DISTRIBUTION SHEET

To	From	Page 1 of 1
Distribution	Data Quality Objectives and Technical Support	Date 4/26/95
Project Title/Work Order		EDT No.
Tank Safety Screening Data Quality Objective, WHC-SD-WM-SP-004, Rev. 1		ECN No. 166544

Name	MSIN	Text With All Attach.	Text Only	Attach./ Appendix Only	EDT/ECN Only
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ENGINEERING CHANGE NOTICE

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1. ECN 166544

Proj. ECN

2. ECN Category (mark one)	3. Originator's Name, Organization, MSIN, and Telephone No.	3a. USQ Required?	4. Date
Supplemental [] Direct Revision [X] Change ECN [] Temporary [] Standby [] Supersedure [] Cancel/Void []	Hunt, J. W. 8E100, T6-07, 373-1013	[] Yes [X] No	April 20, 1995
	5. Project Title/No./Work Order No.	6. Bldg./Sys./Fac. No.	7. Approval Designator
	Tank Safety Screening Data Quality Objective/WHC-SD-WM-SP-004, Rev. 1/ N4A2K	N/A	~~N/A~~ S Q (SHK 8/25/95)
	8. Document Numbers Changed by this ECN (includes sheet no. and rev.)	9. Related ECN No(s).	10. Related PO No.
	WHC-SD-WM-SP-004, Rev. 0	N/A	N/A

11a. Modification Work	11b. Work Package No.	11c. Modification Work Complete	11d. Restored to Original Condition (Temp. or Standby ECN only)
[] Yes (fill out Blk. 11b) [X] No (NA Blks. 11b, 11c, 11d)	N/A	N/A Cog. Engineer Signature & Date	N/A Cog. Engineer Signature & Date

12. Description of Change

Reissue as Rev. 1, in its entirety.

13a. Justification (mark one)

Criteria Change	[X]	Design Improvement	[]	Environmental	[]	Facility Deactivation	[]
As-Found	[]	Facilitate Const	[]	Const. Error/Omission	[]	Design Error/Omission	[]

13b. Justification Details

Document revision was done to reflect modification of decision variables and analytical methods, use of metrics, and clarifications based on studies conducted since issue of the Rev. 0 document. The Rev. 1 document becomes the baseline DQO for tank safety screening. Attachment A is added.

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

See Distribution Sheet

~~RELEASE STAMP~~

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DATE APR 27 1995

STA 4

A-7900-013-2 (11/94) GEF095

A-7900-013-1 (11/88)

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

18. Change Impact Review: Indicate the related documents (other than the engineering documents identified on Side 1) that will be affected by the change described in Block 12. Enter the affected document number in Block 19.

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

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

Document Number/Revision	Document Number/Revision	Document Number Revision

20. Approvals

Signature	Date	Signature	Date
OPERATIONS AND ENGINEERING		ARCHITECT-ENGINEER	
Cog. Eng. J. W. Hunt *John W Hunt*	4/27/95	PE	
Cog. Mgr. D. G. Baide *D G Baide*	4/27/95	QA	
QA T. C. Trible *T.C. Trible*	4/26/95	Safety	
Safety J. A. Harvey *[signature]*	4/26/95	Design	
Environ.		Environ.	
Other: Prog Mgr. G. T. Dukelow *G T Dukelow*	4/27/95	Other	
Characterization Process Engineering Manager, J. P. Sloughter *[signature]*	4-28-95		
		DEPARTMENT OF ENERGY	
		Signature or a Control Number that tracks the Approval Signature	
		ADDITIONAL	

RELEASE AUTHORIZATION

Document Number:	WHC-SD-WM-SP-004, REV.1
Document Title:	Tank Safety Screening Data Quality Objective
Release Date:	April 27, 1995

This document was reviewed following the procedures described in WHC-CM-3-4 and is:

APPROVED FOR PUBLIC RELEASE

WHC Information Release Administration Specialist:

Kara M. Broz — April 27, 1995

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DISCLAIMER

SUPPORTING DOCUMENT		1. Total Pages 59
2. Title Tank Safety Screening Data Quality Objective	3. Number WHC-SD-WM-SP-004	4. Rev No. 1
5. Key Words Characterization, Criticality, Data Quality Objective, DNFSB, DQO, Ferrocyanide, Flammable Gas, Organics, Safety Screening	6. Author Name: John W. Hunt Signature Organization/Charge Code 71300/N4A2K	

7. Abstract

The Tank Safety Screening Data Quality Objective (DQO) will be used to classify 149 single shell tanks and 28 double shell tanks containing high-level radioactive waste into safety categories for safety issues dealing with the presence of ferrocyanide, organics, flammable gases, and criticality.

Decision rules used to classify a tank as "safe" or "not safe" are presented. Primary and secondary decision variables used for safety status classification are discussed. The number and type of samples required are presented. A tabular identification of each analyte to be measured to support the safety classification, the analytical method to be used, the type of sample, the decision threshold for each analyte that would, if violated, place the tank on the safety issue watch list, and the assumed (desired) analytical uncertainty are provided.

This is a living document that should be evaluated for updates on a semiannual basis. Evaluation areas consist of: identification of tanks that have been added or deleted from the specific safety issue watch lists, changes in primary and secondary decision variables, changes in decision rules used for the safety status classification, and changes in analytical requirements.

This document directly supports all safety issue specific DQOs and additional characterization DQO efforts associated with pretreatment and retrieval. Additionally, information obtained during implementation can assist in resolving assumptions for revised safety strategies, and in addition, obtaining information which will support the determination of error tolerances, confidence levels, and optimization schemes for later revised safety strategy documentation.

8. RELEASE STAMP

TANK SAFETY SCREENING DATA QUALITY OBJECTIVE

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April 1995

MASTER

TANK SAFETY SCREENING DATA QUALITY OBJECTIVE

EXECUTIVE SUMMARY

This Tank Safety Screening Data Quality Objective (DQO) will be used to classify 149 single-shell tanks and 28 double-shell tanks containing radioactive waste into specific safety categories for safety issues dealing with the presence of ferrocyanide, organics, and flammable gases, as well as criticality. Issues related to the vapor safety issue will be handled elsewhere. Safety screening for high-heat tanks has already been completed as part of that program's activities. Decision rules used to classify a tank as "safe" or "not safe" are presented. Decision variables used for safety status classification are discussed. The number and type of samples required for safety screening is presented. Data are presented in tables that identify each analyte to be measured, the analytical method to be used, the type of sample, the decision threshold for each analyte that would, if violated, place the tank on the safety issue Watch List, and the assumed (desired) analytical uncertainty.

This safety screening DQO focuses on the following items:

1. Sampling all Watch List tanks for conditions other than those that placed it on a Watch List. Such conditions include the presence of oxidizable fuel or high concentrations of flammable gasses. The DQO affirms the presence of conditions that originally placed the tank on the Watch List.

2. Sampling all non-Watch List tanks for all safety concerns.

3. Determining if tanks are above the threshold levels (safety specifications). Such tanks are to be labeled "not safe" and further evaluated employing safety issue-specific DQOs.

At least two vertical profiles of the liquid and solid portions of the tank shall be obtained as part of this screening activity. If valid assay data exist from prior sampling efforts, replication of those assays need not be done. In addition to sampling the solid and liquid wastes, the dome spaces of all tanks shall be sampled for flammable gas content. Table ES-1 identifies a common set of simple analytes that form the basis of this screening DQO.

Table ES-1. Analytes for Safety Screening DQO.

Analyte	Safety issue
Fuel energy value (J/g)/(cal/g)	Ferrocyanide, organics, and flammable gas
Fissiles, heavy metals, and related assays[2] or Total alpha	Criticality[1]
Weight percent (wt%) water	Ferrocyanide, organics, and flammable gas
Gas composition (% lower flammability limit [LFL])	Flammable gas

Notes:

[1]The criticality program does not presently have a DQO. Therefore, for criticality safety validation, this safety screening DQO includes a requirement for criticality screening to include either fissile materials, neutron sorbers, and poisons or total alpha concentration.

[2]Within a tank group, only selected tanks will be analyzed for fissiles, heavy metals and related assays. Other tanks in the same tank group will be analyzed for total alpha. Selected tanks will be determined by information from tank groupings and other historical data.

This document shall be evaluated periodically to determine whether information gained from characterization or other data affects its validity.

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ACRONYMS

DOE	U.S. Department of Energy
DQO	Data Quality Objective
DSC	Differential scanning calorimetry
DST	Double-shell tanks
GC	Gas chromatography
LFL	Lower flammability limit
MS	Mass Spectrometer
PQL	Practical Quantification Limit
RSST	Reactive System Screening Tool
SST	Single-shell tanks
TCP	Tank characterization plan
TGA	Thermogravimetric analysis
TOC	Total organic carbon
TWRS	Tank Waste Remediation System
WTSP	Waste Tank Safety Program

TANK SAFETY SCREENING DATA QUALITY OBJECTIVE

1.0 INTRODUCTION

The Tank Waste Remediation System (TWRS) has adopted a Data Quality Objective (DQO) process to define the information needs required to support programmatic decisions (Babad et al. 1994b). The tank safety screening DQO, one of a series of TWRS safety and programmatic DQOs, defines the data needed for the Waste Tank Safety Program (WTSP) to determine that the 149 single-shell tanks (SSTs) and the 28 double-shell tanks (DSTs) at the Hanford Site have been appropriately categorized as to whether or not safety issues exist for each tank. This represents the first application of safety DQOs to the SSTs and DSTs at the Hanford Site. For more information, see Babad et al. (1994b).

