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1 ECN

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2 ECN Category (mark one) Supplemental <input type="checkbox"/> Direct Revision <input checked="" type="checkbox"/> Change ECN <input type="checkbox"/> Temporary <input type="checkbox"/> Standby <input type="checkbox"/> Supersedure <input type="checkbox"/> Cancel/Void <input type="checkbox"/>		3 Originator's Name Organization MSIN and Telephone No Melvin R Adams, Data Development and Interpretation, R2-12, 373-6167		4 USQ Required? [] Yes [X] No		5 Date 01/31/00	
		6 Project Title/No /Work Order No Tank 241-U-103		7 Bldg /Sys /Fac No 241-U-103		8 Approval Designator N/A	
		9 Document Numbers Changed by this ECN (includes sheet no and rev) HNF-SD-WM-ER-712, Rev 1		10 Related ECN No(s) N/A		11 Related PO No N/A	
12a Modification Work [] Yes (fill out Blk 12b) [X] No (NA Blks 12b 12c 12d)		12b Work Package No N/A		12c Modification Work Complete N/A		12d Restored to Original Condition (Temp or Standby ECN only) N/A	
		Design Authority/Cog Engineer Signature & Date				Design Authority/Cog Engineer Signature & Date	
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14a Justification (mark one) Criteria Change [X] Design Improvement [] Environmental [] Facility Deactivation [] As Found [] Facilitate Const [] Const Error/Omission [] Design Error/Omission []							
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Tank Characterization Report for Single-Shell Tank 241-U-103

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U S Department of Energy Contract DE-AC06-96RL13200


EDT/ECN ECN-655990 UC 2070
Org Code 74B20 Charge Code 102227/AJ60
B&R Code EW 3120074 Total Pages 24

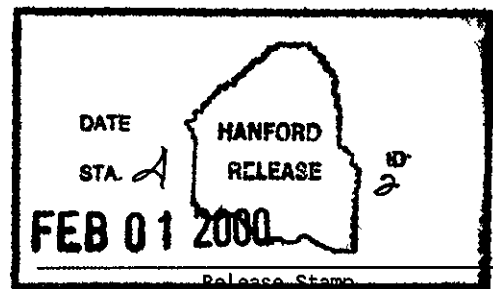
Key Words Waste Characterization, Single-Shell Tank, SST, Tank 241-U-103, Tank U-103, U-103, U Farm, Tank Characterization Report, TCR, Waste Inventory, TPA Milestone M-44

Abstract This document summarizes the information on the historical uses, present status, and the sampling and analysis results of waste stored in Tank 241-U-103. This report supports the requirements of the Tri-Party Agreement Milestone M-44-15B

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Some of the reports herem 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 December 21, 1999

Tank 241-U-103

Sampling Events

Reports

Tank Interpretive Report

Constituent Groups

Anions

Inorganics

Metals/Nonmetals

Organics

PCBs

Physical Properties

Radionuclides

~~WHE~~
WHE-SD-WM-ER-712, R2
Table of Contents

Data Dictionary to Reports in this Document	1
Tank Interpretive Report For c \temp\dict doc241-U-103	2
c \temp\dict doc241-U-103Tank Information Drivers	2
Vapor Space Phenomenology Is the vapor space homogeneous? How does the composition of headspace change with time? How do atmospheric changes and interactions with interconnected (cascading) tanks affect headspace concentrations?	6
Tank History	7
Tank Comparisons	8
Disposal Implications	9
Scientists Assessment of Data Quality and Quantity	10
Sampling and Analysis	10
Data Quality	11
Clarification and Explanation of Data Tables and Figures	11
Unique Aspects of the Tank	12
Best-Basis Inventory Derivation	12
Reference List	17

Data Dictionary to Reports in this Document

Report	Field	Description
Tank Interpretive Report		Interprets information about the tank answering a series of six 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 c \temp\dict doc241-U-103

c \temp\dict doc241-U-103 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-U-103 include the *Tank Safety Screening Data Quality Objective* (Dukelow et al 1995), the *Tank Farms Waste Transfer Compatibility Program* (Fowler 1999b), the *Memorandum of Understanding for the Organic Complexant Safety Issue Data Requirements* (Schreiber 1997), the *Data Quality Objective to Support Resolution of the Organic Solvent Safety Issue* (Meacham et al 1997), the *Data Quality Objective to Support Resolution of the Flammable Gas Safety Issue* (Bauer and Jackson 1998), the *Data Quality Objectives for Tank Hazardous Vapor Safety* (Osborne and Buckley 1995), and the *Recommendation 93-5 Implementation Plan* (DOE-RL 1996). The extent to which these information drivers have been satisfied are discussed below.

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

The data needed to screen the waste in tank 241-U-103 for potential safety problems are documented in *Tank Safety Screening Data Quality Objective* (Dukelow et al 1995). These potential safety problems are exothermic conditions in the waste, flammable gases in the waste and/or tank headspace, and criticality conditions in the waste. A full vertical profile of the tank waste, taken from two risers separated as widely as practicable, is required for the Safety Screening analysis. In 1996-1997, the core sampling method used was push mode. Because of the hardness of the waste or the presence of debris, core 175 was incomplete. A third core, 182, was taken from riser 13 to satisfy programmatic requirements. The data used for evaluation of safety screening requirements were taken from the two complete cores: core 176 which came from riser 7, and core 182. Bates and Shekarriz (1996) directed the use of retained gas samplers (RGS) during the 1996-1997 sampling effort.

