0050783 1. ECN 653793 ENGINEERING CHANGE NOTICE ----Proj. ECN Page 1 of 2 4. USQ Required? 3. Originator's Name, Organization, MSIN, 5. Date 2. ECN Category and Telephone No. (mark one) John M. Conner, Data Assessment [] Yes [X] No 05/25/99 Supplemental [] and Interpretation, R2-12, 373-Direct Revision [X] Change ECN [] 2711 Temporary [] 6. Project Title/No./Work Order No. 7. Bldg./Sys./Fac. No. 8. Approval Designator Standby [] Supersedure [] Tank 241-B-102 241-B-102 N/A Cancel/Void [] 9. Document Numbers Changed by this ECN 10. Related ECN No(s). 11. Related PO No. (includes sheet no. and rev.) WHC-SD-WM-ER-405, Rev. 0-D 623839 N/A ECNs: 625690. 634632. 644475 12a. Modification Work 12b. Work Package 12c. Modification Work Complete 12d. Restored to Original Condition (Temp. or Standby ECN only) No. N/A N/A N/A Yes (fill out Blk. 12b) [X] No (NA Blks. 12b, Design Authority/Cog. Engineer Design Authority/Cog. Engineer 12c, 12d) Signature & Date Signature & Date FX7 No 13b. Design Baseline Document? [] Yes 13a. Description of Change This ECN has been generated in order to update the document to reflect results of recent data/information evaluation. Replace pages: ES-1 through ES-4, ES-7, ES-8, 5-3, 5-4, 6-1, 6-2, and 7-1 through 7 3 S 14a. Justification (mark one) **FX1** [] F1 Γ1 Criteria Change Design Improvement Environmental Facility Deactivation [] [] ٢٦ As-Found Facilitate Const Const. Error/Omission Design Error/Omission 14b. Justification Details A tank characterization report page change revision is required to reflect the results of recent evaluation of data/information pertaining to adequacy of tank sampling for safety screening purposes (Reynolds et al. 1999, Evaluation of Tank Data for Safety Screening, HNF-4217, Rev. 0, Lockheed Martin Hanford Corporation, Richland, Washington). RELEASE STAMP 15. Distribution (include name, MSIN, and no. of copies) .99 le. See attached distribution. DATE: HANFORD RELEACE TA

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Tank Characterization Report for Single-Shell Tank 241-B-102

John M. Conner Lockheed Martin Hanford Corp., Richland, WA 99352 U.S. Department of Energy Contract 8023764-9-K001

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EXECUTIVE SUMMARY

This tank characterization report summarizes the information on the historical uses, present status, and the sampling and analysis results of waste stored in the single-shell underground storage tank 241-B-102. This report supports the requirements of the *Hanford Federal Facility Agreement and Consent Order* Milestone M-44-08 (Ecology et al. 1994).

Tank 241-B-102 is located in the 200 East Area B Tank Farm at the Hanford Site. The tank went into service in 1945 by receiving metal waste produced by the bismuth phosphate process. It is the second tank in a "cascade" connecting it to tanks 241-B-101 and 241-B-103. Tank 241-B-102 was sluiced in 1953 to remove the metal waste for uranium recovery. The tank was later used to store waste from the 242-B Evaporator. The tank also received cladding removal waste supernate from the Plutonium-Uranium Extraction (PUREX) process and supernate from the fission product recovery process at B Plant.

A description and status of the tank are summarized in Tables ES-1 and ES-2 and Figures ES-1 and ES-2 following this summary. The tank was made inactive in 1978 and interim stabilized in 1985 after salt well pumping. The tank has undergone intrusion prevention in 1985 and is considered to be sound. As of October 31, 1994 the waste inventory for tank 241-B-102 shows the tank contains 121 kiloliters (kL) (32,000 gallons [gal]) of waste. This includes 15 kL (4,000 gal) of supernate, 68 kL (18,000 gal) of sludge and 38 kL (10,000 gal) of salt cake (Hanlon 1994). Based on waste level measurements near

ES-1

the edge of the tank, the tank only contains an estimated 18.5 centimeters (cm) (7.3 inches [in.]) of waste, which is expected to be mostly salt cake from the 242-B Evaporator operations (Brevick et al. 1994a). Because the tank has a dished bottom, waste depth near the center may be about 48.5 cm (19.1 in.). The tank is a non-watch list, low-heat load tank, whose contents are classified as noncomplexed waste.

This report discusses the auger sampling and analysis event that occurred on October 16, 1994, and a vapor sampling event on August 30, 1995, to meet the requirements defined in *Tank Safety Screening Data Quality Objective* (Babad and Redus 1994). Because safety screening only requires analyses for differential scanning calorimetry (DSC), moisture, total alpha, and flammable gases, the chemical and radiochemical composition estimate of the waste is based primarily on the *Historical Tank Content Estimate* (Brevick et al. 1994b).

