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Tank Characterization Report for Single-Shell Tank 241-C-104

M. R. Adams

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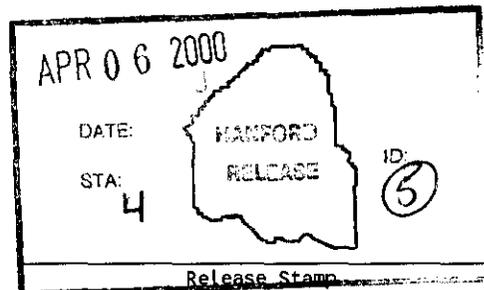
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This report prepared especially for ARCHIVE TCR on 4/3/00

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 April 3, 2000.

Tank: 241-C-104

Sampling Events:

162

165

247

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 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 241-C-104

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-C-104 include the Safety Screening Data Quality Objective (DQO) (Dukelow et al. 1995), the Organic Solvent Safety Issue DQO (Meacham et al. 1997), the Organic Complexant Safety Issue Memorandum of Understanding (MOU) (Schreiber 1997), the Historical DQO (Simpson and McCain 1997), the Hazardous Vapor Screening DQO (Osborne and Buckley 1995), the HLW Feed Processing DQO (Patello et al. 1999), and the Waste Feed Delivery (Confirm Tank T) DQO (Nguyen 1999).

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-C-104 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.

Differential scanning calorimetry (DSC) analyses to assess the exothermic conditions in the waste were not performed on 1998 core samples, as the 1996 core samples had already met the criteria for the DQO. Comparisons were made between the 1996 core analytical results and the DQO decision limits. Thirteen of fourteen DSC samples exhibiting exothermic behavior had a 95 percent confidence interval upper limit for the result and duplicate mean below the safety screening limit of 480 J/g. The highest individual sample result from the sample that exceeded the 95 percent confidence interval was 372 J/g (dry weight) from the drainable liquid of core 162 segment 3. The highest one-sided 95 percent confidence interval upper limit on the mean from the same segment was 603 J/g (dry weight). The mean total organic carbon (TOC) calculated for the core 162 segment 3 drainable liquid was 5,088 µg/g with a 95 percent confidence interval upper limit of 7,798 µg/g, well below the 45,000 µg/g limit for TOC.

Under the direction of the *Tank 241-C-104 Push Mode Core Sampling and Analysis Plan* (Homi 1996) headspace vapor measurements were taken during the 1996 sampling event. The results from the combustible gas meter readings are 0 percent of the LFL as reported in the "*IH Sniff Data*" Standard Report. Headspace vapor measurements were also taken in February and March of 1994, and the result of 0.2 percent of the LFL for hydrogen (68 ppmv) was the highest recorded for the sampling event (Huckaby and Bratzel 1995). These results are all well below the action level of 25 percent of the LFL.

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The threshold limit for criticality is 1 g/L of plutonium. Assuming that all alpha activity is from ^{239}Pu , and using a maximum sample density of 1.97 g/mL, 1 g/L of ^{239}Pu is equivalent to 31.2 $\mu\text{Ci/g}$ of alpha activity for the solids. $^{239/240}\text{Pu}$ was measured directly for core 165 segment 3, subsegment B, the segment having the highest total alpha. The $^{239/240}\text{Pu}$ was 4.3 $\mu\text{Ci/g}$, well below the threshold limit. Alpha activity in all liquid samples was below detection limits. Therefore, criticality is not a concern for this tank.

An evaluation of tank data for safety screening was completed in Reynolds et al. (1999) for all tanks sampled since 1989, to determine if requirements of the DQO had been met. It was concluded that the 1996 sampling event and analytical evaluation for safety screening that occurred in 1997 for tank 241-C-104 (Baldwin et al. 1997) were acceptable based on the criteria of the DQO.

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-C-104 in March 1994, and the total nonmethane organic vapor concentration measured by gas chromatography/mass spectrometry was 28.1 mg/m^3 , with a standard deviation of 0.7 mg/m^3 (Huckaby and Bratzel 1995). The measured concentration was judged high when considering the active ventilation in tank 241-C-104. However, the classification of active ventilation for tank 241-C-104 is based on the cascade line connection between tanks 241-C-104 and 241-C-105 (an actively ventilated tank). No exhauster is used directly on tank 241-C-104.

The recorded waste volume in tank 241-C-104 has declined steadily since the tank was declared inactive in 1980. The volume loss was attributed in part to increased ventilation and evaporation (McKinney 1999b). No organic liquid waste surface area estimation was done for tank 241-C-104 in Huckaby and Sklarew (1997). The 1998 in-tank video shows a dry, cracked surface. No surface moisture is evident. 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 is expected to be closed for all tanks in 2000.

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 TOC analyses were performed on the 1996 core samples to address the organic complexant issue. No DSC results were above the 480 J/g limit. The largest TOC value (31,600 $\mu\text{g/g}$) was from core 165 segment 4, and had a 95 percent confidence interval of 35,700 $\mu\text{g/g}$. This is below the 45,000 $\mu\text{g/g}$ TOC limit. The data indicate that a propagating reaction in the waste is unlikely.