Results obtained using differential scanning calorimetry (DSC) indicated that none of the 1996-1997 core liquid samples, or the 1999 grab samples obtained from tank 241-U-103 exceeded the safety screening decision threshold of 480 J/g (Steen 1997). The maximum average exotherm was 323 J/g (dry weight) from core 176, segment 3, drainable liquid. The highest one-sided 95 percent confidence interval upper limit on the mean was 455 J/g (dry weight) from the same sample. The sample from core 182, segment 8, lower half exhibited a result of 507 J/g (dry weight), but three subsequent re-runs failed to reproduce the high DSC results. None of the liquid samples from the 1999 grab sampling effort exhibited DSC results above the limits (Steen 1999). The maximum average exotherm from the 1999 grab samples was 205 J/g (dry weight), and the maximum upper limit to the 95 percent confidence interval on the mean was 281 J/g (dry weight). A liquid sample obtained in the 1995 grab sampling effort exhibited a mean result of 944 J/g (dry weight), the

maximum upper limit to the 95 percent confidence interval on the mean was 1,050 J/g (dry weight) (Esch 1995)

As requested in Carpenter (1995), samples of the headspace of tank 241-U-103 were obtained for measurement. Prior to obtaining the samples, the headspace was measured for flammability (Caprio 1995). The results were reported as 0 percent of the Lower Flammability Limit (LFL). As requested in Sasaki (1997), headspace vapor measurements were obtained prior to obtaining the 1996-1997 core samples. The "IH Sniff Data" standard report states that headspace vapor measurements during riser setup were up to 9 percent of the LFL. Flammable gas in the tank headspace was detected using a combustible gas meter at up to 19 percent of the LFL, during core sampling (subsequent samples acquired by the vapor sampling system exhibited flammable gas at about 6 percent of the LFL). All results were below the action level of 25 percent of the LFL.

The threshold limit for criticality, based on the total alpha activity, is 1 g/L. Assuming that all alpha is from ^{239}Pu , and using the maximum sample density of 1.9 g/mL, 1 g/L of ^{239}Pu is equivalent to 32.4 $\mu\text{Ci/g}$ of alpha activity. The maximum total alpha result, from the 1996-1997 core samples, was 0.689 $\mu\text{Ci/g}$, with a 95 percent confidence interval upper limit of 0.944 $\mu\text{Ci/g}$. Therefore, criticality is not a concern for this tank.

The requirement of the *Tank Safety Screening Data Quality Objective* (Dukelow et al. 1995) that a profile of the tank waste be acquired from two risers separated as widely as practicable was fulfilled. With the exception of the DSC mean result of 944 J/g from the 1995 grab samples, all required analyses exhibited results below action or notification levels.

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?

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 safety issue is expected by September 30, 2001 (Johnson 1997).

As stated in the safety screening DQO section, the headspace vapor measurements performed in 1995 and 1996-1997 all show results well below the action limit of 25 percent of the LFL.

Retained gas samples (RGS) were taken as part of the 1996-1997 push mode core sampling effort, as directed by Bates and Shekarriz (1996) and documented in Mahoney et al. (1997). Retained Gas Samples were taken of core 176, segments 2, 5, 7, 8, and 9, and of core 182, segment 4. No specific notification limits are associated with the RGS analyses.

According to Mahoney et al. (1997), the retrieved gas in tank 241-U-103 contains 22 mol percent hydrogen, 40 mol percent nitrous oxide, 36 mol percent nitrogen, 1.2 mol percent ammonia, and 1.0 mol percent "other gases." Residual ammonia ranged from 49,000 $\mu\text{mol/L}$ for core 176, segment 5, to 2,300 $\mu\text{mol/L}$ for core 176, segment 2. The corrected gas fractions for individual segments ranged from 0.077 for core 176, segment 8, to 0.441 for core 176, segment 2. The best estimate of total tank retained gases based on Barometric Pressure Estimate (BPE) gas volume is 200 m^3 at in-tank conditions, which corresponds to an overall gas fraction of 0.1161.

In 1995, samples of the tank 241-U-103 headspace vapor were collected and analyzed by WHC Sampling and Mobile Laboratories (Huckaby and Bratzel 1995). The results are documented in the *Vapor Characterization of Waste Tank 241-U-103 Results for Samples Collected on 2/15/95* (Ligotke et al 1995). Ammonia, nitrous oxide, and hydrogen were detected. The most abundant constituent detected was nitrous oxide, which did not contribute appreciably to the flammability of the headspace. Additionally, three triple sorbent trap samples were provided to the Oak Ridge National Laboratory for analysis for organic compounds. The results can be found in Dindal et al (1995), as well as in LMHC (1999c).

Tank 241-U-103 is equipped with a standard hydrogen monitoring system (SHMS) for the collection of vapor-phase data that support resolution of flammable gas issues. The SHMS monitors hydrogen continuously. From the installation date (March 1995) through June 1999, eleven hydrogen gas release events (GREs) were documented for tank 241-U-103 based upon SHMS data. The maximum volume of hydrogen released from tank 241-U-103 in a single GRE was 4.44 m³ June 28, 1999 to July 6, 1999. The maximum concentration of hydrogen measured by the SHMS was 1,260 ppm June 6, 1999. This is well below the action level of 6,250 ppm of hydrogen. These releases are documented in *Results of Vapor Space Monitoring of Flammable Gas Watch List Tanks* (McCain 1999). The referenced document also contains preliminary information concerning ventilation rates for tank 241-U-103.

Organic Solvent Safety Issue DQO Does an organic solvent pool exist that may cause a fire or ignition of organic solvents in entrained waste solids?

