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Systems Engineering Study: Tank 241-C-103 Organic Skimming, Storage, Treatment, and Disposal Options

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Abstract: This report evaluates alternatives for pumping, storing, treating and disposing of the separable phase organic layer in Hanford Site Tank 241-C-103. The report provides safety and technology based preferences and recommendations. Two major options and several variations of these options were identified. The major options were: 1) transfer both the organic and pumpable aqueous layers to a double-shell tank as part of interim stabilization using existing salt well pumping equipment or 2) skim the organic to an above ground before interim stabilization of Tank 241-C-103. Other options to remove the organic were considered but rejected following preliminary evaluation.

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FOSTER WHEELER ENVIRONMENTAL CORPORATION

**Tank 241-C-103 Systems Engineering
Study: Separable Phase Organic
Skimming, Storage, Treatment, and
Disposal Options**

Volume 1
WHC-SD-WM-ES-384 REV 0

FINAL

September 30, 1996

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Tank Waste Remediation System
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EXECUTIVE SUMMARY

This engineering study documents a systems engineering evaluation of alternatives for pumping, storing, treating, and disposing of the separable phase organic layer in Hanford Site Tank 241-C-103. This study is designed to provide safety and technology based preferences and recommendations for the Westinghouse Hanford Company (WHC) Decision Review Board and the Decision Maker, the U.S. Department of Energy (DOE). This report also documents WHC Review Board recommendations and stakeholder positions on recommended tank waste removal options.

Previous studies recommended pumping both the Tank 241-C-103 organic and the aqueous layers to a double-shell tank (DST) as part of interim stabilization through existing transfer lines without organic separation. As a result, WHC recommended this action to the DOE. The Chemical Reactions Sub Tank Advisory Panel (CRS TAP) agreed that there would be no unacceptable short-term safety implications associated with salt well pumping both layers, but disagreed with WHC's recommendation on the basis that there would be serious deleterious impacts on future activities. This CRS TAP decision was made during the 12th and 13th meetings held July 21 to 23 and August 30 to September 13, 1995. The Defense Nuclear Facility Safety Board (DNFSB) and the Washington State Department of Ecology (Ecology) also expressed concerns of the recommendation to pump both layers from Tank 241-C-103 to a DST. The DOE, Richland Operations Office requested WHC perform a systems engineering evaluation of alternatives that would address the concerns of the CRS TAP, DNFSB, and Ecology. This engineering study is the result of the DOE request.

For this evaluation, two major options and several variations of these options were identified. The major options were: (1) transfer both the Tank 241-C-103 organic and pumpable aqueous liquid layers to a DST as part of interim stabilization using existing salt well pumping equipment or (2) skim the Tank 241-C-103 organic to an aboveground tank before interim stabilization of the tank. Several other options to remove the organic layer from Tank 241-C-103 were also considered but rejected following preliminary evaluation. These options included: (1) adding material to the tank to absorb the organic, (2) distilling the organic with a hexone-distillation unit, (3) processing the organic through the 242-A Evaporator, (4) processing the organic through the Liquid Effluent Retention Facility, (5) processing the organic through the Effluent Treatment Facility, and (6) no action (i.e., leaving the material in Tank 241-C-103).

Regardless of the option chosen, separable phase and soluble organics would have created unacceptable impacts to the Tank Waste Remediation System (TWRS) Pretreatment process flowsheets in use at the beginning of this study. Potential impacts included the likelihood that separable phase organics would form and accumulate during sludge washing and carry over to filtration and ion exchange systems. In addition, there is increasing evidence that 87,000 L (23,000 gal) of process organic is still present in the Hanford Site waste tank system. Due primarily to the results of this study, the current TWRS process technical baseline now includes a system for organic separation and storage to address this issue.

If salt well pumping both the aqueous and organic layers from Tank 241-C-103 to a DST is chosen as the preferred option by DOE, the recommended receiving tank is Tank 241-AP-107. This tank was chosen based on availability, storage capacity, lack of solids heel, contents compatibility, and long-term planning impacts. However, the transferred organic layer would not appreciably degrade or evaporate in Tank 241-AP-107 because of the low temperature of the tank and lack of supernatant liquid circulating capabilities. Modifications to Tank 241-AP-107 to enhance degradation and evaporation of the organic were predicted to cost up to \$50 million. Other tanks are better suited for organic degradation and evaporation, but are currently not available to receive the Tank 241-C-103 organic.

If skimming the organic layer from Tank 241-C-103 prior to interim stabilization is chosen as the preferred option by DOE, the organic could be placed in an aboveground tank that meets U.S. Department of Transportation shipping criteria. If skimming and disposal outside the Hanford Site tank farm system is chosen, it is recommended that the organic be disposed through an offsite incinerator. It is likely that the organic could be washed sufficiently onsite with a sodium salt solution of ethylenediaminetetraacetic acid to meet one or more offsite incinerator vendor receipt specifications. One offsite vendor is currently contracted to receive similar organic waste from the Plutonium/Uranium Extraction (PUREX) Plant.

This engineering evaluation concluded that there are no significant safety or technical differences between the major organic removal options if organic treatment is incorporated in

the TWRS flowsheet. Prior to the decision by WHC to change the TWRS Pretreatment processes to treat organic, the technical issues were significant enough that skimming was the preferred option. With the decision to change the TWRS Pretreatment processes, the differences between the options are smaller and would be affected primarily by the predicted impacts from stakeholders concerns. Thus, there is no safety and technology based preferred option for the removal and disposal of the Tank 241-C-103 organic identified in this engineering evaluation.

Subsequent to review of the draft of this engineering evaluation and based on further study and programmatic decisions, the WHC Review Board upheld the previous WHC recommendation that Tank 241-C-103 be interim stabilized on the current stabilization schedule by salt well pumping both the aqueous and separable organic liquid to Tank 241-AP-107. After considering the WHC Review Board's most recent recommendation of salt well pumping, the CRS TAP again agreed that there are no unacceptable near-term safety implications associated with salt well pumping, but did not alter the previous recommendation that the organic layer be removed from Tank 241-C-103 prior to pumping the liquid layer to a DST. The CRS TAP position appeared to be based on concern for transferring the safety issue from Tank 241-C-103 to a DST. Information provided to the CRS TAP, in addition to completion of a Safety Analysis Report on organics in tanks, should address this concern.

The DNFSB staff has indicated that they will have no formal position. Ecology has continued to support skimming the organic layer prior to pumping the liquid to a DST and is finalizing its concerns with DOE concerning the salt well pumping of both layers.

The DOE is the Decision Maker for this action. The DOE will make a final determination on the Tank 241-C-103 organic removal options based on the information provided in this report, stakeholder concerns, and programmatic needs to ensure regulatory requirements are met in a fiscally responsible manner.

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ACRONYMS AND ABBREVIATIONS

ALARA	as low as reasonably achievable
A/O	aqueous to organic ratio
CC	complexed concentrate
CRS TAP	Chemical Reactions Sub Tank Advisory Panel
CWC	Central Waste Complex
DBP	dibutyl phosphate
DCRT	double-contained receiver tank
DNFSB	Defense Nuclear Facility Safety Board
DOE	U.S. Department of Energy
DOT	U.S. Department of Transportation
DQO	data quality objective
DSSI	Diversified Scientific Services Incorporated
DST	double-shell tank
Ecology	Washington State Department of Ecology
EDTA	ethylenediaminetetraacetic acid
EPA	U.S. Environmental Protection Agency
ETF	Effluent Treatment Facility
FY	fiscal year
HEPA	high efficiency particulate air
HLW	high-level waste
INEL	Idaho National Engineering Laboratory
ISO	International Standards Organization
LATA	Los Alamos Technical Associates
LERF	Liquid Effluent Retention Facility
LLW	low-level waste
LSA	low specific activity
LWTC	Liquid Waste Tank Car
NaDBP	sodium dibutyl phosphate
NaOH	sodium hydroxide
Na ₂ MBP	sodium monobutyl phosphate
Na ₃ PO ₄	trisodium phosphate
NEPA	National Environmental Policy Act
NPH	normal paraffin hydrocarbon
OH	hydroxide
PUREX	Plutonium/Uranium Extraction
RCRA	<i>Resource Conservation and Recovery Act</i>
REDOX	Reduction/Oxidation
SAR	safety analysis report
SARP	Safety Analysis Report for Packaging
SST	single-shell tank
TBP	tributyl phosphate
TOC	total organic carbon
Tri-Party Agreement	<i>Hanford Federal Facility Agreement and Consent Order</i>
TWRS	Tank Waste Remediation System
USQ	unreviewed safety question

ACRONYMS AND ABBREVIATIONS (con't)

WAC	Washington Administrative Code
WERF	Waste Experimental Reduction Facility
WHC	Westinghouse Hanford Company

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1.0 INTRODUCTION

Tank 241-C-103 is a single-shell underground storage tank used to store hazardous and radioactive waste that was generated during defense production operations at the Hanford Site. This tank is known to contain about 17,300 L (4,570 gal) of floating separable phase organic liquid comprised primarily of tributyl phosphate (TBP) and normal paraffin hydrocarbon (NPH). The liquid organic is floating on an aqueous supernatant layer of approximately 503,000 L (133,000 gal) and a sludge layer of approximately 230,000 L (62,000 gal).

This engineering study documents a systems engineering multi-variable evaluation of options for pumping, treating, and disposing of the separable organic layer in Tank 241-C-103. This study consists of two volumes. Volume 1 contains the report methodology (Section 2), history (Section 3), impacts to Tank Waste Remediation System (TWRS) processes (Sections 4 through 7), organic treatment and disposal options (Section 8), environmental permitting impacts (Section 9), organic removal options evaluation (Section 10), a summary of the engineering evaluation (Section 11), review board results (Sections 12 and 13), and a current status (Section 14). The background, organic removal options, key assumptions, decision criteria, major issues addressed, and functions and requirements are described in the remainder of this section. Volume 2 contains supporting information including copies of memos, additional technical data, and other documentation. Volume 2 is structured to correspond to each section in Volume 1 (e.g., more detail on tank farm history is found in Volume 2, Section 3).

1.1 BACKGROUND

As a result of previous studies (Parazin 1994; Geschke and Milliken 1995; Dukelow et al. 1995), Westinghouse Hanford Company (WHC) recommended to the U.S. Department of Energy (DOE) that Tank 241-C-103 be interim stabilized by transferring the organic and aqueous liquids to a double-shell tank (DST) for interim storage. The Chemical Reactions Sub Tank Advisory Panel (CRS TAP) subsequently disagreed with this assessment during the 13th meeting held August 30 to September 1, 1995. The CRS TAP stated:

While there appear to be no unacceptable, near-term safety implications associated with immediate salt well pumping, it is our belief this action would have serious, deleterious impact on future activities (such as solid and liquid separation and ion exchange, due to the mixing of organic and sludge or saltcake) leading to undesirable increases in cost and personnel exposure. Consequently, we believe it would be prudent to remove the organic layer from [Tank] 103-C prior to interim stabilization and suggest required actions for this removal be initiated immediately. In order to avoid a recurrence of this problem, we suggest the removed organic be stored without mixing with other waste that contains sludge or saltcake. (See Volume 2, Section 1.1)

During a separate meeting, the Defense Nuclear Facility Safety Board (DNFSB) expressed similar concern.

Based on this response, DOE requested that WHC revisit the decision on stabilizing tanks with floating organic layers, especially Tank 241-C-103, to (1) verify that the overall TWRS program objectives have been adequately designed and (2) provide adequate technical justification as to why the recommendation expressed by the CRS TAP should not be adopted (Volume 2, Section 1.2).

1.2 ORGANIC REMOVAL OPTIONS

Several options have been proposed to remove the separable phase organic layer from Tank 241-C-103. The primary options evaluated in this report are described in Section 1.2.1 and options that were removed from further consideration are described in Section 1.2.2.

1.2.1 Primary Options Evaluated

The two primary organic removal options evaluated in this report are shown in Figure 1-1 and described below.

- **Option A:** Transfer the pumpable separable phase organic and aqueous liquids to a single DST for interim storage using existing salt well equipment. The potential fate of the organic once it has been pumped to a DST is shown in Figure 1-1.
- **Option B:** Skim the separable phase organic and transfer it to an aboveground storage tank for eventual disposal. The remaining liquid would be pumped by salt well to a DST for interim storage and subsequent processing in the TWRS Pretreatment system. As shown on Figure 1-1, Option B has several sub options for the ultimate disposition of the organic depending on the choice of aboveground storage tank (Section 6). These sub options include the following:
 - Skim or pump the organic tank to a DST for storage or destruction
 - Process the organic and send it offsite for treatment and disposal
 - Store the organic in the aboveground tank until organic disposition is better defined.

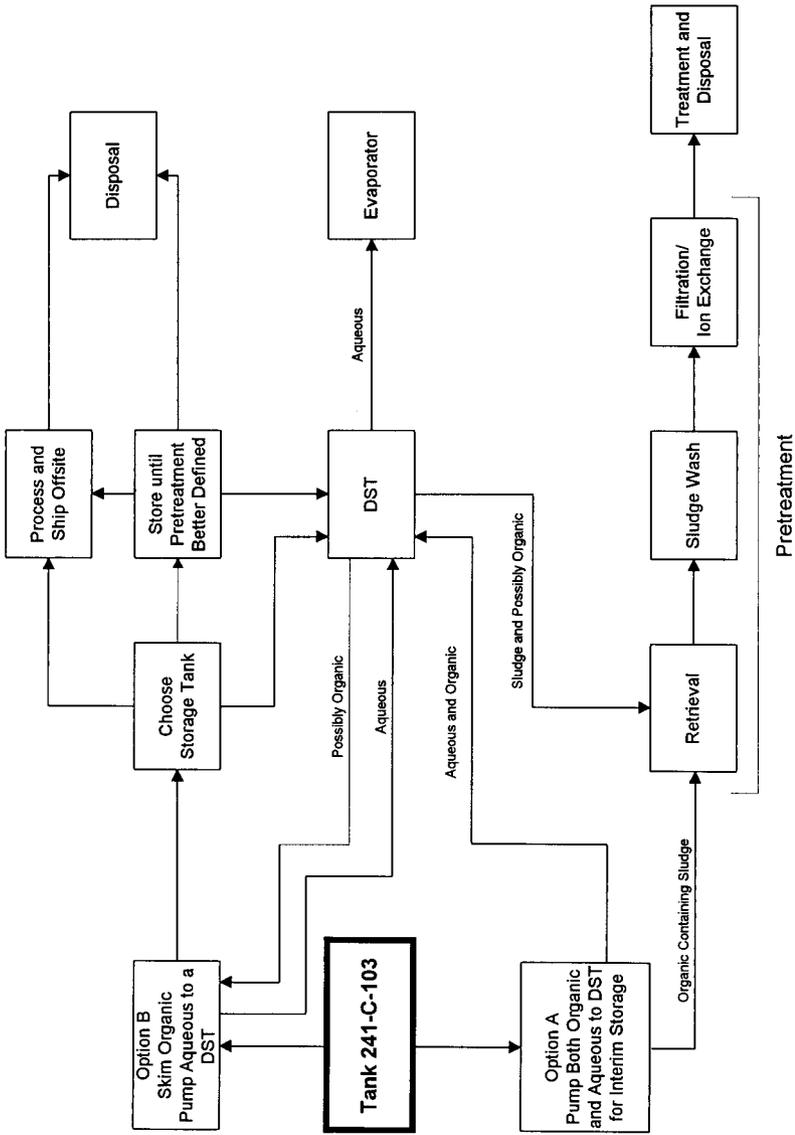


Figure 1-1. Overview of Primary Organic Removal Options.

1.2.2 Removal Options Removed from Further Consideration

Some organic removal options were rejected based on preliminary evaluations. These options included: (1) adding material to the tank to absorb the organic, (2) distilling the organic with a hexone-distillation unit, (3) processing the organic through the 242-A Evaporator, (4) processing the organic through the Liquid Effluent Retention Facility (LERF), (5) processing the organic through the Effluent Treatment Facility (ETF), and (6) no action (i.e., leaving the material in the tank). These rejected options are briefly discussed in Sections 1.2.3.1 through 1.2.3.6 and identified references.

1.2.2.1 Add Material to the Tank. Adding an adsorbent or absorbent material such as charcoal to the tank to absorb the organic was rejected for the following reasons.

- Adding a solid to the tank would directly increase solids that must be processed, thus increasing the amount of feed material being processed.
- Any addition campaign would have to include extensive testing, compatibility studies, and process impact studies.
- The required review and approval process could result in long delays.
- This process does not remove or treat the organic, only binds it. The organic would still require disposal.

1.2.2.2 Distill the Organic. Distilling the organic with a hexone distillation unit was rejected because the distillation system used at the Hanford Site in the past had significant problems with TBP breakdown products and high boiling kerosene residuals (Cowan et al. 1992). Problems included the need for several process outages to remove tar from the feed weir and to flush the overflow drain line.

1.2.2.3 Process through the 242-A Evaporator. This option was previously reviewed and rejected (Bartley 1994; SAIC 1994). Based on equilibrium data, most of the relatively insoluble TBP/NPH would be expected to discharge with the process condensate, resulting in little organic reduction. The discharged material would likely be sent to the LERF.

1.2.2.4 Process through LERF. Separable phase organic cannot be pumped to the LERF because of material incompatibilities with the LERF liner. Based on compatibility testing, the LERF liner material would be likely to have between 14.1% and 32.2% elongation if contacted by Tank 241-C-103 separable organic (Parazin 1994; Bartley 1994).

1.2.2.5 Process through ETF. The ETF is not designed for high concentration organic (DOE-RL 1993). High organic concentrations would shut down or greatly impact nearly every system. Dilution and fixed feed would require years of full time operation at flow rates and capacities greater than current expectations (Bartley 1994; SAIC 1994).

1.2.2.6 No Action. The no action alternative was evaluated by Dukelow et al. (1995), but was not considered for this evaluation because stabilization must be performed to prevent leakage and to meet Tri-Party Agreement requirements.

1.3 KEY ASSUMPTIONS

During this evaluation, the following key assumptions were made.

- (1) **Tank 241-C-103 should not be the driver to change the TWRS Pretreatment processes:** If TWRS Pretreatment processes must be updated to address the presence of organic, the driver should be organic known or projected to exist in other Hanford Site tanks.
- (2) **Stakeholders will continue to resist Tank 241-C-103 organic coming into contact with tank sludge and the organic being sent to a DST unless a clear life-cycle resolution is provided:** These stakeholders include the DNFSB, CRS TAP, and Washington State Department of Ecology (Ecology).
- (3) **DST storage capacity will continue to be critical and will be affected by organic:** Any DST receiving organic from Tank 241-C-103 would have restrictions that could affect meeting storage capacity limitations.
- (4) **Permitting changes will not prevent skimming:** If skimming is performed, it is likely that permit changes will be required. It is assumed that regulatory agencies will approve these changes if sufficient time is provided and stakeholder values are addressed.
- (5) **A decision is required in the near future to prevent impacts on stabilization and allow for obtaining funding:** The *Hanford Federal Facility Agreement and Consent Order* (Tri-Party Agreement) milestones for interim stabilization are still at least two years away. However, a long lead time is required to ensure permitting issues are addressed, funding is obtained, and testing is completed if the skimming option is selected.
- (6) **Characterization of all other potential organic containing tanks will not be completed before a decision for Tank 241-C-103 is required:** Characterization efforts have long lead times. The WHC characterization program is currently under great pressure to meet other commitments. Shifting these priorities is not likely.

1.4 DECISION CRITERIA

Three sets of criteria have been used to evaluate the various options for removing the separable phase organic from Tank 241-C-103. These criteria are described below; additional information is provided in Section 10.

- The decision criteria in Dukelow et al. (1995) included public safety, worker safety, environmental compliance, feasibility, and cost.
- The decision criteria developed by the decision support board included land area, cost, health and safety, schedule, processing rates, separation fractions of high-level and low-level waste, immobilized waste radionuclide concentrations, immobilized waste volume, and immobilized waste oxide loading and are listed in Table 1-1.

The decision support board developed key criteria based on the *Public Values Related to Decisions in the Tank Waste Remediation System Program* (Armocost et al. 1994) and the *TWRS Mission Analysis* (Baynes and Knutson 1995). The decision support board reviewed all stakeholder values and mission goals and determined those that could reasonably be evaluated and provided justification where necessary (Volume 2, Section 1.3). The decision support board also identified key technical experts to answer questions based on the table of decision criteria. These questions were designed to elicit sufficient information to develop a record of decision based upon the decision criteria (Volume 2, Section 1.4). Answers to the questions were used to support the evaluation process described in Section 10.

- The WHC decision review board decision criteria included total costs, schedule, flexibility, technical risk, health and safety, regulatory compliance, and stakeholder values.

All three sets of decision criteria addressed the same basic issues, including cost, safety, scheduling, flexibility, operability, system impacts, and stakeholder concerns. The criteria developed by Dukelow et al. (1995) were used in this report to evaluate the primary organic removal options. This was done for two reasons: (1) to allow a direct comparison of the evaluation results of this study with the results obtained by Dukelow et al. (1995) and (2) the criteria developed by Dukelow et al. (1995) essentially included all of the decision criteria developed by the decision support board, with the exception of stakeholder concerns, which are included in the reevaluation of the Dukelow et al. (1995) results (Section 10.3). Table 1-2 shows the relationship between the criteria developed by Dukelow et al. (1995) and the criteria developed by the decision support board.

Table 1-1. Decision Support Board Criteria for Removing and Processing Separable Phase Organic from Tank 241-C-103.

End Calculated Metrics	Qualitative Metrics
Land Area (Acreage - LLW Volume)	Affect of direct feed to ETF
Cost <ul style="list-style-type: none"> • Life-cycle cost • Repository cost (HLW volume) • D&D cost (from impacted facilities) • Operating cost for storage 	Potential for noncompliance with major regulatory drivers (e.g., Part B permits)
Health and Safety <ul style="list-style-type: none"> • Injury/Fatality • Man-rem 	Technological risks
Schedule <ul style="list-style-type: none"> • SST stabilization completion • TWRS process completion • Time for interim Tank 241-C-103 stabilization (leak potential) 	Local economic benefits
	Safety issues mitigated or realized
Processing Rates <ul style="list-style-type: none"> • Waste Retrieval • Pretreatment • Immobilization 	Radionuclide concentrations for immobilization using different options
	Potential for immobilized waste needing rework
	Potential inability to immobilize waste
	Effects of DST utilization
Separation Fractions of HLW and LLW <ul style="list-style-type: none"> • Sludge Washing • Ion Exchange 	Secondary waste costs
Immobilized Waste Radionuclide Concentration <ul style="list-style-type: none"> • LLW • HLW 	N/A
Immobilized Waste Volume <ul style="list-style-type: none"> • LLW • HLW 	N/A
Immobilized Waste Oxide Loading <ul style="list-style-type: none"> • LLW • HLW 	N/A

D&D - decontamination and decommissioning
 SST - single-shell tank
 TWRS - Tank Waste Remediation System
 ETF - Effluent Treatment Facility

LLW - low-level waste
 HLW - high-level waste
 DST - double-shell tank
 N/A - not applicable

Table 1-2. Comparison of Criteria Used to Evaluate Organic Removal Options.

Decision Support Board End Calculated Metric ¹	Criteria Used by Dukelow et al. (1995) ²	Explanation
Land Area (LLW volume)	D. Feasibility E. Cost	D. Organic will affect the operability of the filtration and ion exchange systems, and the amount of secondary waste, which could increase LLW volumes. E. The greater the area needed, the higher the expected costs.
Cost	E. Cost C. Env. Compliance	E. There are potential cost increases associated with organic in the TWRS Pretreatment processes (eg. more frequent filter/resin changes). C. There is the potential for additional costs due to non-compliance with regulatory drivers.
Health and Safety	A. Public Safety B. Worker Safety	A. There is the risk of a solvent fire due to the presence of organic. B. There is the risk of toxic gases due to the presence of organic - also increased industrial safety worker radiation exposure risks because the presence of organic in some processes will require more frequent maintenance.
Schedule	A. Public Safety B. Worker Safety E. Cost	A & B. Potential safety concerns (e.g., solvent fire and toxic vapor hazards) will affect the schedule if processing is delayed due to the presence of organic. E. The costs of scheduled slippage, particularly in the Pretreatment systems, could be a major factor.
Processing Rates	D. Feasibility E. Cost	D. Organic may foul processing equipment, which would affect the operability and implementation. E. Lower process rates will potentially increase the operating costs.
Separation Fractions of HLW and LLW	D. Feasibility E. Cost	D. Improper separation could result in either increased HLW volumes or unacceptable LLW radionuclide concentrations. E. Greater volumes or rejected concentrations increase costs.
Immobilized Waste Radionuclide Concentration	D. Feasibility E. Cost	D. Maintaining proper immobilized waste radionuclide concentrations is crucial to successful disposal. E. Improper concentrations result in re-work and additional costs.
Immobilized Waste Volume	E. Cost	E. Volumes and costs are directly proportional.
Immobilized Waste Oxide Loading	D. Feasibility	D. For some options, the impacts on waste oxide loading could prevent organic processing

1 See Table 1-1 for a complete list of the decision support board criteria

2 See Table 10-1 for a complete list of the Dukelow et al. (1995) evaluation criteria

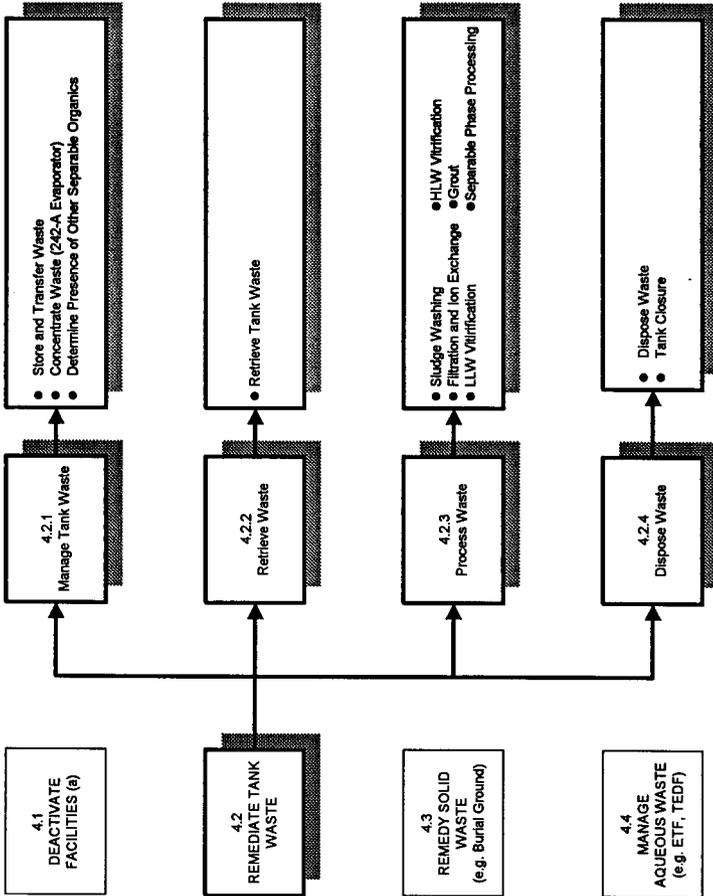
1.5 MAJOR ISSUES ADDRESSED

The approach used for this study was designed to address stakeholder concerns and provide extensive information from technical experts for analysis by the decision support board, decision review board, and DOE. The decision support board determined that there were several major areas of concern that needed to be addressed. These areas are summarized below.

- **New information has been identified since Dukelow et al. (1995):** Since Dukelow et al. (1995) recommended pumping both the organic and aqueous to a DST, new information has been identified, prompting a reevaluation of costs and impacts to the TWRS Pretreatment processes (Section 10).
- **A better history of separable phase organic in the Tank Farms could be helpful:** More knowledge on the current existence and past practices regarding separable phase organic, particularly TBP and NPH resulted in a better understanding of the organic in Tank 241-C-103 and other tanks (Section 3). This aspect of the study expanded on previous work, particularly that of Sederburg and Reddick (1994).
- **Impacts of separable phase organic and degradation products on existing retrieval, processing, and disposal waste flowsheets are unknown:** The TWRS Pretreatment flowsheets were established with the assumption that separable phase organic would not be present (Orme 1995). The impacts of the separable phase organic on the Pretreatment flowsheets required additional evaluation (Section 4).
- **Regulations and source term evaluations have changed:** In the time since the previous reports were written, changes to the U.S. Department of Transportation (DOT) regulations have occurred and better source term evaluations have been made. Impacts from these changes were evaluated (Section 6).
- **Benefits of processing and disposal options not clear:** The potential benefits of different methods for processing and disposal of the organic were determined. New testing data and information on a Plutonium/Uranium Extraction (PUREX) Plant contract with an outside vendor to receive and process separable phase organic were included (Section 8).
- **Disagreement over the acceptability of separable phase organic in a DST:** Previous recommendations indicated that the separable phase organic would be acceptable in a receiver DST (Dukelow et al. 1995; Geschke and Milliken 1995). The CRS TAP disagreed. A more comprehensive evaluation of separable phase organic chemistry was required (Section 8).

1.6 FUNCTIONS AND REQUIREMENTS

The TWRS operations potentially involved with pumping, treating, and disposing the floating organic were evaluated based upon the *TWRS Functions and Requirements Document* (WHC 1995a) and *TWRS Baseline System Description* (Johnson 1995). An abbreviated version of the TWRS functional hierarchy is provided in Figure 1-2. The functions evaluated in this systems engineering study are **Manage Tank Waste** (Function 4.2.1), **Retrieve Waste** (Function 4.2.2), **Process Waste** (Function 4.2.3), and **Dispose Waste** (Function 4.2.4). Each of these is part of **Remediate Tank Waste** (Function 4.2).



(a) Numbers in this figure correspond to functional hierarchy numbers from the TWRS Functions and Requirements Document (WHC 1995), not the sections of this engineering study.

Figure 1-2. TWRS System Engineering Functional Hierarchy.

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2.0 REPORT METHODOLOGY

This engineering study follows, to the extent practical, the WHC *TWRS Systems Engineering Manual Decision Management (Interim Procedure)* (TSEP-07). To ensure that appropriate requirements were met, a representative of the WHC Systems Engineering group was involved in preparing this engineering study. The elements of the decision management procedure applicable to this engineering study are described in the following sections.

2.1 STATEMENT OF DECISION

This engineering study is designed to determine the best approach for removing the floating organic layer in Tank 241-C-103. This removal could include pumping, treatment, and disposal. The analysis will use a multi-variable evaluation approach and take into consideration any potential impacts on TWRS Pretreatment flowsheets, processes, and operations.

2.2 DECISION MAKER

The decision maker is the individual or organization that declares the formal outcome of the decision making process. The final decision maker for this engineering study will be DOE. This report will provide the best available information, preferences, and limitations to support making this decision.

2.3 DECISION ACTION OFFICER

The decision action officer prepares relevant decision documentation and monitors the decision making process to ensure timely progress. For this engineering study, the decision action officer is Gary Dukelow (WHC). He has direct control over staff resources to set the goals and priorities needed to evaluate these options and direct implementation of any decisions. Because this multi-variable evaluation affects several different groups, he does not have the authority to set priorities, budgets, and schedules for all individuals involved.

2.4 DECISION SUPPORT BOARD

The decision support board supports the decision maker by providing additional review of decision-related information and by bringing additional technical expertise into the consideration of technical options. This board was convened at the start of the process to develop the decision plan based on four activities: (1) identify the applicable functions and requirements, (2) determine major issues to be addressed, (3) identify appropriate stakeholder values and decision criteria, and (4) determine required information. The decision support board is composed of primarily WHC and Foster Wheeler Environmental Corporation personnel with additional support from Los Alamos Technical Associates (LATA). Decision

support board members possess experience in performing this type of evaluation and a familiarity with Tank 241-C-103. Some of the personnel changed during the process to allow for additional expertise in target areas.

2.5 DECISION REVIEW BOARD

The decision review board is an internal WHC board chartered to review decisions with potentially significant impacts to the Hanford Site. The board for this Tank 241-C-103 decision was formed in March 1996 to review this systems engineering study. The results of the decision review board's review are contained in Section 12. Members of the board were:

J. E. Truax	Chairman
P. M. Daling	Secretary
N. W. Kirch	Process Engineering
G. L. Dunford	Safety
K. A. Gasper	Process Low-Level Waste
M. E. Johnson	Systems Engineering
D. A. Seaver	Decision Management Support
H. J. Wacek	DOE, Richland Operations Office

3.0 HISTORY

The Hanford Site tank farms have received chemical separation process waste since 1944 and separable phase organics since 1952 or earlier. This section provides a brief review of this history, including the history of Tank 241-C-103. Additional historical information is provided in Volume 2, Section 3.

3.1 HISTORY OF SEPARABLE PHASE ORGANIC IN THE TANK FARMS

Tank farms in the Hanford Site 200 Areas have received waste from many onsite facilities and chemical separation processes since 1944 (Anderson 1990; Klem 1990). Between 1952 and 1991, separable phase organic was transferred to the tank farms from fuel reprocessing (PUREX and Reduction/Oxidation [REDOX]), uranium recovery (U Plant), waste fractionization (B Plant), pilot-scale (C Plant), and plutonium finishing (Z Plant) operations. Solvent treatment was an important step in each of the separation processes. It removed contaminants and degradation products that affected fission product decontamination and operational continuity. Except in the REDOX facility, solvent treatment consisted of washing the organic with an aqueous alkaline solution.

Under ordinary circumstances waste from operations other than the PUREX Plant would have been evaporated to remove water and potentially flammable solvents before transfer to the tank farms. Some process upsets occurred and allowed transfer of additional separable phase organic to the tank farms. More information on solvent treatment and process upsets is available in the 1955 to 1967 Hanford Monthly Reports. These are identified in Sederburg and Reddick (1994).

The PUREX Plant discharged much separable phase organic to the tank farms in the unconcentrated organic wash waste stream. As a result, PUREX Plant may have been the most significant contributor of separable phase organic to the tank farms. The floating organic layer in Tank 241-C-103 is the result of waste discharges from past PUREX Plant operations. Tank farm specifications published just before the restart of PUREX Plant in 1983 did not allow for separable phase organic in DSTs. Current specifications allow organic if certain conditions (e.g., temperature) are met.

The sources in the 100, 200, and 300 Areas that discharged waste to the tank farms are described in Volume 2, Section 3.1. Because most of the organic waste that was discharged to the tank farms came from PUREX Plant, discussion of PUREX Plant organic waste discharges is emphasized below in Section 3.1.1; a more detailed discussion is provided in Volume 2, Section 3.1. Sampling activities to determine the presence of organic currently stored in the tank farms are described in Section 3.1.2.

3.1.1 Organic Waste Discharges

The PUREX Plant began operations in 1955 and began discharging accumulated organic along with high-level (boiling) waste soon after. An estimated 2,490,000 L (657,100 gal) of organic was discharged to the tank farms over the operational lifetime of the PUREX Plant (1955 to 1972 and 1983 to 1991) (Sederburg and Reddick 1994). The organic discharged to tank farms consisted of TBP, TBP degradation products, and diluents. A summary of waste tanks that likely received separable organic directly from the PUREX Plant is estimated in Table 3-1.

The estimates of quantities of organic that each tank received from PUREX Plant do not represent the total amount of organic present in the tanks due to losses and gains in tank volumes during intertank transfers. Many intertank transfers occurred over the years, which adds to the complexity of determining the fate and distribution of organic in the tank farms. Transfer information from the *History of the 200 Area Tank Farms* (Anderson 1990) and *History of Organic Carbon in the Hanford HLW Tanks: HDW Model Rev. 3* (Agnew 1996) show that the SST organic waste receivers experienced many intertank transfers. The intertank transfers during the 1950s, 1960s, and 1970s were mainly among the A, AX, and C Tank Farms, although several transfers that included organic waste went to the B, BX, BY, S, SX, TX, TY, and U Tank Farms. During the 1950s and 1960s the A and AX Tank Farms stored self-concentrating waste and received frequent organic wash waste for storage and destruction of soluble and entrained organic. Later operations improved treatment and reuse of solvents, reducing the amount disposed. The combination of mixing, high alkalinity ($\text{pH} \geq 10$), degradation product emulsifiers, solids/cation catalysts, and high radiation source term of the wastes reduced the quantity of separable phase organic that was stored in the A and AX Tank Farm tanks.

Separable phase organic waste that was added to C Tank Farm and then transferred to other single-shell tanks (SSTs) could have survived destruction due to unfavorable conditions for chemical and radiolytic degradation (e.g., poor mixing of the light-phase organic and heavy-phase aqueous liquids, low temperature and radiation source term history, unfavorable alkalinity, and/or low concentrations of waste components that appear to accelerate TBP destruction). It is difficult to identify waste tanks that currently contain significant residual process solvents based on waste process history and transfer records.

The B Plant waste fractionation process was started in 1968 and removed ^{137}Cs and ^{90}Sr fission products from PUREX and selected REDOX high-level stored wastes. The removal of these high heat radionuclides permitted immobilization of waste as a salt cake in the SSTs. The extracted cesium and strontium were purified and encapsulated.

A continuous solvent extraction process was used to remove strontium; ion exchange and precipitation processes were used for cesium removal. The solvent extraction process used a 20 wt% di-2-ethylhexyl phosphoric acid, 10 wt% TBP, and 70 wt% NPH organic for extraction of strontium from chelated aqueous waste. Solvent extraction processing was started in 1968 and continued until 1978. A continuous alkaline wash was used to remove degradation products from the organic.

Table 3-1. Summary of Waste Tanks That Received Organic from PUREX Plant.

Tank	Volume of Organic ² (gal)	Time Period	Organic Disposition	Year Sludge Retrieved
A-101 ¹	93,200	1956 - 1968	Degradation, Evaporation, Waste Transfer	1975 - 1976
A-102 ¹	80,100	1956 - 1963	Degradation, Evaporation, Waste Transfer	1972 - 1976
A-103 ¹	48,700	1956 - 1967	Degradation, Evaporation, Waste Transfer	1974 - 1976
A-104 ¹	140,000	1958 - 1968	Degradation, Evaporation, Waste Transfer	1974 - 1975
A-106 ¹	68,200	1960 - 1968	Degradation, Evaporation, Waste Transfer	1970 - 1973
AW-101 ²		1982 - 1991	Degradation, Evaporation, Waste Transfer	None
AW-104 ²	72,000	1982 - 1991	Degradation, Evaporation, Waste Transfer	None
AX-101 ¹	11,700	1965 - 1967	Degradation, Evaporation, Waste Transfer	1975 - 1976
AX-102 ¹	11,700	1966 - 1967	Degradation, Evaporation, Waste Transfer	1976
AX-103 ¹	24,100	1965 - 1968	Degradation, Evaporation, Waste Transfer	1976 - 1977
AX-104 ¹	20	1968	Degradation, Evaporation, Waste Transfer	1977 - 1978
C-101	3,800	1968	Evaporation, Waste Transfer	1952 - 1953
C-102	17,200	1968 - 1969	Evaporation, Waste Transfer	1953
C-104	76,400	1969 - 1972	Evaporation, Waste Transfer	None
C-110	4,000	1956 - 1957	Evaporation, Waste Transfer	None
C-111	600	1956	Evaporation, Waste Transfer	None
Unknown	5,400	1955		
Total	657,100	1955 - 1991		

Notes:

- 1 These tanks stored self-concentrating waste and received intermittent organic wash waste during the 1950s and 1960s.
- 2 Organic sent to AW tanks cannot be positively identified due to lack of transfer records. The only certainty is that this organic was sent to DSTs.
- 3 Volume of organic based on estimated average of 0.0176 gal organic/gal of carbonate waste plus organic wash waste streams for SSTs.

Essential material consumption information shows that about 400,000 L (107,000 gal) of B Plant organic were used during strontium extraction. Initial estimates suggest that about 155,000 L (41,000 gal) of organic were discharged to the SSTs. The remaining organic (~66,000 gal of mostly NPH) was discharged as vapor components to the process condensate crib and stack gaseous effluent. Historical records and process flowsheet information show that there were no discards of spent process organic from B Plant to organic cribs. Recent analysis of the Tank 241-C-106 core sample shows the sludge contains B Plant organic.

3.1.2 Tank Farm Sampling Activities and Current Organic Volume Estimates

The first core sample from Tank 241-C-103 to indicate separable organic was analyzed in 1986 (Weiss and Schull 1988). Some separable phase organic exists in other tanks based on core and head space vapor sample results; it is likely present in smaller quantities than in Tank 241-C-103. Visual identification of a separable organic layer in core samples may be difficult and will depend on the quantity, density, and color of the organic phase. The SSTs that have been interim stabilized have only a small volume of drainable liquid remaining; some organic could be sorbed on waste solids (Schulz 1968).

A screening methodology has been developed by WHC Tank Waste Safety that uses vapor characterization data (Bratzel 1996) with an evaporative model to estimate size of solvent pools that feed vapor into tank head spaces and pose significant risk from accidental solvent fires (Grigsby and Postma 1996). Results show that Tanks 241-BY-103, 241-C-102, and 241-C-103 meet or exceed derived criteria for solvent fire risk and need additional evaluation.

An alternate screening methodology based on NPH head space concentration and Raoult's Law was used to identify SSTs that may contain significant NPH and/or TBP liquid organic and therefore pose potential impacts to TWRS processing. A 0.1 mole fraction value for NPH was used as initial criteria based on engineering judgement. A total of six SSTs exceeded the NPH criteria (Tanks 241-TY-103, 241-C-103, 241-T-111, 241-BX-104, 241-BY-108, and 241-C-102). An estimate of the organic volume for some of these tanks could not be developed from available data. Table 3-2 summarizes available information on vapor sample results for SSTs potentially containing separable phase organic.

Tank characterization information was used to estimate the organic inventory for several tanks. The inventory of Tank 241-C-103 is about 17,300 L (4,570 gal) of NPH TBP, Tank 241-BY-108 about 420 L (110 gal) of NPH with trace TBP, and Tank 241-C-204 about 5,000 L (5,600 kg) of TBP with trace NPH. Table 3-3 and Table 3-4 summarize the estimated organic inventory for 21 tanks. The 28,400 L (7,500 gal) of organic exists as a separate floating layer, solubilized in the aqueous supernatant liquid and/or combined with the salt cake and sludge solids based on information to date.

The above information was used to develop a preliminary estimate of the process organic that may remain in the DSTs and SSTs (Klem 1996). A projected volume of 87,000 L (23,000 gal) was the average total value from several projected estimates each

Table 3-2. Summary of Available Information on Single-Shell Tanks Potentially Containing Separable Phase Organic. (sheet 1 of 2)

Tank	Bases for Separable Phase Organic ¹ in Tank		
	NPH Detected in Vapor Sample of Tank Head Space	Documentation	Mole fraction NPH in liquid organic waste ⁶
TY-103	Yes	OWW added 1968 ³ , 242-T bottoms	Max 0.510
C-103	Yes	OWW added, 242-A bottoms, ~17,300 L TBP-NPH in 1995	Max 0.489
T-111	Yes	-	Max 0.221
BX-104	Yes	OWW added ³	Max 0.144
BY-108	Yes	ITS bottoms and recycle ³ , ~420 L NPH estimated from recent core sample	Max 0.141
C-102	Yes	OWW added 1968 ³ , ~136,100 L TBP-NPH in 1972 ⁵	Max 0.132
BY-107	Yes	ITS bottoms and recycle	Max 0.099
B-103	Yes	OWW added 1969 ³	Max 0.051
C-110	Yes	OWW added 1956-7 ³ , ~15 L TBP estimated from recent core sample	Max 0.026
C-101	Yes	OWW added 1968 ³	Max 0.013
TY-104	Yes	OWW added 1970 ³	Max 0.013
BX-107	Yes	~10 L TBP based on recent core sample	Max 0.013
BY-103	Yes	OWW added 1969 ³ , ITS bottoms	Max 0.010
BY-104	Yes	ITS & 242-A bottoms	Max 0.009
BY-110	Yes	242-A bottoms ³	Max 0.008
A-101	Yes	OWW added ³ , 242-A & S bottoms	Max 0.003
BY-105	Yes	ITS bottoms and recycle ¹	Max 0.003
T-107	Yes	242-T bottoms, ~60 L NPH from recent core sample	Max 0.003
AX-102	Yes	OWW added ³ , 242-A bottoms	Max 0.002
BY-106	Yes	ITS bottoms and recycle ³	Max 0.001
BY-112	Yes	70% TBP 30% NPH in 1968 sample ² , ITS bottoms and recycle ³	Max 0.001
TX-118	Yes	OWW added ³	Max 0.001
U-110	Yes	-	Max 0.001
BY-111	Yes	OWW added 1957, ITS bottoms and recycle ³	0.000
B-111	No Vapor Sample	OWW added ³ , ~20 L TBP estimated from recent core sample	-
C-106	Yes	~70 L TBP-NPH estimated from recent core sample	Not Available
C-107	Yes	-	0.000

Table 3-2. Summary of Available Information on Single-Shell Tanks Potentially Containing Separable Phase Organic. (sheet 2 of 2)

Tank	Bases for Separable Phase Organic ¹ in Tank		
	NPH Detected in Vapor Sample of Tank Head Space	Documentation	Mole fraction NPH in liquid organic waste ⁵
C-108	Yes	OWW added 1970 ³	0.000
C-109	Yes	-	0.000
C-111	Yes	OWW added 1956 ³	0.000
C-112	Yes	OWW added 1975 ³ , ~410 L TBP-NPH estimated from recent core sample	0.000
C-204	Yes	~5,800 L TBP estimated from recent core sample ⁴	Not Available
S-102	Yes	OWW added ³ , 242-S evap. bottoms	0.000
S-104	No Vapor Sample	~1,150 L NPH estimated from recent core sample	-
S-111	Yes	OWW added ³ , 242-S bottoms and recycle	0.000
T-104	Taken/Not Yet Analyzed	OWW added ³ , ~3,300 L NPH estimated from recent core sample	Not Available
TX-105	Yes	OWW added 1971, 242-T bottoms and recycle ³	0.000
TY-101	Yes	-	0.000
U-103	Yes	OWW added, 242-S bottoms ³	0.000
U-105	Yes	OWW added, 242-S & T bottoms and recycle ³	0.000
U-106	Yes	OWW added, 242-S bottoms and recycle ³	0.000
U-107	Yes	OWW added ³ , 242-S bottoms	0.000
U-203	None detected	-	0.000
U-204	None detected	-	0.000

Notes:

- 1 A NPH mole fr ≥ 0.1 in the liquid organic waste is considered significant.
- 2 Based on information in *Characterization of the Organic Material in the 112 BY Tank* (Schulz 1968).
- 3 Based on information in *A History of the 200 Area Tank Farms*, (Anderson 1990) or *History of Organic Carbon in Hanford HLW Tanks: HDW Model Rev 3* (Agnew 1996)
- 4 Personal communication with J. A. Campbell (PNNL) January 1996. Assumes sludge sample is valid and uniform distribution of TBP in sludge.
- 5 Based on information in *Liquid Organic Waste Collection and Disposal* (Hall 1972a)
- 6 Based on vapor sample results and Raoult's Law.

Table 3-3. Summary of Single-Shell Tank Sample Results for Tri-Butyl Phosphate and Normal Paraffin Hydrocarbon Organic.

SST	Core/Auger Sample ¹ TBP ($\mu\text{g/g}$)	Projected TBP ¹ (gal/kg)	Projected NPH ¹ (gal/kg)	Total (gal)
C-204	334,000	1,543/5,682	TBD	TBD
BY-108	< 0.1	< 1/ < 0.1	110/320	110
C-112	205	28/100	80/230	108
BY-110	Below detection level	-	TBD	TBD
C-106	55	16/60	2/5	18
C-110	14	4/15	TBD	TBD
B-111	22	6/24	TBD ²	TBD
BX-107	7	3/13	TBD ²	TBD
C-103	No data	2,740/10,100	1,830/5,260	4,570
S-104	No data	-	305/880	TBD
T-104	No data	-	880/2,530	TBD
T-107	No data	-	15/40	TBD
Total	-	4,340/15,990	3,222/9,265	7,562

Notes:

- 1 Based on information in tank characterization reports, conversation with J. A. Campbell (PNNL) and August 1996 tank characterization data base. Assumed solids density was 1.5 g/cc. Solid/liquid volumes as listed in Hanlon (1995).
- 2 Sample taken before 12/91 and contaminated by NPH hydrostatic head fluid used in core sampler.

Table 3-4. Summary of Double-Shell Tank Results on Aqueous Soluble Organic.

DST	Aqueous Supernatant Sample TBP ($\mu\text{g/L}$)	Projected Soluble TBP ¹ (gal/kg)	Estimated Equilibrium Floating Organic Layer ² (gal)	
			30 % TBP 70 % NPH	70 % TBP 30 % NPH
AP-101	< 500 (9/94)	<0.5/<1.7	<0.8	<0.8
AP-102	Below Detection Level (4/93)	-	TBD	TBD
AP-103	Below Detection Level (4/94)	-	TBD	TBD
AP-104	190 - 8,800 (5/96)	3.7/13.8	2.9	<0.8
AP-106	110 - 1,100 (6/95)	0.5/1.8	<0.3	<0.3
AP-107	1,400 - 1,900 (6/95)	1.6/5.9	<0.7	<0.7
AP-108	Below Detection Level - 16 (9/94)	<0.1/<0.1	<0.2	<0.3
AW-102	Below Detection Level (4/94)	-	TBD	TBD
AW-106	Below Detection Level (4/94)	-	TBD	TBD
Total	-	6/23.2	<4.9	<2.9

Notes:

- 1 Based on Simpson (1994) and recent waste feed transferred to 242-A Evaporator per personal conversation with E.Q. Le (WHC).
- 2 Based on preliminary solubility model; assumes no chemical or radiation degradation to achieve average TBP concentration of supernatant. Total not included in volume calculations due to uncertainties.

having comparable levels of uncertainty. The estimates ranged from 34,000 L (9,000 gal) to 148,000 L (39,000 gal) (see Volume 2, Section 3.4).

Remains and location of the 270,000 L (72,000 gal) of organic discharged to the DSTs (AW Farm) from 1982 to 1991 Purex operations are unknown (Table 3-1). Some of this organic should be detected or observed because it was recently transferred to the tanks. However, no significant amount organic has been reported to date.

3.2 TANK 241-C-103 HISTORY

This section briefly describes the long-term process history of Tank 241-C-103 and its recent history involving the separable phase organic layer. Additional information is provided in Volume 2, Section 3.2. A summary of Tank 241-C-103 history is provided in Figure 3-1.

3.2.1 Process History

Tank 241-C-103 is a single-shell underground storage tank used to store hazardous and radioactive waste that was generated during defense production operations at the Hanford Site. This tank is known to contain about 17,300 L (4,570 gal) of floating separable phase organic liquid comprised primarily of TBP and NPH. The liquid organic is floating on an aqueous supernatant layer of approximately 503,000 L (133,000 gal) and a sludge layer of approximately 235,000 L (62,000 gal). Tank 241-C-103 received waste until July 1979. The tank was partially isolated in December 1982 (Welty 1988).

The organic liquid in Tank 241-C-103 is believed to have resulted from the transfer of solvent rich organic wash waste from Tank 241-C-102 in November 1975 (Volume 2, Section 3.3). The organic liquid currently is a mixture of approximately 67 wt% TBP and 33 wt% NPH, the primary organic compounds that make up the PUREX Plant solvent. Partial evaporation of the organic liquid during periods of forced ventilation between 1975 and 1992 has reduced the volume of the liquid and depleted the more volatile hydrocarbons that were initially present in the NPH. The organic liquid has a density of 0.876 g/mL and a viscosity of 4 cP at 25 °C (Pool and Bean 1994).

3.2.2 Organic Removal and Safety Evaluation History

The history of organic removal and safety evaluations including earlier events, unreviewed safety questions (USQs), and previous studies are discussed in the following sections.

3.2.2.1 Earlier Events. The need for a mechanism to deal with separable phase organic in Hanford Site tanks has been known for over 20 years (Hall 1972a). A safety analysis of floating organic layers also dates back to this time period (Hall 1972b). The initial effort to

remove organic from the tanks then containing separable phases, including Tank 241-C-102, was cancelled in either 1974 or 1975 after no separable organic was detected in C Tank Farm tank samples.

Odors in the C Tank Farm have been present for several years. In the late 1980s, the issue of organics in Tank 241-C-103 again received considerable attention after employees exposed to gases and vapors in the C Tank Farms received medical attention. As a result, several gaseous monitoring activities were undertaken. In addition, the fiscal year (FY) 1991 Tri-Party Agreement milestones resulted in the study of ways to remove the organic layer in support of SST stabilization (Scully 1990; Dunford 1990).

3.2.2.2 Unreviewed Safety Question. A USQ was declared in 1992 because the existing Safety Analysis Report (SAR) (Boyles 1989) did not address the potential flammability of a floating organic layer in Tank 241-C-103 (WHC 1992). This USQ was closed in 1994 after several actions were taken. One was the completion of a Justification for Continued Operation (Carothers 1993). Another was the completion of the original *Safety Analysis of Exothermic Reaction Hazards Associated with the Organic Liquid Layer in Tank 241-C-103* (Postma et al. 1995), which has since been revised to include several additional concerns including the impacts of organic in contact with the sludge.

3.2.2.3 Previous Studies. Several related studies were performed to evaluate the best method for removing the Tank 241-C-103 organic (Parazin 1994). Two key findings came to light during preparation of the Preliminary Design Criteria, which prompted the reassessment of the mission and its possible deferral.

- Objective, quantified data became available which significantly reduced concerns related to the toxic vapor and flammability issues originally raised by the presence of the floating organic (Postma et al. 1995).
- New, less restrictive DOT regulations will allow pumping the organic to an aboveground tank for storage or shipment offsite for processing.

Based on this new information, studies were performed that supported pumping the organic directly from Tank 241-C-103 to a DST (Bartley 1994; Dukelow et al. 1995; Geschke and Milliken 1995). See Sections 1.1 and 6.2 for additional information.

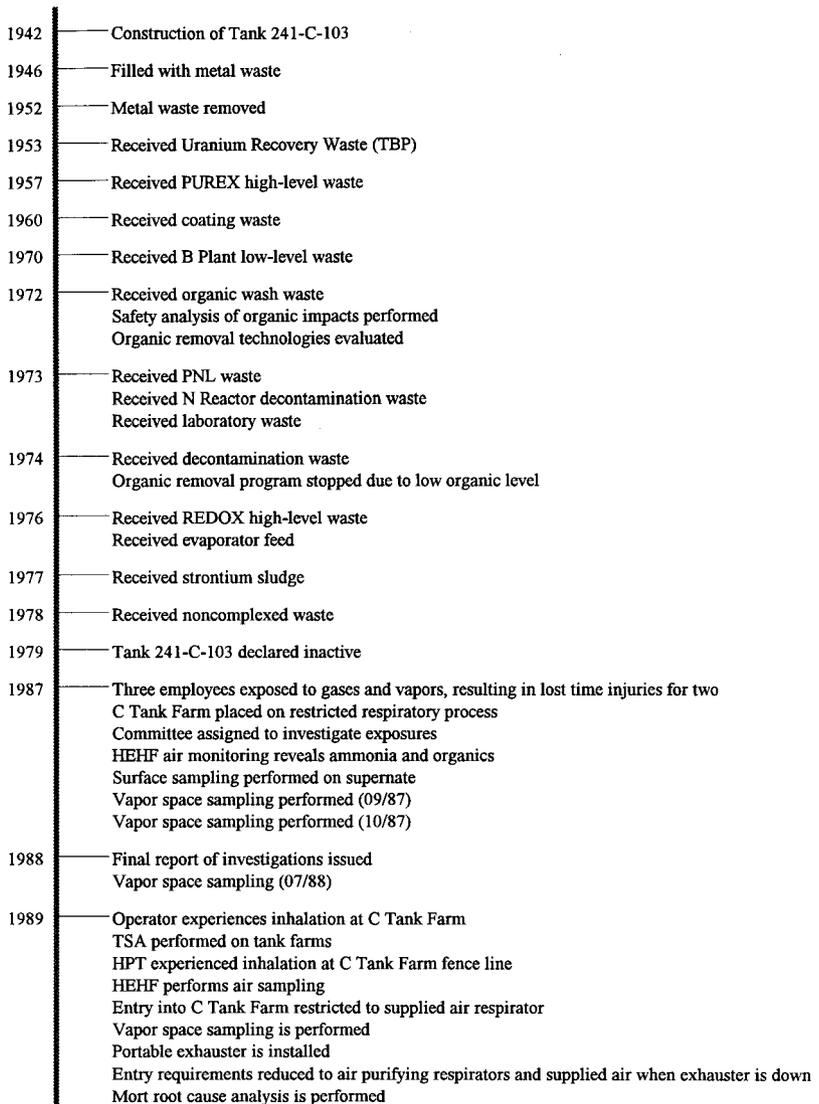


Figure 3-1. Tank 241-C-103 Timeline. (sheet 1 of 2)

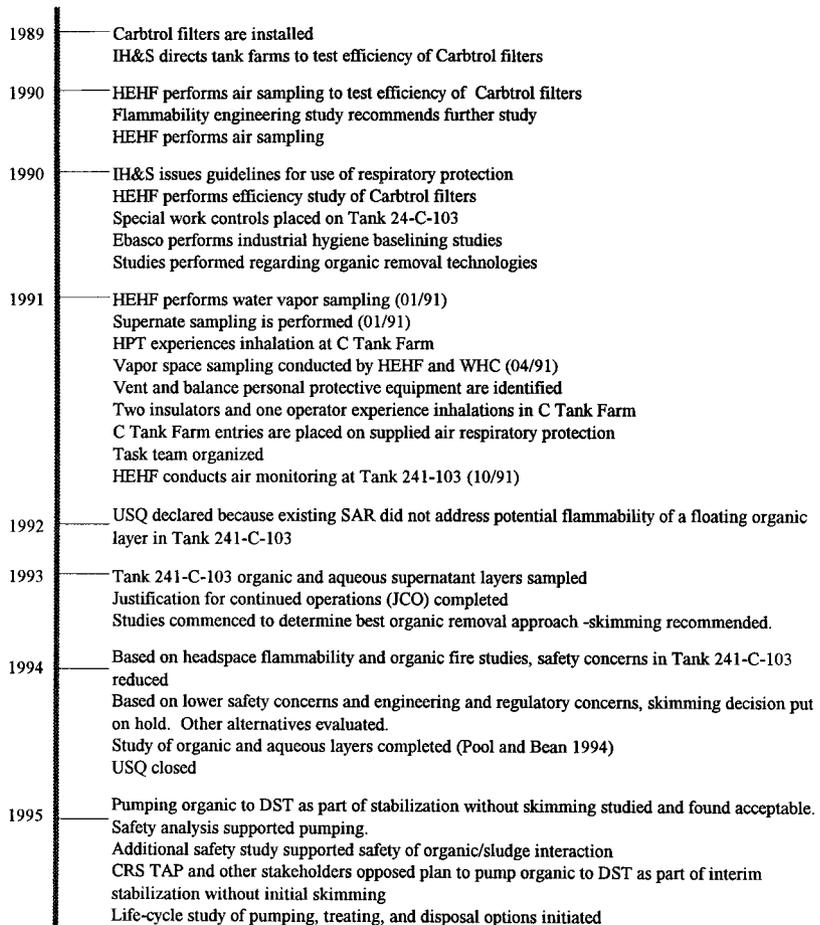


Figure 3-1. Tank 241-C-103 Timeline. (sheet 2 of 2)

4.0 IMPACTS ON DOUBLE-SHELL TANKS AND PRETREATMENT PROCESSES

The TWRS Pretreatment processes must be changed to address separable phase organic regardless of the actions for Tank 241-C-103 for two reasons: (1) separable organic is likely present in several other waste tanks and (2) a separate organic phase will likely form during sludge wash and caustic leaching. This engineering evaluation was completed prior to the decision to modify the TWRS process technical baseline. The information gathered for this evaluation was the primary driver to add a decanter system for separation of aqueous and organic phases after sludge wash (Orme et al. 1996).

This section evaluates the initial impacts if Option A - pump both layers to a DST. This section describes the impacts of separable phase organic if the Pretreatment processes are not modified, and provides recommendations for modifying the Pretreatment processes. The overall organic removal options evaluation (Section 10) includes scenarios for both modified Pretreatment and unmodified Pretreatment processes.

As determined in this section, if the Pretreatment processes are not changed there will be significant impacts regardless of the organic removal option chosen. The organic exists as a separate floating layer, solubilized in the aqueous supernatant liquid, and/or combined with the salt cake and sludge solids. The TBP will transfer between an aqueous soluble and separable organic phase depending on conditions. The TWRS functions included in this section are primarily **Manage Tank Waste** (Function 4.2.1), **Retrieve Waste** (Function 4.2.2), and **Process Waste** (Function 4.2.3).

4.1 MAJOR ASSUMPTIONS

The major assumptions for this section are necessary to evaluate the impact if there are no changes to the Pretreatment processes. The major assumptions are listed below.

- There will be no change to the Pretreatment flowsheet or processes. Impacts if Pretreatment is changed are addressed in Section 10.
- The Tank 241-C-103 organic removal action will result in organic contaminated sludge or separable phase organic that must be processed through the Pretreatment processes.
- At least 99% retrieval of the SST waste will be acceptable by regulatory agencies for tank closure.

4.2 PUMPING BOTH AQUEOUS AND ORGANIC PHASES TO A DST USING EXISTING PUMPING EQUIPMENT

The transfer of the organic and aqueous from Tank 241-C-103 to a DST would likely use existing interim stabilization equipment and procedures. Pumping could be performed

with a jet pump or a submersible turbine pump in a salt well. The liquid would be transferred through a double-contained receiver tank (DCRT) where the pH would likely be adjusted (by adding sodium hydroxide) to meet DST storage criteria and then transferred to a DST for interim storage until the waste was retrieved for pretreatment and disposal. Costs for this pumping are estimated to be between \$500,000 and \$1 million (Appendix A; Dukelow et al. 1995).

Prior to any DST use for separable phase organic storage, the compatibility data quality objective (DQO) that prevents separable phase organic additions to DSTs must be modified. A survey of the 28 DSTs was performed to identify potential alternate locations for placing TBP-NPH separable phase organic from Tank 241-C-103. Table 4-1 summarizes this survey information. Tank 241-AP-107 was identified as the preliminary candidate tank. The use of Tank 241-AP-107 accomplishes the following:

- Avoids mixing the separable phase organic with dilute waste that requires evaporation at the 242-A Evaporator (no impact on LERF and ETF treatment of condensate)
- Segregates waste types and complies with DOE Order 5820.2A
- Minimized potential flammable gas generation from reaction of precipitated organic solids with high heat sludge such as neutralized current acid waste.
- Appears to meet waste volume projection, waste compatibility (e.g., total organic carbon [TOC]), and future programmatic impacts of storage and processing (including Phase I privatization) assuming efficient TBP degradation and NPH evaporation.

The potential use of this DST for organic storage would not impact current safety (Harris 1994; Geschke and Milliken 1995; Postma et al. 1995) and waste management planning assumptions (Certa et al. 1996; Powell et al. 1996). However, long-term disposal of organic through destruction and evaporation is not currently considered usable (Section 8.3).

The transfer and storage of Tank 241-C-103 separable phase organic to the DST system would add some new interface requirements and/or require implementation of existing controls. The procedural requirements for adding organic to a DST have previously been identified (Bartley 1994; Geschke and Milliken 1995). The expected transfer and storage interface impacts, requirements, and controls include the following.

- There could be increased degradation of mechanical and chemical seals by frequent contact with separable phase organic liquid and vapor components. The DST system should be evaluated and compatible materials should be used for pump seals, high efficiency particulate air (HEPA) filters, electrical feed through seals, and other components that could contact the liquid organic or organic vapors. These effects are likely minimal because there is considerable

Table 4-1. Double-Shell Tank Supernatant Summary Based on FY 1998 Projections.

Tank	Projected Waste Type ¹	Safety Issue ²	Other Impacts ³	Projected Supernatant Volume ⁴ (L)	Available Space Volume ⁵ (L)	Solids Volume ⁶ (L)	Vent ⁴
101-AN	DSSF		Priv. Phase I LLW	3.68E06	6.30E05	0	A
102-AN	CC		Priv. Phase I LLW	3.95E06	2.00E04	3.40E05	A
103-AN ⁷	DSSF	FG WL	Priv. Phase I LLW	3.62E06	6.90E05	0	A
104-AN ⁷	DSSF	FG WL	Priv. Phase I LLW	3.02E06	1.29E06	0	A
105-AN ⁷	DSSF	FG WL	Priv. Phase I LLW	4.29E06		0	A
106-AN	CC		Priv. Phase I LLW	4.47E06	0	6.00E04	A
107-AN	CC		Priv. Phase I LLW	3.68E06	1.20E05	5.10E05	A
101-AP	DSSF		Priv. Phase I LLW	3.39E06	9.2E05	0	A
102-AP	CP		LLW Staging	4.16E06	1.50E05	0	A
103-AP	DN		LLW Staging	1.02E05	4.20E06	0	A
104-AP	DN		Priv. Phase I, LLW Staging	4.23E06	8.00E04	0	A
105-AP	CC		Waste Evap Feed	7.56E04	4.23E06	0	A
106-AP	DSSF		Priv. Phase I, LLW Staging	3.03E06	1.28E06	0	A
107-AP	DN		Scheduled for CC waste from SSTs	1.17E05	4.19E06	0	A
108-AP	DN		LLW Staging	3.10E06	1.21E06	0	A
101-AW ⁷	DSSF	FG WL	Priv. Phase I	3.94E06	3.70E05	3.20E05	A
102-AW ⁷			Evap Feed	Not Assessed	N/A	N/A	A
103-AW ⁷	NCRW		High TRU Sludge	5.41E05	2.4E06	1.37E06	A
104-AW ⁷	DN	FG	High TRU Sludge	5.68E05	3.06E06	7.22E05	A
105-AW ⁷	NCRW		Priv. Phase I	4.31E06	0	1.22E06	A
106-AW ⁷			Evap Feed	Not Assessed	N/A	N/A	A
101-AY ^{5,7}	CC	FG		1.48E06	1.93E06	3.1E06	A ⁶
102-AY ⁵	DN		May Change Waste	2.98E06	6.2E05	1.20E05	A ⁶
101-AZ ^{5,7}	NCAW		Priv. Phase I	2.95E06	7.30E05	0	A ⁶
102-AZ ⁵	NCAW		May change waste, May cause FG Issue	2.67E06	1.00E04	1.04E06	A ⁶
101-SY ⁷	CC	FG WL		6.81E04	1.11E05	4.13E06	A
102-SY ⁷	PPF		High TRU Sludge	1.40E05	4.10E06	6.90E04	A
103-SY ⁷	CC	FG WL		6.43E05	3.66E06	2.17E06	A

Notes:

- 1 DST waste types are defined in Appendix B.
- 2 Tanks with Flammable Gas (FG) Unreviewed Safety Question and/or Watch List (WL) tanks based on Barton (1996).
- 3 Based on information in Cerna et al. (1996) and Powell et al. (1996).
- 4 Tank has active (A) or passive (P) ventilation system.
- 5 These tanks contain air-lift circulators for mixing supernatant.
- 6 These tanks are scheduled to be placed on a recirculated air vent system (W-30 Project) in December 1996.
- 7 These tanks contain an ENRAP surface level gauge.

DSSF = double-shell slurry feed NCAW = neutralized current acid waste
 CC = complexed concentrate PFP = Plutonium Finishing Plant
 CP = concentrated phosphate N/A = not applicable
 DN = dilute noncomplexed waste TRU = transuranic
 NCRW = neutralized cladding removal waste

evidence of other organics present (Section 3.1.2) and there have been no known failures due to organics.

- There will be increased difficulty in detecting the waste surface level by standard continuity methods (FIC gauges or manual tape). ENRAF gauges have the capability to measure the waste surface level (including floating organic) and are replacing the older FIC gauges.
- Specification SD-RE-TI-003 should be implemented and the liquid level should be maintained a minimum of 0.9 m (3 ft) above the pump suction level when separable phase organic is detected in the 242-A Evaporator feed tank.
- The waste temperature should be maintained below 73 °C (160 °F) (Harris 1994) to minimize accumulation of separable phase organic vapors in the overhead system.
- NPH vapor will condense and return to the DST and/or be released to the atmosphere via the existing forced air ventilation system; specification OSD-T-151-00017 should be implemented to prevent accumulated organic liquid waste discharges to the ground by design of ventilation equipment, sampling, and administrative control.
- There is the potential formation of a second aqueous phase from sodium dibutyl phosphate (NaDBP) buildup in supernatant, based on recent Pacific Northwest National Laboratory findings in sodium hydroxide (NaOH) solutions at high ionic strength.

4.3 SLUDGE RETRIEVAL FROM TANK 241-C-103

Retrieval systems will mobilize and remove enough tank waste to meet tank site closure requirements. Mobilized waste will be transferred by pumps to DSTs for interim storage before processing. The referenced waste mobilization equipment is past-practice (hydraulic) sluicing for SST waste and mixer pumps for DST waste. Alternate retrieval methods, including those identified through the Acquired Commercial Technologies for Retrieval program, will be used to retrieve waste from SSTs or DSTs if past-practice sluicing or mixer pumps do not meet waste mobilization and removal requirements.

Hydraulic sluicing will be employed as the primary waste retrieval technology in many of the SSTs, including Tank 241-C-103. Hydraulic sluicing involves contacting the solid waste with the sluicing liquid to form a slurry which would be pumped directly to a DST farm for storage prior to processing. The sluicing liquid would be decanted liquid from the DST receiving tank. Pump and sluicing assemblies in an SST are shown in Figure 4-1.

Regardless of the organic removal option chosen, organic will be present in the sludge. Extensive Hanford Site experience with past-practice sluicing of sludge during the

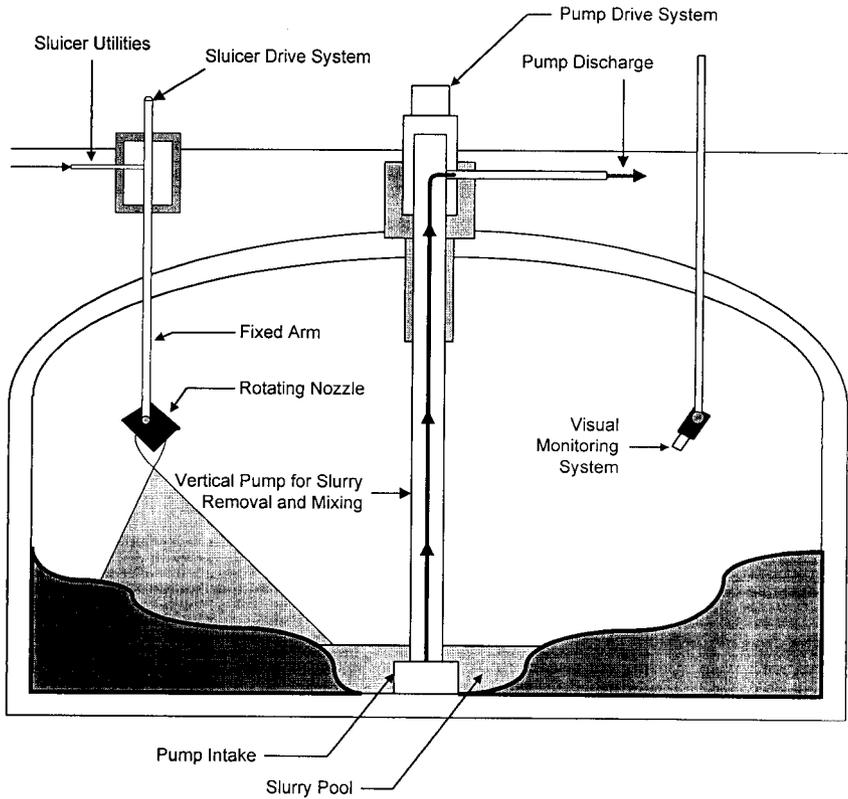


Figure 4-1. Pump and Sluicing Assemblies in a Single-Shell Tank.

uranium and strontium recovery campaigns provides confidence that no significant retrieval rate or efficiency impacts would be observed in the presence of separable phase organic. The 1,300-L/min (350-gal/min) sluicing jet is expected to mobilize sludge and salt cake present in Tank 241-C-103 even if the entire organic layer were to remain in the sludge.

The impacts of sludge retrieval from Tank 241-C-103 on decision criteria if the organic is not skimmed prior to sluicing are not expected to be significantly different than if the organic were skimmed. With the exception of cost, the concerns described in Table 1-1 (e.g., low-level waste [LLW] volume, health and safety impacts, schedule, and process rates) will not be significantly affected. Impacts are more fully described in Volume 2, Section 4.1.

There are cost impacts due to possible damage of the pump seals. The elastomer seals in the transfer pump are not compatible with the organic and may fail before all pumping is completed. Because of radiation exposure concerns, the elastomer seals in the transfer pump can only be replaced on a pump that has not been used in highly radioactive services. Thus, a new transfer pump with compatible seals might have to be used for retrieval of Tank 241-C-103 sludge. Acceptable elastomer materials are discussed in Volume 2, Section 4.1.1.1. This organic transfer pump might be used for retrieval of other SST waste to reduce the cost impact. The cost for procurement and installation of a new pump is approximately \$437,000.

4.4 TANK CLOSURE

Ecology plans to close the Hanford Site SSTs in accordance with Washington State Administrative Code (WAC) Chapter 173-303-610. It is assumed that 99% of the waste will be retrieved from the SSTs (Tri-Party Agreement). Once the waste has been retrieved, the tank system will be closed. Three options are available for closure: clean closure, modified closure, and closure as a landfill. A decision on closure has not been made. Although some amount of organic waste may remain in the SSTs following retrieval, this waste will not preclude closure as a landfill. If it can be demonstrated that clean closure is impractical, then the tank system can be closed as a landfill. Closure as a landfill will require post-closure care and monitoring. The impacts of organic sludge retrieval are pertinent to any tank containing separable phase organic, including Tank 241-C-103.

Closing a tank farm with or without organic skimming will have similar impacts on decision criteria. The amount of residual organic left in the tank following sluicing in either case is expected to be similar and insignificant with respect to environmental risk.

4.5 SLUDGE WASHING

The primary goal of sludge washing/solids pretreatment is to reduce the final volume of high-level waste (HLW) resulting from the treatment of tank waste. The HLW component is reduced through the separation of soluble radioactive and nonradioactive contaminated

components of the waste from the insoluble contaminated sludges/solids. The principle nonradioactive components that need to be separated from the tank waste include sodium, aluminum, chromium, nitrate, nitrite, sulfate, and phosphate. The process must also produce a waste stream that is compatible with the radionuclide separation process of the supernatant pretreatment process. The steps involved in in-tank processing of tank waste are outlined in Figure 4-2 (MacLean 1995).

4.5.1 Impacts of Organic on Sludge Washing

The sludge wash material from Tank 241-C-103 will contain both dissolved organic and some small amount of separable phase organics. Once this material (or organic containing material from any tank) is transferred to the designated DST for sludge washing, NaOH (caustic) will be added as part of the caustic leaching process. During caustic leaching, additional separable organic (primarily TBP) will form and collect from the soluble organic due to the higher salt concentrations, higher caustic levels, and higher temperatures. Formation of this separable organic layer from soluble organics is a primary driver for the need to change pretreatment (Orme et al. 1996).

Some of the aqueous soluble TBP will react with the caustic to form butanol, sodium phosphate, and sodium dibutylphosphate (DBP). The butanol, sodium phosphate, and some if not all of the DBP would likely remain in solution. Based on ventilation studies, flammable gas generation is not an issue (Bartley 1994).

Following the first water washing step, the sludge will settle and excess liquid phase organic will float on top of the aqueous solution together with some solids. The aqueous liquid will then be decanted off of the sludge and sent to the filtration and ion exchange processes (Section 4.6). The decanting pump has a floating suction that draws liquid from 15 cm (6 in.) below the top of the liquid surface; this design leaves a 15-cm (6-in.) liquid layer on top of the sludge. The vortex created by aqueous pumping could cause organic carryover to filtration and ion exchange operations. The layer not decanted, which should include any floating organic left in the tank, will be mixed with the HLW sludge after the second water washing and decanting step. The HLW sludge will be transferred to a vitrification plant feed tank for incineration. Any phosphate in the organic will be incinerated and incorporated into the HLW glass product.

4.5.2 Impacts of Sludge Washing on Decision Criteria

The sludge washing system is not currently designed to handle organic material. Due to the recent decision to modify TWRS Pretreatment, it is likely that organic decanting will occur after the sludge wash system (Orme et al. 1996). The measured values (e.g., LLW volume, cost, health and safety impacts, schedule, and process rates) that could be affected by the presence of organic in the DST are described below.

4.5.2.1 Low-Level Waste Volume. The LLW volume could be impacted if the inlet point to the in-tank sludge wash decant pump were lowered, thus reducing efficiency. The primary LLW volume impact would be to the filtration and ion exchange systems (Section 4.6).

4.5.2.2 Cost and Schedule. The potential additional cost impacts associated with sludge washing if the organic is not skimmed or decanted after sludge wash would be due primarily to schedule impacts and possible shutdowns. The system could be shutdown for the following reasons:

- Potential safety concerns (similar to those that have been raised in Tank 241-C-103)
- Potential for carryover to downstream systems
- No mechanism to identify and remove separable phase organic.

The annual Pretreatment budget is estimated to be \$130 million. The cost associated with extension of the Tank Waste Safety and Operations Program is estimated to be \$400 million per year (Foster Wheeler 1995). Even a short shutdown or schedule extension would cause measurable budget impacts.

4.5.2.3 Health and Safety. Potential health and safety impacts associated with sludge washing if the organic is not skimmed would be the same as those that currently exist in Tank 241-C-103: solvent fire hazard and toxic vapor hazard. The risk of fire due to solvents was determined to be well within risk acceptance guidelines (Dukelow et al. 1995). Active ventilation in the DST should adequately remove any organic vapors (Bartley 1994; Geschke and Milliken 1995).

4.5.2.4 Process Rates. Because the sludge washing equipment was not designed to handle organic, the effect of the organic on the equipment is unknown. The 17,300 L (4,570 gal) of organic in Tank 241-C-103 is a relatively small volume and would likely have no major effect on processing rates; however, this has not been tested. Some organic may be tarry and clump or foam and cause equipment blockages. The equipment that could be adversely affected by the organic includes the decanting pump designed to remove the liquid floating on the sludge and the slurry pump to transfer the slurry to the treatment units. Any fouling of the equipment would cause delays or shutdowns in processing, lower overall process rates, and schedule slippage. If the inlet point was lowered from 15 cm (6 in.) to allow a larger buffer, sludge wash efficiency would be affected.