Currently, the WTSP has identified six safety issues (Reep 1993, Gasper 1993):

- Ferrocyanide
- Organic
- Flammable Gas
- Criticality
- High Heat Conditions
- Vapor

Only the ferrocyanide, organic, flammable gas, and criticality safety issues are examined in this tank safety screening. All tanks have been previously screened for high heat conditions using thermocouple and heat transfer data. The vapor program is being handled separately. Validation of a lack of criticality concerns is included in this screening document to affirm the technical basis for closing the unreviewed safety question (Braun 1994), because issue closure is being based, in part, on only a partial list of tank specific analyses.

Application of the screening module shall be performed on tanks that are both on, and not on, the existing safety issue Watch Lists. Safety classification of waste tanks consists of three categories: "safe," "conditionally safe," and "unsafe" (Grumbly 1993). This DQO uses two safety classifications, "safe" or "not safe." The "safe" classification means that a tank meets "safe" criteria for energetics or flammable gas concentration as defined in Grumbly (1993). The "not safe" classification means that a tank is either "conditionally safe" or "unsafe," as defined in Grumbly (1993). If a tank falls into the second ("not safe") category, additional analysis, as defined in the specific safety issue DQOs, shall define whether the tank is "conditionally safe" or "unsafe."

Use of the safety screening DQO is restricted to providing data for placing a tank on a safety issue Watch List by identifying the tank as potentially "not safe." Safety issue-specific DQOs define data requirements to support the removal of a tank from a safety issue Watch List. The logic to support the removal of a tank from a safety issue Watch List. The logic underlying safety screening (see Figure 1) has been adapted from Page 28 of the Department of Energy response to Defense Nuclear Facility Safety Board characterization concerns, namely *Recommendation 93-5 Implementation Plan* (DOE 1994). Applying the tank safety screening DQO process is the first step. This is accomplished and reported within 45 days after the sampling event, based on the date that the last sample or segment was delivered to the analytical laboratory. Real-time notification of the potential for a "not safe" tank is provided by Hanford Analytical Services to the Waste Tank Safety Program, Tank Farm Operations, and the Waste Tank Characterization Program whenever analysis indicates a tank may be classified as "not safe." This early notification should occur before data validation has been performed.

As stated earlier, the high heat issue (Wang 1993) is not examined as part of safety screening. To determine whether a safety issue exists, the primary decision variable for determination of a high-heat safety issue is the in-tank waste temperature distribution, which is a function of heat generation rate, thermal conductivity, heat transfer paths, and other variables. This screening has already been conducted, and 11 SSTs are actively monitored because of high-heat-generating waste (Bander 1993a, 1993b, and 1994). Only one of these (tank 241-C-106) requires forced-air cooling and water additions. This tank is being addressed under a separate DQO (Wang et al. 1994).

Vapor safety concerns are also not examined as part of safety screening. A separate vapor issue program examines potential vapor releases from tanks for vapor species identification and toxicological evaluation. The program relies on identifying the specific composition of the vapor by sampling the richest source of vapor (that found in the tank dome space). The program also monitors key vapor constituents at leak and exit points on the tanks and in the working environment above the tanks, and employs personnel monitoring techniques for assuring worker safety (Osborne 1993).

2.0 SAFETY SCREENING DECISION LOGIC

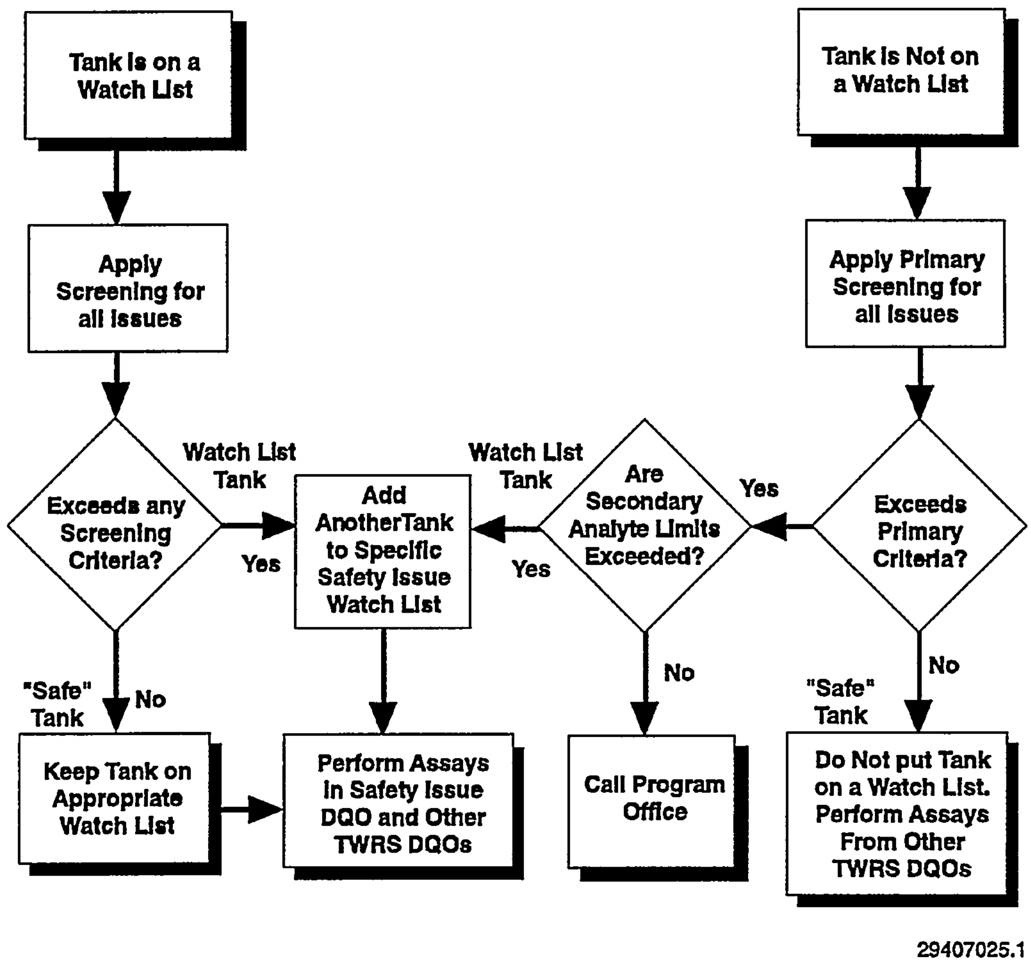
2.1 THE QUESTIONS

Two questions are addressed by this safety screening DQO:

1. If a tank is on a safety issue Watch List, should it be added to another safety issue Watch List? If so, which one?

2. If a tank is not on a safety issue Watch List, should it be placed on a safety issue Watch List? If so, which one?

Figure 1. Detailed Safety Screening DQO Decision Logic.



2.2 DECISIONS TO BE MADE

The decisions to be made for either or both questions presented in Section 2.1 are:

1. After safety screening data have been collected for each of the SSTs and DSTs, which safety issue Watch List, if any, should each specific tank be on?

2. If a tank is currently on a specific safety issue Watch List, evaluation of the tank screening data will support three decisions:

   a. Decision 1. If the tank exceeds safety issue screening criteria, the tank remains classified as "not safe." By definition, tanks on a Watch List fall into this category.

   b. Decision 2. If the tank is classified as "not safe," the tank must be included in the corresponding specific safety issue, and actions appropriate to that safety issue must be taken to assure the safety of the tank. Sampling and analyses required from characterization are controlled by the specific safety issue DQO.

   c. Decision 3. If the tank does <u>not</u> exceed any safety screening criteria, the tank is further evaluated to remove it from the Watch List in accordance with the applicable DQO or other safety program-sponsored studies.

3. If a tank is <u>not</u> currently on a specific safety issue list, evaluation of the tank screening data will support four decisions.

   a. Decision 1. If the tank does not exceed a safety issue screening criterion (see Table 3), the tank is classified as "safe." No further characterization associated with the safety programs is needed.

   b. Decision 2. If the tank exceeds safety screening criteria, the tank is classified as "not safe."

   c. Decision 3. If the tank is classified as "not safe" relative to energetics, the tank must be screened for secondary analytes (see Table 4) to determine to which Watch List it belongs.

   d. Decision 4. If the tank is classified as "not safe," the tank must be included in the corresponding specific safety issue and actions appropriate to that safety issue must be taken to assure the safety of that tank. Sampling and analyses required from characterization are controlled by the specific safety issue DQO.

3.0 DATA REQUIREMENTS

3.1 APPLICABILITY

This Safety Screening DQO applies to all 177 Hanford Site SSTs and DSTs. Although tables in this section deal with the SSTs and DSTs, except for defining sampling intervals (which will need to be decided on a case-by-case basis, all other aspects of this DQO apply to various process and other miscellaneous underground storage tanks. This safety screening DQO requires that a vertical profile of the waste be obtained from at least two widely-spaced vertical samples (e.g., risers). See Section 3.2 for the rationale underlying this requirement. Such an effort need be done only once for each tank, assuming the quality of the data obtained supports appropriate safety classification of the tanks. Such sampling can be done by core drilling, by auger sampling (for shallow tanks) and/or by obtaining liquid supernates samples at several levels (e.g., grab samples).

3.2 ANALYTES OF CONCERN

One result of the studies done to define this safety screening DQO is the documenting of a commonality of assays that cut across safety issues. The flammable gas issue and the criticality issue apply to both SSTs and DSTs. A secondary concern of the flammable gas issue is the question of whether a given crust in a tank is sufficiently fuel rich and dry so that it poses a potential for crust burn, should a flammable dome gas be ignited (McDuffie 1994). Because the organic and ferrocyanide tanks can also generate flammable gases (e.g., ammonia and hydrogen), they, too, require verification that the dome space is below the lower flammability limit (LFL) criterion.

