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ENGINEERING CHANGE NOTICE

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Proj. ECN

2. ECN Category (mark one)	3. Originator's Name, Organization, MSIN, and Telephone No.	4. USQ Required?	5. Date
Supplemental [] Direct Revision [X] Change ECN [] Temporary [] Standby [] Supersedure [] Cancel/Void []	Juergen H. Rasmussen, Data Assessment and Interpretation, R2-12, 373-1128	[] Yes [X] No	05/26/99
	6. Project Title/No./Work Order No. Tank 241-AZ-102	7. Bldg./Sys./Fac. No. 241-AZ-102	8. Approval Designator N/A
	9. Document Numbers Changed by this ECN (includes sheet no. and rev.) WHC-SD-WM-ER-411, Rev. 0-C	10. Related ECN No(s). ECNs: 627032, 612283, 644481	11. Related PO No. N/A

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[] Yes (fill out Blk. 12b) [X] No (NA Blks. 12b, 12c, 12d)	N/A	N/A Design Authority/Cog. Engineer Signature & Date	N/A Design Authority/Cog. Engineer Signature & Date

13a. Description of Change

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

This ECN has been generated in order to update the document to reflect results of recent data/information evaluation.

Replace pages:

ES-7 through ES-10, 1-1, 1-2, 5-13 through 5-16, 6-1, 6-2, and 7-1 through 7-4

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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	[]

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).

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

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1. ECN (use no. from pg. 1) ECN-653814

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

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

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

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

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

21. Approvals

	Signature	Date		Signature	Date
Design Authority			Design Agent		
Cog. Eng. J.H. Rasmussen	[signature]	6/4/99	PE		
Cog. Mgr. K.M. Hall	Kathleen M. Hall	6/4/99	QA		
QA			Safety		
Safety			Design		
Environ.			Environ.		
Other			Other		

DEPARTMENT OF ENERGY

Signature or a Control Number that tracks the Approval Signature

ADDITIONAL

Tank Characterization Report for Double-Shell Tank 241-AZ-102

Juergen H. Rasmussen
Lockheed Martin Hanford Corp., Richland, WA 99352
U.S. Department of Energy Contract 8023764-9-K001

EDT/ECN: ECN-653814 UC: 2070
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Abstract: N/A

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RECORD OF REVISION	(1) Document Number WHC-SD-WM-ER-411	Page i

(2) Title
Tank Characterization Report for Double-Shell Tank 241-AZ-102

CHANGE CONTROL RECORD

(3) Revision	(4) Description of Change - Replace, Add, and Delete Pages	Authorized for Release (5) Cog. Engr.	(6) Cog. Mgr. Date
0	(7) Initially released 07/27/95 on EDT-612174.	G.W. Ryan	J.G. Kristofzski
0-A RS	Incorporate per ECN-627032.	R.D. Schreiber	J.G. Kristofzski
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		MJ Kupfer 7/9/97	K.M. Hodgson 7/21/97
0C RS	Incorporate per ECN 644481	M. J. Kupfer	K. M. Hodgson
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		JHRasmussen	Kathleen M. Hall 6/4/99