4.6 FILTRATION/ION EXCHANGE

The soluble radionuclides (cesium, technetium, chelated strontium, and transuranic elements) separated during in-tank processing would be sent to the filtration system and the ion exchange columns as part of the aqueous phase for further treatment. Separable phase

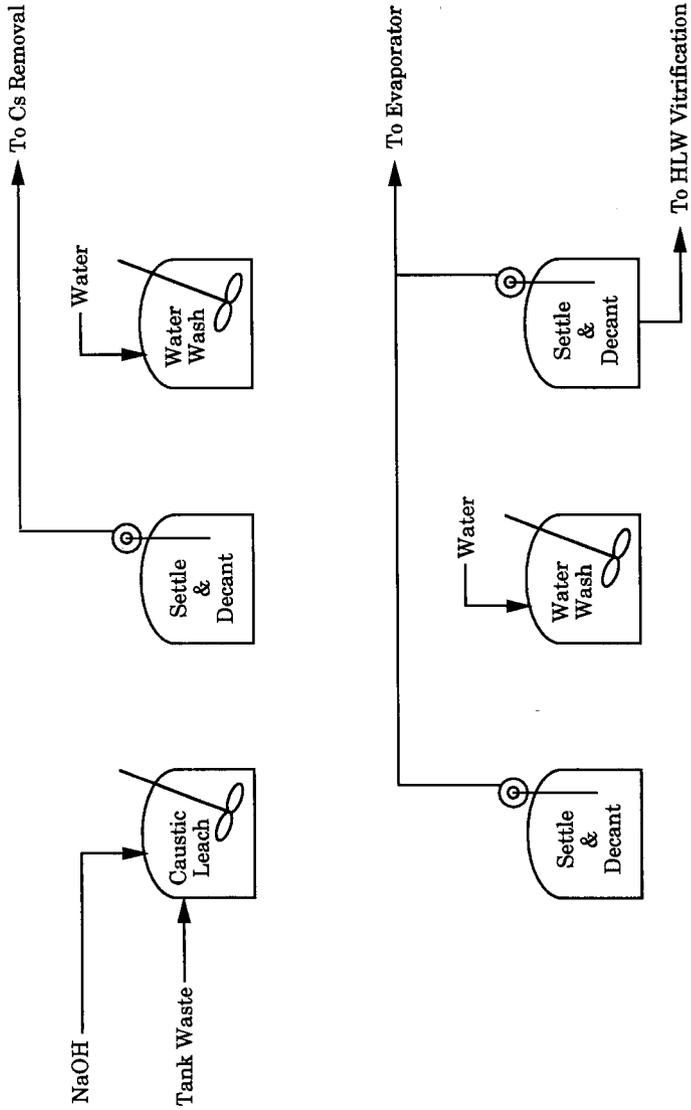


Figure 4-2. In-Tank Processing of Waste (from MacLean 1995).

organic and dissolved organic would likely greatly affect these processes. Additional filtration and ion exchange information is provided in Volume 2, Section 4.2. The impacts of organic on sludge retrieval are pertinent to any tank containing separable phase organic or dissolved TBP or NPH, including Tank 241-C-103.

4.6.1 Impacts of Organic on Filtration/Ion Exchange

The WHC Disposal Engineering and Process Technology Group makes the following recommendations based on a literature search regarding the impacts of separable phase organic on filtration and ion exchange (Volume 2, Section 4.2).

- All of the separable phase organic should be removed prior to filtration/ion exchange to avoid irreversibly coating the ion exchange media.
- Preliminary evidence indicates that the dissolved or emulsified TBP in the aqueous phase of the Tank 241-C-103 supernate should be removed to a level below 1 mg TBP per liter of aqueous feed to minimize the volume of secondary waste, ensure that product specifications are met, and avoid operational problems with the filtration and ion exchange systems.

Dissolved or emulsified TBP at levels as low as 1 mg TBP/L in the aqueous feed resulted in significant deposition of a separable organic phase on the leading part of the ion-exchange bed. Recent laboratory batch equilibrium tests show that TBP deposition or coating of exchanger material reduced cesium removal for both regenerable and non-regenerable exchangers. The cesium batch equilibrium coefficient was reduced by 80% for resorcinol formaldehyde and 50% for engineered crystalline silicotitanate based on tests with Oak Ridge National Laboratory Melton Valley waste (Volume 2, Section 4.2).

4.6.2 Impacts of Filtration/Ion Exchange on Decision Criteria

The measure values (LLW volume, cost, health and safety impacts, schedule, and process rates) that could be affected by the presence of organic in the filtration/ion exchange process streams are described in the following sections.

4.6.2.1 Low-Level Waste Volume. The amount of secondary waste (LLW) generated due to the presence of organic in the waste stream could be significant. Secondary waste that would result from the presence of organic is discussed in Section 4.6.2.5, Process Rates.

4.6.2.2 Cost. The additional cost impacts associated with filtration/ion exchange if the organic is not skimmed or decanted would potentially be high. According to Eager (Volume 2, Section 4.2) "normal operating costs could increase by a factor of four due to the added volume assuming that a TBP containing supernate could not be evaporated to the 5 to 7 molar cesium ion-exchange feed specification. This cost may be insignificant however based on the relatively small volume of the [Tank] C-103 supernate."

4.6.2.3 Health and Safety. Potential health and safety impacts associated with filtration/ion exchange if the organic is not skimmed or decanted would be the industrial safety risks and increased dose rates associated with more frequent filter/ion exchange resin changes and increased handling of the spent resin.

4.6.2.4 Schedule. Any adverse effect of organic in the filtration/ion exchange feed stream on the process rate (Section 4.6.2.5) would similarly affect the schedule. In addition, schedule delays would have a direct effect on the total cost.

4.6.2.5 Process Rates. The filtration/ion exchange process rates would be adversely affected by the presence of organic in the feed stream. In the case of filtration, separable organic phases such as TBP or NPH-type hydrocarbons would likely coalesce on the surface of the filter and increase the flow resistance. In addition, a separable TBP phase on the filter would be difficult to remove. In the case of ion exchange, TBP in either a separable phase or emulsified form would likely coalesce or wet the surface of the ion exchange media where the feed entered the column. This would likely cause a pressure drop. Channeling could also result, causing portions of the bed to be bypassed. Both of these would reduce the efficiency of the ion-exchange bed. Flow restriction would affect the process rates and severe restrictions could cause the ion exchange beds to be "dumped" before the desired loading was reached; this would increase the volume of secondary waste.

4.7 PRETREATMENT MODIFICATIONS

Based primarily on the information developed for this study, the Pretreatment system will be changed to address separable phase organics (Orme et al. 1996). Direct impacts to retrieval and sludge washing would likely be minor and could include premature failure of materials. Impacts to the filtration and ion-exchange processes could be major and could include costly shutdowns. In designing the retrieval and sludge washing system, the following should be evaluated and addressed as necessary:

- Behavior of organic in sludges
- Stable emulsions with aqueous
- Interfacial crud with solids
- Solid agglomerates
- Phase separation characteristics
- Effects of changing the sludge wash discharge suction.

For the filtration and ion-exchange processes, the following should be evaluated and addressed as necessary.

- All of the separable phase organic should be removed prior to filtration/ion exchange to avoid irreversibly coating the ion-exchange media.

- The dissolved or emulsified TBP in the aqueous phase of the Tank 241-C-103 supernate should be removed to a level established through additional tests and study to minimize the volume of secondary waste, ensure that product specifications are met, and avoid operational problems with the filtration and ion-exchange systems.
- The use of a decanter should be evaluated for removing organics.

5.0 ORGANIC SKIMMING

The need for a means to remove the organic from the C Tank Farm using a floating decant suction and dispose of it outside of the tank farm system was first proposed by Hall (1972a, 1972b). This effort was halted in 1975 after no separable phase organic was detected in C Tank Farm samples. Removal of the organic through skimming was again identified when there was concern regarding flammability (SAIC 1994; Parazin 1994). This section reviews the skimming system that would be used if skimming is the organic removal option selected by WHC and DOE (see Sections 1.2.1, 2.2, and 2.5). More information on this system is provided in Appendix A-2 of *Removal of Floating Organic in Hanford Waste Tank 241-C-103 Restart Plan* (Parazin 1995). Organic skimming is part of Function 4.2.1 Manage Tank Waste.

5.1 SKIMMING EQUIPMENT SELECTION

Methods for skimming the organic layer from Tank 241-C-103 have been studied at length (Parazin 1995). The best method includes in-tank equipment consisting of riser shielding, a mast, a hydraulic drive unit and motor, a Waukesha¹ pump, a Douglas Engineering skimmer (modified), and organic layer measuring probe (Figure 5-1). A drawing of the skimmer is provided in Figure 5-2.

The skimmer was selected based on results of preliminary testing of the most promising off-the-shelf technologies. These technologies included density-type skimmers in combination with hydrophobic filters and mechanical weirs. The density skimmers with hydrophobic filters did not prevent aqueous carryover and were rejected. The mechanical Douglas Engineering weir skimmer performed adequately but required modifications. After some iterations, the model 650-SHX Skim-Pak² was selected as the best skimming option. The 650-SHX Skim-PakTM better compensated for the density of the aqueous layer and provided a more chemically resistant weir flap. In testing this newest model, it was determined that there was no aqueous carryover when the device was carefully controlled (Figure 5-3). This quality, combined with other controls such as pipe radiation monitoring would probably preclude the need for an aboveground organic/aqueous separator. Additional testing would be required prior to use in Tank 241-C-103.

The skimmer outlet will be connected to the pump inlet using a Kynar³ tubing coil. This will allow the skimmer to float freely while still being attached to the pump. The pumping system satisfactorily tested included a WaukeshaTM universal positive displacement pump Model 18 (modified), a Ross Operation Torqmotor⁴ MG Series Roller Vane Motor, and a Paul-Munroe Rucker hydraulic drive unit.

¹Waukesha is a registered trademark of United Dominion Industries.

²Skim-Pak is a trademark of Douglas Engineering, a division of U.S. Hydrex, Inc.

³Kynar is a registered trademark of Pennwalt Corporation.

⁴Torqmotor is a registered trademark of E.I. du Pont de Nemours & Co.

The ultrasonic level measurement device tested was constructed and operated by Surveillance Systems Engineering of WHC. The tested version included self-calibration capability consisting of two wires fixed above the sonic horn and spaced approximately 6.5 mm from each other. When both calibration wires are placed in the same liquid layer, the speed of sound for the liquid in that layer can be determined by measuring the difference in the time it takes for the sound wave reflection to return from each calibration wire. The thickness of an organic liquid layer can be determined using the known speed of sound and the difference in time it takes for a sound wave reflection to return from each interface.

5.2 SIMULANT

A simulant of the organic and aqueous layers was used for all equipment testing. The formula for the simulant was developed primarily by the personnel who performed the most comprehensive analysis of Tank 241-C-103 liquid layers and is based on the results of Pool and Bean (1994). The following nonradioactive simulants were developed to approximate the density, surface tension, and emulsion disengaging times of the actual Tank 241-C-103 waste.

- **Tank 241-C-103 Organic Phase Simulant Composition**

70 wt% TBP

30 wt% NPH

- **Tank 241-C-103 Aqueous Phase Simulant Composition**

0.035 molar Na₂SO₄ (sodium sulfate)

0.043 molar CsNO₃ (cesium nitrate)

0.540 molar NaNO₂ (sodium nitrite)

0.023 molar Na₂HPO₄ (disodium phosphate)

0.215 molar Na₂CO₃ (sodium carbonate)

0.005 molar Cs₂CO₃ (cesium carbonate)

0.210 molar NaHCO₃ (sodium bicarbonate)

0.062 molar NaF (sodium fluoride)

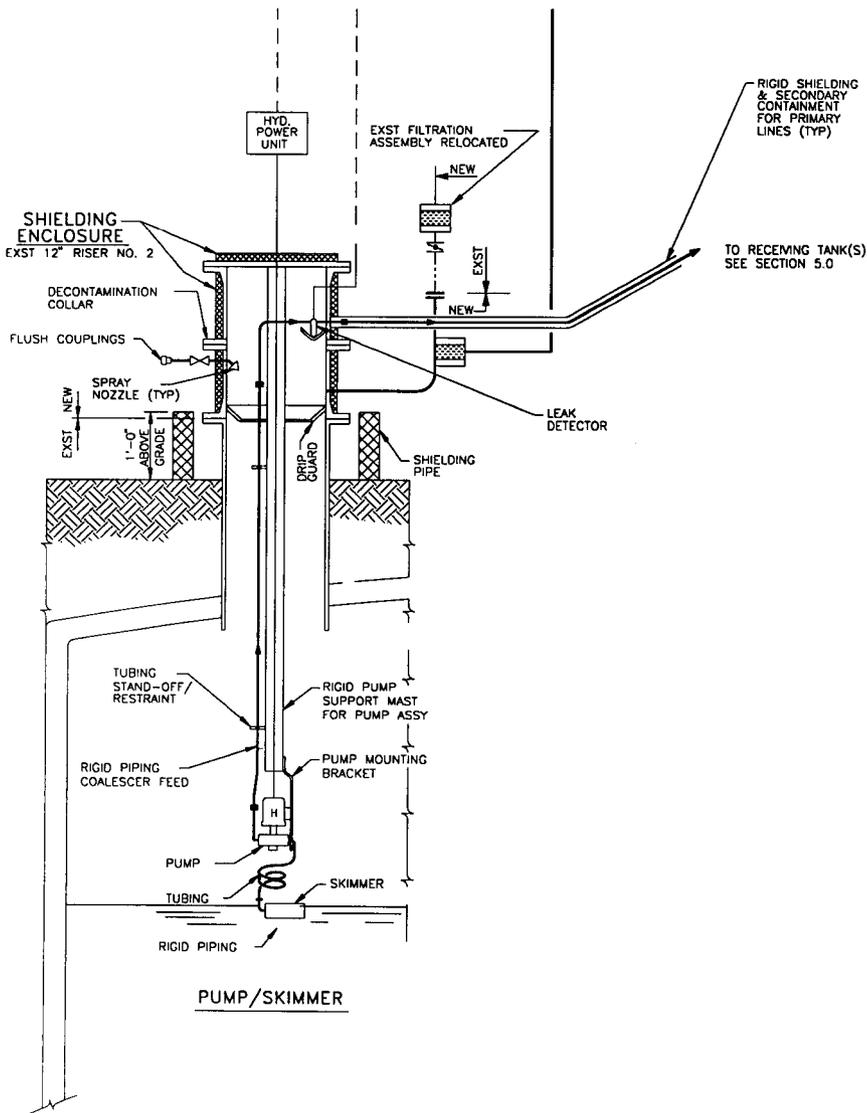
0.108 molar NaOH (sodium hydroxide)

75.02 ppm BRIJ⁵ 35 (polyoxyethylene (23) lauryl ether⁶)

The measured specific gravities of the organic and aqueous simulants were 0.91 and 1.074 respectively. The pH of the aqueous simulant was approximately 9.9.

⁵BRIJ is a registered trademark of ICI Americas, Inc.

⁶This surfactant was added to the Tank 241-C-103 aqueous simulant to adjust the emulsion disengaging time.



* Based on Parazin (1995).

Figure 5-1. Pump and Skimmer Arrangement.*

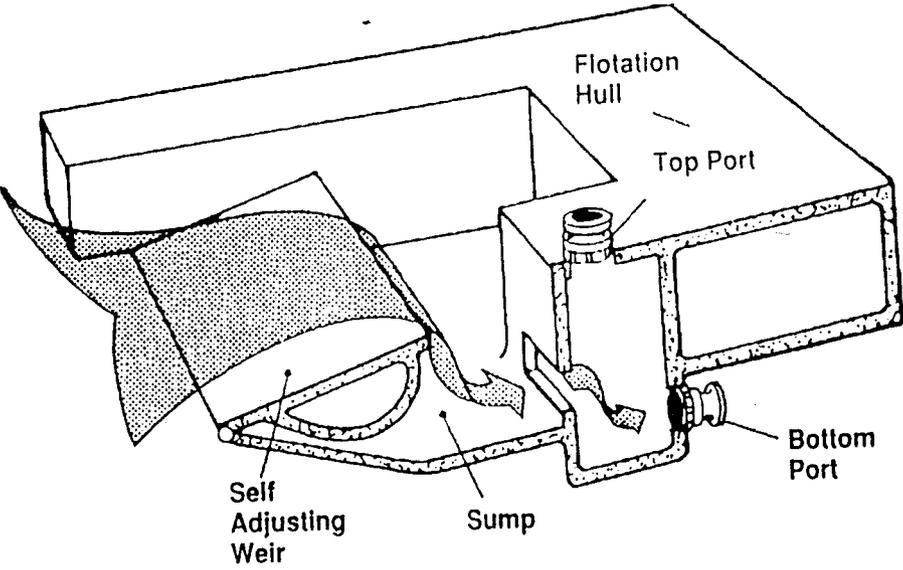
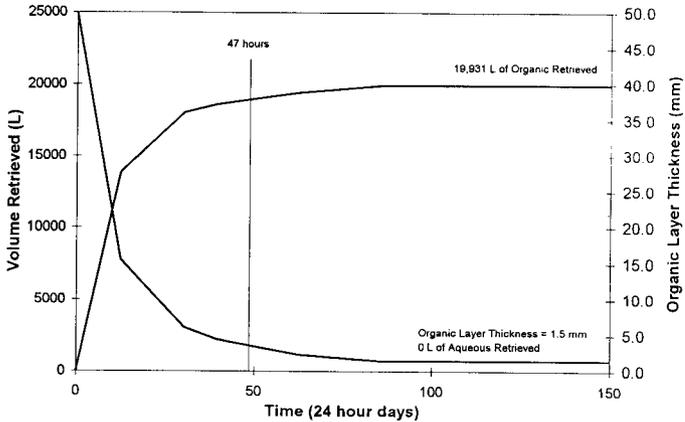


Figure 5-2. Skim-Pak™ Skimmer Head Model 650-SHX.



Starting Organic Volume	20,540 L	5,427 gal
Tank cross sectional area	410 m ²	4,418 ft ²
Final organic layer thickness	1.5 mm	
Volume of organic retrieved	19,931 L	5,266 gal
Volume of aqueous retrieved	0 L	0 gal

Flowrate Assumptions		
H _{org} > (mm)	Q _{Total} (lpm)	X _{org} (% Org.)
25.0	20.00	100%
17.5	12.90	100%
12.7	3.80	100%
8.8	4.30	100%
6.4	3.40	100%
4.8	1.10	100%
3.2	0.57	100%
2.0	0.44	100%
1.2	0.32	100%

H_{org} = Height of organic
 Q_{Total} = Total skimming flow rate
 X_{org} = % pumped liquid that is organic

* Based on Parazin (1995).

**Figure 5-3. Estimation of 650-SHX Skim-Pak™
 Skimmer Operation In Tank 241-C-103.**
 Estimate for Minimum Aqueous Phase Retrieved'

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6.0 ABOVEGROUND STORAGE

If the organic is skimmed from Tank 241-C-103, either an aboveground tank will be used or the organic will be sent directly to the tank farms transfer system. An aboveground tank will be required if the organic will be directly processed to be shipped offsite, stored aboveground, or transported aboveground. The decision regarding the aboveground storage tank options is presented in this section. The decision logic is presented in Figure 6-1, which is based on Figure 1-1.

Four general types of bulk aboveground storage tank (packaging) approaches are reviewed in this section to identify the general issues involved in packaging the organic liquid material from Tank 241-C-103. The LR56/H cask system and various unshielded tanks were evaluated. In some cases both new and used equipment were evaluated. Also reviewed was the use of laboratory (lab) packs. If the container is intended for long-term storage, rather than solely transportation and temporary storage, then only those tanks that can be dedicated for long-term use should be used. The aboveground system that provides the most flexibility is a new International Standards Organization (ISO) tank. Either the LR56/H cask system or rail car could be used for organic transfer if it is successfully demonstrated that DST storage or disposal is acceptable. The LR56/H cask system could also be used as an initial receiving and washing tank.

Because of changes to the DOT regulations, aboveground storage is a more viable option than during previous evaluations (Dukelow et al. 1995; Bartley 1994). These DOT changes and changes to the source code previously used are also discussed in this section. The actions in this section are primarily managed as part of the TWRS Function 4.2.1, **Manage Tank Waste**.

6.1 MAJOR ASSUMPTIONS

For this review the following major assumptions were made.

- **Radionuclide concentration:** It was assumed that the radionuclide concentrations reported by Pool and Bean (1994) are representative of current concentrations in Tank 241-C-103.
- **Aqueous carryover:** It was assumed for radiation and DOT purposes that in-tank aqueous carryover would be 0.2%. Methods to control aqueous carryover, including line monitoring and aqueous separation will be used if separable aqueous is pumped from Tank 241-C-103.

6.2 DOT AND SOURCE TERM CHANGES

Because of current DOT regulations, it is now likely that the organic from Tank 241-C-103 can be pumped to an aboveground tank and shipped offsite with no

radiochemical processing. Radiochemical processing may still be necessary to meet treatment vendor specifications. In addition, use of a more representative radiation dose source-term resulted in significantly lower predicted contact dose rates.

6.2.1 DOT Regulation Changes

Previous DOT regulations limited offsite shipments of bulk radioactive liquids by highway to 10% of the low specific activity (LSA) requirements. These regulations would have required the tank contents to be processed prior to offsite shipment. The Hanford Site currently has no processing facilities available for organic material.

Current regulations (DOT 49 CFR 173) allow shipments up to the LSA limits. In addition, the LSA limit for several radionuclides is now higher. The organic in Tank 241-C-103 is well below the new LSA-II limit (Volume 2, Section 6.1).

Current DOT regulations also permit the use of more types of containers. Under the previous regulations, none of the aboveground tanks available for storage of separable phase organic were DOT approved. Under the new system, at least two systems, the LR56/H cask system and the ISO tanks, are DOT-approved for offsite shipment.

Although DOT regulations may allow for offsite shipment without processing, treatment vendor specifications would likely force the need for some treatment (Section 8.1).

6.2.2 Source Term Reevaluation

Previous aboveground tank dose rate estimates utilized an inflated source term. The source term used was based on preliminary data, not the most recent data (Pool and Bean 1994). A review of this preliminary data indicated that the samples taken for alpha and beta analysis included some aqueous or emulsion layer (Volume 2, Section 6.2). This resulted in levels approximately 20 times greater than that found by Pool and Bean (1994). These inflated levels were also not consistent with the 2 to 5 mR/hr radiation measurements taken on the original sample bottles (Volume 2, Section 6.3).

The correct radiation estimate is approximately 60 mR/hr on contact with an aboveground unshielded tank. Several assumptions were made for this estimate including 0.2% aqueous layer carryover and tank size. See Volume 2, Section 6.4 for the radiation estimate calculation. There is still the potential for aqueous carryover. If the pumping system malfunctions and aqueous is pumped to the aboveground tank, radiation levels would be significantly higher. The skimming methods identified in Section 6.2 are designed to minimize aqueous carryover. The aboveground systems will include methods to detect and address aqueous carryover.

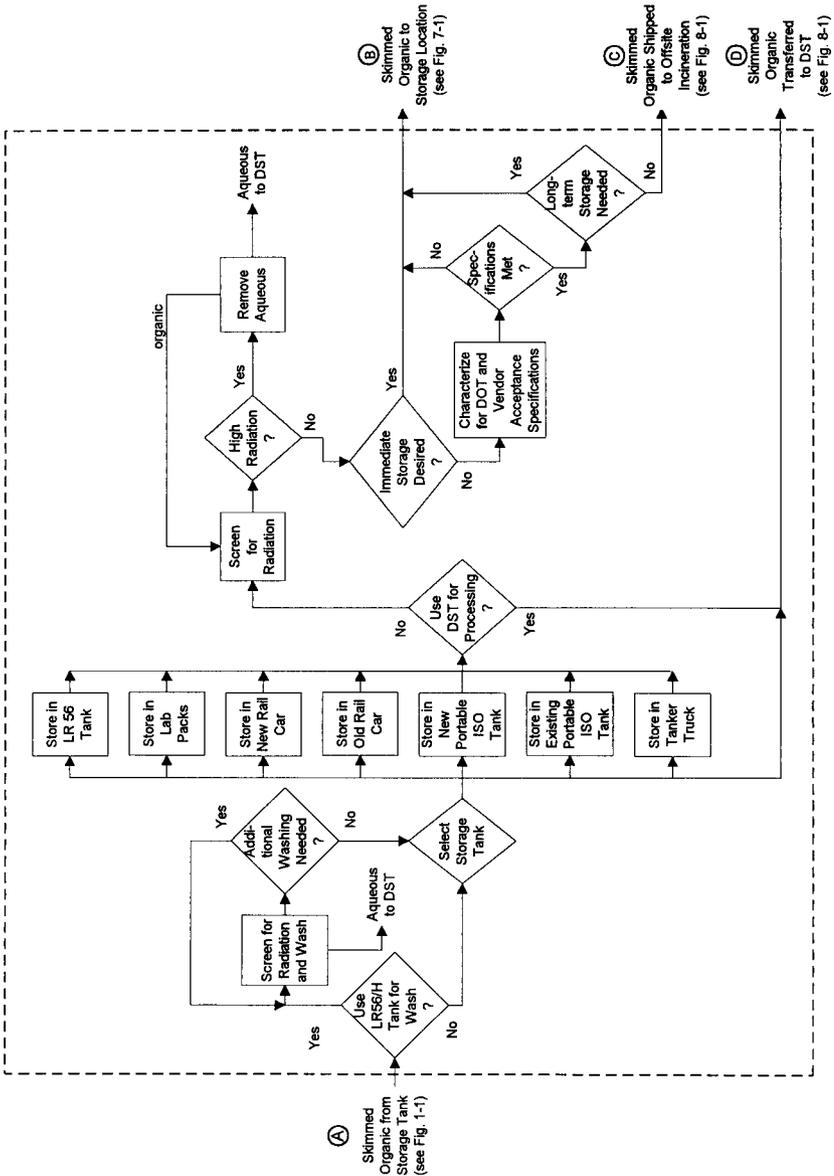


Figure 6-1. Initial Processing and Storage Tank Options.

6.3 ABOVEGROUND STORAGE TANKS

Four general types of bulk aboveground storage tanks were reviewed to identify the general issues involved in packaging the organic liquid from Tank 241-C-103: (1) LR56/H cask system, (2) portable ISO tank, (3) cargo tanker truck, and (4) liquid waste tank car/rail. These reviews are provided in Sections 6.3.1 through 6.3.4. A review of the use of lab packs is provided in Section 6.3.5. The aboveground tank that provides the most flexibility for organic storage and transport is a new ISO tank. The LR56/H cask system or the ISO tank may be used as an initial radionuclide removal tank. These options are described in Section 6.6. Additional information, including the advantages and disadvantages of the aboveground storage tank options, is provided in Volume 2, Section 6.1. A summary of the advantages and disadvantages of each storage container is provided in Table 6-1.

6.3.1 LR56/H Cask System

The LR56/H cask system is a complex shielded tanker with a liquid capacity of 4,000 L (1,100 gal) (Figure 6-2). The packaging was designed and manufactured in France and is certified in that country to transport Type B quantities of liquid. The TWRS program has procured a LR56/H cask which is available for use. At the Hanford Site, the shipment of the LR56/H cask within Site boundaries will be authorized by the *Safety Analysis Report for Packaging (SARP) (Onsite) LR56/H Cask System* (Smith 1996). The LR56/H cask system is new and has not been radioactively contaminated. If it is used on systems other than Tank 241-C-103 and contaminated prior to skimming, there may be impacts on meeting DOE and processing limits, which could require extensive decontamination prior to use.

The LR56/H cask system may be the preferred route if there is additional concern for aqueous carryover or the washing system is found to be acceptable for meeting offsite vendor receipt specifications (Section 8.1).

6.3.1.1 Cost. The cost to use the LR56/H cask system, including personnel and services, is estimated in Appendix A. Another cost for the LR56/H cask system is the SARP revision cost. The cost for a revision is estimated to be \$15,600. This cost includes source term definition, gas generation analysis, procedures, and reviews.

If the Tank 241-C-103 organic liquid source term can be shown to be Type A, or meet the definition of LSA-II material, then the LR56/H cask system can be used with no revision to the SARP, although some safety evaluations of the material compatibility and gas generation rates will be required.

6.3.1.2 Schedule and Availability. The LR56/H cask system is on the Hanford Site now, but its availability is contingent upon the development of the aboveground transfer system and tank modifications.

Table 6-1. Aboveground Storage Tank Options Key Advantages and Disadvantages.

	LR56/H Cask System	New ISO Tank	Existing ISO Tank	Cargo Tanker Truck	New Rail Car	Old Rail Car	Lab Packs
Key Advantages	Shielded Pumping equipment installed	Provides most flexibility of options Meets DOT regulations Long-term storage	Meets DOT regulations Long-term storage	Large capacity	Large capacity Transport high Rad	Large capacity Transport high Rad	Storage at CWC
Key Disadvantages	Cannot use for long term storage 1,000-gal capacity		Limited volume None available	Cannot use for long term storage Current trucks may contaminate organic	Expensive Have to install spur Limited in where to send	Have to install spur Limited in where to send Contaminated with transuranics	Cannot ship offsite Labor intensive

6.3.1.3 Exposure. All radionuclides are orders of magnitude lower than the operational source term authorized in the LR56/H cask system SARP (Smith 1996) when the aqueous fraction is 0.2%

6.3.1.4 Compatibility with TBP/NPH. Compatibility with the seals is unknown. However, compatibility is not anticipated to be a concern with the spray wash capability. The use of detergent-type solutions for use in the spray wash should be investigated as only water has been tested as a wash liquid. The only seals that will be in direct contact with the waste will be the easily replaceable seals integral to the "Zenith" load-in/out connections. The only major seal that may be in contact with the waste within the LR56/H cask itself are the helicoilflex seals on the three top flanges, which are replaceable with some difficulty. The seals of most concern from a packaging standpoint are the double o-ring seals on the three containment vessel lids. However, these seals will not be in contact with the waste because they are outboard of the flange seals. The remainder of the cask internals (instrumentation and piping) should be investigated for any other organic parts. In all cases, these components can be removed and retrofitted, with some difficulty.

6.3.1.5 Compatibility with Existing Systems. The LR56/H cask system onboard vacuum pump is not capable of pumping organic liquid directly from Tank 241-C-103. As a result, a separate pumping system would be required. The LR56/H cask system would have to mate with both the Tank 241-C-103 pumping system and whatever receiving tank or system is used. The primary modification required for compatibility with the receiving system involve integration of the Zenith connectors with a double contained hose.

6.3.2 Portable ISO Tank

An unshielded portable tank (e.g., DOT specification 51, ISO tank) such as that used to transport the PUREX Plant nitric acid to the United Kingdom may be used to transport and store the Tank 241-C-103 organic liquid (Figure 6-3). Portable tanks are now approved by DOT for transporting radionuclides as industrial packages by any mode including highway and rail (49 CFR 173.427).

6.3.2.1 Cost. Costs associated with this option include hardware and documentation costs. Hardware costs should be minimal if existing equipment is used. It may be possible to obtain one of the portable tanks that was used for the PUREX Plant nitric acid shipments to the United Kingdom.

A standard ISO tank fits within a 605-cm (long) by 259-cm (wide) by 244-cm (high) (238- by 102- by 96-in.) frame. The maximum capacity of such a tank is 24,000 L (6,300 gal). An extended ISO tank (considerably more expensive) is 732 cm (288 in.) long and has a maximum capacity of 29,000 L (7,700 gal). This added capacity would allow for in-tank washing (Section 6.7).

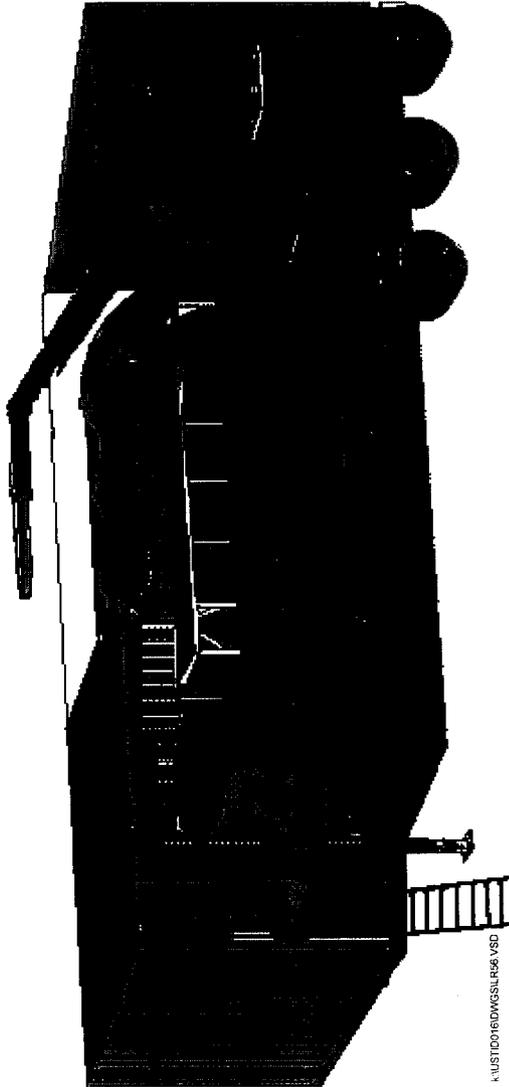


Figure 6-2. LR56/H Cask System.

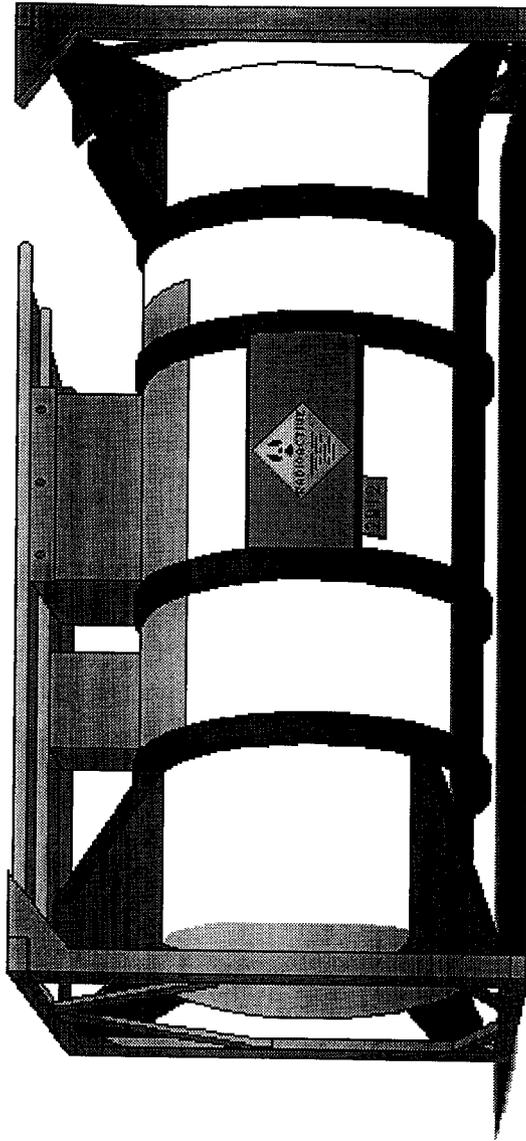


Figure 6-3. Portable ISO Tank.

The estimated cost for obtaining a new 29,000-L (7,700-gal) ISO tank with a treatment system is \$295,000, including engineering, procurement, instrumentation, ventilation, and SARP development (Appendix A).

Safety evaluations will be required, particularly if the tank is used for long-term storage. If an ISO tank is used and the liquid meets LSA requirements, documentation will be limited. A cost-benefit for using an ISO tank is that the tank can be reused. Most of the existing Hanford Site ISO tanks are now in Savannah River. If a new tank is used, it could be incorporated into the TWRS Pretreatment program if it is determined that an organic receiver tank or other liquid receiver tank is required.

6.3.2.2 Schedule. The schedule for obtaining an approved packaging system depends on the type of system selected and the status of the hardware. Less than six months will be needed if an existing system is used. Somewhat greater than six months is needed for a new system. Both of these times are reasonable if a SAR for the entire process is required.

6.3.2.3 Exposure. Radiation dose rates for an unshielded (bulk) tank will be on the order of 25 mR/hr at 1 m (3 ft) for a homogeneous mixture containing 0.2% aqueous material. The contact dose rate is approximately 60 mR/hr (Volume 2, Section 6.4).

6.3.2.4 Availability. There are no available portable ISO tanks. Most of the portable tanks used in the nitric acid shipping campaign were given to the Savannah River Site. The two remaining tanks on the Hanford Site are owned and scheduled for use by B Plant. The status of such packagings could change as the facility mission shifts. The ISO tank availability should not impact the decision to skim or not skim the organic.

6.3.3 Cargo Tanker Truck

An unshielded cargo tanker truck, similar to a gasoline tanker truck, may be used to transport the Tank 241-C-103 liquid. The radionuclides in previously contaminated cargo tanks may affect meeting DOT limits and processing requirements.

6.3.3.1 Cost. The use of an onsite packaging system that does not comply with all DOT requirements must be documented and authorized in a Safety Evaluation for Packaging. The cost of performing the necessary safety analyses and preparing such a document in accordance with the approved WHC packaging program is approximately \$40,000.

6.3.3.2 Schedule. The schedule for obtaining an approved packaging system depends on the type of system selected and the status of the hardware. If existing hardware is employed, then the schedule will be limited by the time necessary to prepare the Safety Evaluation for Packaging, typically two to six months. Otherwise, the long lead item will be the packaging procurement which could take more than six months.

6.3.3.3 Exposure. Radiation dose rates for an unshielded (bulk) tank will be on the order of 25 mrem/hr at 1 m (3 ft) for a homogeneous mixture containing 0.2% aqueous material. The contact dose rate is approximately 60 mrem/hr (Volume 2, Section 6.4).

6.3.3.4 Availability. The availability of existing tanks must be determined from the custodian facilities of the tanks such as 222-S Laboratory. The status of such packagings may change as the facility missions shift. It is preferable to establish a rough schedule and scope for the Tank 241-C-103 operation in order to investigate whether existing tanks can be used.

6.3.4 Liquid Waste Tank Car (Rail)

The packaging systems evaluated in this section are the single-shell Liquid Waste Tank Car (LWTC) which is described in the onsite SARP (WHC 1995b) and new double-shell LWTC. The single-shell LWTCs contain transuranic radionuclides that would likely affect meeting DOT limits and any processing requirements.

6.3.4.1 Cost. Aside from operations, the costs associated with obtaining single-shell LWTC should be minimal. There are four LWTCs onsite, two of which are not in use. The SARP requires that the tank certifications including the hydrostatic test be current before use. Recently, a new double-shell LWTC was purchased for \$700,000. Regardless of LWTC used, a rail spur would have to be installed. The spur cost is estimated to be more than \$1 million.

6.3.4.2 Schedule and Availability. The single-shell LWTCs should be immediately available for as long as needed. Double-shell LWTCs should be available this year.

6.3.4.3 Exposure. Radiation dose rates are expected to be similar to those calculated for the cargo and portable tank except for the heel present at the bottom of the single-shell LWTCs which can generate a substantial dose. Decontamination of the LWTC prior to use may reduce this dose and would likely be required to meet as low as reasonably achievable (ALARA) goals.

6.3.4.4 Compatibility with TBP/NPH. The LWTCs are stainless steel. If gaskets and other seals are compromised, then they can be replaced upon completion of the operation. If a tank is intended for storage, then it should be specifically designed and evaluated for this function.

6.3.4.5 Compatibility with Existing Systems. Approved bulk containers for radioactive liquid load and unload from the top. There are no integral pumps in the onsite cargo tanks or LWTCs. Loading and unloading of the LWTC requires specialized equipment currently available only in a few facilities such as the 204-AR Unloading Facility and the 340 Facility.

6.3.5 Lab Packs

Lab packs are nominal capacity 57-L (15-gal) liquid containers inside 55-gal drums. Appropriate absorbent material is packed around the 57-L (15-gal) container. The only benefit of using lab packs is that the organic could then be sent to the Central Waste Complex (CWC). One major disadvantage is that the Tank 241-C-103 organic could not be shipped offsite in a lab pack. To be shipped in a lab pack, the material must meet DOT Limited Quantity Requirements. To do so, each container would have to hold less than 300 mL of organic. Therefore, lab packs would have to be transferred into an acceptable shipping container.

6.4 GENERAL PACKAGING SAFETY AND REGULATORY ISSUES

There are other general packaging safety and regulatory issues that would have to be addressed prior to final determination of an aboveground storage system. These issues include reviewing National Environmental Policy Act (NEPA) work, updating receiving facility SARs, and verifying package safety. These additional issues are more fully described in Volume 2, Section 6.1.

6.5 PREFERRED TANKS

This section identifies the preferred tanks for different disposal options.

6.5.1 Offsite Shipment or Long-Term Aboveground Storage Options

If the organic is to be shipped offsite or stored aboveground for an extended period of time, a new aboveground ISO tank is the preferred option for storing the organic liquid from Tank 241-C-103. The new aboveground ISO tank provides the most flexibility; has no contamination that may impact offsite shipment; can be built to accommodate aqueous removal, pumping, and/or washing requirements; and is DOT-approved for offsite shipment. All other options have at least one significant flaw that could significantly impact the removal effort.

Pumping to an aboveground tank will be costly. Several additional internal and external reviews will be required. These reviews will be more involved because this pumping is a new operation and includes the floating organic layer. The studies necessary to support these reviews and the reviews themselves are estimated to cost between \$1 and \$2 million.

6.5.2 DST Storage and Disposal Option

If it is determined by WHC and DOE that transferring the organic from Tank 241-C-103 into a DST is the preferred storage or disposal option, either using the LR56/H cask system or building a railroad spur and using an existing railcar could be used as transport tanks because both are available and can be used onsite. The benefit of the LR56/H cask is that it is highly shielded and any aqueous carryover would also be shipped to the DST with no impacts on the driver. However, the LR56/H cask volume is less than the full organic volume. A rail car could receive the entire volume, but rail spurs would have to be built to Tank 241-C-103 and possibly to the receiving tank.

6.5.3 Other Decision Criteria Impacts

Several decision criteria have been reviewed including cost, schedule, process rates, waste volume, and significant qualitative measures. There are no known significant health and safety differences with any of the tank options. The other measure values are considered either not applicable or to have relatively similar outcomes for each option.

6.6 USE OF THE LR56/H CASK SYSTEM AS AN INITIAL WASH TANK

A pumping scheme that includes both a new ISO tank and the LR56/H cask system could increase the chances for successful pumping. There are advantages and disadvantages to this approach. Advantages include a shielded tank, pump suction at the tank low point, several pumping methods, and internal spray wash. Disadvantages include concerns regarding adding and removing the wash solution and measuring the height of the organic/aqueous interface.

Based on initial laboratory testing with actual Tank 241-C-103 waste samples, it has been determined that 0.1 molar sodium ethylenediaminetetraacetic acid (EDTA) will reduce the organic radionuclide concentrations by approximately 95% after two washes (Lumetta 1996). This testing also indicated that radionuclide receiving specifications could be met for offsite treatment vendors.

7.0 LONG-TERM STORAGE

If skimming is required, long-term storage should be anticipated. The decision on storage location and radionuclide removal through washing will be dependent on variables including disposal option chosen, initial radionuclide removal, and costs. Storage location options include the CWC, B Plant, aboveground storage in tank farms, T Plant, and belowground storage in tank farms. This long-term storage decision is shown in Figure 7-1, which is based upon Figure 1-1. The activities in this section are managed primarily by TWRS Function 4.2.1, **Manage Tank Waste**. Other functions would be involved if either CWC, T Plant, or B Plant storage were used.

7.1 LONG-TERM STORAGE LOCATIONS

This section provides information on each of the current long-term storage options, including CWC, B Plant, tank farms aboveground storage, T Plant, and tank farms belowground storage. A summary of the advantages and disadvantage of each potential long-term storage location is provided in Table 7-1. Additional information is provided in Volume 2, Section 7.1.

7.1.1 Central Waste Complex Storage

The CWC in 200 West Area is designed and permitted to store *Resource Conservation and Recovery Act* (RCRA) waste and mixed waste, including organic liquid. The solid waste disposal group that runs this complex is also chartered with determining the best methods to ultimately dispose of this type of waste and has contracted to have a thermal treatment unit be built offsite that could receive this type of waste. Presently, the CWC does not accept bulk liquids and there are no plans in the future to accommodate bulk liquids for storage. Liquids are accepted in lab pack form only, which may make future radionuclide removal efforts more difficult.

7.1.2 B Plant Storage

B Plant currently has approximately 17,000 L (4,600 gal) of separable phase organic in two B Plant canyon tanks (27-3 and 28-3). The organic originally consisted of 20 wt% di-(2 ethylhexyl)-phosphoric acid, 10 wt% TBP, 70 wt% NPH. This organic has contacted 30,000 Ci of strontium for the last 15 years and currently contains 404 Ci of ⁹⁰Sr and 65 Ci of ¹³⁷Cs. The organic constituents have likely changed somewhat due to hydrolysis and radiolysis and contain approximately 10% by volume solids. Waste codes that apply to this organic are nine D-listed codes, five F-listed codes, and two Washington State Toxicity Codes. Initial efforts to identify a washing method to remove the strontium and other radionuclides in preparation for offsite shipment and disposal have been unsuccessful.

There is an outdoor storage pad to contain B Plant organic in an aboveground DOT approved ISO tank (see Section 6.3 for a discussion of storage tanks). Tank farms could store the 19,000 L (5,000 gal) of organic from Tank 241-C-103 in this same pad.

7.1.3 Tank Farms Aboveground Storage

If an aboveground tank, such as an ISO tank, is used, a RCRA compliant temporary storage pad will be built at C Tank Farm near Tank 241-C-103. The requirements for establishing a pad in the tank farms are contained in Volume 2, Section 7.3. The C Tank Farm cannot be used as a long-term storage location because of other activities scheduled in the area and plans for closing down the area.

7.1.4 T Plant Storage

Storing the organic from Tank 241-C-103 at T Plant is not a viable storage location. Although this facility has both prior experience and available tanks, separable organics are neither in the safety basis document nor part of the facility permit.

7.1.5 Tank Farms Belowground Storage

Belowground storage options in the tank farms include storage in a DST, SST or DCRT. These options are described in the following sections.

7.1.5.1 DST Storage. The potential impacts from DST storage include chemical degradation and evaporation. These impacts are described in Section 8.3. If the Pretreatment process is changed to address both separable phase in tanks and organic in sludge, then DST storage may be acceptable. The currently identified DST for receiving this organic is Tank 241-AP-107 (Sections 4.2 and 8.3).

7.1.5.2 SST Storage. SST storage is not considered an option due to the potential for leakage and requirements for interim stabilization.

7.1.5.3 DCRT Storage. The primary candidate DCRTs for storage of the organic are Tank 241-BX-244 and Tank 241-A-244. These tanks were chosen because of capacity, integrity, history, and availability. Additional information is provided in Volume 2, Section 7.4. Storage in a DCRT is not currently considered viable because the DCRTs have generally poor access and high radiation levels. Radionuclide contamination of the organic also is a concern.

Table 7-1. Key Advantages and Disadvantages of Long-Term Storage Locations.

	Central Waste Complex	B Plant	Tank Farms Aboveground	T Plant	Tank Farms Aboveground		
					DST	SST	DCRT
Key Advantages	<p>Facility permitted for material type</p> <p>Small quantity of organic compared to facility capacity</p> <p>Facility already has large organic volume</p>	<p>Experienced handling organic</p> <p>Current safety basis includes organic</p> <p>Only 1 pad needed for B Plant and Tank 241-C-103 organic</p>	<p>Tank farms owns and controls area</p> <p>Storage pad design already developed</p> <p>Storage location for B Plant and based on access and dose control</p>	<p>Facility not scheduled for shutdown</p> <p>Experience with separable phase organic</p> <p>Tank space available for radionuclide removal</p>	<p>Criteria exists for storage</p> <p>Tank available</p> <p>No major permitting or safety basis issues</p>	<p>No storage pad needed</p> <p>Volume available for radionuclide separation</p> <p>Could also handle B Plant organic</p>	
Key Disadvantages	<p>Liquid must be in lab packs</p> <p>Hard to pump</p> <p>Rehandling lab packs</p> <p>Final disposal not identified</p>	<p>Completed B Plant design does not include C-103 organic</p> <p>Harder to process organic due to high dose rate area</p> <p>May extend B Plant shutdown time</p>	<p>May have to build 2 pads</p> <p>Requires additional operation and maintenance support</p> <p>No radionuclide removal capability</p>	<p>Organic not in safety basis</p> <p>Not permitted for organic</p> <p>Storage pad still required</p>	<p>Material likely need skimmed again</p> <p>Further radionuclide contamination of organic</p> <p>Does not remove material from tank farm system</p>	<p>High potential for leakage</p> <p>Interim stabilization issues</p> <p>Potential for leaks</p> <p>Schedule impacts</p> <p>Radionuclide contamination</p>	<p>Questionable condition of tanks</p> <p>Potential for leaks</p> <p>Schedule impacts</p> <p>Radionuclide contamination</p>

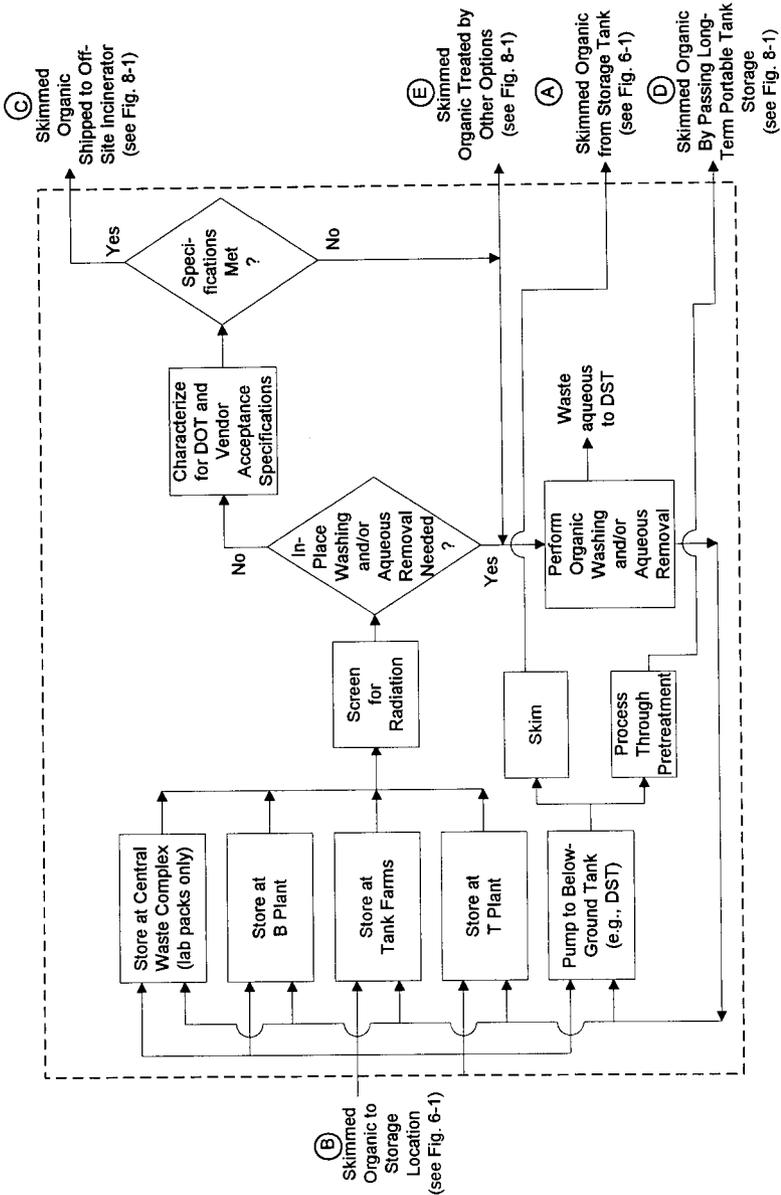


Figure 7-1. Storage Location Options.

7.2 SUMMARY AND PREFERRED OPTIONS

If skimming is required, the preferred option for long-term storage and washing is dependent upon many decisions that have not been made. Of the aboveground storage locations available, storage in tank farms (e.g., in an ISO tank) is the likely choice. Storage at CWC is not a viable option because the organic can only be stored in lab packs. T Plant storage is not a viable option. B Plant storage is a viable option but funds are not available this fiscal year to support the project. Storage of the organic in a DCRT or similar small underground storage tank in tank farms is not recommended for several reasons including high potential radiation doses, difficulty in removing radionuclides from the tanks, and difficulties in operating these tanks.

7.3 OTHER DECISION CRITERIA IMPACTS

All of the long-term organic storage options could result in radiation exposure. Because the dose rate from the organic is expected to be low (Section 6.2), most dose will come from either aqueous carryover or from the storage system. Aqueous carryover can be minimized by using the LR56/H tank as a wash tank. The storage location with the highest potential exposure is pumping to a tank farms belowground tank. Storage at B Plant could also result in higher doses and temporary shielding would likely be required.

The two options that could cause the highest increases in the LLW volume and process rates are storage at the CWC and pumping to a tank farms belowground tank. The CWC impacts stem from the need for numerous storage containers and the need for additional handling. Tank farms belowground tank impacts stem from schedule impacts and the impacts of adding separable phase organic to the tank farms system.

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8.0 ORGANIC TREATMENT AND DISPOSAL OPTIONS

This section describes the potential methods that can be used to destroy or solidify the organic for ultimate disposal. The options evaluated in this section are to ship the organic to an offsite thermal treatment system; treat the organic onsite by incineration, electrochemical treatment, steam reforming, grouting, or vitrification; or destroy TBP and evaporate NPH in an onsite DST. The treatment and disposal options are outlined in Figure 8-1. The ultimate disposal method will be dependent on the treatment option chosen and decisions regarding Pretreatment processes. Treatment options previously rejected, including processing in the 242-A Evaporator, LERF, and ETF are described in Section 1.2.3. A summary of key advantages and disadvantages is provided in Table 8-1.

The activities in this section may be governed by each of the TWRS Functions: **Manage Tank Waste** (Function 4.2.1), **Retrieve Waste** (Function 4.2.2), **Process Waste** (Function 4.2.3), and **Dispose Waste** (Function 4.2.4), depending on the option chosen.

8.1 OFFSITE TREATMENT

Offsite thermal treatment is currently used for disposal of the PUREX Plant separable phase organic. This method could also be used for disposal of the Tank 241-C-103 organic. The existing PUREX Plant organic disposal contract is with Diversified Scientific Services Incorporated (DSSI). This contract could also be used for Tank 241-C-103 organic; however, radionuclide removal washes are required to meet DSSI acceptance criteria. The Waste Experimental Reduction Facility (WERF) at Idaho National Engineering Laboratory (INEL) would also be able to receive this material after radionuclide removal washes. Other potential vendors are available but would have difficulty receiving this waste. These vendors include the Toxic Substances Control Act Incinerator at Oak Ridge National Laboratory, and ATG at the Hanford Site, Washington. More information on each of these vendors is provided in Volume 2, Section 8.1.

As identified in Section 6.2, the Tank 241-C-103 organic will likely meet all DOT shipping criteria without further radionuclide removal. The Tank 241-C-103 organic can be contained in a DOT-approved shipping container for interim storage before offsite shipment. One offsite treatment approach would be to fully characterize the organic and place a request for bid through the Commerce Business Daily for treatment. It is possible that a company will place a bid to accept this material without further radionuclide removal or other processing. Depending on cost, this may be the best option.

8.2 ONSITE TREATMENT OPTIONS

There are several options available for onsite treatment of Tank 241-C-103 organic. These options include incineration, electrochemical treatment, steam reforming, solidification, and vitrification. All of these options are also considered for offsite treatment by contractors.

In general, onsite treatment is not preferred for treating Tank 241-C-103 organic. The costs to build and permit treatment facilities are not currently justified. This is particularly true when other options are available. The only onsite option available for Tank 241-C-103 organic is the LLW vitrification system, which is part of current TWRS planning.

8.2.1 Onsite Incineration

Onsite incineration is not recommended for treatment of Tank 241-C-103 organic. The potential permitting requirements for a true incinerator are daunting and include numerous public meetings, regulatory involvement, and lengthy delays with no assurance of final approval. Many of the other options are preferred, particularly when dealing with the relatively small organic volume in Tank 241-C-103. When the WHC solids waste group was evaluating options for organic destruction, an offsite thermal treatment system was preferred.

8.2.2 Electrochemical

The use of electrochemical treatment for Tank 241-C-103 organic is not recommended for the following reasons.

- Testing has been done only on aqueous soluble chelating agent organic. There has been no testing on floating or emulsified organic. Laboratory feasibility testing would be required.
- Other technologies exist that have no development costs or associated risks. Alternate techniques, based on estimated capital and operating costs for electrochemical treatment, are much more economical.

Electrochemical treatment was investigated and selected as a backup technology for destruction of chelating agents as part of the Initial Pretreatment Module to be used for processing all tank waste at the Hanford Site. Electrochemical treatment operates at near ambient pressure and temperature, and has been used for decades in producing both inorganic (e.g., chlorine, sodium chlorate) and organic (e.g., adiponitrile) chemicals. A number of laboratory scale tests were done on simulated Tank 241-SY-101 wastes that contained dissolved organic and nitrates/nitrites. Electrochemical treatment reduced the TOC from 6.3 to 0.13 g/L during these tests. Dilution of the Tank 241-C-103 pure organic phase to these initial conditions, 6.3 g/L TOC, would increase the volume to be treated by a factor of 117.

Based on expected operating conditions and power requirements, and an assumed power cost of \$0.05 per kWh, it was calculated that approximately \$11 of electricity would be required to treat one pound of Tank 241-C-103 organic.

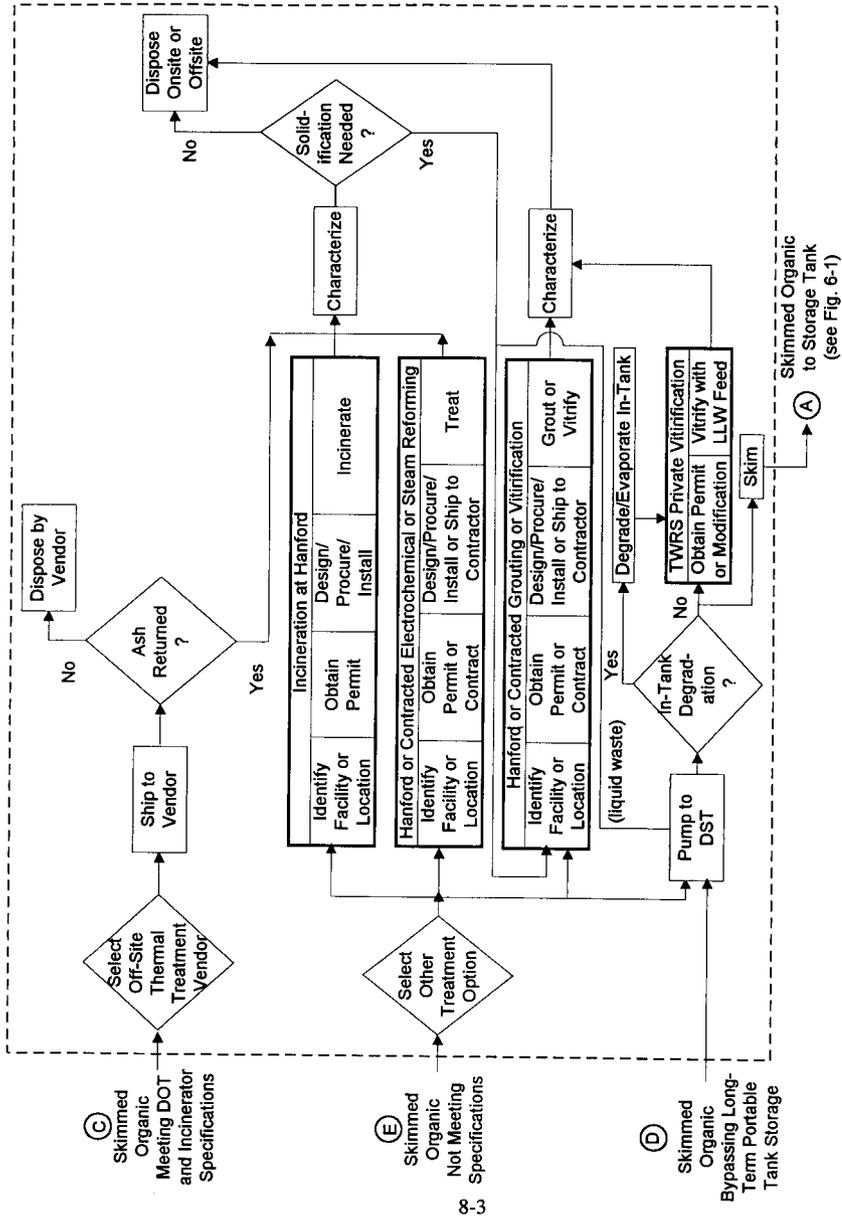


Figure 8-1. Treatment and Disposal Options.

Table 8-1. Advantages and Disadvantages of Organic Disposal.

	Offsite Treatment	Onsite Treatment			DST Addition	
		Electrochemical	Steam Reforming	Solidification		Vitrification
Key Advantages	<p>Several potential vendors</p> <p>May result in no return of solids</p> <p>May not have to do any radionuclide removal</p> <p>Possibly use PUREX contract</p>		<p>Results in dry ash</p> <p>Proven system available</p>	<p>Puts organic in stable form</p>	<p>Vitrification a likely TWRS process</p> <p>LLW Vitrification impacts for ASH feed very low</p>	<p>Degrades or evaporates organic</p> <p>Once degraded or evaporated, no further concerns</p>
Key Disadvantages	<p>No vendor currently identified licensed to receive predicted radionuclide concentrations without washing</p> <p>Shipping</p> <p>May have to have solids returned for disposal contract if necessary</p>	<p>Does not put organic into a form that is readily disposable</p> <p>Would require building special plant</p>	<p>Would require building special plant</p>	<p>Very large volume increase</p> <p>No solidification formula currently identified</p>	<p>Vitrification not a guaranteed process for TWRS</p> <p>Impact of organic liquid feed likely, low but may be costly</p> <p>HLW feed of either ash or liquid may result in Yucca Mountain impacts</p>	<p>Stakeholder acceptance</p> <p>Cost for acceptance and cost for equipment addition</p> <p>Ensuring acceptable DST is available at time required</p> <p>Time required for degradation</p>

8.2.3 Steam Reforming

If a separate organic treatment system must be built on the Hanford Site for the organic in the underground storage tanks, steam reforming is the best candidate treatment system. Steam reforming is a proven, mature technology that readily destroys organic waste. The organic is contacted with high temperature steam, which converts the organic into carbon dioxide and hydrogen. The steam reforming system evaluated for this review is owned by Scientific Ecology Group and uses the patented Synthetica Detoxifier system. An example steam reforming process is provided in Figure 8-2. The steam reforming system employs two-stage steam reforming; once during the evaporation/pyrolysis stage and once within a secondary reactor over a catalyst bed. The U.S. Environmental Protection Agency (EPA) has indicated that this technology would not require control as an incinerator (Volume 2, Section 8.2).

Small quantities of carbon dioxide and water vapor would be vented off along with trace amounts of methane gas. The resulting product would be dry material that could be used as dry feed or removed from the steam reformer evaporator and placed directly into a WHC multi-purpose canister or similar system for direct burial. Using this dry material as feed for the LLW treatment system would prevent potential impacts to HLW disposal (see Section 8.2.5).

The vendor costs for steam reforming are estimated to be approximately \$2 million, not including installation into a plant. Additional costs for WHC involvement, including permitting, safety reviews, and other support have not been estimated. Additional information on steam reforming is provided in Volume 2, Section 8.2.

8.2.4 Grouting (Solidification)

Solidification by grouting is not currently a preferred disposal method. The two primary reasons for not using this method are that no current solidification formulation exists and there is an increased burial volume of the final product. Volume 2, Section 8.3 provides a brief review of the solidification formulation uncertainties.

The solidification of Tank 241-C-103 organic would result in greater waste volume than would treatment by thermal systems. Solidification volume increases of four to seven times the original volume are not uncommon and would result in a final disposal volume of between 76,000 and 130,000 L (20,000 and 35,000 gal). Thermal treatment would reduce the volume to about 2,600 L (700 gal) of solids. These solids could be packaged for direct burial or vitrification.

8.2.5 Vitrification

Vitrification could be used to receive either the liquid separable organic layer or the ash created from a thermal treatment. Ash feed impacts would likely be minor. Accepting

the liquid layer could impact the melter offgas treatment. A more fundamental issue is if vitrification will be used on the Hanford Site.

Vitrification cannot be considered a viable option for processing the separable organic layer from Tank 241-C-103 in the near future because of impacts from the current TWRS privatization effort. The TWRS privatization includes two aspects that affect this option: (1) vitrification is not a required technology and (2) there is no separable organic waste stream in the TWRS privatization flow sheet (Orme 1995).

If vitrification is used, processing the material with the LLW vitrification system would be preferred because it could be diluted with much larger quantities of melter feed with less potential negative impacts and would not impact HLW disposal (see Section 8.4). Accommodating the phosphate ash would not be a problem. Processing the additional phosphate ash derived from Tank 241-C-103 organic with the nominal composition of a double-shell slurry feed tank would only increase the glass P_2O_5 content by approximately 0.1 wt%.

The area of greatest uncertainty in vitrifying the Tank 241-C-103 organic material would be the potential decomposition and/or volatilization in the melter and the residues contained in the melter offgas. Using fairly conservative assumptions, it is estimated that processing the organic liquid could result in flammable organic gases in the offgas to about 1.0% of the offgas volume when quenched to 30 °C (86 °F). The additional cost to process the liquid organic are difficult to estimate because no vitrification design has been identified. An estimate of \$2 to \$10 million is probably reasonable. Costs for solid ash feed would be significantly less because offgas impacts are not expected. Additional information on vitrification is provided in Volume 2, Section 8.4.

8.3 DOUBLE-SHELL TANK ORGANIC DEGRADATION AND EVAPORATION

This section describes the treatment process for removal of separable phase organic in a DST. Interim storage is discussed in Section 4.2 and 7.1.5. An in-tank treatment operation is long and expensive. The following items would impact removal of the organic:

- High cost of initial equipment procurement and installation
- High personnel cost due to slow rate of organic destruction/evaporation
- High cost of equipment replacement and disposal.

To clearly demonstrate that disposal to a DST is acceptable, additional testing has been performed and models have been developed to account for hydrolysis, radiolysis, and evaporation. This section reviews this testing and these models. Additional information on these models is contained in Volume 2, Sections 8.5 through 8.8. This section also includes a discussion of a likely receiving DST and cost impacts of this option. The final DST, if this option is chosen, would be highly dependent on the SST interim stabilization schedule, privatization, waste volume, pumping time, and addition of new equipment to the selected DST for efficient destruction of TBP and evaporation of NPH.

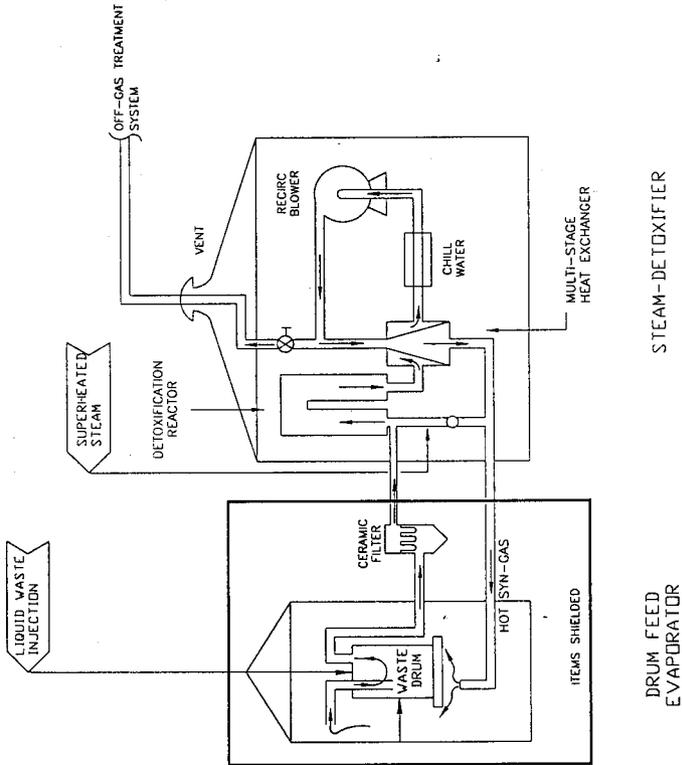


Figure 8-2. Steam Reforming Process.

The addition of separable phase organic to the DST system would affect the aqueous waste quality due to solubility of TBP and NPH organic, organic entrainment, and coating of solids with the organic. The effect on subsequent TWRS Pretreatment processing would be minimized by selecting a DST that does not require waste evaporation or near term processing, contains little or no solids, has the capability to heat and maintain waste temperature above ambient temperature, has sufficient supernatant and free hydroxide ion, has the capability to efficiently mix/disperse light phase organic into aqueous supernatant, and is equipped with a forced ventilation system for removal of NPH and volatile degradation products (e.g., butanol, hydrogen gas, and alkanes). There is no single DST that meets all these requirements; however, Tank 241-AP-107 appears the best candidate for interim storage and removal of the organic by chemical and radiation destruction of TBP and evaporation of NPH. Table 8-2 summarizes the parameters for hydrolysis of TBP based on solubility and reaction rates in sodium hydroxide solution. Table 8-3 summarizes the tank requirements for TBP destruction and NPH evaporation.

Table 8-2. Summary of Preferred Process Conditions for Alkaline Hydrolysis of TBP Based on Sodium Hydroxide Data.

Conditions	Aqueous/Organic Volume Ratio	Free OH (molar)	Temperature (°C)
Minimum	20	0.5 - 1.1	≥ 40
Ideal	200	0.5 - 2.2	≥ 50

8.3.1 Hydrolysis, Radiolysis, and Evaporation

Alkaline hydrolysis, radiolysis, and evaporation are the dominant processes for reducing the separable phase organic level during interim storage in a DST or other tank. This section briefly describes the impacts of each of these removal processes on separable phase organic added to a DST, particularly Tank 241-AP-107. Additional information on these removal processes is provided in Volume 2, Sections 8.5 through 8.8.

A 1-mg/L TBP aqueous phase target value was used for establishing the end point for alkaline hydrolysis. This value is believed to minimize operating problems with cesium ion exchange (see Section 4.6). No target value was established for NPH due to lack of data on potential impacts. The solubility of NPH is about 4 mg/L in water. The impacts to filtration/ion-exchange from soluble NPH are unknown.

Typical TBP degradation products include butanol, NaDBP, sodium monobutyl phosphate (Na_2MBP), trisodium phosphate (Na_3PO_4), hydrogen gas (H_2), methane (CH_4), ethylene (C_2H_4), ethane (C_2H_6), various other hydrocarbons, and a polymer of unknown composition (Schulz and Navratil 1984). Organic vapor emissions, namely NPH and butanol, will increase during hydrolysis, radiolysis, and evaporation. Previous studies indicated that ventilation rates less than 10 ft^3/min are adequate to control flammable vapor

Table 8-3. Summary of Waste Tank Requirements for Efficient Removal of Separable Phase Organic.

Requirement	Purpose/Concern	Current Status Tank 241-AP-107
Waste Mixing	Solubilize/emulsify TBP organic in aqueous phase for reaction with NaOH.	NONE
Waste Heating	Add heat to achieve acceptable reaction rate for TBP destruction and NPH evaporation.	NONE
Temperature Monitoring	Measure and control temperature of waste during TBP hydrolysis and NPH evaporation.	ACCEPTABLE Tank has thermocouple tree; manual readout
Organic Liquid Surface Monitoring	Measure liquid level with floating organic (ENRAF gauge).	NONE Tank has FIC gauge.
Regulatory Offgas Monitoring	Measure NPH or other organic emission to atmosphere as required by Ecology.	NONE Continuous air monitoring and record sampler on AP Tank Farm primary exhaust.
Active Ventilation System	Exhaust NPH to atmosphere for disposal; no condensate collection tanks and NPH recycle. Assumes Ecology approval.	ACCEPTABLE Once through adjustable flow ventilation system for AP Tank Farm
Air Sparge	May accelerate NPH removal.	NONE
Materials Compatibility	Impact from degradation of pump seals, HEPA filters etc by frequent contact with TBP and NPH.	UNKNOWN
Complexed Concentrate (CC) Waste Type	Waste does not require evaporation at 242-A. Increased soluble TOC from TBP and NPH degradation does not impact waste. Some soluble organic components may accelerate TBP destruction.	ACCEPTABLE Scheduled to store > 100,00 gal CC waste from SSTs; meets programmatic impacts of waste compatibility, storage and processing.
No High Heat Solids	Minimizes potential flammable gas generation and/or temperature control problem from potential organic solids.	ACCEPTABLE Current waste temperature is ~20 °C. Solids inventory is zero.

emissions from these removal mechanisms (Bartley 1994; Milliken and Geschke 1995). The average forced air ventilation rate for the AP Tank Farm is 120 ft³/min per tank and varies from approximately 90 to over 300 ft³/min.

8.3.1.1 Hydrolysis. An aqueous phase medium of high dielectric constant such as water is required to support the alkaline hydrolysis reaction. First order dependence upon both hydroxide (OH) and TBP concentration supports the proposal of a bimolecular mechanism for the TBP-NaOH reaction (Burger 1955; Schulz and Navratil 1984). The reaction slows after the first hydrolysis to NaDBP. Subsequent degradation to Na₂MBP and Na₃PO₄ are very slow reactions by NaOH hydrolysis (Burger 1955).

A preliminary model was developed for predicting time requirements for alkaline hydrolysis of TBP at several different conditions. The constant volume batch isothermal model was developed from TBP destruction rate data in 1.0 molar NaOH (Kennedy and Grimley 1953) and solubility of TBP in NaOH solutions (Higgins et al. 1959; Johnson and Dillon 1953; Schulz and Navratil 1984).

A sensitivity analysis was performed to evaluate aqueous to organic (A/O) volume ratio, temperature and OH concentration on TBP hydrolysis. Maximum TBP destruction rates occurred at an A/O ratio of 200, 50 °C (120 °F), and > 0.5 < 2.2 molar free hydroxide. Maximum TBP destruction was 99.93% and occurred at A/O of 20 and 0.5 molar OH for both 40 and 50 °C (100 and 120 °F). The time requirements were 570 days at 50 °C (120 °F) and 1,440 days at 40 °C (100 °F) to achieve 99.93% TBP destruction. Increased maximum TBP destruction could be achieved in a shorter time period by using high A/O process conditions. Temperature and NaOH control both TBP solubility and reaction rate. Maximum A/O ratio can only be achieved by mixing the organic with aqueous waste of the DST.

Mixing of TBP with soluble chelating agents, degradation products such as NaDBP (TBP degradation product), sodium stearate (potential NPH oxidation product), and other organic in waste may increase the solubility of TBP in the aqueous phase and/or help TBP-NPH form a micro emulsion that does not readily disengage (personal communication with D.M. Camaioni [PNNL], January 1996). Recent laboratory tests with simulated complexed concentrate waste (Camaioni et al. 1995) showed more rapid TBP degradation than could be predicted from NaOH solution (Hallen 1996). See Volume 2, Section 8.5 for more information on mixing options.

8.3.1.2 Radiolysis. Radiolysis provides little destruction compared to hydrolysis. If the Tank 241-C-103 organic and aqueous is mixed with the Tank 241-AP-107 contents (A/O = 26), only approximately 1 to 3% of the TBP would be degraded through radiolysis by the predicted time for hydrolysis removal of all TBP. Table 8-4 summarizes radiolytic destruction of TBP at several conditions. If complexed concentrate (CC) waste was added to the tank, the radiolysis rate would increase, but not exceed approximately 12% under reasonable time frames.

Table 8-4. Estimated Typical TBP Destruction by Radiolysis of 18,900 L of Tank 241-C-103 Organic at Potential Storage Conditions.

Tank	Description ¹	Gamma Energy Disposition ² (Rad/h)	Estimated TBP Destruction by Gamma Radiolysis ³	
AP-107	Organic mixed with existing aqueous + Tank C-103 aqueous (A/O = 26)	65	~3% based on 1,440 days hydrolysis at A/O = 20, 0.5 M OH, 40 °C	~1% based on 570 days hydrolysis at A/O = 20, 0.5 M OH, 50 °C
AP-107	Organic as floating layer above existing aqueous + Tank C-103 aqueous (A/O = 26)	40	~4% based on 1,440 days and no hydrolysis; ~15% after 10 years and no hydrolysis	~1% based on 570 days and no hydrolysis; ~15% after 10 years and no hydrolysis
AP-107	Organic mixed with existing aqueous + CC waste (A/O = 100)	330	~11% based on 285 days hydrolysis at A/O = 100, 0.5 M OH, 40 °C	~5% based on 115 days hydrolysis at A/O = 100, 0.5 M OH, 50 °C
AP-107	Organic as floating layer above existing aqueous + CC waste (A/O = 100)	140	~9% based on 285 days and no hydrolysis; ~75% after 10 years and no hydrolysis	~3% based on 115 days and no hydrolysis; ~75% after 10 years and no hydrolysis
AP-107	Organic mixed with existing aqueous + aqueous from Tank C-103 + CC waste (A/O = 126)	290	~12% based on 285 days hydrolysis at A/O = 100, 0.5 M OH, 40 °C	~5% based on 115 days hydrolysis at A/O = 100, 0.5 M OH, 50 °C
AP-107	Organic as floating layer above existing aqueous + aqueous from Tank C-103 + CC waste (A/O = 126)	130	~9% based on 285 days and no hydrolysis; ~85% after 10 years and no hydrolysis	~4% based on 115 days and no hydrolysis; ~85% after 10 years and no hydrolysis

Notes:

- 1 Preliminary planning assumptions.
- 2 Source of information is Boothe (1996).
- 3 Basis is no NPH evaporation or degradation. TBP G values based on Volume 2, Section 8.5.
- 4 See Appendix B for waste definitions.

If CC waste addition is planned, further testing with actual waste is needed to ensure that steady state and abnormal hydrolysis/radiolysis conditions do not exceed criteria for flammable gas and organic salts. Formation and disposal of tarry-like solids or polymers (e.g., recent observation of black oil substance in Tank 241-C-106 sludge sample and tarry substance in 1958 A-24 condensate crib sample) is another area of concern and requires further study.

8.3.1.3 Evaporation. Evaporation is the primary mechanism for removal of NPH and other diluents from the DST. A model was developed to predict organic evaporation rates based on NPH only. This model was based primarily upon data developed to predict organic evaporation in Tank 241-C-103 (Wood and Claybrook 1994) and is fully described in Volume 2, Section 8.8. Sensitivity analyses performed on the evaporation model indicated that there is a very strong relationship between the tank temperature and the evaporation rate. At this time, the temperature in Tank 241-AP-107 is approximately 20 °C (70 °F). At this temperature, the model predicts that it would take in excess of 100 years for 90% of the NPH to evaporate. However, it is anticipated that the conditions in Tank 241-AP-107 might be changed by addition of equipment, and that the temperature in the tank will be closer to 40 °C (100 °F). In this case, 90% of the NPH would be evaporated in less than 40 years. Figure 8-3 shows the relationship between the NPH evaporation rate and the tank temperature.

8.3.2 Costs

Survey of the 28 DSTs showed that Tank 241-AP-107 was the preferred tank for interim storage of separable phase organic (Section 1.2). The tank is not equipped for efficient removal of the organic by hydrolysis and evaporation processes.

The primary cost benefit of organic removal in DST is that there would be no additional processing costs once the material was degraded or evaporated. However, this is offset by the costs for obtaining approval and costs for adding equipment to Tank 241-AP-107. If other tanks become available, the cost for using them to store and treat the organic should be evaluated.

Mixing and heating of the aqueous and separable organic phases in the DST are needed for efficient degradation of the TBP and evaporation of the NPH. Potential mixing methods include mixer pump, air lift circulator, and supernate recycle.

