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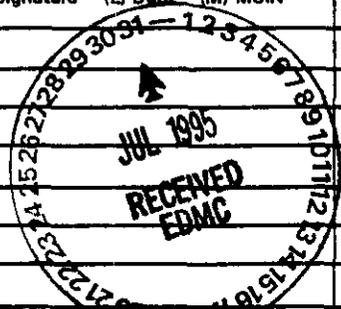
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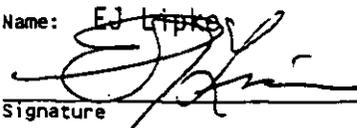


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7. Abstract

This document provides a summary and status of the Hanford Tank Waste Remediation System Safety Program, including current hazards and accident analysis, safety issues in progress, and the approach for their resolution. The TWRS Safety Program is the vehicle that defines the basis for the near term Hanford Tank Waste Characterization Strategy. The safety analysis that defines the safety basis is presented together with a listing of the evaluation basis accidents that were considered and incorporated in the Accelerated Safety Analysis (ASA). The ASA defines the hazards and develops accident analysis and associated Operational Safety Requirements (controls) that, when implemented, will provide an adequate safety envelope for tank farm operations. The ASA is scheduled for completion and approval in CY 1995.

The focus of the characterization effort is to first address those technical issues identified in establishing the safety basis. The principal technical safety issues of flammable gas, noxious vapor, organic solvent, organic complexant, ferrocyanide, high-heat, criticality and tank structural integrity from the ASA are reviewed. A summary of the information required to further address these safety issues is presented.

The Safety Program, through Data Quality Objectives (DQOs), establishes the requirements for analytical data to confirm the models used in the safety analysis, reduce the uncertainty associated with the calculations, and confirm the conservatism of the source term. This additional characterization information will provide the basis for confirming, adjusting, or eliminating controls at the Hanford waste tanks to assure adequate protection of the public, workers and the environment.

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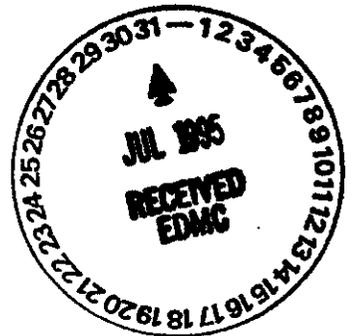
# TWRS Safety Basis

Prepared for the U.S. Department of Energy  
Office of Environmental Restoration and  
Waste Management



**Westinghouse**  
**Hanford Company** Richland, Washington

Management and Operations Contractor for the  
U.S. Department of Energy under Contract DE-AC06-87RL10930



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# TWRS Safety Basis

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Date Published  
June 1995

Prepared for the U.S. Department of Energy  
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## EXECUTIVE SUMMARY

This document provides a summary and status of the Hanford Tank Waste Remediation System Safety Program, including current hazards and accident analysis, safety issues in progress, and the approach for their resolution. The TWRS Safety Program is the vehicle that defines the basis for the near term Hanford Tank Waste Characterization Strategy. The safety analysis that defines the safety basis is presented together with a listing of the evaluation basis accidents that were considered and incorporated in the Accelerated Safety Analysis (ASA). The ASA defines the hazards and develops accident analysis and associated Operational Safety Requirements (controls) that, when implemented, will provide an adequate safety envelope for tank farm operations. The ASA is scheduled for completion and approval in CY 1995.

The focus of the characterization effort is to first address those technical issues identified in establishing the safety basis. The principal technical safety issues of flammable gas, noxious vapor, organic solvent, organic complexant, ferrocyanide, high-heat, criticality and tank structural integrity from the ASA are reviewed. A summary of the information required to further address these safety issues is presented.

The Safety Program, through Data Quality Objectives (DQOs), establishes the requirements for analytical data to confirm the models used in the safety analysis, reduce the uncertainty associated with the calculations, and confirm the conservatism of the source term. This additional characterization information will provide the basis for confirming, adjusting, or eliminating controls at the Hanford waste tanks to assure adequate protection of the public, workers and the environment.

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## LIST OF TERMS

AWF	Aging Waste Facility
ASA	Accelerated Safety Analysis
CES	Consensus Exposure Standard
DCRT	Double-Contained Receiver Tank
DST	Double-Shell Tank
DQO	Data Quality Objectives
EBA	Evaluation Basis Accidents
ISOR	Interim Operational Safety Requirements
ISB	Interim Safety Basis
LFL	Lower Flammability Limit
OSR	Operational Safety Requirements
SAR	Safety Analysis Report
SHMS	Standard Hydrogen Monitoring Systems
SST	Single-Shell Tank
TOC	Total Organic Carbon
TSR	Technical Safety Requirements
TRAC	Track Radioactive Constituents Report
USQ	Unreviewed Safety Question

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## 1.0 INTRODUCTION

This document provides a summary of the Hanford Tank Waste Remediation System safety basis. Historically the Hanford Waste Tank Safety Program was focused on resolution of specific safety issues that were identified from a variety of sources. These issues include flammable gas, noxious vapor, organic solvent, organic complexant, ferrocyanide, high-heat, criticality and tank structural integrity. A systematic approach to waste tank safety has included the development of a safety basis through the application of safety analysis methodology.

The TWRS Accelerated Safety Analysis (ASA) has been developed over the past two years and is currently undergoing DOE-RL and independent reviews prior to submittal to DOE HQ for approval. The ASA will provide the necessary documentation to define the safety envelope for conducting safe tank farm operations.