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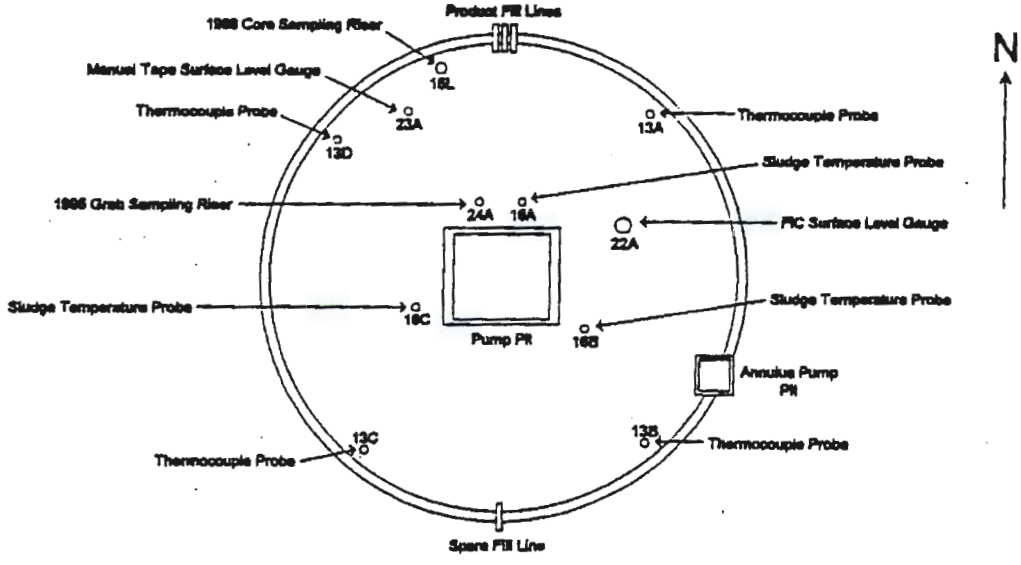
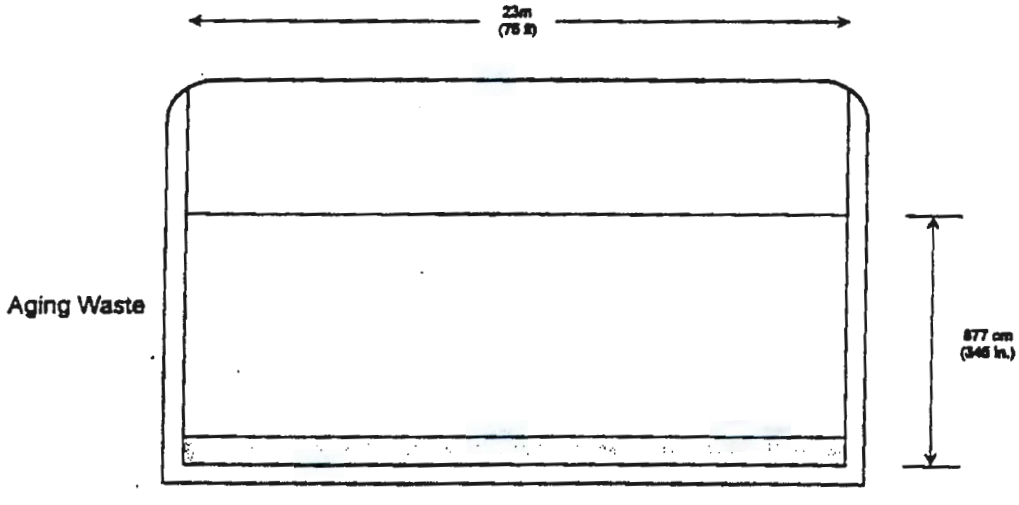
Figure ES-1. Tank 241-AZ-102.

Tank 241-AZ-102



Waste Profile of Tank 241-AZ-102



Total Tank Volume: 3,790 kL (1,000 kgal)
Current Waste Volume: 3,590 kL (949 kgal)
Current Sludge Volume: 360 kL (95 kgal)
Current Supernate Volume: 3,230 kL (854 kgal)

operational capacity of 3,710 kL (980 kgal), currently contains 3,590 kL (949 kgal) of waste, 3,230 kL (854 kgal) existing as supernatant and 360 kL (95 kgal) in the form of sludge (Hanlon 1995). The sludge measured 333 kL (88 kgal) when last sampled (May 1989), while the supernatant constituted 3,230 kL (854 kgal) upon its most recent sampling (February 1995).

This report summarizes four sampling and analysis events. The first two sampling events occurred in August and October of 1987 and the results are presented and used in this report only for comparison with the more recent sampling events. The third sample was taken in 1989 to support retrieval, pretreatment, and disposal and is used to represent sludge composition and properties. Finally, supernatant composition is based on grab samples taken in February of 1995 to evaluate waste compatibility. The grab samples were taken as prescribed in the *Data Quality Objectives for the Waste Compatibility Program*, WHC-SD-WM-DQO-001 (Carothers 1994).