A preliminary cost estimate was developed for Tank 241-AP-107 based on available information for addition of two mixer pumps and other equipment to DST 241-AZ-101 (Kohlman 1995; KEH 1995) and modified expense costs for operation of Tank 241-SY-101 (Galbraith and Parazin 1995) for five years. The rough-order-of-magnitude total cost estimate is \$48 million. See Volume 2, Sections 8.9 and 8.10 for additional information. Some additional cost would be associated with the installation of additional equipment.

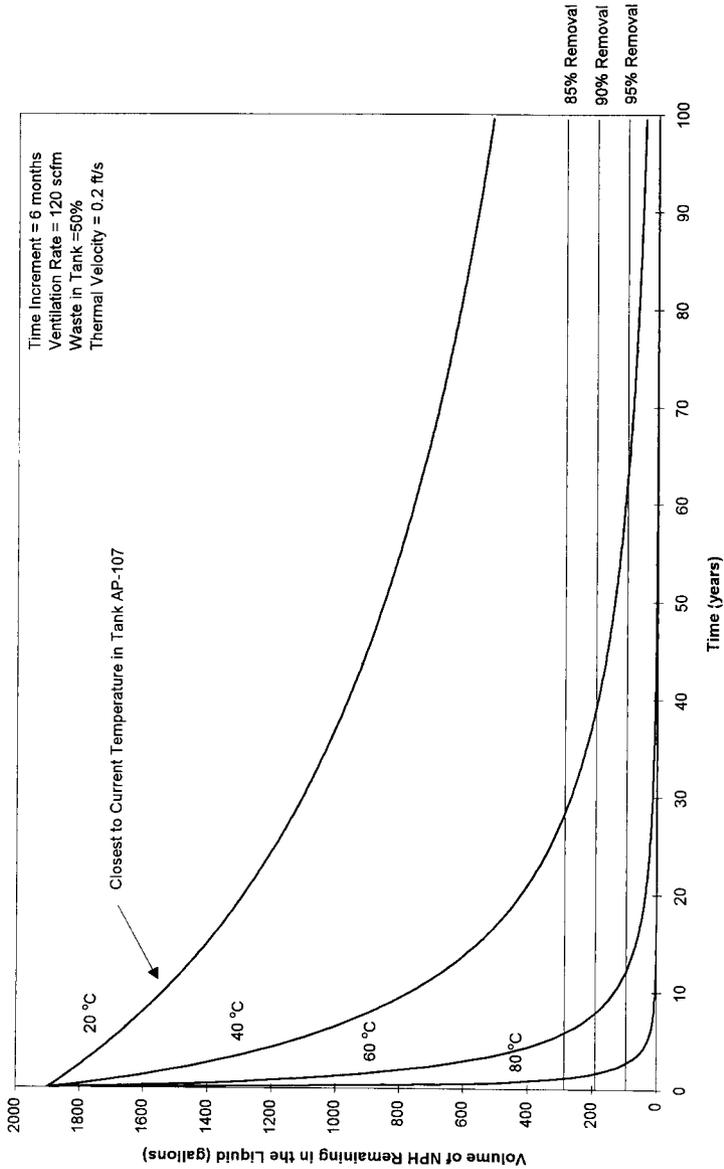


Figure 8-3. Time Required to Achieve 85%, 90%, and 95% Removal of NPH at Varying Temperatures.

The costs for obtaining approval cannot be easily predicted. Stakeholders have generally been skeptical of the benefits of adding the Tank 241-C-103 organic to a DST (Section 1). In addition, evaporation of the NPH would result in some increase in emissions that could affect permits. The combination of these two nonmechanical impacts could easily result in between \$1 and \$2 million in additional costs, that may still not result in approval. The minimum total cost for destruction of the Tank 241-C-103 organic in a DST is approximately \$50 million.

8.4 ULTIMATE DISPOSAL

The ultimate disposal form of the organic will depend upon the process used. If it is acceptable to add the Tank 241-C-103 organic to a DST, the ultimate disposal will be through normal TWRS Pretreatment processing. The current Pretreatment flowsheets can process some soluble organic. The TWRS process technical baseline contains a modified mass balance diagram that addresses both soluble and separable organic (Orme 1996). If offsite thermal processing is used, at least one vendor will keep the ash, thus reducing disposal impacts. Most other processes will result in an ash that must be disposed. If vitrification is used, this ash would make a good feed to the LLW treatment system (see Section 8.2.5 and Volume 2, Section 8.4). Feed to the LLW vitrification is preferred to HLW vitrification because of potential repository impacts. Volume 2, Section 8.11 provides information on these potential impacts. The DOE-RW (repository program) licensing strategy for the proposed Yucca Mountain federal repository in Nevada is to limit the nuclear waste disposal to..."only spent nuclear fuel and high-level radioactive waste that do not include components regulated as hazardous wastes under the Resource Conservation and Recovery Act." The Hanford Site SSTs, including Tank 241-C-103, are considered RCRA tanks and have been identified as containing F listed waste solvents and D characteristic waste metals for toxic characteristic leaching procedure. As a result the issue of RCRA waste and Yucca Mountain disposal must be addressed for both Tank 241-C-103 and the remaining HLW streams.

Dose rates on material returned from thermal processing would be much higher than dose rates on material sent. Assuming a bulk density of 0.3 to 0.4, dose rates on contact with a full 55-gal drum are estimated to be between 400 and 500 mrem/hr (see Volume 2, Section 12).

8.5 ORGANIC DISPOSAL SUMMARY AND PREFERENCES

The key advantages and disadvantages of the organic disposal options are provided in Table 8-1. Based on these advantages and disadvantages and the other information provided in this section, the following preferences are provided:

- Offsite treatment is the preferred option if adding the organic to a DST is not approved

- If stakeholder support is gained for adding the organic to a DST, this then would be the preferred option
- If the organic remains onsite for an extended period of time, onsite treatment through the vitrification system should be pursued
- The ultimate disposal form will be dependent upon the disposal method. Most disposal methods will result in a solid waste. Feeding this waste to the LLW treatment system is preferred to the HLW treatment system because of potential disposal impacts at Yucca Mountain.

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9.0 ENVIRONMENTAL PERMITTING IMPACTS

This section describes activities that could require environmental permitting to support the organic removal options evaluated in Section 10. These impacts are based upon discussions with Tank Farms Permitting personnel and Environmental Regulatory personnel. There are currently no regulations that will clearly stop any of the organic removal options evaluated. With proper planning, there also should be no schedule impacting delays. The permitting impacts identified in this section are only estimates and the final permitting requirements will be determined after approval of an organic removal option. The permitting impacts described in this section are divided into pumping organic and aqueous directly to a DST, skimming the organic to an aboveground tank, and washing the organic in an aboveground tank.

9.1 PUMPING ORGANIC AND AQUEOUS DIRECTLY TO A DST

There are no additional permitting requirements for this activity. However, a notification may be required. Any action that results in separable organic sent to a DST would have to include a change to the compatibility data quality objective.

9.2 SKIMMING TO AN ABOVEGROUND TANK

Skimming to an aboveground tank, regardless of the length of storage time will likely require the following:

- **Hanford Facility Dangerous Waste Part A Permit modification (DOE-RL 1993)** - A modification for aboveground storage was previously prepared but was not submitted due to delay in the skimming decision (Parazin 1995). If a Notice of Intent is needed as part of the modification, it may include a 150-day public hearing period. The regulators have recently waived the Notice of Intent requirements for other permit actions. Other actions as part of the review would be a NEPA review and Washington State Environmental Policy Act review. The cost for this modification is estimated to be approximately \$6,000 for the Part A modification and \$11,000 if a Notice of Intent is required.
- **Air permit review** - An air permit review will be required and will likely include a Notice of Construction to Ecology and the Washington State Department of Health because there is the potential for increased release of toxic air pollutants. The Notice of Construction would include a review of any technology used to reduce emissions. The cost for this review could vary from \$5,000 to \$25,000.
- **NEPA impacts** - The present NEPA Environmental Impact Statement covers putting the organic in an aboveground tank.

If the skimmed material is sent to a DST, the compatibility DQO would have to be changed.

9.3 WASHING IN AN ABOVEGROUND TANK

Washing the organic in an aboveground tank will likely require the following.

- **Hanford Facility Dangerous Waste Part A Permit modification (DOE-RL 1993)** - The permit modifications required for skimming could also include changes to allow washing for no additional cost.
- **Air permit review** - The air permit review required for skimming could also include a review of washing for no additional cost.
- **NEPA impacts** - If the ISO tank is used for washing, it is likely that only a Categorical Exclusion would be required. This would cost approximately \$10,000. If the LR56/H cask system is used, an Environmental Assessment may be required because there are already at least two Categorical Exclusions in progress. It is likely that the regulators agencies may want all of the NEPA related documents put under one Environmental Assessment. This may cost approximately \$100,000.

10.0 EVALUATION OF ORGANIC REMOVAL OPTIONS

Two primary options and one sub option were evaluated for removing the organic from Tank 241-C-103: Option A - transfer the pumpable separable phase organic and aqueous liquids to a single DST for interim storage using existing salt well equipment, Option B - skim the separable phase organic and transfer it to an aboveground storage tank for eventual disposal, and Option B1 - skim the separable organic and transfer it to a DST. These options were based upon the general options for this evaluation (Section 1.2.1) and previous evaluations (Dukelow et al. 1995). The evaluation was based on the following elements.

- **TWRS Pretreatment Considerations (Section 10.1)** - Two major cases were evaluated: (1) there will be no changes to the TWRS Pretreatment process to accommodate organic and (2) the TWRS Pretreatment flowsheet and processes will be changed to accommodate organic.
- **Review of Previous Evaluations (Section 10.2)** - The results of previous organic removal evaluations were reviewed, including the evaluation criteria and scaling used.
- **Reevaluation of Results Based on New Information (Section 10.3)** - The results described in Section 10.2 were reevaluated based on the new or revised information.

The information and numerical values in this section were developed by the Decision Support Board prior to the recommendations of the WHC Review Board (Section 12) and review by the CRS TAP (Section 13). To maintain the integrity of the original engineering evaluation, no numbers were changed as a result of WHC Review Board or stakeholder decisions.

10.1 TWRS PRETREATMENT CONSIDERATIONS

Two major cases were evaluated based on different assumptions regarding potential changes to the TWRS Pretreatment flowsheets. These cases are described below.

- **Pretreatment Case 1:** There will be no change to the TWRS Pretreatment flowsheet or processes (see Section 4). Potential impacts to TWRS Pretreatment if the processes are not updated to accommodate organic are listed below:
 - Incompatibility of organic with waste retrieval components (e.g., the organic may degrade elastomer seals)
 - Formation of foams and emulsions that may foul process equipment and cause schedule delays

- Increased waste volumes because of additional processing volumes and secondary waste generation
 - Increased health and safety risks associated with organic (e.g., solvent fire and toxic vapors)
 - Increased industrial safety risks and increased worker dose rates associated with more frequent filter/resin changes caused by organic in the treatment stream
- **Pretreatment Case 2:** The TWRS Pretreatment flowsheet and processes will be updated to adequately process the separable phase and entrained organic.

10.2 REVIEW OF PREVIOUS EVALUATIONS

Previous reports recommended pumping the organic and the aqueous waste to a DST through existing transfer lines without organic separation (Bartley 1994; Dukelow et al. 1995). This pumping would result in the organic contacting the sludge. A safety evaluation of the pumping activity indicated that pumping could be performed with some system modifications (Geschke and Milliken 1995). The safety conditions in the tank, both before and after pumping, were reviewed and found to be acceptable by Postma et al. (1995). The CRS TAP, DNFSB, and Ecology disagreed with this analysis and requested additional study (Section 1.1). This section reviews the results of *Recommended Alternatives for Interim Stabilization of Tank 241-C-103* (Dukelow et al. 1995) that recommended pumping the organic and aqueous to a DST. Section 4.2 provides additional information.

10.2.1 Review of Previous Evaluation Criteria and Scaling

The Dukelow et al. (1995) report used a scaling system of -3 (worst) to +3 (best) to evaluate selected criteria for the removal of the organic from Tank 241-C-103. These criteria included public safety, worker safety, environmental compliance, feasibility, and cost. The criteria, subdivisions of the criteria, and weighting factors used by Dukelow et al. (1995) to evaluate four organic removal options are provided in Table 10-1.

The Dukelow et al. (1995) system was also used for this comparison with some modifications. The Dukelow criteria were compared to the criteria originally developed by the Decision Support Board (Section 1.4) and found to be comparable (Table 1-2). In addition the rating system and weighting factors were reviewed and found to be acceptable. The principle modification was the addition of stakeholder concerns.

Table 10-1. Evaluation Criteria*.

Criteria	Weighting Factor	Criteria Subdivisions
A. Public Safety	3	<ol style="list-style-type: none"> 1. Solvent fire risk 2. Waste transfer risk
B. Worker Safety	3	<ol style="list-style-type: none"> 1. Radiation protection 2. Toxic gases 3. Industrial safety
C. Environmental Compliance	2	<ol style="list-style-type: none"> 1. Administrative 2. Soil column contamination 3. Tri-Party Agreement considerations
D. Feasibility	1	<ol style="list-style-type: none"> 1. Operability 2. Implementation 3. Decontamination and decommissioning (waste handling)
E. Cost	2	<ol style="list-style-type: none"> 1. Implementation 2. Life-cycle 3. Pretreatment/disposal/site cleanup

*From *Recommended Alternative for Interim Stabilization of Tank 241-C-103* (Dukelow et al. 1995)

10.2.2 Review of Previous Options Evaluated and Results

Dukelow et al. (1995) evaluated four options: (1) no action, (2) typical salt well pumping, (3) skimming to a DST, and (4) skimming and aboveground storage. Of those four options, only Option 2 through 4 are applicable to this report. These options are described below using the nomenclature of Option A and B to be consistent with the terms used in this report. Because skimming to a DST is a subset of Option B, it is designated as Option B1.

- **Option A - Typical Salt Well Pumping:** The salt well pumping option would include the transfer and storage of organic solvent and pumpable aqueous liquids to a DST using the existing salt well pumping equipment. This would also provide interim storage until the waste was retrieved for pretreatment and disposal.
- **Option B - Skimming and Aboveground Storage:** The skimming and aboveground storage option would include the skimming and storage of most of the organic into an aboveground storage tank. The pumpable liquids remaining in Tank 241-C-103 would subsequently be transferred to a DST by salt well pumping.
- **Option B1 - Skimming to a DST:** The skimming option would include the skimming, transferring, and storage of most of the organic into a suitable DST. The pumpable liquids remaining in Tank 241-C-103 would subsequently be transferred to a different DST by salt well pumping.

These options were evaluated against each criteria identified in Table 10-1. A summary of the evaluation results is provided in Table 10-2. The evaluation scores for each option were: (A) typical salt well pumping (score = 0.9), (B) skimming to an aboveground tank (score = -4.8), and (B1) skimming to a DST (score = -2.5). For this evaluation process, the higher the positive number the better the rating. Based on this rating, typical salt well pumping was the organic removal option recommended by Dukelow et al. (1995).

10.3 REEVALUATION OF RESULTS BASED ON NEW INFORMATION

Since the previous report recommending typical salt well pumping of both phases to a DST was published (Dukelow et al. 1995), new or revised information that directly affects the decision criteria has been gained (e.g., cost data, radiation exposure estimates, and stakeholders concerns) and has been provided throughout this engineering evaluation. A reevaluation of the decision criteria was performed based on this new information. The same scaling system of -3 (worst) to +3 (best) was used to reevaluate each criteria from Dukelow et al. (1995) based on the new information, as described in the following sections.

Table 10-2. Previous Ratings For Removing Organic From Tank 241-C-103^a.

Criteria	Rating for Options Evaluated ^{b,c}		
	Option A ^d Typical Salt Well Pumping	Option B ^d Skimming to Aboveground Tank	Option B1 ^d Skimming to a DST
A. Public Safety (3)	-1.5 weighted average	-1.5 weighted average	-1.5 weighted average
1. Solvent fire risk	0	0	0
2. Waste transfer risk	-1	-1	-1
B. Worker Safety (3)	0 weighted average	-3.0 weighted average	-1.0 weighted average
1. Radiation protection	0	-2	-1
2. Toxic gases	0	0	0
3. Industrial safety	0	-1	0
C. Environmental Compliance (2)	2.7 weighted average	2.0 weighted average	2.0 weighted average
1. Administrative	0	0	0
2. Soil column contamination	1	1	1
3. Tri-Party Agreement	3	2	2
D. Feasibility (1)	-0.3 weighted average	-0.3 weighted average	-0.7 weighted average
1. Operability	0	0	0
2. Implementation	0	-2	-1
3. Decontamination & decommissioning	-1	1	-1
E. Cost (2)	0 weighted average	-2.0 weighted average	-1.3 weighted average
1. Implementation	0	-2	-1
2. Life-cycle	0	-1	0
3. Pretreat/dispose/cleanup	0	0	-1
F. Stakeholder Concerns (1)	Not Rated	Not Rated	Not Rated
Total Rating	0.9	-4.8	-2.5

^a From *Recommended Alternative for Interim Stabilization of Tank 241-C-103* (Dukelow et al. 1995). Some numbers have changed due to math errors in original report.

^b Scaling of -3 (worst) to +3 (best).

^c No action option not reported. Some action will be required; no action is not a feasible option.

^d Options A, B, and B1 were called Options 2, 4, and 3, respectively, in Dukelow et al. (1995).

10.3.1 Criteria A - Public Safety

There was no new information regarding this criteria; therefore, public safety was not reevaluated.

10.3.2 Criteria B - Worker Safety

Radiation protection was evaluated as Part 1 of the worker safety criteria. The Dukelow et al. (1995) worker safety, radiation protection ratings for each option were: (A) typical salt well pumping (score = 0), (B) skimming to an aboveground tank (score = -2), and (B1) skimming to a DST (score = -1) (Table 10-2).

The original estimates for radiation exposure were based on preliminary data. In addition, the potential impacts of radiation on a DST and on the TWRS Pretreatment processes were not fully evaluated. Without a clear plan, any organic put into a DST may have to be skimmed at a later date. This skimming would result in the same dose as skimming the organic from Tank 241-C-103.

10.3.2.1 Pretreatment Case 1. If the TWRS Pretreatment process is not changed to accommodate organic, the dose due to difficulties in the filtration and ion exchange Pretreatment process would make typical salt well pumping the worst case for radiation exposure. New scores for the worker safety, radiation protection evaluations for each option are: (A) typical salt well pumping (score = -2), (B) skimming to an aboveground tank (score = -1), and (B1) skimming to a DST (score = -1) (Table 10-3).

10.3.2.2 Pretreatment Case 2. If the TWRS Pretreatment process is updated as scheduled to accommodate organic, the impacts to radiation protection would be the same for all options. New scores for the worker safety, radiation protection evaluations for each option are: (A) typical salt well pumping (score = -1), (B) skimming to an aboveground tank (score = -1), and (B1) skimming to a DST (score = -1) (Table 10-4).

10.3.3 Criteria C - Environmental Compliance

Impacts to the Tri-Party Agreement were the biggest contributor to the environmental compliance ratings. The Dukelow et al. (1995) environmental compliance, Tri-Party Agreement evaluation ratings for the four options were: (A) typical salt well pumping (score = 3), (B) skimming to an aboveground tank (score = 2), and (B1) skimming to a DST (score = 2) (Table 10-2).

Options A, B, and B1 could be completed in time to meet Tri-Party Agreement milestones. Typical salt well pumping was rated higher in Dukelow et al. (1995) because of its potential to be completed before Tri-Party Agreement milestone dates. If there is a

Table 10-3. Reevaluation of Ratings Assuming Pretreatment Case 1 (No Change to TWRS Flowsheet^a).

Criteria	Rating for Options Evaluated ^{b,c}		
	Option A ^d Typical Salt Well Pumping	Option B ^d Skimming to Aboveground Tank	Option B1 ^d Skimming to a DST
A. Public Safety (3)	-1.5 weighted average	-1.5 weighted average	-1.5 weighted average
1. Solvent fire risk	0	0	0
2. Waste transfer risk	-1	-1	-1
B. Worker Safety (3)	<u>-2.0 weighted average</u>	<u>-2.0 weighted average</u>	-1.0 weighted average
1. Radiation protection	-2	-1	-1
2. Toxic gases	0	0	0
3. Industrial safety	0	-1	0
C. Environmental Compliance (2)	2.0 weighted average	2.0 weighted average	2.0 weighted average
1. Administrative	0	0	0
2. Soil column contamination	1	1	1
3. Tri-Party Agreement	2	2	2
D. Feasibility (1)	<u>-1.0 weighted average</u>	0 weighted average	-0.7 weighted average
1. Operability	-1	0	0
2. Implementation	-1	-1	-1
3. Decontamination & decommissioning	-1	1	-1
E. Cost (2)	<u>-3.3 weighted average</u>	-2.0 weighted average	<u>-2.7 weighted average</u>
1. Implementation	-2	-2	-2
2. Life-cycle	-2	-1	-1
3. Pretreat/dispose/cleanup	-1	0	-1
F. Stakeholder Concerns (1)	<u>-2</u>	<u>2</u>	<u>-1</u>
Total Rating	<u>-7.8</u>	<u>-1.5</u>	<u>-4.9</u>
Total Rating w/o Stakeholder Concerns	<u>-5.8</u>	<u>-3.5</u>	<u>-3.9</u>

^a Since this original engineering evaluation was performed, WHC has determined that the TWRS Pretreatment flowsheet will change to accommodate both soluble and separable organic. This case is now provided primarily for comparisons.

^b Changes from Table 10-2 are underlined.

^c Scaling of -3 (worst) to +3 (best).

^d Options A, B, and B1 were called Options 2, 4, and 3, respectively, in Dukelow et al. (1995).

Table 10-4. Reevaluation of Ratings Assuming Pretreatment Case 2 (Changes to the TWRS Flowsheet).

Criteria	Rating for Options Evaluated ^{a,b}		
	Option A ^c Typical Salt Well Pumping	Option B ^c Skimming to Aboveground Tank	Option B1 ^c Skimming to a DST
Criteria (Weight)			
A. Public Safety (3)	-1.5 weighted average	-1.5 weighted average	-1.5 weighted average
1. Solvent fire risk	0	0	0
2. Waste transfer risk	-1	-1	-1
B. Worker Safety (3)	<u>-1.0 weighted average</u>	<u>-2.0 weighted average</u>	-1.0 weighted average
1. Radiation protection	<u>-1</u>	<u>-1</u>	-1
2. Toxic gases	0	0	0
3. Industrial safety	0	-1	0
C. Environmental Compliance (2)	<u>2.0 weighted average</u>	2.0 weighted average	2.0 weighted average
1. Administrative	0	0	0
2. Soil column contamination	1	1	1
3. Tri-Party Agreement	<u>2</u>	2	2
D. Feasibility (1)	<u>-0.3 weighted average</u>	0 weighted average	-0.7 weighted average
1. Operability	0	0	0
2. Implementation	0	<u>-1</u>	-1
3. Decontamination & decommissioning	<u>-1</u>	1	-1
E. Cost (2)	0 weighted average	-2.0 weighted average	-1.3 weighted average
1. Implementation	0	-2	-1
2. Life-cycle	0	-1	0
3. Pretreat/dispose/cleanup	0	0	-1
F. Stakeholder Concerns (1)	<u>-2</u>	<u>2</u>	<u>-1</u>
Total Rating	<u>-2.8</u>	<u>-1.5</u>	<u>-3.5</u>
Total Rating without Stakeholder Concerns	<u>-0.8</u>	<u>-3.5</u>	-2.5

^a Changes from Table 10-2 are underlined.

^b Scaling of -3 (worst) to +3 (best).

^c Options A, B, and B1 were called Options 2, 4, and 3, respectively, in Dukelow et al. (1995).

benefit to completion before these milestones, the benefit would be much smaller than the differences indicated in Dukelow et al. (1995), particularly when compared to stakeholder concerns.

New scores for the environmental compliance, Tri-Party Agreement evaluations, for each option, regardless of whether changes are made to the TWRS Pretreatment process, are: (A) typical salt well pumping (score = 2), (B) skimming to an aboveground tank (score = 2), and (B1) skimming to a DST (score = 2) (Tables 10-3 and 10-4).

10.3.4 Criteria D - Feasibility

The Dukelow et al. (1995) evaluation weighted average ratings for the feasibility criteria were: (A) typical salt well pumping (weighted average = 0.3), (B) skimming to an aboveground tank (weighted average = -0.3), and (B1) skimming to a DST (weighted average = -0.7) (Table 10-2).

Since Dukelow et al. (1995) was published, several operability and implementation issues regarding skimming have been addressed (Section 5). Regardless of the organic removal option chosen, there will be feasibility issues, including modifications to the transfer system necessary to perform typical salt well pumping and difficulty in finding a suitable DST.

10.3.4.1 Pretreatment Case 1. The new evaluation weighted averages for the feasibility criteria, assuming no changes are made to the TWRS Pretreatment process, are: (A) typical salt well pumping (weighted average = -1.0), (B) skimming to an aboveground tank (weighted average = 0), and (B1) skimming to a DST (weighted average = -0.7) (Table 10-3).

10.3.4.2 Pretreatment Case 2. The new evaluation weighted averages for the feasibility criteria, assuming the TWRS Pretreatment process is updated to accommodate organic, are: (A) typical salt well pumping (weighted average = -0.3), (B) skimming to an aboveground tank (weighted average = 0), and (B1) skimming to a DST (weighted average = -0.7) (Table 10-4).

10.3.5 Criteria E - Cost

Cost differences were the largest factor for recommendation of typical salt well pumping in Dukelow et al. (1995). The Dukelow et al. (1995) cost evaluation weighted average ratings for the three options were: (A) typical salt well pumping (weighted average = 0), (B) skimming to an aboveground tank (weighted average = -2.0), and (B1) skimming to a DST (weighted average = -1.3) (Table 10-2).

It was estimated by Dukelow et al. (1995) that skimming costs would be approximately an order of magnitude higher than pumping costs (approximately \$1 million

versus \$8 million). It was assumed that the skimming cost for removal of organic from a DST would be absorbed by the TWRS Pretreatment process. If there are no changes to the Pretreatment process, Option A, typical salt well pumping, will have the greatest cost and greatest impact to the TWRS Pretreatment process. These impacts will be the same for any tanks containing separable phase organic in the aqueous or sludge, or soluble TBP. In addition, skimming costs have been refined and are now estimated to be less than half of the previous estimate (Appendix A).

10.3.5.1 Pretreatment Case 1. The cost evaluation weighted averages, assuming that no changes are made to the TWRS Pretreatment process, are: (A) typical salt well pumping (weighted average = -3.3), (B) skimming to an aboveground tank (weighted average = -2.0), and (B1) skimming to a DST (weighted average = -2.7) (Table 10-2).

10.3.5.2 Pretreatment Case 2. Based on the new cost information, it is difficult to rate one option significantly higher or lower than another until more information is available regarding potential changes to the TWRS Pretreatment flowsheets. Therefore, the scores for each option assuming that the TWRS Pretreatment process will be updated to accommodate organic are the same as the original scores from Dukelow et al. (1995) (Table 10-4).

10.3.6 Criteria F - Stakeholder Concerns

Stakeholder concerns were not factored into the evaluation performed by Dukelow et al. (1995). Skimming to an aboveground tank is clearly the preference of both the DNFSB, CRS TAP, and Ecology. Skimming to a DST would likely be the second preference. For this evaluation, the stakeholder concerns were assigned a weighting of 1. As a result, the ratings for stakeholder concerns, regardless of whether the TWRS Pretreatment process is updated to accommodate organic, are: (A) typical salt well pumping (score = -2), (B) skimming to an aboveground tank (score = 2), and (B1) skimming to a DST (score = -1) (Tables 10-3 and 10-4).

10.4 SUMMARY OF EVALUATION RESULTS

Summaries of the new evaluation ratings for the four options are provided in Tables 10-3 and 10-4. Two Pretreatment processing cases were evaluated: (1) Pretreatment Case 1 - assumes no change to the TWRS Pretreatment flowsheets (Table 10-3) and (2) Pretreatment Case 2 - assumes that the TWRS Pretreatment flowsheets will be updated as scheduled to accommodate organic (Table 10-4). Also included in each table is the new evaluation criteria of stakeholder concerns. Because the extent of changes to the TWRS Pretreatment flowsheets are unknown at this time, Table 10-4 assumes the changes to the TWRS Pretreatment flowsheets will adequately process the organic without additional skimming of organic from the receiver DST. If no changes will be made to the TWRS Pretreatment flowsheets, skimming is the preferred option, regardless of stakeholder

Table 10-5. Summary of Total Ratings for Each Option.^a

Assumption Evaluated	Option A ^c Typical Salt Well Pumping	Option B ^c Skimming to Aboveground Tank	Option B1 ^c Skimming to a DST
Previous Rating ^b	0.9	-4.8	-2.5
Pretreatment Case 1 - No Changes to TWRS Pretreatment Process	-7.8	-1.5	-4.9
Pretreatment Case 1 - No Changes to TWRS Pretreatment Process (excluding stakeholder concerns)	-5.8	-3.5	-3.9
Pretreatment Case 2 - TWRS Pretreatment Process Updated	-2.5	-1.5	-3.5
Pretreatment Case 2 - TWRS Pretreatment Process Updated (excluding stakeholder concerns)	-0.8	-3.5	-2.5

^a The higher the positive number, the more preferred the alternative.

^b Based on *Recommended Alternative for Interim Stabilization of Tank 241-C-103* (Dukelow et al. 1995).

^c Options A, B, and B1 were called Options 2, 4, and 3, respectively, in Dukelow et al. (1995).

concerns. If the TWRS Pretreatment flowsheets will be updated to accommodate organic, inclusion of stakeholder concerns in the evaluation will affect the selection of an organic removal option. A summary of the ratings for each option is presented in Table 10-5.

10.4.1 Sensitivity Analysis

The evaluation results indicate that stakeholder concerns or impacts to TWRS Pretreatment flowsheets will be significant enough to potentially change the recommended option. With the possible exception of Pretreatment Case 1 - no changes to the TWRS Pretreatment process, a sensitivity analysis would result in further indicating the small differences between these options and the impact of TWRS Pretreatment and stakeholder concerns.

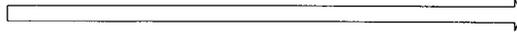
10.4.2 Budget Considerations

Because of shrinking budgets, funding may not be available to aggressively pursue the all feasible options. Appendix A provides cost data on the various options. There is currently no fiscal year 1997 funding for addressing the organic in Tank 241-C-103. This engineering report was designed to review total costs to the extent practical. The following should be factored into any decision limited by near-term budget restrictions.

- The cost to skim and the cost to pump directly to a DST are now estimated to be closer than previously estimated (see Appendix A).
- If the organic is placed in or transferred to a DST, there is a real possibility that it would have to be skimmed from the DST in the future; therefore, the total cost will be the cost to pump it to a DST plus the cost to skim it from a DST.
- There is only one DST currently identified that could receive this organic.
- Stakeholders will likely continue to be concerned with any action that results in organic/sludge contact or organic added to a DST.
- Because organics are likely in other tanks, consolidation of this material to a single DST with future skimming from only one tank will reduce total costs.

A comparison of near-term cost and stakeholder concerns is provided in Figure 10-1.

Increasing Stakeholder Concern



1. Skim, process, and ship the organic offsite
2. Skim the organic to an ISO tank, store until Pretreatment process impacts are known
3. Skim to an LR56/H cask or other transport tank, pump into a DST for interim storage only
4. Pump both organic and aqueous directly to a DST for interim storage (stabilize Tank 241-C-103 in place)



Increasing Cost

Figure 10-1. Tank 241-C-103 Organic Removal Near-Term Cost and Stakeholder Concern Options Overview.

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11.0 ENGINEERING EVALUATION SUMMARY

This report was designed to determine the impacts of various options for removal of the separable phase organic layer in Tank 241-C-103. A systems engineering approach was used to: (1) identify the key stakeholder concerns as a basis for evaluating the options, (2) develop appropriate questions for cognizant personnel to obtain required information, and (3) evaluate the information to support development of preferred and alternate options.

11.1 PREFERRED OPTION EVALUATION

The preferred option will be more strongly influenced by the future direction of the new TWRS process technical baseline and stakeholder concerns than by differences in cost, future potential worker exposures, or other stakeholder concerns. As a result, no preferred organic removal option has yet been identified. This study has identified several key factors used in the evaluation, listed below.

- Costs for skimming, processing, and disposal of organic material are less than previously estimated.
- The impacts to the Revision 1 TWRS Pretreatment flowsheets from separable phase organic will be significant. The recent TWRS process technical baseline addresses the organic issue.
- Organic has been found in the core samples of several tanks. Because of the presence of organic in sludge, the TWRS Pretreatment flowsheets will likely require modifications.
- Only one DST (Tank 241-AP-107) is currently available to receive the organic from Tank 241-C-103. Tank 241-AP-107 will not support in-tank destruction of the organic without major modifications and costs.
- None of the options evaluated clearly determined a preferred option based on health, safety, or environmental impacts.
- All of the options evaluated have had some level of formal safety analysis.
- There will be permitting issues but these issues should not prevent either of the primary options provided sufficient scheduling time is allowed and stakeholder concerns are addressed.

The primary organic removal option evaluated in this report include: Option A - pump both the organic and aqueous phases to a DST (e.g., as part of interim stabilization) and Option B - skim the organic to an aboveground storage tank. There are several disposal options associated with Option B. A summary of the costs for Options A and B (including

the Option B disposal options) is provided in Table 11-1. A summary of the total ratings for each option evaluated is provided in Section 10, Table 10-5.

- The lowest initial cost is to pump both phases to a DST for interim storage. This cost does not address future costs for treatment and disposal.
- If the TWRS Pretreatment flowsheets are updated to include organic, skimming and offsite disposal is the best rated option by a very narrow margin if stakeholder values are considered in the evaluation.
- Pumping to a DST is the best rated option if the TWRS Pretreatment flowsheets are updated and stakeholder values are not considered in the evaluation.

The final decision on the removal of the floating organic layer from Tank 241-C-103 will be made by the decision maker, DOE. The final decision will likely be based on a comparison of costs and stakeholder concerns. The following considerations will affect the final decision.

- Any option involving skimming is estimated to cost at least \$2 million. The decision then becomes the value of spending the additional \$1.2 million for ultimate disposal or to put the material back into a DST and rely on future disposal technology development.
- The cost difference between (1) skimming and storing in an aboveground and (2) skimming, processing, and disposing is less than \$1 million.
- Stakeholders will likely continue to resist any option that results in organic contact with the sludge or organic transferred to a DST for later disposal.

11.2 TWRS PRETREATMENT IMPACTS

The impacts to the Revision 1 TWRS Pretreatment flowsheet from separable phase organics can be significant. Operational continuity, schedule, cost, and other criteria would be impacted if either the option of pumping both phases to a DST or the option of skimming and transferring the organic to a DST with subsequent retrieval are chosen without the addition of an organic handling system.

Direct impacts to retrieval and sludge washing would likely be minor and include premature failure of materials. Impacts to the filtration and ion exchange processes could be major (e.g., plug the filtration process and foul the ion exchanger) and cause costly shutdowns. Any shutdown may impact schedules. At an annual budget of \$400 million, repeated shutdown could easily result in losses greater than \$100 million.

Table 11-1. Summary of Cost Estimates for Organic Removal Options*.

Option	Cost Estimate	Assumptions
Option A - Pumping both phases to a DST as part of interim stabilization (no disposal or treatment option identified)	Between \$500,000 and \$1 million	<ul style="list-style-type: none"> • \$500,000 estimate assumes submersible pumping with no special treatment of the organic layer. \$100,000 to \$200,000 estimated to separate layers in DCRT. (Appendix A) • \$1 million estimate from Dukelow et al. (1995)
Option B - Skimming, treatment, temporary storage, and disposal of the organic (skimming to aboveground tank)	\$3,400,000	<ul style="list-style-type: none"> • Organic pumped directly into 7,700-gal ISO tank • LR56/H cask equipped to store and treat organic (for contingency purposes) • ISO tank equipped to treat organic
Skimming and storing the organic in ISO tank (no disposal option identified)	\$2,500,000	<ul style="list-style-type: none"> • Organic pumped directly into 7,700-gal ISO tank • ISO tank not equipped to treat organic
Skimming and transferring the organic to a DST using the LR56/H cask (no disposal or treatment option identified)	\$2,200,000	<ul style="list-style-type: none"> • Organic pumped directly into LR56/H cask system (no treatment)

* All information summarized from Appendix A unless otherwise noted.

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12.0 DECISION REVIEW BOARD RECOMMENDATIONS

The WHC Decision Review Board considered the options for the organic layer in Tank 241-C-103, including costs, estimates for various stabilization options, effects on Pretreatment, data from previous studies, waste compatibility issues, stakeholder concerns, impacts on waste volume projections, the current stabilization schedule for Tank 241-C-103, and emergency pumping plans. Following the meeting, a decision was made and a recommendation forwarded to DOE (Volume 2, Section 12.1).

Subject to testing required to meet the tank farm waste compatibility DQOs, the Board concluded that interim stabilization of Tank 241-C-103 should consist of salt well pumping of both the aqueous and separable organic liquid to Tank 241-AP-107 on the current stabilization schedule. The basis for the recommended alternative included the following significant considerations:

- (1) The technical work and a previous study (Dukelow et al. 1995) indicate there is no safety problem in allowing the separable organic layer to be mixed with the sludge in Tank 241-C-103 as a result of interim stabilization. Additionally, auger and core samples of Tanks 241-C-106 and 241-C-204 show separable TBP to be present in the waste solids. Vapor and core samples analyzed to date indicate there are other tanks that contain separable organics. The auger samples from Tank 241-C-102 confirm the existence of TBP in the waste solids and validate vapor sample results from that tank which indirectly indicated the presence of separable organics. There is no evidence of adverse reactions or any unusual behavior in these tanks.
- (2) The CRS TAP's major concern regarding pumping to a DST was the potential impact on TWRs Pretreatment. Waste incompatibility resulting from commingling of Tank 241-C-103 separable organic with other waste was perceived as a lesser issue than Pretreatment impacts, based primarily on a judgement that stakeholders would support emergency pumping to an approved DST if a leak were to develop in Tank 241-C-103.
- (3) Emerging data from SST solids (Tanks 241-C-103, 241-C-106, 241-C-204, and others) demonstrate the need for an organic treatment operation on the headend of the Privatization Phase 2 disposal process.
- (4) In addition to the existing separable phase organic in Tank 241-C-103, it is possible additional contributions will occur as the organic now dissolved in the aqueous phase or combined with salt cake and sludge solids is rendered insoluble through pH adjustment during waste pretreatment processing. It is estimated that as little as 380 L (100 gal) of separable organic in a tank would degrade the disposal ion exchange performance. This supports the need for an organic treatment capability on the headend of the Phase 2 disposal process.

- (5) The Decision Board did not believe it would be cost effective to skim the organic from Tank 241-C-103 to an aboveground tank since plans must be developed for removing organic from a DST as part of the Phase 2 disposal process in any event.

Incorporation of a simple organic removal process in the FY 1996 revision of the TWRS Process Technical Baseline (DOE-RL Milestone T33-96-204) was completed for the Privatization Phase 2 process (Orme et al. 1996). The contract for Phase 2 is expected to be let in 2005. By that time, the first 10 SSTs will have been retrieved, including Tank 241-C-103. It is expected that the magnitude of the organic treatment and disposal problem will be fully understood at that time, and resolution incorporated in the Privatization Phase 2 disposal process. In the interim, the separable phase organic will be managed in the DST system in accordance with the existing authorization basis. The FY 1996 Operational Waste Volume Projection (Tri-Party Agreement Milestone M-46-00C due September 30, 1996) will confirm that storage of organic waste in the DSTs does not affect available storage capacity nor interfere with Privatization Phase 1 disposal activities.

13.0 RECENT CRS TAP AND DNFSB REVIEWS

This section summarizes the CRS TAP and DNFSB reviews performed after this engineering study was completed and the WHC Review Board made the recommendation to pump all liquid contents to a DST.

13.1 CRS TAP REVIEW

A presentation on this engineering study and the recommendations of the WHC Review Board was given to the CRS TAP during the 20th meeting June 11 to 13, 1996. The CRS TAP agreed with the WHC Review Board that there would be no unacceptable near-term safety impacts associated with salt well pumping both layers from Tank 241-C-103 to a DST, but indicated that there would be serious deleterious impacts on future activities. In addition, the CRS TAP expressed concern that the receiving DST would become a watch list tank. The presentation did not alter the CRS TAP's position of recommending separable organic removal prior to pumping the Tank 241-C-103 liquid layer to a DST. WHC plans to issue safety documentation that will provide the basis for resolution of the safety issue. This will include storage of solvents in both SSTs and DSTs. The CRS TAP commented positively on the WHC commitment to develop appropriate flowsheets to address the presence of organics in the TWRs Pretreatment processes. Volume 2, Section 1.2, contains the 13th CRS TAP meeting summary letter that recommended removal of the organic prior to pumping the tank liquid, and Volume 2, Section 14.1 contains excerpts from the 20th CRS TAP meeting that upheld the recommendation from the 13th CRS TAP meeting.

13.2 DNFSB REVIEW

The DOE and WHC have had several conversations with the DNFSB since this engineering study was initially completed. The DNFSB has continued to express a general preference for removing the organic prior to interim stabilization but indicated that due to this engineering study, safety and technology are no longer primary drivers preventing the pumping of both layers to a DST. As a result, the DNFSB will focus on other more urgent issues and will not take a formal position.

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14.0 CURRENT STATUS

No decision has yet been made regarding the organic layer in Tank 241-C-103. The DNFSB has no formal position. The CRS TAP have continued to express concern but identified that there is no unacceptable, near-term safety implications associated with immediate salt well pumping. Ecology has continued to express concern to DOE regarding pumping both the separable organic and aqueous layers to a DST. These concerns are still being discussed. The DOE will make a final determination based upon the information provided, stakeholder concerns, and programmatic needs to ensure regulatory requirements are met in a fiscally responsible manner.

The FY 1996 TWRS process technical baseline was approved and transmitted to Ecology (Orme et al. 1996). It contains a modified mass balance that addresses both soluble and separable phase organic.

The issue of organics in DSTs is continuing to be addressed as part of *Safety Evaluation of Potential Impacts from Organic in Hanford Tanks* (Grigsby and Postma 1996). This SARR is scheduled to be finalized in the near future. The information in this SARR will further address CRS TAP concerns for transferring safety issues from Tank 241-C-103 to a DST.

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APPENDIX A
COST ANALYSIS

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COST ESTIMATE FOR										
C-103 ORGANIC SKIMMING,										
TREATMENT, TEMPORARY STORAGE										
AND DISPOSAL										
ASSUMPTIONS:										
ORGANIC PUMPED DIRECTLY INTO 7700 GALLON ISO TANK										
LR-66 EQUIPPED TO STORE AND TREAT ORGANIC (FOR CONTINGENCY PURPOSES)										
ISO TANK EQUIPPED TO TREAT ORGANIC										
			FTE	TIME (DAYS)	HRS	COST (\$60/HR)	SUB TOTAL			
PROJECT MANAGEMENT										
	ENGINEER		2	300	4800	\$ 288,000.00				
	MISC. SUPPORT		0.5	260	1040	\$ 62,400.00	\$ 350,400.00			
COMPLETE DESIGN OF OVERALL SYSTEM										
	ENGINEERS		3	60	1440	\$ 86,400.00				
	DESIGNERS		4	60	1920	\$ 115,200.00	\$ 201,600.00			
7700 GALLON ISO TANK W/ TREATMENT SYSTEM										
	ENGINEERING (SPECIFICATION PREP/APPROVAL)					\$ 9,000.00				
	PROCURE ISO TANK					\$ 126,000.00				
	MISC. INSTRUMENTATION/VENTILATION					\$ 100,000.00				
	SARP					\$ 60,000.00	\$ 295,000.00			
LR 56										
	MODIFICATIONS					\$ 50,000.00				
TESTING										
	PNL TESTING OF MIXING PARAMETERS					\$ 40,000.00				
	SYSTEM MOCKUP TESTING									
	ENGINEER		2	30	480	\$ 28,800.00				
	TECHNICIAN		2	15	240	\$ 14,400.00	\$ 43,200.00			
TEMPORARY STORAGE PAD (2 EA)										
	BUILD TEMPORARY STORAGE PAD					\$ 100,000.00				
SAFETY ASSESSMENT (UPDATE DRAFT)										
	PERFORM HAZ OPS		10	4	320	\$ 19,200.00				
	UPDATE SA		1	80	640	\$ 38,400.00				
	PEER REVIEW		6	5	240	\$ 14,400.00				
	PROJECT REVIEW		2	5	80	\$ 4,800.00				
	INCORPORATE COMMENTS		1	20	160	\$ 9,600.00				
	FOLLOW DOE APPROVAL		1	20	160	\$ 9,600.00	\$ 96,000.00			
PERMITTING										
	PART A PERMIT APPLICATION									
	PART A COSTS					\$ 5,600.00				
	NOI COSTS					\$ 11,200.00				
	AIR PERMIT		1	30	240	\$ 14,400.00				
	NEPA (ENVIRONMENTAL ASSESSMENT)					\$ 100,000.00	\$ 131,200.00			
FABRICATION/PROCUREMENT										
	SKIMMER SYSTEM					\$ 31,000.00				
	MISC. PIPING/ASSEMBLY (USING HANFORD SHOPS)					\$ 150,000.00				
	CHEMICALS					\$ 25,000.00	\$ 206,000.00			

COST ESTIMATE FOR C-103 ORGANIC SKIMMING AND STORAGE IN ISO TANK						
ASSUMPTIONS:						
ORGANIC PUMPED DIRECTLY INTO 7700 GALLON ISO TANK						
ISO TANK IS NOT EQUIPPED TO TREAT ORGANIC						
		FTE	TIME (DAYS)	HRS	COST (\$60/HR)	SUB TOTAL
PROJECT MANAGEMENT						
	ENGINEER	2	300	4800	\$ 288,000.00	
	MISC. SUPPORT	0.5	260	1040	\$ 62,400.00	\$ 350,400.00
COMPLETE DESIGN OF OVERALL SYSTEM						
	ENGINEERS	3	60	1440	\$ 86,400.00	
	DESIGNERS	4	60	1920	\$ 115,200.00	\$ 201,600.00
7700 GALLON ISO TANK W/ TREATMENT SYSTEM						
	ENGINEERING (SPECIFICATION PREP/APPROVAL)				\$ 9,000.00	
	PROCURE ISO TANK				\$ 82,000.00	
	MISC. INSTRUMENTATION/VENTILATION				\$ 100,000.00	
	SARP				\$ 60,000.00	\$ 261,000.00
TESTING						
SYSTEM MOCKUP TESTING						
	ENGINEER	2	30	480	\$ 28,800.00	
	TECHNICIAN	2	15	240	\$ 14,400.00	\$ 43,200.00
TEMPORARY STORAGE PAD (2 EA)						
	BUILD TEMPORARY STORAGE PAD				\$ 100,000.00	
SAFETY ASSESSMENT (UPDATE DRAFT)						
	PERFORM HAZ OPS	10	4	320	\$ 19,200.00	
	UPDATE SA	1	80	640	\$ 38,400.00	
	PEER REVIEW	6	5	240	\$ 14,400.00	
	PROJECT REVIEW	2	5	80	\$ 4,800.00	
	INCORPORATE COMMENTS	1	20	160	\$ 9,600.00	
	FOLLOW DOE APPROVAL	1	20	160	\$ 9,600.00	\$ 96,000.00
PERMITTING						
PART A PERMIT APPLICATION						
	PART A COSTS				\$ 5,600.00	
	NOI COSTS				\$ 11,200.00	
	AIR PERMIT	1	30	240	\$ 14,400.00	
FABRICATION/PROCUREMENT						
	SKIMMER SYSTEM				\$ 31,000.00	
	MISC. PIPING/ASSEMBLY (USING HANFORD SHOPS)				\$ 150,000.00	
READINESS REVIEW						
	STONE AND WEBSTER				\$ 43,000.00	
	WHC SUPPORT FOR RR ACTIVITIES	5	20	800	\$ 48,000.00	\$ 91,000.00

PROCEDURES/WORK PACKAGE PREPARATION							
PLANNER			2	70	1120	\$ 67,200.00	
COG. ENG			0.5	260	1040	\$ 62,400.00	
SCHEDULER			0.25	20	40	\$ 2,400.00	\$ 132,000.00
OPERATIONS							
TRAINING							
			1	60	480	\$ 28,800.00	
			5	20	800	\$ 48,000.00	\$ 76,800.00
PERFORM RISER INSPECTION (2 RISERS)							
			4	6	192	\$ 11,520.00	
			1	6	48	\$ 2,880.00	
			1	6	48	\$ 2,880.00	
			1	6	48	\$ 2,880.00	
			1	6	48	\$ 2,880.00	
			1	10	80	\$ 4,800.00	\$ 27,840.00
INSTALL SKIMMER SYSTEM AND VIDEO CAMERA							
			5	10	400	\$ 24,000.00	
			2	10	160	\$ 9,600.00	
			3	10	240	\$ 14,400.00	
			3	10	240	\$ 14,400.00	
			1	10	80	\$ 4,800.00	
			2	12	192	\$ 11,520.00	
			8	3	192	\$ 11,520.00	
OPERATE SKIMMER							
							\$ 90,240.00
			3	15	360	\$ 21,600.00	
			1	15	120	\$ 7,200.00	
			2	15	240	\$ 14,400.00	
			1	15	120	\$ 7,200.00	
			1	15	120	\$ 7,200.00	
			1	20	160	\$ 9,600.00	
REMOVE SKIMMER/DECON/MOVE TANK							
							\$ 67,200.00
			4	10	320	\$ 19,200.00	
			2	10	160	\$ 9,600.00	
			3	10	240	\$ 14,400.00	
			3	10	240	\$ 14,400.00	
			1	10	80	\$ 4,800.00	
			2	12	192	\$ 11,520.00	
			8	3	192	\$ 11,520.00	\$ 85,440.00
DISPOSE OF SKIMMER SYSTEM (20 DRUMS @\$400/DRUM)							
						\$ 8,000.00	
STORE ORGANIC (1 YR)							
			2	52	832	\$ 49,920.00	
TOTALS							
					21384	\$ 1,892,840.00	
CONTINGENCY (33%)							
					7056.72	\$ 624,637.20	
TOTALS							
					28440.72	\$ 2,517,477.20	

COST ESTIMATE FOR C103 ORGANIC SKIMMING AND TRANSFER TO DST USING THE LR-56							
ASSUMPTIONS:							
ORGANIC PUMPED DIRECTLY INTO LR-56 (NO TREATMENT)							
			FTE	TIME (DAYS)	HRS	COST (\$60/HR)	SUB TOTAL
PROJECT MANAGEMENT							
	ENGINEER		2	300	4800	\$ 288,000.00	
	MISC. SUPPORT		0.5	260	1040	\$ 62,400.00	\$ 350,400.00
COMPLETE DESIGN OF OVERALL SYSTEM							
	ENGINEERS		3	60	1440	\$ 86,400.00	
	DESIGNERS		4	60	1920	\$ 115,200.00	\$ 201,600.00
LR-56							
	MODIFICATIONS					\$ 10,000.00	
TESTING							
SYSTEM MOCKUP TESTING							
	ENGINEER		2	30	480	\$ 28,800.00	
	TECHNICIAN		2	15	240	\$ 14,400.00	\$ 43,200.00
TEMPORARY STORAGE PAD (1 EA)							
	BUILD TEMPORARY STORAGE PAD					\$ 60,000.00	
SAFETY ASSESSMENT (UPDATE DRAFT)							
	PERFORM HAZ OPS		10	4	320	\$ 19,200.00	
	UPDATE SA		1	80	640	\$ 38,400.00	
	PEER REVIEW		6	5	240	\$ 14,400.00	
	PROJECT REVIEW		2	5	80	\$ 4,800.00	
	INCORPORATE COMMENTS		1	20	160	\$ 9,600.00	
	FOLLOW DOE APPROVAL		1	20	160	\$ 9,600.00	\$ 96,000.00
PERMITTING							
PART A PERMIT APPLICATION							
	PART A COSTS					\$ 5,600.00	
	NOT COSTS					\$ 11,200.00	
	AIR PERMIT		1	30	240	\$ 14,400.00	
FABRICATION/PROCUREMENT							
	SKIMMER SYSTEM					\$ 31,000.00	
	MISC. PIPING/ASSEMBLY (USING HANFORD SHOPS)					\$ 150,000.00	
READINESS REVIEW							
	STONE AND WEBSTER					\$ 43,000.00	
	WHC SUPPORT FOR RR ACTIVITIES		5	20	800	\$ 48,000.00	\$ 91,000.00
PROCEDURES/WORK PACKAGE PREPARATION							
	PLANNER		2	70	1120	\$ 67,200.00	
	COG ENG		0.5	260	1040	\$ 62,400.00	
	SCHEDULER		0.25	20	40	\$ 2,400.00	\$ 132,000.00

DON'T SAY IT --- Write It!

DATE: May 18, 1995

TO: DB Engelman

R1-49

FROM: DK DeFord

R2-80

Telephone: 373-5727

cc: TE Rainey

R2-54

DT Vladimiroff

R2-80

SUBJECT: Initial planning for pumping C-103, T-104, T-107

As requested, I have attempted to capture what we know about the requirements to pump any one of these three tanks in the near future. Attached are preliminary project schedules with resource loading and costs.

Recognize that these tend to be best-case projections. Our experience has been that we identify as many of the tasks and associated costs as possible prior to kick-off, then the cost doubles after the engineering effort begins in earnest. We should probably address this in our resource loading strategy, but for now it means that for any one of these tanks to be pumped in the coming fiscal year will cost around \$500K.

C-103

Assumptions: The schedule assumes submersible pumping, with no special treatment of the organic layer. WHC and DOE have proposed this strategy; Ecology is fighting it. The BX-106 pump controls will be reused to the extent possible at C-103. A pump is already on hand. The tank contains 133,000 gallons of supernate. This will require approximately 20 transfers from CR-003 over the course of pumping. Projected cost: \$220K+

Unknowns: If a jet pump is preferred, it will add to the cost. If additional measures are required for the organic waste, then it's anybody's guess. (I would estimate no less than \$100K to separate the layers within the DCRT, as one proposal suggests. More exotic proposals have been made as well.) Although characterization is complete, additional decisions have yet to be made regarding where the waste can be sent for storage; additional studies would also cost more.

T-104:

Assumptions: Tank is similar to T-111; the emergency skid would simply be moved over. No major hang-ups that we know of at this time. Projected Cost: \$265K+

T-107:

Assumptions: The only reason to choose T-107 is if we could run the submersible pump already in place. If not, it would have to be disposed of and then we start over with a standard saltwell/jetpump installation and expense. There is only 9,000 gallons of supernate, 16,000 total liquid to pump. Projected Cost: \$210K+

To: Phil Bartley, Foster-Wheeler Fax 372-5801
From: Doug DeFord, WHC Phone 373-5727

Here is the 5/18 memo I mentioned. The current estimate for T-104 is 300K to prepare for pumping, 300K to pump for 5 months or so.

Actual costs for previous C-farm tanks don't apply because:

- (1) they were saltcake tanks with interstitial liquid only, whereas C-103 is supernate only;
- (2) the pumps were in place in the waste for 3-4 years prior to our project, so they were caked up and corroded, causing poor performance and frequent failures. Also the ancillary equipment was all the old style and derelict at that, so maintenance and refurbishment was a huge expense. C-103 will be all new equipment and a very short pumping duration (ie. days to weeks.)
- (3) The CR-Vault was not in service at the time we needed it, so we had to refurbish it as well; now that is done and not required again for C-103.

Were there other questions I am now forgetting? Call me--

dkd

APPENDIX B
SUMMARY OF HANFORD SITE WASTE TANK DEFINITIONS

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B.0 SUMMARY OF HANFORD SITE WASTE TANK DEFINITIONS

B.1 WATCH LIST TANK

An underground storage tank containing waste that requires special safety precautions because it may have serious potential for release of high level radioactive waste because of uncontrolled increases in temperature or pressure. Special restrictions have been placed on these tanks by "safety Measures for Waste Tanks at Hanford Nuclear Reservation," Section 3137 of the National Defense Authorization Act for Fiscal Year 1991, November 5, 1990, Public Law 101-510, (also known as the Wyden Amendment).

B.2 AGING WASTE (AGING)

High level, first cycle solvent extraction waste from the PUREX plant, following evaporative concentration, denitration, and neutralization (NCAW).

B.3 CONCENTRATE COMPLEXANT (CC)

Concentrated product from the evaporation of dilute complexed waste.

B.4 CONCENTRATED PHOSPHATE WASTE (CP)

Waste originating from the decontamination of the N Reactor in 100 N Area. Concentration of this waste produces concentrated phosphate waste.

B.5 DILUTE COMPLEXED WASTE (DC)

Characterized by a high content of carbon including organic complexants: ethylenediaminetetraacetic acid (EDTA), citric acid, and hydroxyethylthylenediaminetriacetic acid (HEDTA), are the major complexants used during strontium recovery processing at B Plant. Main sources of DC waste in the DST system are salt well liquid inventory (from SSTs).

B.6 DILUTE NONCOMPLEXED WASTE (DN)

Low activity liquid waste originating from T and S Plants, the 300 and 400 Areas, PUREX facility (decladding supernatant and miscellaneous wastes) 100 N Area (sulfate waste), B Plant, salt wells and PFP (supernate).

B.7 DOUBLE SHELL SLURRY (DSS)

Waste that exceeds the sodium aluminate saturation boundary in the waste evaporator without exceeding receiver tank composition limits. for reporting purposes, DSS is considered a solid.

B.8 DOUBLE-SHELL SLURRY FEED (DSSF)

Waste concentrated just before reaching the sodium aluminate saturation boundary (6.5 molar hydroxide) in the evaporator without exceeding receiver tank composition limits. The DSSF is not as concentrated as DSS.

B.9 PUREX DECLADDING (PD)

PUREX Neutralized Cladding Removal Waste (NCRW) is the portion of the PUREX plant neutralized cladding removal waste stream; received in Tank Farms as a slurry. NCRW solids are classified as transuranic (TRU) waste.

B.10 PLUTONIUM FINISHING PLANT (PFP) TRU SOLIDS

Transuranic (TRU) solids fraction from PFP Plant operations. Supernatant fraction covered under dilute non-complexed waste.

Source of information is Hanlon 1995 (Waste Tank Summary report for Month Ending September 30, 1995, WHC-EP-0182-90, December 1995) and Gasper 1995 (TWRS Waste Pretreatment Glossary, WHC-SD-WM-TI-692, April 1995).



FOSTER WHEELER ENVIRONMENTAL CORPORATION

**Tank 241-C-103 Systems Engineering
Study: Separable Phase Organic
Skimming, Storage, Treatment, and
Disposal Options**

Volume 2
WHC-SD-WM-ES-384 REV 0

FINAL

September 30, 1996

Prepared by

P.L. Bartley
Foster Wheeler Environmental Corporation

G.T. Dukelow
M.J. Klem
Westinghouse Hanford Company

J.A. Reddick
Los Alamos Technical Associates

Prepared for

Westinghouse Hanford Company
Tank Waste Remediation System
Task 016 of Order No. MGK-SVV-186918

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VOLUME 2

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VOLUME 2

Volume 2 of this report provides supplemental information. This information would normally be placed in attachments and appendices. Due to the size of the document, and the understanding that there may be wide dissemination of this document, a two volume approach was adopted. In this way, most readers, who would only be interested in the information in Volume 1, have a smaller document. Those with the need for more information can access both volumes.

For consistency, each section in Volume 1 has a corresponding section in Volume 2. Subsection numbers are based on information needs, not corresponding subsections in Volume 1.

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- 1.2 Letter - DOE requesting WHC reevaluate Tank 241-C-103 Pumping Decision
- 1.3 Tables - Quantification of Mission Need Objectives Tables
- 1.4 Questions - To System Experts Regarding Tank 241-C-103 Organic Impacts

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Volume 2 contains no additional information.

SECTION 3 - HISTORY

- 3.1 Addendum - History of Separable Phase Organic in the Tank Farms
- 3.2 Addendum - Tank 241-C-103 History
- 3.3 DSI - Tank 241-C-103 Transaction History - Post January 1976
- 3.4 Memo - Preliminary Estimate of Projected Process Organic Volume in Waste Tanks

SECTION 4 - IMPACTS ON DOUBLE-SHELL TANKS AND PRETREATMENT PROCESSES

- 4.1 Impacts of Sludge Retrieval on Tank 241-C-103
- 4.2 DSI - Impacts of Separable Phase Organics on Filtration and Ion Exchange

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SECTION 7 - LONG-TERM STORAGE

- 7.1 Long-Term Storage
- 7.2 Memo - Rate Guidance for Activity Data Sheet (ADS) Development For the Use of Hanford Site Solid Waste Facilities
- 7.3 Addendum - Tank Farms Aboveground Storage Long-Term Storage Pad Impacts
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SECTION 8 - TREATMENT AND DISPOSAL OPTIONS

- 8.1 Addendum - Offsite Incineration Options Information
- 8.2 Letters - Steam Reforming Technology and EPA Review of Permitting Requirements
- 8.3 DSI - Grout Impacts
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- 8.5 Addendum - DST Hydrolysis and Radiolysis Information
- 8.6 DSI - Dose Rates to Organic in DSTs
- 8.7 DSI - Flammable Gas Review of High-Level Waste Tanks
- 8.8 Addendum - DST Evaporation Information
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- 8.10 DSI - Preliminary Cost Estimate - Separable Phase Organic Removal in Tank 241-AP-107
- 8.11 DSI - Issues/Impacts/Risks with Processing Tank 241-C-103 Separable Organic Material Into Hanford Immobilized High-Level Waste Product(s) Slated For Disposal in a Federal Geologic Repository
- 8.12 DSI - Dose Rate Calculations for a Drum Containing Waste From Tank C-103

SECTION 9 - ENVIRONMENTAL PERMITTING IMPACTS

Volume 2 contains no additional information.

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SECTION 10 - ORGANIC REMOVAL OPTIONS EVALUATION

Volume 2 contains no additional information.

SECTION 11 - ENGINEERING EVALUATION SUMMARY

Volume 2 contains no additional information.

SECTION 12 - WHC EVALUATION REVIEW BOARD RESULTS

Letter - Recommendation on Tank 241-C-103 Floating Organic Layer

SECTION 13 - CRS TAP AND DNFSB REVIEW RESULTS

Volume 2 contains no additional information.

SECTION 14 - CURRENT STATUS

Letter - Chemical Reactions Sub Tank Advisory Panel (CRS TAP) Comments
Prepared During the June 11-13, 1996, CRS TAP Meeting

SECTION 15 - REFERENCES

Volume 2 contains no additional information.

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VOLUME 2
SECTION 1 - INTRODUCTION

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VOLUME 2

**Section 1.1
Meeting Minutes - 13th Meeting of
the Chemical Reactions Sub-Panel**

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Billy C. Hudson
P.O. Box 271, Lindsborg, KS 67456
Phone/Fax: (913) 227 4378

September 12, 1995

Professor Mujid S. Kazimi
Massachusetts Institute of Technology
Room 24-102
Cambridge, Massachusetts 02139

Dear Mujid:

The 13th meeting of the Chemical Reactions Sub-Panel (CRS) was held at Richland, WA, August 30–September 1, 1995. The agenda and list of attendees are attached. TAP representatives comprised Charles Forsberg, Scott Slezak, Tom Larson, Tom Kress, Dave Campbell, Lou Kovach and me. The following comments and suggestions represent our unanimous position.

General Comments and Suggestions

Gas release event in 105-AN. As discussed on page 4, we find the peak, measured hydrogen concentration (1.7%) in the ventilation system to be significant and suggest immediate actions be taken to establish necessary controls and determine future actions.

Interim stabilization of 103-C with the organic layer in place. As discussed below, we see no technical reason for immediate saltwell pumping of the supernate from 103-C. Furthermore, it is our belief this action (without first removing the floating organic layer) would have serious, deleterious impact on future activities leading to undesirable increases in cost and personnel exposure. Consequently, we believe it would be prudent to remove the organic layer from 103-C prior to interim stabilization and suggest required actions for this removal be initiated immediately.

Specific Comments and Suggestions

Flammable Gas Overview. We appreciated the review of recent waste activity in tanks 103-AN, 105-AN, and 103-SY. We found the GRE observed in 105-AN to be especially significant. Based on data presented (1.7% hydrogen concentration in the ventilation system, implying greater than 1/4 LFL in the dome space), a safety issue appears to exist comparable in type to that perceived for 101-SY prior to mitigation. In line with this observation, we suggest:

1. Quickly establishing appropriate, additional administrative and operational controls (such as increased ventilation flow rate) to minimize risk;
2. Proceeding with the safety analyses to determine allowable operations (such as appropriate tank and waste-characterization activities);

Comments and suggestions regarding interim stabilization of 103-C.

In the event of an emergency such that the liquid in 103-C must be removed without separation of the organic layer, the near-term safety implications associated with salt well pumping appear to be acceptable. However, no such emergency appears to exist. We believe sufficient analyses have been performed to establish that there are no significant, near-term, safety-related risks associated with the continued storage of existing waste in 103-C. Furthermore, there has been no indication that 103-C is leaking.

While there appear to be no unacceptable, near-term safety implications associated with immediate salt well pumping, it is our belief this action would have serious, deleterious impact on future activities (such as solid and liquid separation and ion exchange, due to the mixing of organics and sludge or saltcake) leading to undesirable increases in cost and personnel exposure. Consequently, we believe it would be prudent to remove the organic layer from 103-C prior to interim stabilization and suggest required actions for this removal be initiated immediately. In order to avoid a recurrence of this problem, we suggest the removed organics be stored without mixing with other waste that contains sludge or saltcake.

Following removal and separate storage of the organics, the aqueous supernate could be removed from 103-C by saltwell pumping and stored in a DST, as proposed.

Sudharsan memo. A memo entitled "PRELIMINARY REPORT ON SUBPANEL MEETING REGARDING TANK WASTE CHEMICAL REACTIONS, Aug. 30-Sept., 1995" was received from "SUDHARSAN INTERNATIONAL, INC." This memo and our associated comments are contained in attachments 1 and 2.

Future Meetings

The next CRS meeting is planned for September 20-21, with a close-out session the morning of the 21st. Other currently planned meeting times include October 10-12, and November 28-30.

Sincerely,

Billy C. Hudson,
Chairman, CRS

Attachment 1**Suggested 241-C-10 topics for presentation and discussion****I. Political constraints and considerations**

1. A clear description of the TPA-milestone requirements concerning interim stabilization.
2. A clear description of the TPA-milestone requirements concerning the organic layer problem.
3. Renegotiation of TPA requirements.

II. Proposed-action advantages, disadvantages, and cost-related issues

1. A Systems Engineering study to determine potential effects the proposed C-103 salt-well pumping and waste transfer would have on the whole TWRS process, not just safety-related aspects.
2. Impact of the proposed action on ultimate disposal (safety, cost, etc.).
3. Impact of the proposed action on ultimate disposal versus removing the organic layer before (or during) interim stabilization.
4. Potential increased cost in required TWRS operations following the proposed action.
5. Potential advantages and disadvantages of the proposed action.
6. The technical basis for concluding that saltwell pumping will successfully remove the floating organic layer as well as the aqueous supernate.
7. Factors considered in deciding to interim stabilize now without removing the organic layer.
8. Other methods for interim stabilization besides salt well pumping.
9. Technical advantages of the proposed action over other alternatives.
10. The various methods for removing organics and how they were evaluated.
11. Cost of removing the organic layer before salt well pumping.

12. A comparison of costs for TWRS corresponding to removing the organic layer before and after interim stabilization, including costs after interim stabilization.
13. A comparison of various methods for separating the organic layer inside and outside of C-103 (technical difficulties, costs, political constraints, overall TWRS activities, etc.).
14. Projected costs, dose, etc. for the organic layer problem separate from interim stabilization.
15. Advantages of not separating the organic layer at this time.
16. Why the proposed action is the best way to deal with the organic layer problem (from the TWRS perspective) from now until completion of waste treatment.

III. History and characterization issues

1. The current physical and chemical condition of C-103 waste.
2. The history of floating organic material in C-103 in terms of types and volumes added, current type and volume, mechanisms for destruction or alteration (aging), and resulting end products.
3. The basis for the amount of floating organic in C-103 (4100-5500 gal).
4. Comparison of simulants used to perform flow-sheet studies with material at C-103.
5. A history of experience at other tanks for actions similar to those proposed at C-103.
6. Contents and conditions in the proposed receiver tank.
7. Physical and chemical properties of the mixture (in the receiver tank) versus current properties of individual wastes.
8. Possible chemical reactions and end products resulting from the proposed action.

IV. Safety-related issues

a. 241-C-103

1. The technical basis for assuming a slow burning rate in the event of a pool fire.
2. The possible existence, extent, and combustion of organics on the inside surface of the dome.
3. Possible ignition sources during transfer (e.g., static charge buildup and discharge).
4. Technical basis (evidence) for assuming the absence of vertical stratification of NH_3 , H_2 , and N_2O in the C-103 dome space and the maximum credible volume of flammable gas in the dome space.
5. Quantity and configuration of organic material left in C-103 after salt well pumping.
6. The possible existence and combustion of residual organics on the sludge.
7. Possible effects of sludge permeation by residual organics.
8. Possible chemical reactions (including catalytic effects) between residual organic material and the sludge in C-103 after or during pump down.
9. Aerosol release factors for water evaporated from sludge (0.002) and why it is different than for solvent smoke (0.03). [Tom Kress would like to see a copy of the Mishima document from which these were taken.]
10. The technical basis for heat transfer via thermocapillary and thermogravitational convection as being governed by $q = -k(dT/dx)^3$. [Tom Kress would like to see backup documentation.]
11. The temperature history for C-103, explanations for any observed spikes, possible maximum temperatures in the tank consistent with these spikes, possible effects removal of the supernate might have on peak temperature, and the possible relations between the implied peak temperatures and safety (including conditions imposed by residual organics and the possibility of ignition).
12. The possibility of generating or releasing a mixture of flammable gases during or after the proposed action or during retrieval.
13. Potential problems resulting from tank depressurization following a burn (e.g., choked or blocked air flow during depressurization).

VOLUME 2

Section 1.2

**Letter - DOE Requesting WHC Reevaluate
Tank 241-C-103 Pumping Decision**

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9504249 B

WHC CC Recd: 09/21/95 pm



Department of Energy

Richland Operations Office
P.O. Box 560
Richland, Washington 99352

SEP 20 1995

95-TSD-118

President
Westinghouse Hanford Company
Richland, Washington

Dear Sir:

TANK C-103 ORGANIC LAYER

The thirteenth meeting of the Chemical Reaction Sub-Panel (Sub-TAP) was held at Hanford, August 30, 1995, thru September 1, 1995. The adequacy of stabilizing Tank C-103 with the floating organic layer was discussed. The Westinghouse Hanford Company (WHC) has done an excellent job in evaluating and resolving the safety issues associated with the organic layer. However, a programmatic issue appears to have surfaced. The Sub-TAP responded, that although no near-term unacceptable safety implications exist with salt well pumping, they recommend that the floating layer be removed separately prior to salt well pumping. Not doing so, they believe, would have serious, deleterious impact on future program activities (such as solid and liquid separation and ion exchange, due to the mixing of organic and sludge or salt cake) leading to undesirable increases in cost and personnel exposure. They suggested that the required actions for this removal be initiated immediately, to ensure that the layer could be removed prior to an emergency condition created by the tank leaking. They further recommend, that once removed this organic should be stored separately and not be added to the double-shell tanks to avoid future mixing potential with sludge and salt cake. The organic layer was removed prior to salt well pumping in Tank C-102, and is believed to be prudent for this tank. The state has also questioned the wisdom of letting this organic mix with the solid wastes during stabilization.

WHC is requested to revisit the decision on stabilizing tanks with floating organic layers, especially Tank C-103, to verify that the overall THRS program objectives have been adequately system engineered. Please provide adequate technical justification as to why the recommendation expressed by the Sub-TAP should not be adopted. If it appears that implementation of the Sub-TAP recommendation is appropriate, please submit appropriate change control document with cost and schedule information, and ensure that planning for dealing with tanks adequately addresses floating organics .

A response on what course of action WHC plans to take is requested within 15 working days of receipt of this letter.

WHC
95-TSD-118

-2-

SEP 20 1995

If you have any questions, please contact M. F. Jarvis, Ph.D, of my staff on 376-4550.

Sincerely,

R. E. Gerton
for Ronald E. Gerton, Director
Tank Safety Analysis Division

TSD:REG

cc: C. O'Dell, EM-36, HQ

VOLUME 2

Section 1.3

Quantification of Mission Need Objectives Tables

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Table 1.3-1. Quantification of Mission Need Objectives.
(Stakeholder Values)

Stakeholder Value	Technical Performance Measures	Evaluate?	Notes
Protect Public/Worker Health and Safety	Time series of contaminant concentration measurement from all contamination monitoring sites, onsite and offsite	No	All alternatives will have appropriate treatment. Will not affect the discharge or rate of release of contaminants.
	Worker fatalities or injuries for construction/operation	Yes	Estimate injury/death rate from FTEs.
Protect Environment and Clean up to the level necessary for future use	Number of latent local cancer fatalities and incidences	Yes	Estimate exposure rate for workers from FTEs and operation. Public exposure not evaluated. Considered to have little impact.
	TWRS effluent contamination levels as sent to ETF	No	Evaluate effects of direct feed or organic to ETF as volume to ETF increases, environmental impact is increased.
	Cumulative amount of land made restrictive to future use	Yes	Volume of immobilized LLW (including vit & grout), convert to acreage. New facilities will be noted.
	Measures of soil fertility	No	No direct soil contact. Affects of land usage covered elsewhere.
Protect the Columbia River	Number of animal/plants adversely affected	No	No direct soil contact. Affects of land usage covered elsewhere.
	Concentrations of radionuclides at the site wells and at locations in the river	Yes	Schedule time for removal of all pumpable liquids from C-103 interim stabilization (leak potential).
Ensure Compliance	Number of fish casualties and their contamination levels	No	Covered by evaluation time for interim stabilization of Tank C-103 (leak potential).
	Number of requirements not met or in compliance with	Yes	Identify potential noncompliance with major regulatory drivers (e.g., TPA, Part B)
Reduce Costs	Cost savings at completion of major cleanup milestones	No	Evaluating change in cost in 1995 dollars for life cycle of each option. Level of detail does not allow for annual cost calculations or milestones.
	Annual TWRS mission cost profiles	No	Evaluating change in cost in 1995 dollars for life cycle of each option. Level of detail does not allow for annual cost calculations or milestones.
	Repository costs	Yes	Will evaluate in 1995 dollars, base on rad and HLW volume \$ per canister.
Enhance Technology Development	Number of cleanup problems encountered that available technologies cannot solve	Yes	Qualitatively discuss technological risks for each option. Identify where technology not currently available.
Capture Economical Development Locally	Annual profits and revenues of businesses not related to Hanford.	No	Will note any local economical benefits (e.g., onsite treatment options considered better due to higher employment).
Protect Rights of Native American Indians	Acreage available	Yes	Evaluate acreage affected by LLW disposal. Evaluated as part of Protect Environment. Sting locations not evaluated.

Table 1.3-2. Quantification of Mission Need Objectives.
(Mission Goals) Sheet 1 of 2

Mission Goals	Technical Performance Measures	Evaluate?	Notes
Operate and Maintain Facilities to provide continued safe storage and environmentally sound storage	Amount of operating costs needed for maintaining the TWRs in a safe condition (safety storage prior to treatment)	Yes	Capture operating costs for storage (e.g., leave in C-103, build tank, pump to DST).
	Number of safety issues mitigated; timeliness of resolution	Yes	Qualitatively discuss issues mitigated or realized.
	Overall TWRs total operating efficiency	Yes	Impacts on stabilization schedule; effects on DST utilization.
Retrieve Tank Waste	Instantaneous and time-average waste retrieval rates	Yes	Rate impact from retrieving (1) separable phase organic and (2) organic contaminated sludge. Convert rate impact to schedule impact, if any. Other impacts/risks/uncertainties.
	Total operating efficiency (TOE) for retrieval	Yes	
Pretreat Tank Waste	Achieved pretreatment facility or process waste throughput rates	Yes	
	Achieved waste transfer rates	Yes	Rate impact from pretreating (1) separable phase organic and (2) organic contaminated sludge. Convert rate impact to schedule impact, if any. Other impacts/risks/uncertainties.
	Achieved pretreatment and processing total efficiency factor (potential process upsets)	Yes	
	Achieved waste separation factors	Yes	LLW radionuclide concentration and volume for each option. Affects of direct feed of (1) separable phase organics (radionuclide and organic) to vitrification process; (2) organics through the TWRs system to vitrification, and (3) organic source ash to vitrification. Discuss possible groud impacts.
	Achieved waste loading	Yes	
Immobilize and dispose of any remaining mixed or LLW	Immobilized LLW volume	Yes	
	Quantity of immobilized waste form needing rework	Yes	Qualitative discussion of potential problems
	LLW immobilization throughput rate (potential process upset)	Yes	Evaluate process rate (e.g., kg/day throughput)
Close the Underground Storage Tanks	Amount of residual SST and DST wastes	No	All tanks assumed clean to acceptable level.

Table 1.3-2. Quantification of Mission Need Objectives.
(Mission Goals) Sheet 2 of 2

Mission Goals	Technical Performance Measures	Evaluate?	Notes
Immobilize High Level and TRU Constituents of Waste to Minimize Safety and Environmental Risk and Enable Permanent Disposal	HLW immobilization throughput rate (potential process upsets)	Yes	Affects to throughput rate, curie loading, and waste oxide loading from direct feed of separable phase organics to vitrification process and to entire system, and organic source ash to vitrification.
	Achieved waste loading in HLW form	Yes	
	Quantity of immobilized waste form needing rework	Yes	Qualitative discussion of potential problems
	Immobilized HLW volume	Yes	HLW volume for each option.
	Achieved HLW/LLW waste separation factors	Yes	Identify separation factors and impacts in Sludge Wash and Ion Exchange.
Minimize Waste Volume Disposed to Lessen Impact on Repository and Hanford Land Use	Achieved radionuclide and chemical loading in immobilized waste form	Yes	Covered in LLW and HLW sections.
	Achieved immobilized waste form volume	Yes	Covered in LLW and HLW sections.
	Results of durability test on immobilized waste forms	Yes	Qualitative discussion of waste form failure potential from organics. Include organic concentration limits where possible. (1) Liquid Organic, (2) Incinerated Organic, (A) Vitrification, (B) Groul.
	Effluent volumes produced by TWRS	No	Impact assumed proportional to LLW and HLW volumes, which are evaluated.
Transfer Excess Facilities and Equipment to Environmental Restoration Mission Area	Measured contamination levels in effluent released to ETF	No	Measured impact of direct organic feed to ETF as part of stakeholder value "Protect the Environment". Insufficient information to evaluate secondary impacts (i.e., condensate increases from processing organic through other unit operations).
	Capital costs for ETF	No	
	Actual number of active facilities	Yes	Each cost analysis will include number of facilities. This will be converted to D&D costs.