The results from the ASA have demonstrated that the waste tanks can be safely managed with the appropriate controls as specified in the Interim Operational Safety Requirements (IOSRs). Continued characterization by deliberate sampling of the waste will be used to (a) further confirm the models of waste behavior used in the safety analysis, (b) reduce the uncertainty associated with the calculations, and, (c) confirm the conservatism of the source term data used in the analysis. This additional characterization information will thus provide the basis for confirming, reducing or eliminating controls presently in place through the IOSRs. Included in this document is (a) a description of the Hanford Waste Tank Safety Program, (b) a discussion of the principal safety issues, and (c) a summary of specific near-term waste characterization data. This document is issued in conjunction with Dove et al. (1995) and Brown et al. (1995) and should be viewed in the context of the characterization plan established in these companion documents.

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## 2.0 TANK WASTE REMEDIATION SYSTEM SAFETY PROGRAM

The objective of the Tank Waste Remediation System (TWRS) project is safe and efficient storage and ultimate disposal of Hanford Site tank waste. In order to meet the objective, several activities have been on-going relative to the identification and resolution of potential waste storage safety issues, completion of updated safety analysis and required documents, incorporation of necessary controls into tank farm operations, and the definition of necessary information and characterization data to support model development and safety issue resolution.

### 2.1 SAFETY ISSUES

Several tank farm safety issues have been previously identified and significant progress has been made to resolve and close these safety issues with appropriate documentation and/or controls. The major safety issues are related to the potential for flammable gas generation, storage, and release; organic solvent combustion reactions; exothermic ferrocyanide-nitrate reactions; deflagration associated with organic complexants; criticality; high heat generating waste; and tank structural integrity. Identification and progress toward resolution of these safety issues helped focus attention to the fact that the original safety basis for the Hanford Waste Tanks was lacking and that specific controls needed to be implemented in order to be assured that the health and safety of the public, workers and environment were being adequately protected. The resolution of the remaining safety issues requires information from laboratory energetics and waste degradation studies, assessment of existing sample data, evaluation of historical data, and use of various waste tank models to predict waste thermal behavior. The aggressive approach to resolve the waste tank safety issues resulted in significant progress in understanding the hazard potential of tank waste. Further data needs to close out these issues or refine controls are discussed in Section 3.

### 2.2 SAFETY ANALYSIS

Significant progress has been made in defining and understanding a safe operating envelope for the tank farm facilities. Development of the safe operating envelope required integration of the current evolution of characterization data and an understanding of the safety issues to conservatively develop the safety basis for continued waste storage. An Interim Safety Basis (ISB) was issued in November 1993 to establish the authorization basis for the Tank Farm Facilities as part of implementation of DOE Order 5480.23, *Nuclear Safety Analysis Reports*. The ISB provided the basis for interim operations and controls (Interim Operational Safety Requirements, [IOSRs]) until an upgraded Safety Analysis Report (SAR) for the tank farm facilities is completed.

Because of the significance of the safety issues associated with the Hanford Site waste tanks, a strategy was developed in mid FY 1993 to accelerate the hazards and accident analyses for the waste tanks. The development of a full SAR that addressed each of the topics specified by the DOE Order would follow, based on the completed hazards and accident analyses. The updated hazards and

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accident analyses are documented in an Accelerated Safety Analysis (ASA) which provides a systematic identification of facility hazards, an identification and evaluation of potential accident sequences and associated consequences, and a conservative basis for establishment of appropriate controls or interim Operational Safety Requirements (IOSRs). The identification and progress toward resolution of the safety issues provided significant input to the ASA.

### 2.2.1 Application of Data to Determine Source Terms

Because of the variability of waste in the waste tanks, conservative assumptions were used to develop an upper bound for safe operations. Radiological and toxicological source terms were developed from a combination of theoretical models, recent characterization sampling, and historical sample data. Existing data were evaluated from all sources to determine representative and bounding source term concentrations for radioactive isotopes and hazardous chemical species. Data from further waste characterization efforts will result in reducing the conservatism in the source terms used in the ASA analysis, and may allow relaxation of some of the IOSR established controls.

The development of source terms required the selection of concentrations of specified radionuclides and toxic chemicals in different waste types. The selection process resulted in the compilation of sample data into groups for nine different waste types for radionuclide source terms and five different waste types for toxic chemical source terms. The sample data were drawn from the Westinghouse Hanford Company (WHC) characterization library, the Tank Characterization Data Base, Tank Characterization Reports, and other data collected by the characterization program. Predicted concentrations of the radionuclides and analytes taken from the TRAC computer code and the Layering Model developed by Los Alamos National Laboratory were also utilized.

The information and data were interpreted by senior personnel representing the analytical laboratories, process chemistry, TWRS engineering, plant operations and safety analysis. The purpose of the review was to ensure that the concentration values selected were appropriate, that the values were defensible, and that the values chosen would result in the highest expected doses (bounding) for each waste form. Sample concentrations were ranked from the highest to the lowest value. The highest valid sample was used as the concentration for that radionuclide or analyte.

The total dose is the sum of the contributions from all radionuclides or analytes, all of which are not of equal significance relative to health effects. Because the highest, reasonable analyte concentrations were selected for each waste type, it is unlikely that new sample data will result in source terms that would produce higher unit doses. The unit doses used in the ASA, therefore, provide bounding or conservative radiological or toxicological consequences. As a result it is not required that the characterization program analyze the waste tanks for radionuclides and toxic chemicals concentrations for the purposes of ensuring waste tank safety. As waste samples are taken during the characterization program, the radionuclide and toxic chemical concentrations should be measured and reviewed to verify that

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the combined results remain less than the bounding values used in the safety analysis.

### 2.2.2 Development of Safety Envelope

The safety analysis as documented in a SAR for a nuclear facility is intended to define an operating envelope including necessary controls to ensure that the facility can be operated, maintained, shut down and decommissioned safely in compliance with applicable laws and regulations. The ASA documents the hazards and accident analysis information that will be used in the upgraded Hanford Site Tank Farm SAR. The ASA presents the systematic identification of facility hazards, the selection of accident scenarios, and the evaluation of credible accident scenarios analyzed for potential consequences. When the ASA is approved the results of the hazards and accident analyses, in combination with the IOSRs, will define the facility's safety envelope. The selection of safety class equipment and the performance of unreviewed safety question (USQ) determinations will be based on this safety envelope. Results presented in the ASA indicate that the tank farms can be safely maintained within acceptable bounds utilizing appropriate design features and controls.