The auger sampling and analysis event did not fully comply with the safety screening data quality objectives. Because of the low levels of waste in the tank, it was possible to obtain a limited amount of sample from only one riser. Only about 25 percent of the expected auger sample quantity was recovered. However, this amount has proved to be sufficient to resolve the safety screening concerns (Reynolds et al. 1999). Variability in the analytical results was greater than desired (+ 10 percent) because of sample heterogeneity.

The average of four DSC results from the lower auger region of the average sample showed an exotherm (267 joules [J] per gram $[g] \pm 32$ J/g) that was about two times below the safety screening criteria. The average of six values for weight percent water for this

same auger region was 17.4 wt% with a standard deviation of \pm 3.3 wt%. The DSC results for sample from the upper region of the auger was considerably lower (175 J/g) and the weight percent water was slightly higher (20.5 percent).

The heat generated by the radioactivity in the tank is estimated to be very low (97 British thermal units per hour [Btu/hr]) based on the historical inventory estimates. The highest recorded temperatures for the tank have been between 20 °Celsius (C) and 30 °C and are consistent with the estimated low heat load for the tank.

The total alpha results (<0.36 microcuries per gram [μ Ci/g]) indicate that the plutonium concentration is well below the safety screening criteria (41 μ Ci/g). However, the total alpha less than values are too large to determine if the waste is above or below the transuranic classification limit (100 nanocuries per gram [nCi/g]).

The flammable gas concentration measurement in the tank vapor space was 0 percent of the lower flammability limit, which satisfies the safety screening criterion.

Based on the sample and analysis results, the waste in the tank does not appear to present any immediate safety concerns. However, the inability to sample a second riser and the poor recovery for the sample analyzed make it impossible to assess the uncertainty and variability of the waste properties in the tank. The shallow waste depth of this tank (approximately 7.1 inches) contributed to the difficulty in retrieving two separate cores, per the safety screening optimal requirements. However, a technical review panel (Reynolds et al. 1999) has determined that the auger samples provided sufficient, if not optimal sampling to close the safety screening issue. The analytical results, historical information and low waste volume do not offer justification for additional sampling and analysis.

The concentration and tank inventory for chemical and radiochemical components in the waste is summarized in the attached table. These estimates are based on the historical tank layer model (Brevick et al. 1994b). This model predicts that the waste is mostly salt cake from the 242-B Evaporator; therefore, the waste is high in sodium salts. Uranium is expected to be moderately high because of residual metal waste from the bismuth phosphate process. Even though the model does not indicate the presence of any organic carbon, the waste transfer history indicates that organic complexants may have entered the tank from the fission product recovery process. This may explain the observed exotherms in the safety screening analyses.



Figure ES-1. Riser Configuration for Tank 241-B-102.





Total Tank Volume: 2,010 kL (530 kgal) Current Waste Volume: 121 kL (32 kgal) Saitcake Volume: 37.9 kL (10 kgal) Sludge Volume: 68.1 kL (18 kgal) Supernate Volume: 15 kL (4 kgal)

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Several of the duplicate results for DSC and TGA exceed the \pm 10 percent safety screening criteria. The duplicate TGA percent water from the immediate sample taken from flutes 5 and 6 agreed very well (relative percent difference [RPD] = 4.8 percent) but the DSC RPD of 25.7 percent exceeded the safety screening duplicate criteria. The RPD for the TGA percent water results for the composite samples from flutes 1 to 5 and 5 to 9 also exceeded the 10 percent RPD criteria. These TGA samples were rerun in duplicate after a low standard recovery (93.6 percent). Only the rerun data results are reported in Table 4-2. Even though the RPD of the reruns improved from the initial analysis, they still exceeded the 10 percent criteria. The average RPD and standard deviation for these two sets of duplicate data was 24 ± 9 percent. Because of the repeated variability in the duplicates and the reruns, the large RPDs are believed to be caused by sample heterogeneity and not the analytical method.

The TGA and DSC method use very small sample sizes (10 mg). If the sample is not homogeneous (evenly moist), the variability in taking the 10 mg sample will be large. This moisture heterogeneity becomes more of a problem when handling small quantities of sample because the potential for the sample to dry out is greater. Less than 10 g of sample was being handled for these analyses. Because drying out may not affect the DSC results like the TGA, it may explain why the DSC exothermic results for the two composite samples agree when the TGA results do not. In summary, all of the data were within the quality control limits except the RPD data for percent water, and that departure does not seem excessive considering the observed heterogeneity of the sample.

5.2 TANK WASTE PROFILE

The small depth of waste in the tank, the few analytes tested, the poor sample recovery and the sampling of a single riser do not allow a very good assessment of the distribution of properties. A comparison of the results from the upper (1 to 5) and lower flutes may give an indication of changes in the waste moisture and DSC properties.