The data needed to address the organic solvent screening issue are documented in *Data Quality Objective to Support Resolution of the Organic Solvent Safety Issue* (Meacham et al 1997). The DQO requires that headspace samples be analyzed for total nonmethane organic compounds. Vapor samples were taken from tank 241-U-103 in February 1995, and the total nonmethane organic vapor concentration calculated from the concentration of individual compounds measured at a reference 0° temperature by gas chromatography/mass spectrometry was about 7.2 mg/m³ (Huckaby and Bratzel 1995). These samples were collected in triple sorbent traps. A similar summation of organic compounds measured in SUMMA™ samples from tank 241-U-103 exhibited an estimated total organic vapor concentration of 11 mg/m³. The disagreement is largely due to the different estimated concentrations of the dominant alcohols in the two sample types. The organic solvent surface area was estimated at 0.04 m² (Huckaby and Sklarew 1997), which was well below the 1 m² limit.

The organic program has determined that even if an organic solvent pool does exist, the consequence of a fire or ignition of organic solvents is below risk evaluation guidelines for all tanks (Brown et al 1998). The organic solvent issue was closed for all tanks in December 1998 (Owendoff 1998).

Organic Complexant Safety Issue MOU Does the possibility exist for a point source ignition in the waste followed by a propagation of the reaction in the solid/liquid phase of the waste?

The data required for the organic complexant issue are documented in *Memorandum of Understanding for the Organic Complexant Safety Issue Data Requirement* (Schreiber 1997).

Differential scanning calorimetry and total organic carbon (TOC) analyses were performed to address the organic complexant issue

As discussed in the Safety Screening DQO section, the maximum average exotherm was 323 J/g (dry weight) from core 176, segment 3, drainable liquid, with a one-sided 95 percent confidence interval upper limit on the mean of 455 J/g (dry weight) (Steen 1997). A result of 507 J/g (dry weight) was obtained from core 182, segment 8, but the result was not reproduced in subsequent re-runs. None of the liquid samples obtained in the 1999 grab sampling effort exceeded the safety screening limits. The maximum average dry weight exotherm for the 1999 grab samples was 205 J/g, from liquid grab sample 3U-99-2, and the highest 95 percent confidence interval upper limit on the mean was 281 J/g (Steen 1999).

The maximum mean TOC value was 16,300 µg/mL (11,500 µg/g) in core 175, segment 2R, drainable liquid, which on a dry weight basis is 2.34 weight percent. The mean TOC value for core 176, segment 7, solids was 14,000 µg/g, which on a dry weight basis is 2.72 weight percent (Steen 1997). The maximum solid and liquid results from the 1999 grab samples were both below the values from the 1996-1997 core samples. Both values from the core samples were well below the organic complexant action level of 4.5 percent dry weight. The data suggest that a propagating reaction in the waste is unlikely.

A comparison of the energetic equivalents of the TOC values with the DSC values for core 175, segment 2R, and core 176, segment 7, reveals that the TOC equivalent values were well above the DSC results. The comparison is made using the energy equivalence of sodium acetate, i.e., 4.5 weight percent sodium acetate is equal to 1,200 J/g, and, since the exact mix of compounds in the tank is unknown, it is assumed that all of the TOC in the waste is in the form of acetate. The energetic equivalent of the TOC value for the mean liquid sample results from core 175, segment 2R, was 624 J/g versus 158 J/g by DSC, the TOC equivalent value for the mean solid sample results from core 176, segment 7, was 733 J/g versus 123 J/g by DSC (Steen 1997).

The organic complexants safety issue was closed for all tanks in December 1998 (Owendoff 1998).

Compatibility DQO Will safety problems be created as a result of mixing waste in interim storage? Do operations issues exist which should be addressed before waste is transferred?

The requirements of the *Tank Farms Waste Transfer Compatibility Program* (Fowler 1999b) include the safety considerations and decision rules for criticality, corrosion, emissions, energetics, and flammable gas accumulation. The operational issues of heat generation of commingled waste, segregation of complexant waste, and high phosphate waste are addressed in Fowler (1995).

Saltwell pumping of tank 241-U-103 to tank 241-SY-102 began on September 26, 1999, and is projected to continue intermittently over the next 3 years. A compatibility assessment using the 1999 grab sample results was completed before saltwell pumping began. The analytical results are reported in Steen (1999), and assessed in Fowler (1999c). All requirements for transfer were met. In addition, assurance that tank 241-U-103 would remain within specifications for fuel content and distribution was demonstrated in Fowler (1999a). The time to reach 25 percent of the LFL in tank 241-SY-102 (55 days) was presented in Hu (1999).

Hazardous Vapor Screening DQO Do hazardous storage conditions exist associated with gases and vapors in the tank?

The headspace of tank 241-U-103 was vapor sampled in February 1995. According to *Vapor Space Characterization of Waste Tank 241-U-103: Results from Samples Collected on 2/15/95* (Ligotke et al 1995), the ammonia value of 730 ppmv exceeded the 8 hour recommended exposure limit of 25 ppmv set by the National Institute of Occupational Safety and Health (NIOSH 1995). Note, however, that the ammonia measurement was not taken in the worker's breathing area, where the 25 ppmv limit actually applies. Eleven organic compounds were detected above the 5 ppbv reporting level, and 13 tentatively identified compounds were found above the 10 ppbv reporting level. The flammability of the tank headspace was measured at less than 2 percent of the LFL.

Hazardous vapor screening is no longer an issue because headspace vapor (sniff) tests are required for the safety screening DQO (Dukelow et al 1995), and the toxicity issue was closed for all tanks (Hewitt 1998).

Vapor Space Phenomenology Is the vapor space homogeneous? How does the composition of headspace change with time? How do atmospheric changes and interactions with interconnected (cascading) tanks affect headspace concentrations?