The ferrocyanide and organics programs focus predominately on SSTs, although the DSTs will be screened for these concerns. There are fewer safety screening analytes than safety issues because organic and ferrocyanide programs share a concern with fuel-oxidizer concerns, for which energetics is the best determinant. This commonality of analytes is illustrated in Table 1.

Table 1. The Commonality of the Primary Analytes to be Measured for Safety Screening Classification.

Analyte to be measured (decision variable)	FeCN	Organics	Flammable gas	Criticality
Fuel energy content [J/g or cal/g dry, weight basis]	x	x	x	
^{239}Pu and ^{240}Pu, Fe, Mn, U, Cr, Ni, Al, Na, Si, specific gravity, bulk density or Total alpha				x[2]
Wt% Water[1]	x	x	x	
% LFL of Gases			x	

Notes:

[1]Moisture (water) is a key characteristic for determining the risk from a secondary crust burn, and so is a part of the flammability issue.

[2]Within a tank group, only selected tanks will be analyzed for fissiles, heavy metals, and related assays. Other tanks in the same tank group will be analyzed for total alpha. Selected tanks will be determined by information from tank groupings and other historical data.

Specific data requirements and decision thresholds (criteria) are indicated in Table 2. Based on the data collected for each analyte, an upper (90%) confidence value will be computed for average values. This value will be compared to the decision threshold to classify a tank as "safe" or "not safe." This value is based on the authors' engineering judgement.

This DQO assumes a needed precision related to the practical quantification limit (PQL) and a needed ±10% (or less) accuracy related to the primary safety specification. Three considerations allowed the authors to choose the required uncertainties defined in the analytical requirements tables (see Tables 3 and 4).

1. The precisions were demonstrated with blind samples. Hanford Site Laboratories are capable of meeting these accuracies based on the tests that have been performed.

2. The analytical uncertainties proposed correspond to the values that are being established by the specific safety issue DQOs.

3. The expected cost of achieving a higher precision and accuracy is substantially higher, yet higher precision and accuracy levels do not appear to enhance the decision process significantly.

Table 2. Decision Variables and Criteria Used for Safety Issue Classification to Classify Tank as "Safe."

Safety issue	Primary decision variables	Primary decision criterion
Ferrocyanide	Total fuel content (energetics)	≤ 480 J/g (115 cal/g)[3]
	Wt% water	See Figure 4-1 in Meacham et al. (1994)
	Flammability of gases	≤ 25% LFL all flammable gases
Organics[1]	Total fuel content (energetics)	≤ 480 J/g (115 cal/g)[3]
	Wt% water[2]	≥ 17 wt%
	Flammability of gases	≤ 25% LFL all flammable gases
Flammable Gas	Flammability of gases	≤ 25% LFL all flammable gases
Criticality[4, 5]	Total ^{239}Pu and ^{240}Pu or Total alpha	< 1 g/L

Notes:

[1]The present safety specification for organic Watch List tanks is related to total organic carbon (TOC). Although energetics is a more accurate measure of tank risk, the existence of a TOC specification (see Babad and Turner 1993) requires measurement of this parameter. TOC assay is required by only the organic DQO (Babad et al. 1994a).

[2]A moisture (water) determination by thermogravimetric analysis is required to interpret the energetics measurement. Therefore, although listed separately, the moisture (water) assay is an integral part of determining the energetics of the waste.

[3]The criterion of 480 J/g (115 cal/g) dry weight basis represents a conservative compromise between the data found by the ferrocyanide, flammable gas and organics programs. The 480 J/g (115 cal/g) is the lowest value defined by any of the safety programs; it is the most conservative value. In all instances, this data is conservative relative to the risk caused by the presence of energy-rich materials in the waste because this energy is less than 50% of what is needed to achieve propagation in a dry system.

[4]Collecting data on plutonium and neutron poisons in the sludges provides the assurance that the assumptions in the criticality safety assessment (Braun 1994) are indeed correct and verified. Should analytical results exceed the fissile material concentration limit, constraints will be placed on the tank while the data is being reviewed for safety implications. An unreviewed safety question screen will also be done on the results in accordance with Westinghouse Hanford Company (WHC) and U.S. Department of Energy (DOE) procedures. Heavy metal analytes, as well as specific gravity and bulk density measurements, are needed as additional analyses for criticality calculations.

[5]Within a tank group, only selected tanks will be analyzed for fissiles, heavy metals, and related assays. Other tanks in the same tank group will be analyzed for total alpha. Selected tanks will be determined by information from tank groupings and other historical data.

Table 3. Analytical Requirements for Safety Screening.

Analyte to be measured	Sampling interval	Analytical method[4]	Required analytical uncertainty
Total fuel energy content (Energetics in J/g or cal/g dry weight basis)	Half segment (sludge) Half segment (saltcake) Drainable liquid[1]	Differential scanning calorimetry supported by thermogravimetric analysis (TGA)[2]	±10% of decision threshold of 480 J/g (115 cal/g) dry wt% basis. PQL[3] (sample dependent)
% Water (on unhomogenized samples)	Half segment (sludge) Half segment (saltcake) Drainable liquid[1]	Thermogravimetric analysis (TGA)	±10% of decision threshold assumed to be 17% water. PQL = 2%
Gas composition (used to estimate % of LFL for all gases)	Dome space sampling or monitoring Homogenized	Gas chromatography/mass spectrometer (GC/MS) Gas-specific monitoring gauges, when installed (may be used as a check on vapor sampling, e.g., Whitaker Gauge)	Unknown (to be determined in the vapor analysis DQO being prepared by flammable gas program).

Table 3. Analytical Requirements for Safety Screening.

Analyte to be measured	Sampling interval	Analytical method[4]	Required analytical uncertainty
Fissile materials and neutron sorbers and/or poisons[5]	Sludge - Take the bottom-most half segment (with respect to the tank) of every segment	<u>Selected tanks of a tank group[6]:</u> Perform ^{239}Pu and ^{240}Pu concentration analysis	Best laboratory practices.
		Determine iron, manganese, uranium, chromium, nickel, aluminum, sodium, and silicon concentrations by inductively coupled plasma analysis	±10% of decision threshold of 1 g/L fissile materials. PQL (sample dependent)
		Determine specific gravity and bulk density	
	Saltcake and drainable liquids - Take the bottom-most half segment (with respect to the tank) of every segment	Total alpha concentration	
	Sludge - Take the bottom-most half segment (with respect to the tank) of every segment	<u>Remaining tanks of a tank group:</u> Total alpha concentration	±10% of decision threshold of 1 g/L fissile materials. PQL (sample dependent)
	Saltcake and drainable liquids - None		

Table 3 Notes:

[1]For Ferrocyanide Watch List Tanks, the sampling interval is quarter segment (sludge) and half segment (saltcake).

[2]Half segment using duplicate half samples. If one of the pairs of duplicates exceed the limit, another pair of duplicates should be run. If analytical uncertainty is still too high, use TGA or a larger sample as defined in Table 7-2 of Babad et al. (1994a).

[3]Practical quantification limit is usually taken as 10 x the method detection limit. For this DQO, the term is used to represent the lowest analyte value needed to make defensible safety assumptions.

[4]All appropriate blanks and standards will be defined in the tank characterization plan (TCP). A 45-day turnaround for reporting on all assays required by this DQO, other than criticality, is desired. The fissile materials assays for criticality should be available in a 90-day turn-around period.

[5]These analyses are not required to be completed within the 45-day time period.

[6]Within a tank group, only selected tanks will be analyzed for fissiles, heavy metals, and related assays. Other tanks in the same tank group will be analyzed for total alpha. Selected tanks will be determined by information from tank groupings and other historical data.

Finally, to help create tank-specific individual tank characterization plans (TCPs), Table 3 lists the primary analytical requirements for safety screening. Table 4 lists the analyses to be done if a non-Watch List tank exceeds energetics screening. These analyses will allow a tank to be placed on the appropriate Watch List or for operating controls to be placed on that tank (e.g., criticality concerns). Table 4 also defines the analyte to be measured, the sampling interval for that analyte, and the analytical methods desired, and refers to sources that describe the desired precision and accuracy required from that assay.

The assays described in Tables 3 and 4 shall be performed in compliance with the requirements defined in the *Hanford Analytical Services Quality Assurance Plan* (DOE/RL 1994), when implemented. Examples of how Tables 3 and 4 work in accord with the decision logic are provided below.

Example 1. If a tank that is currently on the flammable gas Watch List shows energetics above the screening criteria, it needs to be evaluated relative to placement on the organic or ferrocyanide Watch List by evaluating the results of the measurement of secondary analytes (see Table 4).

Example 2. A tank having a low total cyanide and a high TOC is obviously a candidate for the organic Watch List. The opposite is true for ferrocyanide tanks. Should neither the TOC nor the cyanide analysis prove sufficient to categorize the safety issue, a more detailed, applied, research-oriented evaluation of the problem would be required.

Example 3. If a tank is on the ferrocyanide Watch List but analysis of samples from the tank shows no energetics of concern, then the other analytes required by the ferrocyanide DQO are invoked to support removing that tank from the Watch List.

Table 4. Analysis to Be Performed if a Tank Exceeds Energetics Screen or if Total Alpha Specification is Exceeded.

