1 of 1

Ferrocyanide Safety Program: Data Requirements for the Ferrocyanide Safety Issue Developed Through the Data Quality Objectives (DQO) Process

J. W. Buck
C. M. Anderson
B. A. Pulsipher
J. J. Toth
P. J. Turner
Pacific Northwest Laboratory

R. J. Cash
G. T. Dukelow
J. E. Meacham
Westinghouse Hanford Company

Date Published
December 1993

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

**Westinghouse
Hanford Company**

P.O. Box 1970
Richland, Washington 99352

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

Approved for Public Release

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Date Received: <i>1/4/94 KMB</i>		INFORMATION RELEASE REQUEST		Reference: WHC-CM-3-4	
Complete for all Types of Release					
Purpose			ID Number (include revision, volume, etc.) WHC-EP-0728		
☐ Speech or Presentation ☐ Full Paper (Check only one suffix) ☐ Summary ☐ Abstract ☐ Visual Aid ☐ Speakers Bureau ☐ Poster Session ☐ Videotape			List attachments. N/A		
			Date Release Required 12/30/93		
Title Ferrocyanide Safety Program: Data Requirements for the Ferrocyanide Safety Issue Developed Through the Data Quality Objectives (DQO) Process				Unclassified Category	
				Impact Level 4	
New or novel (patentable) subject matter? ☒ No ☐ Yes If "Yes", has disclosure been submitted by WHC or other company? ☐ No ☐ Yes Disclosure No(s).			Information received from others in confidence, such as proprietary data, trade secrets, and/or inventions? ☒ No ☐ Yes (Identify)		
Copyrights? ☒ No ☐ Yes If "Yes", has written permission been granted? ☐ No ☐ Yes (Attach Permission)			Trademarks? ☒ No ☐ Yes (Identify)		
Complete for Speech or Presentation					
Title of Conference or Meeting N/A			Group or Society Sponsoring		
Date(s) of Conference or Meeting		City/State		Will proceedings be published? ☐ Yes ☐ No Will material be handed out? ☐ Yes ☐ No	
Title of Journal					
CHECKLIST FOR SIGNATORIES					
Review Required per WHC-CM-3-4		Yes	No	Reviewer - Signature Indicates Approval	
				Name (printed)	Signature Date
Classification/Uncontrolled		☐	☒		
Nuclear Information		☐	☒		
Patent - General Counsel		☒	☐	S. W. Berglin	<i>[Signature]</i> 12/30/93
Legal - General Counsel		☒	☐	S. W. Berglin	<i>[Signature]</i>
Applied Technology/Export Controlled Information or International Program		☐	☒		
WHC Program/Project		☒	☐	R. J. Cash	<i>[Signature]</i> 12-29-93
Communications		☒	☐	W. P. Whiting	<i>[Signature]</i> 12-30-93
RL Program/Project		☒	☐	R. F. Christensen	<i>[Signature]</i> 1-4-94
Publication Services		☒	☐	R. A. Conner	<i>[Signature]</i> 1-4-94
Other Program/Project		☒	☐	J. L. Scott	<i>[Signature]</i> 12-30-93
Information conforms to all applicable requirements. The above information is certified to be correct.					
References Available to Intended Audience		Yes	No	INFORMATION RELEASE ADMINISTRATION APPROVAL STAMP Stamp is required before release. Release is contingent upon resolution of mandatory comments.
Transmit to DOE-HQ/Office of Scientific and Technical Information		☒	☐		
Author/Requestor (Printed/Signature) Date					
R. J. Cash <i>[Signature]</i> 12/29/93					
Intended Audience				Date Cancelled Date Disapproved	
☐ Internal ☐ Sponsor ☒ External					
Responsible Manager (Printed/Signature) Date					
J. C. Fulton <i>[Signature]</i> 1/3/94					

**FERROCYANIDE SAFETY PROGRAM: DATA REQUIREMENTS FOR
THE FERROCYANIDE SAFETY ISSUE DEVELOPED THROUGH
THE DATA QUALITY OBJECTIVES (DQO) PROCESS**

ABSTRACT

This document records the data quality objectives (DQO) process applied to the Ferrocyanide Waste Tank Safety Issue at the Hanford Site by the Pacific Northwest Laboratory and Westinghouse Hanford Company. Specifically, the major recommendations and findings from this Ferrocyanide DQO process are presented so that decision makers can determine the type, quantity, and quality of data required for addressing tank safety issues. The decision logic diagrams and error tolerance equations also are provided. Finally, the document includes the DQO sample-size formulas for determining specific tank sampling requirements.

This page intentionally left blank.

SUMMARY

Since 1944, underground storage tanks located at the Hanford Site in Richland, Washington, have stored highly radioactive and nonradioactive waste. Currently, there are approximately 277,000 m³ (60 Mgal) of high-level radioactive waste in 177 tanks. Recently, a number of safety concerns with regard to worker and public health have arisen concerning these tanks. As a result, the U.S. Department of Energy (DOE) has made the resolution of these safety issues its highest priority at the Hanford Site.