It is not known directly if the vapor headspace in tank 241-U-103 is homogeneous. However, the headspaces of three tanks which exhibit relatively cool waste temperatures and measurable quantities of vapors of interest (tanks 241-B-103, 241-TY-103, and 241-U-112) were sampled and analyzed for hydrogen, carbon dioxide, ammonia, and selected organic vapors (Huckaby et al 1997). Tanks with relatively cool waste temperatures were chosen because they presented the "worst case" of non-homogeneity. The low thermal gradient between the waste surface and the headspace vapors in a cool tank produces less convection and mixing than in a tank with a relatively warm or hot waste surface. After sampling from 2 different risers at 4 different depths at a time when the waste temperature was at or near the temperature of the headspace vapors, it was found that the headspaces of all 3 tanks were homogeneous for all intents and purposes. Tank 241-U-103 exhibits cool waste temperatures and measurable quantities of a variety of headspace vapors. The results and conclusions of the study indicate that, unless a reason for heterogeneity exists, such as a GRE, or a large change in the relative temperature of the waste surface and the headspace, the headspace in tank 241-U-103 is most likely homogeneous.

Tank 241-U-103 is passively ventilated and has its own filtered breather riser. As barometric pressure falls, the tank may exhale air, waste gases, and vapors. Barometric pressure typically rises and falls on a diurnal cycle, producing an average daily exchange of air equal to about 0.46 percent of each tank headspace. Changes in the concentration of tank headspace due to barometric pressure changes are consequently very slow. The ventilation rate of tank 241-U-103 was measured using a tracer gas. The gas was injected into the tank headspace and its concentration measured as a function of time. Huckaby et al (1998) reported average ventilation rates of 2.2 m³/hr and 5.2 m³/hr (78 ft³/hr and 180 ft³/hr). The tank was also found to exchange headspace vapors with tank 241-U-102 through the cascade line at estimated rates of 1.6 m³/hr to 12.6 m³/hr (57 ft³/hr to 445 ft³/hr).

Heat Load Estimate A factor in assessing tank safety is the heat generation and temperature of the waste. Heat is generated in the tanks from radioactive decay. The heat load estimate based on the process history was 3.68 kW (12,600 Btu/hr) (Agnew et al. 1997a). The heat load estimate based on the tank headspace temperature was 1.9312 kW (6,593 Btu/hr) (Kummerer 1995). The tank heat load based on the Best-Basis Inventory (See Standard Report "Best-Basis Inventory [Radioactive]") was 2.84 kW (9,700 Btu/hr). These estimates are below the limit of 7.6 kW (26,000 Btu/hr) that separates high and low heat load single-shell tanks (LMHC 1999a).

Table 1-2 Heat Load Estimate Based on the Best-Basis Radionuclide Inventory

Radionuclide	Waste Inventory (Ci)	Specific Activity ¹ (W/Ci)	Heat Load (W)
Strontium-90	7.52E+04	0.00670	5.04E+02
Cesium-137	4.69E+05	0.00472	2.34E+03
Total	-	-	2.84E+03

Notes ¹Includes daughter isotopes

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Tank History

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

The U Tank Farm was constructed during 1943 and 1944 in the 200 West Area. The U Tank Farm contains twelve 100-series tanks and four 200-series tanks. Built according to the first-generation design, the U Tank Farm was designed for non-boiling waste with a maximum fluid temperature of 104 °C (220 °F). Tank 241-U-103 is the third in a cascade series of three tanks that includes tanks 241-U-101 and 241-U-102. Each tank in the cascade series is set 0.305 m (1 ft) lower in elevation from the preceding tank. The cascade overflow height is approximately 4.9 m (16 ft) from the tank bottom and 0.61 m (2 ft) below the top of the steel liner. Tank 241-U-103 has a capacity of 2,010 kL (530 kgal), a diameter of 22.9 m (75.0 ft), and a liner height of 5.8 m (18 ft) as measured from the tank bottom centerline (Leach and Stahl 1993). Saltwell pumping of the tank began September 26, 1999, and is ongoing. As of October 1, 1999, tank 241-U-103 contained 1,722 kL (455 kgal) of non-complexed waste and is listed as sound.

Agnew et al. (1997b) provides a history of the waste in tank 241-U-103. Tank 241-U-103 first received metal waste from T Plant via the cascade line in February 1947 and was full by July 1947. In January 1952, waste was sent to tank 241-TX-115 to prepare the tank to receive waste from the test sluicing of tank 241-U-101. Flush water from miscellaneous sources was added to the tank in the first quarter of 1952. Metal waste from tank 241-U-101 was sluiced to tank 241-U-103 from April to November 1952. Supernatant from tank 241-U-102 was transferred to tank 241-U-101 through tank 241-U-103 and the 244-CR Vault to mobilize the metal waste sludge. Sluicing of tank 241-U-103 for uranium recovery began in December 1952, and the tank was cleaned out during August 1953. Supernatant from tanks 241-TX-115, 241-U-104, 241-U-101, and 241-U-102 was used to sluice the solids in tank 241-U-103.

Tank 241-U-103 again began receiving metal waste through the cascade from tank 241-U-102 from the second quarter of 1953 to the second quarter of 1954. Waste from tank 241-U-103 was sluiced to the uranium recovery process during November 1955. Final cleanout of the tank was initiated in November 1956 and completed in December 1956.