The fuel content of the supernatant was measured by differential scanning calorimetry (DSC) and no exotherms were found, denoting that the fuel content of the supernatant is low. Although a similar analysis was not performed on the core sample, the secondary TOC analysis called for in the current safety screening DQO (Dukelow et al. 1995) in the event the DSC threshold is exceeded was performed. The TOC results are well below the 30,000 μg/g threshold, satisfying the analysis requirement per the safety screening DQO. If the sludge is sampled again the analyses should include an evaluation of the fuel content by DSC to provide an estimate of the future compatibility of this sludge with other waste types. The waste is approximately 90% supernatant, and the sludge moisture content was found to be 51% (by weight), which more than satisfies the 17 wt%

water requirement of the safety screening DQO (Babad and Redus 1994). The tank has a substantial heat load of <58,441 W (<199,457 Btu/hr), which is to be expected due to the high concentration of ^{90}Sr in aging waste. Although notable, the heat load is still far below the 4,000,000 Btu/hr design limit (Bergmann 1989). The estimated level of $^{239/240}Pu$ in the tank sludge, 3.14 μCi/g, is below the safety screening threshold of 41.3 μCi/g (Babad and Redus 1994). Standard hydrogen monitoring system (SHMS) monitoring data and confirmatory grab samples show that the active ventilation system and other controls now in place maintain the tank headspace well below the LFL. The tank was actively mixed by air lift circulators during the years it received NCAW waste from PUREX. Since only minor transfers have occurred since then, the single 1989 core sample and the 1995 grab samples are sufficient to meet the intent of the safety screening DQO.

The 1995 supernatant analysis indicates that the liquid meets compatibility assessment criteria. The supernatant $^{239/240}Pu$ and ^{241}Am levels are below the transuranic classification limit of 100 nCi/g. The TOC concentration in the supernatant is 1.50 g/L, well below the organic complexant classification criteria of 10 g TOC/L. It should be noted, however, that the transfer of the waste in tank 241-AZ-102 to a non-aging waste DST will likely result in a violation of heat load limits for the receiving tank.

The concentration and tank inventory estimates for the major constituents and analytes of concern in the sludge and liquid above the sludge are summarized in Table ES-2. The sludge contained high concentrations of Fe, Na, and Al, and relatively high concentrations of zirconium, chromium, cadmium, uranium, nickel, SO_4^{2-}, NO_2^-, and NO_3^-. The results for iron, sodium, aluminum, uranium, SO_4^{2-}, NO_2^-, and NO_3^- are consistent with what was

expected to be in aging waste, and nickel and chromium are expected corrosion products from PUREX piping and process equipment. Also expected due to aging waste composition were the high levels of ^{90}Sr, ^{137}Cs, ^{106}Ru, and ^{241}Am.

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1.0 INTRODUCTION

This report presents an overview of double-shell underground storage tank 241-AZ-102 (tank 241-AZ-102) and its waste contents. It provides estimated concentrations and inventories for the waste components based on the latest sampling and analysis activities and background tank information. This tank characterization report for tank 241-AZ-102 describes the results of the four most recent sampling events. The first occurred in August of 1987 with the taking of a sludge and supernatant sample (Herting 1987). The second took place in October of 1987 and also included a sludge and supernatant sample (Herting 1988). A core sample consisting of two segments was obtained in 1989 (Gray et al. 1993). Finally, the tank waste was grab sampled in February of 1995 (Rollison 1995, 1995b, and 1995c). Tank 241-AZ-102 is in active service; future plans include combining the waste in tank 241-AZ-102 with that in tank 241-AZ-101. Therefore, the composition of the tank waste can be expected to change. This report will be revised periodically to reflect new sample information and other changes. This report supports the requirements of the *Hanford Federal Facility Agreement and Consent Order* Milestone M-44-08 (Ecology et al. 1994).

1.1 PURPOSE

The report summarizes the information about the use and contents of tank 241-AZ-102. When possible, this information will be used to assess issues associated with safety, operations, environmental, and process development activities. This report also provides a reference point for more detailed information about tank 241-AZ-102.

1.2 SCOPE

The samples taken in 1987 were primarily intended to determine the composition of the solids which had accumulated on the floor of the tank. Chemical and radiochemical waste components were measured on the supernatant and sludge. No physical or thermodynamic analyses were performed. Other than total organic carbon (TOC), no specific organic analyses were performed.

The core sample obtained in 1989 was taken to characterize the neutralized current acid waste (NCAW) stored in tank 241-AZ-102 for support of retrieval, pretreatment, and disposal processes. Early characterization of NCAW was particularly important because at the time it was expected to be the first waste retrieved and vitrified in the Hanford Waste Vitrification Plant (Gray et al. 1993). Chemical, radiochemical and physical properties were measured on the supernatant and sludge phases of this sample. Other than TOC, no specific organic analyses were performed; and thermodynamic analyses were not conducted.