Analyte to be measured	Sampling interval[2]	Analytical method[3]	Required analytical uncertainty
Total organic carbon (TOC)[1]	Half segment (sludge) Half segment (saltcake) Drainable liquid	Direct persulfate oxidation Furnace oxidation used for ferrocyanide and as backup method if energetics and TOC do not correlate	See Babad et al. (1994a and 1994b)
Total cyanide assay	Half segment (sludge) Half segment (saltcake) Drainable liquid	Micro cyanide distillation (e.g., Pacific Northwest Laboratory method)	See Meacham et al. (1994)
Total fuel energy content (Energetics in J/g or cal/g dry weight basis)	Half segment (sludge) Half segment (saltcake) Drainable liquid	Reactive system screening tool (RSST) (adiabatic calorimetry) if greater than or equal to 480 J/g (115 cal/g)[4]	
Fissile materials and neutron sorbers and/or poisons[5]	Sludge - Take the bottom-most half segment (with respect to the tank) of every segment Saltcake and drainable liquids - None	Perform ^{239}Pu and ^{240}Pu concentration analysis Determine iron, manganese, uranium, chromium, nickel, aluminum, sodium, and silicon concentrations by inductively coupled plasma analysis Determine specific gravity and bulk density	Best laboratory practices. ±10% of decision threshold of 1 g/L fissile materials. PQL (sample dependent).

Table 4 Notes:

[1]TOC, not energetics, is the present interim safety criteria for organic Watch List tanks. If the energetics is above 480 J/g (115 cal/g), then a screen for organics is to be run.

[2]Homogenized subsegments.

[3]All appropriate blanks and standards will be defined in the TCP. A 45-day turnaround for reporting on all assays required by this DQO, other than criticality, is desired.

[4]Adiabatic calorimetry in an RSST, or in an equivalent device, is used to validate assays that straddle the decision point. Using a large sample provides a more accurate measure of the waste's bulk energetics.

[5]If total alpha > 1g/L, the assays described are to be performed.

3.3 AN APPROACH TO TANK GROUPING

With present knowledge of the tanks, determination cannot be made, with any degree of confidence, of the minimum number of samples required to characterize the tank volume. Until data from specific sampling events are obtained that could lead to estimation of the distribution and variability of various waste components, simple models for physical laydown of the water must be relied upon. Such a model is based on the assumption that waste was laid down in the tank in essentially horizontal beds (e.g., "pseudo pancake"), one on top of another. Although a particular added waste layer might pitch out, it is unlikely that two widely-spaced vertical profiles of a tank would miss any safety analyte whose concentration and volume were sufficient to indicate a potential safety problem. The basis for the laydown model is discussed below.

The model presupposes, in accord with historical information, that the waste was added in the form of slurry (which was allowed to settle) through one or more tank risers (inlet pipes), or entered the tank in mostly liquid form from the overflow "cascade" pipes in linked SSTs. Figure 2 (top portion) illustrates a tank that is pseudo-pancake in configuration and that may be approximated by two radially separated cores. The second portion of the figure illustrates a tank that is non-pseudo pancake in configuration, in which the center composition of the waste cannot be assumed to approximate the composition at the edges of the waste.

Liquid waste was removed from a tank by means of a floating pump or other pump placed in the freestanding liquid. Solid waste was removed from tanks from the top surface by either mechanical sluicing and/or use of mixer pumps. Solids removal by mechanical sluicing and/or use of mixer pumps could have removed most of the waste (the predominant past operating practice). More recently, sluicing was often focused on the center of the tank only, to reduce the possibility of a tank leak caused by exposing tank walls. Historical records, including photographs, document both practices.

Alternative liquid removal methods resulted in stabilizing the tanks to reduce the available free liquid that could leak. Saltwell pumping from the bottom of a tank was used to remove drainable liquids, an operation that slowly removed the fluid from the waste solids, leaving the drained solids behind. Tank stabilization occasionally resulted in the settling of the saltcake as the drainable liquids were removed, leaving a depression in the center of the tank. This should not have mixed the contents of the waste.

Based on consideration of waste transfer into and out of tanks, a conceptual physical laydown model was developed and used, assuming that a minimum of two widely-spaced vertical profiles of a tank were needed to screen the tank. The proposed physical laydown model and associated grouping will be evaluated by:

- Comparison to sampling information. As sampling information is obtained, classification of tanks on a Watch List will be refined by evaluating the spatial (and sampling) variability within and between tank groups.
- Evaluation against historical transfer records. Historical information (e.g., Anderson 1990, Hanlon 1993) will be validated in terms of tank similarity based on waste transfers, waste type compositions, physical in-tank waste configurations, and validated sample and analysis data.

4.0 CONCLUSION

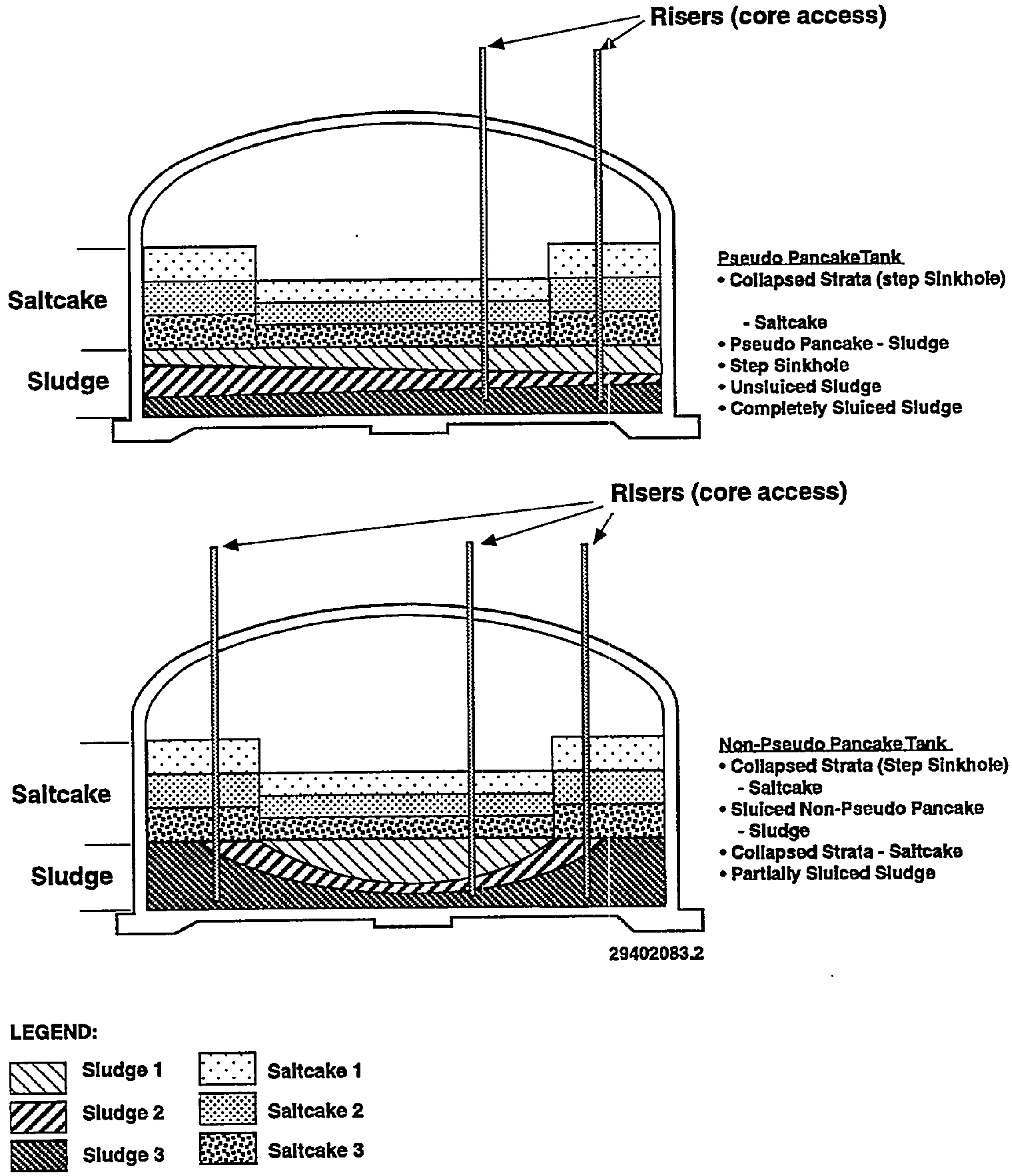
A safety screening module has been developed that allows for rapid classification of the 177 SSTs and DSTs containing high-level radioactive waste. The objective of the safety screening is to support tank safety issue resolution and to help identify if any additional tanks should be on a Watch List. Tanks that are already on a safety issue Watch List will be screened to confirm that the tank should remain on the original Watch List or if the tank should be added to another safety issue Watch List. Tanks that are not on safety issue Watch Lists will be screened to confirm either that the tank should remain classified as a "safe" tank or that the tank should be added to a safety issue Watch List.

The safety screening activity has been narrowed to the following issues: ferrocyanide, flammable gas, organic safety concerns, and criticality. Concerns related to high heat and vapor are not subject to this screening activity. Key parameters to be measured during screening have been reduced to four analytes: energetics; water; composition of the flammable gases in the dome space; and either total alpha or ^{239}Pu, ^{240}Pu, and heavy metals concentration. As other data are required, they will be obtained through application of specific safety program or other TWRS DQOs.

Once sampling efforts are complete, updated values of analyte precision and accuracy (relative standard deviations) will be computed using standard statistical methods. Such computations will be performed for various facies of the physical model. The criteria for total precision and accuracy estimates include complete and statistically valid estimates of laboratory variability, sample variability, and spatial variability. Optimal sampling and analysis plans can then be developed if needed.

Safety screening decision variables, criteria for placing a tank on a Watch List, and decision logic will be evaluated periodically for updates.

Figure 2. Tank Laydown Models - Sludge and Saltcake.



The purpose of such evaluation is to ensure that high confidence in placing an unsafe tank on a Watch List is maintained while performing sampling and assays in a cost-effective manner.