In the first quarter of 1957, the tank received metal waste and water. Waste was sluiced from the tank to the uranium recovery process in the second quarter of 1957. Tank 241-U-103 was filled with REDOX high-level waste supernatant from tanks 241-SX-102 and 241-SX-111 during the fourth quarter of 1958. The tank remained inactive until the first quarter of 1974 when waste was sent from tank 241-U-103 to tanks 241-S-101 and 241-S-110. From the first quarter of 1974 to the second quarter of 1976, the tank received flush water from miscellaneous sources. Tank 241-U-103 began receiving evaporator bottoms waste from tank 241-TX-106 in the second quarter of 1975 and from tank 241-TX-118 in the third quarter of 1975. Waste was sent from tank 241-U-103 to tanks 241-U-111 and 241-TX-118 during the first quarter of 1976, nearly emptying the tank. Additional evaporator bottoms waste was received by tank 241-U-103 from tanks 241-TX-108 and 241-T-101 during the second quarter of 1976. Tank 241-U-107 also sent Pacific Northwest Laboratory wastes to tank 241-U-103 during the second quarter of 1976. In addition, tank 241-U-103 exchanged evaporator waste with tank 241-S-102 during the second quarter of 1976.

Tank 241-TX-108 sent evaporator bottoms waste to tank 241-U-103 during the third quarter of 1976, as tank 241-U-103 became the staging tank for the 242-S Evaporator with tank 241-S-102 as the feed tank. Waste was sent to tank 241-S-102 during the fourth quarter of 1976 with evaporator bottoms waste being received into tank 241-U-103 from tank 241-S-102 during the first quarter of 1977. The tank received waste from tank 241-TX-103 and sent waste to tank 241-U-111 during the first quarter of 1977.

In the second quarter of 1977, tank 241-SY-102 became the feed tank for the 242-S Evaporator and continued the exchange of feed and bottoms waste with tank 241-U-103. This ended in the fourth quarter of 1977 with a final exchange of waste with tank 241-SY-102. In the fourth quarter of 1977, $\text{HNO}_3/\text{KMnO}_4$ (partial neutralization feed) was also added to the tank from evaporator operations. The tank was declared inactive in 1978. The tank contains REDOX (R1) sludge and Supernatant Mixing Model Saltcake 1/Supernatant Mixing Model Saltcake 2 (SMMS1/SMMS2) saltcake and supernatant.

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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?

According to Agnew et al (1997a) tank 241-U-103 currently contains 242-S Evaporator saltcake (SMMS1 and SMMS2). The tank also contains a small R1 sludge heel that roughly fills the dished tank bottom. Agnew et al (1997a) calls this sludge layer Metal Waste (MW), but it is thought to be R1 because most, if not all, of the MW was sluiced out of the tank in the second quarter of 1957. Tank 241-U-103 is the last tank in a cascade of three that includes tanks 241-U-101 and 241-U-102. Because of the cascade, the contents of the three tanks were essentially the same until the mid-1950's. However, following the removal of metal waste from the U Tank Farm, the tanks in

the cascade operated individually to receive and transfer waste. Selected tanks in other tank farms, especially S, T, SX, and U, have waste types similar to those in tank 241-U-103.

Analytical data from different segments from tanks 241-S-101, 241-S-102, 241-S-106, 241-S-109, 241-S-111, 241-SX-106, 241-U-106, 241-U-108, and 241-U-109 were determined to be representative of SMMS2 waste. Analytical results from these tanks provide insight into the composition of the SMMS2 layer in tank 241-U-103. These comparisons are of particular value for estimating the compositions of tanks such as 241-U-111, which is expected to contain significant quantities of SMMS2 waste and for which limited core sample data are available. Analytical data from different segments from tanks 241-S-101, 241-S-102, 241-SX-106, 241-SY-103, 241-U-102, 241-U-106, and 241-U-107 are of use to provide insight into the composition of the SMMS1 layer in tank 241-U-103. Tank 241-U-103 contains a thin layer of R1 sludge, mostly in the dished bottom of the tank. The layer is difficult to sample because it is so small and because it may only be reached through the center riser (Riser 13). Analytical data from different segments from tanks 241-S-101, 241-S-107, 241-S-111, 241-SX-103, and 241-SX-105 may provide insight into the composition of the R1 sludge layer.

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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?

Given what is known about the waste types and behaviors in tank 241-U-103, several items should be considered in regard to waste retrieval. The liquid waste in tank 241-U-103 contains high levels of dissolved salts which may precipitate under certain conditions. Portions of the waste may be considerably harder than other portions, or may contain debris. Tank 241-U-103 is on the Watch List for the flammable gas issue (Public Law 101-510), and the waste retains ammonia and other flammable gases. The levels of organic solvents and fissile material should be taken into consideration when planning waste transfer.

A compatibility assessment was performed in preparation for saltwell pumping which specified measures required to safely transfer supernatant and drainable liquids to the double shell tank system (Fowler 1999c). Analysis of the waste in the tank revealed that precipitation of solids in the transfer line should be considered when assessing dilution and pumpability requirements. However, the low waste temperature will tend to reduce the potential for solids precipitation during pumping and plugging of the transfer line.

As of October 1, 1999, supernatant makes up approximately 1 kgal of waste in tank 241-U-103 (LMHC 1999b). The remaining waste in tank 241-U-103 is mostly a moist to dry saltcake. Push mode core methods were used to retrieve samples. Poor recoveries were obtained in the case of core 175. It was thought that the sampler hit a piece of equipment or a tool, or that possibly the waste was very hard under riser 2. This indicates that the saltcake may require softening to be retrieved, or retrieval equipment should be designed to remove hard solids or pieces of equipment or tools.

Another concern for tank 241-U-103 is the retained gas in the liquid and solid waste layers. Standard Hydrogen Monitoring System data showed that the tank headspace has remained below the

alarm point of 6,250 ppmv Mahoney et al (1997) reports that, based on estimated solubilities and RGS measurements, the waste in tank 241-U-103 contains about 11.6 volume percent of free gas. Of this volume of free gas, about 22 mol percent is hydrogen and 40 mol percent is nitrous oxide. Flammable gas issues should be carefully considered before waste retrieval methods are implemented.