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VOLUME 2

Section 1.4

**Questions to Systems Experts Regarding
Tank 241-C-103 Organic Impacts**

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MANAGE TANK WASTE (4.2.1)

Storage and Transfer

Subfunction Experts: J. P. Sederburg
N. W. Kirch
J. A. Reddick
D. E. Place

Conditions: (1) Leave aqueous and organic in tank until retrieval for processing
(2) Pump both organic and aqueous to same DST (a) at same time, (b) skim and pump separately
(3) Pump organic and aqueous to different DSTs
(4) Pump organic to (a) aboveground tank (mobile or stationary), (b) other DCRT, (c) B Plant, (d) PUREX

Answer the questions below based on the four conditions.

Note: Unless noted, "Organics" means TBP/NPH and breakdown products (including DBP).

General Information:

1. If any question can not be answered, what additional information, testing, cost etc. will be required to obtain the answer?
2. In all cases, provide references, were possible, justification where not.
3. This information will be condensed and formatted to fit into a 5-10 page section on Managing Tank Waste . This information will also be fed into other sections, including evaluating four options for removing the C-103 organic layer. Please keep answers as short and clear as possible.
4. Drawings and clean, one line diagrams are encouraged if it helps the overall understanding.
5. Disk copies of all information are needed where possible.

Questions:

1. What problems does it cause? Why? How?
 - Safety (including chemical and radiation exposures)
 - DST utilization
 - Ability to meet interim stabilization and retrieval criteria (retrieval subfunction experts have also been asked this questions on retrieval impacts)

2. What regulatory issues would exist for the four conditions? Explain.
3. What are the interface changes with other unit operations or system functions (e.g. where does the organic go)? Include ventilation and closure (controlled, clean, and stable for full transfer route). Why? How?
4. Is there a DST available with no impact from aqueous and/or organic on existing contents? Explain.
5. Are any MUSTs, DCRTs or other existing tanks acceptable for interim storage? Explain.
6. Does mixing TBP/NPH, including degradation products, with other organics (e.g., chelating agents) cause additional problems? Why? How?
7. Now that flammability is not an issue, does the pumping strategy change? Why? How?
8. What are the Ops impacts from different conditions (e.g. closure of C farm)? Why? How?
9. Can this option be successfully completed within the TPA Milestone date (1999)? With modification of the TPA Milestone date? Why? How?
10. What are the 1995 equivalent life cycle cost (rough order of magnitude) impacts including:
 - Capital
 - Operation cost
 - Number of facilities
 - D&D
 - FTEs (including construction, ops and D&D)
11. What impact is there if separable phase organics are present in other tanks that must be processed? Is the impact volume dependent? Explain.
 - Cost
 - Schedule
 - Exposure
12. Are the existing cost estimates for pumping organic to aboveground tank (\approx \$8-10 million) and pumping to organic/aqueous simultaneously to DST (\approx \$1 million) still applicable? Justified. (Note: This cost was a major concern of the CRS TAP.)
13. What happens when organic comes into contact with sludge in SST or DST? Why? How? Any testing data?

14. What is the maximum layer of separate organic that can be left in tank C-103?
15. Can anything be done in the storage vessel to increase evaporation and/or degradation of organic? Why? How?
16. When is tank C-103 expected to leak? Is it expected to leak before the TPA Milestone date (1999)?
17. Describe these subfunctions in one to two paragraphs each based upon the engineering functional hierarchy (e.g., manage tank waste [4.2.1, see Attachment 4 for short chart]).
18. Determine the presence of other separable phase organics. Provide clear justification (LATA). If present, how much and where located (e.g. DST, MUSTs, DCRTs)?

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RETRIEVE WASTE (4.2.2)

Retrieve Tank Waste

Subfunction Experts: G. R. Bloom
G. L. Crawford
K. D. Boomer

- Conditions:**
- (1) Organic previously pumped to a tank other than SST or DST (i.e. MUST or aboveground) and not processed through TWRS. Aqueous pumped to DST and processed through TWRS
 - (2) Leave organic in C-103 until ready to pretreat waste. Process organic and aqueous through TWRS.
 - (3) Aqueous and organic previously pumped from C-103 to one DST. Process organic and aqueous through TWRS.
 - (4) Aqueous and organic previously pumped from C-103 to separate DSTs. Process organic and aqueous through TWRS.
 - (5) Organic previously pumped to a tank other than SST or DST (i.e. MUST or aboveground), Aqueous previously pumped to DST. Organic and aqueous retrieved and processed through TWRS.

Answer the questions below based on the five conditions.

Note: Unless noted, "Organics" means TBP/NPH and breakdown products (including DBP).

General Information:

1. If any question can not be answered, what additional information, testing, cost etc. will be required to obtain the answer?
2. In all cases, provide references, were possible, justification where not.
3. This information will be condensed and formatted to fit into a 5-10 page section on Retrieve Tank Waste. This information will also be fed into other sections, including evaluating four options for removing the C-103 organic layer. Please keep answers as short and clear as possible.
4. Drawings and clean, one line diagrams are encouraged if it helps the overall understanding.
5. Disk copies of all information are needed where possible.

Questions:

1. How much organic is a problem? Why?
 - Emulsion formation of liquid
 - Mobilization of solids (e.g., organic contaminated C-103 sludge or organic contaminated DST solids (sludge and saltcake)
 - Pumping slurries
 - Degradation product volatilization (e.g., butanol)
 - Supernatant with high concentration of degradation products
 - Are there currently organic limits? Basis?
 - Foam buildup in the tank headspace (formation of a soap type foam from mixer pump)
 - Temperature impacts from pumping activities (e.g., temperature increase from mixer pump - volatilization)
 - Waste residues
2. What problems does it cause? Why? How?
 - Safety (including chemical and radiation exposures)
 - Throughput (including rate, output volumes, and DST utilization)
 - Scheduling (including startup and production)
 - Ability to meet cleanup criteria
3. Will it require a major change in the design of the subfunction (e.g., tanks, facilities, materials of construction)? Why? Include possible solutions, technological risks, and interim solutions.
4. What regulatory issues would exist for the five conditions? Explain.
5. Are there any new issues? Why?
6. What are the interface changes with other unit operations or system functions (e.g. where does the organic go)? Include ventilation and closure. Why? How?
7. Does mixing TBP/NPH, including degradation products, with other organics (e.g., chelating agents) cause additional problems? Why? How?
8. What are the 1995 equivalent life cycle cost (rough order of magnitude) impacts including:
 - Capital
 - Operation cost
 - Number of facilities
 - D&D
 - FTEs (including construction, ops and D&D)

9. What impact is there if separable phase organics are present in other tanks that must be processed? Is the impact volume dependent? Explain.
 - Cost
 - Schedule
 - Exposure

10. Describe this subfunction in one to two paragraphs based upon F&R criteria and the engineering functional hierarchy (e.g., retrieve waste [4.2.2, see Attachment 4 for short chart]).

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PROCESS WASTE (4.2.3)

Sludge Washing

Subfunction Experts: D. E. Place
G. T. MacLean

- Conditions:** (1) Base Case
(2) Separable Phase Organics
(3) Organic in Sludge
(4) Organic in Supernate

Answer the questions below based on the four conditions.

Note: Unless noted, "Organics" means TBP/NPH and breakdown products (including DBP).

General Information:

1. If any question can not be answered, what additional information, testing, cost etc. will be required to obtain the answer?
2. In all cases, provide references, where possible, justification where not.
3. This information will be condensed and formatted to fit into a 5-10 page section on Sludge Washing. This information will also be fed into other sections, including evaluating four options for removing the C-103 organic layer. Please keep answers as short and clear as possible.
4. Drawings and clean, one line diagrams are encouraged if it helps the overall understanding.
5. Disk copies of all information are needed where possible.

Questions:

1. What are the HLW/LLW partitioning effects? Why?
 - Radionuclides
 - Metals (aluminum, chrome)
 - Anions (phosphate)
2. What problems does it cause? Why? How?
 - Safety (including chemical and radiation exposures)
 - Throughput (including rate, radionuclide and organic concentration, output volumes)
 - Scheduling (including startup and production)

3. How much organic is a problem? Why?
 - Is there currently a limit? Basis?
4. Will it require a major change in the design of the system (e.g., tanks, facilities, materials of construction)? Why? Include possible solutions, technological risks, and interim solutions.
5. What regulatory issues would exist for the four conditions? Explain.
6. Are there any new issues? Why?
7. What are the interface changes with other unit operations or system functions (e.g. where does the organic go)? Why? How?
8. Does mixing TBP/NPH, including degradation products, with other organics (e.g., chelating agents) cause additional problems? Why? How?
9. What are the 1995 equivalent life cycle cost (rough order of magnitude) impacts including:
 - Capital
 - Operation cost
 - Number of facilities
 - D&D
 - FTEs (including construction, ops and D&D)
10. What impact is there if separable phase organics are present in other tanks that must be processed? Is the impact volume dependent? Explain.
 - Cost
 - Schedule
 - Exposure
11. Describe this subfunction in one to two paragraphs based upon F&R criteria and the engineering functional hierarchy (e.g., process waste [4.2.3, see Attachment 4 for short chart]).

PROCESS WASTE (4.2.3)
Filtration and Ion Exchange

Subfunction Experts: K. M. Eager
J. A. Reddick
M. J. Klem

Conditions: (1) Base Case
(2) Separable Phase Organic
(3) Soluble Organic in Supernate

Answer the questions below based on the three conditions.

Note: Unless noted, "Organics" means TBP/NPH and breakdown products (including DBP).

Conditions (2) and (3) include organic contaminated fine solids.

General Information

1. If any question can not be answered, what additional information, testing, cost etc. will be required to obtain the answer?
2. In all cases, provide references, where possible, justification where not.
3. This information will be condensed and formatted to fit into a 5-10 page section on Filtration and Ion Exchange. This information will also be fed into other sections, including evaluating four options for removing the C-103 organic layer. Please keep answers as short and clear as possible.
4. Drawings and clean, one line diagrams are encouraged if it helps the overall understanding.
5. Disk copies of all information are needed where possible.

Questions:

1. What are the HLW/LLW partitioning effects? Why?
 - Radionuclides
 - Mass of materials

2. What problems does it cause? Why? How?
 - Safety (including chemical and radiation exposures)
 - Throughput (including rate, radionuclide and organic concentration, output volumes)
 - Scheduling (including startup and production)
3. How much organic is a problem? Why? How?
 - Is there currently a limit? Basis?
4. Will it require a major change in the design of the subfunction (e.g., tanks, facilities, materials of construction)? Why? Include possible solutions, technological risks, and interim solutions.
5. What regulatory issues would exist for the three conditions? Explain.
6. Are there any new issues? Why?
7. What are the interface changes with other unit operations or system functions (e.g. where does the organic go)? Why? How?
8. Does mixing TBP/NPH, including degradation products, with other organics (e.g., chelating agents) cause additional problems? Why? How?
9. What are the 1995 equivalent life cycle cost (rough order of magnitude) impacts including:
 - Capital
 - Operation cost
 - Number of facilities
 - D&D
 - FTEs (including construction, ops and D&D)
10. What impact is there if separable phase organics are present in other tanks that must be processed? Is the impact volume dependent? Explain.
 - Cost
 - Schedule
 - Exposure
11. Describe this subfunction in one to two paragraphs based upon F&R criteria and the engineering functional hierarchy (e.g., process waste [4.2.3, see Attachment 4 for short chart]).

PROCESS WASTE (4.2.3)

LLW Vitrification

Subfunction Experts: J. W. Shade
G. E. Stegen
C. N. Wilson

- Conditions:**
- (1) Base Case
 - (2) Separable Phase Organic - Direct feed bypassing TWRS pretreatment processes
 - (3) Organic Originated Ash - Feed from incinerator
 - (4) Separable Phase Organic - Carryover through normal TWRS pretreatment processes

Answer the questions below based on the four conditions.

Note: Unless noted, "Organics" means TBP/NPH and breakdown products (including DBP).

General Information

1. If any question can not be answered, what additional information, testing, cost etc. will be required to obtain the answer?
2. In all cases, provide references, where possible, justification where not.
3. This information will be condensed and formatted to fit into a 5-10 page section on LLW Vitrification. This information will also be fed into other sections, including evaluating four options for removing the C-103 organic layer. Please keep answers as short and clear as possible.
4. Drawings and clean, one line diagrams are encouraged if it helps the overall understanding.
5. Disk copies of all information are needed where possible.

Questions:

1. What problems does it cause? Why?
 - Safety (including chemical and radiation exposures)
 - Throughput (including rate, radionuclide and organic concentration, output volumes)
 - Scheduling (including startup and production)

2. How much organic is a problem? Why?
 - Is there currently a limit? Basis?
3. What will be the immobilized waste oxide loading? Why?
4. Will it require a major change in the design of the subfunction (e.g., tanks, facilities, materials of construction)? Why? Include possible solutions, technological risks, and interim solutions.
5. What regulatory issues would exist for the four conditions? Explain.
6. Are there any new issues? Why?
7. What are the interface changes with other unit operations or system functions (e.g. where does the organic go)? Why? How?
8. Does mixing TBP/NPH, including degradation products, with other organics (e.g., chelating agents) cause additional problems? Why? How?
9. Discuss possible grout impacts.
10. Discuss potential for immobilized waste needing rework.
11. Discuss waste form failure potential.
12. What are the 1995 equivalent life cycle cost (rough order of magnitude) impacts including:
 - Capital
 - Operation cost
 - Number of facilities
 - D&D
 - FTEs (including construction, ops and D&D)
13. What impact is there if separable phase organics are present in other tanks that must be processed? Is the impact volume dependent? Explain.
 - Cost
 - Schedule
 - Exposure
14. Describe this subfunction in one to two paragraphs based upon F&R criteria and the engineering functional hierarchy (e.g., process waste [4.2.3, see Attachment 4 for short chart]).

PROCESS WASTE (4.2.3)

Grout

Subfunction Experts: J. W. Shade
W. J. Powell

Cases: (1) Base Case - Vitrification melter condensate to drums
(2) Alternate case - Grout replaces HLW vitrification for 3 million gallons from DSTs to go to vaults

Conditions: (1) No change
(2) Separable Phase Organic - Direct feed bypassing TWRS pretreatment processes
(3) Organic Originated Ash - Feed from incinerator
(4) Separable Phase Organic - Carryover through normal TWRS pretreatment processes

Answer the questions below based on the four conditions and two cases. Each conditions is answered for each case.

Note: Unless noted, "Organics" means TBP/NPH and breakdown products (including DBP).

General Information

1. If any question can not be answered, what additional information, testing, cost etc. will be required to obtain the answer?
2. In all cases, provide references, were possible, justification where not.
3. This information will be condensed and formatted to fit into a 5-10 page section on Grout. This information will also be fed into other sections, including evaluating four options for removing the C-103 organic layer. Please keep answers as short and clear as possible.
4. Drawings and clean, one line diagrams are encouraged if it helps the overall understanding.
5. Disk copies of all information are needed where possible.

Questions:

1. What problems does it cause? Why?
 - Safety (including chemical and radiation exposures)
 - Throughput (including rate, radionuclide and organic concentration, output volumes)
 - Scheduling (including startup and production)
2. How much organic is a problem? Why?
 - Is there currently a limit? Basis?
 - What are the effects of organic feed composition changes? Explain.
3. What are the impacts on:
 - Setup time
 - Compressive strength
 - ANSI 16.1 durability
 - Other
4. Will it require a major change for each case in the design (e.g., tanks, facilities, materials of construction)? Why? Include possible solutions, technological risks, and interim solutions. What are the impacts on hydrogen gas generation?
5. What regulatory issues would exist for the four conditions? Explain.
6. Are there any new issues? Why?
7. What are the interface changes with other unit operations or system functions (e.g. where does the organic go)? Why? How?
8. Does mixing TBP/NPH, including degradation products, with other organics (e.g., chelating agents) cause additional problems? Why? How?
9. What are the benefits of grout compared to other processing (e.g. vitrification)?
10. Discuss potential for immobilized waste needing rework.
11. Discuss waste form failure potential.
12. What are the 1995 equivalent life cycle cost (rough order of magnitude) impacts including:
 - Capital
 - Operation cost
 - Number of facilities

- D&D
 - FTEs (including construction, ops and D&D)
13. What impact is there if separable phase organics are present in other tanks that must be processed? Is the impact volume dependent? Explain.
- Cost
 - Schedule
 - Exposure
14. Describe this subfunction in one to two paragraphs based upon F&R criteria and the engineering functional hierarchy (e.g., process waste [4.2.3, see Attachment 4 for short chart]).

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PROCESS WASTE (4.2.3)
HLW Vitrification

Subfunction Experts: S. L. Lambert
G. E. Stegen
C. N. Wilson

- Conditions:**
- (1) Base Case
 - (2) Separable Phase Organic - Direct feed bypassing TWRS pretreatment processes
 - (3) Organic Originated Ash - Feed from incinerator
 - (4) Separable Phase Organic - Carryover through normal TWRS pretreatment processes

Answer the questions below based on the four conditions.

Note: Unless noted, "Organics" means TBP/NPH and breakdown products (including DBP)

General Information

1. If any question can not be answered, what additional information, testing, cost etc. will be required to obtain the answer?
2. In all cases, provide references, where possible, justification where not.
3. This information will be condensed and formatted to fit into a 5-10 page section on HLW Vitrification. This information will also be fed into other sections, including evaluating four options for removing the C-103 organic layer. Please keep answers as short and clear as possible.
4. Drawings and clean, one line diagrams are encouraged if it helps the overall understanding.
5. Disk copies of all information are needed where possible.

Questions:

1. What problems does it cause? Why?
 - Safety (including chemical and radiation exposures)
 - Throughput (including rate, radionuclide and organic concentration, output volumes)
 - Scheduling (including startup and production)

2. How much organic is a problem? Why?
 - Is there currently a limit? Basis?
3. What will be the immobilized waste oxide loading? Why?
4. Will it require a major change in the design of the subfunction (e.g., tanks, facilities, materials of construction)? Why? Include possible solutions, technological risks, and interim solutions.
5. What regulatory issues would exist for the four conditions? Explain.
6. Are there any new issues? Why?
7. What are the interface changes with other unit operations or system functions (e.g. where does the organic go)? Why? How?
8. Does mixing TBP/NPH, including degradation products, with other organics (e.g., chelating agents) cause additional problems? Why? How?
9. Discuss potential for immobilized waste needing rework.
10. Discuss waste form failure potential.
12. What are the 1995 equivalent life cycle cost (rough order of magnitude) impacts including:
 - Capital
 - Operation cost
 - Number of facilities
 - D&D
 - FTEs (including construction, ops and D&D)
13. What impact is there if separable phase organics are present in other tanks that must be processed? Is the impact volume dependent? Explain.
 - Cost
 - Schedule
 - Exposure
14. Describe this subfunction in one to two paragraphs based upon F&R criteria and the engineering functional hierarchy (e.g., process waste [4.2.3, see Attachment 4 for short chart]).

WASTE PROCESSING (4.2.3)

Separable Phase Processing:

This section addresses possible means for processing the C-103 and potential additional separable phase organics.

Subfunction Experts: J. A. Reddick

- Conditions:**
- (1) Onsite Incineration
 - (2) Process Onsite (PUREX, B Plant)
 - (3) Electrochemical
 - (4) Low Temperature Hydrothermal
 - (5) Solid Sorbents as Part of Disposal Form (e.g., Kitty litter)
 - (6) Solid Sorbents as part of processing on-site (e.g., Activated alumina)
 - (7) Caustic Hydrolysis
 - (8) Other

Answer the questions below based on the four conditions.

Note: Unless noted, "Organics" means TBP/NPH and breakdown products (including DBP).

General Information

1. If any question can not be answered, what additional information, testing, cost etc. will be required to obtain the answer?
2. In all cases, provide references, where possible, justification where not.
3. This information will be condensed and formatted to fit into a 5-10 page section on LLW Vitrification. This information will also be fed into other sections, including evaluating four options for removing the C-103 organic layer. Please keep answers as short and clear as possible.
4. Drawings and clean, one line diagrams are encouraged if it helps the overall understanding.
5. Disk copies of all information are needed where possible.

Questions:

1. What problems does it cause? Why?
 - Safety (including chemical and radiation exposures)
 - Throughput (including rate, radionuclide and organic concentration, output volumes)
 - Scheduling (including startup, production, and TWRS schedule)
2. What technology development is needed? Why? Include possible solutions, technological risks, and interim solutions.
3. What regulatory issues would exist for the four conditions? Explain.
4. What are the interface changes with other unit operations or subfunction functions (e.g. where does the organic go)? Why? How?
5. Does mixing TBP/NPH, including degradation products, with other organics (e.g., other solvents, chelating agents) cause additional problems? Why? How?
6. What will be the final disposal product?
7. What are the 1995 equivalent life cycle cost (rough order of magnitude) impacts including:
 - Capital
 - Operation cost
 - Number of facilities
 - D&D
 - FTEs (including construction, ops and D&D)
8. Describe each subfunction in one to two paragraphs.
9. What impact is there if separable phase organics are present in other tanks that must be processed? Is the impact volume dependent? Explain.
 - Cost
 - Schedule
 - Exposure

DISPOSE WASTE (4.2.4)

Dispose Waste and Tank Closure

Subfunction Experts: G. E. Stegen
J. W. Shade
B. A. Higley
E. H. Randklev

Conditions: (1) Base Case C-103 Closure (Organic skimmed first)
(2) Base Case DST (Organic either skimmed or non present)
(3) Organic in C-103 Waste Residue
(4) Organic in DST Waste Residue

Answer the questions below based on the four conditions.

Note: Unless noted, "Organics" means TBP/NPH and breakdown products (including DBP).

General Information

1. If any question can not be answered, what additional information, testing, cost etc. will be required to obtain the answer?
2. In all cases, provide references, where possible, justification where not.
3. This information will be condensed and formatted to fit into a 5-10 page section on LLW Vitrification. This information will also be fed into other sections, including evaluating four options for removing the C-103 organic layer. Please keep answers as short and clear as possible.
4. Drawings and clean, one line diagrams are encouraged if it helps the overall understanding.
5. Disk copies of all information are needed where possible.

Questions:

1. What problems does it cause? Why?
 - Safety (including chemical and radiation exposures)
 - Scheduling (including startup, duration, and completion of tank closure activities)
 - Closure sampling requirements
2. How much organic is a problem? Why?
 - Is there currently a limit? Basis?

3. Will it require a major change in the closure activities? Why? Include possible solutions, technological risks, and interim solutions.
4. What regulatory issues would exist for the four conditions? Explain.
5. Are there any new issues? Why?
6. What are the interface changes with other unit operations or system functions? Why? How?
7. Does mixing TBP/NPH, including degradation products, with other organics (e.g., chelating agents) cause additional problems? Why? How?
8. Discuss possible tank backfill material impacts.
9. What are the 1995 equivalent life cycle cost (rough order of magnitude) impacts including:
 - Capital
 - Operation cost
 - Number of facilities
 - D&D
 - FTEs (including construction, ops and D&D)
10. What impact is there if separable phase organics are present in other tanks that must be processed? Is the impact volume dependent? Explain.
 - Cost
 - Schedule
 - Exposure
11. Describe this subfunction in one to two paragraphs based upon F&R criteria and the engineering functional hierarchy (e.g., dispose waste [4.2.4, see Attachment 4 for short chart]).

Additional Questions:

Note: These questions are not related to the conditions above.

1. Identify the following for HLW. Provide justification and references.
 - Interim storage cost/volume
 - Shipping cost/volume
 - Burial cost/volume

2. Identify the following for LLW. Provide justification and references.
 - Cost/volume
 - volume/acreage
 - volume/facility
 - cost/facility

3. How would, or could, we dispose of an alternate waste stream? Provide costs where possible. Initially assume 5,000 gallons of separable phase organics. Include impacts of greater quantities.
 - Ash (from on-site incinerator)
 - Organic liquid filtered and treated (e.g., B Plant, PUREX) for offsite processing or sale
 - Organic on solid sorbent

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VOLUME 2

SECTION 3 - HISTORY

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VOLUME 2

Section 3.1

Addendum - History of Separable Phase Organic in the Tank Farms

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3.1 HISTORY OF SEPARABLE PHASE ORGANIC IN THE TANK FARMS

The Hanford Site 200 Areas tank farms have received waste from many onsite facilities and chemical separation processes since 1944 (Anderson 1990; Klem 1990; Agnew 1996). Between 1952 and 1991 separable phase organic was transferred to the tank farms from fuel reprocessing (Plutonium/Uranium Extraction [PUREX], Reduction/Oxidation [REDOX]), uranium recovery (U Plant), waste fractionization (B Plant), semi-works pilot plant (C Plant), and Plutonium Plant (Z Plant) operations. Solvent treatment was an important step in each of the separation processes. Solvent treatment removed contaminants and degradation products that affected fission product decontamination and operational continuity. Except for REDOX operations (Section 3.1.2.2), solvent treatment consisted of washing the organic with an aqueous alkaline solution.

Under ordinary circumstances waste from operations other than PUREX Plant would have been evaporated to remove water and potentially flammable solvents before transfer to the tank farms. Some process upsets occurred that allowed transfer of additional separable phase organic to the tank farms. More information on solvent treatment and process upsets is available in the Hanford Monthly Reports.

The PUREX Plant discharged separable phase organic to the tank farms in the unconcentrated organic wash waste stream. As a result, PUREX Plant may have been the most significant contributor of separable phase organic to the tank farms. The floating organic layer in Tank 241-C-103 is the result of waste discharges from past PUREX Plant operation. Tank farm specifications published just before restart of PUREX Plant in 1983 did not allow for separable phase organic in DSTs.

The sources in the 100, 200, and 300 Areas that discharged waste to the tank farms are described in Sections 3.1, 3.2, and 3.3, respectively. Sampling activities to determine the presence of organic currently stored in the tank farms are described in Section 3.4.

3.1.1 100 Area

Waste from occasional cleaning activities at the N Reactor was shipped via railcar to the tank farms. Volumes were small compared to the waste from processing plants (Section 3.1.2). This waste is not known to have contained separate phase organic, so no further analysis has been conducted.

3.1.2 200 Areas

The 200 Areas contain large-scale processing plants and laboratories, including B Plant (bismuth phosphate and waste fractionization processes), S Plant (REDOX process), PUREX Plant, U Plant (tributyl phosphate [TBP] process), C Plant (Semi-works), T Plant (bismuth phosphate process), UO₂ Plant, and Z Plant (plutonium finishing). The impacts on tank farms from process waste discharges are described in the following sections.

3.1.2.1 B Plant and T Plant (Bismuth Phosphate Process). T Plant and B Plant were the original facilities used to chemically extract plutonium from fuel discharged from Hanford Site reactors. The bismuth phosphate process did not use organic solvents and would not have discharged separate phase organics to the tank farms. T Plant operated from December 1944 through August 1956 and B Plant operated from April 1945 through October 1952.

3.1.2.2 B Plant (Waste Fractionization Process). B Plant was modified in the early 1960s for removal of ^{137}Cs and ^{90}Sr fission products from PUREX and selected REDOX high level stored wastes. The removal of these high heat radionuclides permitted immobilization of waste as a salt cake. The extracted cesium and strontium were purified and encapsulated.

A continuous solvent extraction process was used to remove strontium; ion exchange and precipitation processes were used for cesium removal. Process wastes were not concentrated during current waste processing (1968 to 1971) due to the high level of radioactivity and limitations of the B Plant ventilation system.

The solvent extraction process used a 20 wt% di-2-ethylhexyl phosphoric acid (D2EHPA), 10 wt% TBP, and 70 wt% NPH organic for extraction of strontium from chelated aqueous waste. Strontium extraction processing was started in 1968 and continued until 1978. A continuous alkaline wash was used to remove degradation products from the organic.

Essential material consumption information shows that about 107,000 gal of B Plant organic were used during strontium extraction. Initial estimates suggest that about 41,000 gal of organic were discharged to the SSTs (Klem 1996). The remaining organic (~66,000 gal of mostly NPH) was discharged as vapor components to the process condensate crib and stack gaseous effluent. Historical records and process flowsheet information show that there were no discards of spent process organic to organic cribs.

3.1.2.3 S Plant (REDOX Process). The REDOX process was an improvement over bismuth phosphate processing due to lower costs, improved throughput, recovery of uranium, and increased plutonium recovery. REDOX was a solvent extraction process that used hexone (methyl isobutyl ketone) as the organic phase.

The REDOX process involved countercurrent flows of aqueous solution and organic in solvent extraction columns. Hexone was recovered for reuse via a still, which separated it from accumulated fission products.

The S Plant operated from January 1952 to December 1966. Selected Hanford Works Monthly reports indicate that hexone was unintentionally lost through the waste system. Examples are listed below.

- The S Plant reports solvent losses averaging 350 gal/day during the month of April 1952, saying it "gets into the waste system... D-5 is overloaded... Recovery in D-5 is impaired when the unit is flooded." The S Plant also reported troubles with organic emulsions and the presence of an oily film on

the hexone, due to degradation products. How much of the losses went to tank farms was not stated (HW-24321, p. 8).

- The Hanford Works Monthly Report for April 1952 confirms the average solvent loss of 350 gal/day during the month and states that “high and low losses are experienced periodically, related to waste cell operation” (HW-24337). The solvent emulsion was suspected to result from a chemical (tricresyl phosphate) in the tygon tank lining of an S Plant aluminum nitrate nonahydrate (ANN) storage vessel. The S Plant processed 75 tons of uranium during the month. Solvent was within specifications for MIBK [hexone], mesityl oxide, isopropyl diketone, 1,1-dinitroisobutane, oxidizing normality, and pH. The plant suspected the addition of ANN to the hexone created the non-oily residue and the organic distillation column removed about 90% of it.
- In May 1952, S Plant processed 79 tons of uranium and there was no bypass of the hexone still (HW-24605).
- In June 1952, S Plant was pushing its capacity, estimating up to a maximum of 4 tons per day. Approximately 44.8 tons of uranium were processed. Solvent losses averaged 200 gal per day for the month (HW-24928).
- In July 1952, S Plant operated 76.7% of the time, and processed 3.16 tons of uranium per operating day for a total of 77.2 tons. Hexone losses averaged 270 gal per day. 8,000 gal of new hexone were brought into the plant. Also, a waste condensate stripper was upset when “hexone entered the salt waste receiver via the IAW” (HW-25193).

Based on these monthly reports, S Plant appears to have added some separate phase hexone to the tank farms. In the nearly 30 years since the plant ended operations, separate phase hexone, which is volatile, would have evaporated. Some of it may have been soluble and would have degraded in the waste tanks.

Under normal operating circumstances the plant appears to have distilled the hexone, so that only dissolved organic would have exited with the waste to the tank farms. Process upsets did, however, apparently contribute some hexone to the waste stream. Quantifying the amount would require a material balance over the S Plant flowsheet to determine the normal distribution of hexone losses and an examination of all of the chemical processing department's monthly reports from 1952 through 1966. The monthly reports identify periods of abnormal operation and tend to quantify total monthly solvent losses.

3.1.2.4 PUREX Plant. The PUREX Plant began operations in 1955 and began discharging accumulated organic along with high-level (boiling) waste soon after. Engineering records from 1955 describe the expectations that organic solvent would be discharged to the tank farms with the waste.

While the appreciable quantities of PUREX Plant solvent will be present in the PUREX Plant wastes routed to the [tank] farm, virtually all of the diluent and a large fraction of the TBP will be removed by steam distillation while boiling, and the remaining quantities of organic material will be either accumulated as a separate layer at the top of the mass at a relatively low temperature or diffused through the mass in very low concentrations (Tomlinson 1955).

The practice of discharging organic along with the PUREX Plant high-level waste was occasionally modified to separate the organic from the high-level waste because the organic, which was distilled from the boiling waste in Tank 241-A-103, was blamed for restricting the percolation rate in the tank farm condensate crib. Segregated organic was temporarily routed to the C Tank Farm for storage in September 1956. The PUREX Plant operations were later modified to recycle accumulated organic to reduce separate phase organic discharges. By the time PUREX Plant began its last operational period in 1983, the plant did not expect to discharge organic in a separate layer. Tank farm specifications were revised in 1983 to permit PUREX Plant separable phase organic to be added to the DSTs (Harris 1994).

An estimated 657,100 gal of organic was discharged to the tank farms over the operation lifetime of the PUREX Plant from 1955 through 1991 (Sederburg and Reddick 1994). A summary of the distribution of the organic from 1955 through 1991 is shown in Table 3.1-1. Of the 657,100 gal of organic transferred to tank farms from PUREX Plant, 655,000 gal were estimated to be from organic wash waste and 2,000 gal were estimated to be from high-level waste. The organic wash waste contained approximately 350 times more organic per gallon than high-level waste. For the calculations to determine the amount of organic discharged to each tank from 1956 to 1969, all of the organic was assumed to be distributed via the organic wash waste. For the tables and calculations in the following sections, the annual estimated organic discharged from PUREX Plant is from *TBP and Diluent Mass Balances in the PUREX Plant at Hanford, 1955-1991* (Sederburg and Reddick 1994); the annual estimated volumes of PUREX Plant organic bearing waste (organic wash waste) and high-level waste were assembled from *A History of the 200 Area Tank Farms* (Anderson 1990), which contains quarterly summaries of PUREX Plant transfer records.

The organic discharged to tank farms consisted of TBP, TBP degradation products, and three diluents (Shell E-2342, Soltrol-170, and NPH). At startup, PUREX Plant organic consisted of 30% by volume TBP in Shell E-2342. From September 1961 to February 1966, PUREX Plant organic consisted of 30% by volume TBP in Soltrol-170 and from February 1966 to 1991, PUREX Plant organic contained 30% by volume TBP in NPH.

The properties of TBP and its degradation products dibutyl phosphate (DBP) and monobutyl phosphate (MBP) are listed in Table 3.1-2. The properties of Shell E-2342, Soltrol-170, and NPH are listed in Table 3.1-3. Shell E-2342 contained cyclic paraffins, Soltrol-170 contained highly branched alkanes, and NPH contained normal (straight chain) alkanes. A summary of the organic sent each year to the tank farms is presented in Table 3.1-4; the amount of each type of organic sent to the tank farms is summarized in Table 3.1-5. A summary of waste tanks that received separable organic directly from the PUREX Plant is given in Table 3.1-6.

Table 3.1-1. Estimate of Total Organic Discharged to the A, AX, and C Tank Farms from 1955 through 1969. (sheet 1 of 2)

Year	Total Organic (gal)	Unknown (gal)	Tank A-101 (gal)	Tank A-102 (gal)	Tank A-103 (gal)	Tank A-104 (gal)	Tank A-105 (gal)	Tank A-106 (gal)	Tank AX-101 (gal)
1955	5,199	5,199	0	0	0	0	0	0	0
1956	32,458	0	7,201	8,577	13,078	0	0	0	0
1957	44,332	0	24,447	4,165	14,754	0	0	0	0
1958	42,829	0	12,670	19,936	9,983	240	0	0	0
1959	34,400	0	8,048	18,231	4,646	3,475	0	0	0
1960	40,980	0	1,920	12,755	2,703	23,400	0	282	0
1961	63,202	0	11,624	6,401	0	30,146	0	15,031	0
1962	46,369	0	0	6,560	0	35,733	0	4,076	0
1963	30,238	0	10,929	3,476	0	11,017	0	4,816	0
1964	32,148	0	9,566	0	0	15,173	0	7,379	0
1965	49,421	0	0	0	0	7,988	0	23,077	2,839
1966	33,793	0	3,496	0	2,706	7,031	0	7,189	533
1967	24,582	0	3,002	0	806	4,925	0	5,107	8317
1968	15,173	0	232	0	0	877	0	1,283	?
1969	15,909	0	0	0	0	0	0	0	0
1970	37,871	0	0	0	0	0	0	0	0
1971	26,242	0	0	0	0	0	0	0	0
1972	9,722	0	0	0	0	0	0	0	0
1973	0	0	0	0	0	0	0	0	0
1974	0	0	0	0	0	0	0	0	0
1975	0	0	0	0	0	0	0	0	0
1976	0	0	0	0	0	0	0	0	0
1977	0	0	0	0	0	0	0	0	0
1978	0	0	0	0	0	0	0	0	0
1979	216	216	0	0	0	0	0	0	0
1980	0	0	0	0	0	0	0	0	0
1981	0	0	0	0	0	0	0	0	0
1982	421	0	0	0	0	0	0	0	0
1983	11,389	0	0	0	0	0	0	0	0
1984	19,240	0	0	0	0	0	0	0	0
1985	12,827	0	0	0	0	0	0	0	0
1986	10,309	0	0	0	0	0	0	0	0
1987	8,470	0	0	0	0	0	0	0	0
1988	7,729	0	0	0	0	0	0	0	0
1989	0	0	0	0	0	0	0	0	0
1990	1,391	0	0	0	0	0	0	0	0
1991	245	0	0	0	0	0	0	0	0
Total	657,086	5,415	93,165	80,101	48,676	140,015	0	68,160	11,589

Table 3.1-1. Estimate of Total Organic Discharged to the A, AX, and C Tank Farms from 1955 through 1969. (sheet 2 of 2)

Year	Tank AX-102 (gal)	Tank AX-103 (gal)	Tank AX-104 (gal)	Tank C-101 (gal)	Tank C-102 (gal)	Tank C-104 (gal)	Tank C-110 (gal)	Tank C-111 (gal)	AW Tank Farm (gal)
1955	0	0	0	0	0	0	0	0	0
1956	0	0	0	0	0	0	3,005	597	0
1957	0	0	0	0	0	0	966	0	0
1958	0	0	0	0	0	0	0	0	0
1959	0	0	0	0	0	0	0	0	0
1960	0	0	0	0	0	0	0	0	0
1961	0	0	0	0	0	0	0	0	0
1962	0	0	0	0	0	0	0	0	0
1963	0	0	0	0	0	0	0	0	0
1964	0	0	0	0	0	0	0	0	0
1965	0	15,507	0	0	0	0	0	0	0
1966	6,735	6,103	0	0	0	0	0	0	0
1967	1,131	1,274	0	0	0	0	0	0	0
1968	3,882	1,184	17	3,849	3,849	2,584	0	0	0
1969	0	0	0	0	13,315	37,871	0	0	0
1970	0	0	0	0	0	26,242	0	0	0
1971	0	0	0	0	0	9,722	0	0	0
1972	0	0	0	0	0	0	0	0	0
1973	0	0	0	0	0	0	0	0	0
1974	0	0	0	0	0	0	0	0	0
1975	0	0	0	0	0	0	0	0	0
1976	0	0	0	0	0	0	0	0	0
1977	0	0	0	0	0	0	0	0	0
1978	0	0	0	0	0	0	0	0	0
1979	0	0	0	0	0	0	0	0	0
1980	0	0	0	0	0	0	0	0	0
1981	0	0	0	0	0	0	0	0	421
1982	0	0	0	0	0	0	0	0	11,389
1983	0	0	0	0	0	0	0	0	19,240
1984	0	0	0	0	0	0	0	0	12,827
1985	0	0	0	0	0	0	0	0	10,309
1986	0	0	0	0	0	0	0	0	8,470
1987	0	0	0	0	0	0	0	0	7,729
1988	0	0	0	0	0	0	0	0	0
1989	0	0	0	0	0	0	0	0	1,391
1990	0	0	0	0	0	0	0	0	248
1991	0	0	0	0	0	0	0	0	0
Total	11,748	24,068	17	3,849	17,164	76,429	3,971	597	72,022

Table 3.1-2. Properties of TBP, DBP, and MBP.

	Tributyl Phosphate (TBP)	Dibutyl Phosphate (DBP)	Monobutyl Phosphate (MBP)
Formula	$(n-C_4H_9O)_3PO$	$(n-C_4H_9O)_2(OH)PO$	$(n-C_4H_9O)(OH)_2PO$
Molecular weight	266.32	210.2	154.1
Color	colorless	pale yellow	colorless
Odor	mildly sweet	--	--
Density (g/mL at 25 °C)	0.9730	1.065	1.220
Refractive index (n 20/D)	1.4245	1.4260	1.419
Refractive index (n 25/D)	1.4226	1.4227	1.429
Melting point (°C)	< -80	--	--
Specific heat (cal/g°C at 25 °C)	0.41	--	--
Latent heat of vaporization (cal/g-mole)	14,680	--	11,400
Boiling point (°C at 760 mm Hg pressure)	289	190 (decomposition temperature)	105 (decomposition temperature)
Boiling point (°C at 25 mm Hg pressure)	177	--	--
Boiling point (°C at 1 mm Hg pressure)	121	--	--
Vapor pressure (mm Hg at 100 °C)	ca. 1.0	--	--
Vapor pressure (mm Hg at 25 °C)	0.006	--	--
Flash point (°F, tag closed cup)	295 (146 °C)	--	--
Solubility in water (g/L at 25 °C)	0.39	18	--

Table 3.1-3. Properties of Shell E-2342, Soltrol-170, and NPH.

	Shell E-2342	Soltrol-170	NPH
Period of Use	1955 to 1961	1961 to 1966	1966 to 1989
Density at 25 °C (g/mL)	0.801	0.773	0.76 (max)
Viscosity (cP at 25 °C)	1.7	2.3	1.8
Boiling range (°C)	-	208-239	174-252
Aromatic content	0.1 vol%	Nil	0.2 wt% max as 1,2,3,4 tetrahydronaphthalene
Naphthalene content	about 80 vol%	Nil	-
Iodine number	-	<1.1 bromine number	0.1 wt% max olefins as wt% 1-tetradecene
Solubility in water	<0.004 g/L at 25 °C and 50 °C	very slight	<0.005 g/L between 25 °C and 50 °C
Composition	about 80 vol% 5 and 6 carbon cycloparaffins (cyclopentane, cyclohexane)	mixture of highly branched aliphatic hydrocarbons	mixture of C10 to C14 straight chain (normal) aliphatic hydrocarbons

Notes:

Properties are taken from Sederburg and Reddick (1994).

NPH is more resistant than TBP to chemical and radiolytic degradation.

Shell E-2342 and Soltrol-170 were more susceptible to chemical and radiolytic degradation than NPH.

Table 3.1-4. Yearly Estimate of PUREX Plant Organic Sent to the Tank Farms.

Year	TBP (gal)	TBP-dp (gal)	Shell E-2342 (gal)	Soltrol-170 (gal)	NPH (gal)	Total Organic (gal)	Vol% of Total Discharge	Total Organic (tank inches)	Monthly Average (tank inches)
1955	1,613	31	3,552			5,199		1.89	0.16
1956	10,086	195	22,178			32,458		11.80	0.98
1957	13,775	266	30,291			44,332		16.12	1.34
1958	13,308	257	29,264			42,829		15.57	1.30
1959	10,689	206	23,505			34,400		12.51	1.04
1960	12,734	246	28,000			40,979		14.90	1.24
1961	19,639	379	31,200	11,984		63,202		22.98	1.92
1962	14,408	278		31,682		46,369		16.86	1.41
1963	9,155	215		20,869		30,239		11.00	0.92
1964	9,733	228		22,186		32,147		11.69	0.97
1965	14,329	336		34,757		49,421		17.97	1.50
1966	13,192	309		2,689	17,601	33,791		12.29	1.02
1967	7,197	169			17,195	24,561		8.93	0.74
1968	6,233	146			8,792	15,171		5.52	0.46
Subtotal 1955-1968	156,094	3,260	167,988	124,168	43,587	495,098	75.3%	180.04	
1969	4,778	112			11,019	15,909		5.79	0.48
1970	7,363	1,835			28,673	37,871		13.77	1.15
1971	6,018	1,499			18,725	26,242		9.54	0.80
1972	2,305	574			6,844	9,722		3.54	0.29
1973	0	0			0	0		0.00	0.00
4	0	0			0	0		0.00	0.00
5	0	0			0	0		0.00	0.00
1976	0	0			0	0		0.00	0.00
1977	0	0			0	0		0.00	0.00
1978	0	0			0	0		0.00	0.00
1979	0	0			216	216		0.08	0.01
1980	0	0			0	0		0.00	0.00
1981	0	0			0	0		0.00	0.00
Subtotal 1969-1981	20,464	4,020	0	0	65,477	89,961	13.7%	32.71	
1982	272	149			0	421		0.15	0.01
1983	1,493	834			9,062	11,389		4.14	0.35
1984	3,905	2,176			13,159	19,240		7.00	0.58
1985	2,348	1,309			9,169	12,827		4.66	0.39
1986	1,762	983			7,564	10,309		3.75	0.31
1987	1,306	729			6,434	8,470		3.08	0.26
1988	1,149	642			5,938	7,729		2.81	0.23
1989	0	0			0	0		0.00	0.00
1990	68	38			1,285	1,391		0.51	0.04
1991	0	0			246	246		0.09	0.01
Subtotal 1982-1991	12,302	6,861	0	0	52,857	72,021	11.0%	26.19	
Total	188,860	14,141	167,988	124,168	161,922	657,080	100.0%	238.94	

Notes:

TBP-dp denotes TBP degradation products.

Data for 1955 to 1964 are from HAPO/Chemical Processing Department Monthly Reports.

or 1965 through 1991 are from Essential Material Consumption Records.

estimate is based on Sederburg and Reddick (1994).

Sections 3.1.2.4.1 through 3.1.2.4.3 describe discharges of PUREX Plant waste to the tank farms from 1955 through 1991. The amount of organic present in the waste was estimated as described in each of the sections. Between 1956 and 1969 the organic waste was combined with neutralized current acid waste and transferred with the high-level boiling waste to self-concentrating or self-boiling tanks. After 1969, the organic wash waste was sent to a low-level waste tank in the C Tank Farm (Anderson 1990). PUREX Plant was shut down in 1972; when it was restarted in 1983, the organic wash waste was transferred to double-shell tanks.

Table 3.1-5. Estimate of Each Organic Sent to the Tank Farms.

Organic	Time Frame	Estimate of Organic Sent to Tank Farms (gal)
TBP	1955-1991	188,860
TBP degradation products*	1955-1991	14,141
Shell E-2342	1955-1961	167,988
Soltrol-170	1961-1966	124,168
NPH	1966-1991	161,922
Total		657,097

* Identified degradation products of TBP generated in the PUREX Plant are DBP, MBP, butanol, and phosphoric acid.

The estimates of organic that each tank received from PUREX Plant do not represent the total amount of organic that any one tank may have stored. Many intertank transfers occurred over the years, primarily between the A, AX, and C Tank Farms. These transfers add to the complexity of determining the fate and distribution of organic in the tank farms. Transfer information from the *History of the 200 Area Tank Farms* (Anderson 1990) shows that the SST organic waste receivers experienced many intertank transfers. The intertank transfers during the 1950s and 1960s were mainly among the A, AX, and C Tank Farms. Several organic waste transfers went to B, BX, BY, SX, TX, and TY Tank Farm from Tanks 241-C-101 and 241-C-102 beginning 1968. During the 1950s and 1960s A and AX tank farms stored self-boiling waste and received frequent organic wash waste for storage and destruction of soluble and entrained organic. The combination of time, boiling temperature, air-lift circulation mixing, alkalinity, solids/cation catalysts, and high radiation source term reduced the separable phase organic that was added to the A and AX Tank Farm tanks. Some organic is believed to have polymerized based on Schulz and Navratil (1984). Black tarry solids or "black oil" may have formed from TBP and/or the diluents. Further study is needed. Some material could have been transferred to other SSTs in supernate and/or sludge wash liquids.

Separable phase organic waste that was added to C Tank Farm and then transferred to other SSTs could be expected to have survived destruction due to unfavorable conditions for

Table 3.1-6. Summary of Waste Tanks That Received Organic from PUREX Plant.

Tank	Volume of Organic ² (gal)	Time Period	Organic Disposition	Year Shelves Retrieved
A-101 ¹	93,200	1956 - 1968	Degradation, Evaporation, Waste Transfer	1975 - 1976
A-102 ¹	80,100	1956 - 1963	Degradation, Evaporation, Waste Transfer	1972 - 1976
A-103 ¹	48,700	1956 - 1967	Degradation, Evaporation, Waste Transfer	1974 - 1976
A-104 ¹	140,000	1958 - 1968	Degradation, Evaporation, Waste Transfer	1974 - 1975
A-106 ¹	68,200	1960 - 1968	Degradation, Evaporation, Waste Transfer	1970 - 1973
AW-101 ²		1982 - 1991	Degradation, Evaporation, Waste Transfer	None
AW-104 ²	72,000	1982 - 1991	Degradation, Evaporation, Waste Transfer	None
AX-101 ¹	11,700	1965 - 1967	Degradation, Evaporation, Waste Transfer	1975 - 1976
AX-102 ¹	11,700	1966 - 1967	Degradation, Evaporation, Waste Transfer	1976
AX-103 ¹	24,100	1965 - 1968	Degradation, Evaporation, Waste Transfer	1976 - 1977
AX-104 ¹	20	1968	Degradation, Evaporation, Waste Transfer	1977 - 1978
C-101	3,800	1968	Evaporation, Waste Transfer,	1982 - 1953
C-102	17,200	1968 - 1969	Evaporation, Waste Transfer	1953
C-104	76,400	1969 - 1972	Evaporation, Waste Transfer	None
C-110	4,000	1956 - 1957	Evaporation, Waste Transfer	None
C-111	600	1956	Evaporation, Waste Transfer	None
Unknown	5,400	1955	-	-
Total	657,100	1955 - 1991	-	-

Notes:

- 1 These tanks stored self-concentrating waste and received intermittent organic wash waste during the 1950s and 1960s.
- 2 Organic sent to AW tanks cannot be positively identified due to lack of transfer records. The only certainty is that this organic was sent to DSTs.
- 3 Volume of organic based on estimated average of 0.0176 gal organic/gal of carbonate waste plus organic wash waste streams for SSTs.

good chemical and radiolytic degradation (e.g., poor mixing of the light phase organic and heavy phase aqueous liquids, low temperature and radiation source term history, unfavorable alkalinity and/or insufficient waste components that appear to accelerate TBP destruction). It is difficult to identify waste tanks that currently contain significant residual process solvents based on waste process history and transfer records.

Recent vapor space sampling results can be used to identify SSTs that may contain separable phase organic. An NPH mole fraction value was determined for the liquid organic phase in the tank using Raoult's Law, available vapor space sampling information, head space temperature of the tank, and pure component vapor pressure (Bratzel 1995, and personal communication with J.L. Huckaby (PNNL) January 1996).

An NPH mole fraction of ≥ 0.1 was used as criteria to identify SSTs that may contain significant separable phase organic and impact TWRS processing. Tanks 241-BX-104, 241-BY-108, 241-C-102, 241-C-103, 241-T-111 and 241-TY-103 exceeded the mole fraction criteria (Table 3.1-7). They include tanks identified by tank safety as significant risk from accidental solvent fires (Grigsby and Postma 1996). A volume estimate of the NPH-TBP organic could not be developed from available vapor sample information.

Tank characterization information was used to project an organic inventory for several tanks. The Tank 241-C-103 inventory is about 17,300 L (4,570 gal) of NPH TBP, Tank 241-BY-108 about 420 L (110 gal) of NPH with trace TBP, and Tank 241-C-204 about 5,000 L (5,600 kg) of TBP with trace NPH. Similar information is available for 9 other SSTs and 9 DSTs. The current estimated organic inventory is about 28,400 L (7,500 gal) in 21 tanks. This organic exists as a separate floating layer, solubilized in the aqueous supernatant liquid and/or combined with the salt cake and sludge solids based on information to date.

The above information was used to develop a preliminary estimate of the residual process organic that may remain in the DSTs and SSTs. The estimate is needed for initial sizing of an aqueous-organic decanter system for waste pretreatment (Klem 1996). A projected volume of 87,000 L (23,000 gal) was the average total value from several projected estimates each having comparable levels of uncertainty. The estimates ranged from 34,000 L (9,000 gal) to 148,000 L (39,000 gal).

3.1.2.4.1 Discharges to Tank Farms - 1955 through 1969. Between startup and 1969 PUREX Plant discharged accumulated organic along with the high-level (boiling) waste. The practice was occasionally modified to divert separated organic from the high-level waste because organic that was distilled from Tank 241-A-103 (boiling) was blamed for causing an emulsion problem that restricted the percolation rate (organic oxidation products and fungus growth) in the Tank Farm A-8 condensate crib. In August 1956, segregated organic was routed, at least temporarily, to Tank 241-C-110 for storage (HW-45115). According to the Chemical Processing Department Monthly Report for October 1957 (HW-53499), organic treatment aqueous waste was routed to Tank 241-A-101 "to avoid accumulation in any single tank." The operating philosophy was to distribute organic-bearing waste among several tanks, a practice that would enhance distillation and degradation of organic.

Table 3.1-7. Summary of Available Information on Single-Shell Tanks Potentially Containing Separable Phase Organic. (sheet 1 of 2)

Tank	Bases for Separable Phase Organic ¹ in Tank		
	NPH Detected in Vapor Sample of Tank Head Space	Documentation	Mole fraction NPH in liquid organic waste ⁶
TY-103	Yes	OWW added 1968 ³ , 242-T bottoms	Max 0.510
C-103	Yes	OWW added, 242-A bottoms, ~ 17,300 L TBP-NPH in 1995	Max 0.489
T-111	Yes	-	Max 0.221
BX-104	Yes	OWW added ³	Max 0.144
BY-108	Yes	ITS bottoms and recycle ³ , ~ 420 L NPH estimated from recent core sample	Max 0.141
C-102	Yes	OWW added 1968 ³ , ~ 136,100 L TBP-NPH in 1972 ⁵	Max 0.132
BY-107	Yes	ITS bottoms and recycle	Max 0.099
B-103	Yes	OWW added 1969 ³	Max 0.051
C-110	Yes	OWW added 1956-7 ³ , ~ 15 L TBP estimated from recent core sample	Max 0.026
C-101	Yes	OWW added 1968 ³	Max 0.013
TY-104	Yes	OWW added 1970 ³	Max 0.013
BX-107	Yes	~ 10 L TBP based on recent core sample	Max 0.013
BY-103	Yes	OWW added 1969 ³ , ITS bottoms	Max 0.010
BY-104	Yes	ITS & 242-A bottoms	Max 0.009
BY-110	Yes	242-A bottoms ³	Max 0.008
A-101	Yes	OWW added ³ , 242-A & S bottoms	Max 0.003
BY-105	Yes	ITS bottoms and recycle ⁶	Max 0.003
T-107	Yes	242-T bottoms, ~ 60 L NPH from recent core sample	Max 0.003
AX-102	Yes	OWW added ³ , 242-A bottoms	Max 0.002
BY-106	Yes	ITS bottoms and recycle ³	Max 0.001
BY-112	Yes	70% TBP 30% NPH in 1968 sample ² , ITS bottoms and recycle ³	Max 0.001
TX-118	Yes	OWW added ³	Max 0.001
U-110	Yes	-	Max 0.001
BY-111	Yes	OWW added 1957, ITS bottoms and recycle ³	0.000
B-111	No Vapor Sample	OWW added ³ , ~ 20 L TBP estimated from recent core sample	-
C-106	Yes	~ 70 L TBP-NPH estimated from recent core sample	Not Available
C-107	Yes	-	0.000

Table 3.1-7. Summary of Available Information on Single-Shell Tanks Potentially Containing Separable Phase Organic. (sheet 2 of 2)

Tank	Bases for Separable Phase Organic ¹ in Tank		
	NPH Detected in Vapor Sample of Tank Head Space	Documentation	Mole fraction NPH in liquid organic waste ²
C-108	Yes	OWW added 1970 ³	0.000
C-109	Yes	-	0.000
C-111	Yes	OWW added 1956 ³	0.000
C-112	Yes	OWW added 1975 ³ , ~410 L TBP-NPH estimated from recent core sample	0.000
C-204	Yes	~5,800 L TBP estimated from recent core sample ⁴	Not Available
S-102	Yes	OWW added ³ , 242-S evap. bottoms	0.000
S-104	No Vapor Sample	~1,150 L NPH estimated from recent core sample	-
S-111	Yes	OWW added ³ , 242-S bottoms and recycle	0.000
T-104	Taken/Not Yet Analyzed	OWW added ³ , ~3,300 L NPH estimated from recent core sample	Not Available
TX-105	Yes	OWW added 1971, 242-T bottoms and recycle ³	0.000
TY-101	Yes	-	0.000
U-103	Yes	OWW added, 242-S bottoms ³	0.000
U-105	Yes	OWW added, 242-S & T bottoms and recycle ³	0.000
U-106	Yes	OWW added, 242-S bottoms and recycle ³	0.000
U-107	Yes	OWW added ³ , 242-S bottoms	0.000
U-203	None detected	-	0.000
U-204	None detected	-	0.000

Notes:

- 1 A NPH mole fr ≥ 0.1 in the liquid organic waste is considered significant.
- 2 Based on information in *Characterization of the Organic Material in the 112 BY Tank* (Schulz 1968).
- 3 Based on information in *A History of the 200 Area Tank Farms*, (Anderson 1990) or *History of Organic Carbon in Hanford HLW Tanks: HDW Model Rev 3* (Agnew 1996)
- 4 Personal communication with J. A. Campbell (PNNL) January 1996. Assumes sludge sample is valid and uniform distribution of TBP in sludge.
- 5 Based on information in *Liquid Organic Waste Collection and Disposal* (Hall 1972a)
- 6 Based on vapor sample results and Raoult's Law.

The A-24 condensate crib replaced the A-8 condensate crib in January 1958. In September 1958 the A-24 crib was sampled, yielding a "black, tarry substance" thought to be the condensation products of diluent (Shell E-2342) due to high temperature and radiation. Shell E-2342 contained naphthenes (cyclic paraffins). Recent samples from Tank 241-C-106 sludge also indicate a black oily substance. No correlation between these samples has been found.

Through the end of 1968, approximately 495,000 gal of organic were discharged to the tank farms. The greatest rate of organic discharges to the tank farms occurred in 1961 (Table 3.1-4). Tanks that received both high-temperature self-concentrating waste and organic waste directly from PUREX Plant through the end of 1968 include Tanks 241-A-101, 241-A-102, 241-A-103, 241-A-104, 241-A-106, 241-AX-101, 241-AX-102, 241-AX-103, and 241-AX-104. The amount of organic wash waste and high-level waste that was transferred to each tank from 1956 through 1969 is presented in Tables 3.1-8 and 3.1-9, respectively. The estimate of total organic each tank routed to organic wash waste and/or high-level waste from 1956 through 1969 is presented in Table 3.1-1.

Most of the organic waste generated from 1955 through 1968 was deliberately distilled from the self-concentrating waste. After distillation, alkaline-soluble products of degraded organic remained in the tanks.

Table 3.1-8 shows that there were few transfers of organic to the tank farms between 1956 and 1961 that were specifically called out as organic waste. Anderson (1990) states that organic waste was combined with high-level waste (which was discharged to the A and AX Tank Farms) until 1969. Organic waste volumes were probably combined with the high-level waste volumes for reporting purposes, since all of the records indicate that the organic went to the high-level waste tanks. It appears the organic was called out as a separate shipment when it wasn't sent to the primary high-level waste receiver. This happened six times between 1956 and 1961; there were three transfers to C Tank Farm (Chemical Processing Department Monthly Reports indicated that organic wash waste was occasionally sent to C Tank Farm), one transfer to Tank 241-A-102 in a year that it did not receive high-level waste (1957), and two transfers to Tank 241-A-103 in 1957 and 1958. In the case of the last two transfers, it appears that the waste volume notes in Anderson (1990) were more detailed than earlier notations.

The estimate of total organic discharged during each year of PUREX Plant operations (Sederburg and Reddick 1994) was used to calculate the amount of organic that was discharged to each tank with the organic wash waste and high-level waste between 1956 and 1969 (Table 3.1-1), with the following assumptions.

- For the years 1959 through 1961, the distribution of organic followed the distribution of high-level waste, except in the six cases where organic wash waste was called out separately.
- In the six cases during 1956 through 1961 where the organic wash waste discharges were called out separately, the amount of organic present in the

Table 3.1-8. Organic Wash Waste Discharged to the A, AX, and C Tank Farms from 1955 through 1969. (sheet 1 of 2)

Year	Total Organic Wash Waste (gal)*	Total Organic Wash Waste (gal)	Tank A-101 (gal)	Tank A-102 (gal)	Tank A-103 (gal)	Tank A-104 (gal)	Tank A-105 (gal)	Tank A-106 (gal)	Tank AX-101 (gal)
1955	5,199	0	0	0	0	0	0	0	0
1956	32,458	205,000	0	0	0	0	0	0	0
1957	44,332	384,000	0	237,000	92,000	0	0	0	0
1958	42,829	115,000	0	0	115,000	0	0	0	0
1959	34,400	0	0	0	0	0	0	0	0
1960	40,979	0	0	0	0	0	0	0	0
1961	63,202	0	0	0	0	0	0	0	0
1962	46,369	2,389,000	0	338,000	0	1,841,000	0	210,000	0
1963	30,239	2,053,000	742,000	236,000	0	748,000	0	327,000	0
1964	32,147	1,856,000	554,000	0	0	876,000	0	426,000	0
1965	48,421	1,619,000	0	0	0	262,000	0	756,000	93,000
1966	33,791	1,711,000	177,000	0	137,000	356,000	0	364,000	27,000
1967	24,561	1,890,000	231,000	0	62,000	379,000	0	393,000	640,000
1968	15,171	1,833,000	28,000	0	0	106,000	0	155,000	?
1969	15,909	0	0	0	0	0	0	0	0
Total	511,007	14,055,000	1,732,000	811,000	406,000	4,568,000	0	2,631,000	760,000

Table 3.1-8. Organic Wash Waste Discharged to the A, AX, and C Tank Farms from 1955 through 1969. (sheet 2 of 2)

Year	Tank AX-102 (gal)	Tank AX-103 (gal)	Tank AX-104 (gal)	Tank C-101 (gal)	Tank C-102 (gal)	Tank C-104 (gal)	Tank C-110 (gal)	Tank C-111 (gal)
1955	0	0	0	0	0	0	0	0
1956	0	0	0	0	0	0	171,000	34,000
1957	0	0	0	0	0	0	55,000	0
1958	0	0	0	0	0	0	0	0
1959	0	0	0	0	0	0	0	0
1960	0	0	0	0	0	0	0	0
1961	0	0	0	0	0	0	0	0
1962	0	0	0	0	0	0	0	0
1963	0	0	0	0	0	0	0	0
1964	0	0	0	0	0	0	0	0
1965	0	508,000	0	0	0	0	0	0
1966	341,000	309,000	0	0	0	0	0	0
1967	87,000	98,000	0	0	0	0	0	0
1968	469,000	143,000	2,000	465,000	465,000	0	0	0
1969	0	0	0	0	?	?	0	0
Total	897,000	1,058,000	2,000	465,000	465,000	0	226,000	34,000

* Annual estimate of total organic discharged to the tank farms is from Sederburg and Reddick (1994)

Table 3.1-9. High-Level Waste Discharged to the A, AX, and C Tank Farms from 1955 through 1969. (sheet 1 of 2)

Year	Total Organic (gal)*	Total High-Level Waste (gal)	Tank A-101 (gal)	Tank A-102 (gal)	Tank A-103 (gal)	Tank A-104 (gal)	Tank A-105 (gal)	Tank A-106 (gal)	Tank AX-101 (gal)
1955	5,199	0	0	0	0	0	0	0	0
1956	32,458	1,699,000	424,000	505,000	770,000	0	0	0	0
1957	44,332	2,057,000	1,338,000	0	719,000	0	0	0	0
1958	42,829	3,398,000	1,055,000	1,660,000	663,000	20,000	0	0	0
1959	34,400	4,287,000	1,003,000	2,272,000	579,000	433,000	0	0	0
1960	40,979	6,702,000	314,000	2,086,000	442,000	3,827,000	0	33,000	0
1961	63,202	4,453,000	819,000	451,000	0	2,124,000	0	1,059,000	0
1962	46,369	2,458,000	0	0	0	0	0	2,458,000	0
1963	30,239	1,517,000	0	0	0	0	1,365,000	152,000	0
1964	32,147	1,398,000	0	0	0	0	1,398,000	0	0
1965	49,421	1,557,000	267,000	0	0	0	0	0	0
1966	33,791	1,449,000	70,000	0	0	93,000	0	137,000	0
1967	24,561	2,432,000	0	0	0	0	0	0	925,000
1968	15,171	453,000	0	0	0	0	0	0	196,000
1969	15,909	164,000	0	0	0	0	0	0	3,000
Total	511,007	34,024,000	5,290,000	6,974,000	3,173,000	6,497,000	2,763,000	3,839,000	1,124,000

Table 3.1-9. High-Level Waste Discharged to the A, AX, and C Tank Farms from 1955 through 1969. (sheet 2 of 2)

Year	Tank AX-102 (gal)	Tank AX-103 (gal)	Tank AX-104 (gal)	Tank C-101 (gal)	Tank C-102 (gal)	Tank C-104 (gal)	Tank C-110 (gal)	Tank C-111 (gal)
1955	0	0	0	0	0	0	0	0
1956	0	0	0	0	0	0	0	0
1957	0	0	0	0	0	0	0	0
1958	0	0	0	0	0	0	0	0
1959	0	0	0	0	0	0	0	0
1960	0	0	0	0	0	0	0	0
1961	0	0	0	0	0	0	0	0
1962	0	0	0	0	0	0	0	0
1963	0	0	0	0	0	0	0	0
1964	0	0	0	0	0	0	0	0
1965	0	1,290,000	0	0	0	0	0	0
1966	0	687,000	462,000	0	0	0	0	0
1967	0	0	1,507,000	0	0	0	0	0
1968	0	4,000	253,000	0	0	0	0	0
1969	76,000	45,000	40,000	0	0	0	0	0
Total	76,000	2,026,000	2,262,000	0	0	0	0	0

* Annual estimate of total organic discharged to the tank farms is from Sederburg and Reddick (1994)

waste was estimated by using the average amount of organic discharged per gal of waste from 1962 through 1968 (0.0176 gal of organic per gal of waste). Table 3.1-10 summarizes the organic discharges for the six cases described above, based on calculations using the average composition of waste from 1962 through 1968.

- For the years 1962 through 1969, the distribution of the organic was assumed to be the same as the distribution of organic wash waste (Table 3.1-8).

Table 3.1-10. Total Organic Discharged in Separate Shipments Between 1956 and 1958, Estimated from the Average Waste Composition from 1962 through 1968.

Year	Tank 241-A-102 (gal)	Tank 241-A-103 (gal)	Tank 241-C-110 (gal)	Tank 241-C-111 (gal)	Total (gal)
1956	0	0	3,005	597	3,602
1957	4,165	1,617	966	0	6,748
1958	0	2,021	0	0	2,021

The amount of organic discharged to each tank from 1956 through 1961, and 1962 through 1968 is summarized in Table 3.1-1 and was calculated as follows:

- For 1956 to 1961, the total organic in organic wash waste sent to the tank farms (Table 3.1-10) was subtracted from the total organic sent to the tank farms (Table 3.1-1) and the result was multiplied by the volume percent distribution of high-level waste (high-level waste discharged to the tank divided by the high-level waste discharged to all tanks for that year [Table 3.1-9]) to give the estimated total organic discharged to each tank each year. For the six cases listed in Table 3.1-10, the amount of organic discharged separately to each tank was added to the total.
- For 1962 to 1968, the volume percent of the total organic waste stream sent to the tank (organic wash waste discharged to the tank divided by organic wash waste discharged to all tanks for that year [Table 3.1-8]) was multiplied by the total organic discharged to the tank farms that year (Table 3.1-1) to give the estimated total organic discharged to each tank each year.

There is no record of where 5,400 gal of organic used by PUREX Plant prior to hot startup was discharged to in 1955. There is also no record of where 216 gal of organic were discharged to in 1979. There is no definite accounting for 15,900 gal of organic discharged from PUREX Plant in 1969. The distribution shown in Table 3.1-1 was estimate based on the reported sum of PUREX Plant organic wash waste and cladding waste sent to Tanks 241-C-102 and 241-C-104.

3.1.2.4.2 Discharges to C Tank Farm - 1969 through 1980. Between 1969 and the end of single-shell tank operations in December 1980, C Tank Farm received organic wash waste from PUREX Plant (Table 3.1-1). In addition, supernatant from self-concentrating tanks was occasionally transferred to the C Tank Farm. Tanks 241-C-102 and 241-C-104 received PUREX Plant organic waste directly from PUREX Plant; however, numerous intertank transfers also included moving organic wash waste into Tanks 241-C-103, 241-C-107, and 241-C-108. Waste transfers out of the C Tank Farm moved waste that potentially contained organic into other tank farms in both the 200 East and 200 West Areas. The total organic stored in and transferred through the C Tank Farm is estimated to be 50,000 gal from early operations (1955 through 1968) and 90,000 gal from 1969 through 1981; a total of about 140,000 gal.

Most of the organic that was stored in the C Tank Farm has probably evaporated; it was divided into several tanks, which provided more surface area for evaporation. The elevated temperatures of the C Tank Farm tanks probably contributed to evaporation; although they were at lower temperatures than the self concentrating tanks, they were not cold. Operational logbooks indicate that Tank 241-C-102 was observed "steaming" (per P. Sederburg, WHC). The only separate layer of organic known to currently exist in the C Tank Farm is approximately 4,600 gal floating in Tank 241-C-103. Organic may remain in other C Tank Farm tanks. A 1972 inventory of the C Tank Farm indicated a total of 44,000 gal of PUREX Plant organic waste in the primary receiver tanks; 36,000 gal in Tank 241-C-102 and 8,000 gal in Tank 241-C-104. In 1975, these organics were consolidated into Tank 241-C-103. The volume of organic that remained in Tank 241-C-103 in 1995 was approximately 4,600 gal, which corresponds to a volume reduction of approximately 89% over 20 years.

3.1.2.4.3 Discharges to AW Tank Farm - 1983 through 1991. In 1983, when PUREX Plant operations were restarted, the organic wash waste was planned to be transferred to DSTs in the AW Tank Farm. The estimated total volume discharged was approximately 72,000 gal (Table 3.1-1). The organic in the AW Tank Farm may never have formed a definite separable layer. The organic that was discharged from PUREX Plant after 1980 consisted of small amounts of dissolved material and entrained droplets of organic. The dispersion in droplets created considerable surface area to support alkaline hydrolysis of the TBP. In addition, the active ventilation in the DSTs in the AW Tank Farm probably enhanced evaporation.

Tanks 241-AW-101 and 241-AW-104 were designated as miscellaneous waste receivers for PUREX Plant waste (per P. Sederburg, WHC). Waste from Tanks 241-AW-103, 241-AW-104, and 241-AW-105 was processed in the 242-A Evaporator; an organic film was discovered in the evaporator condensate during this operation. In the mid-1980s, Tank 241-AW-101 was emptied and refilled with the evaporated waste. Tank 241-AW-104 may also retain some of the PUREX Plant organic wash waste. The actual distribution of organic waste to AW Tank Farm tanks or other DSTs has not been established because transfer records are not available.

3.1.2.5 U Plant (TBP Process). The U Plant housed a process that was used to recover uranium from tank waste. The TBP process at U Plant was similar to the PUREX Plant process, except that it did not recover plutonium. The organic used in solvent extraction was TBP in diluent. The U Plant ran the TBP process from March 1952 to January 1958.

The U Plant had concerns similar to REDOX and PUREX Plant in that it treated its solvent for reuse in the plant and made notes regarding solvent losses. The plant rate for April 1954 was 11.03 tons of uranium per operating day, with an average of 10.03 tons per day. A total of 302 tons were processed. "Solvent consumption was 7.3 and 1.6 gal of diluent and TBP respectively for each ton of new uranium, excellent phase decanting and entrainment losses" (HW-31734). This report indicates that U Plant was a potential routine source of separate and emulsified organic to the tank farms. U Plant flowsheets and the remainder of the applicable monthly reports have not been analyzed to develop a quantitative estimate.

The Uranium Recovery Technical Manual describes plans for how the plant was to be operated (HW-19140). Actual operations did not always follow these plans, so a review of flowsheets and monthly reports would be necessary to quantify solvent losses to the tank farms. U Plant planned to use a solution of 12.5% TBP in a kerosene type diluent, but had not chosen the diluent at the time the manual was published. Provisions were made for continuous and batch type solvent treatment to clean the solvent of contamination so it could be reused in the plant. Planned operations called for neutralization of the organic wash waste, followed by waste concentration. Under ordinary circumstances, it appears that separated organic would have been removed from the waste in the concentration step. (It would have been disposed as a condensate. Condensates were generally not sent to the tank farms.)

The Uranium Recovery Technical Manual states that organic losses would occur due to two mechanisms. One was solubility of TBP in the aqueous phase, expected to be 7.5 gal TBP per 10 tons of uranium processed. The other was entrainment of organic in the aqueous phase totalling 30 gal of TBP and 210 gal of diluent per 10 tons of uranium processed (HW-31734, p. 1103). The destination of the organic losses is not described in the manual. U Plant expected to have total losses of 40 gal TBP and 210 gal of diluent per operating day.

The Uranium Recovery Technical Manual also states that the plant had no facilities for disposal of large quantities of solvent. Provisions were made so that it could be pumped to drums. Events such as replacement of degraded solvent or disposition of solvent at plant shutdown may be recorded in the Chemical Processing Department monthly reports.

Before 1954, uranium recovery wastes were sent untreated to the tank farms. In November 1955, scavenging of these wastes was begun at 241-CR. The scavenged supernatant was disposed to the ground until 1957 (Anderson 1990.) U Plant waste, called "TBP waste," was discharged to tanks in TX, TY, and C Tank Farms. Some also went to T Tank Farm.

3.1.2.6 C Plant (Semi-works). C Plant is a much smaller facility than PUREX Plant, B Plant, T Plant, S Plant, U Plant, or Z Plant. C Plant was designed as a contact maintained pilot plant, although it was later modified for cesium and strontium recovery. C Plant was started up in 1952 and operated until 1954 as a pilot plant for the REDOX process. In 1954, C Plant was converted to use as a pilot plant for the PUREX Plant process. C Plant was shut down in 1956. It was restarted for strontium recovery in 1961 and operated through 1967 recovering fission products from high level waste.

C Plant would have used several organics over its lifetime, including hexone, TBP, diluents, and di (2 ethylhexyl) phosphoric acid. On at least one occasion in 1961, spent organic was disposed to a specific organic retention crib. This was done at the end of a campaign to produce strontium carbonate (HW-72666). C Plant was equipped with batch and continuous solvent treatment steps. It appears that organic washes were passed through a concentrator, which would remove separated organic. In 1965, plant specifications stated that "if the solvent does not perform satisfactorily, it may be sent to a crib" (RL-SEP-20). Discharge of separate phase or entrained organic to the tank farms or abnormal operations were not discussed in these reports.

3.1.2.7 UO₃ Plant. The UO₃ Plant received solutions of recovered uranium from the other processing plants and produced uranium oxide. This plant operated calciners and would not have discharged separable phase organics to the tank farms.

3.1.2.8 Z Plant (Plutonium Finishing). The Z Plant operated with much smaller quantities of chemicals than did the other processing plants. The Z Plant received plutonium nitrate solutions for further processing. The plant produced plutonium metal and oxide and recovered americium. Waste from Z Plant was cribbed until May 1973 when waste was sent to TX farm via a new underground transfer line.

The Z Plant plutonium reclamation operation used an 80% carbon tetrachloride and 20% TBP solvent extraction process for plutonium scrap recovery. The downstream waste treatment operation used a 70% carbon tetrachloride and 30% dibutyl butyl phosphonate process for residual plutonium and americium recovery. Some soluble and entrained separable phase organic was transferred with the aqueous waste to the tank farms. The amounts could not be determined and are very small compared to the PUREX organic.

3.1.3 300 Area

Waste from the 300 Area was collected in tanks and transported to the tank farms via railcar. The amount of waste discharged from the 300 Area is small compared to the waste from processing plants (Section 3.2). Some of this waste probably originated in research laboratories and hot cells. Chemicals used in the 300 Area facilities were identified by Klem (1990). No further analysis has been conducted for this waste because it would not have been a routine or significant source of separate phase organics.

3.1.4 Tank Farm Sampling Activities

The first core sample from Tank 241-C-103 to indicate separable organic was analyzed in 1986 (Weiss and Schull 1988). Some separable phase organic exists in other tanks based on core and head space vapor sample results; it is likely present in smaller quantities than in Tank 241-C-103. Visual identification of a separable organic layer in core samples may be difficult and will depend on the quantity, density, and color of the organic phase. The SSTs that have been interim stabilized would have only a small volume of drainable liquid remaining and some organic may be sorbed on waste solids (Schulz 1968).

Sampling in Tank 241-C-102 after the removal of the organic indicates the possibility that some organic remains in the tank. Auger samples from Tank 241-C-102 taken in 1995 to determine if organic is present contained sludge waste that was "greasy" (per P. Sederburg, WHC). Salt well pumping from the tank was also difficult, and plugging of the salt well screen was frequent, indicating the possible presence of organic. Earlier sampling of Tank 241-C-102 was attempted in 1986 by push-mode core sampling, but sample recovery was poor. This sampling effort used NPH as the hydrostatic head fluid; therefore, NPH could be present simply from the sampling effort. Sample data from core samples obtained from Tank 241-C-107 to determine if organic is present indicate that parts of the sample were oily or appeared to contain oil. The hydrostatic fluid for these samples was water, not NPH.

A screening methodology has been developed by WHC Tank Waste Safety that uses vapor characterization data (Bratzel 1996) with an evaporative model to estimate size of solvent pools that feed vapor into tank head spaces and pose significant risk from accidental solvent fires (Grigsby and Postma 1996). Results show that Tanks 241-BY-103, 241-C-102, and 241-C-103 meet or exceed derived criteria for solvent fire risk and need additional evaluation.

An alternate screening methodology based on NPH head space concentration and Raoult's Law was used to identify SSTs that may contain significant NPH and/or TBP liquid organic and therefore pose potential impacts to TWRS processing. A 0.1 mole fraction value for NPH was used as initial criteria based on engineering judgement. A total of six SSTs exceeded the NPH criteria (Tanks 241-TY-103, 241-C-103, 241-T-111, 241-BX-104, 241-BY-108, and 241-C-102). An estimate of the organic volume for some of these tanks could not be developed from available data. Table 3.1-7 summarizes available information on vapor sample results for SSTs potentially containing separable phase organic.

Tank characterization information was used to estimate the organic inventory for several tanks. The inventory of Tank 241-C-103 is about 17,300 L (4,570 gal) of NPH TBP, Tank 241-BY-108 about 420 L (110 gal) of NPH with trace TBP, and Tank 241-C-204 about 5,000 L (5,600 kg) of TBP with trace NPH. Table 3-3 and Table 3-4 of Volume 1 summarize the estimated organic inventory for 21 tanks. The 28,400 L (7,500 gal) of organic exists as a separate floating layer, solubilized in the aqueous supernatant liquid and/or combined with the salt cake and sludge solids based on information to date.

The above information was used to develop a preliminary estimate of the process organic that may remain in the DSTs and SSTs (Klem 1996). A projected volume of 87,000 L (23,000 gal) was the average total value from several projected estimates each having comparable levels of uncertainty. The estimates ranged from 34,000 L (9,000 gal) to 148,000 L (39,000 gal).

Remains and location of the 72,000 gal of organic discharged to the DSTs (AW Farm) from 1982 to 1991 PUREX operations are unknown (Table 3.1-6). Some of this organic should be detected or observed because it was recently transferred to the tanks. However, no significant amount organic has been reported to date.