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

Historical DQO: Is the waste inventory generated by a model based on process knowledge and historical information (Agnew et al. 1997a) representative of the current tank waste inventory?

The purpose of the historical evaluation is to determine whether the Hanford Defined Waste (HDW) model, based on process knowledge and historical information (Agnew et al. 1997a), predicts tank inventories that are in agreement with current tank inventories. If the historical model can be shown to accurately predict the waste characteristics as observed through sample characterization, then there is a possibility that the amount of total sampling and analysis needed may be reduced. Data requirements for this evaluation are documented in *Historical Model Evaluation Data Requirements* (Simpson and McCain 1997). Historical DQO issues (Simpson and McCain 1997) have largely been replaced by the Best-Basis Inventory assessment (see Question 7). The following discussion of the historical DQO evaluation is presented for information.

Tank 241-C-104 is considered a spatially complex tank. For spatially complex tanks, the historical DQO (Simpson and McCain 1997) requires the analyses of the solids of each core. The analyses are DSC, TGA, total inorganic carbon/total organic carbon (TIC/TOC), gamma energy analysis (GEA) (¹³⁷Cs) ion chromatography (IC) (all anions), total uranium, Sr-90 (beta counting), total beta and inductively coupled plasma spectroscopy (ICP) (all metals). A composite for each of the two cores retrieved in 1996 was made.

The subsegment level data from tank 241-C-104 suggests a vertically heterogeneous structure. The concentration behavior of aluminum, uranium, and zirconium as a function of depth implies a highly layered waste matrix. This condition was expected because of the relatively high level of transfer activity that occurred in this tank. Interpretation of the subsegment data is clouded by the asymmetrical distribution of waste in the tank. The trends observed hold true in both cases.

The top region of the tank, consisting of approximately 48 cm (19 inches), appears to be zirconium cladding waste, with some aluminum cladding waste mixed in. The mixture and concentrations of analytes in this material (aluminum at approximately 1 percent, nickel at about 1.5 percent, uranium and iron between 2 and 5 percent, and zirconium between about 1 percent and 8 percent) supports this interpretation.

The upper middle region of the tank, consisting of segments 2 and 3 in core 162 and segments 2 to 4 in core 165, does not appear to be a single waste type, but rather a mixture of several wastes, and appears to be laterally heterogeneous. The aluminum concentration modestly increases, and uranium iron and nickel stay about the same. The zirconium concentration drops substantially below 1 percent in core 162 but maintains a concentration of about 9 percent in core 165, which also suggests lateral heterogeneity. Other analytes that were not present in substantial quantities in the previous segments are now present (manganese and silicon between 1 percent and 3 percent) in core 162, where they are not present in core 165.

The lower middle region of the tank, consisting of segment 5 in core 165 does not have a corresponding sample in core 162. Compositionally, this sample is much different from the others observed. Aluminum concentrations are modest, about 1 percent, and zirconium concentrations are even lower, about 0.2 percent to 0.3 percent in the upper subsegment. Zirconium concentrations in

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the lower subsegments jumps to 5 percent. Iron and nickel vary significantly between the two subsegments (between 1 percent and 5 percent), and uranium is at about 1 percent.

The lower region of the tank, consisting of segment 4 in core 162 and most of segment 6 in core 165, changes composition abruptly. Aluminum concentrations go from between 3 to 5 percent to almost 20 percent. Iron and nickel concentrations fall to below 1 percent, and uranium remains about 1 percent. Zirconium concentrations drop below 0.5 percent. These analytes in the above concentrations are suggestive of aluminum cladding waste.

The process history indicates that a small residual heel of metal waste may lie at the very bottom of this tank. The sampling data available to support that premise are very limited. The lowest subsegment from core 165 has a uranium concentration of about 3 percent, possibly indicating a transition layer from the cladding waste. That uranium concentration is not out of the range observed in some aluminum cladding waste samples, thus in this case the analytical evidence is inconclusive. The measured constituent concentrations for the core composites are given in the *Analytical Results* standard report.

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

The data required to support vapor screening are documented in *Data Quality Objective for Tank Hazardous Vapor Safety Screening* (Osborne and Buckley 1995). The two issues addressed in the DQO are vapor headspace exceeding 25 percent of the LFL, and the potential for worker hazards associated with the toxicity of constituents in any fugitive vapor emissions from the tank.

Tank 241-C-104 was vapor sampled in March 1994 in accordance with Osborne et al. (1994) and WHC (1995). Flammability results were well below action limits. No measured headspace constituents exceeded the National Institute of Occupational Safety and Health recommended exposure limits (Huckaby and Bratzel 1995). Vapor results are documented in *Tank 241-C-104 Headspace Gas and Vapor Characterization Results for Samples Collected in March 1994* (Huckaby and Bratzel 1995). The measured concentrations of inorganic gases and vapors would have a negligible effect on the flammability of the tank 241-C-104 headspace.

Hazardous vapor screening is no longer an issue for tank 241-C-104 because the safety screening DQO (Dukelow et al. 1995) addresses the concern by requiring headspace vapor (sniff) tests. With the present work controls in place, an unacceptable inhalation risk to workers from tank farm vapors does not exist in steady-state conditions, and the hazardous vapor screening toxicity issue was closed for all tanks (Hewitt 1998).