Sample results showed that the tank waste has low total alpha concentrations, alleviating criticality concerns during retrieval and processing. Organic solvent surface areas are also low compared to threshold limits. The flammable gas concentrations in the tank headspace ranged from 0 to 19 percent of the LFL. The vapors of tank 241-U-103 were within health hazard threshold limits for all analytes measured except ammonia (Ligotke et al 1995). Note, however, that the ammonia was not measured in the worker's breathing zone, where the 25 ppmv limit actually applies. The vapors were measured during steady state conditions, the waste may behave differently during retrieval operations such as sluicing, mixing, or pumping.

Assessments that could be conducted to better address disposal implications include evaluating potential impediments to pretreatment and estimating the number of glass logs that tank 241-U-103 waste will produce. These assessments are beyond the scope of the current effort.

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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

All appropriate DQO and waste issues have been addressed for this tank and accepted by the Project Hanford Management Contract River Protection Project. No additional sampling and analyses are necessary to satisfy current safety issue requirements for this tank. Additional sampling may be necessary to better understand the physical characteristics of the waste from a disposal perspective. Issues related to permits, retrieval of the saltcake, and retrieval of the sludge are not completely understood by the current analytical information. Given the schedule for Phase II disposal, this additional analytical/physical information has a moderate priority from a strictly technical point of view. This additional information on the behavior of the waste may be adequately understood by sampling tanks with similar waste types. None of the Disposal DQOs has been applied to this tank.

Data Quality

The samples collected in the 1996-1997 core sampling event, the 1995 and 1999 grab sampling events, and in the 1995 vapor sampling event were analyzed with approved and recognized sampling and laboratory procedures and in accordance with the tank sampling and analysis plan (Sasaki 1997), and tank characterization plan (Carpenter 1995). The laboratory procedures for the core sample analysis can be found in the standard report "Analytical Methods and Procedures." Quality control (QC) parameters assessed in conjunction with tank 241-U-103 samples included standard recoveries, spike recoveries, duplicate analyses, and blanks. Appropriate QC footnotes were applied to data outside QC parameter limits. Analytical results and data quality are discussed in the tank 241-U-103 data packages (Steen 1997 and Steen 1999).

Propagating reactive systems screening tool analyses were to be performed on the individual solid sample exhibiting the highest DSC exotherm greater than 480 J/g. One solid sample exhibited an exothermic reaction greater than 480 J/g, (core 182, segment 8, lower half), but the result was not reproducible by duplicate analysis.

The vast majority of QC results were within the boundaries specified in the sampling and analysis plans. Small discrepancies noted in the analytical reports and footnoted in the "Analytical Results" standard report should not impact the data validity or use.

Data anomalies were observed in the results for titanium and silicon. Silicon was high in the samples from core 176, segment 9, and from core 182, segment 10, presumably due to laboratory contamination. Titanium was high in the samples from core 182, segment 10. Because of the suspect nature of these data, they were excluded from the calculated means for the tank.

Hydrostatic head fluid (HHF) was used during the 1996-1997 core sampling event (Steen 1997). The hydrostatic head fluid used to obtain core samples is water spiked with lithium bromide. Lithium is measured by ICP, and bromide is measured by IC. The presence of lithium bromide in the tank samples is an indication of intrusion into the tank samples by the HHF. A calculation is performed for segments with elevated lithium and bromide results to correct the weight percent water based on the lithium and bromide results. If the HHF intrusion based on analytical results is greater than 50 weight percent water by thermogravimetric analysis (TGA), the data are considered not representative of the tank waste and are excluded from the "Means and Variances" standard report. Although many of the core samples were intruded by HHF, none of the results from the 1996-1997 core sampling effort were contaminated greater than 50 weight percent of TGA, and no data were removed from the calculated means for that reason (LMHC 1999b).

Clarification and Explanation of Data Tables and Figures

"Description of Tank" standard report: the saltcake volume and the total waste volume of the tank shown in this standard report differs from the Hanlon (1999) volume. This is because the volumes shown in the "Description of Tank" standard as well as in the "Best Basis Inventory Derivation" were based on the volumes listed in Sasaki et al. (1998). For additional discussion, refer to question 7, "Best-Basis Inventory Derivation."

"Core Profile" standard report the sludge layer identified by the "Core Profile" standard report in core 182, segment 10, lower half, has analyte concentrations representative of R1 sludge. No actual facie or visual change as a result of depth, however, was noted in the extrusion worksheets.

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Unique Aspects of the Tank

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

The waste types in tank 241-U-103 are relatively well defined and understood. The same waste types can be found in a number of other tanks, particularly in the U, S, and SX tank farms. Based upon visual observations of the extrusion photographs, the waste is mostly a dark gray to gray-brown saltcake with varying consistencies. The waste below riser 2 may contain very hard material or it may contain metallic debris or tools. The sampler was unable to penetrate the waste below the second segment. The riser was abandoned and the sample rig moved to the center riser, number 13, where a complete profile of the tank was obtained. As mentioned in Question 4 of this report, the waste in tank 241-U-103 contains a relatively large volume of free gas entrained in the solid and liquid phases of the waste (Mahoney et al. 1997).

The photographic montage of the tank 241-U-103 interior shows the waste surface to be an opaque, dark-yellow to black liquid covering approximately 2/3 of the waste surface, with greyish-white solids appearing above the remaining 1/3. Interim stabilization began September 26, 1999. The tank contained 49.2 kL (13 kgal) of supernatant and 1770 kL (468 kgal) of total waste at that time. As of October 1, 1999, 4 kL (1 kgal) of supernatant and 1720 kL (455 kgal) of total waste remained in the tank. The photograph montage taken September 13, 1988, therefore, does not likely represent the current appearance of the tank waste surface.