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ATTACHMENT A

WHC-SD-WM-DQO-012, Rev. 0

Data Requirements for the Safety Screening Issue Developed Through the Data Quality Objectives Process

Consisting of 34 Pages Including Introduction

INTRODUCTION:

Any strategy describing the overall approach to safe storage and disposal of waste must identify the problems and decisions requiring characterization data. Requirements for obtaining tank characterization information are developed through the use of the Data Quality Objectives (DQO) process. The DQO process addresses each decision or group of related decisions to specify data needs.

The initial attempt at performing the DQO process to address safety issues revealed points where significant assumptions would be required to proceed. Although the problems and decisions were identified, details of the error tolerances and confidence levels were difficult to develop. Attempts to optimize the data collection for each tank were affected by the limited locations from which samples could be obtained and concerns that samples did not represent overall waste contents. The complexity of sampling made it impossible to design a high confidence data acquisition scheme based solely on multiple samples, and necessitated review of the overall strategy for obtaining data and resolving issues.

A revised safety strategy for the storage of tank waste was developed, focused on ensuring safe operations over a range of waste material rather than on characterizing waste in great detail. The revised safety strategy includes several assumptions about the nature of the waste which require verification through additional sample analysis. Should these assumptions be shown to be well founded, the approach to screening the waste for safety issues and resolving those issues is considerably simplified. The following draft of the data requirements, based on the revised safety strategy, has been prepared.

Clearly any assumptions must be addressed before proceeding with the revised safety strategy. The preceding minor revisions to the baseline DQO document were found to be adequate to perform safety analyses in the near term, while specific additional information needs are pursued to verify the assumptions in the revised safety strategy. In addition to resolving the assumptions, the near term sampling events will obtain information which will support the determination of error tolerances, confidence levels, and optimization schemes in the finalized version of the revised safety strategy DQO. The approach taken in the revised baseline DQO document, simply requesting multiple samples per tank, is the appropriate first step to finalizing the optimization requirements.

The DQO process is iterative in nature. It is anticipated that the data collected in the near term, based on the revised baseline DQO document, will provide the added information needed to provide complete DQO requirements for longer term characterization. As such, the following revised safety strategy DQO may continue to undergo further development and revision as this added information becomes available. At the appropriate time after the revised safety strategy DQO is completed, the necessary reviews and approvals will be conducted and the document will become the new baseline.

WHC-SD-WM-DQO-012, Rev. 0

DATA REQUIREMENTS FOR THE SAFETY SCREENING ISSUE DEVELOPED THROUGH THE DATA QUALITY OBJECTIVES PROCESS

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T. M. Brown

April 1995

EXECUTIVE SUMMARY

This document applies the Data Quality Objectives process to the safety screening issue, and establishes data requirements for answering, on a tank-by-tank basis, all questions regarding safety of the 177 Hanford Site high-level waste storage tanks relative to the following danger potentials:

1) *Potential for buildup of flammable gases in the tank dome spaces or for dome space pressurization from gas releases*

2) *Potential for chemical reactions that produce hazardous consequences, such as toxic or radioactive releases or tank structural damage*

3) *Potential for release of toxic substances into the atmosphere.*

Application of the Data Quality Objectives process to the safety screening issue is directed toward ensuring continued safe storage of Hanford Site wastes through confirming the absence of dangerous potentials, providing bases for setting operating controls to mitigate safety problems, or giving bases for declaring unsafe conditions that require remediation. In practice, the safety screening process refers specific, potential safety issue problems to the appropriate safety programs, whose decision processes are covered in program-specific Data Quality Objectives, process, or strategy documents. The referral action is coupled with notification to operating management of recommendations for placement of proper work controls.

Decisions that drive safety screening require inputs that do not necessarily need to be obtained by future sampling and analysis or monitoring alone. All available sources of characterization information (including historical process information) are studied in order to create the most efficient sampling and analysis plan. The Data Quality Objectives decision process will be optimized by applying it subjectively to each tank on an individual basis. The process will be applied in preparation of the Tank Characterization Plans, not at the generic Data Quality Objectives levels. Sampling and Analysis Plans will be developed from the Tank Characterization Plans and will provide sampling crews and laboratories with the detailed plans required to obtain the necessary Data Quality Objectives information.

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DQO	Data Quality Objective
TCP	Tank Characterization Plan
SST	Single-Shell Tank
DST	Double-Shell Tank
TOC	Total Organic Carbon
LFLA	Lower Flammability Limit Approach
LFL	Lower Flammability Limit
CES	Consensus Exposure Standard

DATA REQUIREMENTS FOR THE SAFETY SCREENING ISSUE DEVELOPED THROUGH THE DATA QUALITY OBJECTIVES PROCESS

1.0 SCOPE OF THE SAFETY SCREENING DATA QUALITY OBJECTIVES PROCESS

The primary scope of the safety screening Data Quality Objectives (DQO) process is to ensure interim safe storage of single-shell tank (SST) and double-shell tank (DST) wastes. Specifically, the safety screening DQO process will determine if a tank is currently under safe storage conditions or if operating controls need to be initiated to provide interim safe storage conditions for the tank. The specific safety programs (Flammable Gas, Organic, and Ferrocyanide) will review the need for additional operating controls and will provide tank upgrades and/or mitigation as necessary for extended safe storage. This DQO follows the technical basis for safety screening outlined in *Approach for Tank Safety Characterization of Hanford Site Waste* (Meacham et al. 1995a).

For the safety issues involving chemical reactions (flammable gas, organic solvents, ferrocyanide, and organic complexants), the approach to safety characterization is based on the fact that rapid exothermic reactions cannot occur if either fuel, oxidizer, or temperature (initiators) is not sufficient or controlled. Because specific limits of fuel, oxidizer, and temperature (initiators) must be satisfied for a chemical reaction to occur, waste can be stored safely if the conditions for reaction are not met. Therefore, the characterization approach is to confirm that one of the conditions of fuel, oxidizer, or temperature (initiators) is not sufficient or that at least one condition is controlled.

The approach to characterization has been influenced by the progress made since mid-1993: (1) completion of safety analyses on ferrocyanide, criticality, organic solvent in tank 241-C-103, and sludge dryout: (2) successful mitigation of tank 241-SY-101; (3) demonstration of waste aging in laboratory experiments and from waste sampling; and (4) increased understanding of the information that can be obtained from dome space sampling. All these accomplishments have helped refine the direction of safety characterization.

Sources of data for safety characterization include: (1) reviews of process flowsheets, waste transfer records, monitoring data, and historical sample data; (2) visual inspections of the waste; (3) interrogation of the tank dome space using standard hydrogen monitors and vapor sampling; (4) moisture monitoring; and (5) analyses of waste samples obtained from liquid grab sampling, surface auger sampling, and full-depth core sampling. Dome space vapor sampling is being used to confirm that flammable gas does not accumulate in the SSTs, and to determine whether organic solvents are present. The dome spaces of tanks that may contain significant quantities of flammable gas will be monitored continuously using standard hydrogen monitors.

To understand more fully what the characterization needs are for exothermic chemical reaction issues, it is necessary to determine the depth of "near surface." Preliminary calculations (Appendix D in Meacham et al. 1995) have examined heat transfer through waste in contact with a high-temperature initiation source. These calculations suggest "near surface" is the top 2 to 14 cm of waste. A more rigorous study, to be completed in June 1995, will examine potential accident scenarios to better quantify "near surface." Results from this study could lead to reducing characterization needs for this issue to material only limited depths beneath the surface.

For the noxious vapors safety issue, characterization will consist of dome space vapor sampling of most of the Hanford Site waste tanks. Sampling specifically for criticality is not required to confirm interim safe storage; however, analyses for fissile material will be conducted as waste samples are obtained for other reasons. High-heat tanks will be identified through temperature monitoring coupled with thermal analyses.

In addition, the safety screening DQO process provides linkage with other safety issues (i.e., transfer of key issues that are outside the scope of this DQO process to other DQO processes) and Tank Waste Remediation System functional elements. The safety screening DQO does not change the Watch List status of the tanks. Safety issues regarding high heat and criticality are not addressed in this DQO process. As well, high concentrations of flammable gases in non-flammable gas tanks from episodic releases are not considered within the scope of this DQO process, but will continue to be studied by the Flammable Gas Safety program for possible future inclusion in the safety screening DQO process.

The safety screening approach is the same for SSTs and DSTs. However, the application of safety screening will be different for SSTs and DSTs. Safety screening will be applied to all SSTs. After safety screening of an SST is performed and any necessary controls (if any) are implemented, that tank is considered to be under safe storage conditions until a transfer occurs from the tank. Upon transferring any material from an SST, as is the case with interim stabilization, safety screening will again be applied to the tank to ensure that it is still under safe storage conditions.

Safety screening will be applied only once to all DSTs.. The screening will be performed to baseline the safe storage status of the DST. If any waste transfer occurs (either to or from the DST) after safety screening has been performed, then the DQO for Tank Farm Waste Compatibility Program will be applied to that tank (Fowler 1995). The waste compatibility DQO process will ensure that a DST remains under safe storage conditions after any waste transfers to or from that tank.

The safety screening DQO will consider all available sources of characterization information to provide the necessary decision inputs needed to address safety screening issues. The use of historical characterization information is necessary to ensure that the most efficient sampling and analysis plans are produced to meet the DQO data needs requirements.

The safety screening DQO will be applied separately to each tank. The seventh step of the DQO process (optimization) will not be performed until the Tank Characterization Plans (TCPs) are written. Sampling and analysis decisions, (e.g., number of samples, analytical methods, etc.), will not be made in this report but will be developed in the TCPs and sampling and analysis plans.