The hazards analysis was used to validate that the selection of accidents analyzed in the ASA were an appropriate spectrum of bounding and representative events, referred to as evaluation basis accidents (EBAs). The hazard evaluation process also provides a thorough qualitative evaluation of the spectrum of potential accidents involving identified hazards.

The hazards analysis considered a comprehensive range of potential process-related hazards as well as those hazards associated with internal and external events for all 177 large waste tanks. The hazards analysis forms the basis for understanding facility worker protection, environmental protection, selecting or confirming potential evaluation basis accidents (EBAs) to be further developed and quantified, and determining the facility hazard classification.

Consideration was given during the hazards analysis process to normal operations and potential hazards experienced by facility workers. Though the hazards to facility workers were identified during the hazards identification, they are not evaluated as part of the accident analyses. Worker safety and environmental protection are adequately covered by other WHC programs (e.g., Radiological Safety, Industrial Safety, Emergency Preparedness, and Environmental Protection) that have been implemented to comply with DOE and other federal regulations, codes, and standards.

Consistent with the requirements of DOE Order 5480.23, the hazard identification and analysis does not include consideration of sabotage or other malevolent acts of commission or omission. These events are addressed under the vulnerability assessment analyses of, and provisions for, tank farm facility security protection.

The analysis results of the selected EBAs provided the bases for development of controls needed for protection of the public and co-located workers. The unmitigated consequences and associated likelihoods of the evaluation basis

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accidents were compared to WHC risk acceptance guidelines (WHC 1993). If the unmitigated consequences and likelihoods exceeded the risk acceptance guidelines, appropriate design features; safety systems, structures and components (SSCs); or administrative controls were identified to reduce the consequence or frequency of the accidents to acceptable levels.

Each EBA was described in the following order:

- Accident scenario
- Accident frequency
- Radiological source term and unmitigated consequences
- Toxicological source term and unmitigated consequences
- Mitigated or prevented radiological consequences
- Mitigated or prevented toxicological consequences
- Systems, structures, components (SSCs), design features, or controls required to meet risk acceptance guidelines.

Table 1 provides a list of the EBAs that were analyzed in the ASA and for which radiological and toxicological consequences were determined.

A primary purpose of the accident analysis is to identify whether SSCs, design features, or controls are required for prevention or mitigation of postulated accidents. Including this information in the documentation of the evaluation basis accidents provided easy identification of the safety functions that required consideration for the Interim Operational Safety Requirements. The Interim Operational Safety Requirements included the definition of acceptable conditions, safe boundaries, bases thereof, and management or administrative controls required to ensure safe operation of the Tank Farms.

Table 1. List of Evaluation Basis Accidents Analyzed in ASA

Type of Accidents	ASA Accident Name
Waste Storage Tank Accidents	Tank Dome Collapse
	SST Flammable Gas Headspace Deflagration
	DST/AWF Flammable Gas Headspace Deflagration
	DCRT Flammable Gas Headspace Deflagration
	Ferrocyanide Exothermic Propagating Reaction
	Organic Exothermic Pool Fire (in progress)
	Tank Bump
	Steam Release From Waste
	Pressurization From Steam Jet Pumping
	Criticality
Tank Ventilation Accidents	SST Passive Ventilation (90% Filtration)
	SST Passive Ventilation (0% Filtration)
	SST Passive Ventilation (Filter blowout)
	SST Active Ventilation (90% Filtration)
	SST Active Ventilation (0% Filtration)
	SST Active Ventilation (Filter Blowout)
	DST Active Ventilation (90% Filtration)
	DST Active Ventilation (0% Filtration)
	DST Active Ventilation (Filter Blowout)
	AWF Active Ventilation (90% Filtration)
	AWF Active Ventilation (0% Filtration)
	AWF Active Ventilation (Filter Blowout)
Waste Transfer Accidents	Leak or Break from Single Encased Pipeline
	Spray Release From Waste Transfer System
	Pipeline Break From Excavation

Table 1. List of Evaluation Basis Accidents Analyzed in ASA

Type of Accidents	ASA Accident Name
204-AR Waste Handling Facility Accidents	Railcar Spill (with and without fire)
	Unfiltered Ventilation System Release From Catch Tank
	Local Combustible Material Fire Inside Building
	Sodium Hydroxide Spill
244-AR Vault Storage/Handling Accidents	Unfiltered Release From Vent Ventilation Stack
	Unfiltered Release From Canyon Exhaust Ventilation system
	Hydrogen Gas Deflagration Inside Storage Tanks During Passive Ventilation

**2.2.3 Status of Accelerated Safety Analysis**

The ASA was submitted to the DOE, Richland Operations Office (DOE-RL) in March 1995. DOE-RL then subjected the ASA to independent review which was completed in early June 1995. Comments from the independent review are currently being resolved. Evaluation of the independent review comments and proposed resolutions indicates that the ASA successfully defines the hazards, develops appropriate accident analyses, and identifies necessary operational safety requirements to provide an adequate safety basis for tank farm operations. The IOSRs that result from the ASA were submitted to DOE-RL in May 1995 and are currently undergoing independent review.

Upon approval, the ASA hazard and accident analyses will form the nucleus of the new authorization basis. Resolution of current issues such as the USQ on flammable gas or the analysis of condensed phase organic nitrate reactions will be entered as changes to the authorization basis. The proposed IOSRs are not fully implemented at this time and will be implemented upon approval. In some cases, implementation will amount to relaxation of current IOSRs, while for other cases, implementation will result in new controls.