The supernatant grab samples acquired in 1995 were taken to support tank operations in assessing the compatibility of tank 241-AZ-102 supernatant with other waste for transfer purposes. The technical basis for this compatibility assessment is described in the *Data Quality Objectives for the Waste Compatibility Program* (Carothers 1994). The sampling and analysis were performed as described in *Tank 241-AZ-102 Tank Characterization Plan* (Schreiber 1995). The supernatant was analyzed for a smaller set of metals and radiochemical constituents than the 1989 core sampling event to comply with the requirements of Schreiber (1995). Thermodynamic analyses including thermo-gravimetric analysis (TGA) and differential scanning calorimetry (DSC) analysis were performed.

Tank 241-AZ-102 is equipped with a standard hydrogen monitoring system (SHMS). Dome headspace vapor grab samples are obtained periodically from the SHMS to verify the monitoring data. The SHMS monitoring data are documented in *Results of Vapor Space Monitoring of Flammable Gas Watch List Tanks* (McCain and Bauer 1998). Tank 241-AZ-102 confirmatory grab sample results are documented in Goheen (1998).

While the tank was not sampled specifically for safety screening, the data obtained from the 1989 core sample, the 1995 grab samples, and the SHMS confirmatory headspace grab samples were sufficient to perform a safety screening (Reynolds et al. 1999).

Terms such as waste types, waste generating processes, etc., generally are not defined in this document; detailed explanations of these and many other Tank Farm/Hanford Site terms can be found in the *Tank Characterization Reference Guide* (De Lorenzo et al. 1994).

middle. Vertical variability within the sludge layer was then examined by looking for trends in the data as a function of tank depth. Of the analytes with concentrations over 10,000 μg/g, aluminum, sodium, and uranium generally showed an increasing concentration as a function of depth, whereas the opposite was generally true for iron, zirconium, and nitrite. Most of the radionuclides showed a decreasing concentration as a function of depth. Given these mixed results, it is difficult to make any conclusions regarding the disposition of waste within the sludge layer.

5.4 COMPARISON OF ANALYTICAL AND TRANSFER HISTORY INFORMATION

A comparison of the transfer history of tank 241-AZ-102 and analytical data shows some correlation in terms of overall characteristics. For example, ^{241}Am, which was a constituent of NCAW, appears in a relatively insoluble form in the tank sludge. Tank layering and waste chronology, however, are difficult to establish by evaluating process history and analytical results. Most of the waste which entered the tank was composed of three types: B Plant aging waste and complexant concentrate which initially filled the tank and were subsequently removed; and NCAW, which makes up the present day tank contents. Because of the difficulty in sluicing waste below 5,000 gal, it is possible that a minute heel of B Plant waste and complexant concentrate still exists in the tank. The layer samples from the 1989 core may or may not have encountered the heel. The layer results for TOC, an indicator of complexant concentrate waste, were inconclusive in showing evidence of the waste, as results were missing for the bottom-most layer where this waste would be found. This was also the case for TIC. The other samples were not designed to describe heterogeneity.

The ^{241}Am which appears in relatively high concentrations in the 1987 and 1989 sludge samples is a component of the waste stream from PUREX in which americium was separated from other TRUs in the solvent extraction process. Strontium, a component of aging waste which forms relatively insoluble compounds, is present in high concentrations in the sludge sampled in 1987 and 1989. Cesium, a highly soluble component of aging waste, is present in the 1987 and 1989 sludge samples and in the 1995 supernatant samples.

Large quantities of iron were used in the form of ferrous sulfamate in the PUREX second solvent extraction step which reduced the valence of plutonium to the +3 state. The iron, which is assumed to exist in the hydroxide form, shows up in all of the data used in this report in the sludge analyses in relatively high concentrations and does not appear in the supernatant analyses above detectable levels.

Zirconium is a primary ingredient in the zircalloy cladding for the N-reactor fuel. Although NCAW does not come from decladding operations, enough zirconium carried over (from the decladding operation) in the NCAW waste stream for it to appear in waste samples.

Cadmium was used as a neutron poison to reduce the chance of inadvertent criticality during process operations, and appears as a major constituent in the solid portion of the waste (Schofield 1991).

Chromium and nickel appear in the NCAW waste stream as a consequence of normal corrosion of the process piping and components of PUREX, and both are major constituents of the waste in tank 241-AZ-102 (Schofield 1991).