HLW Feed Processing DQO: Do the samples taken from tank 241-C-104 and the subsequent laboratory analysis meet the needs of the privatization high-activity waste DQO (Patello et al. 1999)?

Three cores were retrieved from tank 241-C-104 in 1998, and core 247 was provided in support of Waste Feed Delivery (WFD) Phase I characterization per Schreiber (1998). However, the requirements of the *Low-Activity Waste and High Level Waste Feed Data Quality Objective* (Patello et al. 1999) were not applied per customer direction (McKinney 1999a). Archived material is available for future analyses to address the DQO.

Waste Feed Delivery DQO (Confirm Tank T): Does the waste feed meet specifications as a feed source for tank waste privatization (Nguyen 1999)?

Tank 241-C-104 has been selected as a Phase I source tank for High Level Waste (HLW) sludge feed for vitrification. The data required to support waste feed delivery for Phase I high level 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* (Nguyen 1999). The DQO outlines three criteria for determining if the waste is appropriate for use as feed material. The criteria include assessing the feed characteristics, physical and rheological characteristics, and quantity properties of the tank waste. The laboratory tests outlined in Herting et al. (1999) were designed to obtain the data needed to address the DQO. The analyses required were performed in accordance with McKinney (1999a), and the results were discussed in O'Rourke (2000).

The solids were analyzed for feed characteristics according to the "envelope D" list shown in Table 2-3 (Nguyen 1999). Some constituent analyses requested in Table 2-3 were not performed due to the lack of adequate methods at the 222-S Laboratory. These analytes (Pd, Pr, Rb, Rh, Ru, Ta, Te, W, Y, ^{total}Cs, and ²³⁸Pu) are of limited interest for waste retrieval, but will become increasingly important for melter operations (O'Rourke 2000).

The Privatization Contract requires that the waste feed does not contain a separable organic layer. No separable organic phase was apparent after 30 minutes of centrifugation of the target dilution duplicate samples.

Measurements of physical and rheological properties of the waste are needed to confirm that the waste can be effectively mixed and transferred to the privatization contractor. Limits established for the properties of viscosity, specific gravity, and volume percent solids were based on an analysis of the capability of the proposed transfer routes (Galbraith et al. 1996). The mean viscosities of the core composite samples at dilution levels 60 g solids/L, 100 g solids/L, and 140 g solids/L (the target dilution is 100 g solids/L), measured at 45 °C, 65 °C, and ambient temperatures, were all below the viscosity limit set at 10 cP. The highest mean viscosity at these dilution levels was 5.5 cP, calculated from samples in the dilution level 140 g solids/L at ambient temperature. Density was measured for the samples at the three dilution levels and each of the results yield a specific gravity below the 1.5 limit. The highest specific gravity measurement (1.308) was assigned to the settled solids from the 140 g solids/L sample. The volume percent solids calculated at the target dilution of 100 g solids/L (37.1 percent) exceeded the limit of 30 percent. The target dilution may have to be increased to meet the volume percent solids criteria.

Shear strength was measured for the segment samples from core 247 prior to the preparation of the composites, as requested in Herting et al. (1999). The shear strength measurements ranged from 31 Pa to 760 Pa, and tended to increase with the sample depth in the tank. The shear strength could not be measured for two samples collected from segment 5. These two segments were sufficiently hard that the shear vane could not be pushed into the sample material (O'Rourke 2000).

The inputs for the quantity decision include the measurement of insoluble solids in the waste feed. A minimal amount of tank solids is expected to dissolve, therefore the dissolution rate was not measured for tank 241-C-104 waste per customer direction (McKinney 1999a). The total number of canisters of HLW glass that will be produced by treating the tank contents can be calculated from

component concentrations. Sufficient data were obtained for these components to allow an accurate estimate of the total HLW glass canisters, and are found in O'Rourke (2000).

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 3,700 W (12,600 Btu/hr) (Agnew et al. 1997a). The heat load estimate based on the tank headspace temperature was 3,343 W (11,410 Btu/hr) (Kummerer 1995). The tank heat load based on the Best-Basis Inventory (see Standard Report *Best-Basis Inventory [Radioactive]*) was 4,411 W (15,051 Btu/hr) as shown in Table 1-3. These estimates are below the limit of 7,600 W (26,000 Btu/hr) that separates high and low heat load single-shell tanks (LMHC 1999).

Table 1-3. Heat Load Estimate Based on the Best-Basis Radionuclide Inventory.