**2.3 OPERATIONAL CONTROLS**

The accident analysis of the ASA calculated the consequences for unmitigated accidents and identified a range for the accident sequence event frequencies. For each accident sequence, if the consequence and frequency were outside of the Risk Acceptance Guidelines (WHC 1993), additional physical and/or administrative controls were established that would either prevent the postulated accident or reduce the calculated consequences or likelihood of the

accident. The controls will be incorporated into the Interim Operational Safety Requirements (Technical Safety Requirements when the SAR is completed) for the facility.

An example of the controls are those used for tanks containing flammable gases. The unmitigated consequences and associated likelihood of a flammable gas deflagration with a tank dome collapse were above the Risk Acceptance Guidelines. Controls were, therefore, developed to prevent a gas deflagration. The controls were specific to the accumulation of flammable gases within the tank vapor space, monitoring vapor space flammability concentrations, limiting or preventing ignition sources, and minimizing intrusive activities to reduce hazard exposure.

The results from the ASA have demonstrated that the waste tanks can be safely managed with appropriate controls as specified in the IOSRs. Continued characterization by deliberate sampling of the waste will be used to (a) further confirm the models of waste behavior used in the safety analysis, (b) reduce the uncertainty associated with the calculations, and, (c) confirm the conservatism of the source terms used in the analysis. This additional characterization information will thus provide the basis for confirming, reducing or eliminating controls presently in place through the IOSRs.

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### 3.0 DISCUSSION OF WASTE TANK SAFETY ISSUES

#### 3.1 SAFETY RELATIONSHIP WITH CHARACTERIZATION PROGRAM

The objective of safe waste storage and disposal requires that the waste tank characterization strategy be structured to provide priority support to addressing tank farm safety issues in the most efficient manner.

Appropriately, the characterization program is focused on first addressing those technical issues associated with the analyses used in establishing the safety basis. Information from the characterization program will be analyzed and compared to existing technical information, waste behavior models, and/or assumptions used in establishing the safety basis. The new information will be used to resolve current safety issues and other safety issues that may be identified in the future. The safety basis is a living document and will be revised as needed based on new information and issue resolution. Operational controls will be confirmed, modified, or eliminated through the IOSRs as appropriate. The characterization basis and plan will be appropriately revised in order to continually focus on obtaining the most important information with the largest potential for ensuring adequate protection of the public, workers and environment. This parallel path approach to safety and characterization is shown in Figure 1.

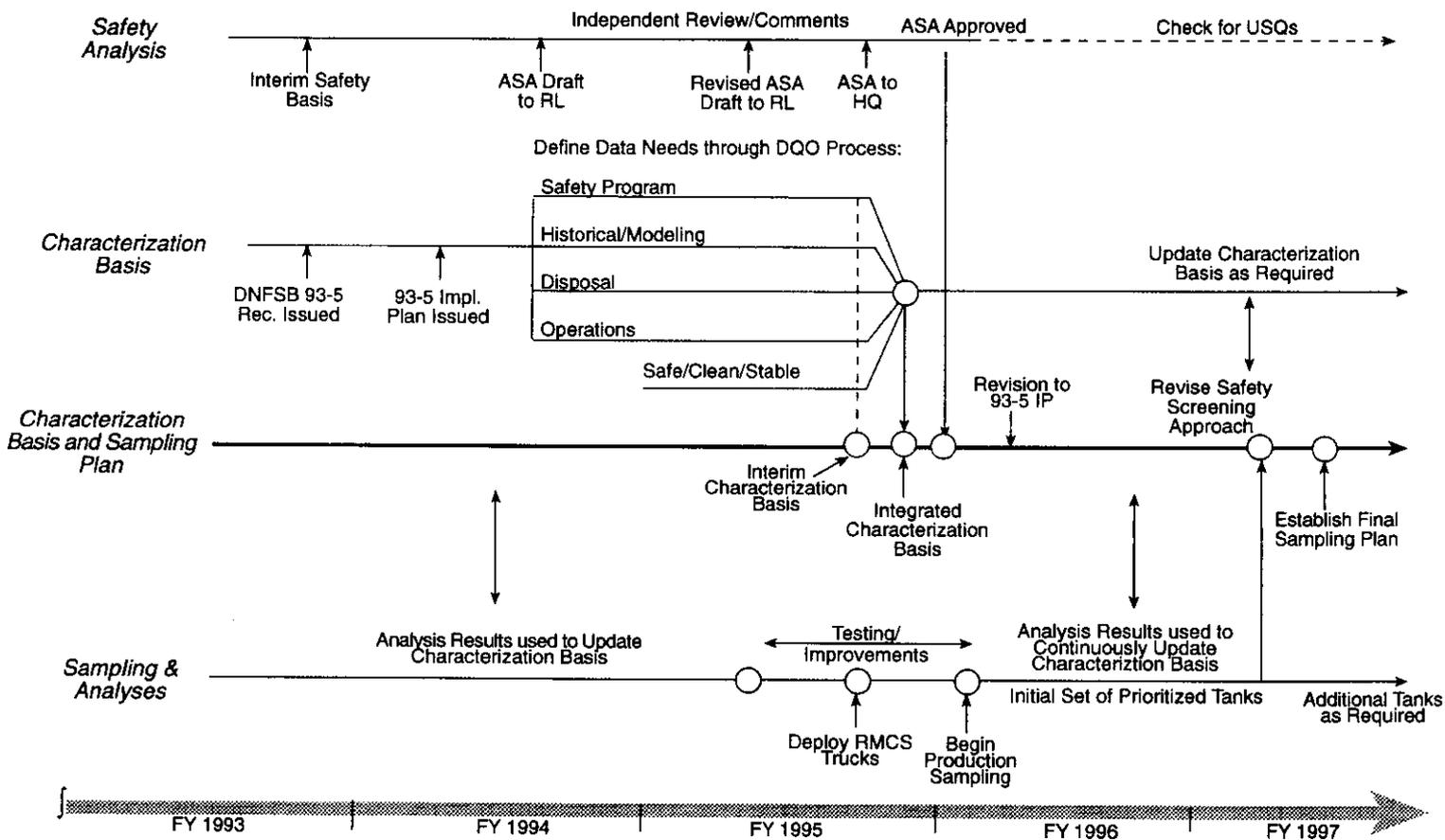
The safety program and characterization approach for resolving priority safety issues related to flammable gas, noxious vapor, organic solvent, organic complexant, ferrocyanide, high heat generating waste, criticality and tank structural integrity has been influenced by the significant progress made to date. The progress includes: (1) completion of safety analyses for flammable gas, ferrocyanide, criticality, organic solvent (tank 241-C-103), and sludge dry out; (2) successful mitigation of tank 241-SY-101 safety issues; (3) demonstration of actual and simulated waste energetics; (4) demonstration of waste degradation (aging resulting in lower energy products) in laboratory experiments and limited waste sampling for ferrocyanide and organics; (5) completion of laboratory tests to define conditions required for condensed phase propagating reactions, and (6) developing an increased understanding of safety related information that can be obtained from tank headspace sampling.