5.5 EVALUATION OF PROGRAM REQUIREMENTS

The waste compatibility Data Quality Objectives (DQO) (Carothers 1994) outlined the requirements that must be applied to the 1995 grab sample data in order to assess the compatibility of tank 241-AZ-102 waste with that in other tanks. This compatibility assessment is presented in this section. The TCP for the 1995 grab sampling event (Schreiber 1995) specified that the obtained samples were not to be safety screened due to the fact that only one riser was sampled instead of the two required by the safety screening DQO (Babad and Redus 1994). Although DQOs were not in existence when the 1989 core sample was taken, the requirements of the safety screening DQO have been compared with the analytical results.

5.5.1 Safety Evaluation

The data criteria identified in the safety screening DQO (Babad and Redus 1994) is used to assess the safety aspect of the waste in tank 241-AZ-102. Although the sludge and supernatant weren't specifically sampled for safety screening, the sampling and analyses performed for other programs were adequate to satisfy the intent of the safety screening DQO. The safety screening DQO identifies several primary and secondary factors for consideration. The safety screening DQO optimization guidelines cal for two full cores of the solid phase and a number of grab samples in the liquid phase unless unique characteristics of the waste drive a need for more or fewer samples. In the case of tank 241-AZ-102, the tank contents were mixed by air lift circulators while the tank received NCAW wastes from PUREX. Therefore, the solids layer will not exhibit the lateral inhomogeneity seen in unmixed tanks where solids deposition patterns may be affected by the proximity to waste inlet and outlet lines. The supernatant phase was mixed by both the air lift circulators and by thermal convection due to radioactive decay heat. Consequently, the single 1989 core sample and the three 1995 grab samples are adequate for safety screening.

The waste fuel energy value is normally determined using DSC analysis of the waste material. DSC analyses were performed on the 1995 grab samples; no exotherms were found. No DSC analyses have been performed on the sludge in tank 241-AZ-102. The current safety screening DQO (Dukelow et al. 1995) requires total organic carbon analysis as a secondary analyte in the event that the DSC threshold is exceeded. Total organic carbon analyses of the sludge were performed, and were well below the threshold limit.

Large amounts of moisture reduce the potential for propagating exothermic reactions in the wastes. Because the waste in tank 241-AZ-102 is 90% liquid by volume, the moisture content of the sludge is expected to be high. The waste is approximately 90% supernatant, and the 1989 centrifuged sludge moisture content was found to be 63% (by weight), which more than satisfies the 17 wt% water requirement of the safety screening DQO (Babad and Redus 1994). This value more than satisfies the 17% criteria established by the safety screening DQO.

Another factor in assessing the safety of the tank waste is the heat generation and temperature of the wastes. Heat is generated in the tanks primarily from radioactive decay. The major contributors for tank 241-AZ-102 are ^{90}Sr, ^{106}Ru, and ^{137}Cs. The estimated heat generated from the isotopes in the tank is <58,441 W (<199,457 Btu/hr) as shown in Table 5-8. This heat load is high when compared to other double-shell tanks, but is expected because of the aging waste. The maximum heat limit for tank 241-AZ-102 is 4,000,000 Btu/hr (Bergmann 1989), so the heat load is only about 5% of this maximum limit. Temperature data for the previous year (December 1993 through December 1994) is displayed graphically in Figure 2-6. In that time the temperature has ranged from 78 °C (172 °F) to 83 °C (181 °F), excluding one suspect spike.

Table 5-8. Tank 241-AZ-102 Projected Heat Load.

Radionuclide	Curies* (Ci)	Watts
^{241}Am	<36,097	<1,206
^{137}Cs	3,712,801	14,554
$^{239/240}Pu$	<1,568	<49
^{106}Ru	<3,570	<0.2
$^{89/90}Sr$ (supernatant)	5,793	39
^{90}Sr (sludge)	6,366,730	42,593
Total watts		<58,441

*Analyte values from the liquid portion of the tank were added to the sludge portion. Therefore, the total tank inventory is based on 1987 sludge and 1995 liquid grab sample results.