A statistical test known as the t-test was conducted on the percent water and DSC data to determine if there was any difference between the upper and lower halves (flutes 1 to 5 and 5 to 9, respectively) of the auger sample. The t-test generates a statistic called a p-value, which is compared with a standard significance level ($\alpha = 0.05$). If a p-value is below 0.05, there is sufficient evidence to conclude that the subsample means are significantly different from each other. However, if a p-value is above 0.05, there is not sufficient evidence to conclude that the subsamples are significantly different from each other. The results of the t-test for percent water indicated that there was not a significant difference between the upper and lower halves of the sample (p-value = 0.065). For the DSC values, the t-test indicated that the lower half of the sample had a significantly larger DSC value than the upper half (p-value = 0.010). The large variability in the TGA percent water analyses makes it difficult to distinguish differences in moisture between the upper and lower auger regions.

5.3 COMPARISON OF ANALYTICAL AND TRANSFER HISTORY INFORMATION

Because of the few analytical requirements for the safety screening characterization, the comparison of the analytical results from the 1994 sampling event with the historical transfers and estimated inventories is very limited. The less than values for the total alpha results ($<0.356 \ \mu$ Ci/g) corresponding to the 1994 sampling event are too high to compare to the *Historical Tank Content Estimate* (Brevick et al. 1994a) plutonium estimate (0.11 μ Ci/g). Percent water results are not comparable because they depend on how much the waste has dried out over time. There are no historical estimates for DSC results other than fuel based on total organic carbon (TOC) or cyanide. The *Historical Tank Content Estimate* estimates that there is no TOC in tank 241-B-102. However, records indicate that the tank received waste from the fission product recovery process at B Plant during its latter years of service. Because this process used organic complexants, some of the complexants could have been transferred to the tank and may explain the exothermic reactions that were observed in the DSC analysis.

5.4 EVALUATION OF PROGRAM REQUIREMENTS

The 1994 auger sampling event was performed to meet the safety screening DQO (Babad and Redus 1994). Therefore, only these safety program requirements can be assessed. There is insufficient data to evaluate operational, environmental, or process development programs.

5.4.1 Safety Evaluation

The data criteria identified in the safety screening DQO is used to assess the safety aspect of the waste in tank 241-B-102. The 1994 auger sampling event was not able to retrieve the optimal amount of materials from the tank, because of the low level of waste. However, a technical panel has reviewed the data form the subsequent analyses and determined that the sampling information was sufficient to establish that the safety screening issue for this tank is closed (Reynolds et al. 1999). The reproducibility (duplicate RPD) of the TGA percent water results exceeded the 10 percent criteria established in the DQO because of sample heterogeneity. A comparison of the safety screening decision limits and the analytical results is provided in Table 5-2.

The waste fuel energy value is normally determined using DSC analysis of the waste material. An exotherm was observed for the waste that had an onset temperature of 320 °C. The maximum average energy output observed for the exotherm on a dry weight basis was 278 J/g. This is about two times lower than the safety screening criteria of 523 J/g. There are no analyses for TOC or cyanide to identify the source of the fuel but historical transfer information indicates that the tank received B Plant waste in the 1970's that may have contained organic complexants.

6.0 CONCLUSIONS

The sludge in tank 241-B-102 has only been sampled and analyzed in October 1994. Supernate analyses information from the 1970's are no longer applicable. Because the 1994 auger sampling event was focused only on safety screening criteria, the chemical and radiochemical composition of the waste must be estimated from historical information (Brevick et al. 1994a). The waste is expected to contain mostly salt cake with high concentrations of sodium and aluminum. The analysis of the 1994 auger sample indicated that the plutonium concentration was well below criticality levels. The DSC analysis of the waste did exhibit an exotherm indicating the possible presence of organic carbon. However, the maximum average dry weight exotherm (278 J/g) was lower than the safety screening criteria. TGA analysis of the waste indicated that the percent moisture level in the waste was near the safety screening criteria of 17 percent.

The 1994 auger sampling and analysis event for tank 241-B-102 did not meet all the requirements for the safety screening DQO. The inability to sample a second riser and the poor recovery of waste from the other riser make it impossible to estimate the sampling uncertainty and variability in the waste composition. Even though the percent water is very near the safety screening criteria limits, existing DSC data indicate that the fuel level in the waste is below the established safety limit (523 J/g). In addition, historical information on heat generation rates and tank temperatures do not indicate that excessive heat is being generated in the waste. Additional sampling and analysis could provide a better understanding of the variability of the waste composition. However, the auger sampling has provided enough materials for analysis and determination that the safety screening issue for this tank is closed. Based on the small waste volume, these analytical results and historical information about the waste, there is no justification for performing additional sampling and analysis of the tank (Reynolds et al. 1999).

A 1995 vapor space sampling event for tank 241-B-102 was completed to address the vapor flammability portion of the safety screening DQO. Flammable gases were found to be 0 percent of the lower flammability limit.

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