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Best-Basis Inventory Derivation

Question 7 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 RPP process flowsheet 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. The inventories for certain tanks are changing as the result of waste being transferred into or out of the tanks. The process of updating the inventories for these tanks is being performed on a quarterly basis. Single-shell tank 241-U-103 is being saltwell pumped and, therefore, the inventory of this tank will be updated quarterly until the interim stabilization criteria are met. A re-evaluation of the best-basis inventories for tank 241-U-103, as of October 1, 1999, was performed and is documented in the following text. The following information was used in this evaluation.

- Statistical means based on analytical data from the October 1996 to April 1997 push mode and March 1999 grab samples from tank 241-U-103 (See "Means and Confidence Intervals" Standard Report)
- Templates S1 Saltcake, S2 Saltslurry, and R1 Sludge, based on input from analytical results from other tanks and HDW (Agnew et al 1997a)

The following table represents how the available data are used to derive Best-Basis Inventories for tank 241-U-103. Note that the waste volumes according to Hanlon (1999) are different from the volumes used for the Best Basis Inventory. This is because the Hanlon report had not accounted for the saltwell pumping which began September 26, 1999, and will continue until interim stabilization activities are completed for tank 241-U-103. Additionally, the Hanlon report does not account for the volume of retained gas. Three waste phases were identified for the tank: supernatant, saltcake, and sludge. Inventories were computed for each phase separately, with the exception of the retained gas, and then summed to obtain the overall inventory.

Table 7-1 Tank 241-U-103 Best-Basis Inventory Source Data

Waste Phase	Waste Type	Applicable Concentration Data	Associated Density	Associated Volume ¹
Supernatant	SMMS1/SMMS2	1996-1997 core liquid means	1.41 g/mL	1 kgal (4 kL)
		1999 liquid grab means	1.44 g/mL	
		S2-saltslurry supernate HDW	1.83 g/mL	
Saltcake	SMMS1/SMMS2 (retained gas)	None	N/A	51 kgal (193 kL)
	SMMS1/SMMS2 (liquids)	1996-1997 core liquid means	1.41 g/mL	67 kgal (254 kL)
		1999 liquid grab means	1.44 g/mL	
		S1-saltcake supernate HDW	1.83 g/mL	
	SMMS2 (solids)	1996-1997 core sampling, drained solids	1.71 g/mL	86 kgal (326 kL)
		S2 saltslurry template (8/99 sample/HDW)	1.59 g/mL	
	SMMS1 (solids)	1996-1997 core sampling, drained solids	1.71 g/mL	238 kgal (901 kL)
		S1 saltcake template (8/99 sample HDW)	1.65 g/mL	
Sludge	R1 (retained gas)	None	N/A	1 kgal (4 kL)
	R1 (solids)	1996-1997 core 182, seg 10 lower half	1.9 g/mL	11 kgal (41.6 kL)
		R1 Sludge template (8/99 sample/HDW)	1.75 g/mL	
Total Tank	Overall Tank Volume			455 kgal (1722 kL)

Notes for Table 7-1

¹Note that the total volume of the tank waste is different from the Hanlon (1999) volume by 1 kgal. The sludge and saltcake volumes (Sasaki et al. 1998), were derived from extrusion data. The total volume in kiloliters was calculated by multiplying the total volume in kgal by 3.7854.

1. Retained gas volumes were calculated based on results from the RGS analyses (Mahoney et al. 1997). The best estimate of the retained gas in tank 241-U-103, determined using the barometric pressure effect method, is $200 \text{ m}^3 \pm 60 \text{ m}^3$ at in-tank conditions. Assuming no gas retention by the supernatant, and using the volumes of sludge and saltcake listed in Sasaki et al. (1998), the volume fraction of retained gas in the saltcake and sludge is

$$(200 \text{ m}^3) (1,000 \text{ L/m}^3) (1 \text{ gal}/3.785 \text{ L}) / (442,500 \text{ gal} + 12,500 \text{ gal}) = 0.1161$$

The volume of retained gas in the saltcake is

$$(442,500 \text{ gal}) (0.1161) = 51,374 \text{ gal (or } 194,450 \text{ L)}$$

The volume of retained gas in the sludge is

$$(12,500 \text{ gal}) (0.1161) = 1,451 \text{ gal (or } 5,492 \text{ L)}$$

The volume of the sludge is

$$(12,500 \text{ gal}) (1 - 0.1161) = 11,049 \text{ gal}$$

2. The liquid and solid fractions in the saltcake were calculated by first correcting the volume for the retained gas, then by using the volume fractions of liquids and solids from the extrusion data from core 182. The volume of saltcake, corrected for retained gas is

$$(442,500) (1 - 0.1161) = 391,126 \text{ gal}$$

From core 182 extrusion data, the volume fraction of drainable liquid was 0.1723, the volume fraction of solids was 0.8277. The volume of interstitial liquid is

$$(391,126 \text{ gal}) (0.1723) = 67,391 \text{ gal (or } 255,075 \text{ L)}$$

The volume of the solids is

$$(391,126 \text{ gal}) (0.8277) = 323,735 \text{ gal (or } 1,225,336 \text{ L)}$$