Radionuclide	Waste Inventory (C)	Decay Heat Generation Rate (W/C)	Heat Load (W)
Strontium-90	5.79E+05	0.00669	3,873
Cesium-137	1.14E+05	0.00472	538
Total	-	-	4,411

Bounding Concentration Limits:

Sample results from tank 241-C-104 were screened against current bounding concentrations limits used to develop the authorization source term, derived from the Final Safety Analysis Review (Adams 1999). These bounding concentration limits are found in Tables 4-1 and 4-2 in HNF-SD-PROC-021 Rev. 3, Section 18.0. Several solid sample results from americium-241, beryllium, and cadmium were initially found to exceed the bounding concentration limits, which used an estimated density of 1.6 g/mL to calculate the limits. When the appropriate sample densities were used to recalculate the bounding concentration limits for the subsamples or composites which had results exceeding the limits, the two americium-241 sample results were just below the new bounding concentration [$38.8 \mu\text{Ci/g} * (1.83/1.6) = 44.4 \mu\text{Ci/g}$]. Two beryllium sample results, S96T004950 and S96T004957 (with a range from 15 $\mu\text{g/g}$ to 30 $\mu\text{g/g}$), slightly exceeded the new bounding concentration limits of $\sim 13 \mu\text{g/g}$. The four cadmium core sample results, S96T004889, S96T004893, S96T004894, and S96T004824 (with a range from 868 $\mu\text{g/g}$ to 6,130 $\mu\text{g/g}$), exceeded the bounding concentration of 840 $\mu\text{g/g}$. Three of the cadmium results with mean concentrations ranging from 1,490 $\mu\text{g/g}$ to 6,130 $\mu\text{g/g}$ were from the portion of the waste with an average density of 1.83 and a new higher calculated bounding concentration limit of 960 $\mu\text{g/g}$. The cadmium sample with the lowest duplicate result of 827 $\mu\text{g/g}$ had a subsegment density of 1.55 and exceeded the new calculated lower bounding concentration limit of 813 $\mu\text{g/g}$ for that subsegment. Since the analytical data for beryllium and cadmium represent tank waste and there appears to be no quality assurance

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problems with the data, notifications were made for further study concerning those six sample results exceeding the bounding concentration limits.

Tank History

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

The 241-C Tank Farm was constructed during 1943 and 1944 in the 200 East Area. The C Tank Farm contains twelve 100-series tanks, and four 200-series tanks. Tank 241-C-104 is first in a cascade series of three tanks that includes tanks 241-C-104, 241-C-105, and 241-C-106. The 100-series tanks have a capacity of 2,006 kL (530 kgal), a diameter of 22.9 m (75.0 ft), and an operating depth of 4.9 m (16 ft). Tank 241-C-104 currently contains 995 kL (263 kgal) of complexant concentrate waste and is listed as sound (Hanlon 2000). Tank descriptions and figures are presented in standard reports *Description of Tank*, *Tank Plan View*, *Tank Profile View*, and *Riser Configuration Table*.

Tank 241-C-104 went into service in 1946 when it began to receive metal waste (MW) from B Plant (Agnew et al. 1997b). The MW began to cascade to tank 241-C-105 in the first quarter of 1947. Additions of MW continued until November 1947, when the tank and the cascade series were full. The tank remained full until 1953, when water was added and waste was sent to tank 241-C-106. Tank 241-C-104 was sluiced and the waste was sent to U Plant for uranium recovery in 1953. Water was added to the tank in 1954, and MW slurry was sent to U Plant for uranium recovery in 1954 and the first quarter of 1955, effectively emptying the tank. The tank remained empty until the fourth quarter of 1955 when it received tri-butyl phosphate waste (TBP) supernatant and MW from tank 241-C-112. Cladding waste was received from PUREX and was transferred to tanks 241-C-101 and 241-C-105 in 1956, and PUREX cladding waste was received again and cascaded to tank 241-C-105 in 1957.

Tank 241-C-104 received supernatant from tank 241-C-105 in 1960, and received waste from the 244-CR vault in 1965. Activity in the tank increased in the time period between 1969 and 1976. During this time tank 241-C-104 received supernatant waste from tanks 241-A-101, 241-A-102, 241-A-103, 241-AX-103, 241-C-101, 241-C-103, 241-C-106, 241-C-107, 241-C-108, 241-C-109, 241-C-110, 241-C-111, 241-C-112, 241-C-201, 241-C-202, 241-C-203, 241-C-204, 241-TY-101, and 241-U-107. The tank also received cladding waste, organic wash waste, thoria high-level waste, low-level waste, and high-level waste from PUREX. Decontamination waste was sent from the 244-CR vault to tank 241-C-104 in 1970 and again in 1974. Waste was sent from 241-C-104 to tanks 241-B-103, 241-BX-101, 241-BX-103, 241-C-102, 241-C-103, 241-C-105, 241-C-107, 241-C-108, 241-S-107, 241-SX-106, 241-TX-101, 241-U-102, and 241-U-106.

From 1976 to 1980, tank 241-C-104 exchanged supernatant with tank 241-A-102. Supernatant was sent to tanks 241-AZ-101 and 241-AX-102 in 1978. The tank received supernatant waste from 241-C-103 in 1979. Tank 241-C-104 was removed from service in 1980.

A 1985 saltwell pumping event for tank 241-C-104 is documented in Agnew et al. (1997b). Tank 241-C-104 was recorded as having sent 79.5 kL (21 kgal) to tank 241-AW-105. However, the record could not be corroborated with other evidence, such as a compatibility study or the tank

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stabilization evaluation (Boettger 1997), and the tank 241-AW-105 process history record (Agnew et al. 1997a) was never updated to incorporate the waste transfer. Therefore, it is assumed that the saltwell pumping event did not occur.