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Section 3.2

Addendum - Tank 241-C-103 History

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3.2 TANK 241-C-103 HISTORY

3.2.1 Process History

Tank 241-C-103 is one of 16 single-shell tanks (SSTs) located in the C Tank Farm within the 200 East Area of the Hanford Site. The tank is nominally 23 m (75 ft) in diameter and 9 m (31 ft) from the inside of the center of the roof dome to the tank bottom. The center of the domed tank top is buried beneath approximately 9 ft of earth. The dome supports 11 steel pipe risers through which the tank contents may be assessed. Tank 241-C-103 is also directly connected to Tank 241-C-102 by an underground cascade line (7.6-m (25-ft)-long, 7.6-cm (3-in.)-diameter). When Tank 241-C-102 was full, the cascade line allowed the overflow of liquid to Tank 241-C-103. There is also a similar cascade line connecting tanks 241-C-101 and 241-C-102. Tank 241-C-103 has a rated storage capacity of 530,000 gal.

Tank 241-C-103 was first placed into service in August 1946, and initially received metal waste from the bismuth phosphate process at B Plant (Anderson 1990). The metal waste was retrieved in 1953 for uranium recovery. Later, uranium recovery (TBP process) and coating waste from the PUREX Plant process along with other PUREX Plant wastes were discharged directly into the tank or cascaded into the tank from the primary receiver tank, Tank 241-C-102. After this period, the tank received numerous other radioactive liquid waste streams from a variety of Hanford Site sources. Tank 241-C-103 received wastes until July 1979, after which time it was inactivated. The tank was partially isolated in December 1982 (Welty 1988).

The organic liquid in Tank 241-C-103 resulted from the transfer of PUREX Plant organic wash waste containing elevated levels of PUREX Plant solvent to Tank 241-C-102, with subsequent transfer of all Tank 241-C-102 free liquid to Tank 241-C-103 in November 1975. In 1969, Tank 241-C-102 was observed to contain a 250- to 330-mm (10- to 13-in.) layer of organic material, or a volume of approximately 104,100 to 135,300 L (27,500 to 35,750 gal) (Anderson 1990). Estimates of the total volume of organic transferred to Tank 241-C-103 range up to 284,000 L (75,000 gal) (Welty 1988). Currently, the Tank 241-C-103 liquid organic layer is believed to be about 38 to 51 mm (1.5 to 2 in.) thick (Huckaby 1993), corresponding to a volume of 15,500 to 20,800 L (4,100 to 5,500 gal). Huckaby (personal communication 1996) indicated the level most likely is 1.5 in but to compensate for potential errors, a band of 1.5 to 2 in was reported. For this report, a level of 5,000 gal has generally been used. The liquid organic is floating on an aqueous supernatant liquid approximately 1.2 m (4 ft) thick (503,000 L [133,000 gal]). The supernatant liquid sits on top of a 235,000-L (62,000-gal) sludge layer. The total waste content is approximately 738,000 L (195,000 gal) with a total waste depth of 2.0 m (6 ft 8 in.) (Hanlon 1994).

Based on sample results, the liquid organic phase contains approximately 1.3 wt% water and 25 wt% unidentified materials which include inorganic salts comprised primarily of silicates and phosphates. The organic liquid itself is a mixture of approximately 67 wt%

TBP and 33 wt% NPH, the primary organic compounds that make up the PUREX Plant solvent. Partial evaporation of the organic liquid during periods of forced ventilation, between 1975 and 1992, has reduced the volume of the liquid and depleted the more volatile hydrocarbons that were initially present in the NPH. The organic liquid has a density of 0.876 g/mL and a viscosity of 4 cP at 25 °C (Pool and Bean 1994).

The relative stability of the waste surface level in Tank 241-C-103 is an indication that the tank does not undergo periodic venting of gases from the stored waste. The surface level data for Tank 241-C-103 was charted for the period 1980 through 1991 (Burke 1991). The data indicate a decrease in the surface level of the tank of about 4 cm (1.6 in.) over the 11-year period, which Burke attributes to the evaporation of water.

There is the potential for an interstitial solids layer at the interface between the organic and aqueous phase. Discussions with the engineer in charge of the last sampling activity indicated that this is not likely because of the following (Huckaby 1996):

- There is a lot of water migrating through (or around) the organic layer, condensing on the walls and other surfaces of the tank, and causing a constant dripping throughout the tank. This was reported as causing a constant rippling of the surface.
- This migration of water up and dripping down results in washing of the organic, including any entrained solids and would tend to remove these solids.
- The solids would be more dense than either the organic or aqueous phase.
- All four organic samples were very clear, even though the samples were drawn with a "bottle-on-a-string" from 35 ft above the surface of the liquid in approximately 1.5 inches of organic.

Huckaby (1996) did note that the surface was opaque so a visual confirmation of the presence of an interstitial layer could not be done.

Even though it is likely that there is not an interstitial solids layer, current plans include the use of a radiation monitor on the skimmer pump discharge line to shut off the pump in the event of radiation levels inconsistent with the organic radionuclide concentrations previously determined (Pool and Bean 1994) and that may affect DOT certification.

3.2.2 Organic Removal and Safety Evaluation History

Earlier events

The need for a mechanism to deal with separable phase organic in tanks has been known for over twenty years (Hall 1972a). Safety analysis of floating organic layers also

dates back to this time period (Hall 1972b). The initial effort to remove organic from the tanks then containing separable phases, including Tank 241-C-102, was cancelled in either 1974 or 1975 after no separable organic was detected in C-Farm tanks sampled. In the late 1980s, the issue of organics in Tank 241-C-103 again received considerable attention after employees exposures to gases and vapors in the C Tank Farms. As a result, several gaseous monitoring activities were undertaken. In addition, the FY 91 Tri-Party Agreement milestones resulted in studying ways to remove the organic layer in support of single-shell tank stabilization (Scully 1990; Dunford 1990).

USQ

An unreviewed safety question (USQ) was declared in 1992 because the existing Safety Analysis Report (SAR) (Boyles 1989) did not address the potential flammability of a floating organic layer in Tank 241-C-103 (WHC 1992). This USQ was closed in 1994 after several actions were taken. One was the completion of a Justification for Continued Operation (Carothers 1993). Another was the completion of the original *Safety Analysis of Exothermic Reaction Hazards Associated with the Organic Liquid Layer in Tank 241-C-103, SARR 001*, which has since been revised to include addressing several additional concerns including organic coming into contact with the sludge (Postma et al. 1995).

Previous Studies

Several studies were performed to evaluate the best method for removing this organic (Parazin 1994). Two key findings came to light during preparation of the Preliminary Design Criteria (PDR) which prompted the reassessment of the mission and its possible deferral.

- Objective, quantified data became available which significantly reduced concerns related to the toxic vapor and flammability issues originally raised by the presence of the floating organic (Postma et al. 1994)
- Due to Department of Transportation limits, once the organic was removed from the tank and stored, there was no clear disposal paths nor options. There were no DOT approved containers for this radionuclide concentration, the DOT limits for shipping were very restrictive, and no processing paths were available.

Based on this information and these limitations, studies were performed that supported pumping the organic directly from Tank 241-C-103 to a DST (Bartley 1994; Dukelow et al. 1995, Geschke and Milliken 1995). The recommendation was returned by the Chemical Reaction Sub Tank Advisory Panel (CRS TAP) in September 1995, with a request to evaluate the broader range of alternatives. Many of the questions involved either impacts of the organic layer and the sludge layer and life-cycle costs of transferring the organic layer to a DST. The Defense Nuclear Safety Board has expressed similar concerns.

This engineering report reevaluates the alternatives from a life-cycle perspective, particularly impacts on TWRS. This report also incorporates changes made to DOT regulations, utilizes more accurate source terms for shielding calculations, and incorporates additional testing results on the skimming system. The impact of these two items is significant. Current DOT regulations now allow higher radionuclide concentrations to be shipped and approves the use of shipping tanks that can be used to receive the Tank 241-C-103 organic. The more accurate source terms indicate that less shielding will likely be required. The additional skimming system testing, using a new modified skimmer, indicate that the amount of aboveground equipment can be reduced.

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Section 3.3

DSI - Tank 241-C-103 Transaction History - Post January 1976

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From: Tank Farms Plant Engineering 13331-88-600
 Phone: 3-4556 2750E/200E/A121 R1-51
 Date: September 22, 1988
 Subject: TANK 103-C TRANSACTION HISTORY - POST JANUARY 1976

To: D. A. Dodd T6-50 A. W. Lilly R3-54
 G. L. Dunford *GHJ* R1-51 R. E. Van der Cook S6-07
 G. N. Hanson S5-04 KGC/LB

- References: (1) Internal Memo, D. A. Dodd to K. G. Carothers, "Final Report of Tank Vapor Space Sampling of 241-C-101, -102, and -103," May 4, 1988.
- (2) Internal Memo, F. M. Jungfleisch to K. G. Carothers, "Historical Perspectives of Wastes in Tank 241-C-103," November 6, 1987.
- (3) RHO-CD-213, Vol. II, Waste Storage Tank Status and Leak Detection Criteria, Revised February 11, 1984.
- (4) Internal Letter, J. C. Hall to R. C. Roal, "Safety Analysis - Storage of Organic Waste in Underground Tanks," June 27, 1972.
- (5) Internal Letter, T. D. Anderson to W. L. Godfrey, "Organics in 102-C Tank," October 2, 1969.

The Reference (2) memo summarizes an evaluation of waste management transactions for tank 103-C spanning the period from March 1946 through December 1975. The objective of this evaluation was to determine the types of wastes that were sent to the tank and to identify tanks with similar histories. A review of tank farm surveillance records for tank 103-C shows that waste transactions actually occurred through July 1979. Thus, this memo extends the transaction history from the December 1975 date to the present time.

Tank 103-C remained active until July 1979, after which no wastes were transferred into or out of the tank. During the period in question, the tank served as a primary receiver for insoluble strontium-leached solids from both B Plant and AR Vault during the PUREX Acidified Sludge (PAS) secondary recovery operations. Other wastes transferred into tank 103-C originated from supernatant pumping tanks in the 200 East Area that were historically either primary receivers of waste or secondary receivers of waste from other tanks. Tanks involved in these transfers included tanks 107-C, 108-C, 109-C, 110-C, 111-C, and 112-C. Besides the PAS strontium-leached solids, other waste types contributing to the tank transactions include Hot Semiworks Waste (HS), Cesium Recovery Waste (CSR) and

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13311-28-600

Strontium Recovery Waste (SRR) from Fission Product Recovery, B Plant High-Level Waste (B), B Plant Low-Level Waste (BL), PUREX Coating Waste (CWP), PUREX Organic Wash Waste (OWW), PUREX Low-Level Waste (PL), PUREX High-Level Waste (P), Thoria Waste (TH), Strontium Semiworks Waste (SSW), N Reactor Waste (N), Battelle Northwest Waste (BNW), and Decontamination Waste (DW).

Most of the supernate that remained in tank 103-C after removing it from service in July 1979 probably originated from wastes added subsequent to May 12, 1977. At that time, the tank was pumped down to a minimum liquid level of 31.4 inches. The sludge levels reported for the first quarter 1977 and third quarter 1977 were 20 inches and 50 inches respectively. At most, about 11 inches of supernate remained after pumping to the above minimum level. Much of this heel (if aqueous) could have been removed during the subsequent nine fill/decant cycles that occurred prior to deactivating the tank.

The major source of waste received in tank 103-C during the last two fill/decant cycles originated from tank 107-C. A best estimate of waste types in tank 107-C at the time shows N, BNW, and OW received from tank 104-C via tank 107-U. The records also show minor quantities of waste originating from tank A-101 (SRR and PL waste) and PUREX High-Level Waste (P) being received in tank 104-C prior to making the final waste transfer into tank 107-C. Secondary sources of waste over this period includes about 0.2 inch from tank 109-C, 2.6 inches from tank 110-C, and 1.2 inches from tank 112-C. The most likely origin of waste in these tanks is tank 110-C, tank 103-8X, and tank 110-C, respectively. Waste types from these secondary sources include B, BL, CSR, CWP, and OWW.

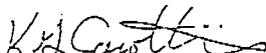
One final possibility to consider is the presence of a separable organic phase in tank 103-C resulting from transfer of waste from tank 102-C. Such a layer is suspected due to a total organic carbon (TOC) concentration of 7400 ppm (parts per million) measured on a surface sample taken from the tank in September 1987 (Reference [1]). The last transfer from tank 102-C occurred on November 14, 1975, during P-10 pumping stabilization efforts, with the waste routed to tank 103-C. Subsequent tank 102-C photographs taken on May 18, 1976, "revealed a dry, lumpy surface of sludge with very shallow puddles of liquid visible." (Reference [3]) Prior to the November 1975 P-10 pumping, tank 102-C had stood inactive since the fourth quarter of calendar year 1969. During this same quarter, a 10 to 13 inch deep top layer of organic was found in the tank (Reference [5]). Because tank 102-C had been a receiver for PUREX OWW, the 36,000 gallon organic waste inventory was taken to be a mixture of tributyl-phosphate and normal paraffin hydrocarbons (TBP-NPH) (Reference [4]). Given the success in pumping tank 102-C down below the sludge level, it is likely that a portion of the organic layer was transferred to tank 103-C. Also, because of its lower specific gravity, the organic would most likely remain in tank 103-C during subsequent fill/decant cycles.

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Given the tank 103-C transactions occurring between December 1975 and July 1979, other candidate tanks for containing waste similar to that stored in tank 103-C include tank 104-C and tank 107-C. As discussed above, the majority of the liquid waste presently stored in tank 103-C (excluding any floating organic layer originating from the earlier tank 102-C transfer) was received from tank 107-C. Tank 107-C has stood inactive since completing the tank 103-C transfers. Similarly, the last transfer made from tank 103-C was routed to tank 104-C and represents the last receipt of waste by tank 104-C.

In conclusion, the tank 103-C transaction history for the period December 1975 until the present time basically substantiates the findings of the Reference (2) study with only one exception. The important findings are summarized below along with the single exception.

- o Detailed composition data on the waste sources contributing to the tank inventory are required in order to assess the hazardous chemicals that could occupy the tank vapor space.
- o A mixture of TBP-NPH organic and associated degradation products from PUREX Plant processing activities is probably present in the tank. This represents an exception to the earlier study findings.
- o DW, BNW, and N wastes may contain chemicals or degradation products of chemicals that could exhibit volatility. Because many of the products used in decontamination operations are proprietary, knowledge of the chemical make-up of these products are unknown.
- o Tank 104-C and tank 107-C represent high potential candidate tanks to investigate for problems similar to those experienced in tank 103-C.


K. G. Carothers, Principal Engineer
Tank Farms Plant Engineering

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Section 3.4

Memo - Preliminary Estimate of Projected Process Organic Volume in Waste Tanks

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From: Process Technology
Phone: 372-0235 H5-27
Date: September 18, 1996
Subject: PRELIMINARY ESTIMATE OF PROJECTED PROCESS ORGANIC VOLUME IN WASTE TANKS

73510-96-029

To: D. J. Washenfelder H5-27

cc: A. L. Boldt H5-49
P. J. Certa H5-61
G. T. Dukelow S7-14
R. A. Kirkbride H5-27
M. J. Klem H5-27
M. J. Kupfer H5-27
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73510 File/LB H5-27

This evaluation develops an initial projected estimate of residual process organic that may remain in the DSTs and SSTs from PUREX (Shell E-2342, Soltrol-170 and normal paraffin hydrocarbon (NPH) diluents, tributyl phosphate [TBP]) and B Plant (NPH, di-2-ethylhexyl phosphoric acid [D2EHPA], TBP) solvent extraction operations. It is based on extrapolation of data from 21 tanks to a total of 139 tanks using three approaches. The 139 tanks are known or suspected to contain TBP, NPH, and/or paraffinic residues based on the Los Alamos National Laboratory Hanford Defined Waste (LANL HDW) Model Revision 3, core sample results and tank vapor samples (References 2, 3, 5, 6, 7, 8, 9, 11, 12, 14, 17, 18, 19, 20, 21).

Twenty-three thousand (23,000) gallons (78,000 Kg) of process organic are projected to remain in the 139 waste tanks. The projected volume of 23,000 gallons is the average value from several estimates each having comparable levels of uncertainty. The estimates range from 9,000 gallons to 39,000 gallons. The 23,000 gallon estimate is recommended for planning purposes because there has been no detection to date of another large quantity of organic in addition to the 4,600 gallons floating layer in tank 241-C-103.

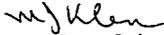
The process organic exists as a separate floating layer, solubilized in the aqueous supernate liquid and/or combined with salt cake and sludge solids based on information to date. The TBP and D2EHPA are slowly degrading to aqueous soluble constituents by on going chemical and radiation processes. The NPH is slowly evaporating to the environment.

A rough estimate of the organic volume present in the waste tanks is needed for initial sizing of an aqueous-organic decanter system for waste pretreatment. The recent tank 241-C-103 systems engineering study identified that both separable and aqueous soluble TBP would impact cesium ion exchange performance (Reference 9).

D. J. Washenfelder
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Information on the process organic volume projection estimates is included in Attachments 1 and 2.

If there are any questions regarding this information please feel free to give me a call on 372-2035.


M. J. Klem, Principal Engineer
Process Technology

kge

Attachments 2

Background

Essential material consumption information of PUREX reprocessing and B Plant strontium recovery operations show that about 1,498,000 gallons of solvent extraction process organic [1,391,000 gallons of diluent-TBP from PUREX (1956 - 1972) & (1982 - 1991) and 107,000 gallons of NPH-D2EHPA-TBP from B Plant (1967 - 1981)] were used at these facilities. Of this amount about 700,000 gallons were discharged to the SSTs and DSTs as soluble and entrained constituents in the high level and organic wash waste (OWW) streams (See Tables 1 and 2 of Attachment 2). Much of this organic is believed to have degraded by chemical and radiation methods to carboxylic salts and/or evaporated during waste concentration and storage operations.

The PUREX operation discharged 657,000 gallons of organic to the waste tanks and 841,000 gallons to organic cribs, process condensate cribs and the stack gaseous effluent based on Reference 16.

There are no records or previous analysis on disposition of B Plant process organic. Initial estimates suggest less than half of the 107,000 gallons of organic was discharged to the SSTs. Historical records and process flowsheet information show that there were no discards of spent process organic to organic cribs. Most of the consumed D2EHPA and TBP organic (including degradation products) and 10 - 20 % of the NPH are estimated to have been discharged to the SSTs. The remaining organic (mostly NPH) was discharged as vapor components to the process condensate crib and the stack gaseous effluent.

Summary of Results

It was not possible to establish an accurate estimate of the current inventory of process organic in the waste tanks due to insufficient information and ongoing in-tank degradation and evaporation processes. Several volume projection estimates were developed by extrapolating information on 9 DSTs and 12 SSTs to a total of 139 tanks that are suspected or known to contain TBP or NPH. Based on these projections a total average volume of 23,000 gallons (78,000 Kg) is recommended for use at this time for preliminary sizing of the organic separation equipment for pretreatment. This volume is recommended because there has been no detection to date of another large quantity of organic in addition to the 4,600 gallons floating layer in tank 241-C-103.

The current organic inventory is about 7,500 gallons (25,300 Kg) of TBP and NPH constituents based on sample results of 21 tanks. The organic exists as a separate floating layer, solubilized in the aqueous supernate liquid and/or combined with salt cake and sludge solids. The 4,300 gallons of known TBP are slowly degrading to DBP and butanol and the 3,200 gallons of NPH are slowly evaporating to the environment. There is insufficient information on D2EHPA in the waste tanks to include it in the calculations at this time (Reference 2). Previous laboratory studies have shown that radiation degradation of D2EHPA is about 50 % faster than TBP (Reference 23).

Three approaches were used to extrapolate the available data. They were based on ratios of original OWW volume, number of tanks that may contain

organic and the TBP/DBP mass ratio. Table 3 summarizes the projected process organic volumes and bases of their calculation. Tables 4 - 7 contain specific tank information. Tables 8 - 10 show the calculations.

Estimates of remaining organic ranged from 15,000 to 22,000 gallons based on the OWW volume ratio method, 17,000 to 35,000 gallons based on tank number ratio method, and 9,000 to 39,000 gallons based on TBP/DBP mass ratio method. Several other values were developed based on other combinations of these ratios (e.g. extrapolation to 177 vs 139 tanks, grouping and/or separation of DSTs and SSTs and uniqueness of the 6,110 gallons of organic in tanks C-103 and C-204). The results either fell within the above ranges or were judged too large (>40,000 gallons) based on information available at this time.

Remains and whereabouts of the 72,000 gallons of process organic discharged to the DSTs (AW Farm) from 1982 - 1991 PUREX operations is unknown (Table 1). Some of this organic should be detected or observed because it was recently transferred to the tanks. However, no significant amount organic has been reported.

Bases of Estimated Process Organic Volumes

A total of 139 tanks (26 DSTs, 113 SSTs; see Tables 4 and 5) received OWW, are known or suspected to contain TBP, NPH and/or paraffinic residues (BY salt cake), and/or vapor sample results show the NPH liquid phase mole fraction is ≥ 0.001 . These tanks include 30 of the 32 organic phenomenology (fuel) issue tanks (exceptions are U-203 and U-204, Reference 1). The organic fuel issue tanks have been identified as most likely to contain high quantities of organic material (complexant and solvent degradation products) and are judged to have potential to become unsafe due to the expected amount of organic fuel, oxidizer and water.

The LANL HDW Rev 3 model (References 7 and 8) results for OWW volume and DBP mass were used to develop the estimates. OWW from PUREX additions to self boiling waste in A & AX tank farm during the 1950's and 1960's are now identified as waste resulting from cesium recovery (CSR) by the LANL HDW model Revision 3. Virtually no TBP and NPH are expected in the CSR due to degradation and evaporation. Several of these tanks were included in the calculations due to subsequent receipt of OWW, mass of DBP and/or vapor sample results (Table 4). The Sort on Radioactive Waste (SORWT) model identified 8 SSTs as containing OWW (Reference 15). These tanks are included in the 139 tank total (see Table 4).

The estimated mass of DBP in the waste tanks was included in the HDW model (see Table 10). Since DBP was used to identify the maximum number of tanks that may contain organic for this estimate a check was made to determine the impact on the estimated average process organic volume that would result from eliminating 24 SSTs and 23,600 Kg DBP from the projection calculations (tank deletion criteria: tank received 0 K gal OWW per HDW model, ≤ 0.000 NPH mole fraction realized from vapor sampling based on Table 4 and did not contain organic based sample results of Table 6). The results gave a 10 % decrease of the estimated average organic volume (23,000 gallons to 21,000 gallons).

The HDW model does not track TBP and NPH organic. It assumes a certain fraction of TBP was lost during processing as soluble DBP and butanol and the remaining TBP was converted to DBP and butanol in the waste tanks by chemical and radiation degradation processes. The model assumes all the NPH has evaporated. The model does not include OWW from B Plant Sr recovery.

Recommended Additional Work

Future work is needed to improve the accuracy of predicting the remaining process organic in waste tanks. Laboratory analyses of liquid and solid waste tank samples for TBP, D2EHPA and NPH constituents, continued vapor space sampling of the SSTs and DSTs, and surface liquid sampling of selected tanks (to be determined based on vapor sample results and other information) for a floating organic layer (e.g. 1985 surface sample from tank 241-AW-105 showed a small floating layer of 30 % TBP 70 % NPH; see Reference 22) are needed.

Additional work would include continued waste tank characterization (Reference 1), documenting waste transfer history (Reference 7 & 8), improving organic inventory estimates (Reference 4), completing alkaline side TBP chemistry of tank C-103 systems engineering study (Reference 9) and continued laboratory efforts to perform enhanced sludge wash tests on actual organic contaminated sludge. These efforts would expand current knowledge of OWW transfers (PUREX and B Plant), waste evaporation, organic diffusion and solubility in the aqueous phase, absorption and removal of organic from solids, and organic degradation by chemical and radiation reactions in high salt waste.

Impact of Process Organic on Pretreatment

The projected 23,000 gallons of process organic will require separation during pretreatment to avoid fouling the cesium ion exchange process. An aqueous-organic phase decanter system should be sized to handle the expected aqueous flow rate from retrieval and enhanced sludge washing. The receiving, washing, and storage tanks should be sized to handle 5,000 gallons batches of organic. The 5,000 gallon batch size is based on the largest quantity of separable phase organic identified to date.

Recent PNNL preliminary test results showed that mixing equal volumes of tank 241-C-103 organic and 0.1 M EDTA significantly reduced the radionuclide contamination of the organic for off site disposal (Reference 10). Additional work will need to be performed on organic decontamination after more is known about the quantity and composition of the organic requiring disposal.

The tank 241-C-103 systems engineering study did not attempt to quantify the amount of soluble organic (TBP specifically) that would be carried to the cesium ion exchange system and potentially degrade the exchanger. If enhanced sludge washing and/or the pretreatment evaporator do not sufficiently reduce this organic, then a sorption column before cesium ion exchange may be needed. The sorption column would remove aqueous soluble TBP/NPH and reduce the frequency of ion exchange column flow and/or exchanger fouling problems (Reference 9).

Recent ORNL batch equilibrium test results show that separable phase TBP affects cesium removal performance of both resorcinol formaldehyde and engineered CST exchangers (Reference 13). Further work is needed to determine the impact of aqueous soluble process organic on cesium ion exchange.

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Data Use Caveat:

The data contained in this attachment are preliminary and may be subject to change. Inventory and projection information have not undergone checks and quality reviews. The projected process organic volume is to be used for initial sizing of the aqueous-organic decanter system for pretreatment. Additional work is needed to improve the accuracy of this estimate. An accurate estimate is needed some time in FY 2001 to support preparation of the Privatization Phase II Request for Proposal.

Table 1. SUMMARY OF WASTE TANKS RECEIVING ORGANIC DIRECTLY FROM PUREX PLANT¹

Tank	Volume Organic (Gal)	Time Period	Organic Disposition	Year Sludge Retrieved
A-101 ²	93,200	1956 - 1968	Degradation Evaporation	1975 - 1976
A-102 ²	80,100	1956 - 1963	Degradation Evaporation	1972 - 1976
A-103 ²	48,700	1956 - 1967	Degradation Evaporation	1974 - 1976
A-105	0	N/A	N/A	1968 - 1969
A-104 ²	140,000	1958 - 1968	Degradation Evaporation	1974 - 1975
A-106 ²	68,200	1960 - 1968	Degradation Evaporation	1970 - 1973
AW-101 ³	72,000	1982 - 1991	Degradation Evaporation	None
AW-104 ³		1982 - 1991	Degradation Evaporation	None
AX-101 ²	11,700	1965 - 1967	Degradation Evaporation	1975 - 1976
AX-102 ²	11,700	1966 - 1967	Degradation Evaporation	1976
AX-103 ²	24,100	1965 - 1968	Degradation Evaporation	1976 - 1977
AX-104 ²	20	1968	Degradation Evaporation	1977 - 1978
C-101	3,800	1968	Evaporation Waste Transfer	1952 - 1953
C-102	17,200	1968 - 1969	Evaporation Waste Transfer	1953
C-104	76,400	1969 - 1972	Evaporation Waste Transfer	None
C-110	4,000	1956 - 1957	Evaporation Waste Transfer	None
C-111	600	1956	Evaporation Waste Transfer	None
Unknown	5,400	1955 - 1979	-	-
Total	657,100	1955 - 1991	-	-

Notes:

- 1) Source of information is Reference 9.
- 2) These tanks stored self boiling waste and received intermittent OWW during the 1950's and 1960's.
- 3) Organic sent to AW tanks cannot be positively identified due to lack of transfer records. The only certainty is this organic was sent to DSTs.

Table 2. SUMMARY OF ORGANIC USAGE AT B PLANT BASED ON CONSUMPTION RECORDS

Year	DZEPHA ⁵ Gallons	TBP Gallons	NPH Gallons	Total Gallons
1967 ¹	1,108	696	8,520	10,324
1968 ²	2,714	1,625	12,494	16,833
1969	1,473	940	3,827	6,240
1970	2,260	1,270	10,841	14,371
1971 ³	1,477	862	5,565	7,904
1972	2,635	2,006	8,867	13,508
1973	1,767	867	7,431	10,065
1974	1,685	706	5,138	7,529
1975	635	575	2,325	3,535
1976	1,693	1,550	5,707	8,950
1977	1,840	498	5,382	7,720
1978 ⁴	1,076	563	3,235	4,874
1979	1	1	0	2
1980	0	0	0	0
1981	6	0	0	6
Sub Total	20,370	12,160	79,330	111,860
Current Inventory	760	390	3,450	4,600
Total Used	19,610	11,770	75,880	107,260
Estimate of Evaporation ⁶	TBD	1,000	65,000	66,000
Est Total Discharged to SSTs ⁷	19,610	10,770	10,880	41,260

Notes:

- 1) Amount includes addition to plant for hot startup of solvent extraction system on 1/31/68 to process rare earth crude.
- 2) PAW-ZAW solvent extraction started on 4/20/68.
- 3) End of Sr recovery from PAW-ZAW. No concentration of solvent extraction waste by B Plant evaporator.
- 4) End of Sr recovery from PAS.
- 5) DZEPHA is more susceptible to radiation damage than TBP based on Reference 23.
- 6) Based on Raoult's Law & B Plant vessel ventilation systems. Includes estimated amount discharged to process condensate crib.
- 7) Amount includes degradation products.

Table 3. SUMMARY OF ESTIMATED PROCESS ORGANIC VOLUME IN WASTE TANKS

Organic		Bases of Estimate
Gal	Kg	
7,570	25,300	Present inventory: TCR/TCO or average sample results and amount of waste
14,700	46,100	OMW volume ratio, org of DST & SST combined, 6,110 gal in C-103 & C-204 is unique
22,300	74,000	OMW volume ratio, org of DST & SST combined, 4,570 gal in C-103 is unique
16,600	51,600	Tank number ratio, org of DST & SST combined, 6,110 gal in C-103 & C-204 is unique
25,300	83,800	Tank number ratio, org of DST & SST combined, 4,570 gal in C-103 is unique
35,000	116,200	Tank number ratio, org of DST & SST as separate groups, 4,570 gal in C-103 is unique
8,800	30,000	TBP/DBP mass ratio, known TBP and HDW model DBP, 6,110 gal C-103 & C-204 is unique
39,400	142,700	TBP/DBP mass ratio, known TBP & HDW model DBP, 4,570 gal in C-103 is unique
23,200	77,800	Average estimated amount of organic

Note: Detailed calculations to support these estimates are contained in Tables 8, 9, and 10.

Table 4. SUMMARY OF LANL HDW MODEL REV 3 AND VAPOR SAMPLE RESULTS FOR SSTs

Tank	Volume PUREX OWM ³ K gal	Estimated DBP ⁴ Kg	NPH Liquid Organic Mole Fraction Based on Vapor Sample
A-101 ¹	88.7	20,500	0.003 - 0.004
A-102 ¹	3.6	421	0.001
A-103	33.9	8,700	0.025
A-104		0	
A-105	-	0	
A-106	10.9	1,850	
AX-101	34.5	18,000	0.001
AX-102 ¹	4.2	790	0.001 - 0.002
AX-103	9.2	2,130	0.000
AX-104	-	0	
B-101		1.8	
B-102 ¹	0.2	12.8	
B-103 ¹	0.1	1.2	0.037 - 0.054
B-104	-	1.5	
B-105	0.0	2.8	
B-106	0.1	6.7	
B-107	0.0	0.2	
B-108	0.0	1.3	
B-109 ²	-	1,160	
B-110	-	0	
B-111	0.0	33.4	
B-112 ²	0.0	486	
B-201	-	0	
B-202	-	0	
B-203	-	0	
B-204	-	0	

Note:

- 1) Tank identified as organic fuel issue in Reference 1.
- 2) Tank contains BY salt cake and paraffinic residues per Reference 8.
- 3) Source is Reference 8. Original OWM from A & AX farm fed to Cs-137 IX and now CSR.
- 4) Source of information is Reference 7.

Table 4. SUMMARY OF LANL HDW MODEL REV 3 AND VAPOR SAMPLE RESULTS FOR SSTs

Tank	Volume PUREX, OMW ⁵ K gal	Estimated DBP ⁴ Kg	NPH Liquid Organic Mole Fraction Based on Vapor Sample
BX-101	-	24.7	
BX-102	3.8	0	
BX-103 ⁵	0.1	74.9	
BX-104	6.3	828	0.04 - 0.156
BX-105 ¹	0.5	83.5	
BX-106 ²	0.5	972	
BX-107	0	12.9	0.013
BX-108	-	0	
BX-109	0	4.4	
BX-110 ^{1,2}	0	1,080	
BX-111 ²	0.2	4,590	
BX-112	0	26.0	
BY-101 ²	-	8,980	
BY-102 ^{1,2}	0.3	8,250	0.003
BY-103 ^{2,5}	-	10,000	0.011 - 0.011
BY-104 ²	-	4,520	0.007 - 0.009
BY-105 ²	-	8,650	0.001 - 0.004
BY-106 ²	-	14,000	0.000 - 0.001
BY-107 ²	-	3,820	0.017 - 0.110
BY-108 ^{1,2}	0	1,620	0.032 - 0.156
BY-109 ²	-	9,930	0.013
BY-110 ²	0	5,340	0.003 - 0.011
BY-111 ²	-	11,100	0.000
BY-112 ²	0	7,260	0.001

Note:

- 1) Tank identified as organic fuel issue in Reference 1.
- 2) Tank contains BY salt cake and paraffinic residues per Reference 8.
- 3) Source of information is Reference 8.
- 4) Source of information is Reference 7.
- 5) Tank contains OMW based on SORWT Model per Reference 15.

Table 4. SUMMARY OF LANL HDW MODEL REV 3 AND VAPOR SAMPLE RESULTS FOR SSTS

Tank	Volume PUREX OMW ² K gal	Estimated DBP ³ Kg	NPM Liquid Organic Mole Fraction Based on Vapor Sample
C-101 ⁴	-	0.8	0.009 - 0.015
C-102 ^{1,4}	0	46.6	0.075 - 0.144
C-103 ¹	3.3	841	0.597 - 0.670
C-104 ^{1,4}	0.4	621	
C-105	0	0.4	
C-106	0	0.4	
C-107 ¹	-	0.5	0.000 - 0.001
C-108 ⁴	-	0.7	0.000
C-109	-	0	0.000
C-110 ⁴	0	0	0.006 - 0.028
C-111	0	0	0.000
C-112	0	0	0.000
C-201	-	0	
C-202	-	0	
C-203	-	0	
C-204	-	0	
S-101	25.1	3,630	
S-102 ¹	58.2	7,700	0.000
S-103	38.1	4,980	
S-104	-	58.1	
S-105	27.3	4,740	
S-106	54.6	6,670	
S-107	11.2	1,460	
S-108	36.3	7,260	
S-109	36.6	7,540	
S-110	30.2	5,050	0.000

Notes:

- 1) Tank identified as organic fuel issue in Reference 1.
- 2) Source of information is Reference 8.
- 3) Source of information is Reference 7.
- 4) Tank contains OMW based on SORWT Model per Reference 15.

Table 4. SUMMARY OF LANL HDW MODEL REV 3 AND VAPOR SAMPLE RESULTS FOR SSTS

Tank	Volume PUREX OMW ² K gal	Estimated DBP ³ Kg	NPH Liquid Organic Mole Fraction Based on Vapor Sample
S-111 ¹	45.5	8,810	0.000
S-112	38.7	7,730	
SX-101	8.9	1,270	
SX-102	89.7	12,600	
SX-103 ^{1,4}	96.4	12,000	
SX-104	68.9	9,810	
SX-105	99.4	14,700	
SX-106 ¹	79.6	10,100	0.000
SX-107	-	611	
SX-108	-	0	
SX-109	-	68.3	
SX-110	-	10.8	
SX-111	0.2	15.1	
SX-112	-	8.3	
SX-113	-	0	
SX-114	0.3	47.8	
SX-115	-	2.2	
T-101	3.0	378	
T-102	-	0	
T-103	0	9.7	
T-104	0.1	24.1	
T-105	-	0	
T-106	-	0	
T-107	-	0	0.003
T-108	-	0.5	
T-109	-	1.2	

Note

- 1) Tank identified as organic fuel issue in Reference 1.
- 2) Source of information is Reference 8.
- 3) Source of information is Reference 7.
- 4) Tank contains OMW based on SORWT Model per Reference 15.

Table 4. SUMMARY OF LANL HDW MODEL REV 3 AND VAPOR SAMPLE RESULTS FOR SSTs

Tank	Volume PUREX OX ² K gal	Estimated DBP ³ Kg	NPH Liquid Organic Mole Fraction Based on Vapor Sample
T-110	-	0	
T-111 ¹	-	0	0.200 - 0.257
T-112	-	0	
T-201	-	0	
T-202	-	0	
T-203	-	0	
T-204	-	0	
TX-101	0.8	121	
TX-102	37.6	2,680	
TX-103	15.2	1,200	
TX-104	7.7	543	
TX-105 ¹	119.9	8,690	0.000
TX-106	54.4	4,180	
TX-107	0.9	61.3	
TX-108	18.2	1,280	
TX-109	0	0	
TX-110	76.4	5,430	
TX-111	58.0	4,120	0.000
TX-112	135.9	9,220	
TX-113	114.2	5,800	
TX-114	118.4	6,900	
TX-115	137.3	7,990	
TX-116	53.8	1,460	
TX-117	125	3,590	
TX-118 ¹	20	1,890	0.001
TY-101	-	0.9	0.002

Note:

- 1) Tank identified as organic fuel issue in Reference 1.
- 2) Source of information is Reference 8.
- 3) Source of information is Reference 7.

Table 4. SUMMARY OF LANL HDW MODEL REV 3 AND VAPOR SAMPLE RESULTS FOR SSTs

Tank	Volume PUREX O/W ² K gal	Estimated DBP ³ Kg	NPH Liquid Organic Mole Fraction Based on Vapor Sample
TY-102 ¹	5.9	413	
TY-103	8.2	578	0.199 - 0.541
TY-104 ¹		1.2	0.013
TY-105	-	7.4	
TY-106	-	<0.1	
U-101	-	0	
U-102 ¹	60.5	6,840	
U-103 ¹	73.6	8,590	0.000
U-104	38.4	1,040	
U-105 ¹	70.2	8,470	0.000
U-106 ¹	32.6	5,070	0.000
U-107 ¹	50.4	6,460	0.000
U-108 ¹	66.7	10,600	
U-109 ¹	73.0	11,200	
U-110	-	0	
U-111 ¹	30.3	3,940	0.001
U-112	-	0	
U-201	-	0	
U-202	-	0	
U-203 ¹	-	0	
U-204 ¹	-	0	
Total SST	2,652.6	411,715	-

Note:

- 1) Tank identified as organic fuel issue in Reference 1.
- 2) Source of information is Reference 8.
- 3) Source of information is Reference 7.

Table 5. SUMMARY OF LANL HDW MODEL REV.3 FOR ORGANIC IN DSTs¹

TANK	VOLUME OW ² (1956 - 1972) K gal	VOLUME PL ³ (1983 - 1988) K gal	Estimated DBP ⁴ Kg
AN-101	21.1	47.6	3,270
AN-102	142.6	161.4	23,300
AN-103	123.3	956.8	13,100
AN-104	89.7	654.9	12,800
AN-105	196.4	767.5	23,300
AN-106	2.0	0.1	202
AN-107	95.2	69.9	18,800
AP-101	4.6	129.0	708
AP-102	72.8	4.5	7,480
AP-103	1.0	32.0	176
AP-104	-	-	0
AP-105	46.9	1,512.4	7,610
AP-106	16.9	549.7	2,750
AP-107	-	-	0
AP-108	0.1	96.0	220
AW-101	148.3	2,261.6	18,200
AW-102	34.3	1,132.1	5,570
AW-103	0.0	10.3	24.4
AW-104	0.0	934.5	2,250
AW-105 ⁴	16.5	543.7	2,760
AW-106	37.5	1,227.5	6,160
AY-101	10.7	21.6	5,020
AY-102	0.0	1.1	20.4
AZ-101	4.4	10.8	570
AZ-102	0.3	13.2	60.7
SY-101	214	-	16,900
SY-102	0.0	0.3	1,610
SY-103	103.2	-	9,190
Total DST	1,381.8	11,138.5	182,052

Note:

- 1) Source of information is Reference 7; no NPH vapor samples at this time.
- 2) Reported as transferred from SSTs.
- 3) Waste contains average of 40 % OW based on 1985 - 1990 PUREX records.
- 4) 1985 surface sample identified a small floating layer of 30 % TBP 70 % NPH (Reference 22).
- 5) Source of information is Reference 7.

Table 6. SUMMARY OF SST SAMPLE RESULTS FOR TBP AND NPH ORGANIC

SST	Core/Auger Sample ¹ TBP $\mu\text{g/g}$	Projected TBP ¹ Gallons/Kg	Projected NPH ¹ Gallons/Kg	Total Gallons
C-204	334,000	1,543/5,682	TBD	TBD
BY-108	<0.1	<1/<0.1	110/320	110
C-112	205	28/100	80/230	180
BY-110	Below detection level	-	TBD	TBD
C-106	55	16/60	2/5	62
C-110	14	4/15	TBD	TBD
B-111	22	6/24	TBD ²	TBD
BX-107	7	3/13	TBD ²	TBD
C-103	No data	2,740/10,100	1,830/5,260	4,570
S-104	No data	-	305/880	TBD
T-104	No data	-	880/2,530	TBD
T-107	No data	-	15/40	TBD
Total	-	4,340/15,990	3,222/9,265	7,562

Note:

- 1) Based on information in tank characterization reports, conversation with J. A. Campbell (PNNL) or August 1996 tank characterization data base. Assumed solids density was 1.5 g/cc. Solid/liquid volumes as listed in Reference 14.
- 2) Sample taken before 12/91 and contaminated by NPH hydrostatic head fluid used in core sampler.

Table 7. SUMMARY OF DST RESULTS ON AQUEOUS SOLUBLE ORGANIC

DST	Aqueous Supernatant Sample TBP $\mu\text{g/l}$	Projected Soluble TBP ¹ Gallons/Kg	Estimated Equilibrium Floating Organic Layer ² Gallons	
			30 % TBP 70 % NPH	70 % TBP 30 % NPH
AP-101	<500 (9/94)	<0.5/<1.7	<0.8	<0.8
AP-102	Below Detection Level (4/93)	-	TBD	TBD
AP-103	Below Detection Level (4/94)	-	TBD	TBD
AP-104	190 - 8,800 (5/96)	3.7/13.8	2.9	<0.8
AP-106	110 - 1,100 (6/95)	0.5/1.8	<0.3	<0.3
AP-107	1,400 - 1,900 (6/95)	1.6/5.9	<0.7	<0.7
AP-108	Below Detection Level - 16 (9/94)	<0.1/<0.1	<0.2	<0.3
AW-102	Below Detection Level (4/94)	-	TBD	TBD
AW-106	Below Detection Level (4/94)	-	TBD	TBD
Total	-	6/23.2	<4.9	<2.9

Note:

- 1) Based Reference 20 or recent waste feed transferred to 242-A evaporator per E. Q. Le (WHC).
- 2) Based on preliminary solubility model; assumes no chemical or radiation degradation to achieve average TBP concentration of supernatant. Total not included in volume calculations due to uncertainties.

Table 8. SUMMARY OF PRELIMINARY ORGANIC VOLUME PROJECTION CALCULATIONS BASED ON OWW VOLUME RATIO

139 tanks (26 DSTs, 113 SSTs; see Tables 4 and 5) received OWW, contain TBP, NPH and/or paraffinic residues (BY salt cake), and/or vapor sample results show the NPH liquid phase mole fraction is ≥ 0.001 . The 0.001 value was used as criteria to identify potential tanks containing process organic. Mole fractions were developed from Raoult's Law and vapor sample results. TBP results are available for 18 tanks (9 DSTs 9 SSTs). NPH results are available for 6 SSTs. Information for these tanks was found in August 1996 tank characterization data base and References (2, 3, 5 - 9, 11, 12, 14, 17 - 21).

A) Predict organic in tanks assuming DSTs and SSTs combined (139 total tanks) based on 1) 19 tanks (9 DSTs 10 SSTs) containing a total of 63 gal TBP and 1,390 gal NPH (1,455 gal) and 2) tanks C-103 and C-204 are unique and contain 4,283 gal of TBP and 1,830 gal NPH (6,113 gal). PL2 is waste from PUREX 1983-88 campaign and contains OWW.

Summary of PUREX Organic Wash Waste Streams to Tanks

	HDW Model K gal OWW	HDW Model K gal PL2
SST (2)	3.3(C-103 & C-204)	0
SST (10)	0.1	0
DST (9)	167.2	3,171

	HDW Model K Gal OWW	HDW Model K gal PL2
SST(113)	2,652.6	0
DST(26)	1,381.8	11,138.5

PL2 waste contains about ~40 % OWW based on 1985 - 1990 records of PUREX.

OWW volume = 3,171 K gal (PL2 9 DST)*0.4 = 1,268.4 K gal

OWW volume = 11,138.5 K gal(PL2 26 DST)*0.4 = 4,455.4 K gal

Volume organic = [2652.6 (OWW 113 SST) + 1381.8 (OWW 26 DST) + 4455.4 (OWW/PL2 26 DST) = 8489.8 gal]/[(0.1 (OWW 10 SST) + 167.2 (OWW 9 DST) + 1268.4 (OWW/PL2 9 DST) = 1435.7)]*1455 gal (TBP & NPH in 19 tanks) + 6,113 (C-103 & C-204) = 14,700 gal

B) Predict organic in tanks assuming DSTs and SSTs combined (139 total tanks), based on 1) 2,998 gal TBP and NPH in 20 tanks (9 DSTs 11 SSTs) and 2) tank C-103 contains 4,570 gal TBP & NPH and is unique.

Volume organic = [8489.8 gal OWW (138 tks)]/[1435.6 gal OWW (20 tks)]*[1628 TBP + 1,390 gal NPH = 2,998 gal org (20 tks)] + 4,570 gal (C-103) = 22,300 gal

Table 9. SUMMARY OF PRELIMINARY ORGANIC VOLUME PROJECTION CALCULATIONS
BASED ON TANK NUMBER RATIO

139 tanks (26 DSTs, 113 SSTs; see Tables 4 and 5) received OWW, contain TBP, NPH and/or paraffinic residues (BY salt cake), and/or vapor sample results show the NPH liquid phase mole fraction is ≥ 0.001 . The 0.001 value was used as criteria to identify potential tanks containing organic. Mole fractions were developed from Raoult's Law and vapor sample results. TBP results are available for 18 tanks (9 DSTs 9 SSTs). NPH results are available for 6 SSTs. Information for these tanks was found in August 1996 tank characterization data base and References (2, 3, 5 - 9, 11, 12, 14, 17 - 21).

A) Predict organic in tanks assuming DSTs and SSTs combined (139 total tanks), based on 1) 19 tanks (9 DSTs 10 SSTs) containing a total of 63 gal TBP and 1,390 gal NPH (1,455 gal) and 2) tanks C-103 and C-204 are unique and contain 4,283 gal of TBP and 1,830 gal NPH (6,113 gal).

Volume organic = $(137/19) * 1455 \text{ gal} + 6,113 \text{ gal (C-103 \& C-204)} = 16,600 \text{ gal}$

B) Predict organic in tanks assuming DSTs and SSTs combined (139 total tanks), based on 1) 2,998 gal TBP & NPH org in 20 tanks (9 DSTs 11 SSTs), and 2) and 4,570 gal TBP & NPH org in tank C-103 unique:

Volume organic = $(138/20) * 2998 \text{ gal org} + 4,570 \text{ gal org (C-103)} = 25,300 \text{ gal}$

C) Predict organic in tanks assuming DSTs and SSTs as separate groups (26 DSTs & 113 SSTs), based on 1) 6 gallons TBP in 9 DSTs, 2) 2,992 gallons TBP & NPH org in 11 SSTs, and 3) and 4,570 gal TBP & NPH org in tank C-103 unique:

Volume organic = $(26/9 \text{ DSTs}) * 6 \text{ gal TBP} + (112/11 \text{ SSTs}) * 2,992 \text{ gal org} + 4,570 \text{ gal org (C-103)} = 35,000 \text{ gal}$

Table 10. SUMMARY OF PRELIMINARY ORGANIC VOLUME PROJECTION CALCULATIONS
BASED ON TBP/DBP MASS RATIO

Compare Agnew and Reddick/Sederberg TBP values for PUREX (1956-1991)

Agnew/HDW model predicts 593,767 Kg DBP in waste tanks per Reference 7. Reddick/Sederberg (Reference 16) estimate of 203,000 gal TBP from PUREX converts to 590,011 Kg DBP. Result - good comparison.

Predict mass of DBP added to tanks from organic usage at B Plant (1967-1981) assuming conversion of TBP to DBP (Table 2) and update HDW model for DBP

DBP B Plant to waste tanks = 10,770 gal TBP*3.785 L/gal*(973 g TBP/L)*(g mole TBP/g 266.3 TBP)*(210.2 g DBP/g mole DBP)*(0.001 Kg/g) = 31,308 Kg

Determine revised total mass of DBP in waste tanks assuming TBP degradation to DBP from PUREX and B Plant

593,767 Kg DBP PUREX (HDW Model/Agnew)
+31,308 Kg DBP B Plant (Klem)
625,075 Kg DBP Total

A) Predict organic in tanks assuming 1) the 4,570 gal TBP & NPH in C-103 and 1,543 gal TBP in C-204 are unique and 2) the 1,392 gal NPH in 5 SSTs are unique

Calculate TBP/DBP mass ratio for 16 tanks (9 DSTs + 7 SSTs)

	Measured TBP Kg	HDW Model DBP Kg	
SSTs	212	7,007	
DSTs	<u>23</u>	<u>23,064</u>	
Total	235	30,071	TBP/DBP ratio = 235/30,071 = 0.0078

TBP volume = (0.0078)*625,075 Kg DBP = 4880 Kg = 1,320 gal (16 tanks)

Volume organic = 1,320 gal TBP (16 tanks) + 4,570 gal TBP & NPH (C-103) + 1,543 gal TBP (C-204) + 1,392 gal NPH (5 tanks) = 8,800 gal

B) Predict organic in tanks assuming 1) 4,570 gal TBP and NPH of C-103 unique and 2) 1,392 gal NPH of 5 SSTs are unique

Calculate TBP/DBP mass ratio for 17 tanks (9 DSTs + 8 SSTs)

	Measured TBP Kg	HDW Model DBP Kg	
SSTs	5,900	7,007	
DSTs	<u>23</u>	<u>23,064</u>	
Total	5,923	30,071	TBP/DBP ratio = 5,923/30,071 = 0.197

TBP volume = (0.197)*625,075 Kg DBP = 123,140 Kg = 33,400 gal (17 tanks)

Volume organic = 33,400 gal TBP (17 tanks) + 4,570 gal TBP & NPH (C-103) + 1,392 gal NPH (5 tanks) = 39,400 gal

VOLUME 2
SECTION 4
IMPACTS ON DOUBLE-SHELL TANKS AND PRETREATMENT PROCESS

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VOLUME 2

Section 4.1

Impacts of Sludge Retrieval from Tank 241-C-103

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4.1 IMPACTS OF SLUDGE RETRIEVAL FROM TANK 241-C-103

The safety analysis performed by Geschke and Milliken (1995) indicated that interim stabilization of Tank 241-C-103, without first skimming the organic was acceptable provided additional actions were taken. These additional actions are provided in Table 4.1-1.

4.1.1 Sludge Retrieval from Tank 241-C-103

Hydraulic sluicing will be employed as the primary sludge retrieval technology in the SSTs. The primary features of the sluicers are shown in Figure 4.1-1 (the use of a 4-in. reinforced hose should be noted).

Extensive experience with high-volume hydraulic sluicing has been gained at the Hanford Site during two retrieval campaigns as described in *Hanford Waste Tank Sluicing History* (Rodenhizer 1987). Sluicing retrieval of sludge in SSTs is described for both uranium recovery in the 1950s and again for strontium recovery in the 1960s and 1970s. Approximately 3.8×10^6 gal of solids were sluiced from 55 tanks over 23 years of sluicing operations. Approximately 2.6×10^6 gal of solids were sluiced from 45 tanks in the B, C, T, U, TX, BX, and BY Tank Farms from 1952 to 1957 during the uranium recovery campaign. Approximately 1.2×10^6 gal of solids were sluiced from 10 tanks in the A and AX Tank Farms from 1962 to 1978 during the strontium recovery campaign. The solids volumes given for the past recovery campaigns are insoluble solids only and do not include salt cake. Based on retrieval technology options studies, sluicing is an acceptable retrieval technology.

The goal of sluicing campaigns was to leave only 1 to 2 in. of residual waste in the tank, but sluicing operations were terminated when the retrieval rate dropped below a minimum value. The current cleanliness requirement expressed in the Tri-Party Agreement allows for a 1-in. thick layer of uniformly distributed residual waste in the larger SSTs (500,000- to 1,000,000-gal capacity). This is equivalent to 360 ft³. During past retrieval operations, several tanks were cleaned to below the 360-ft³ requirement; however, many other tanks were left with a waste heel that was difficult to remove. A hard waste heel is known to exist in Tank 241-C-106 and other tanks are suspected of having a hard heel.

4.1.1.1 Materials Compatibility. Some materials used for waste retrieval operations may be incompatible with the organic in Tank 241-C-103; specifically the organic could cause degradation of the elastomer seals and EPDM Type P hoses. The organic may also volatilize and subsequently carry over to the offgas system during high pressure sluicing operations. The elastomer seal materials in some transfer pumps were tested for compatibility with TBP and NPH. The elastomers were exposed to a waste simulant comprised of 70 wt% TBP and 30 wt% NPH at approximately 40 °C. These TBP and NPH concentrations closely approximate those reported in the Tank 241-C-103 liquid sample analysis reported in *Waste Tank Organic Safety Project Analysis of Liquid Samples from Hanford Waste Tank 241-C-103* (Pool and Bean 1994). Results of this compatibility study can be found in Parazin (1994).

Table 4.1-1. Additional Controls Required for Interim Stabilization of Tank 241-C-103.*

GENERAL PROCESS CONTROLS	
1. If the riser is damaged, gas and vapor confinement will be maintained by a torus type gasket on the riser or by installing a temporary glove box until repairs are made to the riser.	3. A technician from the Hygiene, Safety, and Fire Protection organization will be present whenever the riser is open in accordance with the Tank Farm Health and Safety Plan.
2. Flammable gas concentration readings will be taken before intrusive work on the tank. For concentrations above 25% of the LFL, a sample will be taken in accordance with the Tank Farm Health and Safety Plan.	4. All lifts greater than 1.1 kN (250 lb) shall be treated as critical lifts. Critical lifts require additional operator training and rigging inspections in accordance with the Hanford Site Hoisting and Rigging Manual.
TRANSFER CONTROLS	
1. The transfer of waste from Tank 241-C-103 will be routed through the salt well screen prior to pump initiation.	6. All cover blocks will be in place on all facilities along the transfer route before initiating pumping and no cover blocks will be removed during pumping. Surveillance is mandated 72 hours prior to transfer and every 24 hours thereafter for permanent covers (every 12 hours for temporary covers).
2. The transfer rate will be limited to 151 L/min (40 gal/min), based on 1/3 solids carryover. The transfer rate may be revised based on the actual amount of solids carryover.	7. All leak detectors along the transfer route will be tested for operability prior to transfer.
3. If the Floway pump is used, thermal overload protection will be added prior to transfer.	8. All direct buried transfer pipes will be pressure tested prior to transfer.
4. A current drop of 50% (indicating a loss of suction) will shut down the pump.	9. MBDs will be calculated at least hourly during waste transfer operations.
5. Megger testing will be performed on the submersible pump prior to installation.	10. Nonconductivity level measurement gauges will be installed in the DCRT and the receiver tank prior to transfer.
RECEIVING TANK CONTROLS (INTERMEDIARY AND RECEIVER)	
1. Watch List DSTs will not be considered as receiver tanks.	4. If the mean TOC is > 10 g/L at double-shell slurry feed composition, the waste will be transferred to a complexant waste receiver tank in accordance with the waste compatibility program.
2. The DSTs will not exceed their maximum operating limits.	5. If the pH is adjusted in the DCRT, the ventilation flow through the tank will be $\geq 0.14 \text{ m}^3/\text{min}$ (5 ft ³ /min).
3. The receiver tank will have a waste temperature less than 74 °C (165 °F).	6. The operability of the DSTs active ventilation system will be verified prior to transfer.

Notes: *Based on Geschke and Milliken (1995)
 MBD - material balance discrepancy
 DST - double-shell tank
 DCRT - double-contained receiver tank
 TOC - total organic carbon

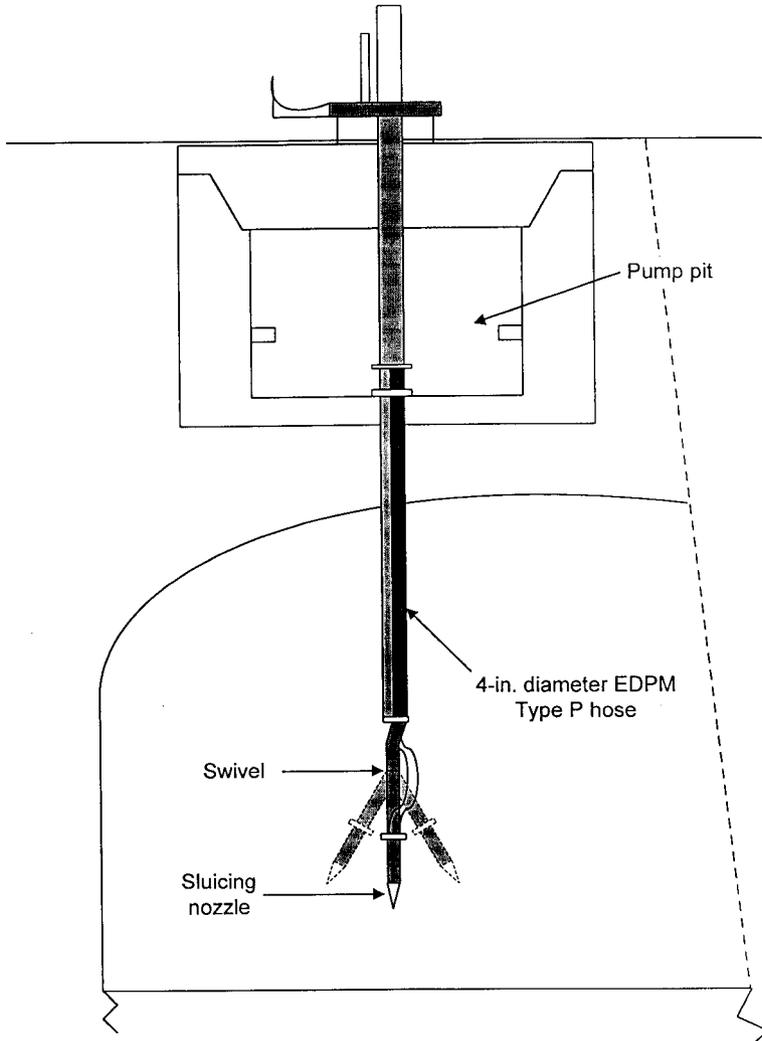


Figure 4.1-1. Sluing Assembly.

Test results for the elastomer seals indicate that EPDM would not be acceptable for long-term exposure.

The chemical resistance tables provided by one supplier of industrial hoses (Gates 1991) do not recommend EPDM hoses for TBP and NPH service. Hose materials recommended for TBP and kerosene (similar to NPH) are chlorinated polyethylene (CPE), cross-linked polyethylene (Gatron), fluorinated thermoplastic (Teflon), and fluorocarbon (Viton, Fluorel) (Gates 1991). Radiation resistance of Teflon is known to be low and is not recommended as a replacement. Cost impacts of hose replacements are minimal for new sluicing systems if the recommended hoses are acceptable for service in SST environments. A metal bellows hose with an outer woven metal sheath is an acceptable alternate that has been used successfully in past Hanford Site sluicing operations. The metal bellows is less flexible and more likely to retain radioactive materials in the bellows convolutes. Residual radioactive material would increase personnel radiation exposure.

The sluicing hose would be exposed to an emulsion of the organic material in the aqueous slurry during retrieval operations. The lower organic concentration in the slurry would reduce the detrimental effect on elastomer hose material.

Elastomer seals are used in the transfer pump, booster pump, and wall nozzle. Radiation resistant elastomer seals are used, but compatibility tests would be required for qualified seal materials. The transfer pumps will be reused in subsequent sluicing operations; however, pump seals can only be replaced on unused pumps due to personnel radiation exposure concerns.

4.1.1.2 Formation of Foams and Emulsions. Sluicing operations can be expected to mix the separable phase organic with the aqueous phase. The amount of organic in the tank would either be the 5,000 gal currently in the tank, if the tank is not skimmed or the residual left after skimming. The emulsified organic resulting from sluicing would be pumped by the transfer pump to the receiving tank. Retrieval rates and efficiencies are not expected to be significantly impacted.

Organic foams may form as the high flow sluicing jets impact the surface of the waste slurries and entrain gas from the head space. Foam volume is not expected to fill the head space or carryover to the offgas treatment system. Should foam volume become significant, defoaming agents should be considered to prevent foam carryover to the offgas treatment system. Foam carryover to the offgas treatment system could be expected to significantly increase pressure drops across high efficiency particulate air (HEPA) filters and subsequently cause filter failure.

Tanks receiving organic material and requiring active ventilation cooling due to the presence of high heat sludges will need to be evaluated to determine if equipment for removing organic vapors in the offgas system will be necessary to meet permitting requirements. The high velocity sluicing nozzles will generate a mist that will include aqueous materials along with any organic present. The high surface area of the mist will increase the vaporization rate of the organic. Organic vapors could be transferred out of the

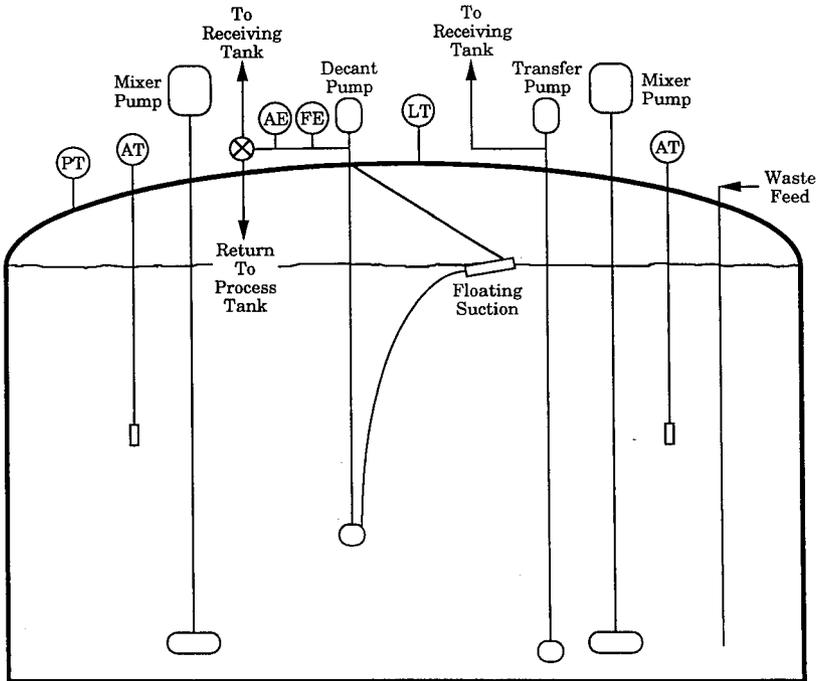
tank to the atmosphere via the active ventilation system. Any HEPA filter system that uses polyurethane could pose a material compatibility problem. The TBP and NPH have caused degradation and failure of such filters in the past.

4.1.2 Sludge Washing

Figure 4.1-2 depicts the equipment and instruments used for in-tank processing. Figure 4.1-3 shows the tanks that will be used for in-tank processing, and the transfer of waste during processing activities.

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AT = Tank Waste Turbidity Profiler or Ultrasonic Sludge Level Monitor
 AE = Decant Pump Discharge Turbidimeter
 FE = Flow Element
 LT = Level Transmitter
 PT = Pressure Transmitter

Figure 4.1-2. In-Tank Processing Equipment and Instruments (From MacLean 1995).

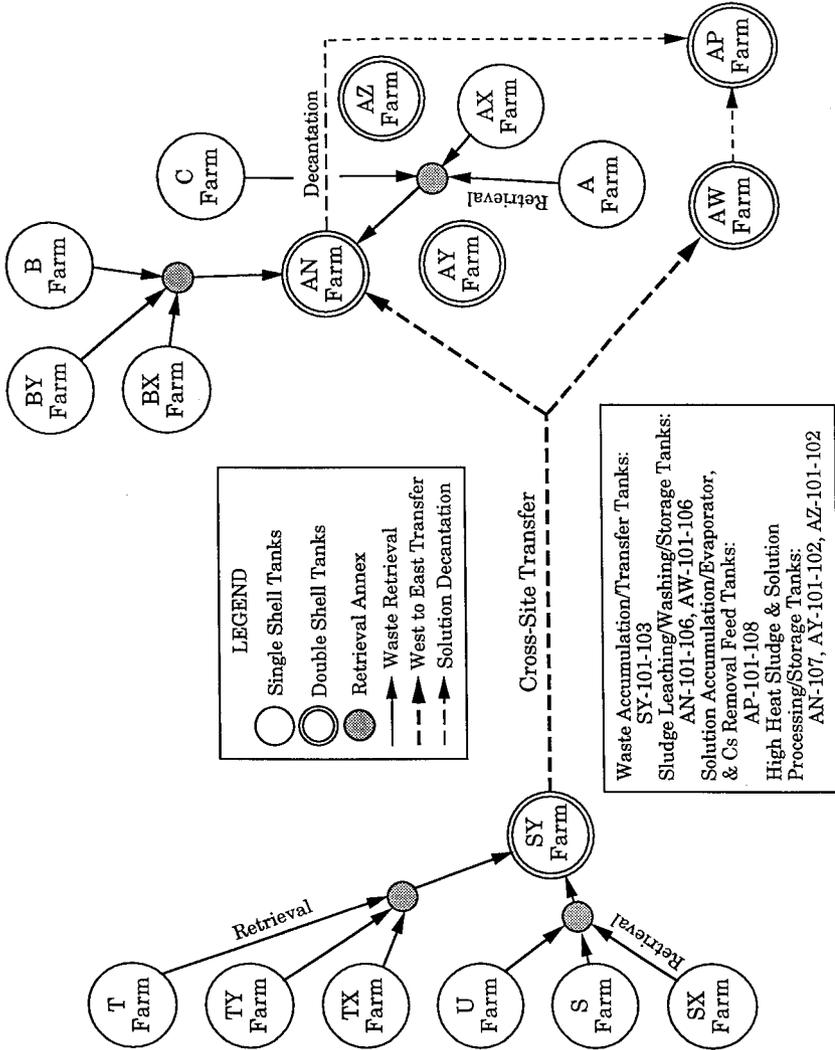


Figure 4.1-3. Tank Waste Retrieval and In-Tank Processing (From MacLean 1995).

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VOLUME 2

Section 4.2

**DSI - Impacts of Separable Phase Organics
on Filtration and Ion Exchange**

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DON'T SAY IT --- *Write It!*

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SUBJECT: Impact of Separable Phase Organics on Filtration and Ion Exchange

REFERENCES

Cheremisinoff, N. P., and D. S. Azbel, 1983, *Liquid Filtration*, Ann Arbor Science Publishers, Woburn, Massachusetts.

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BACKGROUND

Calculations based on inventories of cesium and sodium in tank 241-C-103 (Bean and Pool 1994) and on LLW product requirements listed in the Request for Proposal for TWRS privatization indicate that about 99.7% of the $^{137}\text{Cs}^+$ in tank C-103 will need to be removed (see calculation in Appendix A). Nearly all of the $^{137}\text{Cs}^+$ in tank C-103 is in the aqueous phase. Tank C-103 contains significant amounts of TBP both in a separate layer and either dissolved or emulsified in the aqueous supernate. A question is raised whether or not mixtures of TBP and hydrocarbons will effect the performance of filtration and ion exchange in the TWRS flowsheet. The following discussion presents the results of a literature search which attempts to answer this question.

RECOMMENDATIONS

Information from a search of the literature and from the data found in two independent studies (Mercer 1960 and Skarpelos 1963) in which cesium ion exchangers were tested with Hanford alkaline waste solutions (condensate waste) which had been in equilibrium with an organic layer of TBP/hydrocarbon, indicate that perhaps all of the separable phase TBP fed to a typical bed of cesium ion exchanger (either organic or inorganic) would be filtered out and irreversibly coat the exchanger. A cesium ion exchange system is not likely to be designed as a filter for removing bulk organics. Any use as such, which would be the case if TBP laden supernate is fed to the Cs-IX system, is likely to result in significant cost increases, as well as potential problems in meeting production schedules, and product quality specifications. Therefore it is not recommended to attempt to feed any of the separable organic layer of tank C-103 to a filter or to a bed of cesium ion exchanger (either organic or inorganic).

Not only is it recommended to remove all of the separable organic phase before filtration or cesium ion exchange including emulsified TBP, but it is also recommended to remove the dissolved TBP in the aqueous phase of the C-103 supernate to a level of about 1 mg TBP/L aqueous. Removal of the TBP to this level would minimize the volume of secondary waste from the cesium ion exchange operations, ensure that LAW product specifications are met, and avoid operational problems with the filter and cesium ion exchange system. This conclusion is based on data in Skarpelos (1963) which indicate that dissolved TBP at levels as low as 1 mg TBP/L, in the aqueous feed to beds of organic or inorganic ion exchangers resulted in significant deposition of a separate organic phase on the leading part of the bed which resulted in operational problems (reduced flow at constant pressure drop). TBP concentrations in the aqueous phase of the actual waste solutions tested by Mercer (1960), and Skarpelos (1963) were nearly identical as that reported in the aqueous phase of C-103 (about 100 mg TBP/L). Skarpelos (1963) proposed that the mechanism for the deposition of the separate TBP phase on the ion exchanger was by coalescence of emulsified TBP. A more likely explanation is that the TBP at concentrations of 1 - 100 mg/liter in the aqueous waste solution is soluble, and is adsorbed on the relatively high surface area of the ion exchanger. Once the soluble TBP builds up on the surface of the ion exchanger by the adsorption mechanism it is theoretically possible to coalesce into a separate organic phase such as that observed by Skarpelos (1963).

In order to reduce the concentration of the aqueous phase TBP from about 100 mg/L in C-103 to the recommended 1 mg/L it is recommended to study the following potential technology options; steam stripping, in-tank hydrolysis at high pH, and for final polishing, adsorbent beds such as the ion exchangers themselves in small particle sizes, and activated carbon. Skarpelos (1963) tested granular activated carbon, a membrane separator designed to remove emulsified organics, steam stripping, and beds of small particle size inorganic and organic ion exchangers. The activated carbon effectively removed the soluble TBP but plugged rapidly in much the same way as the beds of ion exchangers themselves. As in the case of the ion exchangers the TBP appeared to be adsorped on the activated carbon then coalesed into a separate organic phase causing a rapid and significant pressure drop across the beds. Attempts to remove the TBP from the activated carbon with a flow of steam at 250°C were largely unsuccessful. Skarpelos (1963) suggests that gas at a higher temperature may remove the TBP. The membrane separator did not remove TBP from the actual aqueous waste solutions tested. This was attributed to a the TBP forming a "very stable emulsion" in the aqueous phase, however it seems more likely that the TBP was actually soluble in the aqueous solution tested and therefore was not removed by the separator. A steam stripper was proven to remove about 98% of the TBP from the aqueous phase and was used consistantly thereafter prior to the ion exchange beds throughout the Skarpelos (1963) experiments. Even with the steam stripper removing TBP to levels of about 2 mg/L some deposition of TBP on the ion exchange beds was still noted with an associated increase in pressure drop. Sacrificial beds of small particle size inorganic and organic ion exchangers were used successfully to reduce the aqueous TBP concentration from about 2 mg/L in the steam stripper effluent to about 1 mg/L which then fed the ion exchange beds. Activated carbon beds were also used in this capacity (i.e. for polishing) although perhaps not quite as successfully.

A question is then raised that if TBP removal from C-103 is necessary before ion exchange, where would be the best place to do it e.g. from C-103 itself, from the sludge wash stage, or at the filtration step?. From a cesium ion exchange perspective it does not matter where the TBP removal takes place only that the organic is removed to the recommended 1 mg TBP/L concentration in the aqueous feed to the ion exchanger. Organic removal from tank C-103 appears to be advantageous in that:

1. The capital and operating costs of in-tank skimming are probably no more costly than those of decanting and removal from a downstream location. However much of the engineering and planning work has been done.
2. In-tank organic removal avoids problems associated with losing some organic (organic may hold-up in "pockets" through the system).
3. Left over organic in the aqueous phase of C-103 would then be subject to further reduction by hydrolysis in the sludge wash stage. This hydrolysis/degradation mechanism may be sufficient to reduce the TBP concentration to the desired 1 mg/L if enough organic is removed through the in-tank skimming process.

COST/PROBLEMS ASSOCIATED WITH THE ORGANIC LAYER

The Skarpelos (1963) and Mercer (1960) documents lack data which would allow an estimation of the volume of secondary waste generated by the cesium ion exchange process as a function of the amount or concentration of TBP in the feed, which thus would allow estimates to be made of the cost increases due to the TBP. It seems reasonable to assume however that the levels of TBP in the Cs-IX feed which were identified as problematic in the lab scale tests are likely to also be problematic in full scale and increase overall costs. This assumption is the bases for the recommended maximum TBP concentration of 1 mg/L in the feed to the cesium ion exchange beds.

If C-103 supernate was processed through a cesium ion exchange system without TBP removal normal operating costs of the cesium ion exchange operation could increase by a factor of 4 due to the added volume assuming that a TBP containing supernate could not be evaporated to the 5 - 7 M Na⁺ Cs-IX feed specification. This cost may be insignificant however based on the relatively small volume of the C-103 supernate.

Flow restriction through the lead ion exchange bed due to TBP adsorbing and coalescing on the first part of bed is likely to be the first problem to manifest itself and has the greatest potential for negative impact. Flow restriction problems could prevent LLW production goals from being met. More severe restrictions in flow could cause beds of ion exchanger to be "dumped early" i.e. before the desired cesium loading point is reached. This would cause an increase in the volume secondary waste, either LLW or HLW depending on the exchanger. "Dumping" beds "early" is also likely to cause production delays if the system for handling the spent exchanger is not designed to deal with excess material. A loss of exchanger performance due to decreased cesium/sodium mass transfer because of formation of a third (TBP) phase "coating" the ion exchange particle is another potential problem associated with TBP in the feed to Cs-IX.

In the case of a non-regenerable exchanger such as the engineered form of the CST (IE-911), the loaded/spent exchanger would best be blended into the HLW melter feed. The result of dumping beds early due to flow restriction problems or the effect of reduced exchanger performance would be to increase the volume of spent exchanger, and HLW glass logs. The sodium to cesium ratio of the C-103 supernate is close to that of the overall waste blend (Orme 1995) such that the rate of production of spent exchanger should be close to that of the average for all waste types. A significant increase in the rate of spent exchanger production, as would occur if TBP was fed to the Cs-IX columns, would likely cause problems and cost increases in the storage and handling of the spent exchanger depending on the amount of overcapacity designed into the spent exchanger handling/storage system. The Skarpelos (1963) and Mercer (1960) reports lack the data which allow estimations of the amount of spent exchanger produced as a function of TBP concentration/mass in the Cs-IX feed. Also no data exists on the spent exchanger handling/storage system nor data on costs associated with it's operation. Due to the lack of these data no estimates are made on the cost increases associated with TBP in the feed to a non regenerable cesium ion exchange system.

In the case of a regenerable organic cesium ion exchange resin such as resorcinol formaldehyde or CS-100, the spent resin would best be disposed of as LLW, i.e. either burned in the LLW melter, or packaged for storage as LLW. Cost increases associated with TBP in the feed to a regenerable cesium ion exchange system would come from the following:

- Decreased resin performance, i.e. increased mass of elution acid used resulting in increased operating/handling costs and an increase in the volume of HLW glass.
- An increase in the rate of spent resin production (very possibly beyond system capacity) which would likely cause problems and cost increases in the storage and handling of the spent resin depending on the amount of overcapacity designed into the system.
- Increase in the cost of storage and/or disposal of the spent resin as LLW.

As in the case of the non-regenerable exchanger data is lacking which relate TBP concentrations/mass in the CS-IX feed to the added volume of elution chemicals (and thus added volume of chemicals to HLW). Also data is lacking on the spent resin handling/storage system which might allow an estimate of costs associated with added spent resin volumes.

It should be noted that in either case (regenerable or non-regenerable exchanger) if TBP is present in the Cs-IX feed in sufficient quantity to adsorb/coalesce on the exchanger, the volume of secondary waste could be minimized by using a sacrificial bed of material prior to the lead Cs-IX bed.

DISCUSSION

A reference on filtration (Cheremisinoff and Azbel 1983) indicates that separate organic phases such as TBP/hydrocarbon, are likely to coalesce on the surface of a filter increasing the flow resistance through the filter due to the viscosity difference between the phases. Essentially the organic phase is likely to adhere to the filter occupying void space and thus restricting flow of the aqueous phase. Furthermore a separate TBP phase on the filter is likely to be difficult to be removed from the filter i.e. by the aqueous phase itself or by back-flushing. A bed of ion exchanger can be considered and will act as a filter to particles of a certain size distribution.

A preliminary literature search indicates that TBP, possibly even in small amounts, is likely to give some problems to a bed of organic or inorganic ion exchange media under conditions of the TWRS or a likely privatization flowsheet. Literature indicates that TBP in either a separate phase or emulsified form is likely to coalesce or wet the surface of the ion exchange media particularly where the feed enters the column. The coalescing organic phase is then likely to form a mat in the first part of the bed, thereby increasing the pressure drop. Channelling may result, and portions of the bed may be by-passed, reducing the efficiency of the bed. Wetting and coating of the ion exchange media by TBP will reduce the diffusion of ions in

and out of the exchange media, resulting in poor kinetics and thus poor performance (Helfferich 1962). Based on this information it is recommended that separate phase organics be removed as much as possible from the feed to ion exchange. Testing is recommended to verify the findings of this literature search and to determine the extent of TBP removal needed.

Literature indicates that soluble organics are a known problem for anion exchangers, however should not pose a problem to the cation exchangers such as those used for cesium removal. This is a general theory however, which should be validated through testing under actual conditions.

Two sets of ion exchange studies (Mercer 1960 and Skarpelos 1963) both of which using actual PUREX tank farm condensate waste indicate that mixtures of tributylphosphate (TBP) and hydrocarbon in alkaline waste at levels similar to those found in the aqueous phase of tank 241-C-103 may be detrimental to cesium ion exchange operations. The PUREX tank farm condensate waste used in both studies had a pH of 10 or lower, and a TBP content of about 0.10 g TBP/L aqueous solution. The aqueous phase waste of tank 241-C-103 has a pH of about 10, and a TBP concentration of about 0.086 g TBP/L. The problems may manifest themselves as decreases performance of the ion exchange media, specifically a decrease in the volume of feed processable given a maximum cesium concentration in the LLW, and/or loss of flow rate through the ion exchange column due to increased pressure drop.

Although the effect of a readily separable phase organic was not specifically tested in these studies, one can assume from the data given that the presence of any separable phase TBP in addition to that present as soluble or emulsified in the aqueous phase would only add to the problem. Neither study provided a quantitative description of the process conditions which brought on the increases in bed pressure drop nor did either report provide adequate quantification of the pressure drops themselves. Further testing, eventually with actual aqueous phase waste from tank 241-C-103 is required to verify and scope the potential for such problems.