This document will follow, in order, the seven steps of the DQO process:

Step 1. State the Problem
Step 2. Identify the Decision
Step 3. Identify the Inputs to the Decision
Step 4. Define the Study Boundary
Step 5. Develop a Decision Rule
Step 6. Specify Acceptable Limits on Decision Errors
Step 7. Optimize the Design

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2.0 STATEMENT OF PROBLEM

This chapter completes the first step of the DQO process: *State the problem.* The problems to be examined are:

1) Is there a potential for exothermic chemical reactions in Hanford Site waste tanks?

2) Is there a potential for an accidental release of a noxious substance in Hanford Site waste tanks?

Possible safety conditions that give cause for concern are summarized below:

- Tank wastes may contain fuel and oxidizers combined in the condensed phase and may support an exothermic reaction. Specific fuels of concern are ferrocyanide and organic compounds.

- Tank wastes may contain organic liquids (pooled or entrained in porous solids) that may burn using atmospheric oxygen.

- Tank wastes may generate and retain flammable gases, giving rise to eventual release of concentrated flammable gas, which could lead to a reaction above the waste surface.

- Tank wastes may generate amounts of noxious vapors greater than the limits specified in the safety documentation (Leach 1993). These vapors include noxious vapors that are not anticipated to be found in the tank dome space.

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3.0 DECISION

3.1 DECISION TO RESOLVE PROBLEM

This chapter completes the second step of the DQO process: *Identify the decision.* **Each tank that is safety screened will either be determined to be under safe storage conditions or will be statused as needing operating controls to provide interim safe storage conditions.**

3.2 DECISION LOGIC

The multiple decision steps that are used to categorize the tanks as under safe storage conditions or as needing operating controls are listed below. The decisions used in the safety screening DQO are listed in a logical order such that some decisions only need to be addressed based on the outcome of previous decisions. Multiple decision steps will be stated in terms of questions that help to formulate the logic in the DQO. The resulting actions to be taken are specified after each decision statement.

Decisions:

1A. Are gases in dome space above 25% of the lower flammability limit (LFL)?

Action if Yes: Implement same controls as for a flammable gas Watch List tank (Schofield 1995). (Note that if the tank is already a flammable gas Watch List tank, the controls stay the same). Notify the Flammable Gas Safety Program. Proceed with the safety screening DQO.

Action if No: Proceed with the safety screening DQO.

Note that the National Fire Protection Association recommends that processes be controlled to less than 25% of the LFL.

1B. Are gases in dome space above the noxious vapor limits?

Action if Yes: Take immediate steps to restrict workers from the area. Refer to the DQO for Generic In-Tank Health and Safety Vapor Issue Resolution (Osborne 1994a). Notify Industrial Hygiene (note that Industrial Hygiene will direct the appropriate controls). Notify the Tank Vapor Issue Resolution Program. Proceed with the safety screening DQO.

Action if No: Proceed with the safety screening DQO.

1C. Do the gases indicate a potential immiscible organic phase entrained in the waste?

Action if Yes: Implement same controls as for an organic Watch List tank (Schofield 1995). (Note that if the tank is already an organic Watch List tank, the controls stay the same). Refer to the organic DQO (Buckley 1995). (Note that as part of the organic DQO, the characterization data will be reviewed for possible inclusion in the Watch List). Notify the Organic Tank Safety Program. Proceed with the safety screening DQO.

Action if No: Proceed with the safety screening DQO.

2. Is the surface moisture high enough to prevent an exothermic propagating reaction from occurring?

Action if Yes: Monitor waste to ensure continued safe interim storage. Safety screening decision process ends here.

Action if No: Proceed with the safety screening DQO.

3. Is the surface fuel content high enough for an exothermic propagating reaction to occur?

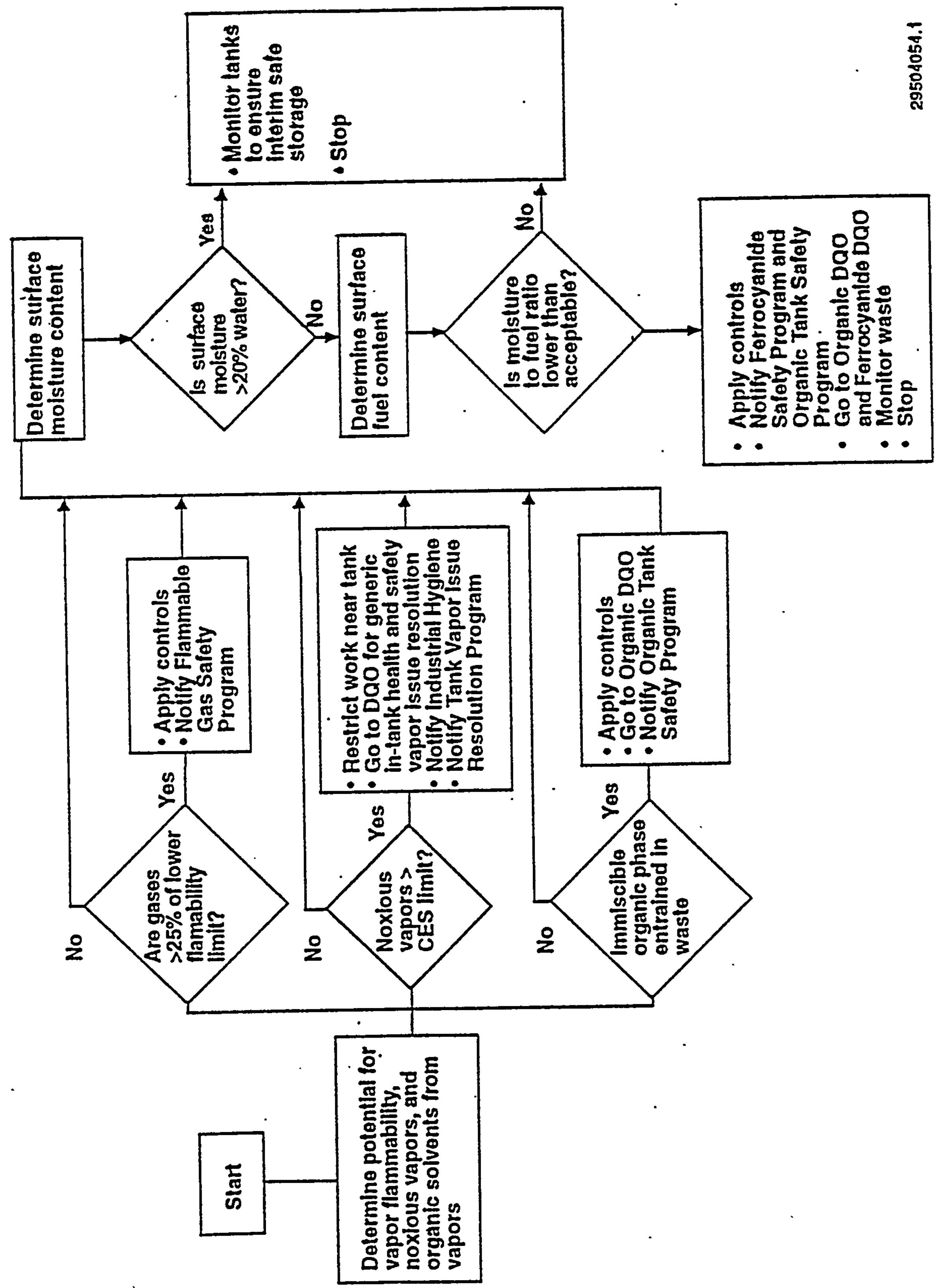
Action if Yes: Implement same controls as for an organic Watch List tank (Schofield 1995). (Note that if the tank is already a Watch List tank, the controls stay the same). Refer to the organic (Buckley 1995) and ferrocyanide (Meacham et al. 1995b) DQOs. (Note that as part of the organic and ferrocyanide DQOs, the characterization data will be reviewed for possible inclusion in the Watch List). Notify both the Ferrocyanide Safety program and the Organic Tank Safety Program. Monitor the waste as in Step 2. Safety screening decision process ends here.

Action if No: Monitor the waste to ensure continued safe interim storage as in Step 2. Safety screening decision process ends here.

Note that in Steps 2 and 3 above, monitoring of the tank is required. After safety screening characterization, monitoring parameters and schedules will be established to ensure safe storage of the waste. If any of the threshold limits are exceeded, monitoring parameters will be immediately established. Monitoring needs may differ for each tank because of differences between tank wastes and the safety margins.

The decision logic that is inherent in the above decision steps is given in Figure 3-1.

Figure 3-1. Logic Diagram for Safety Screening DQO Process.



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4.0 DECISION INPUTS

4.1 INPUTS REQUIRED TO RESOLVE DECISION

This chapter completes the third section of the DQO process: *Identify inputs to the decision.* **The decision inputs that are needed to make the decision are summarized in Table 4-1.**

In Section 3.2, the decision logic that forms the basis of the safety screening DQO was outlined. Decision inputs consist of the information or data that are needed to make the decision. It is important to distinguish at this point the difference between decision inputs and sample measurements. Decision inputs may consist of any piece of information or data that can help make the decision, and do not necessarily need to be from sampling and analysis. In Table 4-1, the decision input is listed along with the reason the decision input is needed. Each of the decision inputs listed below are connected to one of the five decisions listed in Section 3.2. These decisions are also summarized in the first column of Table 4-1 for each of the decision inputs. Note that the limits for the decision inputs are summarized in Section 6.0.

Table 4-1. Summary of Decision Inputs.