Since tank 241-C-104 was declared inactive in 1980, a steady decline in the waste level has been measured (approximately 0.13 inches/mo.). The level losses have been investigated at least six times since the tank was declared inactive, with the conclusion that the decrease in waste level is due to a combination of evaporative losses, surface irregularity, and the slumping and compaction of the waste (McKinney 1999b).

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-C-104 currently contains fourteen different waste types. It is the first tank in a cascade of three that includes tanks 241-C-105 and 241-C-106. Because of the cascade, the three tanks all received metal waste (MW) until the cascade was full in November 1947. Very little MW is expected to remain in the tank, as it was sluiced in the 1950's. The tanks also received cladding waste from Purex Plant (CWP1) in 1957. All three tanks in the cascade have a representative layer of CWP1 waste (Agnew et al. 1997a). Following the addition of CWP1 waste the tanks in the cascade operated individually to receive and transfer waste.

Another significant waste layer found in tank 241-C-104 is Purex cladding waste from a second campaign in the 1960's (CWP2). Tank 241-C-102 is estimated to have over 1,136 kL (300 kgals) of CWP2 waste. Information from tank 241-C-102 could contribute to the understanding of the CWP2 waste in tank 241-C-104. Tanks 241-C-101, 241-C-107, 241-B-109, 241-BX-102, 241-BX-103 and 241-BY-103 have small layers of CWP2 waste, according to Agnew et al. (1997a). The inventories in tanks 241-T-102 and 241-T-103 are primarily CWP2 waste, but the waste volume is small. Analytical data from these tanks are of limited value for comparing with the tank 241-C-104 results.

Tank 241-C-104 is listed as containing primarily complexant concentrate (CC) waste material in Hanlon (2000). Given the analytical data, the assignment of CC to the waste in tank 241-C-104 is incorrect. CC waste, by operating definition (Agnew 1996), contains 20 to 25 mg TOC/mL. The average TOC concentration found in the tank core composites was 14.5 mg/mL. The two other CC tanks that Hanlon (2000) lists are tanks 241-AX-102 and 241-AX-103. The waste designations given to the three CC tanks in Agnew et al. (1997a) show no common waste types between them. However, all three tanks received organic wash waste and low-level waste from Purex Plant in the 1960's. The volumes of sludge waste in tanks 241-AX-102 and 241-AX-103 are small and the waste types are varied between all three tanks. Analytical data from either of the other CC waste tanks would provide limited insight into the waste in tank 241-C-104.

The characterization of individual waste types from tank 241-C-104 analytical results is difficult. Though Agnew et al. (1997b) predicts significant layers of CWP1 and CWP2 waste in the tank, high waste transfer activity occurred and the tank received at least twelve other waste types while in service. A combination of surface irregularity and the slumping and compaction of the waste in tank

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241-C-104 was also noted after the tank was declared inactive. Therefore, the effort to identify waste layers from individual tank core segments provided inconclusive results.

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?

Tank 241-C-104 has been selected as a Phase I source tank for High Level Waste (HLW) sludge feed for vitrification. The tank contains 995 kL (263 kgal) of sludge, which will be sluiced and transferred to a staging tank prior to delivery to the vitrification contractor. Retrieval of the tank waste will require dilution. Laboratory tests were performed per Herting et al. (1999) to determine the amount of dilution required for safe retrieval and transfer of feed. The target dilution assigned was such that the diluted sludge contained 100 grams of solids per liter of diluted sludge. At the target dilution, the measured viscosity and specific gravity for the samples were below the limits set for those properties. Therefore, these properties should not negatively affect the mixing and transferring of the waste to the privatization contractor.

The volume percent solids calculated at the target dilution (37.1g solids per 100g sludge) exceeds the limit set at 30g solids per 100 g sludge for mixing the HLW sludge feed. The target dilution was calculated with the assumption that approximately ten percent of solids in the composite will dissolve upon dilution. Minimal amounts of tank 241-C-104 solids are expected to dissolve during mixing of the HLW feed (McKinney 1998). Therefore, the target dilution may be adjusted after accounting for other inputs such as particle size distribution, dissolution rates, and settling rates.

The shear strength measurements completed on undisturbed sludge from the 1998 sampling event, prior to the dilution studies, ranged from 31 to 760 Pascals and tended to increase with sample depth in the tank. The shear strength could not be measured for the two samples collected from the fifth segment. The shear vane could not be pushed into the hard sample material from these two samples. Difficulty in breaking up the hard waste heal could impact waste retrieval for the tank.

No separable organic phase was apparent after 30 minutes of centrifugation of the target dilution duplicate samples, and organic solvent surface areas were not observed in the 1998 tank video. The flammable gas concentrations in the tank headspace are low (0 percent of the LFL). The vapors measured in the headspace of tank 241-C-104 during steady-state conditions were within health hazard threshold limits for all analytes measured (Huckaby and Bratzel 1995). Therefore, organics should not impact retrieval and disposal of tank 241-C-104 waste.

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 and accepted by River Protection Project (RPP): Safety Screening DQO (Dukelow et al. 1995), Organic Solvent Safety Issue DQO (Meachem et al. 1997), Organic Complexant MOU (Schreiber 1997), Historical DQO (Simpson and McCain 1997), and Hazardous Vapor Screening DQO (Osborne and Buckley 1995). No additional sampling or analyses are necessary to satisfy these requirements for this tank.