Precise data on the solubility of TBP in alkaline supernates similar to that of C-103 is not available. It seems likely that the all the TBP is soluble both at the levels reported to exist in the aqueous phase of C-103, and also in the solutions used in the Mercer (1960) and Skarpelos (1963) reports. If this is so, a question is raised that if the TBP is soluble why does it appear to come out of solution and coalesce on the ion exchange media? Testing to identify the existing form of TBP in alkaline waste type solutions and to identify the mechanisms through which the TBP adsorbs then coalesces as a separate organic phase on the resin may be beneficial.

The following discussions summarize the findings of two studies (Mercer 1960, and Skarpelos 1963) in which actual alkaline waste solutions containing TBP and hydrocarbon mixtures were tested with beds of ion exchange media.

Mercer 1960

Actual condensate waste from PUREX high level waste storage facility was used to test the ability of the zeolite clinoptilolite to exchange cesium ion. PUREX tank farm condensate is produced by self boiling waste stored in underground tanks. Small amounts of TBP were found in the actual condensate waste used in these tests. TBP was the only organic detected. The experiments were conducted at 23°C. Clinoptilolite grain size was 0.42 - 0.50 mm (29 - 35 mesh). The flowrate was 4.0 gal/ft²-min.

More rapid breakthrough of cesium was observed at lower pH (i.e. 5 and 7 as opposed to 9) reportedly due to increasing deposition of organic material preventing access to the exchange sites. Reducing the pH "evidently breaks down an emulsion" of the organic in solution. "At pH 3 a column was rapidly plugged by organic material."

A sample of PUREX tank farm condensate waste was put through a small bed of activated carbon to remove organic material, concentration of tributylphosphate was reduced from 120 ppm (120 mg TBP/L aqueous) to less than 1 ppm (1 mg TBP/L aqueous). No ¹³⁷Cs was detected as having been adsorbed by the carbon bed.

Skarpelos 1963

Ion exchange experiments were conducted with actual PUREX tank farm condensate waste, a waste of pH 9-10 containing 30 to 200 mg of butylphosphates per liter aqueous phase and 10 to 20 mg of hydrocarbons per liter of aqueous solution. The organics were reported as being "emulsified" in the aqueous phase, however this is doubtful as the solutions were reported as have a clear appearance. TBP and the hydrocarbon are likely to be soluble in the aqueous phase at these concentrations. Beds of organic resin and clinoptilolite natural zeolite were tested for their ability to remove cesium, strontium and other radionuclides from the condensate waste. During the first scoping runs problems involving plugging of the ion exchange beds with TBP were encountered. The following is a quote from the report: "Organic matter in the condensate waste, especially in emulsified form, tends to be mechanically removed by natural zeolite clinoptilolite ion-exchange beds. The emulsified globules fill the void spaces in the bed and cause excessive pressure drop after only a fraction of the adsorption capacity is used. Plugging of the bed by organic material is characterized by the formation of a layer of an orange colored wax-like material in the top inch of the bed." From that test run on a large percentage of the work focus was directed at removing the TBP from the feed stream to the ion exchange beds.

The waste used for these tests was the aqueous phase obtained from the lower part of the retention tank 241-A-417. The waste originates as condensed vapors collected from the PUREX tank farm. Tank 241-A-417 is described as having an overflow through which much of the aqueous condensate and any organic matter are periodically overflowed through a proportional sampler to a crib. The aqueous condensate waste used in this study is listed as the following concentrations:

^{137}Cs	10^{-2} uCi/ml
butylphosphates	30 to 200 mg/L
Hydrocarbons	10 to 20 mg/L
Na^+	1 to 2 mg/L
NO_3^-	1 to 5 mg/L
NO_2^-	5 to 10 mg/L
pH	9 to 10

The organic was reported to be present as a very stable emulsion.

Three methods of removing organic matter prior to ion exchange were tried: activated carbon adsorption, and membrane separation, and steam stripping. Steam stripping appeared to be the best solution. A bench scale steam stripper used in these tests was reported to remove about 97% of the entering organics. Beds of activated carbon successfully removed both soluble and emulsified organic. The carbon beds however tended to plug with organic in much the same way as did the unprotected beds of ion exchanger, resulting in high pressure drops at a given flow rate. Membrane separation was expected to remove only emulsified organic. Membrane separation worked with simulated waste but the emulsion in the actual waste was reportedly too stable for separation.

Activated Carbon

The effectiveness of the activated carbon was studied at waste flow rates of 0.25 to 10 gpm/ft² (0.01 to 0.4 column volumes per minute). A 500 ml 1 inch diameter bed of 8 x 30 mesh type SGL activated carbon was used. Feed temperature was 25°C.

The activated carbon reduced the butylphosphate concentrations to >0.1 mg/L. Removal of hydrocarbons was not as efficient; their effluent concentrations varied from 0.5 to 4 mg/L, with the higher values occurring at higher flowrates. Tests indicated that activated carbon can remove about 0.23 g of organic matter per gram of activated carbon. With about 100 mg organic per liter in the condensate, about 1000 column volumes could be treated by the 500 ml bed of activated carbon. Activated carbon removal of organic matter successfully reduced the ion exchange bed hydraulic problems, but there were excessive pressure drops across the carbon beds.

Removal of organic material with the carbon bed did not seem to improve the decontamination efficiency of the clinoptilolite bed for cesium and strontium removal, but rather minimized hydraulic problems in the clinoptilolite bed. Many of these hydraulic problems however were merely transferred to the carbon bed. Another problem with activated carbon was the leaching of aluminum ash present in the carbon by the alkaline solution; later, the aluminum precipitated and tented to plug the downstream beds.

Membrane Separator

A commercial membrane separator (the Selas liquid - liquid separator) for removing emulsified organics, was evaluated for removing organics. The separator was designed to remove entrained liquid contaminants from liquid systems, and to separate immiscible liquids. The separator consisted of porous membranes which coalesce liquids and separate light and heavy phases for discharge. A waste simulant containing about 150 mg TBP/L, and 20 mg hydrocarbon diluent per liter, emulsified in water was prepared to test the separator. When the simulant emulsion was passed through the separator a clear effluent containing about 140 ppm TBP/L and 8 ppm hydrocarbon was produced. Organic matter was not removed from PUREX tank farm condensate after passage through a similar membrane system.

Steam Stripping

Steam stripping was tried to remove both organics and ammonium. Significant quantities of ammonium are thought to reduce the efficiency of cesium removal because Cs^+ is similar to NH_4^+ . The steam stripper consisted of an 8 ft length of 2 inch ID stainless steel (SS) tubing packed with 1/4 inch SS Raschig rings. A reboiler was fabricated from a 2 ft length of 4 inch SS pipe and contained a steam coil made from 10 ft of 3/8 in SS tubing. At a feed rate of 96 ml/min to the stripper and an overhead condensate rate of 6 ml/min, the NH_4^+ concentration in the bottoms ranged from 1 to 4 mg/L, the butylphosphate concentration was less than 1 mg/L and the hydrocarbon concentration varied from 1 to 4 mg/L. Thus the steam stripper removed over 97% of the organics. Waste leaving the steam stripper in the bottom stream had a pH of 5 to 7.

The activated carbon bed was used after the steam stripper in an attempt to remove residual organics, however when the organic in the stripper bottoms averaged 2 mg/L, the organics concentration in the effluent of the carbon bed averaged 1 mg/L, indicated rather limited adsorption. The pressure drop across the carbon bed increased after about 2,000 bed volumes. Stream directed up-flow at 250°F steam at atmospheric pressure through the carbon bed removed about 25% of the hydrocarbon and a negligible amount of the TBP. It is probable that the organic material removed by the steam treatment was present in the interstices of the bed and had been removed from the condensate by filtration rather than adsorption. Higher steam temperatures may remove the adsorbed organics. After the regeneration the carbon bed was effective at removing organics but pressure drops increased at a much high rate than before. The regeneration procedure apparently produced fines which impaired the hydraulic behavior of the bed.

Initial experiments with steam stripping prior to ion exchange used a carbon bed for removal of residual organics. Although the bed worked adequately functioning as a prefilter-adsorber, it's use did not appear practical for large scale application. Later experiments omitted the carbon bed. When used, the carbon bed often removed significant amounts of strontium, cerium, zirconium, and ruthenium, although the results were not always reproducible, and indication that partial removal by carbon might be due to filtration or colloid adsorption.

The steam stripper bottoms was reported as being very clear but residual organics were present as a filterable particulate. In one run (without the carbon bed after the steam stripper) at a flow rate of 1 gpm/ft², the initial pressure drop across an 11 inch deep strong acid cation resin bed was about 0.1 psi. The run was stopped after 6,000 column volumes when the pressure drop across the bed had increased to about 4.9 psi. Most filterable organic material was removed in a 1 inch layer at the top of the bed (some organic was dispersed throughout the bed). Since the organic had adhesive properties which caused considerable resin particle agglomeration, mechanical means were used to break up the agglomerate, and solvent treatment was necessary to dissolve the organic matter adhering to the resin beads before regeneration.

The organic material remaining in the steam stripper bottoms is not easily removed from the ion exchange beds by normal backwashing and regeneration techniques; therefore, filtering is necessary to protect ion exchange beds which are to be regenerated.

Steam stripped condensate was fed to a bed of Amberlite 200 without a prefilter or carbon bed. Pressure drop increased by 20 times after treating over 3,000 liters. The cesium DF was 1,000. The same experiment was done but the feed was acidified to pH 3.4 to 4.1. Cesium DF was 2,000, over 3,000 liters were processed and pressure drop across the bed did not appreciably increase during the run.

Clinoptilolite effectively removed cesium from the steam stripper bottoms stream to a cesium DFs of >1000. Even greater capacities were achieved with strong acid cation resins. When a feed containing 0.44 meq cations/L was passed through the bed of clinoptilolite, about 15,000 bed volumes of feed were treated.

Precoat Filter

The use of a precoat filter with a small particle cation exchange filter aid was considered so that both filtering and cation exchanges adsorption could be handled by one unit operation. Two experiments were performed with steam stripped condensate to evaluate the use ability of thin precoat beds of cation exchangers. In the first the steam stripped IX feed was acidified to a pH of 3.2 with HNO₃ then was passed through 1.7 cm of 200 x 400 mesh strong acid sulfonated polystyrene cation resin at a flow rate of 5 gpm/ft² (10 bed volumes/min). The cesium DF varied from 700 at the beginning of the test to 70 when it's MPC_w value was reached. The MPC_w of cesium in the effluent was reached after 2,250 bed volumes. Pressure drop across the bed increased from 2.1 psi at the start of the test to 3.3 psi at the end.

MPC_w = Maximum Permissible Concentration in Water for Occupational Exposure (168 hr wk) from National Bureau of Standards Handbook 69, June 1959. The cesium MPC_w is listed as 2×10^{-4} uCi/ml.

During another experiment the IX feed was acidified to a pH of 4 and was passed through 2.0 cm of 100 x 230 mesh acid washed clinoptilolite in the sodium format a flow rate of 5 gpm/ft² (10 bed volumes/min). The DFs for cesium ranged from 100 to 400 through 4,500 bed volumes. Pressure drop across the bed did not exceed 2 psi.

APPENDIX A CALCULATIONS

Assumptions

volume of organic layer in C-103 = 17,000 - 18,900 liters

composition of organic layer: TBP 50 vol%
NPH 25 vol%

$^{137}\text{Cs}^+ 0.041 \text{ uCi/g organic soln}$

density of organic layer 0.876 g/ml
density of TBP 0.973 g/ml

volume of aqueous and organic layer = 132,000 gallons (500,000 liters)

composition of aqueous layer: 1.4 M Na⁺
300 ug K⁺/g aqueous soln
80 ug TBP/g aqueous soln
1-3 ug NPH/g aqueous soln

$^{137}\text{Cs}^+ 57.9 \text{ uCi/g aqueous soln}$

density of aqueous layer: 1.078 g/ml

isotopic ratio of cesium in C-103: 0.25 gmoles $^{137}\text{Cs}^+$ per g mole Cs⁺

Calculations

Concentration of TBP in homogenized C-103 supernate:

$$\frac{17,000 - 18,900 \text{ liters org}}{\text{tank C-103}} \left| \frac{0.5 \text{ liters TBP}}{\text{liters org}} \right| \frac{1000 \text{ ml}}{\ell} \left| \frac{0.973 \text{ g TBP}}{\text{ml}} \right| \frac{\text{tank C-103}}{500,000 \text{ liters}} = 17 - 18 \frac{\text{g TBP}}{\text{liter soln}}$$

(1.75 E+07 mg TBP/liter soln), at 1.4 M Na⁺

concentration of TBP in aqueous phase only

$$\frac{80 \mu\text{g BP}}{\text{g aqueous}} \left| \frac{1.078 \text{ g aqueous}}{\text{ml aqueous}} \right| \frac{1000 \text{ ml}}{\text{liter aqueous}} \left| \frac{\text{g BP}}{1,000,000 \mu\text{g}} \right| = 0.086 \frac{\text{g BP}}{\text{liter aqueous}}$$

Which is below the solubility limit of TBP (in water at 25°C) of about 0.39 g TBP/liter.

total inventory of cesium

a) in aqueous layer

$$\frac{57.9 \mu\text{Ci } ^{137}\text{Cs}}{\text{g aqueous}} \left| \frac{1.078 \text{ g}}{\text{ml}} \right| \frac{1000 \text{ ml}}{\text{liter}} \left| \frac{\text{Ci}}{1,000,000 \mu\text{Ci}} \right| \frac{500,000 \text{ liters}}{\text{tank C-103}} = 3.12\text{E}+04 \text{ Ci } ^{137}\text{Cs}$$

b) in organic layer

$$\frac{0.941 \mu\text{Ci } ^{137}\text{Cs}}{\text{g organic}} \left| \frac{0.876 \text{ g}}{\text{ml}} \right| \frac{\text{liters}}{1000 \text{ ml}} \left| \frac{\text{Ci}}{1,000,000 \mu\text{Ci}} \right| \frac{18,000 \text{ liters}}{\text{tank C-103}} = 6.4\text{E}-01 \text{ Ci } ^{137}\text{Cs}$$

which is negligible

total inventory of sodium

$$\frac{1.4 \text{ gmole Na}^+}{\text{liter}} \left| \frac{500,000 \text{ liters supernate}}{\text{tank C-103}} \right| \frac{23 \text{ g Na}^+}{\text{gmole}} \left| \frac{\text{kg}}{1000 \text{ g}} \right| \frac{\text{MT Na}^+}{1000 \text{ kg}} = 16.1 \text{ MT Na}^+$$

Sodium to cesium ratio in C-103 supernate:

$$\frac{1.4 \text{ gmole Na}^+}{\text{liter}} \Big| \frac{500,000 \text{ liters}}{\text{tank C-103}} \Big| \frac{\text{tank C-103}}{3.12 \text{ E}+04 \text{ Ci}^{137}\text{Cs}} \Big| \frac{86.6 \text{ Ci}^{137}\text{Cs}}{\text{g}^{137}\text{Cs}}$$

$$\frac{137 \text{ g}^{137}\text{Cs}}{\text{gmole}^{137}\text{Cs}} \Big| \frac{0.25 \text{ gmole}^{137}\text{Cs}}{\text{gmole Cs}^+} = 6.65 \text{ E}+04 \frac{\text{gmole Na}^+}{\text{gmole Cs}^+}$$

Table A-1. Sodium to Cesium Ratios in Hanford Supernates			
Waste Type	[Na ⁺]:[Cs ⁺]	[Na ⁺]:[K ⁺]	volume @ 5M Na ⁺ (liters)
tank C-103	6.65 E+04	169	1.40 E+05
overall blend	2.41 E+05	1.86 E+02	6.75 E+08
NCAW	9.09 E+03	47	4.97 E+06
CC	9.21 E+04	240	3.88 E+07
DSSF	1.25 E+05	15	9.83 E+07

Cesium Removal Criteria:

The draft Request for Proposal (RFP) for TWRS privatization lists as a key product requirement a cesium concentration in the immobilized LAW form of less than 3 Ci/m³. Assuming that the LLW form was glass (and is thus denser than for example a glass in sulfur form) would give an estimated percent of cesium removal necessary. The percent of cesium removal required from the C-103 supernate is estimated as follows:

$$\frac{3.12 \text{ E}+04 \text{ Ci }^{137}\text{Cs}}{16.1 \text{ MT Na}^+} \left| \frac{23 \text{ MT Na}^+}{\text{MT mole Na}^+} \right| \frac{2 \text{ MT mole Na}^+}{\text{MT mole Na}_2\text{O}} \left| \frac{\text{MT mole Na}_2\text{O}}{62 \text{ MT Na}_2\text{O}} \right|$$

$$\frac{0.25 \text{ MT Na}_2\text{O}}{\text{MT LLW glass}} \left| \frac{2.6 \text{ MT LLW glass}}{\text{m}^3 \text{ LLW glass}} \right| = 935 \frac{\text{Ci }^{137}\text{Cs}}{\text{m}^3 \text{ LLW glass}}$$

$$\frac{(935 \text{ Ci }^{137}\text{Cs} - 3 \text{ Ci }^{137}\text{Cs})}{935 \text{ Ci }^{137}\text{Cs}} (100) = 99.7\% \text{ of the } ^{137}\text{Cs}$$

so about 99.7% of the ¹³⁷Cs⁺ in the supernate of C-103 needs to be removed.

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ABOVEGROUND STORAGE

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VOLUME 2

Section 6.1

**DOT Regulation Changes and Advantages and Disadvantages of
Aboveground Storage Tanks**

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6.1 DOT REGULATION CHANGES AND ADVANTAGES AND DISADVANTAGES OF ABOVEGROUND STORAGE TANKS

This section contains information on new DOT regulations regarding low-specific activity (LSA) requirements. This section also describes the advantages and disadvantages of various aboveground storage tank options.

6.1.1 DOT Regulation Changes

A comparison of the new LSA-II limits and the organic levels in Tank 241-C-103 for an assumed aqueous fraction of 0.2% is provided in Table 6.1-1. Table 6.1-2 shows the LSA-II factors for varying aqueous fractions.

6.1.2 LR56/H Cask System

6.1.2.1 Cost. The SARP doesn't address a payload which is primarily organic (although the presence of small quantities of organics is mentioned). The gas generation analysis is empirically based on Tank 241-SY-101 data. If the Tank 241-C-103 liquid payload does not meet the requirements for Type A quantity or LSA-II, then a revision to the SARP will be needed to fully address all safety issues in the SARP.

6.1.2.2 Advantages and Disadvantages. The advantages and disadvantages of using the LR56/H cask for storage of the Tank 241-C-103 organic are discussed below.

Advantages

- Shielded
- Available
- Designed for shipping materials with high rad levels
- Can ship with aqueous
- Sump installed in bottom can pump from bottom
- Likely easier to complete engineering change notice to existing SARP
- Has an active demister, charcoal, and HEPA filtration system that can also be used passively.
- Onsite transport.

Disadvantages

- Small volume (1,000 gal)
- Can't use for long-term storage
- May have to replace seals
- Still doesn't solve storage problems
- Not yet used onsite.

Table 6.1-1. Comparison of New LSA-II Limits and Organic Levels in Tank 241-C-103.
 Volume = 18,925 L; Density = 0.871 g/mL; Assumed aqueous fraction = 0.20%

	Organic Conc ¹ (μ Ci/mL)	Aqueous Conc ² (μ Ci/mL)	Mixture Concentration (μ Ci/mL)	Mixture (Concentration) (Ci/g)	New DOT LSA II Limit (Ci/g)	LSA-II Factor Concentration/ Limit
Pu-238	7.85E-05	7.07E-03	9.25E-05	1.06E-10	5.41E-08	1.96E-03
Pu-239/240	1.69E-04	1.52E-02	1.99E-04	2.29E-10	5.41E-08	4.22E-03
Pu-241	5.38E-03	4.09E-01	6.19E-03	7.10E-09	2.70E-06	2.63E-03
Am-241	1.56E-04	1.40E-02	1.84E-04	2.11E-10	5.41E-08	3.90E-03
Cm-244	3.70E-05	3.33E-03	4.36E-05	5.00E-11	1.08E-07	4.63E-04
Sr-90	4.79E-01	7.05E+01	6.19E-01	7.11E-07	2.70E-05	2.63E-02
Co-60	6.48E-04	5.10E-02	7.49E-04	8.60E-10	1.08E-04	7.96E-06
Cs-137	3.59E-02	5.78E+01	1.51E-01	1.74E-07	1.35E-04	1.29E-03
Eu-154	2.76E-04	2.10E-02	3.17E-04	3.64E-10	1.35E-04	2.70E-06
Eu-155	2.74E-04	2.08E-02	3.15E-04	3.62E-10	5.41E-04	6.69E-07
Total LSA-II Factor						0.0408³

- (1) From Pool and Bean (1994).
- (2) Based on Pool and Bean (1994). Some activities estimated.
- (3) Factors < 1 can be shipped provided external doses acceptable.

Table 6.1-2. LSA-II Factor for Varying Aqueous Fractions.

% Aqueous¹	LSA-II Factor²
0.00%	0.0319
0.10%	0.0364
0.20%	0.0408
0.30%	0.0452
0.40%	0.0497
0.50%	0.0541
0.60%	0.0586
0.70%	0.0630
0.80%	0.0674
0.90%	0.0719
1.00%	0.0763
(1) LSA Factor results if different %	

6.1.3 Portable ISO Tank Advantages and Disadvantages

The advantages and disadvantages of using either a new or existing ISO tank for storage of the Tank 241-C-103 organic are discussed below.

New Portable ISO Tank

Advantages

- Provides most options for final disposal
- Can lift by crane
- Can ship by rail or on flat bed truck
- Vessel meets DOT shipping criteria
- Can build to size up to 7,000 gal to support in-tank washing
- Can set up to pump heel
- Cylinder shape conducive to heel pumping
- May have resale/site reuse value (e.g., nitric acid tanks at PUREX Plant now in use at Savannah River) - may be reused for TWRS
- Onsite experience
- Existing PUREX Plant containers engineered onsite - much is applicable to new construction - decreases cost
- Can design pump and other openings.

Disadvantages

- Have to start buying at least six months in advance (building tanks takes two months, four months for engineering, etc.)
- Has no shielding
- More expensive than PUREX Plant tanks
- Creates another tank which must ultimately be decommissioned.

Existing Portable ISO Tank

Advantages

- Nearly same as above
- Does not contaminate additional tanks.

Disadvantages

- 4,000-gal size is smaller than a new tank
- Most in Savannah River
- Two onsite owned by B Plant, scheduled for use
- Limited to access in existing tanks.

6.1.4 Cargo Tanker Truck Advantages and Disadvantages

Advantages and disadvantages of using a cargo tanker truck for storage of the Tank 241-C-103 organic are listed below.

Advantages

- Available
- Relatively inexpensive
- Can go anywhere onsite
- Good experience
- Onsite transport
- Offsite transport.

Disadvantages

- Unshielded
- Exposure to driver
- Long-term storage problems
- May contaminate organic
- Maintenance requirements
- Difficult to radiological release truck equipment.

6.1.5 Liquid Waste Tank Car (Rail) Advantages and Disadvantages

Advantages and disadvantages of using either a new (double-shell) railcar or an old (single-shell) railcar for storage of the Tank 241-C-103 organic are listed below.

New Railcar (Double-shell)

Advantages

- Can use spacers (exposure control)
- Volume

- No existing contamination
- Onsite transport.

Disadvantages

- Stuck on rail lines
- Paying for more capacity than needed
- Fewer facilities can take
- Maintenance requirements
- Storage location
- Onsite transport.

Old Railcar (Single-shell)

Advantages

- Can use spacers
- Volume
- Readily available at minimal cost.

Disadvantages

- Same as above except cost
- Contains transuranics
- High dose
- Long-term storage.

6.1.6 Lab Packs Advantages and Disadvantages

Advantages and disadvantages of using lab packs to store the Tank 241-C-103 organic are summarized below. Table 6.1-3 provides the DOT limited quantity requirements for lab packs.

Advantages

- Meets CWC criteria.

Disadvantages

- More difficult to pump tank
- Requires approximately 350 lab packs
- Limits options
- Not acceptable for offsite shipment of this organic material.

This section provides additional general packaging safety and regulatory issues.

- Potential safety and regulatory issues pertaining to transportation include the necessity for identification of the payload, minimization of radiation doses resulting from the operation, and verification of the package safety through appropriate safety analyses, including containment and shielding.

Table 6.1-3. DOT Limited Quantity Requirements for Tank 241-C-103 Organic in Lab Packs.

Volume = 18,925 L; Density = 0.871 g/mL;
Assumed aqueous fraction = 0.20%

Isotope	Mixture Concentration ($\mu\text{Ci/mL}$)	Mixture Activity (Ci)	DOT A2 (Ci) Limit	Type A Activity/Limit
Pu-238	9.25E-05	1.75E-03	0.00541	3.23E-01
Pu-239/240	1.99E-04	3.77E-03	0.00541	6.96E-01
Pu-241	6.19E-03	1.17E-01	0.27	4.34E-01
Am-241	1.84E-04	3.48E-03	0.00541	6.43E-01
Cm-244	4.36E-05	8.25E-04	0.0108	7.64E-02
Sr-90	6.19E-01	1.17E+01	2.7	4.34E+00
Co-60	7.49E-04	1.42E-02	10.8	1.31E-03
Cs-137	1.51E-01	2.87E+00	13.5	2.12E-01
Eu-154	3.17E-04	6.01E-03	13.5	4.45E-04
Eu-155	3.15E-04	5.96E-03	54.1	1.10E-04
TOTAL A2s				6.73E+00

Total A2s present in 18,925 liters = 6.73
 Total A2s present in 15 gallons = $(6.73/18,925) \times 15 \times 3.785$ liters/gal = 0.02
 (49 CFR 173.425) Limited quantity specification: 1E-04 A2s per package
Maximum volume of Tank 241-C-103 waste for limited quantity: 1E-04 x 15/0.02 = 0.07 gal; 0.28 L

(1) See Table 6.1-1 for organic and aqueous concentrations.

- Use of existing, contaminated packagings, especially the LWTC, may result in the contamination of the payload with transuranic isotopes. The effect of such potential contamination of the Tank 241-C-103 organic liquid should be evaluated when selecting a specific packaging.
- Potential safety and regulatory issues related to the storage of the organic liquid in a transport container include the dose rates, leakage detection capabilities, and storage permits.
- Ongoing National Environmental Policy Act work should be reviewed prior to pumping to verify that it will cover Tank 241-C-103 transfers.
- Receiving facility SARs should be reviewed to verify that they cover the planned operations.
- From the standpoint of the LR56/H SARP, the only significant issues will be material compatibility and gas generation. These problems should be solvable, but will need inclusion in the SARP.

6.1.7 Use of the LR56/H Cask as an Initial Wash Tank

This section discusses this option and a potential chemical that could be used for the wash.

6.1.7.1 Processing Advantages. If the organic liquid from Tank 241-C-103 is pumped in batches to the LR56/H cask first, the advantages include:

- Shielded tank
- Pump suction at tank low point
- Several pumping methods
- Internal spray wash
- Active or passive ventilation including demister, charcoal, and HEPA filters.

The likely scenario would be as follows:

- Skim organic to the LR56/H cask: monitor the inlet radiation for indications of aqueous waste carryover, fill tank to accepted volume for washing
- Add radionuclide wash chemicals
- Recycle all liquid through the internal spray wash system
- Let settle
- Pump aqueous to organic receiving tank (e.g. the ISO tank if shipping offsite)

- Repeat wash if necessary
- Pump organic to ISO tank.

The benefit of this approach is that it will be much more likely that the organic in the ISO tank will meet the requirements for an offsite vendor. It is possible that no long-term storage would be required.

6.1.7.2 Processing Concerns. Prior to WHC and DOE approval of using the LR56 for washing, the following should be addressed:

- How is wash solution added to LR56/H?
- What DST receives the EDTA wash solution? (EDTA is a complexant, a candidate tank is Tank 241-AY-101).
- How is wash solution transferred from LR56/H to the receiver tank?
- How many washes are required and how much volume will be generated?
- Does the LR56/H have the means to determine organic/aqueous phase interface?
- EDTA wash tests conducted by Pacific Northwest National Laboratory used a centrifuge to separate organic/liquids and noted "dark solid materials at interface". What implications are there for washing in the LR56/H? **Note:** Communication with Pacific Northwest National Laboratory said they observed a few specks of floating solids at the interface. There were insufficient amounts collected and analyzed. Pacific Northwest National Laboratory stated there was probably no cause for concern. Twenty-four to 48 hours was sufficient for aqueous organic phase separation by gravity.

6.1.8 ISO Tank Washing

The ISO tank could also be used for washing. Even if the LR56/H cask is used for washing, the ISO tank will have to have the necessary equipment to remove aqueous. This equipment would include a bottom suction pump. This pump system could be set up to recirculate the contents of the tank. If a chemical system is added and the general issues identified for washing with the LR56/H tank are addressed, the ISO tank could also be used. One potential issue with using the ISO tank is that of a single wall container. Some additional means of containment (e.g., inside a facility) may be required after a full safety analysis.

REFERENCE

Pool, K.H., R.M. Bean, 1994, *Analysis of Liquid Samples from Hanford Waste Tank 241-C-103*, PNL-9403, Battelle Pacific Northwest Laboratory, Richland, Washington.

VOLUME 2

Section 6.2

**DSIs - Contamination in Organic Samples Used
for Some Early Source Term Calculations**

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Date March 29, 1994

T. Hosaka
File/LB

To Karl Pool

From Sandy Fadeff

Subject Activity on Organic-Aqueous Mix Test

This memorandum is written in response to a request by Karl Pool to evaluate the activity represented by the count rates reported in a previous report (reference memorandum dated March 17, 1994, Tank C103 Organic-Aqueous Mix Test by R. Strebin and S. Fadeff).

The approximate counting efficiency for alpha measurements on a beta counting planchet (1 inch diameter) was determined. From this counting efficiency, the approximate activity of the mix-test sub-aliquots could be determined. In order to determine the approximate counting efficiency for the gamma emitters, a 50 µL aliquot of the unmixed organic layer was plated on the beta counting planchet. This was counted on the gamma counter and a direct ratio was established for the beta plate count rate and the activity determined by L. R. Greenwood on 12/20/93.

The results are summarized below.

1 Liter = 0.26417 gallons

Analyte	90 Minute Sampling		24 Hour Sampling	
	Alpha	39 cpm	1200 pCi/mL	12 cpm
Beta	1.2E+5 cpm	2.2E+6 pCi/mL	66,300 cpm	1.2E+6 pCi/mL
Gamma ¹³⁷ Cs ⁶⁰ Co	5,200 cpm 4 cpm	5.3E+6 pCi/mL 2200 pCi/mL	710 cpm 2 cpm	7.2E+5 pCi/mL 1100 pCi/mL

It is important to note that the reported activities are only approximate; they are based on a rough calibration for the alpha and gamma analytes.

5,567.5 gallons 0.2% Agn.

$$^{137}\text{Cs} (21075.44) \times 1000 \times 1e^{-12} \times (7.2e+5 \times 9.98 + 5.7e7 \times .002) = 17,585$$

$$^{60}\text{Co} = 0.0253$$

5,567.5 with 1% Agn.

$$^{137}\text{Cs} (21075.44) \times 1000 \times 1e^{-12} \times (7.2e+5 \times 9.98 + 5.7e7 \times .002) = 27,225$$

ESA-1800-001 (10/88) 60

$$= 11.2 \times 10^5 \times (110 \times 9.98 + 5.7e7 \times .002) = 0.0337$$

4,000 gal organic

$$^{137}\text{Cs} \frac{15146 \times 1000 \times 7.2e+5 \times 1e^{-12}}{1000} = 10.9$$

$$^{60}\text{Co} \frac{1666 \times 0.0161}{1567.5 \text{ gal organic} \times 0.2\% \text{ Agn}} = 4.95$$

$$^{137}\text{Cs} (5733.68) \times 1000 \times 1e^{-12} \times (7.2e+5 \times 9.98 + 5.7e7 \times .002) = 260712$$

$$^{60}\text{Co} = (5733.68) \times 1000 \times 1e^{-12} \times (110 \times 9.98 + 5.7e7 \times .002) = 260712$$

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K12015

T. Hosaka
L. Greenwood
File/LB

March 17, 1994

KH Pool
RS Strebin and SK Fadeff

Tank C103 Organic-Aqueous Mix Test

A test was performed to determine the partitioning of gamma, alpha, and beta radioactivity when the organic layer is mixed with the aqueous layer. Samples were to be taken after initial phase separation (estimated to be 5 minutes based on simulant studies) and again 24 hours later.

One milliliter each of the organic layer and aqueous layer were placed in a 15 mL plastic centrifuge tube. The mixture was stirred on a vortex mixer for 1 min at a setting of 6. After 5 min the top organic layer was just beginning to separate from a middle emulsion-mix layer. After 14 min the organic portion assumed 3 distinct layers. After 50 min the organic layer consisted of about 2/3 organic and 1/3 emulsion-mix (the third organic layer was no longer evident). In consultation with KH Pool, 50 μ L of the organic layer was sub-sampled after 90 min for gross alpha, gross beta, and gamma analyses. At this time the emulsion layer was still present. After 24 hr the organic layer had apparently attacked the plastic tube resulting in tube softening and deformation. Again, 50 μ L of the organic layer was sampled at this time for gross alpha, gross beta, and gamma analyses. **The available volume of the organic fraction was small and some aqueous or emulsion layer was withdrawn in the sub-samples taken for gross alpha and gamma analyses.** (Emphasis added by P. Bartley, 2/10/96). Therefore, only the beta mount preparations were counted for all analyses.

The counting results are provided in the table below. Because the alpha count is not calibrated relative to the beta planchet geometry, only count rates are presented (as opposed to disintegration rates). The same applies to the gamma counts. However, cross comparisons can be made between the 90 min and 24 hr sampling times as the relative geometries are consistent.

If this experiment is to be repeated, larger organic and aqueous volumes should be used so that subsequent sampling would proceed more effectively. Also a glass screw cap centrifuge tube should be used to avoid the reaction of the plastic with the organic layer.

Analyte	90 min Sampling	24 hr Sampling
Alpha	39 cpm	12 cpm
Beta	121,000 cpm	66,300 cpm
Gamma	5,200 cpm	710 cpm
¹³⁷ Cs	4 cpm	2 cpm
⁶⁰ Co		

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VOLUME 2

Section 6.3

Letter - Information on Tank 241-C-103 Organic Sampling Effort

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Westinghouse
Hanford CompanyInternal
Memo

From: J. L. Huckaby
 Phone: 373-3443 R2-78 7A300-94.003
 Date: February 2, 1994
 Subject: FIELD REPORT FOR COLLECTION OF LIQUID SAMPLES FROM TANK
 241-C-103 ON DECEMBER 15, 1993

To: J. W. Osborne

cc: H. Babad R2-78
 G. Dukelow R2-78
 J. M. Grigsby H4-62
 M. A. Payne R2-31
 D. A. Turner R2-78
 JLN File/LB R2-78

I provided engineering field support for the December 15, 1993 liquid sampling of tank 241-C-103, and was present during the collection of all liquid samples from the tank. I reported the event by cc:Mail to the interested parties the day after the sampling event. For your future reference, I am submitting the following verbatim text of the cc:Mail report I wrote and sent on December 16, 1993:

"Sample job 6, which included the collection of semivolatle organic vapor and aerosol samples, organic and aqueous liquid samples, and the measurement of the organic liquid depth in tank 103-C was completed December 15. All objectives of the sampling event were met. It was determined that the organic waste layer in tank 103-C is between 1.5 and 2 inches thick, 6 100 ml samples of the organic liquid were collected, and 1 100 ml sample of the aqueous liquid was also collected.

Results from the first step of sample job 6, collection of the semivolatle organic vapor and aerosol samples, indicated the fuel content of the headspace to be about 6 to 7 percent of the lower flammability limit.

A special zipcord, designed to locate both the organic surface and the interface between the organic and aqueous liquids, did not detect the organic liquid surface. This would be expected if the organic liquid in the tank is significantly less conductive (has lower concentration of ions) than the simulated organic liquid used to test the special zipcord. The zipcord did, nevertheless, accurately locate the interface between the organic and aqueous liquids. The interface was determined to be 33 ft 0.125 in. below the riser flange.

Visual inspection of the waste surface during the zipcord measurements and the first liquid sampling, allowed by

J. W. Osborne, et al.
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February 2, 1994

7A300-94.003

virtue of a very mild field of only 20 mR at the riser flange, indicated the surface to be about 32 ft 10.5 in. below the riser flange. This location was confirmed by subsequent liquid sampling; a bottle lowered to 32 ft 10 in. returned empty, and careful inspection during the subsequent sampling indicated the sample bottle did not begin to fill (air bubbles were produced while the bottle filled) until the lip of the bottle was at 32 ft 10.5 in. below the riser flange. Given the uncertainties of these measurements, and the fact that sample bottles did fill at 32 ft 10.5 in., the thickness of the organic layer is estimated to be between 1.5 and 2.0 in.

The 6 organic liquid samples were all collected from 32 ft 10.5 in. below the riser flange, essentially at the surface. Surveys indicated the sample bottles to be 2 to 5 mRad/hr on contact. The organic liquid is a clear (as opposed to opaque or cloudy), bright red liquid. It looks like cranberry juice or red wine. All sample bottles were filled completely, with minimal air trapped in each bottle. At the temperature of the tank, the liquid appeared nonviscous, being maybe about as viscous as water. Two of the samples collected contained drops of a clear, immiscible liquid, which rested on the bottom of the bottles. These drops were apparently water, and provide fairly good evidence that the samples were indeed organic.

The single aqueous liquid sample was collected 34 ft 10.5 in. below the riser flange, using an uncorked bottle. The sample bottle was allowed to sink rapidly through the organic and upper aqueous liquid to avoid the inadvertent collection of that liquid. The aqueous sample was surveyed and determined to be about 200 mRad on contact. The aqueous sample was a lighter, brownish red, but also appeared to be a clear liquid.

Five of the organic samples and the aqueous sample have already been shipped to PNL in the 300 area, and analyses will begin December 16. The remaining organic sample is to be shipped to the 222-S lab for adiabatic calorimetry.

Other supplementary information obtained includes the fact that no fog currently exists in the headspace, though a light fog does exist in the riser (this would not exist during warmer seasons). Evidence indicated that the headspace is nearly saturated with water vapor, and that the fog in the riser is composed of water droplets (not organic droplets). Also, temperature readings several feet above the waste and at a position

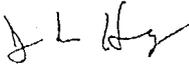
J. W. Osborne, et al.
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February 2, 1994

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10 ft above that were identical, suggesting the headspace is convectively mixed.

A great many thanks are due to all the people who helped directly and indirectly to make this sampling event a success. Tank farm operations conducted the event extremely well; the entire operation was performed in a safe, cooperative, and productive fashion.

Should you require further information on the field sampling event, please contact me at 373-3443.



J. L. Huckaby, Ph.D.
Senior Engineer
Tank Vapor Issue Resolution Program

mjs

VOLUME 2

Section 6.4

DST - Dose Rate Calculation for Organic Waste from Tank 241-C-103

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DON'T SAY IT --- Write It! DATE: January 29, 1996

TO: Jennifer Mercado G2-02

FROM: R. A. Schwarz HO-35

Telephone: 376-5977

SUBJECT: DOSE RATE CALCULATIONS FOR WASTE FROM TANK C 103

1. "Dose Rates Outside a 5,567 Gallon Tank of C 103 Waste," DSI from R. A. Schwarz to T. R. Wilson, dated June 6, 1994

Initial dose rate calculations for organic waster were reported in reference 1. This document describes additional calculations made for the organic waste using the source description provided in Table 1. In Table 1 it is conservatively assumed that there are equal amounts of ^{239}Pu and ^{240}Pu , both of which are set to the total provided in the source reference. Additionally, it is assumed that all of the ^{90}Sr will decay to ^{90}Y and all of the ^{137}Cs will decay to $^{127\text{m}}\text{Ba}$.

This source was used by the Isoshield-PC computer code to calculate the dose rate outside a cylinder 9.5 ft. in diameter with a length of 10.5 ft. This cylinder has a density of 0.868 g/cc and is surrounded by a 3/8 in. thick steel container. The results of this dose rate calculation is provided in Table 2 with a graphical representation of these dose rates shown in Figure 1. Attached to this document is the Isoshield-PC input file used for these calculations.

The surface dose rate from Reference 1 for a source with 17.6 curies of ^{137}Cs and 0.025 curies of ^{60}Co is 173.2 mrem/hr. The current source has 16% of the ^{137}Cs as the previous source and 56 % of the ^{60}Co of the previous source, thus it is expected that this source should be higher than 16 % of 173.2 (17.7 mrem/hr) and lower than 56 % of 173.2 (97 mrem/hr). The source dose rate for the current source is 57 mrem/hr which compares well with what is expected from the previous calculations.

Table 1. Source Term for Tank C 103 Waste

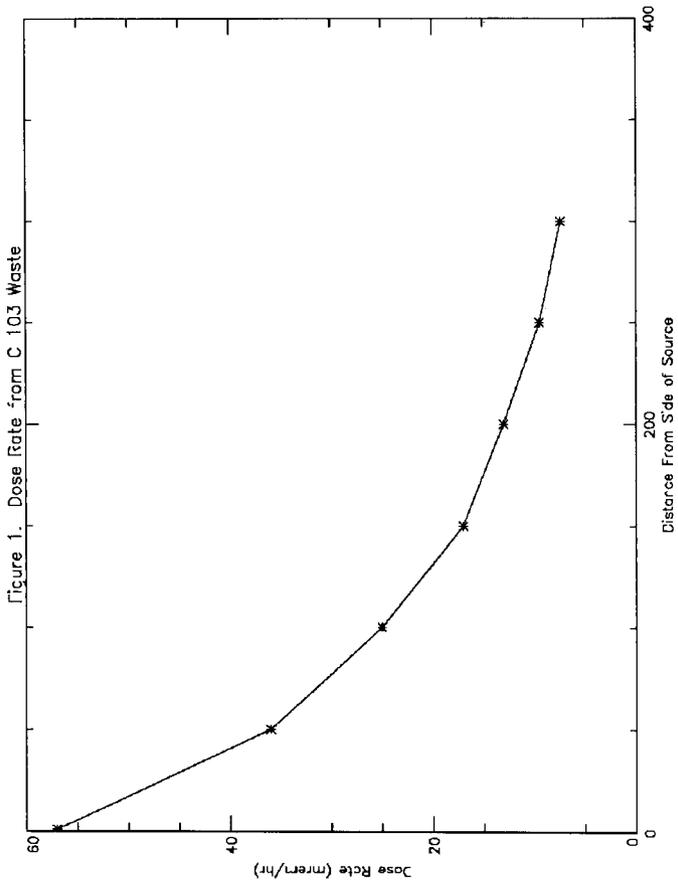
Isotope	Curies
Pu 238	1.75E-03
Pu 239 ¹	3.77E-03
Pu 240 ¹	3.77E-03
Am 241	1.17E-01
Cm 244	3.48E_03
Sr 90	1.17E+01
Y 90 ²	1.17E+01
Co 60	1.42E-02
Cs 137	2.87E+00
Ba 137m ²	2.87E+00
Eu 154	6.01E-03
Eu 155	5.96E-03

¹ ²³⁹Pu set equal to ²⁴⁰Pu which is set equal to total of both.

² Daughter product assumed equal to parent.

Table 2. Dose Rate (mrem/hr) Out the Side Surface

Distance from Side (cm)	Dose Rate (mrem/hr)
1	57
50	36
100	25
150	17
200	13
250	9.5
300	7.4



Attachment: Isoshield-PC Input File

```

0      2 C105 Tank Waste
Dose Rate out the side of the bottle
&input Next=1, Ispec=3, Dunit=1, Option=1, Igeom=7,
Slth=320.04, Y=160.02, Ntheta=10, Npsi=10, Delr=1,
Nshld=2, Jbuf=1, T(1)=144.78, T(2)=0.9525,
X(1)=146.7325,195.7325,245.7325,295.7325,345.7325,395.7325,
445.7325,
weight(492)=1.75e-3, weight(493)=3.77e-3,
weight(494)=3.77e-3, weight(495)=1.17e-1,
weight(496)=3.48e-3, weight(500)=8.25e-4,
weight(82)=11.7, weight(84)=11.7,
weight(335)=2.87, weight(336)=2.87,
weight(415)=6.01e-3, weight(418)=5.96e-3 &
Water 1 0.868
1 Iron 9 7.86
END OF RUN
&Input Next=6 &

```

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VOLUME 2
SECTION 7
LONG-TERM STORAGE

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7.1 LONG-TERM STORAGE

Potential long-term storage locations for the Tank 241-C-103 organic include the Central Waste Complex (CWC), B Plant, tank farms aboveground storage, T Plant, and tank farms belowground storage. These storage locations are described in Sections 7.1.1 through 7.1.5. The options for in-place washing are described in Section 7.1.6.

7.1.1 Central Waste Complex Storage

The CWC already has well over 500 lab packs containing organic materials and several thousand lab packs in total. Presently, this complex has capacity to store over 90,000 lab packs. Approximately 350 drums would be required to lab pack all the organic from Tank 241-C-103 into 55-gal drums. The 350 lab packs from Tank 241-C-103 would be a minor contribution to this total inventory.

The initial tank farm costs for storage at this facility are a flat fee of approximately \$500,000 based upon 15 gal of liquid per lab pack, approximately 350 lab packs, 9 ft³ of volume per 55-gal drum lab pack, and \$160 per cubic foot for storage cost. These costs are scheduled to decrease slightly. This cost does not include the costs for handling and moving these drums. This cost has not been estimated but could be significant.

Current treatment plans for the organic waste in CWC are thermal treatment, stabilization, and solidification. The proposed thermal treatment is by plasma arc through a WHC contracted thermal treatment facility scheduled to be operating in five years. There are potential problems with each of these treatment options.

The timing of the pumping could affect the long-term storage decision. WHC has constructed a RCRA disposal facility, which is not yet operational. Should this facility become operational before the Tank 241-C-103 organic is shipped to CWC, other requirements of acceptance may be imposed, such as some form of treatment that meets RCRA land disposal criteria, liner compatibility, and performance assessment standards for radionuclide migration control.

The advantages and disadvantages of storage in the CWC are listed below:

Advantages

- Facilities already permitted, with necessary safety reviews, for this quantity and type of material
- Small quantity of material compared to capacity of facility
- Facility already contains large quantity of organic material that will require processing

- Facility designed to hold and manage this type of material
- The CWC thermal treatment contract is designed for mixed waste and is committed to treating 5,000 m³ (1.32 x 10⁶ gal) of waste
- Don't have to build a storage pad.

Disadvantages

- Additional characterization is required prior to making any decision regarding CWC storage
- Liquid must be in a lab pack, harder to pump from Tank 241-C-103
- If later radionuclide removal is required, 350 lab packs will have to be handled again
- Characterization costs may be higher because of number of containers
- Dose rate has to be < 100 mrem/hr gamma on outside of 55-gal lab pack. Because the contact reading on a tank containing all of the Tank 241-C-103 organic is expected to be lower, this is not expected to be a problem; however, if entrained solids are pumped, or if aqueous is pumped, dose rates will be higher
- Final disposal is still not identified; life-cycle costs could still be high
- If there is a long delay in pumping, additional requirements may be imposed
- If thermal treatment is not acceptable, stabilization or solidification (binding) may be required, which is generally not a preferred option.

7.1.2 B Plant

The advantages and disadvantages of storing both the B Plant and Tank 241-C-103 organic at B Plant are as follows:

Advantages

- B Plant is experienced at working with separable phase organic
- Current safety basis includes organics
- Only one pad required for storing both B Plant and Tank 241-C-103 organic

- Any radionuclide removal activities could be consolidated
- In that B Plant already has organic, changing any permits and other regulatory documents to include added inventory is easier than for facilities that have no separable organic
- The B Plant pad will include a 4,600 gal backup tank in the event that their tank leaks. This tank can also be used for leakage from the Tank 241-C-103 organic storage tank. However, this tank may be too small for all of the Tank 241-C-103 organic.

Disadvantages

- The B Plant design is completed. This design would have to be modified to include a tank containing Tank 241-C-103 organic.
- The separable phase organic in B Plant is estimated to have a dose of 200 mrem on contact after initial washing. The Tank 241-C-103 organic is estimated to have a dose of 60 mrem or less on contact. If processing of the Tank 241-C-103 liquid is required at the B Plant pad, personnel doses could be high. This could be addressed with temporary shielding.
- Although the likelihood of a release incident is low, combining the B Plant and Tank 241-C-103 source terms would increase employee and offsite worst case exposures. This would be addressed as part of required safety analysis.
- Issues of ownership, ultimate disposal, and emergency action responsibility would have to be addressed by WHC.
- If storage of Tank 241-C-103 organic at B Plant would result in extending the shutdown time for B Plant, there could be major cost and schedule impacts.
- The decision to use B Plant would have to be made soon so that ongoing engineering activities could include the expanded source term. Current cost estimates are \$100,000, which is not budgeted for FY 96.

7.1.3 Tank Farms Aboveground Storage

If longer storage is required, the likely location for a long-term storage pad is in the B Tank Farms because there is more room, the radiation doses are low, access is controlled, and schedules are not impacted. Advantages and disadvantages of long-term aboveground storage at tank farms are as follows.

Advantages

- Tank farms maintains control and ownership of the organic until disposal path determined
- The storage location can be chosen to control access and radiation exposure
- Depending on LR56/H cask use, additional pads may not be required
- A storage pad design has already been developed (Parazin 1994)

Disadvantages

- If long-term storage is required, two pads must be built. It is estimated that two pads would cost approximately \$100,000.
- Requires additional operations and maintenance support
- There are no existing aboveground facilities or tanks to support radionuclide removal activities. The LR56/H tank might be used.

7.1.4 T Plant

The advantages and disadvantages of T Plant storage are as follows:

Advantages

- Facilities not scheduled for shutdown in near future
- Have experience with separable phase organics
- Have tank space that could be used for radionuclide removal.

Disadvantages

- T Plant has no separable phase organics at this time, and as a result does not have the appropriate safety basis, permit allowance or other documentation
- Tanks available would not be adequate to control emissions and have open tops
- No current agreements with state to handle toxic air pollutants in open top tanks
- Storage of an ISO tank or other aboveground tank would require building a pad or inside storage. There are better places to build a pad; inside storage would unnecessarily affect current scheduled and activities.

7.1.5 Tank Farms Belowground Storage

7.1.5.1 Double-Shell Tank. If the Pretreatment process is not changed, interim storage of the organic in a DST is not a recommended approach because:

- The material would likely need to be skimmed again at some future time for approximately the same cost as skimming from Tank 241-C-103.
- Radionuclides in the DST may further contaminate the organic, making any processing attempts more difficult

7.1.5.2 Double-Contained Receiver Tank. Advantages and disadvantages of tank farms DCRT or other belowground storage are as follows:

Advantages

- Does not require the building of additional storage pads or storage pad space
- Would provide necessary volume for radionuclide separation washes
- Depending on tank, could also store and handle B Plant organic

Disadvantages

- Would result in separable phase organic in tank that may contain sludge
- Radionuclides currently in tank may result in more difficulty meeting shipping or disposal criteria
- Condition of tanks may affect ability to remove or treat.

7.1.6 In-Place Washing

This section discusses the options for in-place organic washing. In-place washing is radionuclide removal washing in a storage tank other than Tank 241-C-103. Also discussed is the option of using the hexone distillation unit previously used at the Hanford Site.

7.1.6.1 In-Place Washing Options. The organic in Tank 241-C-103 will meet offsite shipping (i.e., DOT) criteria with no further processing if aqueous carryover is prevented and samples of the organic are consistent with previous results. The ISO tank size recommended is the largest size available, 7,700 gal, to accommodate any in-tank washing. To meet vendor specifications, some washing will likely be required. This washing could be done in the LR56/H. If not washed in the LR56/H, or if additional washing is needed, the ISO tank may be used. It is also possible the LR56/H tank could again be used as a wash tank if further processing is needed.

Once initial screening indicates a likely disposal path, additional characterization, if required will be performed. Based on this characterization, the organic will either be shipped to an offsite thermal treatment or plans would be made for treatment by some other option. Treatment options are reviewed in Section 9.

7.1.6.2 Use of the Hexone Distillation Unit. The distillation unit used for the REDOX Plant mixed waste hexone solvents should not be used for Tank 241-C-103 organics. The distillation unit very successfully distilled near pure hexone but had significant problems with TBP breakdown products and high boiling kerosene residuals (Cowan et al. 1992). These problems included several process outages to remove tar from the feed weir and to flush the overflow drain line.

REFERENCES

- Cowan, R.J., W.F. Heine, and O.R. Rasmussen, 1992, *The Distillation and Incineration of 132,000 Liters (35,000 Gallons) of Mixed-Waste Hexone Solvents from Hanford's REDOX Plant*, WHC-EP-0570, Westinghouse Hanford Company, Richland, Washington.
- Parazin R.S., 1994, *Removal of Floating Organic in Hanford Waste Tank 241-C-103 Restart Plan*, WHC-SD-WM-PLN-092, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

VOLUME 2

Section 7.2

**Memo - Rate Guidance for Activity Data Sheet (ADS)
Development for the Use of Hanford Site Solid Waste Facilities**

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United States Government

Department of Energy

memorandum

Richland Operations Office

DATE: FEB 07 1996
REPLY TO:
ATTN OF: WPD:RFG 96-SWT-047
SUBJECT: RATE GUIDANCE FOR ACTIVITY DATA SHEET (ADS) DEVELOPMENT FOR THE USE OF
HANFORD SITE SOLID WASTE FACILITIES

TO: J. C. Haugen, CH
P. E. Hill, OAK
L. K. Price, OR
A. R. Seepo, SNR
E. W. Gillespie, Portsmouth Site Office
D. Allen, Paducah Site Office
E. Shollenberger, PNR
F. M. Stewart, GO
J. P. Hamric, OH
J. J. Mangeno, NE-60

For your use in ADS preparation, attached is guidance for waste rates through FY 2002. Please note that the actual rates will be established per fiscal year based upon actual receipts. Your office should use the rates established in memorandum 96-SWT-035 for FY 1996.

Offsite generators are currently authorized to ship only Low-Level waste to Hanford at this time. Mixed waste receipts and transuranic waste receipts require EM-30 approval. RL will not accept offsite hazardous waste.

Please note that the attached table requires overhead adders to be applied to them. Currently, the planned adders are as follows:

FY 1997:	15%
FY 1998-2002:	17%

7/2/96

Distribution
96-SWT-047

-2-

Please forward this information to the appropriate federal and contractor staff. Any questions that you may have on this subject may be addressed to me on (509) 376-5494.



R. F. Guercia, Program Manager
Solid Waste Programs
Waste Programs Division

Attachment

cc w/attach:

R. Martinez, EM-38
R. A. Campbell, EM-36
R. D. Pierce, WHC
D. E. McKenney, WHC
R. E. Lang, CH
D. Nakahara, OAK
W. Seay, OR
S. Feinberg, SNR
M. Rafferty, PORTS
W. D. Tidwell, PAD
J. Sage, PNR
D. Turner, GO
D. Hodges, OH

BUDGET GUIDELINE HANDBOOK
SECTION 8

01/08/96

RATE GUIDANCE FOR ADS DEVELOPMENT

	FY 1996 Execution -----	FY 1997 through FY 2002 Planning -----
Waste Pool		
Low Level Waste		
Category 1 (per cu ft)	\$17.86	\$15.75
Low Level Waste Category 3		
Contact Handled (per cu ft)	\$63.63	\$62.89
Low Level Waste Category 3		
Remote Handled (per cu ft)	\$125.00	\$126.10
Transuranic Waste (per cu ft)	\$161.14	\$142.96
Hazardous Waste direct ship offsite (containerized)	\$229.00*	\$186.43
Hazardous Waste LABPACK direct ship offsite (containerized)	\$710.00*	\$593.29
Hazardous Waste direct ship offsite (bulk)	\$710.00	\$679.80
Radioactive Mixed Waste (per cu ft)	\$158.95	\$148.20

*The Hazardous Waste direct ship offsite rate for FY 1996 will come into effect following change control action. The initial planning rate for FY 1996 was \$339.00 per cubic foot. The reduced rate will be possible due to operational changes in the handling of hazardous waste for the remainder of FY 1996. In addition, a new rate for LABPACK direct ship offsite will be added.

The FY 96 execution rates are currently being reviewed and updated rates will be provided after appropriate approvals have been obtained.

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VOLUME 2

Section 7.3

**Addendum - Tank Farms Aboveground Storage
Long-Term Storage Pad Impacts**

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LONG-TERM STORAGE

This section briefly discusses the issues involving long-term storage, if plans call for pumping the organic phase of Tank 241-C-103 into an aboveground tank at the C Tank Farm and then possibly moving the tank to a bermed area at the B Tank Farm for long-term storage.

The long-term storage plans at B Tank Farm and C Tank Farm will be nearly identical. Plans have already been made (Parazin 1994, Rev. 0, Section E, Appendix A, Drawing ES-ER5602-C2). It will be designed in accordance with WAC 173-303-630(7) including the following.

- Collecting and holding spills and leaks
- Holding the additional volume that would result from precipitation of a maximum 25-year storm of 24-hours duration.
- Holding the volume of the trailer mounted container
- Providing positive drainage control
- Removing spilled or leaked waste and accumulated precipitation from the containment system (berm) in as timely a manner as is necessary to prevent overflow.

Leak detection systems in these types of containment are not required. Permit and regulatory impacts are described in Volume 1, Section 9.

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VOLUME 2

Section 7.4

**Draft Information - Alternate Storage of Organic in an Underground
Tank Farms Tank Other than an SST or DST**

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Given: Approximately 5,000 gallons of separable phase organic liquid has been detected to be present in tank 241-C-103.

Required: Evaluate alternate storage of organic in another tank farm facility (73510-95-021).

Discussion: Tank C-103 is one of 149 SSTs. Removing C-103 from the list yields 148 SSTs to consider. However, the 1/1/81 milestone to stop adding new waste to SSTs, combined with the goals of the Interim Stabilization Program suggests that these 148 SSTs not be considered further for storing the 'C-103 Organic.'

There are 28 DSTs. Some (if not all) of these DSTs would be (are) viable tanks to consider for storage of the 'C-103 Organic.' However, the DSTs fall outside the scope of this study because they were the subject of a March 1, 1995 SAIC/FWEC report.

This leaves all 'Tank Farm Tanks other than SSTs and DSTs' to be considered. Of these however, the tanks in the 200 West Area are eliminated from further consideration at this point (if transporting the 'C-103 Organic' by truck or rail becomes an option in the future, then consideration should be given to the C-100 and E-A-1 vessels in the 242-S Evaporator, as-well-as others.

Of the 200 East Area Tanks that remain in consideration, only a few are larger than the potentially 5,000 gallons that may exist in the C-103 tank. Combining this with the approximately 5,000 gallons of organic that exist at B-Plant implies that a tank of greater than 10,000 gallons is desirable. Therefore the small tanks (A-350, A-302-A, AZ-154, and 204-AR-1) are not considered further here, but could be in the future should a different course of action be recommended.

The next tank to remove from consideration is the AX-152 diversion box catch tank because of the dedicated transfer routing. The AX-152 diversion box and associated catch tank are part of the Tank Farm transfer system dedicated to receiving NCAW, and therefore modification of it could result in large radiation exposure and cost for the receipt of 'C-103 Organic.'

Next consideration is given to the A-302-B Catch Tank (which serves the A-152 Diversion Box). This tank has been out of service for some time, its integrity is unknown, little information is readily available regarding the secondary containment, tank orientation, ventilation capability, or auxiliary instrumentation. Furthermore this tank and the diversion box that it served have been isolated and weather sealed making it less desirable yet. Tank A-302-B is not considered further in this report.

The four process vessels/tanks in the 244-AR Vault may be worth considering at some point in time, but because the Vault has been relatively neglected for many years, and there are many questions about integrity, operability, etc. Furthermore it is believed by many experienced operating personnel in and around Tank Farms that to make this facility fit and ready to receive the 'C-103 Organic' would be a very expensive endeavor. The tanks in this facility are not considered further in this report.

After eliminating the above tanks/vessels from immediate consideration 8 tanks result as potentially viable receivers of the 'C-103 Organic.' These tanks are shown in the

attached table along with the associated evaluation parameters that were considered important at this point in the evaluation.

Recommendation:

Further consideration should first be given to the larger of the vessels listed in the attached table, and then if they are not useable for storage processing of the 'C-103/B-Plant Organic' then other tanks should be considered next.

Survey of Viable Receiver, Storage, and/or Reactor Vessels for Separable Phase Organic from Tank 241-C-103 (and/or B Plant)²

Tank	Description of Tank	Tank Status ⁴	Tank Integrity Status ¹¹	Tank Op. Design Cap. (gal)	Current Contents of Tank		Type of and Containment for Tank	Tank Configuration			Transfer Route from Tank ¹⁶ Is an add-on? Same as CR Double Enduse?	Competing Use(s)/Impact of Separable Phase Organic Being Added to Tank	Comments	
					Surface Level ⁴	Volume (gal)		Mixer?	Tank Orient	Ventilation				Instrumentation
A-417	Gas Tank for Air-Free Solvents, 200-A Process Condensate	I	S	44,000 ⁵	W.F.=28	16,520	?	No	?	?	Yes ²	No ¹³	Aglyc. Water Process Condensate, 200-A	TS-200-464, Check to 200-A
244-A	DCRT-244 Receiver	I	S	16,000 ⁵	W.F.=6.02	786	Concrete Vault	No	Vert. Cylinder	A ¹⁰	Yes ⁶	Yes	244-AZ-200 to 200-A (REACT. 244-AZ-200)	
CR-603	DCRT-603 Receiver	O	S	16,000 ⁵	M.T.=42.477	9,200 ⁷	Concrete Vault	Yes	Vert. Cylinder	A ¹⁰	Yes	NA	None	
CR-011	Oil Process Vessel Inventory used with the Process Employed at CR-Vault	O	S	44,000 ⁵	?	?	Concrete Vault	?	Vert. Cylinder	A ¹⁰	Yes	NA	None	
244-BX	DCRT-244 Receiver	I	S	31,000	M.T.=74.25 in.	16,121	Concrete Vault	No	Horiz. Cylinder	A ¹⁰	Yes ¹⁰	Yes	REACT. 244-AZ	
ER-311	Gas Tank for Air-Free Solvents, 200-A Process Condensate	I	S	17,000	FIC=34.4 in.	4,816	None	No	Horiz. Cylinder	P	Yes	Yes	244-AZ-200 to 200-A (REACT. 244-AZ-200)	
AZ-151	Gas Tank for Air-Free Solvents, 200-A Process Condensate	I	S	11,000	FIC=38.2 in.	2,676	?	No	?	P	Yes ¹⁴	No ¹³	AZ-150 to 200-A (REACT. 244-AZ-200)	
C-100 ¹	Process Condensate Catch Tank for 200-A Equipment	I	S	17,000	W.F.=76.53	12,754	Concrete Vault	Yes	Vert. Cylinder	A	Yes ¹⁷	Yes	AZ-150 to 200-A (REACT. 244-AZ-200)	From 200-A

1 The C-100 tank is located in the 200-A Refrigerator.
 2 The relative inactivity of the 244-AZ Vault excludes several possible tanks from consideration.
 3 When PUREX is shutdown, then this tank will be out-of-service and no other competing uses will exist (~1996).
 4 Data as of 1/22/79.
 5 A combination of single and double enclosed transfer lines are used with this tank.
 6 1"-In Service & 0" = Out of Service
 7 Equates to ~50% corrected W.F. reading
 8 Equates to ~75% corrected W.F. reading
 9 Equates to ~55% corrected W.F. reading
 10 Cross coupled with cell ventilation
 11 S = Sound, however no "leak checks" available to reference, therefore if the tank were considered in the future a functional check could be performed combined with a video inspection.
 12 Need jumper modifications/changes in the AX-B Valve Pit & 301-AXX Diversion Box.
 13 Single Line (i.e. no encasement) from diversion box (301-AXX) to tank A-417.
 14 Need jumper modifications/changes in 02D pit of AY-Farm, AX-153 diversion box, and AZ-152 diversion box.
 15 Single Line (i.e. no encasement) from diversion box AZ-152 to Catch Tank at AZ-151.
 16 Need jumper change in 244-A DCRT pit(s).
 17 Need jumper changes in 242-A pump room, and 241-A-A (or 241-A-B) valve pit.
 18 Need jumper modifications/changes in the ER-153 diversion box and 244-BX DCRT pit(s).
 19 Assumption is that the material to be transferred can make it to CR-Vault satisfactorily.

Other miscellaneous Abbreviations:
 A = Forced "Active" Ventilation by some type of machine
 P = "Passive" Ventilation, (i.e. no machine drawing/forcing air through)
 W.F. = Weight Factor
 P = Pressure Indication
 T = Temperature Indication
 FIC = Level Indicating Transmitter manufactured by "Food Instrument Corp."
 M.T. = Manual Tape

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VOLUME 2

SECTION 8 - TREATMENT AND DISPOSAL OPTIONS

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VOLUME 2

Section 8.1

Addendum - Offsite Incineration Options Information

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8.1 OFFSITE INCINERATION

Incineration of the recovered organic from Tank 241-C-103 at an existing DOE facility licensed for radioactive waste is an attractive option. Three such facilities are currently incinerating radioactive waste; the Waste Experimental Reduction Facility (WERF) Incinerator at the Idaho National Engineering Laboratory, the Consolidated Incineration Facility (CIF) at the Savannah River Plant, and the Toxic Substances Control Act (TSCA) Incinerator associated with the Oak Ridge National Laboratory. If the organic phase from Tank 241-C-103 can be incinerated offsite, potential TWRS schedule impact is minimized and development, design, permitting and all capitol costs are avoided. Issues such as packaging, transportation, and approval by each facility's regulatory authority must still be addressed.

While costs have been estimated for incineration at each of the three facilities, the costs do not include further sampling and characterization of the organic phase, recovery of the organic from Tank 241-C-103, washing or other cleaning process to reduce radionuclide concentration (and the cost of dealing with treatment A/O disposal of the used wash solution), packaging, transportation, and permit modifications with the proper authorities. These costs are either common to all offsite treatment options, or difficult to estimate without further effort; i.e., negotiating permit modifications or treatment/disposal of used wash solution.

The basis of determining feasibility of incineration of Tank 241-C-103 organic phase was Table S.1, "Summary Result of Analysis of Organic Supernatant of Tank C-103" from Pool and Bean (1994). In all cases, Table S.1 was faxed to the facility contact for their review and comment. The facility contact was either a waste coordinator or other knowledgeable person on the facility staff. Principal points of discussion were; whether the organic phase was acceptable (or reasons for non-acceptability), whether the facility's permit covered processing offsite waste, other relevant comments and cost associated with processing the organic phase.

Reference:

Pool, K.H. and Bean, R.M., 1994, *Waste Tank Organic Safety Project; Analysis of Liquid Sample from Hanford Waste Tank 241-C-103*, PNL-9403/UC-601, Battelle Pacific Northwest Laboratory, Richland, Washington.

8.1.1 Waste Experimental Reduction Facility

WERF is not equipped with a liquid injection port for direct incineration of pumpable material. All waste is ram fed from a magazine area to the incinerator via 2-ft cube shaped boxes. For liquid wastes, the boxes are filled with an organic absorbent (specially processed corn cobs) and 16 to 24 lb of liquid is distributed throughout the box. The maximum box weight is 60 lb.

WERF has a limit of 1.0 Ci of ⁹⁰Sr per campaign, after which it must be shut down and cleaned. The approximately 5,000 gal of Tank 241-C-103 organic phase would require 10 campaigns to process. In addition, WERF cannot currently accept alpha contaminated waste. Current limits are 0.1 nanocuries/gm ²⁴¹Pu and 0.1 nanocuries/gm all other alpha emitters. Recent wash testing indicates that these levels may be achieved.

The TRU content may require some negotiations prior to processing but was deemed to not be a sticking point. The organic itself would be a "good fuel and [WERF] would like to burn it."

WERF is permitted to accept out-of-state waste since the ash is returned to the waste generator. Hanford would need to have the appropriate permit to receive the ash. The estimated radiation field associated with a barrel containing 150 lb of ash is 1.5 R/hr.

The cost of incinerating the organic phase, based on current operating costs and absorbing 23 lb of organic per box, is \$10 per lb. The cost for 5,000 gal (at 7.27 lb/gal) is \$364,000.

Advantages

- WERF states that Tank 241-C-103 organic would be a "good fuel"
- Can accept out-of-state waste.

Disadvantages

- Cannot accept alpha contamination > 0.1 nCi/g ²⁴¹Pu and > 0.1 Nci/g remaining alpha. This may be met with radionuclide washing.
- WERF limited to 1 Ci of ⁹⁰Sr per campaign. This may be met with radionuclide washing.
- Hanford or INEL must remove radionuclides to meet the 1 Ci ⁹⁰Sr and alpha limits.
- No existing contract.
- Both ash and any separated ⁹⁰Sr returned to the Hanford Site.

Reference:

Personnel Communication with Scott Roesner, waste coordinator of WERF Engineering, (208) 526-5264, INEL, January 23 & 24, 1996; N.K. Rogers, Lockheed Martin, (208) 526-7775.

8.1.2 Consolidated Incineration Facility

The CIF can treat solids at a rate of approximately 900 lb/hr, liquids at 450 lb/hr for organics and 950 lb/hr for aqueous solutions. It does have a liquid injection system for processing liquid wastes without an intermediate step of adsorbing the waste on combustible material.

PUREX type waste has been incinerated at the CIF, and the radionuclides content as listed in Table S.1 of Pool and Bean (1994) is not a concern. The CIF cannot presently take any offsite waste, since its existing waste treatment plan negotiated with the state restricts processing to only SRP wastes. The only exception is for a very small amount of Navy generated nuclear waste. Negotiations with the state would need to be successfully completed for alteration of the waste treatment plan. Politics would be a necessary part of the negotiation. Return of the ash to Hanford or acceptance of some waste from SRP, a "waste exchange," could increase the possibility of success of the negotiation.

A copy of the draft Interim Savannah River Site Waste Acceptance Criteria Manual (SRSWACM), effective Oct. 30, 1995 and expiring April 30, 1996 was requested and received. A cursory exam was made for prohibited wastes, maximum allowable metal concentrations, radionuclide limits, and package content limits. The only major limitation, as given in Table 7 of the SRSWACM, is that a maximum of 639 lb of tributyl phosphate can be accepted into the CIF in a single shipment. Tank 241-C-103 organic phase, if sent to the CIF, would have to be sent in many (approximately 38) shipments.

Cost for processing waste at the CIF, as per the current facility budget plan, is \$0.91 per gallon. This incremental amount may be adjusted depending on the type of waste, but should accurate for PUREX spent solvent type material. The cost for incinerating the 5,000 gal of Tank 241-C-103 waste is \$4,550.

Advantages

- PUREX Plant type waste has been incinerated here
- Current radionuclide concentrations not a concern.

Disadvantages

- Not currently licensed to take any offsite waste (with some minor exceptions)
- Can only take 639 pounds of TBP in a single shipment (approx 38 shipments for Tank 241-C-103 organic)
- May have to return ash to Hanford Site for disposal.

Reference:

Personnel communication with Charles McVay, CIF Waste Acceptance Criteria, (803) 208-8158, Savannah River Site, January 11, 1996.

8.1.3 TSCA Incinerator

The TSCA Incinerator is permitted for processing PCB, RCRA and LLW wastes, and will accept out-of-state waste. Some negotiation with the State of Tennessee for final approval would be required, and Hanford would need to accept the return of the ash. The TSCA incinerator has processed TBP mixed with solvent.

DOE-ORNL has sent out a request for sites that may be interested in using the TSCA Incinerator. A meeting of interested parties on this topic will be held on or about April 1996.

There is currently no cost to DOE generators for processing waste at the TSCA incinerator, since it is fully funded by DOE. Full characterization and transportation are the responsibility of the generator. The average cost to process waste during 1994, calculated by dividing total pounds processed by the facility operating expenditures, equaled \$4.24 per lb.

Unfortunately the radionuclide parameters of the Tank 241-C-103 organic phase for gross alpha, gross beta, ⁹⁰Sr, alpha emitters, and beta emitters are outside of the acceptance limits. Decontamination of the organic phase to less than the 2,000-pCi/g DOT limit would be required prior to processing. The current preferred wash strategy, using EDTA, could not meet this limit.

Advantages

- Will accept out of state waste
- Has experience with TBP mixed with solvent.

Disadvantages

- Radionuclide acceptance criteria too low (2,000 pCi/g)
- Negotiations with the State of Tennessee would be required
- Ash returned to the Hanford Site for disposal.

Reference:

Personnel Communication with Fidel Perez, TSCA Incinerator Division Manager,
(423) 576-5257, Oak Ridge National Laboratory, January 19 and February 1, 1996.

8.1.4 DSSI in Kingston, Tennessee

Advantages

- DSSI is currently accepting PUREX Plant organic, which is very similar to Tank 241-C-103 organic except for the amount of radionuclides

- Existing contract for PUREX Plant can likely be used for other Hanford Site organic
- Contract includes transportation
- They keep the waste residue after treatment; final disposal is achieved.

Disadvantages

- Tank 241-C-103 organic contains a total of 9.1 Ci of ⁹⁰Sr; the organic must be washed at the Hanford Site to meet the DSSI acceptance criteria (including ≤ 1 Ci of ⁹⁰Sr)
- Cost for existing contract is very good, cost for Tank 241-C-103 organic may be different
- Contract will be completed in June 1997.

Cost

- Current contract \$20 per gallon (\$100,000), including shipping, likely to be higher for Tank 241-C-103 because of higher anticipated radionuclide content. Correspondence has commenced with DSSI to determine this impact. No values are currently available.

8.1.5 ATG at the Hanford Site, Washington

The ATG thermal treatment system has not yet been built. This system was contracted by WHC as part of the solid waste strategy for Hanford Site mixed waste. The system design is based on plasma arc treatment of small volume waste batches. According to the contract, a unit is to be permitted and ready to receive Hanford Site waste for thermal treatment in less than five years. The Tank 241-C-103 organic is a prime candidate for this treatment. WHC has committed to the vendor to send 5,000 m³ (1.32 x 10⁶ gal) of waste to the ATG thermal treatment system.

Because the permitting and building process is just beginning, there are several issues that have yet to be resolved. Chief among these issues is if the facility can be built and operating within five years. Other issues include no firm identification of planned radionuclide limits, feed capabilities, and chemical limitations. The system will be designed to receive solids, not liquids, which would result in the need to absorb the Tank 241-C-103 organic unto some other material.

Advantages

- Under Hanford Site control

- Likely designed to accept this type of waste without further radionuclide reduction.

Disadvantages

- Not to be built for approximately five years, likelihood of meeting this time frame is questionable
- Contract is to process small volume waste packages, receipt and processing of large volume batches is outside the current scope
- Licensing restrictions not established, may result in need for radionuclide reduction of waste feed before processing.

Cost

- Unknown.

VOLUME 2

Section 8.2

**Letters - Steam Reforming Technology and EPA Review
of Permitting Requirements**

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STATE OF CALIFORNIA—ENVIRONMENTAL PROTECTION AGENCY

PETE WILSON, Governor

DEPARTMENT OF TOXIC SUBSTANCES CONTROL

1015 P Street, 4th Floor
P.O. Box 8006
Sacramento, CA 95812-0806

(916) 322-3670



April 29, 1993

Mr. William L. Hart, Jr.
Applications Engineer
Synthetica Technologies, Inc.
5327 Jacuzzi Street, #3-0
Richmond, California 94804

SYNTHETICA DETOXIFIER

Dear Mr. Hart:

This letter is in response to your request for a concurrence from the Department of Toxic Substances Control (Department) that the Synthetica Detoxifier is not categorized as an incinerator. Based on the information provided to the Department by Synthetica Technologies, Inc., the Synthetica Detoxifier does not appear to meet the definition of an "incinerator" as defined in 22 CCR and 40 CFR.

By the definitions listed in Section 260.10, Title 40, Code of Federal Regulations (40 CFR) and Section 66260.10, Title 22, California Code of Regulations (22 CCR), an "incinerator" is any enclosed device that:

- (1) uses controlled flame combustion and neither meets the criteria for classification as a boiler, sludge dryer, or carbon regeneration unit, nor is listed as an industrial furnace; or
- (2) meets the definition of an infrared incinerator or plasma arc incinerator.

Federal regulations were amended August 25, 1992 to define infrared incinerators as including an afterburner using controlled flame combustion. It is our understanding that your design does not include an afterburner using controlled flame combustion, and thus is not an infrared incinerator.

Based on the Federal Register, Volume 57, Number 165, page 38562 #8, and on a conversation with Mr. Shiva Garg of United States Environmental Protection Agency (U.S. EPA), Washington, DC (703) 308-8459, the catalytic converter unit (CO Converter) is not considered an afterburner using controlled flame combustion. You might want to contact the California Air Resources Board since the catalytic converter may be regulated as an air pollution control device under the Clean Air Act.

Mr. William L. Hart, Jr.
April 29, 1993
Page Two

The Synthetica Detoxifier process appears to be "thermal treatment," as defined in Section 66260.10, 22 CCR and Section 260.10, 40 CFR. Thermal treatment is regulated by 40 CFR, subpart P, part 265 (for units in interim status) and subpart X, part 264 (for units operating under a RCRA permit), and under similar rules from the State of California.

Thank you for supplying us the information on your detoxifier. If you have any questions, please contact Mr. Eric Nichol at (916) 322-2712.

Sincerely,



Greg Williams
Office of Pollution Prevention
and Technology Development

cc: Mr. Larry Bowerman
U.S. Environmental Protection Agency
75 Hawthorne Street
San Francisco, California 94105

Dr. Terry Galloway
Synthetica Technologies, Inc.
5327 Jacuzzi Street, #3-0
Richmond, California 94804

Ms. Gail Humphreys
Community Environmental Council
930 Miramonte Drive
Santa Barbara, California 93109

Mr. Paul Blais
California Environmental Protection Agency
555 Capitol Mall, Suite 235
Sacramento, California 95814

GW:EN:pl



SCIENTIFIC ECOLOGY GROUP, INC.

December 14, 1995

Mr. Philip L. Bartley, CIH
Foster Wheeler Environmental Corp.
1981 Snyder Road, Suite 3
Richland, WA 99352

SUBJECT: TANK 241-C-103 ORGANIC LAYER

Dear Mr. Bartley:

We appreciate the opportunity to be included as a possible technology in your feasibility study. Based on the process perimeters that you discussed with Jim Hensch we are pleased to provide the following budget data.

Attached, please find relevant technical data on our proposed process. We have attempted to resolve any outstanding questions on the process itself. We are proposing an entirely revitalized waste feed system to handle the subject waste stream.

A ball park estimate based on our understanding of the process requirements is approximately \$1.8 million.

Please keep us in touch and if possible we would like to receive a copy of the full report.

If you have any questions please don't hesitate to give me a call at (509) 736-0626, x 238.

Sincerely,

A handwritten signature in black ink, appearing to read 'Frank H. Jackson', written over a white background.