The potential for criticality is assessed from either total alpha or plutonium analysis. Criticality specifications for double-shell storage tanks are defined in Vail (1994). The safety screening criteria is 1 g/L. This is equivalent to 41.3 μCi of $^{239/240}Pu$/g in the waste, using the sludge density of 1.49 g/mL. The 1989 core data showed that the sludge contained 43.0 μg/g of plutonium (Table 4-2), which translates to 3.14 μCi/g of $^{239/240}Pu$ when using the plutonium isotope weight percentage breakdown given in Gray et al. (1993) and tabulated in Table A-2. The concentration of $^{239/240}Pu$ in the supernatant is $<2.7 \times 10^{-3}$ μg/g, so the total waste inventory of $^{239/240}Pu$ is well below the safety screening limit. The criticality specifications also require the pH of the waste to be greater than 8.0 when the plutonium inventory exceeds 10 kg and the depth of the supernatant liquid exceeds

30 cm. The pH of the supernatant is 12.9, the sludge pH is 11.8, and the supernatant depth exceeds 30 cm, which satisfies the criticality prevention specification since the plutonium inventory exceeds 10 kg in the tank.

Tank 241-AZ-102 is actively ventilated. The headspace hydrogen concentration is monitored by a standard hydrogen monitoring system (SHMS). Grab samples obtained from the SHMS confirm that the concentrations of hydrogen and other flammable gases remain less than 2% of the LFL. The tank is conditionally safe, being maintained well below the LFL by the operation of the active ventilation system.

Tank 241-AZ-102 has been adequately sampled and analyzed to meet the intent of the safety screening DQO. Because the tank was mixed by air life circulators for several years during its final filling cycle, the single 1989 core sample and the three 1995 grab samples are adequate to assess the safety conditions of tank 241-AZ-102. No exotherms were found in the supernatant. While the sludge was not analyzed by DSC, concentrations of the secondary safety screening analyte TOC were far below the 30,000 μg/g threshold level for organic fuel content. Plutonium analyses show that criticality is not a concern for this tank. Flammable gas analyses confirm that the active ventilation system maintains the headspace flammable gas concentrations well below the LFL.

5.5.2 Operational Evaluations

The 1995 supernatant sampling and analysis were performed to evaluate compatibility of tank 241-AZ-102 waste with that in other tanks. Sampling and analysis requirements for assessing waste compatibility have been addressed in the waste compatibility DQO (Carothers 1994). This DQO is based on both safety and operational considerations. Operational considerations include pumpability and corrosion. Comparisons between some of the key criteria for evaluating compatibility and the 1995 supernatant results are summarized in Table 5-9. No viscosity or cooling curve analysis was required since historical information already exists which adequately addresses the potential for line plugging and precipitation of solids during the transfer of waste (Schreiber 1995).

It should be noted that all of the criteria listed in Table 5-9 are met and that the analysis indicates that the waste is compatible with other similar tank waste types. Additionally, low phosphate ($<$360 μg/g) indicates that the potential for insoluble phosphates forming is low and the waste is pumpable. Other operational factors, as defined and discussed in Carothers (1994), need to be considered as part of the overall assessment before the waste is transferred out of the tank.

5.5.3 Process Development Evaluation

The metal analysis of the sludge in 1989 is important for evaluating the disposal waste form (glass) formulations and identifying potential components that may affect the treatment and disposal process. Because the waste sludges may be blended, washed and treated before disposal, there are no specific criteria for the parameters measured. The 1989 physical

6.0 CONCLUSIONS AND RECOMMENDATIONS

The sludge in tank 241-AZ-102 has been sampled and analyzed three times, twice in 1987 and most recently in 1989. The supernatant was also analyzed in the two 1987 samplings. The most recent supernatant sampling occurred in February 1995. The sampling and analysis of tank 241-AZ-102 adequately meets the intent of the safety screening DQO (Reynolds et al. 1999). Airlift circulators operated during the years the tank received NCAW waste from PUREX, and ensured that the single core 1989 core sample and the three 1995 grab samples are adequate for safety screening. The small amount of condensate and PUREX neptunium waste received since then do no appreciably alter these conclusions. The supernatant meets the compatibility assessment criteria.

The sludge contained large quantities of iron, sodium, aluminum, uranium, SO_4^{2-}, NO_2^-, and NO_3^- as expected from the NCAW waste stream. Also found in relatively high concentrations were nickel and chromium, which entered the waste stream through corrosion of PUREX piping and process vessels.

$^{89/90}Sr$, ^{90}Sr, ^{137}Cs, $^{239/240}Pu$, ^{106}Ru, and ^{241}Am were the most abundant radionuclides found in the waste. The heat generated by these and other significant isotopes is approximately <58,441 W (<199,457 Btu/hr). The estimated heat load is far below the 4,000,000 Btu/hr design limit for the tank (Bergmann 1989).

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