Decision Input	Decision	Reason for Requesting Decision Input
Vol% hydrogen	1A. Are gases above 25% of the LFL?	Hydrogen is considered to be the major contributor to the flammability of the tank dome space.
Vol% ammonia	1A.	Ammonia is another contributor to the flammability of the dome space.
Vol% methane	1A.	Contributor to flammability.
Vol% CO	1A.	Contributor to flammability.
[Ammonia]	1B. Are gases above noxious vapors limit?	Respiratory and eye irritant.
[CO_2]	1B.	Simple asphyxiant.
[CO]	1B.	Replaces oxygen in blood.
[NO]	1B.	Respiratory irritant.
[NO_2]	1B.	Respiratory irritant.
[N_2O]	1B.	Respiratory irritant.

Decision Input	Decision	Reason for Requesting Decision Input
Total organic carbon (TOC)	1B.	The presence of TOC in the vapor indicates that other noxious organic vapors could be present.
[Tributyl Phosphate]	1C. Is there an immiscible organic phase?	One of three dominant semivolatile compounds found in past tanks that have been vapor sampled. Indicative of a potential immiscible organic phase in the waste.
[n-dodecane]	1C.	Same as [tributyl phosphate] justification.
[n-tridecane]	1C.	Same as [tributyl phosphate] justification.
Observation of waste surface	2. Is surface of waste wet?	If a continuous aqueous layer is observed on the surface of the waste then it is certain that the surface of the waste contains enough water to stop an exothermic propagating reaction.
Wt% water	2.	A high moisture content (at the surface) indicates that there is enough water to stop an exothermic propagating reaction.
[Fuel]	3. Is surface fuel content too high?	A dry tank is safe if the fuel content is low.

[ ] = Concentrations

The decision inputs summarized in Table 4-1 for decision Steps 1A, 1C, 2, and 3 are referenced in Meacham et al. (1995a). The toxicological compounds from decision Step 1B are referenced in Huckaby and Story (1994).

4.2 POTENTIAL SOURCES OF DECISION INPUTS

It has been stressed throughout this DQO process that decision input sources need not consider only sampling and analysis. The characterization program has access to many other sources of characterization information other than future sampling and analysis work. An in-depth examination of the available (historical) characterization data will ensure that the most efficient sampling plan is produced. These other sources are listed throughout the rest of this section.

In order to optimize the DQO process such that all resources have been considered and that the cost of characterization is truly reduced, the DQO process evaluation considers available data before it considers sampling and analysis. Sources of data other than from sampling and analysis (e.g., historical or models) need to be validated before they are acceptable for use as input sources. Validation of historical data in this context implies that the historical data will be compared with current sampling and analysis data.

Table 4-2 lists possible sources of characterization information and data that need to be considered in the safety screening DQO. This table lists input sources for each of the decision inputs within the scope of this DQO. Only the known input sources are listed. If another input source for any decision input is discovered, it can be added to the list.

Table 4-2. Possible Decision Input Sources.

Decision Input	Possible Input Sources
Vol% flammable compounds (see Decision 1A)	1) Previous vapor sample 2) Dome space sample
Noxious vapor compounds (see Decision 1B)	1) Previous vapor sample 2) Dome space sample
Organic phase compounds (see Decision 1C)	1) Previous vapor sample 2) Dome space sample
Observation of waste surface	1) Surveillance
% Water	1) Previous sampling 2) Tank grouping models 3) Surface sampling
[Fuel]	1) Previous sampling 2) Tank grouping models 3) Surface sampling

[ ] = Concentrations

The possible input sources listed above come from several characterization information and data sources that will be addressed throughout the rest of this section.

There are several sources of previous sampling information. Liquid (and some solid) samples were taken in the early 1970s. A limited amount of core sampling has been done since the early 1980s. Recently, extensive core sampling, as well as supernate and auger sampling, has been performed. Many sources of previous sampling results exist; all sources known to the Characterization Program have been collected in the Tank Characterization Resource Center. A listing of these samples may be found in Sathyanarayana (1994). Other useful sources of previous sampling information include the Tank Characterization Reports, and the Supporting Documents for the Historical Tank Content Estimate Reports (Brevick 1994a, 1994b, 1995). Note that previous sampling data does not generally have the same quality assurance requirements as current laboratory data. Evaluation of these historical sample data is necessary before they are used as input sources.

The next source listed is tank grouping models. Currently, tank grouping models are being developed but none have been completed. A tank grouping model is a model that groups tanks of similar waste type. The model will provide an effective characterization tool because tanks that are in the same group as another tank that has been well characterized may require less sampling. Although these grouping models have minimal current application, they may be more useful in the near future. Other sources of historical model estimates include the Historical Tank Content Estimates (Brevick 1994a, 1994b, 1995), the Waste Status and Transaction Record Summaries (Agnew 1994a, 1994b, 1994c, 1995) and the Hanford Defined Waste document (Agnew 1994d). Again, for these models to be of use as input sources, validation of the models is necessary.

Surveillance data used to provide inputs for the safety screening DQO consist of photographs of the waste surface. These photographs can be obtained from the Tank Waste Remediation Systems surveillance group. Data from the photographs has been summarized in the Historical Tank Content Estimate report (Brevick 1994a, 1994b, 1995). Surveillance information may not be valid if transfer activity has occurred since the time of surveillance; this possibility must be checked before surveillance information is used.

After all other characterization sources have been considered, sampling plans will be made. Evaluation of historical sources of information and data will ensure that the most efficient sampling plans are created--plans that are based on process knowledge of the tank.

5.0 STUDY BOUNDARIES

This chapter completes the fourth step of the DQO process: *Define the study boundaries*. The study boundaries for the decision inputs are summarized in Table 5-1.

Before confidence limits for the decision inputs may be determined, the study boundaries of the desired inputs must be stated. Study boundaries may be subdivided into two parts: physical boundaries and time constraints.

"Physical boundaries" refers to the area of study within the tank. Physical boundaries are stated on an input basis, and are specified in the first column of Table 5-1 for the inputs particular to the safety screening DQO. The physical boundary for the desired input is specified in the second column, and the reason for choosing the specified physical boundary is given in the third column.

"Time constraints" refers to the time frame for which a decision input must be studied or the time frame in which the decision should be made. To date, no time constraints have been specified for determining decisions and decision inputs.

Table 5-1. Study Boundaries for Decision Inputs.

Input	Physical Boundary	Justification for Specified Boundary
Flammable compounds (see Decision 1A)	Dome space	The issue of flammability deals with hydrogen reaction in the tank dome space. Note that flammable gas in solids is dealt with in the flammable gas core DQO (McDuffie 1994).
Noxious vapor compounds (see Decision 1B)	Dome space	Noxious vapor compounds are only an issue if they are released from the tank in gas phase.
Organic phase compounds (see Decision 1C)	Dome space	The presence of these compounds in the dome space indicates the possible presence of an immiscible organic phase in the waste.
Observation of waste surface	Top of tank waste (potential supernate layer)	This is the easiest detection of tank moisture.
Wt% water	Top 14 cm* of waste surface	There is no credible reaction initiator that could start below the waste surface.**
[Fuel]	Top 14 cm* of waste surface	There is no credible reaction initiator that could start below the waste surface.**

[ ] = Concentrations

* This is a preliminary boundary; studies are in progress to finalize this depth.

** Possible exceptions to this rule are lightning strike to equipment and gasoline spills on waste surface, which may initiate a reaction below 14 cm. Operating controls will be used to ensure that equipment is electrically grounded and that gasoline spills will not occur.

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6.0 DECISION RULE

6.1 SUMMARY OF DECISION RULE

This chapter completes the fifth step of the DQO process: *Develop a decision rule.* **The decision rule is summarized in Table 6-1.**

In this section, the logic inherent in the decision steps is summarized, and the action limits associated with each decision input are indicated. It is recognized that some inputs do not necessarily need to be known and are only required depending on the values of previous inputs. The decision rule is tabulated in an "if...then" format that outlines the logic that is to be used when researching or measuring inputs. The numbers given in the "if" statements are referred to as decision thresholds. Note that a decision threshold is provided for every input.

Table 6-1. Decision Rule.

Step No.	Decision No.	IF (Decision Threshold)	THEN
1.	1A.	LFLA ≥ 25% (LFLA is Lower Flammability Limit Approach - See below for definition)	Implement controls for flammable gas Watch List tank (Schofield 1995). Notify Flammable Gas Safety Program. Continue to next step.
2.	1B.	[Ammonia] ≥ 25 ppm AND/OR [CO_2] ≥ 5000 ppm AND/OR [CO] ≥ 35 ppm AND/OR [NO] ≥ 25 ppm AND/OR [NO_2] ≥ 1.0 ppm AND/OR [N_2O] ≥ 25 ppm AND/OR [TOC] ≥ 1.0 ppm	Restrict workers from area. Go to DQO for Generic In-Tank Health and Safety Vapor Issue Resolution (Osborne 1994a). Notify Noxious Vapor Safety Program. Notify Industrial Hygiene. Continue to next step.
3.	1C.	[Tributyl phosphate] ≥ detection limit AND/OR [Dodecane] ≥ detection limit AND/OR [Tridecane] ≥ detection limit	Implement controls for Organic Watch List tank (Schofield 1995). Go to Organic DQO (Buckley 1995). Notify Organic Safety Program. Continue to next step.

Step No.	Decision No.	IF (Decision Threshold)	THEN
4.	2.	Continuous aqueous layer observed on waste surface.	Tank is under safe storage conditions.* -Monitor waste surface to ensure safe interim storage. -Stop here.
5.	2.	Wt% water > 20 wt%	Tank is under safe storage conditions.* -Monitor waste surface to ensure safe interim storage. -Stop here.
6.	3.	[Fuel] < 290 cal/g + 13.5 • wt% water (Note: [Fuel] as determined by differential scanning calorimetry)	Tank is under safe storage conditions.* -Monitor waste surface to ensure safe interim storage. -Stop here.
7.	3.	[Fuel] ≥ 290 cal/g + 13.5 • wt% water (Note: [Fuel] as determined by differential scanning calorimetry)	Potential for propagating exothermic reaction.* Implement controls as for organic Watch List tank (Schofield 1995). Go to Organic (Buckley 1995) and Ferrocyanide (Meacham et al. 1995b) DQOs. Notify Organic and Ferrocyanide Safety Programs. Monitor waste surface. Stop here.