Mr. Frank H. Jackson
Senior Account Executive

FHJ/tam
Attachment

SEG-WO-95-061

P.O. Box 2530
1560 Bear Creek Rd.
Oak Ridge, Tennessee 37831-2530
(615) 481-0222 Fax: (615) 482-7206

P.O. Box 2138
Carlsbad, New Mexico 88220
(505) 887-1673 Fax: (505) 885-4219
8-2-3

1234 Columbia Dr. S.E.
Richland, Washington 99352
(509) 736-0626 Fax: (509) 735-3085

TECHNICAL DATA

The Synthetica Detoxifier® (STD) has been proven to be highly effective on tributylphosphate and kerosene mixtures by full scale pilot testing.

The Synthetica Detoxifier® (STD) consists of a two-step process. As shown in the attached drawing, liquid waste is injected into the first stage Drum Feed Evaporator. The hydrocarbons of the waste are evaporated by a superheated stream of steam and reforming products called "syn-gas", and the reforming reactions start when temperatures reach 600 to 1100°F. Reforming produces CO₂, H₂O, H₂, and a small amount of CH₄. The partially reacted organic vapors and steam mixture is pulled through a 0.3 micron ceramic filter to remove radionuclides, injected with more superheated steam, and passed to the second stage, the steam-detoxifier. In the detoxifier, the reforming reactions are brought to completion in the detoxification reactor over a catalytic bed. A blower provides the motive force for recirculation, and a small amount of syn-gas is vented to the off-gas treatment system to release the gases produced by the reforming process.

Liquids are injected to fill the drum in the Drum Feed Evaporator, then low is stopped to let the evaporation process begin. When the reaction rate begins to fall off, indicating the liquid is mostly vaporized and reformed, more liquid is injected. Inorganics collect in the bottom of the drum and eventually fill the drum. When full, the drum is removed, sealed, and stored for future treatment. The dry ash-like inorganics are suitable for solidification or vitrification treatment.

The simplified design for the Tank C-103 steam reformer differs significantly from the system proposed for the Initial Pretreatment Module (IPM) Technology Selection Meeting. The moving bed evaporator and pneumatic recirculation system which were cited by the IPM selection committee as not being a mature technology have been eliminated. All of the equipment which was cited as being subject to corrosion, erosion, and plugging have also been eliminated.

STEAM REFORMING

Safety and Environmental Control Systems Synthetica Detoxifier and Feed Systems

Introduction

The Synthetica Detoxifier system has several unique design features that makes it ideally suited for an onsite treatment application. The most critical features are:

- The entire system is designed to eliminate the possibility of accidental releases, thus making it safe for the environment as well as for the operators.
- The entire system is designed to be easily operated through the use of simple color touch panels, with a minimum of operator intervention needed, thus eliminating the need for a full-time highly trained operating staff.
- The entire operation is highly automated through the application of the latest computer technology -- distributed process controllers, fail-safe circuitry logic, 4-level redundancy, on-line process modeling, error checking, etc.
- The design of the Synthetica system reflects considerable effort at eliminating potential safety problems. Each potential problem area was examined and engineering/design measures were taken to eliminate the potential of failure resulting in a safety problem or a control function was provided to reduce the likelihood of occurrence of failure.

The various environmental control and safety systems designed into the STD and the associated feeders are described below.

Environmental Control Systems

In steady state operation, the system automatically monitors key operating parameters, such as the temperatures of the waste feeder, heat exchangers, reactor, circulating blower, vessel walls, gas in, gas out, process chemistry, flow rates of the STD feed, vent gas flow, condensate pH levels and hazardous materials in the feed tanks, to ensure that these parameters fall within narrow predetermined ranges.

Operator error problems are eliminated in the system by only allowing certain operator actions to be taken in the color touch screen menu-driven control system. The computer monitoring key process variables will alert the operator if any key variable begins to go out of range. Failure to respond within 5 minutes will result in a sequence of automatic actions possibly leading to a controlled shutdown.

Improper Waste Feed to System - misidentification of the waste and/or improper feeding of this waste into the system for processing could result in the selection of operating conditions that are not optimal for the system, but it is unlikely that the resulting detoxification would drop below 99.99% because process conditions are automatically changed when waste feed differences are detected. An automated,

computer-readable waste detoxification approval control system is used to ensure that this will not happen. Each waste container is uniquely identified.

On-line chemistry sensors are used to monitor the waste feed and to ensure that it matches the profile entered into the computer. Mismatches in process chemistry will result in process changes and possible alarm conditions, followed by a controlled shutdown if there has been no operator intervention.

Hazardous Waste Leaks - a power failure will cause "fail-safe" valves to activate, isolating the STD from the feed stream and the downstream process units. The STD will then cool down at a rate slow enough to allow for any residual waste to be processed while, at the same time, the cooling continues to quench any reactions. Upon power resumption, the STD will automatically come up in total recycle mode, recycling all unconverted residual hazardous materials through the STD until the operating temperatures remain at the recycle level for at least one hour. This ensures that all residues are completely destroyed. Once the STD is clean, the feed and downstream units are restarted and processing is resumed.

In addition, the entire system is under slight negative pressure (-0.1 to -3.0 psig), including all lines and process units. The waste feed streams are kept at -3.0 psig, while the clean gas streams exiting the steam reformer are controlled at -0.1 psig (-2.0 inches W.C.). Any leaks in the part of the process system handling unprocessed hazardous waste would cause outside air to leak into the system, which, if it happened, would be immediately detected by redundant on-line oxygen sensors. The only possibility of waste escaping would be when the system has a leak at the same time the electricity fails; in this event, all valves are closed, isolating the STD and its recycle loop while still allowing steam-reforming to detoxify waste using stored heat in the steam reformer.

Environmental Impact - the only potential impact of concern would be air emissions as there is no discharge to a sewer system. As is discussed elsewhere, the potential of waste leakage has been greatly reduced because of the fail-safe, fault-tolerant design features.

Air emissions, consisting mostly of CO₂ and water vapor, from the process vent are carefully monitored. The following residual gas components are monitored and computer-tracked on a continuing basis:

- benzene
- carbon monoxide
- oxygen
- water vapor
- acid gases
- radioactivity (for those applications on radioactive waste)

Gas chromatograph/mass spectrograph traps are used to collect samples for complete laboratory analysis.

Safety Systems

Electrical - the drum feed evaporator (DFE) electrical equipment meets NFPA 496 (1993) code requirements for Class I, Division 1 locations. All electrical equipment in the steam-reforming detoxifier meets Class I, Division 2 requirements. All electrical hardware is enclosed within pressurized and purged electrical enclosures and can only be accessed by trained maintenance personnel. The highest voltage available on any piece of equipment in the enclosure is 480 vac, 3-phase.

Skin Burns - all hot surfaces have been insulated or shielded to prevent contact with the skin during any maintenance operation while any part of the system is at temperature.

Hazardous Waste Leaks - with all feed lines at negative pressure and flows monitored and controlled by a mass flowmeter, the possibility of this happening is extremely low while the waste is inside the system. Of course, all normal precautions should be taken when handling the waste outside the Synthetica system.

Explosions: Fuel/Air - combustion air is not used by the system and oxygen is only present at very low levels. Therefore, no explosive fuel/air mixtures can exist. An on-line oxygen monitor is used; if any significant oxygen is present (most likely, from air in-leakage), it will trigger an alarm and will begin a programmed air purging operation to restore low oxygen levels and only, if this operation fails, will the system begin a programmed shutdown. The steam rate flowing into the STD is automatically controlled to carry out efficient steam reforming destruction at the maximum hazardous waste input concentration while keeping fuel/air concentrations well below any ignition flash point, should air somehow leak in any quantity into the system. This level is set to ensure that even if the waste happened to be a flammable fuel, the fuel-to-air ratio would never reach dangerous levels. Additionally, the STD has an anti-flashback arrestor which remains cool and quenches any flame that could flash back into the source.

If, despite all of these precautions, an explosion does occur within the STD or the waste feeders, 3 psig to 5 psig rated 2" diameter burst discs, installed on every system, will rupture, preventing vessel failure due to overpressure. These pressure relief systems are vented outside to avoid dangerous ground level concentrations.

Vessel Pressure Failures - all vessels are 316L stainless steel and are kept below atmospheric pressure. Even though none of the STD components are pressure vessels, the entire system is pressure-checked before testing and shipment for mechanical failures. Also, extensive thermal stress analysis has been done, and special mechanical designs developed to ensure long life at high operating temperatures.

Piping Pressure Failures - all process piping is 316 stainless steel and is below atmosphere pressure. Even so, all fittings are 316 stainless steel and 150 psig pressure rated and are capable of a 50-fold over-pressure.

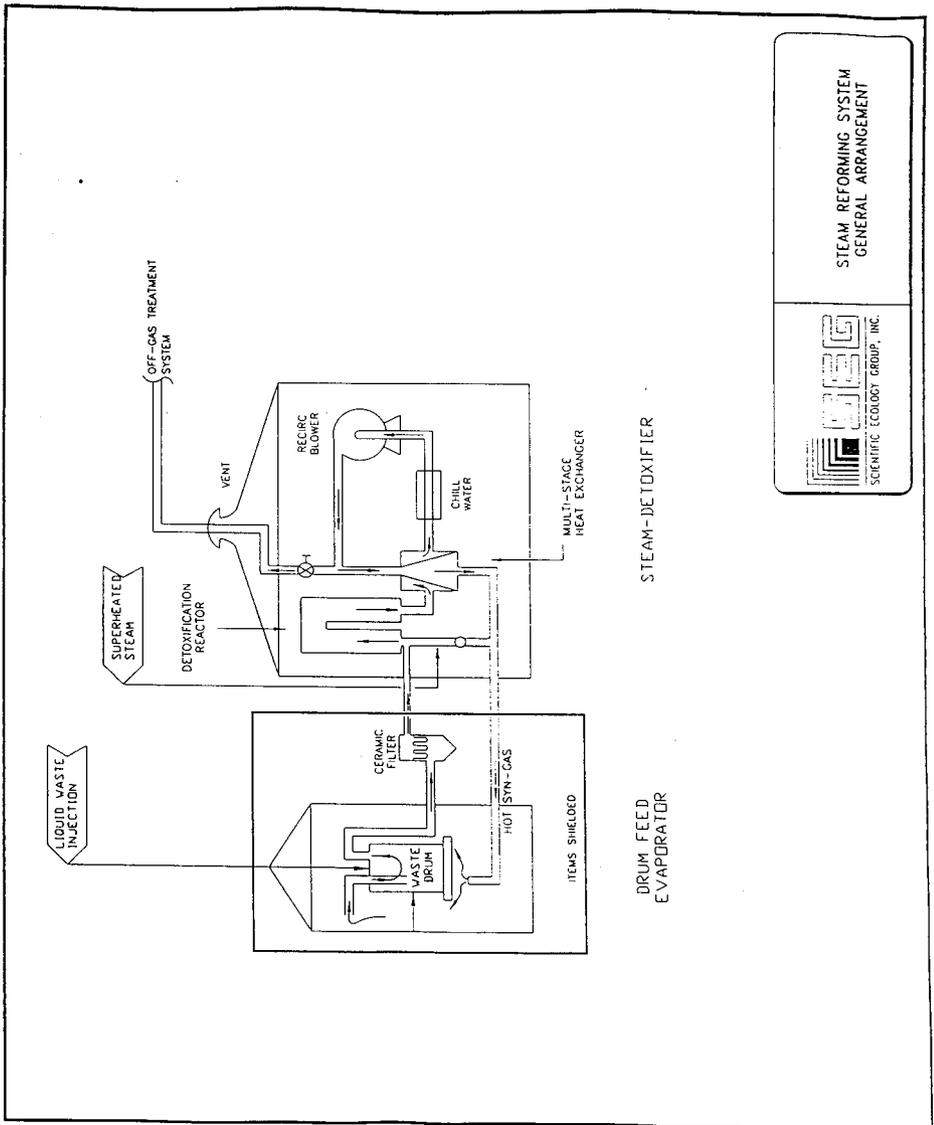
Thermal Shock - an unexpected interruption of site electrical power, while the system is at temperature, will not result in rapid thermal cooling which would thermally shock and destroy or damage the internal components, as shown by extensive computer stress analysis. The STD is designed with proper balance between its thermal storage capacity and heat loss, and it has been demonstrated repeatedly that a power failure results in a safe, low cooling rate that will not damage internals.

There could also occur a failure mode where the electrical power is interrupted to the steam-reformer vessel core, but not to the circulating blower, which could result in thermal shock damage. In this case, the process control system detects the loss of power to the core and stops the blower so as to avoid any thermal shock problems.

Overtemperature - an overtemperature problem could occur with gas flow failure or thermocouple failure. Gas flow sensors would detect the loss of gas flow and would shut down the system. Critical thermocouples are redundant and carefully compared by the process control processor (by "voting" among redundant sensors). If differences are out of range, the system is shut down.

Improper Gas Flow - low gas flow could result in a vessel core overtemperature condition. Redundant thermocouples as well as gas flow sensors prevent this from happening.

Revised: June 22, 1994



SCIENTIFIC ECOLOGY GROUP, INC.



**STEAM REFORMING SYSTEM
GENERAL ARRANGEMENT**

**Hanford Waste TANK 241 C-103 Steam Reforming
Waste Form Data**

Based on the analysis performed to support the Waste Tank Organic Safety Project prepared for Westinghouse Hanford Company by Pacific Northwest Laboratory (March 1994), the following waste form information is provided for the resultant steam reforming technology waste product.

Current requirements:

Steam reforming is a proven, mature technology which readily destroys organic wastes. The steam reformer has been proven effective with surrogate wastes consisting of tributylphosphate, kerosene, and water. When processing the TANK 241 C-103 organic and a portion of the aqueous layers, at least 99.99% of the organic contents will be destroyed, and virtually all of the water will be vaporized to join the steam in the reforming gases. Small quantities of carbon dioxide and water vapor will be vented off along with trace amounts of methane gas. A smaller amount of dry residue will be left in the waste container(s), resulting in an organic content volume reduction ratio of between 100 and 1,000 to one.

Final waste form description:

- Dry; virtually all moisture removed
- Inorganic and totally inert; more than 99.99% of the organics found in the organic and aqueous layers of TANK 241 C-103 will be destroyed as proven in surrogate waste testing
- Significant volume reduction; since the process achieves greater than 99.99% destruction of organics the resultant residue will contain only inorganic materials
- No hydrogen generation problem in the burial container; virtually all hydrogen containing compounds listed in the characterization data provided will be reformed to free hydrogen and the gases removed

- **No solidification or other treatment required to meet high level waste acceptance criteria for dry storage systems**
- **No processing of residue; the container of residue can be removed from the steam reformer evaporator and easily placed directly into a Westinghouse Multi-Purpose Canister (MPC) or similar system**
- **Suitable for storage in the existing footprint for dry storage of spent fuel when packaged in an MPC or similar system**

The remaining residue would contain all of the radioisotopes originally contained in the waste, and, therefore, would remain classified as high level waste. Since there is only remote handling and a minimum number of personnel required to remotely operate the system, the principles of ALARA are readily achieved.

VOLUME 2

Section 8.3
DSI - Grout Impacts

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DON'T SAY IT --- *Write It!*

DATE: February 7, 1996

TO: M.J. Klem

FROM:

J.W.

Shade H5-27

Telephone: 373-5922

cc: P Bartley
 RL Gibby
 WJ Powell
 CN Wilson
 DJ Washenfelder

SUBJECT:

Grout Option for Separable Phase Organic

GROUT OPTION - SEPARABLE PHASE ORGANIC

J.W. Shade and W.J. Powell

Cement/Grout Chemistry

Setting and waste immobilization in waste forms based on hydraulic cements, such as Portland cement, occur through hydration reactions with the cementitious materials, usually calcium silicates and reactive silica. For example formulations for Hanford grout usually consisted of Portland cement, fly ash, and attapulgite clay although slag was sometimes considered for certain formulations. In general, hydration reactions yield primarily complex hydrated calcium silicates (CSH) that develop as a reactive gel around the original anhydrous calcium silicate particles plus calcium hydroxide such that pore fluids are very basic with pH values of about 12. The CSH phase is the "glue" that holds the hydrated particles together. Very little work has been done to evaluate the impact of organics on grout and most of this has emphasized complexants such as EDTA or citric acid and oxalates. In general, organics added to Portland cement based materials are usually considered set retardants because they often inhibit ionic diffusion through the CSH layer or interfere with the crystallization of calcium hydroxide. For grout formulations such those considered for Hanford, specifications for total organic constituents (TOC) in the grout feed has been given as 3.26 g/L (Hendrickson, 1991).

Other types of cements exist in the commercial market that may be useful in immobilizing organics. One of these is a lactose based material, but it has not been investigated for this type of waste. Other organic waste forms include bitumens (asphalt) and polyethylene which have had limited investigation for immobilizing organic constituents. The application of all of these for separable phase organic immobilization would require development activities.

CASE 1: Incinerate TBP/NPH liquids, then grout residue

Residues from incineration of TBP/NPH liquids will probably consist largely of inorganic salts of silicates and phosphates as indicated in the C-103 report (Pool et al, 1994, PNL-9403). Fly ash, which is commonly used in cement blends, is a product from coal combustion as is largely silicate material, partially vitrified. Phosphates can react with calcium hydroxides to form stable calcium phosphates. These types of residues should be readily contained in a cementitious waste form by addition to the dry blend or as a slurry. They could also be gradually fed into a vitrification system.

Case 2: Add TBP/NPH liquids directly to grout dry blend

Specific studies related to grouting TBP/NPH liquids have not been conducted or have not been identified for this application so much of the following is speculative. Inclusion of a separable phase organic waste into a cementitious waste form would require a source of water to initiate hydration reactions. There may be sufficient water in the waste stream or additions may be needed. Once hydration is initiated, some subsequent reactions may be speculated. In high pH systems, TBP decomposes to DBP and MBP acids plus butanol with a theoretical end product of phosphoric acid and butanol. In reality, probably only a small amount of phosphoric acids occurs as the decomposition becomes slow after DBP formation. The phosphoric acid and perhaps some of the other butyl acids may react with the calcium hydroxide to form other phosphates. Also some of the butanol may react with the CSH phase. Since hydration reactions are slow and occur for years in cements, there may be considerable kinetic limitations. Also impacts on waste form volume changes may take considerable time to become evident. In general, however, very little is known about incorporation of separable phase organics in grout so a feasibility and development program would be required.

In general, the following items are expected to be limiting, or limit the quality of the grout:

- Concentrations of organics in the grout feed
- Formulation of the grout dry materials
- Formulation/mix of the grout dry blend to waste liquid ratio
- Compositino of the organics
- Temperature of set
- Degree of mixing and timing

Case 3: Add TBP/NPH liquids to an organic waste form

The development of organic waste forms that typically include matrix constituents such as bitumen (asphalt) or polyethylene as matrices have the potential to immobilize organic contaminants. In general these materials have not been developed to the degree that inorganic waste forms have attained. As with the grout option, organic waste forms will result in a volume increase relative to the original liquid waste volume. Organic waste forms generally involve waste loadings of 20 to 40 percent. Some drawbacks to organic waste forms include susceptibility to oxidation in near surface environments and biodegradation. These processes are usually considered during performance assessments of disposal actions. At this time, it is expected that the use of organic waste forms for TBP/NPH immobilization

will require considerable development work and subsequently development of processing facilities.

DISPOSAL SYSTEM FOR PRODUCT

The only options for disposal of an additional LLW product is in the the LLW Storage and Disposal facility intended to receive the primary LLW products or in existing Hanford Solid Waste facilities. For disposal in the LLW Storage and Disposal facility, a secondary waste form will have to comply with the requirements and packaging restrictions in the ILAW Product Specifications which requires additional testing and characterization. Treating TBP/NPH in the LLW vitrification facility would avoid this qualification requirement because the phosphate would be incorporated into the ILAW product which will already be qualified. For disposal in existing Hanford Solid Waste facilities, the product must comply with WHC-EP-0063-4 which requires selected characterization and documentation. Thus it would be cost effective from the disposal system point of view to avoid having to qualify a separate waste form and include as much waste as possible in the primary waste form.

PERFORMANCE ASSESSMENT ISSUES

Performance assessment analyses of disposal systems require an estimate of waste inventory that will be disposed and a release rate function for contaminants from the waste form and waste package. For both the ILAW Storage and Disposal system and the Solid Waste system, the slight inventory increase represented by 5500 gals of TBP/NPH would probably be trivial relative to the inventory assumed in the respective PA's and may not require further analysis. For a new waste form, however, leach tests to determine release rates must be conducted if the additional inventory represented by the TBP/NPH is significant.

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VOLUME 2

Section 8.4
DSI - Vitrification Impacts

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DON'T SAY IT --- *Write It!*

DATE: February 5, 1995

TO: M.J. Klem

H5-27

FROM: C.N. Wilson

H5-27

Telephone: 376-1141

cc: P Bartley
 RL Gibby
 RA Kirkbride
 SL Lambert
 EH Randklev
 JW Shade
 GE Stegen
 DJ Washenfelder
 CNW file/LB

SUBJECT:

Impact of C-103 Separable Organic on HLW & LLW Vitrification, Rev 1

In response to reference 1, I reviewed information related to the tank C-103 separable phase organic issues and assessed the potential impacts of feeding this material to the melter during vitrification. My original assessment was provided in a DSI dated December 22, 1995. Following our meeting on January 15, 1996 I did some calculations to determine potential flammable gas concentrations in the LLW melter offgas to determine if this is really a safety concern. This DSI is revised from my December 15 DSI to include the results of those calculations, and to include some cost impact estimates (guesses) that were request at the January 15 meeting.

HLW versus LLW Issues

Either the LLW or HLW vitrification plant can be designed to handle the relatively small quantities of separable organic currently estimated to be in tank C-103 if this is specified up front in the design criteria. However, it does not appear that this liquid organic could get to the HLW vitrification plant unless we intentionally separate it out and transfer it to HLW vitrification. Processing this material with LLW would also be preferred in that it could be diluted with much larger quantities of melter feed with less potential negative impacts. Therefore, impacts of processing with LLW are the primary focus of this assessment.

Melter Feed Processing Issues

If this organic material, either solubilized or emulsified in the liquid LLW, causes problems for pretreatment², it would seem likely that the organic phase would be separated and sent to LLW as a separate stream. If not, we should assure that this material is solubilized or emulsified so that it does not phase separate during wet or slurry feed processing.

Processing the organic as a separate stream implies the need for special equipment in the LLWVP to allow blending with the melter feed or a separate feed system which may not be cost effective to process this relatively small amount of organic.

If a privatization vendor elects dried pre-reacted (NO_3/NO_2 reacted with reductant additives) melter feed, the TBP/NPH would likely be volatilized and/or destroyed during feed processing. Another option would be to separately incinerate the organic phase and blend the ash with the LLW melter feed or process this ash in a separate small melter producing a phosphate glass that would have a very high waste loading for this ash.

In a draft DSI addressing potential impacts of TBP/NPH organic on vitrification, Gary Stegen indicates that much of this organic may be lost by evaporation and/or hydrolysis before it reaches vitrification if it is not processed as a separate stream. Gary concludes that we could probably ensure it will mostly evaporate or decompose by selection of the DST it goes to.

Ability of Glass to Accommodate Phosphate Ash

Accommodating the phosphate ash in LLW glass is not a problem. Based on analyses reported in reference 3, the total P_2O_5 expected to report to the glass from the estimated 5500 gallons of TBP/NPH organic phase in tank C-103 would be 3240 kg. This quantity of phosphate could easily be processed with a single DSSF tank. A typical DSSF tank containing 2×10^7 moles of Na would produce about 3,100,000 kg of 20 wt% Na_2O glass containing about 0.2 wt% P_2O_5 based on the nominal DSSF composition data given in reference 4. Processing the additional phosphate ash derived from the 5500 gallons of TBP/NPH with this DSSF tank would only increase the glass P_2O_5 content by about 0.1 wt%. The solubility limit of P_2O_5 in LD6-5412 candidate LLW is about 2 wt%⁵.

Decomposition/Volatilization

The area of greatest uncertainty in processing this organic material during vitrification is its decomposition and/or volatilization behavior in the melter and what residues are contained in the melter offgas. The ideal situation would be if the TBP and its associated products would thermally decompose and oxidize to phosphate ash plus H_2O and CO_2 in the cold cap or melter plenum with the ash all incorporated into the glass. Studies suggest that, when heated in air, TBP thermally degrades to yield flammable organic compounds⁶. Higgins and Baldwin report⁷ that "TBP, and its acid degradation products HDBP and H_2MBP , lost on the average over 80% of the butyl groups as butene isomers when heated at 241-245°C. When TBP decomposed, the gas initially evolved was all butane-1..." A flash point of 118°C has been measured on tank C-103 TBP/NPH organic phase samples³. The flash point of TBP is reported as 146°C and the boiling point is given as "289°C with decomposition" in the Merck Index⁸. Data provided in reference 3 indicates significant volatility of TBP at 100°C and very little organic carbon remaining in the residue after heating to 320°C in vacuum.

Based on the above information, I would expect TBP and associated products to decompose in the coldcap if it were solubilized or emulsified in a slurry melter feed, and that flammable

organic vapors would be evolved. This may be a safety issue requiring design changes to ensure that potentially explosive flammable gas concentrations do not occur in the melter or offgas system. Savannah River (DWPF) uses plenum heaters to maintain the melter plenum at 600°C to 800°C to assure organic (primarily benzene) destruction in the melter.

If organo-phosphates volatilize from the cold cap, or the TBP/NPH is separately fed to the melter, and decomposition and burning occur in the melter plenum, an issue of some concern is how much entrained inorganic phosphate ash will report to the offgas system. The ash produced by burning TBP in the plenum would likely be a fine aerosol. The main concern here would be if entrained phosphate would contribute to a foaming problem in the offgas scrubbers or condensate collection tanks. Another related issue may be if organo-phosphates volatilize during LLW concentration (by evaporation) or melter feed processing and phase separation in condensate collection tanks occurs and/or contributes to foaming in these tanks.

Flammable Organic Vapor Content in Melter Offgas

Organics considered to date in LLW feeds are expected to decompose or react with NO₃/NO₂ in the melter cold cap producing non-flammable gasses such as CO₂, H₂O, N₂ and NO_x. These organics include complexants such as EDTA and citric acid and organic reductants such as sugar that are added to the melter feed to destroy nitrate and nitrite. As discussed above, flammable organic gasses may be liberated from the TBP/NPH C-103 organic when it is heated in the melter.

I did a calculation using what I regard as conservative assumptions to estimate the maximum probable flammable organic content in the LLW melter offgas if the 5500 gallons of TBP/NPH estimated to be in tank C-103 was processed with the LLW feed from a single DST. I assumed a liquid LLW stream with the composition of the DSSF simulant used in the Phase 1 LLW melter vendor tests, which is concentrated to 10 M Na (given at 6 M Na in reference 4). I assumed the DST chosen would contain 2×10^7 moles of Na producing 2×10^6 L of liquid LLW at 10 M Na concentration. The DSSF simulant composition is 3.1 M NO₃⁻, 1.7 M NO₂⁻, 0.27 M CO₃⁼, and contains about 750 g/L H₂O. Assuming the NO₃⁻ and NO₂⁻ would completely react with sugar reductant additive yielding N₂, CO₂ and H₂O by the reactions given as equations (1) & (2) on page 2-3 of US Bureau of Mines LLW melter test report (reference 9), the following moles and volume % compositions are calculated for the offgas exiting the plenum at a temperature >100°C.

Butane (C ₄ H ₁₂)	0.136 x 10 ⁶ moles	0.12%
N ₂	4.8 x 10 ⁶ moles	4.3%
CO ₂	10.8 x 10 ⁶ moles	9.7%
H ₂ O	95.6 x 10 ⁶ moles	85.8%

This exit composition assumes no in leakage of air or added air by a film cooler at the melter exit. If the offgas were quenched to 30°C most of the H₂O would be condensed out with

H₂O partial pressure dropping to 32 mm Hg. Adjusting the composition for quenching to 30°C the following offgas composition is calculated.

Butane (C ₄ H ₁₂)	0.136 x 10 ⁶ moles	0.83%
N ₂	4.8 x 10 ⁶ moles	29.2%
CO ₂	10.8 x 10 ⁶ moles	65.7%
H ₂ O	6.9 x 10 ⁶ moles	4.2%

These calculations assume that the TBP/NPH is 67 wt% TBP as analyzed in reference 3 and do not include the NPH volatiles. Assuming the NPH to be all C₁₂H₂₆, the total moles of butane plus NPH would be about 0.17 x 10⁶, increasing the flammable organic gasses to about 1.0 % of the offgas volume when quenched to 30°C. Factors such as air in leakage and incomplete reductant reaction resulting in NO_x would dilute the organic vapors further.

I do not believe that 1 % flammable gas vapors in the offgas could explode or be a real safety problem, but I will leave that call to the safety people. Hydrogen (H₂) diluted to 2 % in Ar or He is considered a safe mixture for laboratory use that is not explosive when mixed with oxygen, and I would not expect butane to any more explosive than hydrogen at the same volume dilution.

I will keep my calculations for the above on file for any one who wishes to review them.

Additional Costs Estimates for TBP/NPH Vitrification

At the January 15, 1996 meeting it was requested that I provide estimates for added costs associated with processing the C-103 organic as part of LLW vitrification. This is really difficult to do since neither the LLWVP process or design are not defined at this time, and even if they were, a detailed design study would be needed to get good cost estimates for the required modifications.

Assuming the C-103 organic is separated and stored for later processing, equipment will be needed to receive this material and blend it with the melter feed. The LLWVP will likely have a maintenance cell (or melter cut up cell) that could receive the organic in a suitable container or cask. Assuming a slurry fed melter processes the 5500 gal (2 x 10⁴ L) with 2 x 10⁶ L of DSSF LLW concentrated to 10 M Na (LLW from a single DST), the organic would emulsified at 1 % concentration in the LLW. Transfer lines from the maintenance cell with associated pumps and metering equipment will be needed to get the organic to the slurry feed make up tank. As a conservative guess add \$1M to the LLWVP cost. If a process using surfactants to emulsify the organic in the slurry does not work, it may be possible absorb the organic in diatomaceous earth (90% SiO₂) and get it into the slurry feed as part of the glass former additives, which would require more complicated equipment than just pumping it in as a liquid with a surfactant. (\$1M estimated added cost associated with feeding)

Although based on the preceding offgas composition calculations it may not be required, melter modifications to deal with potentially explosive offgas compositions would require added costs. For an Inconel electrode low temperature melter the organic destruction could be accomplished with plenum heaters. Including associated power supplies and jumpers, plenum heaters could add about \$2M to the melter cost. Plenum heaters would not work for a high temperature Joule heated melter, which would require a thermal reactor in the offgas system following the melter. Not being sure what this thermal reactor would look like I will offer a wild guess of \$10M if one is required. Another approach would be to increase air (or inert gas) flow through the melter and offgas system to dilute the flammable gasses to safe concentrations. This would require a larger offgas system to handle the additional gas volumes adding cost. (\$2M to \$10M added cost if organic destruction is required for the offgas)

Another potential impact would be if entrained phosphate aerosol would cause foaming in offgas scrubbers or condensate collection tanks. This may require the use of antifoam additives and more frequent flushing of these systems when the organic is processed.

Melter Testing with Feeds Containing TBP

Feeding of TBP with the melter feed in a small scale LLW melter test could provide data to confirm TBP destruction in the melter, confirm estimates of flammable gasses in the offgas, and determine if there is an issue of phosphate residues contributing to foaming in offgas equipment. An opportunity exists to piggyback such testing onto the FY-1996 "minor components" vitrification testing being conducted in the small scale high temperature melter (SSHTM) at PNNL. PNNL has estimated that \$50k additional funding would likely be needed to cover an additional run segment and analytical costs associated with adding TBP effects to the testing scope.

References

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3. KH Pool, RM Bean, *Analysis of Liquid Samples from Hanford Waste Tank 241-C-103*, PNL-9403, March 1994.
4. C. N. Wilson, *Evaluation of Melter System Technologies for Vitrification of High-Sodium Content Low-Level Radioactive Liquid Wastes -- Statement of Work*, WHC-SD-WM-RD-044, Rev. 0 (1994).
5. Hong Li, *Letter Report - Minor Component Study for Low-Level Radioactive Waste Glasses*, PVTD C95-02.01B, March 1995.

6. WW Schulz, JD Navratil, AE Talbot editors, *Science and Technology of Tributyl Phosphate*, vol 1, pp 151-152.
7. CE Higgins, WH Baldwin, *The Pyrolysis of n-Butyl Phosphate Esters and Salts*, Journal of Organic Chemistry, vol 30, pp 3173-3176, 1965.
8. The Merck Index, 9th edition, Merck & Co, Inc., 1976.
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VOLUME 2

Section 8.5

Addendum - DST Hydrolysis and Radiolysis Information

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8.5 DST HYDROLYSIS AND RADIOLYSIS INFORMATION

Models were developed to predict the TBP and NPH removal rates from a DST by aqueous hydrolysis, radiolysis, and evaporation. Much of the model was made to compare different parameters of hydroxide (OH) concentration, temperature, dose rate, liquid volume and ventilation. This section provides additional information regarding the hydrolysis, radiolysis, and evaporation removal mechanisms.

8.5.1 Tank 241-AP-107

The candidate DST for Tank 241-C-103 organic addition is Tank 241-AP-107, based on guidance from Tank Wastes Process Engineering, Process Control, and Engineering. The use of Tank 241-AP-107 for interim storage of separable phase organic accomplishes the following:

- Avoids mixing separable phase organic with dilute waste that requires evaporation at the 242-A Evaporator (no impact to LERF and ETF treatment of condensates)
- Segregates waste types and complies with DOE Order 5280.2A
- Minimizes potential flammable gas generation from reaction of precipitated organic solids with high heat sludge such as NCAW
- Appears to meet waste volume projection, waste compatibility and future programmatic impacts of storage and TWRS processing assuming efficient TBP degradation and NPH evaporation.

Depending upon the option chosen, waste type addition may include the existing contents plus the contents of Tank 241-C-103, or the contents of Tank 241-AP-107 plus Tank 241-C-103 and suspect or known CC waste from SSTs. The CC waste increases Tank 241-C-103 OH concentration and gamma dose rate, which are important for hydrolysis and radiolysis respectively. The Tank 241-C-103 addition for these calculations included both the organic and aqueous phase. It is reasonable that the aqueous from Tank 241-C-103 will be added to the same tank as the organic (no laboratory boil down information available at the time of writing this report). This provides a quantified aqueous volume to develop conservative model predictions based on sodium hydroxide. Tank 241-AP-107 information relevant to hydrolysis and radiolysis is provided in Table 8.5-1.

8.5.2 Hydrolysis

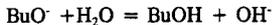
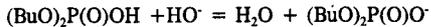
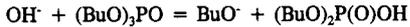
The mechanism of alkaline hydrolysis of TBP occurs by breaking of the P-O bond connecting to the butyl group (Bu):

Table 8.5-1. Summary of Candidate DST Information for Interim Storage of Tank 241-C-103 Aqueous and Separable Phase Organic.

Tank	Current and Projected Waste Type	Estimated Free OH ¹ M	Estimated Gamma Dose Rate to 5,000 gal Separable Phase Organic ²		Temp ³ (°C)
			Dispersed as Supernatant (Rad/hr)	Floating Layer (Rad/hr)	
107-AP	DN	0.15	<0.1	<0.1	15
107-AP	DN + C-103	0.15	65	40	TBD
107-AP	DN + CC ⁴	0.5	330	140	TBD
107-AP	DN + C-103 + CC ⁴	0.5	290	130	TBD

Notes:

- 1 Based on information in Certa et al. (1996).
- 2 Based on preliminary calculations by Boothe (1996).
- 3 Based on January 1996 waste tank surveillance information for DN waste.
- 4 Based on February 1996 information from Waste Tanks Process Engineering (WHC).



The reaction slows after the first hydrolysis to NaDBP. Subsequent degradation to monobutyl phosphate and sodium phosphate are very slow reactions by NaOH hydrolysis (Burger 1955).

The NPH is more resistant to thermal and radiation degradation than TBP and the diluents previously used at the PUREX Plant (Shell E-2342 and Soltrol 170). The NPH degradation produces a variety of reaction products. They include hydrogen gas, carboxylic acid salts, and several other compounds having both higher and lower carbon numbers (< C₁₀ and > C₁₄). The NPH does not hydrolyze in the common use of the term (Samuels et al. 1993). Shell E-2342 diluent contained cycloparaffins. Soltrol 170 diluent contained branched alkanes. The amount of these previously used diluents discharged to waste tanks is known; however, their current inventory is unknown. Condensation products of Shell E-2343 are believed to yield a "black tarry substance" based on September 1958 samples of the A-24 condensate crib.

A preliminary model was developed for predicting time requirements for alkaline hydrolysis of TBP at several different conditions. The constant volume batch isothermal model was developed from TBP destruction rate data in 1.0 M NaOH (Kennedy and Grimley 1953) and solubility of TBP in NaOH solutions (Higgins et al. 1959; Johnson and Dillon 1953; HW-29086; Schulz and Navratil 1984). See Tables 8.5-2 through 8.5-8 for a summary of the TBP data.

Figure 8.5-1 shows the solubility of TBP in water and NaOH solutions at 25 °C. TBP solubility is dependent on the concentration of TBP in the TBP-NPH separable phase organic, temperature, and the aqueous phase NaOH concentration.

The aqueous solubility of TBP decreases as the temperature is increased (Higgins et al. 1959; Schulz and Navratil 1984). The solubility of TBP in water is about 0.42 to 0.44 g/l at 25 °C. The solubility of NPH is about 4 mg/L in water. No additional information of NPH solubility could be located.

Alkaline TBP solubility is related to water solubility by using the Setschenow equation and salting coefficient for NaOH concentration and temperature of solution (Higgins et al. 1959; Schulz and Navratil 1984).

$$\text{Log}[M \text{ TBP in water}/(M \text{ TBP in OH})] = \text{Salting Coefficient} \times \text{OH } M \quad (1)$$

The solubility of TBP in NaOH decreases as the concentration of hydroxide is increased.

Table 8.5-2. Hydrolysis of TBP with 1.02 M Sodium Hydroxide Solution.

Temperature °C	100% TBP (mg/L/h) Reacted	20% TBP Odorless Kerosene (mg/L/h) Reacted
30	0.88	0.708
40	1.96	0.959
50	4.37	2.17
60	9.59	5.79
70	30.4	12.2
100	283	120

Source of data is Kennedy and Grimley (1953).

Table 8.5-3. Solubility of TBP in Water at 25 °C Based on Concentration of TBP in Diluent.

Volume% TBP in Dodecane	TBP g/L Aqueous Phase
0	0
6	0.130
12.5	0.197
25	0.244
50	0.277
71	0.328
100	0.44

Source of data is Johnson and Dillon (1953)

Table 8.5-4. Solubility of 100% TBP in Water.

Temperature (°C)	Solubility (g/L)
3.4	1.075
4.0	1.012
5.0	0.957, 0.95
13.0	0.64
15.0	0.64
16.0	0.42
17.0	0.41
19.0	0.397
22.0	0.380
25.0	0.422, 0.39, 0.44, 0.447
35.0	0.35
45.0	0.29
50.0	0.285

Source of data is Schulz and Navratil (1984)

Table 8.5-5. Salting Coefficient for TBP in NaOH Solution as a Function of Temperature.

Temperature °C	Salting Coefficient
5	0.66
13	0.66
25	0.65

Source of data is Higgins et al. (1959)

**Table 8.5-6. Summary of Second Order Reaction Constants
Based on TBP Solubility in 1.02 M NaOH at 25 °C.**

% TBP in Odorless Kerosene	K	R ²
20	$2.035E10e^{(-17.110/RT)}$	0.983
100	$2.634E11e^{(-18.790/RT)}$	0.993
Combined	$7.395E10e^{(-17.960/RT)}$	0.987

**Table 8.5-7. Summary of Estimated TBP Equilibrium Solubility of Tank 241-C-103
Separable Phase Organic in NaOH Solution.**

Temperature (°C)	NaOH M	A/O Volume Ratio	Aqueous Phase TBP ¹ (mg/L)
40	0.5	20	119
40	0.5	200	119
50	0.5	20	108
50	0.5	200	107
40	1.1	20	49.1
40	1.1	200	49.0
50	1.1	20	44.6
50	1.1	200	44.5
40	2.3	20	8.3
40	2.3	200	8.3
50	2.3	20	7.6
50	2.3	200	7.6

Note:

- 1 Solubility is based on a temperature corrected algorithm from information in Tables 8.5-3, 8.5-4, and 8.5-5.

Table 8.5-8. Graphically Interpolated Total Acid Yields for the Radiolysis of TBP in Aliphatic Diluents.

TBP (g/L)	G (total acid)	
	Dry	H ₂ O Saturated
0	0	0
50	0.38	0.27
100	0.62	0.47
200	1.00	0.73
300	1.32	0.92
400	1.61	1.09
500	1.87	1.24
600	2.13	1.38
700	2.37	1.50
800	2.61	1.62
900	2.83	1.73
973	3.00	1.80

Source of data is Schulz and Navratil (1984)

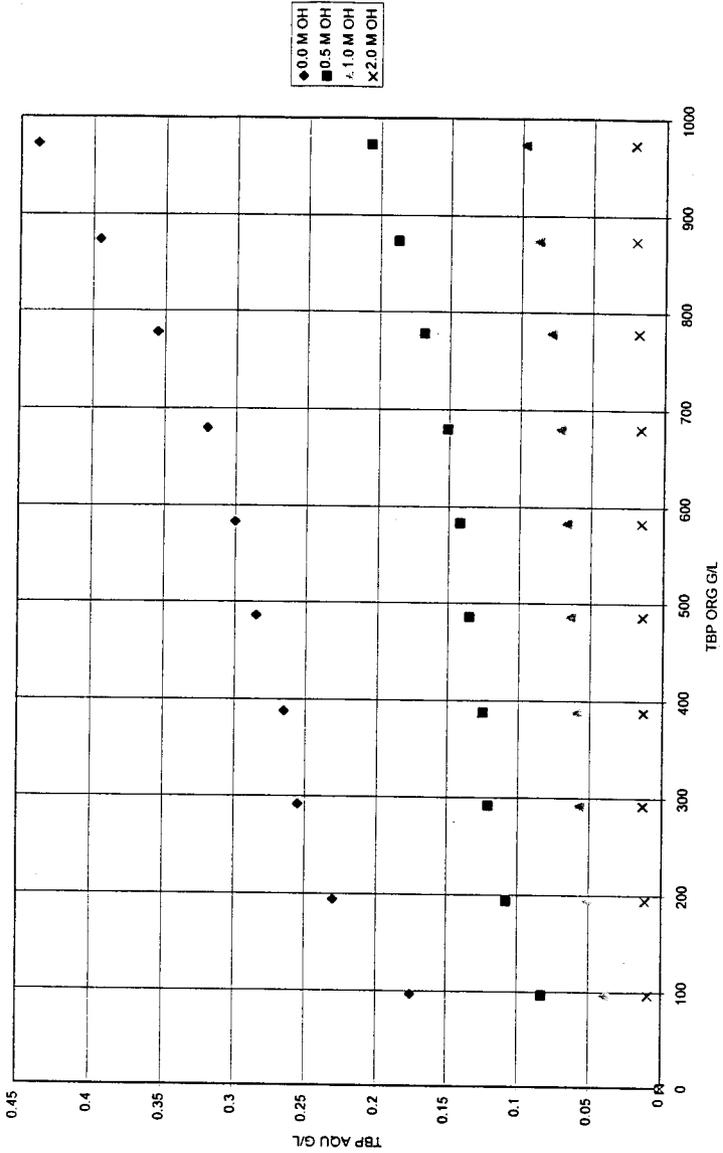


Figure 8.5-1. Predicted TBP Aqueous-Organic Phase Equilibrium Solubility at 25° C.

Aqueous phase TBP solubility is based on 25 °C in water and then corrected for NaOH using the Setschenow equation (Equation 1). Technical literature shows that increasing temperature decreases the solubility of TBP in both water and NaOH solution. The solubility of TBP at 50 °C is about 70% of solubility at 25 °C (see Tables 8.5-3 and 8.5-4).

The preliminary TBP hydrolysis model was based upon a second order rate equation for extrapolation to different temperatures and NaOH concentrations. The hydrolysis of TBP by NaOH takes place only in the aqueous phase and the reaction rate is limited by the solubility of TBP in NaOH solution. TBP hydrolysis may occur at the aqueous/organic interface and significantly increase the reaction rate. The effect of salting agents on TBP solubility in NaOH solution is not clearly understood. The second order reaction rate equations are described below.

$$\text{TBP destruction rate (g mole/L/h)} = K C_{\text{TBP}} C_{\text{OH}} \quad (2)$$

K = rate constant (L/g mole h) = $Ae^{-E/RT}$

C_{TBP} = g mole TBP/L aqueous phase

C_{OH} = g mole/L free OH⁻ aqueous phase

A = 2.634E11 L/g mole h

E = 18,720 cal/g mole activation energy based on 100% TBP destruction in 1.0 M NaOH

T = Temperature K

R = Gas constant, 1.987 cal/g mole K

The integrated rate equation:

$$\text{incremental time (hr)} = [1/K(C_{\text{OH1}} - C_{\text{TBP1}})] \text{Ln}[(C_{\text{TBP1}} C_{\text{TBP2}} + C_{\text{TBP1}} C_{\text{OH1}} - C_{\text{TBP2}}^2) / (C_{\text{TBP2}} C_{\text{OH1}})] \quad (3)$$

The C_{TBP} values are established by a repetitive combination of TBP aqueous phase equilibrium solubility and assumed increment of soluble TBP destruction. TBP is transferred from the separable phase organic to the aqueous phase during the re-equilibration step. The time increment is cumulative. The C_{OH} value was assumed as constant. NaOH as solids or 50 wt% solution could be added to the tank as needed to maintain desired free hydroxide concentration. There is little change of aqueous volume at A/O ratio ≥ 20 by addition of concentrated NaOH. The NaOH heat of solution would add heat to the waste and help TBP hydrolysis.

Individual rate constants (K) were developed by dividing the experimental rate of TBP destruction at 30 to 100 °C by the product of NaOH concentration and predicted equilibrium aqueous phase TBP concentration at 1.02 M NaOH and 25 °C (A/O = 32.6). A graph of $\text{Ln } K$ and reciprocal of absolute temperature was developed using the 20 vol% TBP and 100% TBP experimental data. Figure 8.5-2 shows the results.

A linear regression analysis equation of $\text{Ln } K$ and $1/T$ was developed for 20% TBP, 100% TBP and combined 20 and 100% TBP data. The slope of the line multiplied by gas

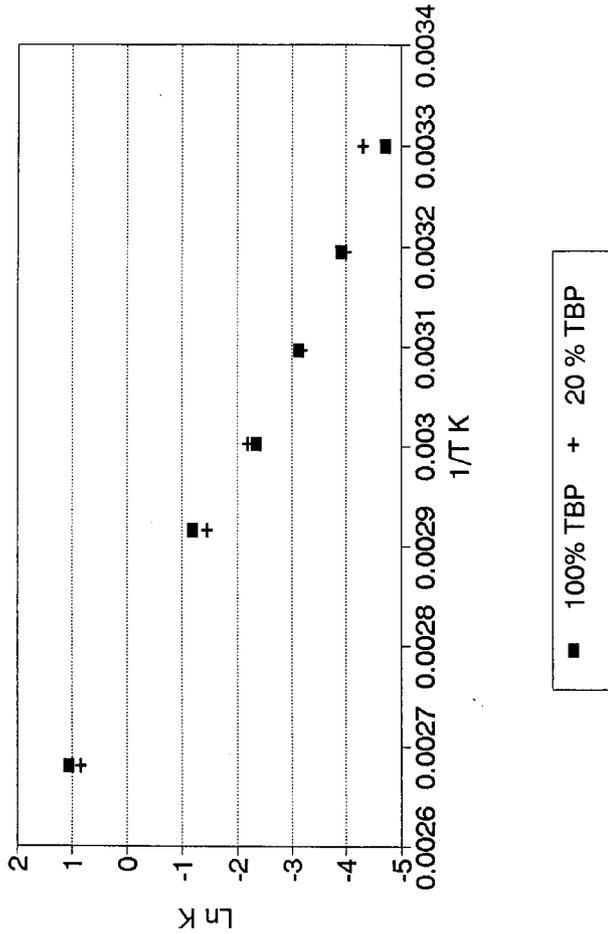


Figure 8.5-2. Second Order Rate Constants for Hydrolysis of TBP in 1M NaOH
Based on Kennedy and Grimley (1953) Data.

law constant (R) 1.987 g-cal/g mole K gives the activation energy. The activation energy was 17,110 cal/g mole for hydrolysis of 20% TBP in odorless kerosene, 18,790 cal/g mole for 100% TBP and 17,960 cal/g mole for combined 20% and 100% TBP data (see Table 8.5-6). The 100% TBP correlation gave the best fit of the data and was used for the modeling.

Figure 8.5-3 compares predicted TBP reaction rates for 20% TBP based on the 100% TBP rate constant correlation. The results compare favorably with experimental values by Kennedy and Grimley (1953) for total TBP destruction of 1 and 10%. The experimental reaction rates were developed at conditions of constant TBP concentration, constant NaOH concentration, constant temperature, and little TBP destruction.

Preliminary sensitivity analysis results are summarized in Table 8.5-9 and shown graphically in Figure 8.5-4 for hydrolysis of 70% TBP 30% NPH to an aqueous phase concentration of 1.0 mg/L TBP. This value is believed to minimize operating problems with cesium ion exchange. No target value could be established for NPH at this time. The modeling parameters are A/O (aqueous to organic volume) ratio of 20 and 200, NaOH concentrations of 0.5, 1.1 and 2.3 M and temperatures of 40 and 50 °C. All three parameters impact the destruction rate of TBP. The NPH does not hydrolyze and must be removed by evaporation.

Based on sensitivity analysis results, maximum TBP destruction rates occurred at A/O of 200, 50 °C and 0.5 to 2.2 M free hydroxide. Maximum TBP destruction was 99.93% and occurred at A/O of 20 and 0.5 M OH at both 40 and 50 °C. The destruction times were 570 days at 50 °C and 1,440 days at 40 °C to achieve 99.93% TBP destruction. Higher total TBP destruction may be achieved in a shorter time period by using high A/O process conditions. NaOH and temperature control both TBP solubility and TBP reaction rate. The maximum A/O ratio can only be achieved by mixing the 18,900 l of Tank 241-C-103 organic with aqueous waste of the DST.

Differences of average TBP destruction rates (See Figure 8.5-3) were partly dependent on the convergence method and size of the increment used by the model for aqueous phase TBP destruction before remixing the aqueous and organic phases. A large destruction increment (30 or 40% vs 10 to 20%) reduced the reaction rate and increased the time requirement due to removal of additional TBP (lower aqueous phase concentrations) before re-equilibration with the organic phase. An aqueous phase TBP destruction increment of $\leq 10\%$ is considered as ideal before resolubilization within the organic phase. Technical literature shows aqueous phase re-equilibration is achieved in less time than 10 minutes by shaking or tumbling (Higgins et al. 1959, Kennedy and Grimley 1953). Larger destruction increments may better represent actual mixing efficiency of light phase organic with the waste in a DST or other interim storage tank.

Mixing of TBP with soluble chelating agents, degradation products such as Na dibutyl phosphate (TBP degradation product) and Na stearate (potential NPH oxidation product) and other organic in waste may increase the solubility of TBP in the aqueous phase and/or help TBP-NPH form a micro emulsion that does not readily disengage (personal communication

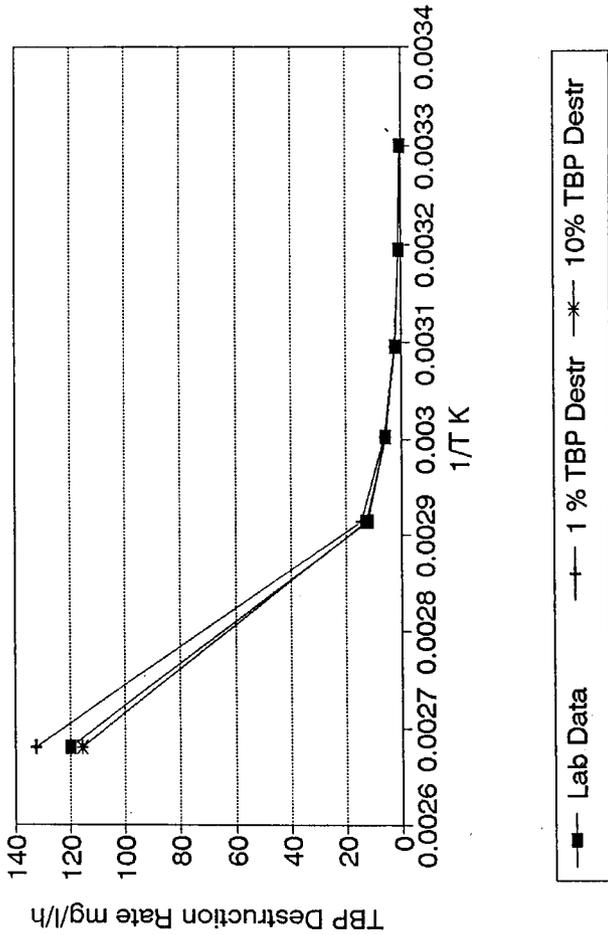


Figure 8.5-3. Comparison of Laboratory and Predicted TBP Destruction Rates for 20% TBP in Odorless Kerosene Based on Rate Constants for 100% TBP.

Table 8.5-9. Summary of Sensitivity Analysis For Alkaline Hydrolysis of 18,900 L of Tank 241-C-103 Organic to 1 mg/L TBP in Aqueous Phase' Based on Preliminary Isothermal Batch Modeling.

Temp (°C)	NaOH (M)	A/O ² Volume Ratio	Average TBP Destruction Rate		Estimated Time (days)	wt % TBP		Aqueous NaDBP ^a (g/L)	
			(mg/L/h)	(g/h)		Destroyed	Aqueous		Organic
50	0.5	200	2.33	8810	50	99.90	0.03	0.07	2.5
50	1.1	200	2.05	7750	60	99.80	0.03	0.07	2.5
40	0.5	200	0.91	3440	130	99.90	0.03	0.07	2.5
40	1.1	200	0.80	3020	150	99.80	0.03	0.17	2.5
50	2.3	200	0.77	2910	160	98.91	0.03	1.06	2.5
40	2.3	200	0.31	1170	390	98.91	0.03	1.06	2.5
50	0.5	20	2.13	800	570	99.93	0.003	0.07	25.4
50	1.1	20	2.02	760	600	99.83	0.003	0.17	25.4
40	0.5	20	0.83	310	1440	99.93	0.003	0.07	25.4
40	1.1	20	0.79	300	1530	99.83	0.003	0.17	25.4
50 ^b	2.3	20	0.76	290	1580	98.94	0.003	1.06	25.1
40 ^b	2.3	20	0.27	100	4440	98.94	0.03	1.06	25.1

Notes:

- 1 Preliminary modeling does not include the following: NPH solubility loss to aqueous phase, temperature effect on aqueous phase TBP solubility, evaporation losses, potential catalytic effect of emulsifiers, cations, or hydrated oxide/hydroxide solids, instantaneous hydrolysis-resolubility and irradiation effects.
- 2 Aqueous to organic (A/O) volume ratio.
- 3 TBP destruction was based on >20% increment before resolubilization to reduce the number of iterations.
- 4 Multiply values by 0.41 to convert NaDBP to organic carbon. Waste containing ≥ 10 g/L TOC after concentration is considered CC waste.

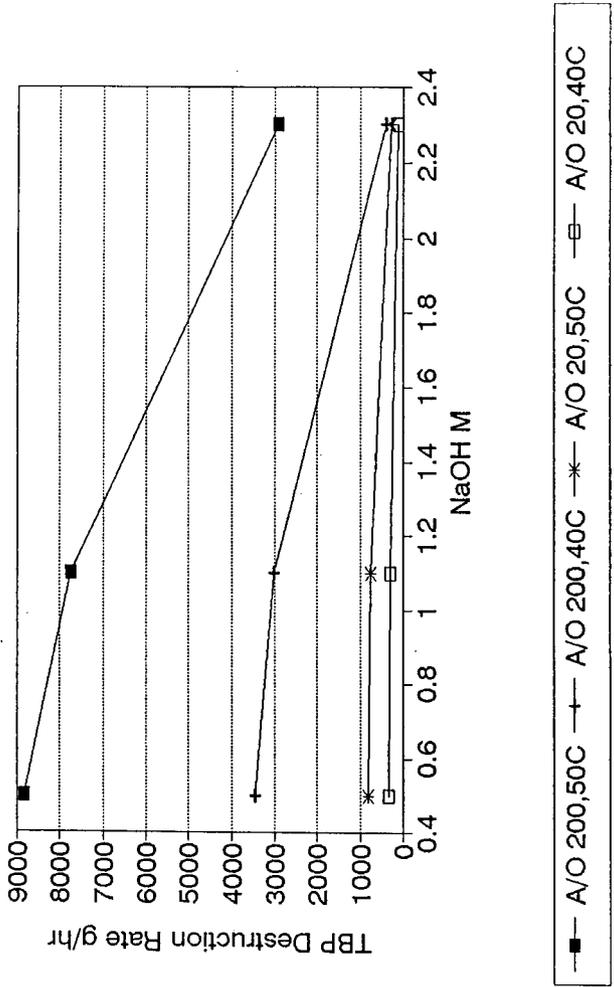


Figure 8.5-4. Sensitivity Analysis of TBP Destruction Rates for Tank 241-C-103 Organic in NaOH Solutions Based on Model.

with D.M. Camiaoni [PNNL] January 1996). FY 95 waste aging laboratory tests with simulated, undiluted Tank 241-SY-101 complexed concentrate waste (Camiaoni et al. 1995) show more rapid TBP degradation than could be predicted from NaOH solution (Hallen 1996).

The TBP rate constants could not be established from FY 95 waste aging tests. There was an estimated 1.5 to 1.9 mg TBP/L/h degradation during the 2- to 4-month storage of emulsified simulated waste feed at 4 °C before testing. Additional degradation may have occurred during 1 to 4 months refrigerated storage of test samples (-10 °C) and/or rewarming of the test samples for analysis. The organic and aqueous components remained together for a total of 3 to 8 months before analysis. The FY 95 waste aging studies show the estimated rate of TBP degradation is about 110 mg/L/h at 50 °C or about 60 times faster than predicted in NaOH solution. The FY 95 test data are summarized in Tables 8.5-10 and 8.5-11. Additional information is needed to understand the mechanism for accelerated TBP destruction and use of the test results in standard rate equations.

Follow-on laboratory scouting studies were performed under uniform mild mixing conditions and indicated that metal ions, surfactants or nitrite ions probably have little effect on the rate of TBP hydrolysis (Hallen 1996). Therefore, previous study results could not be repeated. Mixing may be very important for achieving fast degradation rates of TBP. Further study is required.

8.5.3 Radiolytic Destruction

Radiolysis provides little TBP destruction compared to chemical hydrolysis. If the Tank 241-C-103 organic and aqueous are mixed with the Tank 241-AP-107 contents (A/O = 26), only approximately 1 to 3% of the TBP is degraded through radiolysis by the predicted time for hydrolysis of the TBP. Table 8.9-12 summarizes radiolytic destruction of TBP under several conditions. Results show that up to 12% TBP is destroyed by radiolysis during alkaline hydrolysis based on mixing existing Tank 241-AP-107 waste with Tank 241-C-103 and suspect/known CC waste from the SSTs. Up to 85% TBP destruction is expected if the organic remains as a floating layer atop the supernatant for 10 years. About 15% TBP destruction is estimated after 10 years of storage as a floating layer organic atop Tank 241-C-103 supernatant.

If CC waste addition is planned, further testing with actual waste is needed to ensure that steady state and abnormal hydrolysis/radiolysis conditions (including accelerated TBP destruction and butanol formation) do not exceed criteria for flammable gas and organic salts. The frequent stirring of the waste, low temperature (50 °C) digestion, and 120 ft³/min forced air ventilation are expected to prevent accumulation of potential flammable gas. Formation and disposal of tarry like solids or polymers (eg. recent observation of black oil substance in Tank C-106 sludge sample and tarry substance in 1958 A-24 condensate crib sample) is another concern.

Table 8.5-10. Summary of Waste Aging Studies Data for Unirradiated Hydrolysis Tests with Simulated CC Waste at 1.8 M NaOH and A/O of 20.

Experiment	Temp °C	Test Time (days)	Dose (MGy)	Age of Simulant Before Expt (days)	Time Expt Sample Stored Before Analysis (days)	Total TBP (mg/g)	Average TBP Degradation Rate (mg/L/h)	Est % TBP Degraded Before Expt
SIM 94C	4	0	NA	0 (62 @ ~4 °C)	62 @ -10 °C	18.6	NA	NA
SIM 94C	4	0	NA	466 @ ~4 °C	134 @ -10 °C	8.89	1.5	52 ¹
SIM 94C	4	0	NA	466 @ ~4 °C	116 @ -10 °C	6.37	1.8	66 ¹
SIM 94C	4	0	NA	515 @ ~4 °C	32 @ -10 °C	4.85	1.9	74 ¹
B-1	50	11	0.00	72 @ ~4 °C	118 @ -10 °C	0.05	108 ³	10 ²
B-2	70	11	0.00	84 @ ~4 °C	105 @ -10 °C	0.00	106 ³	11 ²
B-3	90	11	0.00	99 @ ~4 °C	60 @ -10 °C	0.01	103 ³	13 ²
X-1	50	90	0.00	115 @ ~4 °C	28 @ -10 °C	0.00	12.3 ³	15 ²

Source of information is Camiaoni et al. (1995) and undocumented test data dated 1/22/96.

Notes:

- 1 Based on initial analysis of simulant 62 days after make up. Test simulant was stored at ~4 °C. Lab samples were stored at -10 °C. TBP make up target was 15.7 mg/g.
- 2 Based on average TBP degradation rate of 1.73 mg/L/h at 4 °C.
- 3 Assumes no TBP degradation during storage of test samples at -10 °C and warming for analysis.

Table 8.5-11. Head Space Gas Analysis for Unirradiated Simulant SY-SIM-94-C
Aging Experiments at 1.8 M NaOH and A/O = 20.

Experiment	Temp (°C)	Time (days)	H ₂ μmol	CH ₄ μmol	N ₂ μmol	O ₂ μmol	N ₂ O μmol	NO _x μmol	C ₂ H ₆ μmol	RH μmol
B-1	50	11	0.01	1	18	155	0.06	0.2	0.2	9
B-2	70	11	0.01	1	18	155	0.06	0.2	0.2	9
B-3	90	11	5	1	16	132	0.06	0.01	0.01	7
X-1	50	90	0.33	1.25	37	2.4	0.08	0.08	0.3	16

Table 8.5-12. Estimated Typical TBP Destruction by Radiolysis of 18,900 L of Tank C-103 Organic at Potential Storage Conditions.

Tank	Description ¹	Gamma Energy Disposition ² Rad/h	Estimated TBP Destruction by Gamma Radiolysis ³
AP-107	Organic mixed with existing aqueous + Tank C-103 aqueous (A/O = 26)	65	~1 % based on 570 da hydrolysis at A/O = 20, 0.5 M OH, 50 °C
AP-107	Organic as floating layer above existing aqueous + Tank C-103 aqueous (A/O = 26)	40	~1 % based on 570 da and no hydrolysis; ~15 % after 10 yr and no hydrolysis
AP-107	Organic mixed with existing aqueous + CC waste (A/O = 100)	330	~5 % based on 115 da hydrolysis at A/O = 100, 0.5 M OH, 50 °C
AP-107	Organic as floating layer above existing aqueous + CC waste (A/O = 100)	140	~3 % based on 115 da and no hydrolysis; ~75 % after 10 yr and no hydrolysis
AP-107	Organic mixed with existing aqueous + aqueous from Tank C-103 + CC waste (A/O = 126)	290	~5 % based on 115 day hydrolysis at A/O = 100, 0.5 M OH, 50 °C
AP-107	Organic as floating layer above existing aqueous + aqueous from Tank C-103 + CC waste (A/O = 126)	130	~4 % based on 115 da and no hydrolysis; ~85 % after 10 yr and no hydrolysis

Notes:

1 Preliminary planning assumptions. No potential catalytic affect on CC waste.

2 Source of information is Boothe (1996).

3 Basis is no NPH evaporation or degradation. TBP G values based on Table 8.5-8 for water saturated organic.

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VOLUME 2

Section 8.6

DSI - Dose Rates to Organic in DSTs

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DON'T SAY IT --- Write It!

DATE: January 31, 1996

TO: M. J. Klem

FROM: Gary F. Boothe
Phone: 376-0158cc: D. J. Washenfelder
R. A. Kirkbride**SUBJECT: DOSE RATES TO ORGANIC IN DOUBLE-SHELL TANKS**

The attached EXCEL print out, *Energy Deposition In DST*, gives the energy deposition in terms of dose rate (rad/hr) to organic contained in double-shell tanks. Two cases are considered: (1) The dispersed case where the organic is assumed to be uniformly dispersed in the supernate and (2) The layered case where the organic is assumed to be floating on top the supernate.

For the dispersed case, the dose rates in all tanks are calculated, including special cases for 105-AP and 102-AY in which 133,000 gallons of supernate from 103-C are added. For the layered organic case, dose rates for 105-AP (with and without supernate from 103-C), 102-AY (with and without supernate from 103-C), and 102-AZ are calculated with the MICROSIELD code.

The dose rates are approximate, using the following simplifying assumptions:

In the dispersed case, no alpha, beta or gamma energy is lost from the supernate. This assumption is valid only near the center of the supernate. The average error here could be as high as 20% (rough guess) due to gamma losses.

In the layered case, the dose rate is constant throughout the organic layer, and equal to the dose rate 5 cm into the layer. The average error here could be as high as 50% (rough guess) due to microshield calculation techniques.

Other assumptions used are given in the EXCEL printout, including Ci/l of isotopes present, volume of supernate, supernate density, and supernate dimensions. These data were taken from Certa, P. J., et. al., *Preliminary Low-Level Waste Feed Staging Plan*, WHC-SD-WM-RPT-210, Rev. 0, Draft A, January 15, 1996. The energies of alpha, beta and gamma emissions were taken from Kocher, D. C., *Radioactive Decay Data Tables*, Oak Ridge National Laboratory, 1981.

WHC-SD-WM-ES-384 REV 0
ENERGY DEPOSITION IN DST

Energy deposition in dispersed and layered organic within DSTs is given below. Dispersed case assumes no alpha, beta or gamma losses from the supernate. The layered case assumes a constant dose rate equal to the gamma dose rate 5 cm into the organic, as calculated by MICROSIELD.						
SUPERNATE CURIES PER LITER						
FOR THE DISPERSED ORGANIC CASE:						
ISOTOPE	101AN	102AN	103AN	104AN	105AN	106AN
14C	3.23E-08	1.74E-05	1.96E-06	0.00E+00	0.00E+00	4.52E-08
90Sr	1.90E-05	5.48E-02	7.13E-03	4.86E-03	1.59E-03	6.32E-03
90Y	1.90E-05	5.48E-02	7.13E-03	4.86E-03	1.59E-03	6.32E-03
99Tc	9.82E-06	2.95E-04	1.67E-04	1.80E-04	1.75E-04	6.41E-05
137Cs	2.64E-06	1.82E-01	4.24E-01	3.86E-01	2.57E-01	3.53E-02
137Ba	2.51E-06	1.73E-01	4.02E-01	3.67E-01	2.44E-01	3.36E-02
154Eu	1.76E-06	7.58E-04	0.00E+00	0.00E+00	0.00E+00	1.80E-06
235U	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
238U	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
237Np	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	4.69E-10
238Pu	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	4.30E-07
239Pu	8.57E-09	6.37E-05	1.87E-06	1.04E-05	1.04E-05	2.99E-06
240Pu	8.58E-12	1.62E-05	2.87E-07	1.60E-06	1.59E-06	7.38E-07
241Pu	0.00E+00	1.56E-05	3.62E-07	1.59E-06	1.58E-06	2.30E-07
241Am	1.65E-07	5.91E-05	2.24E-06	1.52E-06	1.51E-06	1.62E-05
SUPERNATE VOLUME (LITERS)	3.68E+06	3.95E+06	3.62E+06	3.02E+06	4.29E+06	4.47E+06
SUPERNATE DENSITY (GRAMS/CC)	1.3	1.37	1.5	1.46	1.46	1.37
SUPERNATE THICKNESS (CM)	8.98E+02	9.65E+02	8.84E+02	7.38E+02	1.05E+03	1.09E+03
SUPERNATE DIAMETER (CM)	2286	2286	2286	2286	2286	2286
ALPHA ERGS PER CC-HR	2.03E-01	1.57E+02	4.99E+00	1.50E+01	1.49E+01	2.36E+01
BETA ERGS PER CC-HR	4.76E+00	1.99E+04	1.72E+04	1.53E+04	9.75E+03	2.81E+03
GAMMA ERGS PER CC-HR	6.20E-01	2.45E+04	5.68E+04	5.18E+04	3.44E+04	4.73E+03
SUPERNATE/ORGANIC RAD/HR	7.26E-02	6.10E+02	1.11E+03	9.79E+02	6.45E+02	1.04E+02
GAMMA ONLY RAD/HR	4.77E-03	1.79E+02	3.78E+02	3.55E+02	2.36E+02	3.46E+01
FOR THE LAYERED ORGANIC CASE:						
SUPERNATE Ba-137 CURIES	9.21E+00	6.83E+05	1.46E+06	1.11E+06	1.05E+06	1.50E+05
SUPERNATE Eu-154 CURIES	6.46E+00	3.00E+03	0.00E+00	0.00E+00	0.00E+00	8.03E+00
RAD/HR TO ORGANIC LAYER						

WHC-SD-WM-ES-384 REV 0
ENERGY DEPOSITION IN DST

SUPERNATE CURIES PER LITER						
FOR THE DISPERSED ORGANIC CASE:						
ISOTOPES	107AN	101AP	102AP	103AP	104AP	105AP
14C	0.00E+00	1.96E-07	4.19E-07	4.46E-09	2.52E-14	8.73E-09
90Sr	4.83E-02	1.14E-04	8.71E-04	1.53E-06	2.16E-09	5.72E-03
90Y	4.83E-02	1.14E-04	8.71E-04	1.53E-06	2.16E-09	5.72E-03
99Tc	4.74E-04	6.31E-05	8.58E-05	1.08E-06	1.99E-07	4.46E-05
137Cs	1.38E-01	1.28E-01	1.42E-03	3.92E-03	1.29E-05	1.76E-02
137Ba	1.31E-01	1.21E-01	1.34E-03	3.72E-03	1.23E-05	1.67E-02
154Eu	1.45E-03	4.94E-09	0.00E+00	1.69E-05	0.00E+00	0.00E+00
235U	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
238U	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
237Np	0.00E+00	0.00E+00	0.00E+00	0.00E+00	5.36E-10	0.00E+00
238Pu	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
239Pu	3.55E-05	1.44E-07	7.50E-08	6.97E-09	4.46E-10	2.41E-06
240Pu	9.03E-06	2.22E-08	1.15E-08	1.07E-09	1.61E-10	6.02E-07
241Pu	8.52E-06	3.30E-08	1.70E-08	1.47E-09	1.56E-09	2.14E-07
241Am	3.50E-04	3.67E-07	4.17E-07	1.13E-08	1.50E-12	1.34E-05
SUPERNATE VOLUME (LITERS)	3.68E+06	3.39E+06	4.16E+06	1.02E+05	4.23E+06	7.56E+04
SUPERNATE DENSITY (GRAMS/CC)	1.33	1.32	1.21	1.01	1.28	1.32
SUPERNATE THICKNESS (CM)	8.99E+02	8.27E+02	1.02E+03	2.50E+01	1.03E+03	1.85E+01
SUPERNATE DIAMETER (CM)	2286	2286	2286	2286	2286	2286
ALPHA ERGS PER CC-HR	4.59E+02	6.13E-01	5.83E-01	2.21E-02	1.22E-03	1.90E+01
BETA ERGS PER CC-HR	1.67E+04	4.68E+03	2.62E+02	1.44E+02	4.72E-01	2.02E+03
GAMMA ERGS PER CC-HR	1.87E+04	1.71E+04	1.90E+02	5.28E+02	1.73E+00	2.35E+03
SUPERNATE/ORGANIC RAD/HR	4.77E+02	2.88E+02	5.47E+00	6.78E+00	2.82E-02	5.80E+01
GAMMA ONLY RAD/HR	1.41E+02	1.30E+02	1.57E+00	5.22E+00	1.35E-02	1.78E+01
FOR THE LAYERED ORGANIC CASE:						
SUPERNATE Ba-137 CURIES	4.82E+05	4.11E+05	5.59E+03	3.80E+02	5.20E+01	1.26E+03
SUPERNATE Eu-154 CURIES	5.33E+03	1.67E-02	0.00E+00	1.73E+00	0.00E+00	0.00E+00
RAD/HR TO ORGANIC LAYER						9.98

ENERGY DEPOSITION IN DST

SUPERNATE CURIES PER LITER					
FOR THE DISPERSED ORGANIC CASE:	103C +			103C+	103U+105U+109U
ISOTOPE	105AP	106AP	107AP	107AP	107AP
14C		4.09E-14	8.97E-11		
90Sr	9.64E-04	3.19E-10	2.02E-09	2.03E-04	9.14E-03
90Y	9.64E-04	3.19E-10	2.02E-09	2.03E-04	9.14E-03
99Tc		2.93E-11	5.78E-10		
137Cs	5.79E-02	4.75E-08	8.77E-09	5.19E-02	3.33E-01
137Ba	5.50E-02	4.51E-08	8.33E-09	4.93E-02	3.16E-01
154Eu		2.22E-12	3.27E-09		
236U		0.00E+00	0.00E+00		
238U		0.00E+00	0.00E+00		
237Np		4.54E-14	0.00E+00		
238Pu		0.00E+00	1.53E-11		
239Pu		5.36E-12	1.51E-08		
240Pu		2.81E-14	2.31E-09		
241Pu		1.87E-13	3.45E-09		
241Am		1.61E-11	1.78E-08		
SUPERNATE VOLUME (LITERS)	5.79E+05	3.03E+06	1.17E+05	6.20E+05	1.95E+06
SUPERNATE DENSITY (GRAMS/CC)	1.10	1.38	1.01	1.06	1.35
SUPERNATE THICKNESS (CM)	1.41E+02	7.40E+02	2.86E+01	1.51E+02	4.75E+02
SUPERNATE DIAMETER (CM)	2286	2286	2286	2286	2286
ALPHA ERGS PER CC-HR		2.48E-05	4.00E-02		
BETA ERGS PER CC-HR	2.34E+03	1.81E-03	9.66E-04	1.94E+03	1.43E+04
GAMMA ERGS PER CC-HR	7.76E+03	6.36E-03	1.67E-03	6.96E+03	4.46E+04
SUPERNATE/ORGANIC RAD/HR	1.11E+02	1.13E-04	4.30E-04	9.42E+01	7.92E+02
GAMMA ONLY RAD/HR	7.04E+01	4.61E-05	1.65E-05	6.57E+01	3.31E+02
FOR THE LAYERED ORGANIC CASE:					
SUPERNATE Ba-137 CURIES	3.19E+04	1.37E-01	9.77E-04	3.06E+04	6.14E+05
SUPERNATE Eu-154 CURIES		6.73E-06	3.84E-04		
RAD/HR TO ORGANIC LAYER	44.3		0.00001	41.1	141.2

WHC-SD-WM-ES-384 REV 0
ENERGY DEPOSITION IN DST

SUPERNATE CURIES PER LITER					
FOR THE DISPERSED ORGANIC CASE:					
ISOTOPES	103C+103U+105U+	108AP	101AW	102AW	103AW
14C		2.99E-12	3.69E-07		0.00E+00
90Sr	7.31E-03	1.80E-04	5.63E-04		0.00E+00
90Y	7.31E-03	1.80E-04	5.63E-04		0.00E+00
99Tc		1.54E-04	1.51E-04		0.00E+00
137Cs	2.77E-01	1.10E-01	2.68E-01		4.75E-02
137Ba	2.63E-01	1.05E-01	2.55E-01		4.51E-02
154Eu		1.63E-09	0.00E+00		0.00E+00
235U		0.00E+00	0.00E+00		0.00E+00
238U		0.00E+00	0.00E+00		0.00E+00
237Np		1.15E-11	0.00E+00		0.00E+00
238Pu		1.05E-08	0.00E+00		1.16E-04
239Pu		6.93E-12	1.54E-06		0.00E+00
240Pu		1.06E-12	2.36E-07		0.00E+00
241Pu		1.75E-13	3.04E-07		0.00E+00
241Am		1.55E-12	1.61E-06		0.00E+00
SUPERNATE VOLUME (LITERS)	2.45E+06	3.10E+06	3.94E+06		5.41E+05
SUPERNATE DENSITY (GRAMS/CC)	1.29	1.1	1.51	0	1.04
SUPERNATE THICKNESS (CM)	5.98E+02	7.57E+02	9.62E+02	0.00E+00	1.32E+02
SUPERNATE DIAMETER (CM)	2286	2286	2286	2286	2286
ALPHA ERGS PER CC-HR		1.24E-02	3.84E+00	0.00E+00	1.36E+02
BETA ERGS PER CC-HR	1.19E+04	4.06E+03	9.92E+03	0.00E+00	1.73E+03
GAMMA ERGS PER CC-HR	3.72E+04	1.48E+04	3.60E+04	0.00E+00	6.37E+03
SUPERNATE/ORGANIC RAD/HR	6.32E+02	2.07E+02	6.93E+02	0.00E+00	8.56E+01
GAMMA ONLY RAD/HR	2.88E+02	1.34E+02	2.38E+02		6.12E+01
FOR THE LAYERED ORGANIC CASE:					
SUPERNATE Ba-137 CURIES	6.45E+05	3.25E+05	1.00E+06	0.00E+00	2.44E+04
SUPERNATE Eu-154 CURIES		5.05E-03	0.00E+00	0.00E+00	0.00E+00
RAD/HR TO ORGANIC LAYER	126.6				

WHC-SD-WM-ES-384 REV 0
ENERGY DEPOSITION IN DST

SUPERNATE CURIES PER LITER						
FOR THE DISPERSED ORGANIC CASE:						
ISOTOPES	104AW	105AW	106AW	101AY	102AY	102AY
	103C +					
14C	4.48E-08	5.04E-15		1.89E-06	0.00E+00	
90Sr	6.99E-05	3.77E-11		3.18E-02	1.37E-03	1.21E-03
90Y	6.99E-05	3.77E-11		3.18E-02	1.37E-03	1.21E-03
99Tc	1.36E-05	3.61E-12		9.10E-05	2.24E-05	
137Cs	1.40E-02	2.93E-04		1.25E-01	4.87E-02	5.09E-02
137Ba	1.33E-02	2.78E-04		1.19E-01	4.62E-02	4.83E-02
154Eu	2.44E-06	2.74E-13		0.00E+00	0.00E+00	
235U	0.00E+00	0.00E+00		0.00E+00	0.00E+00	
238U	0.00E+00	0.00E+00		0.00E+00	0.00E+00	
237Np	0.00E+00	1.53E-10		1.69E-07	0.00E+00	
238Pu	0.00E+00	1.40E-07		0.00E+00	0.00E+00	
239Pu	6.87E-08	6.61E-13		9.39E-08	2.06E-05	
240Pu	9.87E-09	3.47E-15		2.57E-08	0.00E+00	
241Pu	1.55E-08	2.13E-14		5.89E-08	0.00E+00	
241Am	1.57E-07	1.98E-12		1.52E-04	1.44E-07	
SUPERNATE VOLUME (LITERS)	5.68E+05	4.31E+06		1.52E+06	2.98E+06	3.48E+06
SUPERNATE DENSITY (GRAMS/CC)	1.07	1.06	0	1.05	1.14	1.13
SUPERNATE THICKNESS (CM)	1.39E+02	1.05E+03	0.00E+00	3.70E+02	7.29E+02	8.50E+02
SUPERNATE DIAMETER (CM)	2286	2286	2286	2286	2286	2286
ALPHA ERGS PER CC-HR	2.70E-01	1.65E-01	0.00E+00	1.79E+02	2.29E+01	
BETA ERGS PER CC-HR	5.27E+02	1.07E+01	0.00E+00	1.23E+04	2.11E+03	2.15E+03
GAMMA ERGS PER CC-HR	1.87E+03	3.93E+01	0.00E+00	1.68E+04	6.52E+03	6.82E+03
SUPERNATE/ORGANIC RAD/HR	2.57E+01	5.31E-01	0.00E+00	3.07E+02	9.86E+01	1.01E+02
GAMMA ONLY RAD/HR	1.75E+01	3.71E-01		1.60E+02	5.72E+01	6.03E+01
FOR THE LAYERED ORGANIC CASE:						
SUPERNATE Ba-137 CURIES	7.54E+03	1.20E+03	0.00E+00	1.81E+05	1.38E+05	1.68E+05
SUPERNATE Eu-154 CURIES	1.38E+00	1.18E-06	0.00E+00	0.00E+00	0.00E+00	0.00E+00
RAD/HR TO ORGANIC LAYER					26.1	29.8

WHC-SD-WM-ES-384 REV 0
ENERGY DEPOSITION IN DST

SUPERNATE CURIES PER LITER					
FOR THE DISPERSED ORGANIC CASE: ISOTOPES	101AZ	102AZ	101SY	102SY	103SY
14C	0.00E+00	2.74E-06	0.00E+00	0.00E+00	0.00E+00
90Sr	2.21E-03	5.43E-02	1.89E-03	1.80E-09	5.37E-03
90Y	2.21E-03	5.43E-02	1.89E-03	1.80E-09	5.37E-03
99Tc	3.46E-04	3.29E-05	2.23E-03	1.44E-07	2.04E-04
137Cs	1.89E+00	1.47E-01	2.85E-01	1.07E-05	6.93E-02
137Ba	1.80E+00	1.40E-01	2.71E-01	1.02E-05	6.58E-02
154Eu	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
235U	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
238U	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
237Np	0.00E+00	2.45E-07	0.00E+00	3.88E-10	0.00E+00
238Pu	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
239Pu	4.14E-07	3.42E-06	1.38E-07	3.23E-10	3.20E-07
240Pu	1.14E-07	3.35E-09	3.51E-08	1.16E-10	8.13E-08
241Pu	1.64E-06	5.40E-08	2.85E-08	1.48E-09	4.99E-08
241Am	1.82E-05	2.20E-04	5.62E-07	1.50E-12	1.62E-06
SUPERNATE VOLUME (LITERS)	2.95E+06	2.67E+06	6.81E+04	1.40E+05	6.43E+05
SUPERNATE DENSITY (GRAMS/CC)	1.27	1.11	1.41	1.29	1.39
SUPERNATE THICKNESS (CM)	7.21E+02	6.52E+02	1.66E+01	3.43E+01	1.57E+02
SUPERNATE DIAMETER (CM)	2286	2286	2286	2286	2286
ALPHA ERGS PER CC-HR	2.19E+01	2.62E+02	8.49E-01	8.82E-04	2.33E+00
BETA ERGS PER CC-HR	6.95E+04	1.85E+04	1.08E+04	3.90E-01	3.82E+03
GAMMA ERGS PER CC-HR	2.53E+05	1.97E+04	3.82E+04	1.43E+00	9.28E+03
SUPERNATE/ORGANIC RAD/HR	4.10E+03	4.27E+02	6.91E+02	2.35E-02	1.82E+02
GAMMA ONLY RAD/HR	2.00E+03	1.78E+02	2.71E+02	1.11E-02	6.68E+01
FOR THE LAYERED ORGANIC CASE:					
SUPERNATE Ba-137 CURIES	5.30E+06	3.74E+05	1.84E+04	1.43E+00	4.24E+04
SUPERNATE Eu-154 CURIES	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
RAD/HR TO ORGANIC LAYER		76.8			

VOLUME 2

Section 8.7

DSI - Flammable Gas Review of High-Level Waste Tanks

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From: Waste Tanks Process Engineering
Phone: 376-5118 R2-11
Date: February 7, 1996
Subject: Flammable Gas Review of High Level Waste Tanks

74A10-96-006

To: G. D. Johnson S7-15
J. H. Wicks R2-50

cc: R. F. Bacon S7-85
J. G. Burton S7-01
R. A. Dodd S5-07
L. F. Ermold S7-84
G. R. Franz S7-81
J. B. Geary S5-07
C. J. Geier R2-36
C. J. Grando R2-54
K. M. Hodgson R2-11
J. O. Honeyman S7-81
M. N. Islam R3-08
N. W. Kirch R2-11
E. J. Kosiancic H5-61
R. E. Lerch S7-85
E. J. Lipke S7-14

W. H. Meader S8-05
G. A. Meyer S2-48
T. Morton S8-05
M. A. Payne S7-84
D. P. Reber T4-08
W. E. Ross S5-07
R. L. Schlosser H4-65
J. P. Slaughter R2-54
J. D. Thomson H6-35
J. E. Truax R2-50
A. M. Umek S7-81
R. J. Van Vleet H4-64
D. J. Washenfelder H5--27
WBB File/LB

- References: 1) Hodgson, K. M., *Evaluation of Hanford Tanks for Trapped Gas*, WHC-SD-WM-ER-526, Rev 0., December 1995, Westinghouse Hanford Company.
- 2) Internal Memo, Quick Screen of 177 Tanks For Flammability Determination, Dated December 19, 1995.
- 3) Hopkins, J. D., *Criteria for Flammable Gas Watch List Tanks*, WHC-EP-0702, August 1994, Westinghouse Hanford Company.
- 4) Hopkins, J. D., *Methodology for Flammable Gas Evaluations*, WHC-SD-WM-TI-724, Rev. 0, December 1995, Westinghouse Hanford Company.
- 5) Whitney, P., *Screening the Hanford Tanks for Trapped Gas*, PNL-10821, October 1995, Pacific Northwest Laboratory.