#### 3.2 SAFETY ISSUES

The approach to characterization for the safety issues continues to evolve as the parameters affecting safe storage and their relationship are better understood. In general, characterization demands are lessened as safety issues become better understood. This section reviews the current safety issues to ensure safe storage and examines the direction of future efforts. Specific near-term characterization requirements to resolve safety issues are presented in Section 4.0.

The High-Level Waste Tank Subcriticality Safety Assessment (Braun et al. 1994) concluded that the waste in the Hanford Site waste tanks is in a form that is favorable to maintaining a large margin of subcriticality because of the small quantities of fissile material and the large amounts of neutron absorbing

Figure 1: Hanford Tank Waste Characterization Strategy



BTFC060095.28

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materials. The characterization program will continue to provide appropriate confirmatory sample data (e.g., fissile material, absorber content, and alkalinity information) as waste samples are obtained for other reasons.

High-heat tanks have been identified through temperature monitoring coupled with thermal analyses. However, only one tank, tank 241-C-106, has demonstrated any significant high-heat load. This tank is scheduled to be retrieved in late 1996. In the meantime, a chiller is being procured for this tank to mitigate potential risk that may be associated with leaks that might result because of accelerated corrosion due to the increased temperature.

Waste tank structural integrity evaluations are being completed for all waste tanks. Structural and seismic evaluations are being completed, and the tank life expectancy is being determined for each tank.

### 3.2.1 Flammable Gases

Flammable gas species (mainly hydrogen and ammonia) are produced at low rates by radiochemical and thermochemical degradation reactions in waste. Vapor from organic solvents may also contribute to headspace flammability. While a mixture of gases may contain flammable constituents, a flammability hazard exists only if a minimum flammability concentration can be retained within the tank head space (i.e., enough to exceed the minimum fuel concentration known as the lower flammability limit [LFL]). Otherwise, the gases will be dissipated to the atmosphere at concentrations too low to represent a flammability hazard.

For a flammable gas to ignite and burn, it must be mixed with an oxidizer (usually oxygen) and be provided sufficient energy to initiate the chemical reaction. A sufficiently dilute mixture of flammable gas (i.e., a concentration below the LFL) and oxidizer will not burn. The National Fire Protection Association recommends that processes be controlled so that flammable gas concentrations are less than 25% of the LFL. U.S. Department of Energy orders require that Hanford Site waste tanks be operated within National Fire Protection Association guidelines; therefore, management efforts must provide assurance that flammable gas levels are maintained below 25% of the LFL.

The flammable gas hazard can be classified according to the mode by which the flammable gases are released from the waste. For a steady-state gas release, gases are released at approximately the rate at which they are formed, and the concern is an accumulation of flammable gases in the tank headspace (i.e., a steady-state flammability hazard). For a limited number of tanks, gases are released episodically at comparatively high rates. For these episodic releases, flammable gas concentrations could exceed 25% of the LFL for brief time periods. Twenty-five Hanford Site waste tanks are on a Flammable Gas Watch List because the waste in these tanks is believed to have the potential to retain hydrogen gas until appreciable quantities are released (Hopkins 1994). Monitors have been installed on these tanks and access controls have been imposed to minimize the potential hazard.

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**Steady-State Release of Flammable Gases.** All DSTs are actively ventilated, and air exchange is rapid enough (except during an episodic release) to keep steady-state bulk hydrogen concentrations in the headspace well below 25% of the LFL (Graves 1994). However, most SSTs are passively ventilated and only exchange air with the environment through relatively slow barometric pressure changes and by instrument air purges. Therefore, potential accumulation of flammable gases in the headspace and risers of all SSTs has been explored.

Preliminary studies (Wood 1993, Graves 1994, Fowler and Graves 1994) have examined accumulation of flammable gases in the headspace and risers of SSTs that are not on the Flammable Gas Watch List. A more detailed study on flammable gas accumulation is currently being developed. However, calculations performed thus far show that gas production and release rates from thermochemical and radiochemical processes are modest and that passive ventilation alone will keep the headspace well below 25% of the LFL. The contribution to the flammable gas mixture from organic solvent vapor is low (Claybrook and Wood 1994) because the bulk of organic solvent remaining in any tank would likely have a low vapor pressure. Sampling data from tank 241-C-103, which contains a floating organic layer, supports this conclusion. Vapors from the organic solvent amount to less than 5% of the LFL (Huckaby and Story 1994, Postma et al. 1994).

**Episodic Release of Flammable Gases.** The ability of waste to retain large amounts of gas is dependent on its physical properties and chemical/radiological composition. The waste retains gases that increase the waste volume (slurry growth) until the gases escape. Slurry gas is only present in a tank headspace at high concentrations when it is released by the waste; therefore, the most direct way to characterize gas may be to sample the waste directly.