[ ] = Concentrations

* See (Meacham et al. 1995a).

Note that in Step 1, a variable is used called the Lower Flammability Limit Approach (LFLA). The LFLA is defined as the percentage of the flammability limit that the tank dome space gases are at. Hence, an LFLA of 100% would mean that the tank dome space gases are at the flammability limit. For the purposes of this DQO, the decision threshold for the LFLA is 25% (as explained in Section 6.2). The LFLA is a function of the concentration of the various flammable compounds in the tank as described below:

$$LFLA(Vol\%)=100\times(\frac{y_{Hydrogen}}{LFL_{Hydrogen}}+\frac{y_{Ammonia}}{LFL_{Ammonia}}+\frac{y_{Methane}}{LFL_{Methane}}+\frac{y_{CO}}{LFL_{CO}})$$

Where:

LFLA = Lower Flammability Limit Approach (Vol%)
y = vapor fraction (Vol%) of specific compound
$LFL_{Hydrogen}$ = 3.5% (LFL for Hydrogen)
$LFL_{Ammonia}$ = 8%
$LFL_{Methane}$ = 5.0%
LFL_{CO} = 12.5%

6.2 JUSTIFICATION OF DECISION THRESHOLDS

In this section, justification will be given for the decision thresholds listed in Table 6-1. These justifications support the technical basis for the decision rule that was summarized in Section 6.1.

The first decision threshold listed in Step 1 of Table 6-1 is related to potential vapor flammability in the dome space above the tank waste. The National Fire Protection Association recommends that processes be controlled so that flammable gas concentrations are less than twenty-five percent of the LFL. Because several different gasses contribute to the overall flammability of the waste, a method is needed to combine the flammability limits of the separate gases into an overall flammability limit. This method is to calculate the Lower Flammability Limit Approach (LFLA) that was defined in Section 6-1. The compounds of concern are hydrogen, ammonia, methane, and carbon dioxide (CO). Hydrogen is the predominant contributor. It should be noted that the flammability limit decreases in the presence of nitrous oxide. This relationship is defined in *Safety Basis for Activities in Double-Shell Flammable Gas Watch List Tanks* (Van Vleet 1994a) and *Safety Basis for Activities in Single-Shell Flammable Gas Watch List Tanks* (Van Vleet 1994b). The adjustments in the defined flammability limit will be incorporated into this DQO at a later time.

Hydrogen gas is generated in radioactive waste containing water as gamma-radiation emitted by decaying radionuclides severs the bonds in water molecules; this is a generic concern. The other flammable gases (e.g., ammonia and methane) are generated by the waste in some Hanford Site DSTs. Production of flammable gas by stored materials will lead to a steady-state concentration of the gas in any vacant container volume. *Steady-state* flammable gas levels in a waste container will depend upon the gas production and mixing rates, and the container's ventilation rate. If a container is adequately ventilated and the flammable gases mix rapidly, then flammable gas levels will likely be less then the 25% of the LFL guideline from the National Fire Protection Association. Some Hanford Site DSTs, most notably tank

241-SY-101, store waste that tends to retain the generated gas until large gas volumes are suddenly released. In these cases, resulting *transient* flammable gas levels are in general dependent upon the amount of gas released, the length of the release time, free volume in the tank, and the ventilation rate. Vapor sampling the Hanford Site waste tanks for safety screening will only provide information about the steady-state flammable gas levels in these tanks; it will not characterize any type of transient flammable gas behavior.

In Step 2 of Table 6-1, the decision threshold is related to the suspected presence of noxious vapors in the tank dome space. Several compounds, which are of concern to overall waste tank safety, are expected to be in many tanks. These compounds are derived from a list of some analytes that were actually detected in a vapor sample from SST C-103. The decision threshold limit is defined as the consensus exposure standard (CES) concentration for the analytes of interest (Osborne 1994b) and (Gerton 1992). The exception to this limit is for total organic carbon (TOC), which is 1 ppm. There are several other noxious organic compounds not specified in this DQO that have a threshold limit of over 1 ppm. The purpose of determining TOC is to screen for the other possible noxious organic compounds.

In determining the CES concentration limits, the *NIOSH Pocket Guide to Chemical Hazards* (NIOSH 1994) was used. Several standard limits are listed in this source, and the CES limit was determined by using the most stringent of the referenced limits. Detection of one or more of these noxious vapor compounds in the dome space above the threshold limit indicates a noxious vapor hazard, of which Westinghouse Hanford Company Industrial Hygiene is advised.

The decision threshold listed in Step 4 specifies the possible detection of an immiscible organic phase within the solid or liquid portion of the tank waste. It was noted in tank C-103 that a vapor-liquid equilibrium existed between certain organics found in the organic layer in the tank waste and the vapor from the tank dome space. Hence, detection of one and/or more of these organic compounds (e.g., n-dodecane, n-tridecane, and tributyl phosphate) in the tank dome space above the decision threshold limit may indicate an immiscible organic phase within the tank (Meacham et al. 1994a). Because the relationship between the dome space concentration and the immiscible organic phase concentration of these compounds is not yet understood, the detection limit has been chosen as the threshold limit. Using the detection limit as the threshold limit is temporary until the true vapor/liquid equilibrium is understood.

In Steps 4 and 5, decision threshold limits are provided for the detection of moisture at the "near surface" (see Section 1.0) of the waste. The decision input listed in Step 4 applies a qualitative assessment of the moisture at the surface of the tank waste. If a photograph of the waste surface indicates that the entire waste surface is covered by an aqueous layer, then the solids waste underneath the aqueous layer is moist enough to stop an exothermic propagating reaction from occurring (Meacham et al. 1994a). If photographic evidence of the waste surface does not indicate an aqueous layer on the waste surface, then separate determination of the moisture at the near surface of the solids waste is necessary. A stoichiometric mixture of fuel and oxidizer will not propagate when the moisture content exceeds 20 wt%.

In Steps 6 and 7, the determination of fuel is made as a result of finding less than 20 wt% moisture in the near surfce of the waste. Waste that is dry may still be safe depending upon the amount (if any) of fuel it contains. Possible fuels to be found in the waste are organics and ferrocyanide. The relationship expressed in Steps 6 and 7 indicate the safe boundary of fuel content based on the amount of water in near surface of the waste (Meacham et al. 1994a).

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7.0 ACCEPTABLE LIMITS FOR DECISION ERRORS

This chapter completes the sixth step of the DQO process: *Specify acceptable limits on decision errors*. **The desired confidence limits for the decision thresholds are listed in Table 7.1.**

In Section 6.1, the decision thresholds were summarized. Because the decision threshold numbers determine the logic flow path in the DQO, it is necessary to know what confidence is required in determining if the decision input meets the threshold. In some cases, the determination of the decision input and its comparison to the decision threshold limit may be based on a qualitative interpretation of the data or information source as compared to a statistical determination of the confidence. In such cases, agreement by the requesting program is needed. An example of such a case is the visual surveillance of the waste surface for water covering the entire surface. This type of data meets the decision input need even though a statistical statement based on multiple measurements is not possible.

Decision input confidence limits will be expressed in the following manner. Each decision input has one or more decision threshold numbers associated with it. For each decision threshold provided, an associated confidence will be expressed. Error limits will be expressed in statistical terms that quantify the probability that the decision input is above or below the decision threshold. For the purpose of this DQO, these confidence requirements only control a false positive type of error (that is, assuming that the tank is under safe storage conditions when it was actually not under safe storage conditions).

The following table provides the desired confidence for each of the decision input threshold limits. The first column gives the decision step and the second column gives the decision threshold associated with the inputs in the decision step. The third column provides the desired confidence for the decision threshold.

Table 7-1. Confidence Requirement for Decision Inputs.

Decision No.	Decision Threshold	Confidence Requirement
1A. (All compounds listed)	LFLA < 25%	95%
1B. (All compounds listed except TOC)	[Noxious compound] < CES-based limit	95%
1B. TOC	TOC < 1.0 ppm	95%
1C. (All compounds listed)	[Organic compound] < Temperature-based threshold limit	95%

Decision No.	Decision Threshold	Confidence Requirement
2.	Continuous aqueous layer observed on waste surface.	High. Aqueous layer needs to be very clear in photograph.
2.	% Water > 20%	95%
3.	[Fuel] < or = 290 cal/g + 13.5 • wt% water	95%

[ ] = Concentrations

Justification for the confidence limits for decisions 1A, 1C, 2, and 3 will be determined through an assessment of the associated risks are not available at this time. Due to lack of a developed risk assessment criterion, these limits will be temporarily referenced as 95% in the above table.

Justification of the 95% confidence limit for Decision 1B is provided in DQO for Generic In-Tank Health and Safety Vapor Issue Resolution (Osborne 1994a). This justification assumes that the true concentration of the noxious vapor compound is in the range of one half of the CES value to full CES value. This justification will need to be developed soon to a true confidence limit.

When these confidence limits are derived, a complete assessment of the risk associated with each decision will need to be performed.

8.0 OPTIMIZATION OF THE DQO PROCESS

This chapter initiates the final step of the DQO process: *Optimize the design.* Optimization of the DQO process consists of researching the decision inputs and optimizing the sampling needs for the DQO. This second step is performed on a tank by tank basis and will be included in the separate Tank Characterization Plans (TCPs).

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