In December 1995 a document (Reference 1) was issued reporting the results of the flammable gas evaluations for 44 tanks, a memo was issued on December 19, 1995 (Reference 2) reporting the results of a quick screen which completed the evaluation of an additional 52 tanks (55 tanks were reported in the memo, but three of these were included in the original 44). The preliminary results of the flammable gas evaluations for the remaining 81 tanks are reported in this memo.

The criteria and methodology used were those used for the previous evaluations and are documented in References 3 and 4. Whenever possible a sample value was used to calculate the steady state concentration. The surface level increases were estimated from surface level data and corrections were made for evaporation if the tank had a liquid surface. In certain cases the surface level was corrected for leaks that were not accounted for in the surface level data. If a tank was flagged by Whitney (Reference 5) then a barometric pressure/surface level analysis was included in the evaluation. If not flagged by Whitney then no attempt was made to include a barometric pressure/surface level analysis.

Attachment 1 summarizes the results of the flammable gas evaluations for all 177 tanks. Tanks previously reported are shaded, the results for the 81 tanks being reported for the first time here are not shaded. The tank numbers of tanks currently on the Flammable Gas Watch List are in bold.

The evaluation of the 81 tanks resulted in 49 tanks passing the criteria and 32 failing the criteria. Of those that failed, 19 are already on the Flammable Gas Watch List. The following tanks failed based only on a calculated steady state: AP-102, B-111, S-104, T-203, TX-116, TX-117, U-110. We have requested that vapor samples be taken from these tanks. When the sample results are available the tanks will be re-evaluated and we expect they will pass all criteria.

Attachment 2 lists all tanks which either are currently on the Flammable Gas Watch List or have failed the evaluation. This list was discussed in the Plant Review Committee meeting of February 6, 1996 and is intended to be used as a quick reference by the shift operations staff.

Final documentation of the tank-by-tank evaluation will be published by March 31, 1996. Before publication, we will complete reviews by the tank Cognizant Engineers and expert review as appropriate.

If you have questions please call me at 376-5118.



W. B. Barton, Manager
Waste Tanks Process Engineering

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Attachment

ATTACHMENT

74A10-96-006

FLAMMABLE GAS EVALUATION

Consisting of 6 pages,
including cover page

Flammable Gas Evaluation					
Tank Number	Recommendation	Quick Screen %LFL	Steady State % LFL	Surface Level Rise % LFL	Barometric Pressure Evaluation % LFL
A-101	Fail		2.43	899.7	379.11
A-102	Pass	Passed			
A-103	Fail		37.12	N/A	55.32
A-104	Pass	Passed			
A-105	Pass	Passed			
A-106	Pass	Passed			
AN-101	Pass		0.09	3.68	No Correlation
AN-102	Pass		0.69	N/A	No Correlation
AN-103	Fail		0.78	334.42	301.1
AN-104	Fail		0.06	503.52	246.16
AN-105	Fail		0.64	742.66	411.29
AN-106	Pass		0.02	6.07	No Correlation
AN-107	Pass		0.34	N/A	No Correlation
AP-101	Pass		10.91	0.01	No Correlation
AP-102	Fail		136.5	N/A	No Correlation
AP-103	Pass	Passed			
AP-104	Pass		4.93	N/A	No Correlation
AP-105	Pass		0.01	0.17	20.92
AP-106	Pass	Passed			
AP-107	Pass		0.4	N/A	Tank Pumped
AP-108	Pass	Passed			
AW-101	Fail		282.87	231.22	378.4
AW-102	Pass	Passed			
AW-103	Pass		0.03	6.26	18.74
AW-104	Fail		0.1	127.15	133.65
AW-105	Pass		0.03	9.04	No Correlation
AW-106	Pass		0.12	6.92	No Correlation
AX-101	Pass		0.54	N/A	No Correlation
AX-102	Pass	Passed			
AX-103	Pass	Passed			
AX-104	Pass	Passed			
AY-101	Fail		0.15	63.91	56.71
AY-102	Pass		0.29	14.4	No Correlation
AZ-101	Pass		0.16	N/A	No Correlation
AZ-102	Pass		0.14	10.26	No Correlation
B-101	Pass		1.02	N/A	No Correlation
B-102	Pass	Passed			
B-103	Pass	Passed			
B-104	Pass		17.78	2.68	No Correlation
B-105	Pass		6.51	13.97	No Correlation
B-106	Pass		5.61	2.68	No Correlation
B-107	Pass		17.58	N/A	No Correlation
B-108	Pass		8.73	1.67	No Correlation
B-109	Pass		11.04	N/A	No Correlation
B-110	Pass		15.2	0.95	No Correlation
B-111	Fail		28.35	N/A	No Correlation
B-112	Pass	Passed			
B-201	Fail		30.29	65.61	No Correlation
B-202	Fail		45.65	32.79	No Correlation
B-203	Pass		1.03	N/A	No Correlation
B-204	Pass		<1.0	N/A	No Correlation
BX-101	Pass	Passed			
BX-102	Pass	Passed			
BX-103	Pass	Passed			
BX-104	Pass		0.24	15.94	18.03
BX-105	Pass	Passed			
BX-106	Pass	Passed			
BX-107	Fail		25.32	3.16	62.22
BX-108	Pass	Passed			
BX-109	Pass		22.47	N/A	No Correlation
BX-110	Pass		6.94	10.69	No Correlation

BX-111	Pass		16.45	7.93	No Correlation
BX-112	Pass		<1	10.88	15.31
BY-101	Fail		14.51	27.66	53.14
BY-102	Fail		24.55	N/A	32.52
BY-103	Fail		0.07	N/A	26
BY-104	Pass		0.92	4.57	No Correlation
BY-105	Fail		0.25	13.48	144.89
BY-106	Fail		0.17	122.93	No Correlation
BY-107	Pass		1.32	1.11	No Correlation
BY-108	Pass		1.71	2.17	No Correlation
BY-109	Fail		0.17	N/A	27.14
BY-110	Pass		0.67	0.66	No Correlation
BY-111	Pass		0.45	N/A	No Correlation
BY-112	Pass		0.26	7.22	No Correlation
C-101	Pass	Passed			
C-102	Pass		0.46	N/A	No Correlation
C-103	Pass		2.21	N/A	No Correlation
C-104	Fail		0.2	N/A	28.82
C-105	Pass		0.06	N/A	No Correlation
C-106	Pass		0.03	N/A	No Correlation
C-107	Fail		0.64	N/A	32.03
C-108	Pass	Passed			
C-109	Pass	Passed			
C-110	Pass		9.04	11.06	No Correlation
C-111	Pass	Passed			
C-112	Pass	Passed			
C-201	Pass	Passed			
C-202	Pass	Passed			
C-203	Pass	Passed			
C-204	Pass	Passed			
S-101	Fail		53.48	109.1	46.96
S-102	Fail		1.98	190.16	226.22
S-103	Fail		19.31	56.54	71.51
S-104	Fail		35.69	N/A	No Correlation
S-105	Fail		6.74	0	44.19
S-106	Fail		42.17	187.36	223.03
S-107	Fail		29.3	138.35	34.14
S-108	Pass		0.04	N/A	No Correlation
S-109	Fail		25.78	15.83	145.11
S-110	Pass		0.32	N/A	No Correlation
S-111	Fail		1.08	79.91	181.05
S-112	Fail		12.96	29.57	No Correlation
SX-101	Fail		0.03	N/A	28.29
SX-102	Fail		1.95	30.44	92.98
SX-103	Fail		0.11	2.21	216
SX-104	Fail		1.22	200.12	10.62
SX-105	Fail		<1	162.11	No evaluation-lack of data
SX-106	Fail		0.37	66.89	78.26
SX-107	Pass	Passed			
SX-108	Pass	Passed			
SX-109	Pass		5.21	N/A	No Correlation
SX-110	Pass	Passed			
SX-111	Pass	Passed			
SX-112	Pass	Passed			
SX-113	Pass	Passed			
SX-114	Pass		0.28	6.08	No Correlation
SX-115	Pass	Passed			
SY-101	Fail		0.11	659.53	572.23
SY-102	Pass		0.01	14.64	No Correlation
SY-103	Fail		0.28	43.35	57.42
T-101	Pass		5.27	10.75	No Correlation
T-102	Pass	Passed			
T-103	Pass	Passed			
T-104	Fail		36.52	N/A	No Correlation
T-105	Pass		14.08	3.56	No Correlation
T-106	Pass	Passed			
T-107	Pass		0.32	13.68	18.54
T-108	Pass	Passed			
T-109	Pass	Passed			

T-110	Fail		17.17	31.81	No Correlation
T-111	Pass		0.39	1.56	5.64
T-112	Pass		4.91	4.73	No Correlation
T-201	Fail		55.37	120.75	No Correlation
T-202	Fail		29.24	41.11	No Correlation
T-203	Fail		72.11	N/A	No Correlation
T-204	Fail		43.09	62.45	No Correlation
TX-101	Pass	Passed			
TX-102	Fail		8.46	1.7	40.32
TX-103	Pass		4.69	7.84	No Correlation
TX-104	Pass	Passed			
TX-105	Pass		0.26	N/A	No Correlation
TX-106	Pass		10.67	N/A	No Correlation
TX-107	Pass	Passed	2.58	N/A	0.65
TX-108	Pass		6.07	3.07	No Correlation
TX-109	Pass		22.5	N/A	No Correlation
TX-110	Pass		20.21	N/A	No Correlation
TX-111	Fail		18.74	17.55	42.8
TX-112	Fail		42.21	66.1	194.95
TX-113	Fail		12.1	23.36	83.7
TX-114	Pass		0.98	13.82	No Correlation
TX-115	Fail		11.85	44.56	93.62
TX-116	Fail		31.64	N/A	No Correlation
TX-117	Fail		56.08	N/A	No Correlation
TX-118	Pass		0.27	0	No Correlation
TY-101	Pass		0.25	1.62	No Correlation
TY-102	Pass	Passed	7.49	4.21	12.41
TY-103	Pass		0.27	N/A	0
TY-104	Pass	Passed			
TY-105	Pass		5.5	12.9	No Correlation
TY-106	Pass	Passed			
U-101	Pass	Passed			
U-102	Fail		47.85	151.56	209.03
U-103	Fail		1.9	158.26	160.72
U-104	Pass	Passed			
U-105	Fail		154.51	270.47	128.52
U-106	Fail		1.19	36.51	20.82
U-107	Fail		1.57	42.18	87.42
U-108	Fail		301.25	179.12	No enough data for evaluation
U-109	Fail		4.95	81.09	117.91
U-110	Fail		22.54	12.11	No Correlation
U-111	Fail		1.06	96.65	No Correlation
U-112	Pass	Passed			
U-201	Pass	Passed			
U-202	Pass	Passed			
U-203	Pass	Passed			
U-204	Pass	Passed			
Original Group =	44	Original Group Number Failed =	29		
Quick Screen =	52				
Final Group =	81	Completed in Final Group =	81		
Remaining =	0			Failed in Final Group =	32
Note:	Bold numbers under surface level rise include a calculated evaporation amount				
	19 of those failing in final group are already on flammable gas watch list				
	22 of 25 flammable gas watchlist tanks failed this evaluation				
	Bold tank numbers are Flammable Watch List Tanks				

Flammable Gas Evaluation Results

Original Flammable Gas Watch List Tanks	Recommendation to DOE for Addition to Flammable Gas Watch List	Additional Tanks Which Failed Criteria
A-101	A-103	
AN-103		
AN-104		
AN-105		
		AP-102
AW-101	AW-104	
AX-101		
AX-103		B-111
	AY-101	
		B-201
		B-202
	BX-107	
	BY-101	
	BY-102	
	BY-103	
	BY-105	
	BY-106	
	BY-109	
	C-104	
	C-107	
S-102	S-101	S-104
S-111	S-103	
S-112	S-105	
	S-106	
	S-107	
	S-109	
SX-101		
SX-102		
SX-103		
SX-104		
SX-105		
SX-106		
SX-109		
SY-101		
SY-103		

Original Flammable Gas Watch List Tanks	Recommendation to DOE for Addition to Flammable Gas Watch List	Additional Tanks Which Failed Criteria
T-110		
		T-201
		T-202
		T-203
		T-204
	TX-102	TX-116
	TX-111	TX-117
	TX-112	
	TX-113	
	TX-115	
U-103	U-102	U-110
U-105	U-106	U-111
U-107		
U-108		
U-109		
Total Count	Total Count	Total Count
25	25	13

Supplied by W B Barton

VOLUME 2

Section 8.8

Addendum - DST Evaporation Information

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8.8 DST EVAPORATION INFORMATION

Evaporation is the primary mechanism for removal of NPH and diluents from the DST. A model based on NPH was developed to predict organic evaporation rates after removal of TBP. This model was based primarily on data developed to predict organic evaporation in Tank 241-C-103 (Wood and Claybrook 1994). The model included vapor pressure correlations in the form of Antoine equation coefficient for each of the organic species. Partial vapor pressures for each species over the liquid were calculated using Raoult's law and updated to reflect the continuously changing organic layer composition. The presence of TBP would reduce the NPH evaporation rate and was not included in the initial analysis.

Diffusion coefficients for calculating the transport of organic from the pool surface into the air are based on a Colburn j-factor correlation that is applicable to evaporation from a flat surface. Evaluation of this correlation requires an air velocity across the pool, which was supplied as a model input in Wood and Claybrook (1994).

The evaporation model solved mass conservation equations for each component of NPH. A lumped parameter approach was employed, which assumed that the gas space will be well mixed. The model allows the user to specify the following input variables: time increment for analysis, initial NPH volume, ventilation rate, waste level in tank, thermal velocity, temperature, and pressure.

Two analyses were initially performed with the evaporation model: (1) a base case analysis modeled the NPH evaporation rate based on conditions expected to exist in the selected DST (Tank 241-AP-107) and (2) a sensitivity analysis determined how changing the input variables would affect the evaporation rate determined in the base case. The base case analysis and the sensitivity analysis are described in the following sections.

8.8.1 Base Case Analysis

The initial run of the evaporation model was performed to determine the base case NPH evaporation rate after TBP removal. The user input variables (initial NPH volume, ventilation rate, waste level in the tank, temperature, and pressure) were chosen as the conditions likely to exist in Tank 241-AP-107. The thermal velocity used is from Wood and Claybrook (1994). The time increment was chosen to represent sufficient iterations to reliably predict the evaporation rate while keeping the number of iterations to an easily managed level. The values of the user input variables for the base case are listed below:

- Time increment 6 months
- Initial NPH volume 1,900 gal
- Initial TBP volume 0 gal
- Ventilation rate 120 std. ft³/min
- Waste level in tank 50%
- Liquid surface area 4,420 ft²

- Thermal velocity 0.2 ft/s
- Temperature 40 °C
- Pressure 760 mmHg.

The base case for NPH evaporation would require approximately 39 years to achieve a 90% removal of the NPH. Figure 8.8-1 shows the volume of NPH remaining in the liquid over time. Figure 8.8-2 shows the breakdown of the NPH constituents (tridecane, tetradecane, dodecane, and pentadecane); dodecane and tridecane are evaporated relatively quickly, while pentadecane and tetradecane remain after 30 years. Vapor concentration of each of the organic species in NPH start out at a maximum of approximately 1.2×10^{-5} lb/ft³ (tetradecane and dodecane) and rapidly fall off (Figure 8.8-3).

8.8.2 Sensitivity Analysis

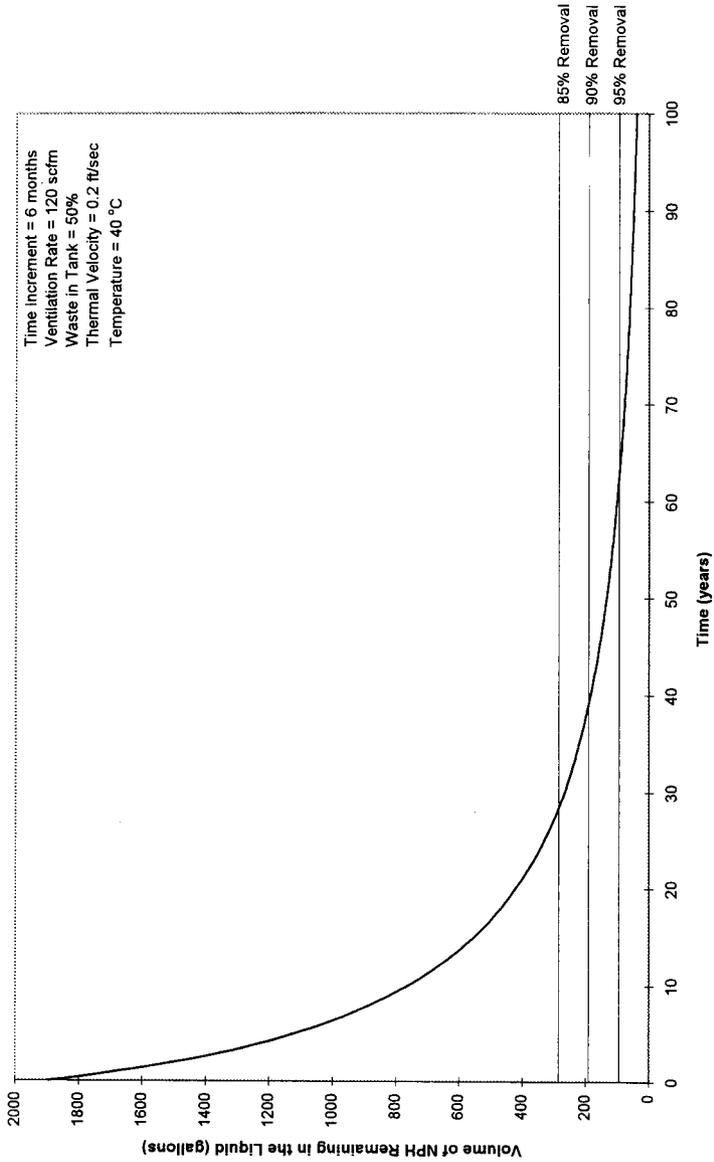
A sensitivity analysis was performed for the user input variables of time increment, ventilation rate, waste level in the tank, thermal velocity, and temperature. The following sections discuss the results of these analyses.

8.8.2.1 Time Increment. As discussed earlier, the base case analysis used time increments of six months. Two additional runs were done, one with three-month time increments, and the other with one-day time increments to determine the sensitivity of the model to the time increment analyzed. Due to the size of the model and the number of iterations required to run the model out to 100 years, the two additional analyses were only carried out to six years. A graph of the three sets of results was created, using data points for each at six month intervals, and the results were compared (Figure 8.8-4). Although there is a small difference in the results over time, it was determined that the results of the base case modeling runs (using the six-month time increment) were within the bounds of uncertainty for the model.

8.8.2.2 Ventilation Rate. The evaporation modeling results presented in Wood and Claybrook (1994) show that the ventilation rate is only a determining factor in the evaporation rate for low ventilation rates. As the ventilation rate climbs above approximately 150 std. ft³/min, the rate of diffusion from the liquid to the air is the determining factor in the evaporation rate.

This report modeled evaporation rates for tank ventilation rates of 50, 120 (base case), 250, and 500 std. ft³/min. The modeling results show that as the ventilation rate increases, the incremental effect on the evaporation rate decreases (Figure 8.8-5). For lower ventilation rates, ventilation is the deciding factor in evaporation rate, but as the ventilation rate gets higher, the diffusion rate of the organic from the surface of the liquid is the limiting factor.

8.8.2.3 Waste Level in the Tank. Two tank waste levels were modeled: 50% of the tank filled with waste (base case), and 80% of the tank filled with waste. Figure 8.8-6 shows that the amount of waste in the tank is not a deciding factor in the rate of evaporation.



8.8-3

Figure 8.8-1. Time Required to Achieve 85%, 90%, and 95% Removal of NPH.

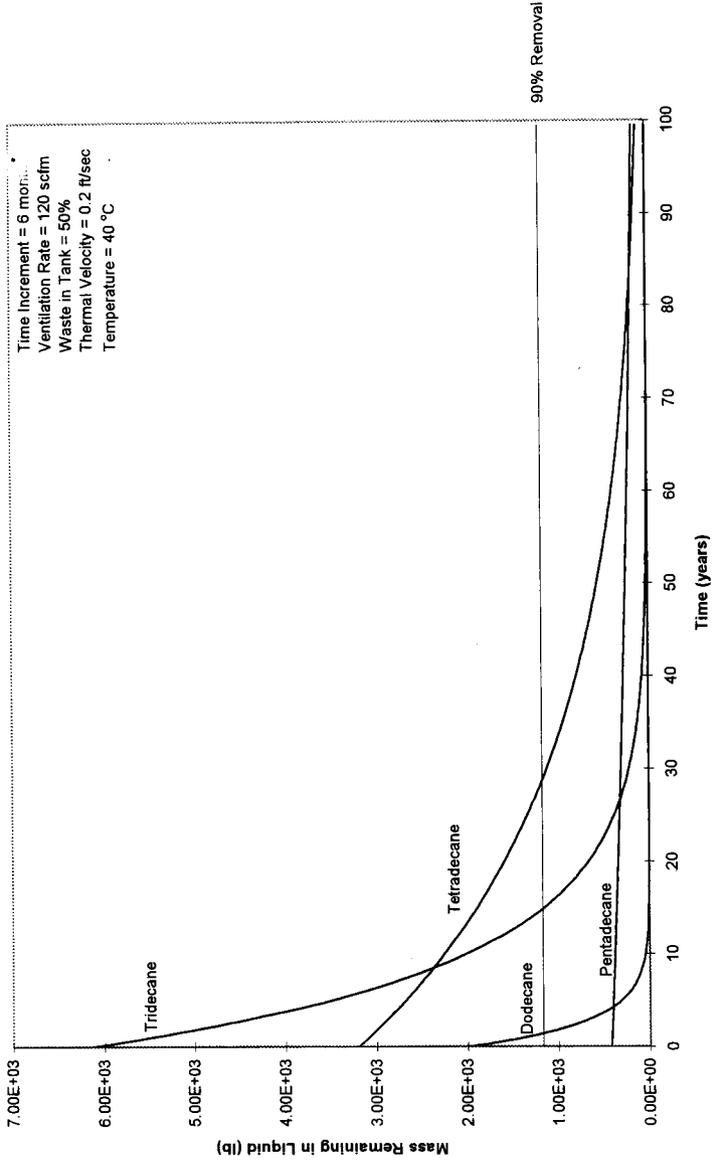


Figure 8.8-2. Mass of NPH Constituents Remaining Versus Time for Base Case Variables.

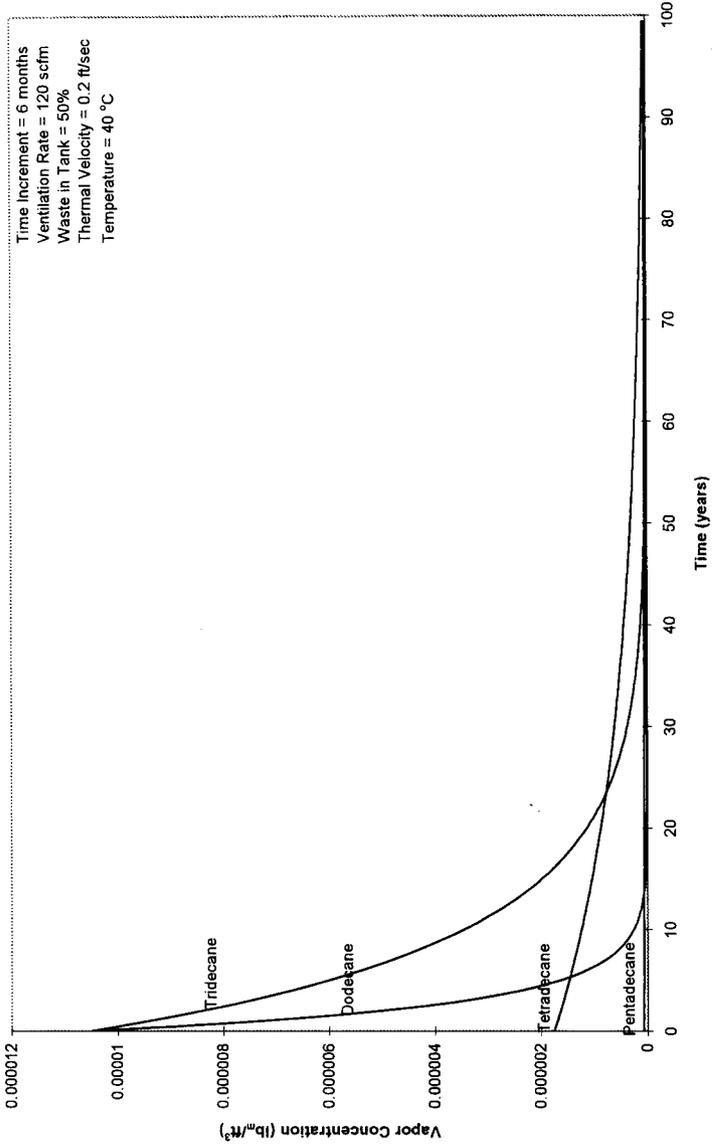


Figure 8.8-3. Vapor Concentration of NPH Constituents Versus Time.

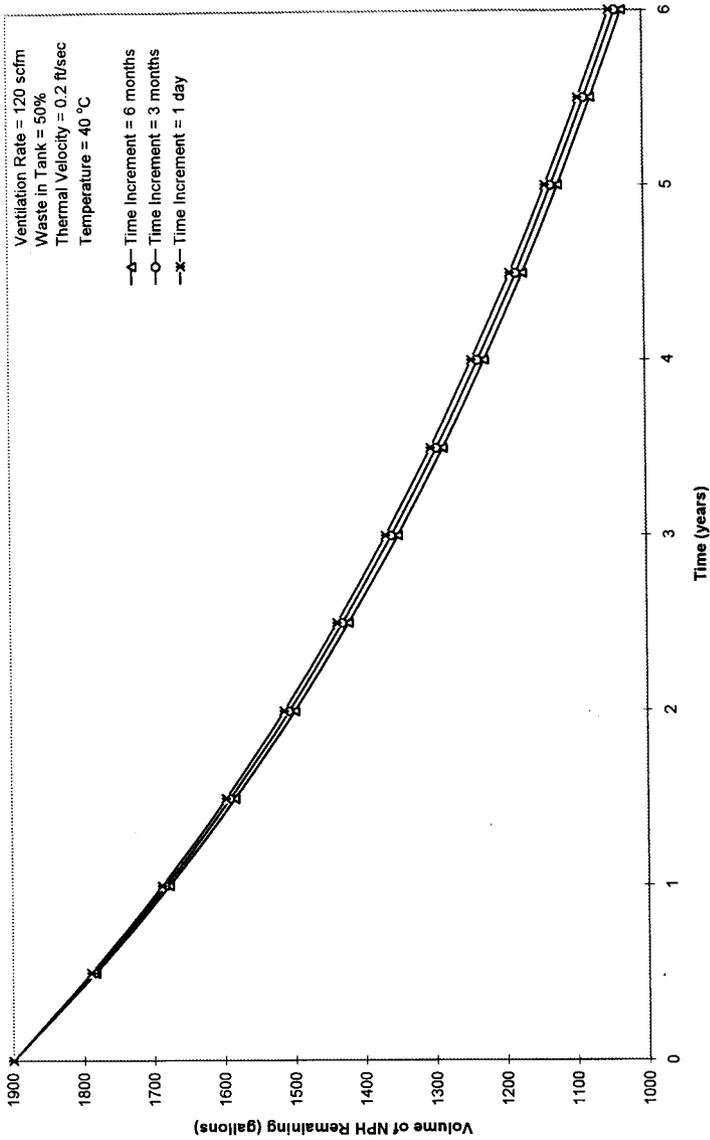


Figure 8.8-4. Volume of NPH Remaining in Liquid for Various Time Increments.

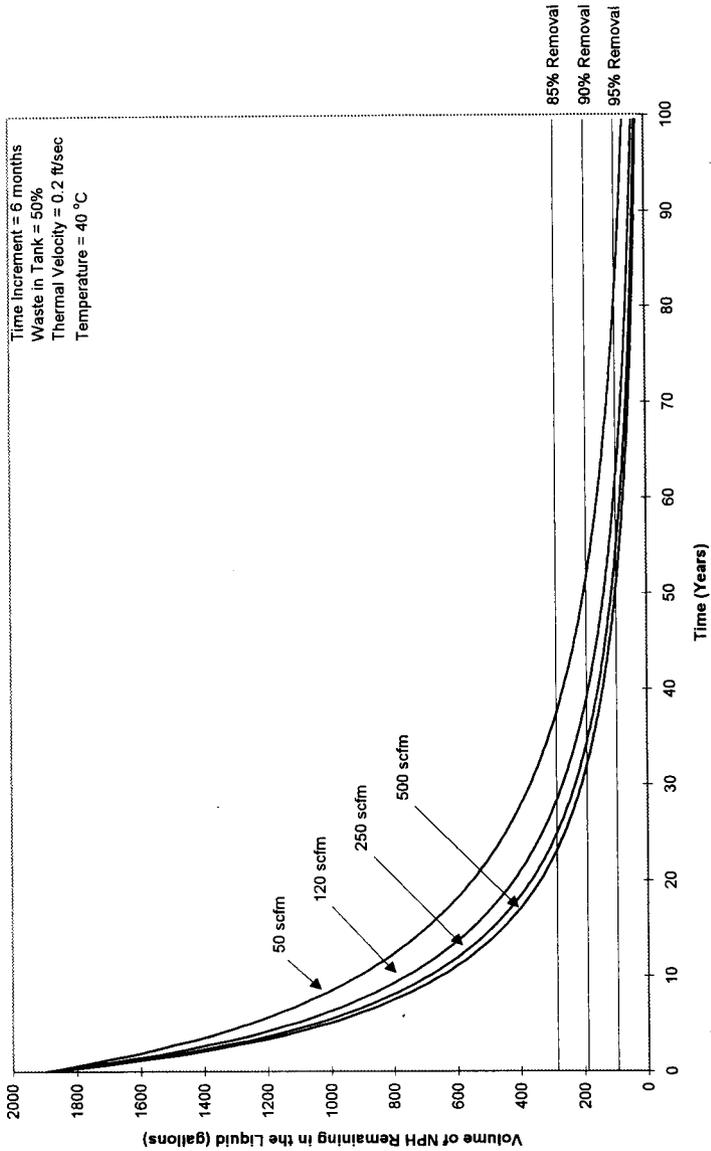


Figure 8.8-5. Time Required to Achieve 85%, 90%, and 95% Removal of NPH at Varying Ventilation Rates.

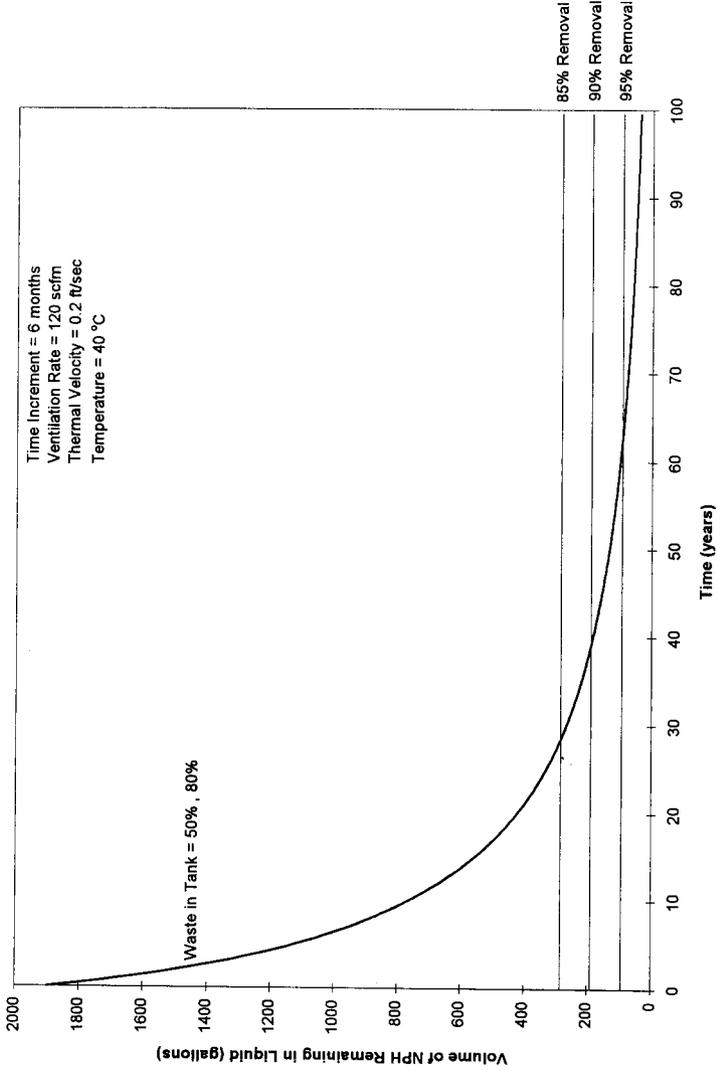


Figure 8.8-6. Time Required to Achieve 85%, 90%, and 95% Removal of NPH at Varying Tank Waste Percentages.

8.8.2.4 Thermal Velocity. The evaporation model developed by Wood and Claybrook (1994) had the user input the velocity of air across the liquid surface. The evaporation model developed for this report had the user input the component of the velocity across the surface that is caused by thermal differences in the tank. A correlation was developed for the component of the velocity that was due to the ventilation of the tank. This was assumed to be equal to the characteristic length of the liquid surface (assumed by Wood to be the radius of the tank) divided by the residence time of the air in the tank (headspace in the tank divided by the ventilation rate).

Models of the velocity of air across the liquid surface due to the temperature difference between the waste and the tank dome indicate that the thermal velocity ranges from 0.1 to 0.5 ft/s (Wood and Claybrook 1994). The evaporation model was run for thermal velocities of 0.1, 0.2 (base case), and 0.5 ft/s. The results of these runs (Figure 8.8-7) show that the thermal velocity could have a large effect on evaporation rates. The time to achieve 90% removal of the NPH ranges from approximately 24 years (0.5 ft/s) to approximately 61 years (0.1 ft/s).

8.8.2.5 Temperature. Varying the temperature inside the tank will have a large effect on the evaporation rate of the NPH. A tank at 20 °C will still have a significant amount of NPH remaining even after 100 years have passed (Figure 8.8-8). However, a tank that is just 20 °C (40 °C) warmer will have evaporated 90% of the NPH in approximately 39 years. At 80 °C, 90% of the NPH will have evaporated in only 1.7 years.

8.8.3 Minimum Removal Time

The time to remove NPH can be minimized using air sparging. Air sparging moves air through the organic, which increases the surface area of the air-liquid interface. Calculations performed to determine the rate of NPH removal predicted that evaporation of 90% of the NPH would be achieved in approximately eight years under base case conditions (Figure 8.8-9). It was assumed that ideal conditions would exist in the tank and that a sufficient portion of the ventilation air would be diverted to the sparging mechanism to produce equilibrium conditions. The assumption of ideal, equilibrium conditions means that the results of the air sparging modeling represent a best case scenario with the minimum time to achieve removal of the NPH.

REFERENCE

Wood, S.A. and S.W. Claybrook, 1994, *Organic Evaporation in Waste Tank C-103*, WHC-SD-WM-ER-344, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

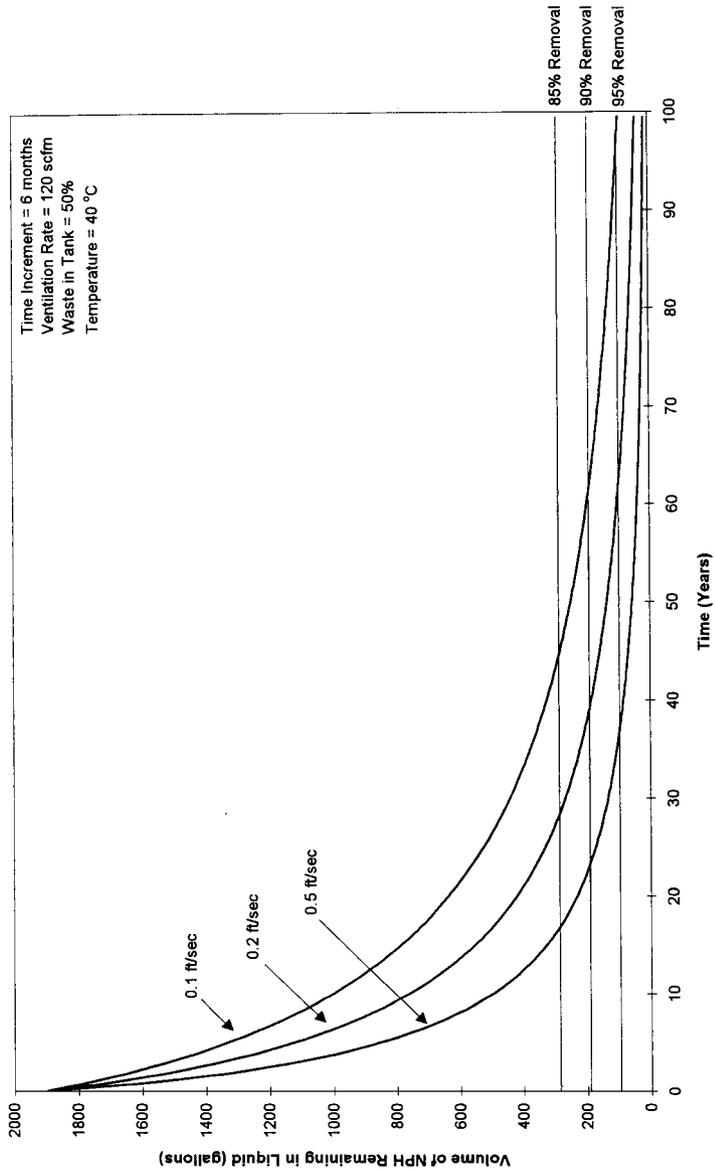


Figure 8.8-7. Time Required to Achieve 85%, 90%, and 95% Removal of NPH at Varying Thermal Velocities.

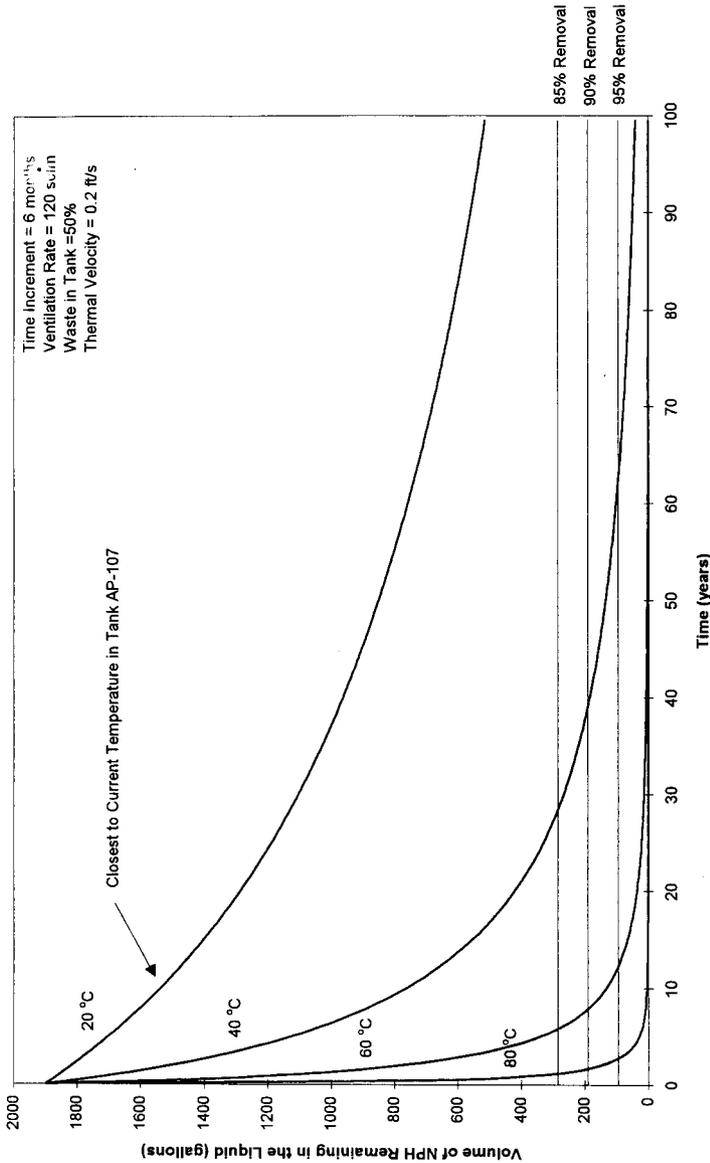


Figure 8.8-8. Time Required to Achieve 85%, 90%, and 95% Removal of NPH at Varying Temperatures.

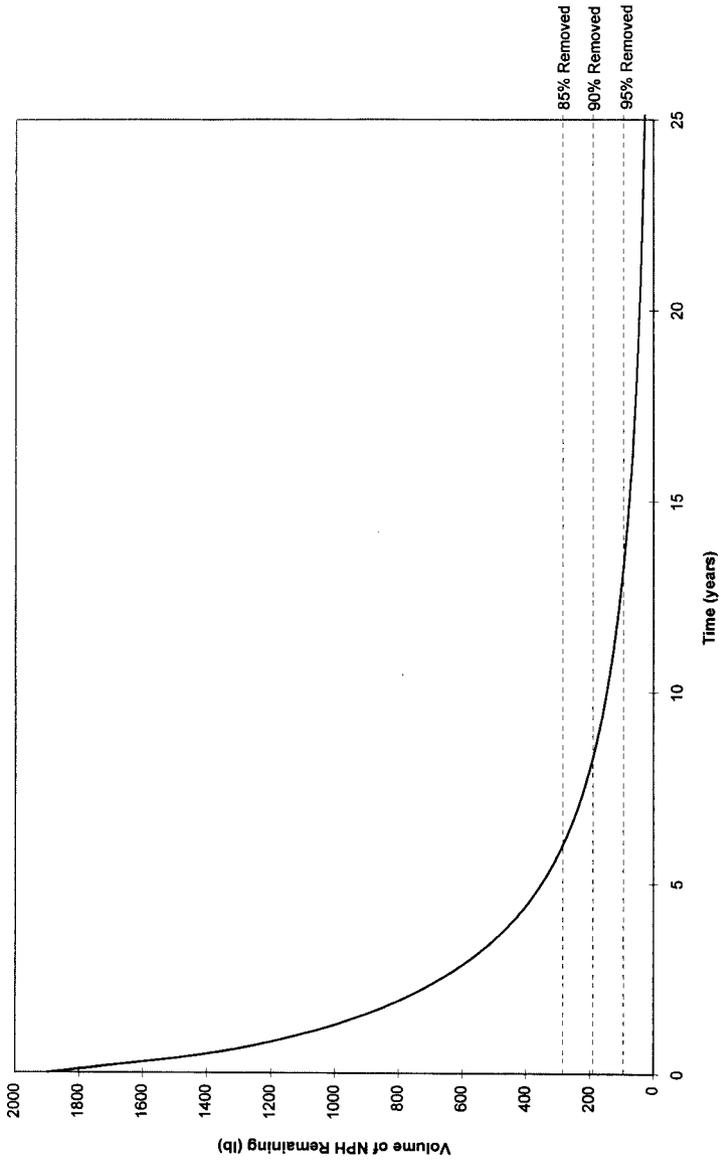


Figure 8.8-9. Volume of NPH Remaining in the Liquid versus Time with Air Sparging.

VOLUME 2

Section 8.9

Addendum - Mixer Pump Costs

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8.9 PROJECT AND OPERATING COSTS FOR MIXER PUMP ORGANIC REMOVAL

Mixing and heating of the aqueous and separable organic phases in the DST are needed for efficient degradation of the TBP and evaporation of the NPH. Potential mixing methods include mixer pump, air lift circulator, and supernate recycle.

Mixer pump hydraulic action would not provide the vigorous surface stirring action to entrain floating organic, form an emulsion, and disperse the organic into the aqueous phase for reaction of the TBP. TBP transfer into the aqueous would occur across the 4,420 ft² surface area between the phases. Mixer pump operation would add energy to the waste and maintain a minimum temperature for good organic removal. The NPH would be removed by evaporation and discharged to the environment by the forced air ventilation system.

When more than approximately 8 ft of supernate or slurry is present in a DST there is a damping effect of the waste on the discharge nozzle jet. The mixer pump discharge jet would create a "rooster tail" at the waste surface and mist in the vapor space if the maximum pump speed is maintained and waste level above the discharge nozzle is less than 8 ft. Normal mixer pump operation will avoid "rooster tail" formation.

Air lift circulator mixing would not provide as vigorous phase mixing action and dispersion as the mixer pump. Several air lift circulators would probably be needed inside the tank for good mixing. The rising bubbles should create an emulsion in the upper aqueous layer. The air flow requirements and entrainment of aqueous and organic in discharge air may create a mist in the vapor space of the tank. Unless the waste or inlet air to the air circulators was heated, the rate of TBP destruction and NPH evaporation would decrease due to cooling. The air lift circulator would help remove NPH faster than by mixer pump stirring action. The addition of air lift circulator(s) to an existing tank may be impractical due to size and number of new penetrations.

The supernate recycle method would better disperse the organic into the aqueous. It would use a skimmer type floating pump suction to remove both organic and aqueous liquid, inline mix the phases and then inject the resulting emulsion well below the surface level of waste in the tank. A heat exchanger on the return line or inside the tank would maintain the waste temperature for good TBP destruction and NPH evaporation. This method could be combined with reduced flow operation of mixer pumps.

The above methods of mixing floating organic and aqueous liquids need additional evaluation. A preliminary cost estimate was developed for Tank 241-AP-107 based on available information for addition of two mixer pumps and other equipment to DST 241-AZ-101 (Kohlman 1995; KEH 1995) and modified expense costs for operation of Tank 241-SY-101 (Galbraith and Parazin 1995) for 5 years. The rough order of magnitude total cost estimate is \$48 million. The cost information is summarized in Table 8.9-1. Additional information is provided in Volume 2, Section 8.10. Some additional cost would be needed to install other equipment as described in Volume I, Section 9.3.

Table 8.9-1. Summary of Preliminary Cost Estimates for Alkaline Hydrolysis of TBP in a DST by Mixer Pump.

Project Capital (\$millions)	Expense (\$millions)	Total (\$millions)	Time (years)
15	33	48	5

Tank 241-AZ-101 should be reevaluated as an alternate to Tank 241-AP-107 for processing separable phase organic. It would use available equipment and save up to \$15 million on project cost and some expense money.

REFERENCES

Galbraith, J. D. and R.J. Parazin, 1995, *Passive Versus Active Mitigation Cost Analysis*, WHC-SD-W236A-ES-013, Rev. 0, Westinghouse Hanford Company, Richland, Washington, April 1995.

KEH, 1995, *Tank 101-AZ Waste Retrieval System Final Project Cost Summary*, W151TAA4, Kaiser Engineers Hanford Richland, Washington, February 1995.

Kohlman, E.H., 1995, *Functional Design Criteria Project W-151 Tank 101-AZ Waste Retrieval System*, WHC-SD-W151-FDC-001, Rev. 3, Westinghouse Hanford Company, Richland, Washington, October 1995.

VOLUME 2

Section 8.10

**DSI - Preliminary Cost Estimate - Separable Phase
Organic Removal in Tank 241-AP-107**

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'DON'T SAY IT --- Write It!

DATE: Mar 29/96

TO: Mike Klem

FROM: Kevin Eager

Westinghouse Hanford Company
Disposal Engineering, Process Technology
MISN H5-27

Telephone: (509) 372-1715

FAX: (509) 372-3973

cc: Phil Bartley Foster Wheeler
John Galbraith

SUBJECT: Preliminary Cost Estimate - Separable Phase Organic Removal in Tank
241-AP-107

REFERENCE

Project W-151, *Tank AZ-101 Waste Retrieval System Final Project Cost Summary*, February 17, 1995, Kaiser Engineers Hanford, Richland, Washington.

Parazin, R. J., and J. D. Galbraith, 1995, *Passive Versus Active Mitigation Cost Analysis*, WHC-SD-W236A-ES-013, Rev. 0, April 1995, Westinghouse Hanford Company, Richland, Washington.

The following cost estimate is for installation of two mixer pumps in tank AP-107 and operation for 5 years followed by disposal i.e. life cycle cost. Costs are based on those given in Project W-151 for mixer pump addition to tank AZ-101 and Parazin and Galbraith (1995) for active mitigation operating costs of tanks SY-101 and SY-103.

Table 1. Preliminary Estimate of Life Cycle Cost	
Project (W-151: Tank 241-AZ-101)	\$ M
Engineering	5.2
Procure and Fab	6.5
Construction	1.2
Other Project Costs	1.9
project total	15
5 yr Operating (Tank 241-SY-101)	
Installation in-tank equipment	10.7
Post installation operating costs	6.5
Spares	7.0
Replacements/equipment	3.0
Disposal of in-tank equipment	3.7
Safety reviews and design reviews	2.0
expense total	33
Grand Total	48

The following changes were made to the baseline costs for Project W-151:

Procure and fabrication:

Cost was reduced by \$1.8 M due to elimination of TWRS control trailer (\$0.2M), site monitor trailer (\$0.4M), equipment removal (\$1.0M), fence relocation (\$0.3M), steam coil upgrade (\$0.9) and addition of anticipated pump pit and transfer lines (\$1.0M).

Other project costs:

Cost based on 15 % value.

The Project W-151 includes: two 300 hp mixer pumps (5000 hr), transfer pump, instrumentation and pump control system, profile thermocouple, and electrical upgrade.

The project excludes: ventilation system upgrades and potential flammability/regulatory off gas monitoring.

The following changes were made to the baseline operating costs given by Parazin and Galbraith (1995) to account for differences in the two cases:

Installation in-tank equipment:

Parazin and Galbraith cost estimate was increased by 8/3 because estimate was for installation of 3 mixer pumps. Mixer pump duty cycle estimated at 25 - 50 %. Pump provides heat for TBP hydrolysis and NPH evaporation.

Post installation operating costs:

The Parazin and Galbraith cost estimate was based on 11 FTEs and 10 years. This was converted to 7 FTEs for 5 years as follows.

$$\frac{20 \text{ million } \$}{(11 \text{ FTE}) (10 \text{ yrs})} \left| \frac{(7 \text{ FTE}) (5 \text{ yrs})}{(11 \text{ FTE}) (10 \text{ yrs})} \right| = 6.5 \text{ million } \$$$

Spares:

Assumes 6 spares; Parazin and Galbraith cost was doubled.

Replacements/equipment

Approximately halved since the Parazin and Galbraith estimate accounted for one tank and 5 yr operation.

Disposal of in-tank equipment

The Parazin and Galbraith estimate was increased by 8/3 because estimate was for disposal of 3 pumps.

Safety reviews and design reviews

Approximately halved since the Parazin and Galbraith estimate accounted for two tanks.

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VOLUME 2

Section 8.11

**DSI - Issues/Impacts/Risks With Processing Tank 241-C-103
Separable Organic Material Into Hanford Immobilized
High-Level Waste Product(s) Slated for Disposal
in a Federal Geologic Repository**

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DON'T SAY IT --- *Write It!*

DATE: February 2, 1996

TO: M.J. Klem/WHC

FROM: E.H. Randklev/WHC

Telephone: 376-1456

cc: R.L. Gibby/WHC
C.N. Wilson/WHC
D.J. Washenfelder/WHC

SUBJECT:

ISSUES/IMPACTS/RISKS ASSOCIATED WITH PROCESSING C-103
SEPARABLE ORGANIC MATERIAL INTO HANFORD IMMOBILIZED HIGH-
LEVEL WASTE PRODUCT(S) SLATED FOR DISPOSAL IN A FEDERAL
GEOLOGIC REPOSITORY

INTRODUCTION

Objective

Per your request in Reference 1, I have reviewed this subject and identified the issues (impacts/risks) that are likely to result from processing the C-103 separable organic material into Hanford immobilized high-level waste (HLW) product(s) destined for disposal in a federal geologic repository.

Scope

I confined my assessment to the set of HLW immobilization processing alternatives considered in Reference 2, by C.N. Wilson/WHC, since they appear to adequately capture the range of likely options that are worth considering.

WASTE (PRODUCT) ACCEPTANCE -- REPOSITORY DISPOSAL

Option 1: Current Standard Form HLW Product

Assume that the first HLW product disposal option for disposing of the separable organic wastes from C-103 is to blend this material into the HLW feed stream for a Hanford HLW vitrification plant that is making the DOE-RW "Standard Form" HLW Product. One major advantage of this particular option is that DOE-RW does not have to be petitioned to evaluate and decide on any new "standard form" product candidates.

NOTE: DOE-RW (repository program) has, to date, only approved one immobilized HLW form product for disposal in the federal repository. Following that candidate evaluation and acceptance decision, DOE-RW defined and baselined (Reference 3) the waste acceptance systems requirements for this particular "standard form" product. The product in question is produced by melt pouring a borosilicate waste glass into a thin walled stainless steel canister, which is then sealed and allowed to cool.

OPTION 1: Potential Issues (Impacts/Risks)

Issue 1. Blending the C-103 separable organic wastes into the HLW feed for vitrification processing and production of the current DOE-RW approved "standard form" HLW disposal product would likely result in a HLW disposal product that may not be capable of complying with the DOE-RW licensing strategy, for the Yucca Mountain repository site.

RATIONALE:

- a. The person in charge of DOE-RW has recently confirmed (Reference 4) that DOE-RW intends to limit the waste disposal in the proposed Yucca Mountain repository to..."only spent nuclear fuel and high-level radioactive waste that do not include components regulated as hazardous wastes under the Resource Conservation and Recovery Act."
- b. Per Reference 5,... "all C Tank Farm SSTs contain designated hazardous waste (including listed wastes)"..., which is so claimed in ... "the SST RCRA Part A permit application." The report, which deals with requirements and actions pertaining to pumping the separable organic layer out of C-103, then states that.. "the organic and aqueous phase are assumed to be a designated hazardous waste for purposes of this report." I obtained a copy of parts of this reference report from a Mr. Phil Bartley, Foster Wheeler Environmental Corp., on referral from M.J. Klem/WHC.
- c. Although there is the prospect for more than one repository, the DOE-RW has not begun work on such a second repository project. Hence, there is no easy way to judge whether this issue would also be applicable to such a second repository site. It is worth noting that this topical issue (i.e., HLW containing hazardous materials) is one that applies to much of the Hanford tank wastes, as implied even in Reference 5. DOE-EM and DOE-RW continue to dialog about the resolution to this issue.

Impacts: Per my limited knowledge of RCRA, Hanford would have to demonstrate, probably by both analysis and testing, that these organic

materials as processed in the HLW melter would (a) not contribute material to the resultant glass product (i.e., they would be volatilized and dealt with in the off-gas system), and/or (b) be processed in the melter (e.g., in the cold-cap/vitrification reactions) into a product that could be claimed as exempt from EPA control as hazardous material.

Risks: My initial opinion is that there is a medium to high risk that the effort to address this HLW product disposal issue would not be practical (i.e., schedule, cost, probability of failure).

Additional Background on Issue 1. :

I have heard informally that this is a DOE-RW position that is driven by the desire to avoid any circumstance that would enable the State of Nevada to claim precedence in controlling the licensing process. The topic of hazardous waste regulations (i.e., the interface between Federal EPA and State EPA regulations) would apparently offer such an opportunity to the State of Nevada. It should be noted that the DOE-RW waste acceptance requirements document (Reference 3) for the "standard form" HLW disposal product do not contain any (HLW product) waste acceptance requirements that explicitly exclude repository acceptance of waste forms containing hazardous wastes. Instead it contains several requirements regarding the extent of characterization and certification that the HLW disposal product producer must do to determine the extent to which such materials are present, if at all.

OPTION 2. Produce a HLW Product that would efficiently incorporate the resultant phosphate ash, etc. from incinerating the C-103 separable organic material.

The Reference 2 discussion does not explicitly say whether the phosphate glass waste form produced by this processing option would be a low-level waste form or a HLW form. It seems to me that there would be few, if any, advantages provided by retrieving and then processing (i.e., any pretreatment and then incineration) the separable organic material in a manner that would require that the resultant canistered waste form (i.e., phosphate glass) to be disposed of as HLW. However, if for some reason such a HLW disposal product was produced, then the following issues, etc. would result:

Issue 1. This new waste form disposal product would have to be proposed to DOE-RW for evaluation and a decision as to whether it would even qualify as a suitable HLW form. Following that decision, the DOE-RW would establish the specific waste acceptance requirements that would apply to such a disposal product (i.e., a metal canistered phosphate waste glass).

NOTE: From this point on the general waste acceptance process, used by DOE-RW, would be about the same for either the currently

approved "standard form" product or a newly approved standard form product.

Impacts: The DOE-RW repository program is under severe budgetary pressures these days, and it has very limited staff resources for working on waste acceptance issues. Hanford/TWRS has recent experience with this problem. The fact is that the DOE-EM is much more interested in getting DOE-RW to make decisions on waste acceptance issues concerning possible repository disposal of DOE-EM spent nuclear fuel, which presents a priority problem for resolving such an issue.

It is also likely that only a small portion of the experience base established by the other DOE HLW vitrification projects would be applicable to gaining waste acceptance approval and product process qualification for such a (new) disposal product. Admittedly, the volume of the production, for this new product, would be very small, by comparison, and that would simplify some aspects of this burden.

Risks: High risks for cost, schedule and probability of success.

Issue 2. The RCRA issue cited in OPTION 1., of this write-up, would still apply and would have to be resolved with DOE-RW, if a HLW disposal product was being produced.

REFERENCES

1. Memo, Process Technology to Distribution, "Subfunction Impacts, Systems Engineering Study on Impact of Tank 241-C-103 Separable Phase Organic on TWRS Program", 73510-95-23, November 21, 1995.
2. Memo, C.N. Wilson to M.J. Klem, "Impact of C-103 Separable Organic on HLW and LLW Vitrification", December 22, 1995.
3. DOE (1994), "Waste Acceptance System Requirements Document" (WA-SRD) Rev. 1, DOE/RW-0351P, Office of Civilian Radioactive Waste Management (DOE-RW), March 1994.
4. (FW) (1995), for WHC per Task Order No. 043 of Order No. MRS-SVV-315924, "Requirements and Actions for Pumping the Tank 241-C-103 Organic Layer to a Double-Shell Tank", Foster Wheeler Environmental Corporation and Science Applications International Corporation, March 1, 1995.

5. Memorandum, D.A. Dreyfus (head of DOE-RW) to Secretary of DOE, via C.B. Curtis (Under Sec.), ISSUE: "The Notice of Intent to prepare an Environmental Impact Statement for a repository at Yucca Mountain to dispose of spent nuclear fuel and high-level radioactive waste will define the fuel and waste types to be considered for disposal in the repository", June 22, 1995.

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VOLUME 2

Section 8.12

DSI - Dose Rate Calculations for a Drum Containing Waste From Tank C 103

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DON'T SAY IT --- Write It!DATE: March 22, 1996

TO: Jennifer Mercado G2-02

FROM: R. A. Schwarz HO-35

Telephone: 376-5977

SUBJECT:DOSE RATE CALCULATIONS FOR A DRUM CONTAINING WASTE FROM
TANK C 103

Dose Rate Calculations have been made for a drum containing waste from tank C 103. The dose rate was calculated radially out from the surface of the drum at 1 cm and 1 meter from the side of the drum for two cases. Table 1 shows the source terms used for the two cases. For case 1, the density of the source is 0.3 g/cc and for case 2 the density is 0.4 g/cc. The dose rates were calculated using the ISO-PC computer code, version 1.98.

The drum was modeled as a cylinder with an internal radius of 28.575 cm and an axial extent of 84.455 cm. A 0.1214 cm thick steel shield was modeled around the source region. The dose rate was calculated radially outward from the center point of the drum at 1 cm and 100 cm. The dose rate was calculated at 1 cm from the surface to approximate a surface dose rate. Table 2 shows the calculated dose rates for these conditions for case 1 and case 2. Attachments 1 and 2 to this DSI contain the ISO-PC input files used for these calculations.

Table 1 Source terms

Isotope	Case 1 (Curies)	Case 2 (Curies)
Pu 238	6.9e-5	9.19e-5
Pu 239	1.48e-4	1.98e-4
Pu 240	1.48e-4	1.98e-4
Pu 241	4.61e-3	6.15e-3
Am 241	1.37e-4	1.83e-4
Cm 244	3.25e-5	4.33e-5
Sr 90	4.62e-1	6.15e-1
Y 90*	4.62e-1	6.15e-1
Co 60	5.58e-4	7.44e-4
Cs 137	1.13e-1	1.51e-1
Ba 137m*	1.13e-1	1.51e-1
Eu 154	2.37e-4	3.16e-4
Eu 155	2.35e-4	3.13e-4

*Assumed to be equal to the parent

Table 2. Dose Rates

Dose Point (distance from side of drum)	Case 1 (mrem/hr)	Case 2 (mrem/hr)
1 cm	402	505
100 cm	23	29

Attachment 1. ISO-PC Input file for case 1

```
0      2 C103 Tank Waste in a drum
Dose Rate out the side of the drum
&input Next=1, Ispec=3, Dunit=1, Option=1, Igeom=7,
Slth=84.455, Y=42.2275, Ntheta=10, Npsi=10, Delr=.1,
Nshld=2, Jbuf=1, T(1)=28.575, T(2)=0.1214,
X(1)=29.696,128.696
weight(492)=6.9e-5, weight(493)=1.48e-4,
weight(494)=1.48e-4, weight(495)=4.61e-3,
weight(496)=1.37e-4, weight(500)=3.25e-5,
weight(82)=0.462, weight(84)=0.462,
weight(335)=0.113, weight(336)=0.113,
weight(415)=2.37e-4, weight(418)=2.35e-4, weight(472)=5.58e-4 &
CONC 16 0.3
1 IRON 9      7.86
END OF RUN
&Input Next=6 &
```

Attachment 2. ISO-PC Input file for case 2

```

0      2 C103 Tank Waste in a drum
Dose Rate out the side of the drum CASE 2
&input Next=1, Ispec=3, Dunit=1, Option=1, Igeom=7,
Slth=84.455, Y=42.2275, Ntheta=10, Npsi=10, Delr=.1,
Nshld=2, Jbuf=1, T(1)=28.575, T(2)=0.1214,
X(1)=29.696,128.696
weight(492)=9.19e-5, weight(493)=1.98e-4,
weight(494)=1.98e-4, weight(495)=6.15e-3,
weight(496)=1.83e-4, weight(500)=4.33e-5,
weight(82)=0.615, weight(84)=0.615,
weight(335)=0.151, weight(336)=0.151,
weight(415)=3.16e-4, weight(418)=3.13e-4, weight(472)=7.44e-4 &
CONC 16 0.4
1 IRON 9 7.86
END OF RUN
&Input Next=6 &

```

VOLUME 2
SECTION 12
CRS TAP AND DNFSB REVIEW BOARD RESULTS

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VOLUME 2

Section 12.1

Letter - Recommendation on Tank 241-C-103 Floating Organic Layer

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Westinghouse
Hanford Company

P.O. Box 1970 Richland, WA 99352

April 26, 1996

9504249 R3

Dr. M. F. Jarvis, Project Director
Safety Issue Resolution Projects
U.S. Department of Energy
Richland Operations Office
Richland, Washington 99352

Dear Dr. Jarvis:

RECOMMENDATION ON TANK 241-C-103 FLOATING ORGANIC LAYER

- References: (1) Letter, E. J. Lipke, WHC, to Dr. M. F. Jarvis, RL, "Tank C-103 Organic Layer," 9504249 R1, dated April 12, 1996.
- (2) WHC-SD-WM-DQO-001, "Data Quality Objectives for Tank Farms Waste Computability Program," Revision 1, dated April 24, 1995.
- (3) WHC-EP-0862, "Recommended Alternative for Interim Stabilization of Tank 241-C-103," dated April 1995.
- (4) Geschke, G. R. and N. J. Milliken, April 1995, "Safety Evaluation for the Interim Stabilization of Tank 241-C-103, WHC-SD-WM-SARR-034, Rev. 0, Westinghouse Hanford Company, Richland, Washington

Reference 1 recently transmitted the systems engineering study for disposition of the floating organic layer in tank 241-C-103. However, a recommendation was not available at that time because additional time was required by the Westinghouse Hanford Company (WHC) Decision Support Board to study the issue. The Decision Board has now reached a conclusion and this letter provides the recommendation to the U.S. Department of Energy, Richland Operations Office (RL).

Subject to testing required to meet the Tank Farm Waste Compatibility Data Quality Objectives (Reference 2), WHC recommends that interim stabilization of 241-C-103 consist of saltwell pumping of both the aqueous and separable organic liquid to 241-AP-107 on the current stabilization schedule. After interim stabilization, about 1900 liters (500 gallons) of organic material will remain in tank 241-C-103. Double-shell tank (DST) 241-AP-107 was identified earlier as the receiver tank in the event of an indicated leak in 241-C-103 prior to interim stabilization. The Tank Waste Remediation System (TWRS) Authorization Basis does not currently include receipt and storage of separable organic liquids. However, Reference 4 does provide the technical

Dr. M. F. Jarvis
April 26, 1996
Page 2 of 3

9504249 R3

basis for amending the authorization basis, and the intent would be to complete that action before any transfer from 241-C-103.

In formulating its recommendation the Decision Board considered safety, cost, pretreatment and waste disposal impacts, previous studies, waste compatibility, cross contamination of wastes by organic residues in transfer lines, stakeholder concerns, impacts on waste volume projections, the current stabilization schedule for 241-C-103, and emergency pumping plans for a range of stabilization options. The basis for the recommended alternative includes the following significant considerations:

- 1) The technical work and a previous study (Reference 3) indicate there is no safety problem in allowing the separable organic layer to be mixed with the sludge in 241-C-103 as a result of interim stabilization. Additionally, auger and core samples of 241-C-102, 241-C-106 and 241-C-204 show separable tributyl phosphate (TBP) to be present in the waste solids. Vapor samples analyzed to date indicate there are other tanks that contain separable organics. The auger samples from tank 241-C-102 confirm the existence of TBP in the waste solids and validate vapor sample results from that tank which indirectly indicated the presence of separable organics. There is no evidence of adverse reactions or any unusual behavior in these tanks.
- 2) The Chemical Reaction SubTAP's major concern regarding pumping to a DST was the potential impact on pretreatment. Waste incompatibility resulting from commingling of 241-C-103 separable organic with other waste was perceived as a lesser issue than pretreatment impacts, based primarily on a judgement that stakeholders would support emergency pumping to an approved DST if a leak were to develop in 241-C-103.
- 3) Emerging data from single-shell tank solids (241-C-103, 241-C-106, and 241-C-204) demonstrate the need for an organic treatment operation on the headend of the Privatization Phase 2 disposal process.
- 4) In addition to the existing separable phase organic in 241-C-103, it is possible additional contributions will occur as the organic now dissolved in the aqueous phase is rendered insoluble through pH adjustment during waste pretreatment processing. It is estimated that as little as 380 liters (100 gallons) of separable organic in a tank would degrade the disposal ion exchange performance. This supports the need for an organic treatment capability on the headend of the Phase 2 disposal process.
- 5) The Decision Board did not believe it would be cost effective to skim the organic from 241-C-103 to an above ground tank since plans must be developed for removing organic from a DST as part of the Phase 2 disposal process in any event.

Dr. M. F. Jarvis
April 26, 1996
Page 3 of 3

9504249 R3

Incorporation of a simple organic treatment process in the FY 1996 revision of the TWRS Process Technical Baseline (RL Milestone T33-96-204 due August 16, 1996) is planned as part of the Privatization Phase 2 process. The contract for Phase 2 is expected to be let in 2005. By that time, the first 10 single-shell tanks will have been retrieved, including tank 241-C-103. It is expected that the magnitude of the organic treatment and disposal problem will be fully understood at that time, and resolution incorporated in the Privatization Phase 2 disposal process. In the interim, the separable phase organic will be managed in the double-shell tank system in accordance with the existing authorization basis. The FY 1996 Operational Waste Volume Projection (TPA Milestone M-46-00C due September 30, 1996) will confirm that storage of organic waste in the double-shell tanks does not affect available storage capacity nor interfere with Privatization Phase 1 disposal activities.

Please direct any questions to Mr. G. T. Dukelow on 373-4479 or Mr. D. A. Turner on 373-2238.

Very truly yours,



R. J. Cash, Manager
Safety Issue Resolution
Tank Waste Remediation System

p11

RL - S. O. Branch
D. H. Irby
J. K. McClusky
B. L. Nicoll
A. H. Wirkkala

CORRESPONDENCE DISTRIBUTION COVERSHEET

Author: G. T. Dukelow
 Addressee: M. F. Jarvis
 Correspondence No.: 9504249 R3

Subject: TANK 241-C-103 FLOATING ORGANIC LAYER

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x per G. T. Dukelow 4/26/96

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*x per D. J. Washenfelder
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VOLUME 2
SECTION 14
CURRENT STATUS

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VOLUME 2

Section 14.1

**Letter - Chemical Reactions Sub Tank Advisory Panel (CRS TAP)
Comments Prepared During the June 11-13, 1996 CRS TAP Meeting**

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Department of Energy

Richland Operations Office

P.O. Box 550

Richland, Washington 99352

9601649B

JUL 13 1996

96-WSD-088

Xc-GTP
-GAD
-JEM

President
Westinghouse Hanford Company
Richland, Washington

Dear Sir:

CHEMICAL REACTIONS SUB TANK ADVISORY PANEL (CRS TAP) COMMENTS PREPARED DURING THE JUNE 11-13, 1996, CRS TAP MEETING

Attached for your review and action is a copy of the letter from Billy C. Hudson to Professor Mujid S. Kazimi dated June 30, 1996. The letter contains comments prepared by the CRS TAP, as a result of the U.S. Department of Energy, Richland Operations Office (RL), and Westinghouse Hanford Company's (WHC) presentations and discussions provided during the 20th meeting of the CRS TAP held in Richland on June 11-13, 1996.

RL requests that WHC review the subject letter and provide a response to each CRS TAP comment by close of business on July 24, 1996.

If you have any questions, please contact me on 372-0947 or your staff may contact Dave Squires on 372-2944.

Sincerely,

J. K. McClusky
J. K. McClusky, Director
Waste Storage Division

WSD:DJS

Attachment

- cc w/attach:
- R. F. Bacon, WHC
- R. J. Cash, WHC
- S. J. Eberlein, WHC
- L. F. Ermold, WHC
- J. O. Honeyman, WHC
- R. E. Lerch, WHC
- G. A. Meyer, WHC
- M. A. Payne, WHC

ACTION - Gary Duke
LEAD



WHC-SD-WM-ES-384 REV 0

Disposition of the 103-C Organic Layer. Tank 103-C is currently on the Organics Watch List because of the floating organic layer. The proposed project (saltwell pumping without removal of the organic layer) would appear to transfer watch list eligibility from 103-C to 107-AP, i.e., a tank with the same floating organic layer would probably remain eligible for the watch list. Furthermore, this action would reduce treatment options available downstream. Alternatively, removal and separate storage of the floating organic layer would provide a simple, technical basis for removing 103-C from the Watch List and, at the same time, not unnecessarily limit future treatment options. Removal of the organic layer could be followed by saltwell pumping for interim stabilization of 103-C. In summary, we remain convinced this alternative represents a preferred path and find no reason to change our position from that given in the 13th CRS meeting summary letter:

"In the event of an emergency such that the liquid in 103-C must be removed without separation of the organic layer, the near-term safety implications associated with salt well pumping appear to be acceptable. However, no such emergency appears to exist. We believe sufficient analyses have been performed to establish that there are no significant, near-term, safety-related risks associated with the continued storage of existing waste in 103-C. Furthermore, there has been no indication that 103-C is leaking.

While there appear to be no unacceptable, near-term safety implications associated with immediate salt well pumping, it is our belief this action would have serious, deleterious impact on future activities (such as solid and liquid separation and ion exchange, due to the mixing of organics and sludge or saltcake) leading to undesirable increases in cost and personnel exposure. Consequently, we believe it would be prudent to remove the organic layer from 103-C prior to interim stabilization and suggest required actions for this removal be initiated immediately. In order to avoid a recurrence of this problem, we suggest the removed organics be stored without mixing with other waste that contains sludge or saltcake.

Following removal and separate storage of the organics, the aqueous supernate could be removed from 103-C by saltwell pumping and stored in a DST, as proposed."

We are pleased the new system engineering study has identified impacts on pre-treatment processing due to the presence of organics (requiring changes in the pre-treatment flow sheets) and that commitment has been made to develop appropriate flow sheets.

There was limited discussion at the meeting concerning estimation of organic pool size using vapor sample data. We would appreciate a presentation on this topic at a future meeting.

DISTRIBUTION SHEET

To	From	Page 1 of 1
Distribution	M. J. Klem	Date 9/30/96
Project Title/Work Order		EDT No. 607745
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