- 3 The volume fractions for S1 Saltcake and S2 Saltslurry were calculated by using the values given in Agnew (1997a) for SMMS1 and SMMS2 saltcake. The SMMS1 volume is 325,000 gal and the SMMS2 volume is 130,300 gal. Assuming that SMMS1 is all saltcake and subtracting the portion of SMMS2 that is supernatant gives a SMMS2 volume of

$$130,300 \text{ gal} - 13,000 \text{ gal} = 117,300 \text{ gal}$$

The fraction of the saltcake that is SMMS1 and SMMS2 is

$$\text{SMMS1} = (325,000 \text{ gal}) / (325,000 \text{ gal} + 117,300 \text{ gal}) = 0.7350$$

$$\text{SMMS2} = (117,300 \text{ gal}) / (325,000 \text{ gal} + 117,300 \text{ gal}) = 0.2650$$

From above, the solids portion of the saltcake is 323,735 gal. The SMMS1 and SMMS2 portions are

$$\text{SMMS1} = (323,735 \text{ gal}) (0.7350) = 237,946 \text{ gal (or 900,623 L)}$$

$$\text{SMMS2} = (323,735 \text{ gal}) (0.2650) = 85,790 \text{ gal (or 324,714 L)}$$

Templates are based on sampling data from tanks that contain the same waste type as tank 241-U-103, supplemented with Hanford Defined Waste (HDW) model data. A multiplier is used to scale the template vector to the sample data using the sample weight percent H₂O and density. A more detailed description of template data is found in Tran (1999).

Waste phases in Table 7-1 were based on the core sampling extrusion observations, the analytical results from the core samples, and the process history of the tank. Further evidence of a supernate layer was provided by in-tank photos, grab samples, and surveillance by level detectors. Extrusion observations and segment analyte concentrations show a saltcake, sludge, and drainable liquid. Waste types (SMMS1/SMMS2 saltcake, sludge) were based on the HDW model presented in Agnew et al (1997a). Although not shown as a distinct facie when extruded, R1 sludge was added as a phase because it is expected based on past 241-U-103 waste transactions and because the analytical results from core 182, segment 10, lower half were more indicative of R1 sludge than of saltcake. Note that Agnew et al (1997a) identifies this layer as metal waste. When establishing the volumes of the different waste phases in the tank, it was assumed that the sludge layer occupied the dished bottom of the tank. The 1996 - 1997 core samples were analyzed on the segment basis only, no composites were made or analyzed. Because the tank has been inactive since 1978, sample data from 1996 - 1997 push mode core samples and the 1999 grab samples are both representative of the waste in the tank.

The analytical means were derived by averaging the individual sample primary and duplicate results to obtain a sample mean. Sample means from the same segment were averaged together to obtain a segment mean, and finally the segment means were averaged to obtain the overall mean for the waste phase. All analytical means were performed using a restricted maximum likelihood (REML) method. The model and the sample means are presented in the Standard Report "Means and Confidence Intervals." Sample data are available for all of the 25 best-basis nonradioactive chemical species for the liquid and saltcake waste phases except mercury. Sample data for radionuclides are

available for cobalt-60, strontium-90, cesium-137, uranium-233, -234, -235, -236, plutonium-239/240, americium-241, total uranium, and total alpha activity. Not all waste phases contain data for the listed radionuclides.

Prior to performing the Best Basis Inventory, the available concentration data are placed in a hierarchy according to completeness, accuracy, and ability to represent the tank contents. The data hierarchy was 1996 – 1997 core sample data, 1999 grab sample data, and template data. For the supernate, the SMMS1/SMMS2 saltcake, the SMMS1/SMMS2 liquids, and the R1 sludge, the preferred concentration data were taken from the 1996 – 1997 core sampling effort. The concentration data for the SMMS1 and SMMS2 saltcake were taken from templates. The SMMS1 saltcake and SMMS2 saltcake were evaluated using template data because of the difficulty determining which waste type was associated with the results from a particular core segment. The data hierarchy was overridden when the preferred concentration data contained a value less than the detection limit and the corresponding value in the next data set was above the detection limit, when the preferred data reported a larger undetected value than the next data set, or when the preferred data did not report the desired analyte.

The associated density values for the inventory calculations are all simple means of the density or specific gravity values for the respective waste type, or they were taken from a template for the respective waste type.

The associated volume of the supernate is in accordance with LMHC (1999b), and reflects the volume of supernate remaining after a period of saltwell pumping beginning September 26, 1999, and continuing to the status date of October 1, 1999. The supernate volume is a transient value. A final number will be determined after saltwell pumping is complete and the waste in tank 241-U-103 has stabilized. The volume of the retained gas in the saltcake and sludge is as explained in note 1 for Table 7-1. An estimate of the total gas volume in the tank (200 m³) was converted to units of liters, then divided by the total volume of saltcake or sludge. As shown in note 2 for Table 7-1, the volume of the solid and liquid fractions of the saltcake was calculated by first correcting the total saltcake volume for retained gas, then using the extrusion data from core 182 to establish the relative fractions of liquid and solid in the saltcake. The volume fractions of the two types of saltcake (SMMS1 and SMMS2) were calculated as explained in note 3 for Table 7-1. The volumes were calculated by using the Tank Layer Model (TLM) values listed in Agnew et al. (1997a) for tank 241-U-103. After correcting the SMMS2 volume for the supernatant volume, and assuming that SMMS1 is all saltcake with no supernatant, the relative fractions of SMMS1 and SMMS2 were multiplied by the TLM volumes to obtain the corrected volumes of SMMS1 and SMMS2.

All inventory calculations were performed using the Best-Basis Inventory Maintenance (BBIM) Tool. The updated best-basis inventory values for tank 241-U-103 can be found in the "Best-Basis Inventory (Non-Radionuclides)" and "Best Basis Inventory (Radionuclides)" Standard Reports. 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).

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