The amount of gas retained in the waste will be estimated from analysis of tank operational data. Tank monitoring data include changes in surface level (resulting from gas release events and changes in atmospheric pressure) and axial waste temperature profiles. New, more accurate level gages and instrument trees (that measure temperature) are being installed in Hanford Site waste tanks. In addition standard hydrogen monitoring systems (SHMS) are also being installed on all flammable gas watch list tanks.

**Near-Term Characterization of Flammable Gases.** Sampling and/or continuous monitoring is being used to confirm that flammable gas does not accumulate in the SSTs. Headspace sampling results from 30 SSTs (none of which are on the Flammable Gas Watch List) indicate that flammability in the headspace and risers is well below 25% of the LFL. Headspace sampling of passively ventilated SSTs for flammable gases will continue until all are sampled. None of these tanks is expected to contain steady state flammable gas concentrations above 25% of the LFL. However, if concentrations greater than 25% of the LFL are measured for non-Watch List tanks, then these tanks would become candidates for continuous gas monitoring and potential mitigation.

The headspace of tanks that are suspected of having waste that releases flammable gases episodically will be continuously monitored for flammable gases. Standard hydrogen monitoring systems (SHMS) have been designed, built,

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and installed on all Flammable Gas Watch List tanks. Standard hydrogen monitoring systems contain instrumentation that support an on-line hydrogen detector and a "gas grab sampler" (WHC 1992).

The near-term characterization requirements are described in the following DQO: *Flammable Gas Tank Safety Program: Data Requirements for Core Sample Analysis Developed Through the Data Quality Objectives (DQO) Process* (WHC-SD-WM-DQO-004). A summary of these characterization needs is presented in Section 4.0.

**Future Characterization of Flammable Gases.** Two techniques are being developed to directly characterize waste for retained gas: (1) a void meter to measure the volume fraction of the gas phase in the waste, and (2) a retained gas sampling system to extract a sample of waste from a tank so that the waste can be analyzed (gas can exist as a distinct phase in the waste, and it can also be adsorbed on solid or dissolved in aqueous liquid phases). In the near future ammonia monitoring capability will be added to the SHMS. Another system is being developed for in-situ measurement of physical properties (density, viscosity, shear strength) which are critical to evaluation of stored gas. Development of these systems is scheduled for completion in FY 1995.

### 3.2.2 Noxious Vapors

Several health and safety issues are related to noxious vapors that may be present in some of the high-level waste tanks at the Hanford Site. Until vapors in the waste tanks are well characterized, the risks to worker health and safety must be maintained low by means of adequate operational controls (Osborne and Huckaby 1994).

A tank-by-tank sampling approach is being pursued to resolve headspace issues dealing with flammability and noxious vapors. Vapor sampling will be conducted on all tanks in the tank farm complex.

Modeling and vapor data from tank 241-C-103 indicate that the tank head spaces are well mixed (Meacham et al. 1995), except during an episodic gas release. To corroborate that the headspace is well mixed, additional headspace sampling at different vertical and horizontal locations will be conducted in selected tanks.

If any compounds are detected inside a tank dome with toxicological properties that exceed their respective trigger points, WHC Industrial Hygiene is advised that gases with toxicological concern are present in the tank headspace. The trigger point has been defined as 50% of the appropriate Consensus Exposure Standard (CES) concentration for all analytes of interest. A CES is generally defined as the most stringent of known regulatory or recommended toxicological values for the occupational setting; including the threshold limit value, permissible exposure limit, recommended exposure limit, and biological exposure limit (Osborne and Huckaby 1994).

The data required to assess toxicity are as follows: (1) identification of chemical compounds in the tank headspace of concern for worker health and

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safety or toxicological importance; (2) estimates of the concentrations of these toxicologically significant compounds in the headspace; and (3) understanding of the toxicological effects of these compounds and the CES for each constituent of concern.

The near-term characterization requirements are described in the following DQO: *Data Quality Objectives for Generic In-Tank Health and Safety Vapor Issue Resolution* (WHC-SD-WM-DQO-002). A summary of these characterization needs is presented in Section 4.0.

### 3.2.3 Organic Solvents

Various separation processes involving organic solvents have been used at the Hanford Site. These organic solvents were inadvertently and/or purposely sent to the underground storage tanks, and subsequent waste transfer operations distributed organic solvents among several of the 177 high-level waste tanks (Sederburg and Reddick 1994). There are three potential hazards associated with organic solvent: (1) contribution to headspace flammability (as discussed above in 3.2.1); (2) ignition of an organic solvent pool; and (3) ignition of organic solvent that is entrained in waste solids.

Currently, one tank (241-C-103) is known to contain an organic solvent pool. Additional tanks that may contain an organic solvent pool will be identified through continued vapor sampling of the tank headspace. Analyses have shown that solvent pool fires are difficult to initiate (Postma et al. 1994). Waste that may contain entrained organic solvent will also be identified through vapor sampling of the tank headspace. These analyses have been integrated into the noxious vapor sampling campaign. If vapor sampling suggests the presence of organic solvent, liquid grab samples and/or near-surface samples will be obtained to better quantify the potential for an organic solvent fire.

The near-term characterization requirements are described in the following DQO: *Data Quality Objectives for Generic In-Tank Health and Safety Vapor Issue Resolution* (WHC-SD-WM-DQO-002). A summary of these characterization needs is presented in Section 4.0.

### 3.2.4 Fuel-Nitrate (Condensed-Phase) Reactions

During the defense mission at the Hanford Site, organic complexants and ferrocyanide were sent to the high-level waste tanks. These compounds have the potential to act as a fuel when combined with an oxidizer. Nitrate salts have also precipitated in the tanks and are a source of oxidizer. For the organic complexant (non-volatile materials) and ferrocyanide safety issues, the approach to safety characterization is based on the fact that propagating reactions cannot occur if either the fuel, oxidizer, or potential initiators (e.g., temperature or energy) are controlled. Because specific limits of fuel, oxidizer, and initiators must be satisfied for a propagating chemical reaction to occur, waste can be stored safely if the conditions for the reaction are not possible. Therefore, the approach for obtaining characterization information is to obtain information that would confirm that one of the conditions of fuel or oxidizer is not present in sufficient quantities or that initiators are absent or can be controlled.

