant has increased from 3017 kL (797 kgal) at the time of sampling (December 15, 1999) to 3251 kL (859 kgal) as currently measured. Flushing of air-lift circulators and mixer pump seal water both contributed to this increase. A multiplier (0.928) was calculated for the supernatant vectors, based on the volume ratios, to adjust the supernatant concentration to the current volume. The multipliers used for the HDW model SMM (1.08) and TLM (0.558) vectors are the ratio of the respective volumes reported in Table 8-1 to the volumes reported in Agnew et al. (1997a). The sludge volume has increased since the original best-basis update was done. The average sludge depth reported by Lambert (1998) was 15.3 inches, which corresponds to a sludge volume of 159 kL (42 kgal), whereas the sludge volume currently calculated is 197 kL (52 kgal). The aluminum concentration has decreased in the supernate since the 1995 grab-sampling event, and increased in the sludge since the 1989 sampling event. Consequently, it can be concluded that the precipitation of aluminum is partially responsible for the sludge growth. Therefore, one can assume that the mass of insoluble constituents in the sludge has stayed the same since the 1989 sampling event, but that the concentration of these constituents has decreased because of dilution by aluminum. The multiplier of 0.808 for the 1989 sludge-vector is the ratio of the sludge volume from Lambert (1998) to the sludge volume in Table 8-1.

The sample data for the sludge were inadequate for several analytes, and a process knowledge vector was created to improve the inventory estimates for them. A high detection limit was obtained for iodine-129 in solids, whereas a low detection limit was obtained for the supernate. Agnew et al. (1997a) assumed that iodine was completely soluble in Hanford waste. This same assumption was made for tank 241-AZ-101 in order to obtain a more reasonable iodine-129 inventory for this tank. Iodine-129 was assumed to have the same concentration in the sludge as in the supernatant. To calculate this concentration in the sludge, the iodine-129 detection limit for the supernatant, in μg/mL, was divided by the sludge density of 1.62 g/mL. There is no reliable sample data for some of the thorium, radium, and protactinium isotopes. These isotopes are primarily formed in the waste as actinide decay products. Agnew et al. (1997a) over predicts the inventory of these isotopes because they assumed that all of the decay products created reactor fuel before January 1, 1994 went to the tanks. In reality, many of those decay products went with the uranium and plutonium products. Therefore, the inventory predicted by Origen2 is likely to be more accurate than the inventory predicted by Agnew et al. (1997a). Origen2 predicts the total tank inventory rather than a by-phase inventory. The thorium (except thorium-232), radium, and protactinium isotopes predicted by Origen2 were assumed to be in the sludge because of their low solubility. The concentrations reported in the process knowledge vector were determined by dividing the Origen2 total tank inventory by the sludge mass. The tank inventory for aluminum predicted by the sample data and the HDW model is approximately 20% below the inventory predicted from PUREX flow sheets and essential material usage. Aluminum has been slowly precipitating in this tank, as is evident by the decrease in supernatant aluminum and increase in sludge depth, and most likely formed a gelatinous layer on the surface of the sludge. The 1999 cores had poor solids recovery (see Question #5), and likely missed the top layer of precipitated aluminum. The 1989 core data for the sludge are not accurate for aluminum because of aluminum precipitation that occurred between 1989 and the 1995 supernate sampling event, but it is believed to have been representative of the sludge aluminum concentration in 1989. An estimate of the amount of aluminum that precipitated was made by subtracting the supernatant aluminum inventory derived from the 1995 grab samples from the supernatant aluminum inventory calculated from the 1989 centrifuged liquid. The quantity aluminum that precipitated between 1989 and 1995 was estimated to be 4,550 kg. The total sludge inventory for the 1989 sludge plus the aluminum that has precipitated since then was divided by the current total sludge mass to obtain the aluminum concentration used in the process knowledge vector.

The densities reported in Table 8-1 for the 1999 liquid core composite means was determined from analytical data, and then recalculated to account for dilution, based on the assumption that water gained had a density of one. The density of the 1999 segment vector was assumed to be the same as the core composite data. The core 269 reconstituted solids means vector density is the mean of the densities reported for this core by Steen (2000a), where the density was reported on the solids without decanting off the centrifuged liquid or building the tank composite. In contrast, the density reported in the *Means and Confidence Interval* Standard Report, which was not used, is the density of the centrifuged solids, and not representative of the in-tank density. The densities of the Origen2 and iodine-129 vectors were assumed to be the same as the core 269 composite density.

White crystals, consisting primarily of sodium aluminate and zeolites, were observed in the supernate segments of the cores (Steen 2000b). The cores were taken in November through December (see *Description of Tank* Standard Report), and, thus, the waste must have cooled in the cores before being transported to the laboratory. Heating tests demonstrate that these white solids do not re-dissolve upon heating to tank temperatures (O'Rourke 2000). These crystals were

incorporated into the composite samples (Templeton 2000c). Grab samples have been taken from this tank since the cores were taken, prior to, during, and after mixer pump operation, but the analytical data are not yet available. No white crystals, however, were visually observed in the new liquid grab samples. Thus, the white crystals observed in the core supernate segments likely precipitated while the cores sat outside before being shipped to the laboratory. Therefore, the Na, Al, and Si (the components of zeolites) concentration of the supernate is possibly underestimated in this analysis, and the concentration of these analytes in the sample-based sludge is possibly over estimated.

Once the best-basis inventories were determined, the hydroxide inventory was calculated by performing a charge balance with the valences of other analytes. This charge balance approach is consistent with that used by Agnew et al. (1997a).

All inventory calculations were performed using the Best-Basis Inventory Maintenance (BBIM) Tool. The updated best-basis inventory for tank 241-AZ-101 can be found in *Best Basis Inventory Estimate (Nonradioactive)* and *Best Basis Inventory Estimate (Radioactive)* Standard Reports.

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