Additional analysis may be necessary to meet the requirements of the HLW Feed Processing DQO (Patello et al. 1999) and the Waste Feed Delivery (Confirm Tank T) DQO (Nguyen 1999). The requirements of the *Low-Activity Waste and High Level Waste Feed Data Quality Objective* (Patello et al. 1999) were not applied per customer direction (McKinney 1999a). Some constituent analyses requested in Nguyen (1999) were not performed because of the lack of adequate methods at the 222-S Laboratory. Sludge washing activities in support of Waste Feed Delivery may be restored in the future as well. Archived sample material should be suitable for these purposes.

Data Quality

The data obtained in the 1994 vapor and 1996 core sampling events were collected and analyzed with approved and recognized sampling and laboratory procedures. The vapor analyses were conducted according to Osborne et al. (1994), while the core analyses were performed in accordance with the sampling and analysis plan (Homi 1996). 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-C-104 samples included standard recoveries, spike recoveries, duplicate analyses, and blanks. Appropriate QC footnotes were applied to data outside QC parameter limits as shown in the standard report *Analytical Results*. Analytical results and data quality for the core samples are discussed in the tank 241-C-104 data package (Fritts 1997). Vapor sampling results and a summary of the data quality are provided in Huckaby and Bratzel (1995). Data quality for the 1998 core samples is not addressed in this section as two cores were sent to the privatization contractor and the third was altered and analyzed for the Waste Feed Delivery (Confirm Tank T) DQO (Nguyen 1999).

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. A brief discussion of these small discrepancies is presented below.

The DSC analyses were performed in duplicate on direct subsamples. Relative percent differences (RPDs) greater than 30 percent were reported for five of the twelve subsamples. The results of four of these samples were near the detection limit for the instrument and resulted in a decrease in precision. No further analysis for these subsamples was requested. A second analysis of core 165, segment 5, upper half (sample number S96T004919) was performed. The results from the second

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analysis were similar to those from the first analysis. Sample inhomogeneity appears to be the cause of the initial high RPD.

The TGA analyses were performed in duplicate on direct subsamples. An RPD greater than 30 percent was reported for one of the twenty three subsamples. A second analysis of core 162, segment 4, lower half (sample number S96T004843) was performed, and sample inhomogeneity appears to be the cause for the initial high RPD. The results from the second analysis were similar to those from the first analysis.

The preparation blanks for the ICP analysis showed Al, Fe, Ni, and Na results above the detection level. The levels of these analytes in the preparation blank are inconsequential when compared to the results for the samples (Fritts 1997).

The TOC subsample from core 165, segment 6, quarter segment D (sample number S96T004881) had a spike recovery of 73.8 percent. If the spike recovery is calculated using the duplicate result, it is within the specified QC range of 75 to 125 percent. This suggests sample heterogeneity, and rerun analyses would not significantly improve the results.

Two TIC subsamples had RPDs slightly outside the QC parameters of ± 20 percent. Four subsamples had spike recoveries slightly outside the QC range of 80 to 120 percent. Reruns were not requested.

Low spike recoveries for the total alpha analysis were reported for core 165, segment 5, lower half (sample number S96T004924) and core 165, segment 6, quarter segment D (sample number S96T004898). These are the result of self-absorption from dissolved solids in the sample. The results for these samples may be biased low. One preparation blank showed a result above the detection level. The preparation blanks also showed strontium-90 activity above the detection level, and two preparation blanks showed cesium-137 activity above the detection level. The activity in these preparation blanks is inconsequential when compared to the results from the sample.

Rerun analysis of sample numbers S96T004850, S96T004852, and S96T004853 show the high RPD results for the GEA analytes to be the result of heterogeneity problems between the sample and duplicate preparation. The levels of cesium-137 and the relatively low RPDs do not warrant the preparation of another fusion digestion for these samples.

A few analytical results from the sampling event were flagged by a computer algorithm using internal quality control standards. These results were reviewed to determine if the data were compromised, and if so, the anomalous value was removed from the *Analytical Results* Standard Report. One copper analysis reported for core 162, segment 4 (sample number S96T004852) showed an RPD of greater than 188 percent, and the duplicate value of 5950 $\mu\text{g/g}$ was removed. One zinc result from the solid composite samples, from core 165 (sample number S96T004956), showed high RPDs (greater than 100%). The zinc value of 1,170 $\mu\text{g/g}$ from the fusion analysis was determined biased (Nguyen 2000) and removed from the *Analytical Results* Standard Report.

The 1996 core sample ICP subsamples were prepared for analysis by three digestion processes: acid, water, and fusion. The fusion digestion process was performed using potassium hydroxide as a reagent and a nickel crucible for the digestion vessel. The results for potassium were biased high

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due to the use of the potassium hydroxide, and the results for nickel were biased high due to leaching from the crucible. Therefore, the results for these analytes from the fusion preparation were not included in the *Analytical Results* Standard Report.