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An important parameter in controlling propagating reactions is an inhibitor such as moisture. In sufficient quantity, moisture will prevent propagating reactions by three main mechanisms: (1) moisture behaves as an inert diluent (lowering the effective fuel concentration); (2) moisture prevents initiation of a propagating reaction (the energy from most credible initiators would be absorbed by the sensible and latent heat of the moisture before the waste reached the critical initiation temperature); and (3) moisture provides a large heat sink that inhibits propagation (for a reaction to propagate, enough energy must be supplied to overcome the sensible and latent heat of the moisture present).

**Fuel and Moisture Criteria.** Experiments have shown that moisture can prevent condensed-phase propagating reactions. Tube propagation tests on waste simulants have shown that propagating reactions cannot occur in waste simulants containing more than 20 wt% moisture. Sufficient moisture content can ensure that a propagating reaction will not occur, regardless of the fuel-oxidizer concentration. That is, if adequate moisture can be confirmed through monitoring, analysis, or sampling, then it can be concluded that condensed phase exothermic reactions will not occur, thus ensuring interim safe waste storage.

The minimum required fuel concentration has been determined using a contact temperature ignition model (Fauske 1995). A necessary (but not sufficient) condition for a condensed-phase propagating chemical reaction is that the fuel concentration be greater than 4.5 wt% total organic carbon (TOC), based on sodium acetate as fuel, or 1200 J/g on an energy equivalent basis (Fauske 1995). For fuel concentrations between 1200 and 2100 J/g, the waste moisture content required to prevent a propagating reaction varies linearly from 0 to 20 wt%. Above 20 wt% moisture, the fuel-moisture linear relationship no longer holds because the mixture becomes a continuous liquid phase, effectively preventing propagating reactions. Note that the TOC criteria depends on the chemical concentration of the waste. Table 2 summarizes the criteria for safe storage.

Table 2. Safe Storage Criteria

Parameter	Criteria
Fuel Concentration	< 1200 J/g
TOC Concentration	< 4.5 wt%
Moisture Concentration	$\geq 0.022 [\text{Fuel (in J/g)} - 1200] \text{ wt\%}$ or > 20 wt%

**Parameters Affecting Fuel Concentration.** Waste tank operations have affected fuel concentration in the tanks. Experiments on waste simulants have shown

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that the high energy organic complexants (i.e., the organic salts that could support a propagating reaction) are highly soluble in the tank supernatant solutions. Subsequent pumping of the tank liquids might have removed most of the organic complexant fuels (Barney 1994).

Ferrocyanide waste stored in Hanford Site tanks has been exposed to caustic solutions and radiation for nearly 40 years. Long-term degradation (aging) of ferrocyanide is known to have occurred through chemical and radiolytic processes in the waste (Lilga et al. 1993, 1994). Analyses of core samples taken from six of the eighteen ferrocyanide tanks reveal fuel values about an order of magnitude less than the original flowsheet concentrations. These remaining fuel values are well below the concentration of concern. Experimental work at Georgia Tech (Ashby 1994) and PNL (Camaioni et al. 1994) have demonstrated that complexants and other organics degrade under radiation and/or chemical oxidation conditions found in tanks. In addition, 101-SY core sample analysis of the originally complexant waste identified extensive chemical degradation products (Campbell et al. 1994).

**Near-Term Characterization of the Condensed Phase.** Current characterization efforts are focused on testing of tank waste samples to confirm that the criteria shown in Table 2 are conservative for actual waste. That is, if the waste meets the energy (fuel value), TOC, or moisture criterion, then the waste will not support a propagating reaction. Waste from selected tanks will be tested for reaction propagation in the same type of adiabatic calorimeter (the Reactive System Screening Tool) that was used to develop the criteria (Fauske 1995).

Near-term sampling efforts are also focused on confirming degradation of ferrocyanide and organic complexant wastes. Full-depth core samples from ferrocyanide tanks will be analyzed for fuel, nickel (a signature analyte of the sodium nickel ferrocyanide scavenging campaign), and total cyanide to confirm ferrocyanide aging. Full-depth cores for organic complexant tanks will be analyzed for organic species to confirm that organic complexants have degraded to less energetic species. In addition, liquid and solid samples from organic complexant tanks will be analyzed to confirm laboratory demonstration that high energy organic complexants are soluble. The near-term characterization requirements are described in the following DQOs: *Data Requirements for the Ferrocyanide Safety Issues Developed Through the Data Quality Objectives Process* (WHC-SD-WM-DQO-007) and *Data Quality Objective to Support Resolution of the Organic Fuel Rich Tank Safety Issue* (WHC-SD-WM-DQO-006). A summary of these characterization needs is presented in Section 4.0.

### 3.2.5 Reaction Ignition

**Credible Ignition Sources.** If the waste has a sufficiently high fuel and low moisture content, a propagating reaction could be initiated if an energy source raised the temperature of the waste to the reaction initiation temperature. The potential for tank farm equipment and operations to initiate propagating reactions has been evaluated (Scaief 1991, Bajwa 1994), and a brief summary is presented in Table 3. All credible initiators would be

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located near the waste surface, with the exception of rotary core drilling incidents and lightning.

Although rotary core drilling incidents and lightning strikes cannot be deemed incredible initiating events, the risk can be mitigated with controls. The rotary core driller is designed with safety interlocks that limit drill bit temperature increases. Ignition from lightning strikes can be prevented by appropriate grounding. The need to further ground the single-shell tanks is being studied because of their unique construction.