The analyses performed on tank waste material sampled in 1996 included the traditional analysis of technetium-99 by radiochemical separation. It was observed that the results were 50 to 100 times higher than expected, and an investigation into the sample matrices and method was initiated. Results from the beta spectral evidence indicated that an incomplete separation of plutonium-241 from technetium-99 caused spectral interference and a false high technetium-99 signal. It was postulated that the sludge material has an organic or other complexant which binds to the plutonium, which is then extracted in the organic phase of the technetium-99 analysis (Troyer 1999). Only sludges with significant concentrations of plutonium or other actinides are expected to exhibit high radiochemical results for technetium-99. For the tank 241-C-104 sludge, the ICP/MS analytical method, rather than the radiochemical separation method, provides good estimation of the actual technetium-99 concentration.

Clarification and Explanation of Data Tables and Figures

Description of Tank Standard Report: The total waste volume of 995 kL (263 kgal) shown in this standard report does not agree with the Hanlon (2000) volume. The total waste volume was adjusted to account for observed tank waste settling and evaporation. The volume of drainable liquid also differs between the standard report and Hanlon (2000) report. The drainable liquid volume in the standard report was derived from 1998 core extrusion observations. The updated volumes will be reflected in a future revision to Hanlon (2000).

Analytical Results and *Sample Analysis Summary* Standard Reports: Two core composites were created using solids from the 1996 sampling event. For core 162, the solid composite results listed are from the homogenization of approximately forty grams of material from each of the six segments recovered, with the exception of segment 1. The amount of material in the core 162 solid composite segment 1 was 7.7 grams, ten percent of recovered solids for the segment. The solid composite results listed for core 165 are from the homogenization of approximately fifty grams of material from each of the four segments recovered from the sampling event. One sample portion listed under core 162 segment 2 is referenced as "Centrifuged Solids". The sample was created from 1996 archived sample material to perform an organic speciation analysis concurrently with ten other samples from six other waste tanks. The majority of the samples in the organic speciation analyses were centrifuged to separate the sludge from the interstitial liquid in the sample. However, it was noted that the sample from tank 241-C-104 was dry and no centrifugation was performed (Esch 1998). As no alteration was made to sample material, the results were included in the standard reports.

The 241-C-104 Means and Confidence Intervals Standard Report: The means for each data set are listed separately in the *241-C-104 Means and Confidence Intervals* Standard Report. Immediately preceding each *Tank 241-C-104 95 Percent Two-Sided Confidence Interval for the Mean Concentration* table is a discussion of the method used to derive those means. The solids sample portion mentioned in the first paragraph of the discussion immediately preceding the *Tank 241-C-104 95 Percent Two-Sided Confidence Interval for the Mean Concentration for Solid 98 Analyses, 96 Comp* table refers to an archived 1996 core 162 composite sample that was analyzed in 1998. The

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solids sample portion mentioned in the first paragraph of the discussion immediately preceding the *Tank 241-C-104 95 Percent Two-Sided Confidence Interval for the Mean Concentration for Solid Core Composite Data* table refers to the data generated from core 162 and core 165 composites. The solids sample portion mentioned in the first paragraph of the discussion immediately preceding the *Tank 241-C-104 95 Percent Two-Sided Confidence Interval for the Mean Concentration for Solid Subdivision Data* table refers to core 162 and core 165 segment data. The liquid sample portion mentioned in the first paragraph of the discussion immediately preceding the *Tank 241-C-104 95 Percent Two-Sided Confidence Interval for the Mean Concentration for Liquid Drainable Liquid* table refers to drainable liquid recovered from two segments in core 162.

The *241-C-104 Average Monthly Tank Surface Level Standard Report*: The graph shows an abrupt 30 cm. (12 in.) increase in level during the first quarter of 1999. This increase is caused by rebaselining the surface level to the tank bottom centerline and does not represent any real transfer of waste.

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 this tank are relatively well defined and understood, and can be found in a number of other tanks. However, changes to the tank waste have occurred since the tank was declared inactive in 1980. Surface level readings taken over the last nineteen years have recorded a waste level decrease at a fairly consistent rate from the tank level baseline established at 110.9 inches (January 27, 1981), to 97.3 inches (January 2, 2000). The recorded decrease was evaluated on several separate occasions, with the conclusions that the waste level reduction was due to waste compaction, surface irregularity caused by waste slumping, and evaporation (McKinney 1999b). A comparison of the densities measured from cores taken in 1986 (1.21 g/mL) and 1996 (1.69 g/mL) support the conclusion of sludge compaction in the tank. The 1998 in-tank video shows the surface level measurement instrument in a dish shaped depression estimated at 5-8 inches deep, which would contribute to the decrease in the waste level measured. While tank 241-C-104 is not considered an actively ventilated tank, it is the first of a three tank cascade series with tanks 241-C-105 and 241-C-106, which are actively ventilated tanks. The pump pits for the two connected tanks were taped in July 1981, which resulted in an increased ventilation in tank 241-C-104. An evaluation done in November 1983 verified that the decrease in level was caused by evaporation due to an operating exhauster (Van Meter 1983).

The compaction and evaporation of the waste is supported by the changes in the surface appearance between the 1982 and 1988 in-tank photographs. The May 1982 in-tank photographs show a wet, level surface, which appears to be covered in a thin sheen of moisture, but no major supernate pools. Holes and pockmarks visible in the photograph are spread uniformly across the surface and seem to be full of liquid. Photographs taken April 1988 show a dry cracked surface with no evident surface moisture. Observations of the waste surface from the in-tank video taken in 1998 are similar to those based on the 1988 photographs.