Table 3. Summary of Operations Evaluation

Operation	Incident Conditions	Location of Heating	Heating Potential
In-tank instrumentation	Electrical overcurrent	Waste surface	<1 J (1)
Still camera photography	Dropping flash unit onto the waste surface, hot filament contacts waste	Waste surface	<70 J (2)
Video camera	Dropping light unit onto the waste surface, hot filament contacts waste	Waste surface	<70 J (2)
Rotary core sampling	Loss of bit cooling and failure to shut down drill sampler causes frictional heating	Bit/waste interface	<66 °C (3)
Vehicle operation above a tank	Rupture of fuel tank on aboveground equipment, fuel leakage into tank, subsequent fire	Waste surface	High (4)
Welding or grinding	Hot slag/sparks contact waste	Waste surface	<100 J (2)
Lightning strikes	Lightning strike on or near a tank or equipment causes lightning current to reach the waste	Arc to waste surface or from immersed object to waste below the surface	>1 MJ (5)

(1) Data from Grigsby et al. (1995)

(2) Preliminary data from Fauske and Associates, Inc.

(3) Safety interlocks limit temperature rise in the waste to 66 °C.

(4) The heating potential depends on the amount of fuel present; localized heating to ignition temperatures is possible (Bajwa 1994).

(5) Data from Cowley (1994)

**Future Characterization of the Condensed Phase.** When the propagation testing of actual waste is completed and the threat from lightning strikes is thoroughly analyzed and/or mitigated, the characterization emphasis will begin to shift from full-depth to near-surface waste. Therefore, future sampling and characterization efforts for safe storage are expected to focus on the presence of moisture in the waste surface (upper 15 cm) (Meacham et al. 1995). However, even the need for near-surface measurements may be reduced depending on the outcome of ongoing ignition source studies.

Preliminary laboratory tests were conducted to quantify the ignition source required to initiate a propagating reaction. These tests indicate that even a small amount of moisture can prevent initiation. With the presence of only 5 wt% free moisture, stoichiometric mixtures of organic complexants and sodium nitrate could not be ignited by 1300 °C steel particles (energy content ranging from 10 to 270 J) or a strong ignition source of about 138 J (energy released in about 3 msec).

These preliminary results suggest that potential ignition sources associated with tank intrusive activities (Table 3) might be ruled out as viable ignition sources. Additional work to quantify ignition energy requirements might reduce or eliminate all credible ignition sources for propagating reactions. Elimination of the credible ignition sources would substantially decrease the need for condensed phase sampling to ensure safe storage.

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#### 4.0 SUMMARY OF INFORMATION REQUIRED FROM EARLY CHARACTERIZATION EFFORTS

Although a safety envelope with appropriate controls has been developed for waste tank operations, it is important that the characterization program focus on providing information that addresses the technical issues associated with the analyses used in establishing the safety basis. Information is, therefore, required from the characterization program to; (a) provide information necessary for complete closure of each safety issue, or (b) further confirm the models used in the safety analysis. Characterization information will also be used to reduce the uncertainty associated with the safety analysis calculations and confirm the conservatism of the source term data used in the analysis. The initial characterization information will thus provide the basis for confirming, relaxing, or eliminating controls presently in place through the IOSRs. Waste characterization will also provide necessary information to establish the safety basis and operational information for pretreatment, retrieval and disposal of the tank wastes.

The following tables summarize the safety needs from the characterization efforts as detailed in the appropriate DQOs. The tables follow the same sequence as the safety issues discussed in Section 3.0.

Table 4. Summary of Characterization Needs For Flammable Gas Safety Issue

Safety Issue	Primary Data Requirements	Secondary Data Requirements
Flammable Gas	Hydrogen Nitrous Oxide Ammonia Methane	Major anions, cations, and water Total Organic Carbon, organic chelating agents, decomposition products, formate and oxalate Stratum identification and description Density of bulk samples, liquid phase and settled solids Rheological properties (viscosity and shear strength) Solids content and settling rate Solubility of solids Bulk enthalpy Radionuclides
Reference: Table III and Table IV, Flammable Gas DQO, WHC-SD-WM-DQO-004		

Table 5. Summary of Characterization Needs for Ferrocyanide and Organic Safety Issues

Safety Issue	Primary Data Requirements	Secondary Data Requirements
Ferrocyanide	Fuel Moisture Nickel Fuel and Nickel	Cations (Al, Bi, Ca, Fe, P, Na) Total Cyanide Total Organic Carbon Total Carbon Particle Size
Reference: Table 7-2 and Table 7-3, Ferrocyanide DQO, WHC-SD-WM-DQO-007		
Organic	Total organic carbon Moisture content in half segment Presence of organic floating layer Tank temperature Total fuel content	Total moisture analysis Principal organic species Equilibrium moisture content <sup>137</sup> Cs and <sup>90</sup> Sr Chromium and manganese oxidation state Chromium and manganese concentration Hydroxide concentration
Reference: Table 7-1 and Table 7-2; Organic Fuel DQO, WHC-SD-WM-DQO-006		

Table 6. Summary of Characterization Needs for Noxious Vapors

Safety Issue	Primary Data Requirements	Secondary Data Requirements
Noxious Vapors	Combustible gas meter measurement	Acetone, acetonitrile, benzene, 1,3-butadiene, butanal, n-butanol, n-hexane, methane, propane nitrile  CO <sub>2</sub> , CO, CH <sub>4</sub> , H <sub>2</sub> , N <sub>2</sub> O, NO, NO <sub>2</sub>  H <sub>2</sub> O  NH <sub>3</sub>  Acetone, acetonitrile, benzene, butanol, n-dodecane, n-hexane, propane nitrile, tributyl phosphate, n-tridecane
Reference: Table 7-1, Attachment A, Health and Safety Vapor Issue DQO, WHC-SD-WM-DQO-002		

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