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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 River Protection Program (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. Since new sample data were recently made available for tank 241-C-104, 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:

- Tank 241-C-104 statistical means based on the 1996 core samples (cores 162 and 165) analyzed in 1996 and 1999 and reviewed in January 2000 (see *Means and Variances Standard Report*).
- Hanford Defined Waste (HDW) model single-shell tank 241-C-104 total inventory estimate (Agnew et al. 1997a).

The following table represents how the available data were used to derive best-basis inventories for tank 241-C-104.

Table 7-1. Tank 241-C-104 Best-Basis Inventory Source Data.

Waste Phase	Waste Type	Applicable Concentration Data	Associated Density	Associated Volume
Sludge	Cladding Waste	Mean concentrations for 1996 core composite solids	1.69 g/mL	995 kL (263 kgal)
		Mean concentrations for 1996 core segment solids		
		Mean concentration for 1999 analysis of 1996 core sample solids		
		HDW Model total inventory estimate	1.46 g/mL	
Total Tank				995 kL (263 kgal)

The waste phase and waste type designations for Table 7-1 were based on core sampling extrusion results and process history. The extrusions from cores 162 and 165 taken in 1996 showed a wet to dry sludge, with one segment of sludge slurry. The waste type of cladding waste was assigned to tank 241-C-104 based on the waste that was received by the tank while it was in operation. Tank

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241-C-104 received approximately fourteen different waste types while in service, but the majority of the inventory was cladding waste received from various Purex Plant campaigns (Agnew et al. 1997b).

Inventories of the sludge phase were calculated using sample solids means based on data from two core samples taken in 1996. Separate means were calculated from the composite data and segment data. An archived sample from the 1996 sampling event was subsampled to perform a reanalysis for the technetium-99 concentration in 1999 to address a discrepancy between 1996 data and the previous BBI value. It was determined that a matrix interference caused a bias in the 1996 technetium-99 results (Troyer 1999). The 1999 results were used to estimate the technetium-99 concentration in this BBI. Three cores were retrieved from tank 241-C-104 in 1998. Two cores were reserved for the Privatization Contractor, and the third was used to carry out tests for the Waste Feed Delivery DQO (physical property tests only). Therefore, data from the 1998 sampling event were not available for the BBI effort.

A drainable liquid volume is usually associated with sludge waste (Field and Vladimiroff 1999), and a volume of 42 kL (11 kgal) was assigned for the tank 241-C-104 drainable liquid phase in Hanlon (2000). However, since tank 241-C-104 was declared inactive in 1980, the tank waste has undergone evaporation and settling and the waste is no longer assumed to be saturated. Less than 100g of drainable liquid were recovered from the 1996 sampling event, and no drainable liquid was recovered from Core 247 in 1998. Therefore, for the purpose of the BBI, no separate liquid waste phase was assessed.

Sample data are available for all 25 best-basis nonradioactive chemical species for the sludge waste phase, but not all radionuclide data are available. The HDW model (Agnew et al. 1997a) tank total inventory data were used where sample data were not available or were qualified.

For the 1996 sampling event, the density value (1.69 g/mL) was derived from the segment subdivision data mean. The HDW model (Agnew et al. 1997a) total tank density was 1.46 g/mL.

The total tank volume of 995 kL (263 kgal) was derived from an averaged surface level measurement from three tank risers in 1996, adjusting for the estimated depth of the dish-shaped depression in one riser containing the Food Instrument Company (FIC) liquid level measurement instrument (McKinney 1999b). The waste recovery from the 1996 core sampling event supports the volume calculated for Table 7-1. The ENRAF measurement instrument replaced the FIC in Riser 8 in 1999. The calculated volume from the January 2, 2000 ENRAF measurement was 931 kL (246 kgal). However, as a result of the depression in the waste and the uneven waste surface in the tank, the calculated volume from the ENRAF measurement underestimates the waste volume of the tank. The volume assigned to the tank in Hanlon (2000) was 1117 kL (295 kgal). The volume was estimated from the process history and the waste additions to the tank until it was removed from service in 1980 (Agnew et al. 1997b). Level decreases since 1980 have been observed and attributed to settling and evaporation (McKinney 1999b). The BBI volume and phase information will be reflected in a future Hanlon report update.

For calculating the BBI, the mean concentrations for 1999 data were preferred, where available. The majority of the analytes were characterized from 1996 analytical data. The 1996 composite data were preferred over the 1996 segment data. However, when comparing mean values below detection limits, the lowest nondetect value was always selected, whether segment or composite data.

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When comparing acid digest and fusion results the higher value was chosen. When neither sample or template data were available for a given analyte, or when available data were below detection limits and the detection limit was higher than the HDW model value, then HDW model results (Agnew et al. 1997a) were used.

All inventory calculations were performed using the Best-Basis Inventory Maintenance (BBIM) Tool. The updated best-basis inventory values for tank 241-C-104 can be found in the "*Best-Basis Inventory (Non-Radionuclides)*" and "*Best Basis Inventory (Radionuclides)*" Standard Reports.

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