To address these safety concerns, the Tank Waste Remediation System (TWRS) was developed by Westinghouse Hanford Company, the Pacific Northwest Laboratory, and DOE to provide an integrated approach to resolution of the waste tank safety issues. The Tank Waste Characterization Plan (TWCP), as part of the TWRS, was initiated to fully characterize the waste contained in the tanks. With support from TWCP and data package information from the analytical laboratories, this characterization process is much more likely to lead to the safe storage, treatment, and disposal of the waste.

Ferrocyanide DQO Process

The data quality objectives (DQO) process, first developed by the U.S. Environmental Protection Agency (EPA) and adapted to the tank safety issues, is being applied to determine the type, quality, and quantity of data required for assessing the issues. The application of the DQO process to tank safety issues provides a comprehensive view of all the facets involved in assessing these tanks.

This particular application of the DQO process was implemented as a template for characterizing tank waste containing ferrocyanide compounds¹ based on historical, monitoring, simulant, modeling, and sampling information. It also provides a link to data requirements that will be developed through the DQO process for other safety issues and TWRS functional elements.

The recommendations and decision logic presented in this report should be used to develop tank-specific characterization plans for all Ferrocyanide Watch List tanks. These tank-specific characterization plans will specify the data requirements for the final data packages developed by the analytical laboratories. The information from these data packages can then be used by decision makers to determine the safety classification of each Ferrocyanide Watch List tank and the appropriate measures needed to ensure continued safe interim storage. Tanks that are not classified as Ferrocyanide Watch List tanks will be addressed through a

¹The term ferrocyanide is used throughout this report to represent all ferrocyanide compounds associated with the tank safety issue, e.g., Na₂NiFe(CN)₆ and NaCsNiFe(CN)₆.

safety screening module. The safety screening module will provide appropriate linkage between the ferrocyanide data requirements and the other safety, or TWRS function, data requirements.

Findings of Ferrocyanide DQO Process

Three important outputs of this particular DQO application are (1) key decision rules for determining the safety status of Ferrocyanide Watch List tanks, (2) recommendations for the number of tank cores [samples] to be taken, and (3) analytical requirements that will feed into the tank-specific characterization plans.

Primary Decision Rules

Two key decision rules were identified during the DQO process that will enable the decision makers to classify the safety status of interim storage of ferrocyanide waste into one of three categories (*safe*, *conditionally safe*, and *unsafe*). These decision rules are defined as follows:

- If the fuel concentration in all homogenized quarter segments¹ is less than 8 wt% as $\text{Na}_2\text{NiFe}(\text{CN})_6$ (on an energy equivalent basis), then the tank is classified as *safe* for interim storage. Otherwise, the tank is classified as *conditionally safe* or *unsafe* for interim storage (the moisture and temperature conditions of the tank resolve the difference between these two categories).
- If the fuel concentration in any homogenized quarter segment is greater than or equal to 8 wt% [energy equivalent $\text{Na}_2\text{NiFe}(\text{CN})_6$] and if the free water² content for that subsegment is greater than $4/3 [\text{Fuel} - 8]^3$, then the tank is classified as *conditionally safe*. Otherwise, the tank is classified as *unsafe* for interim storage.

The temperature of the waste is a secondary data requirement that is used in support of the decision whether a tank is *conditionally safe* or *unsafe*. Temperature is not a core sample data value but is obtained from instrument tree measurements.

¹Quarter segments apply only to sludge samples. For saltcake samples, analyses will only be made on homogenized half segments. Based on historical records, most of the ferrocyanide should be in the sludge.

²Free water is water that can be removed from samples by drying at 120 °C for 18 hours.

³Fuel (wt%) represents the energy value of the sample based on an equivalent wt% $\text{Na}_2\text{NiFe}(\text{CN})_6$. For the Ferrocyanide Watch List tanks, the fuel is expected to be ferrocyanide as $\text{Na}_2\text{NiFe}(\text{CN})_6$ or $\text{NaCsNiFe}(\text{CN})_6$. The total fuel value, determined by calorimetry, will be compared with the total cyanide and total organic carbon determinations to calculate whether ferrocyanide alone accounts for the total fuel value.

Number of Core Samples Required

The primary considerations for defining sampling requirements are the expected spatial, sampling, and analytical variations and the desired levels of protection from making incorrect decisions. Estimates of the expected variations in ferrocyanide and moisture determinations were derived from available core sample data for two tanks on the Ferrocyanide Watch List (Tanks 241-C-109 and 241-C-112).

Desired levels of protection against making decision errors were derived through soliciting input from the decision makers concerning the risks of decision errors. The essence of these discussions was captured in discomfort curves. This process is described in the EPA guidance on the DQO process.

Two spatially distributed cores are required to meet the decision makers' tolerance for making incorrect decisions. If the estimates of variability from the previously sampled two tanks are assumed to be representative, we are ensured a less than 20% chance of concluding that a tank is *safe* when the true fuel concentration is 8%. Likewise, if the true fuel concentration is 15%, there is less than a 1% chance of concluding that the tank is *safe*. Finally, if the true fuel concentration is 4%, there is only a 20% chance of concluding that the tank is either *unsafe* or *conditionally safe*.

Similar statements can be made for the moisture decision rule, and more detail is provided in Section 5 of this report. As more data become available, the estimate of variability should be updated and examined for its effect on sampling requirements.

Analytical Requirements

Table S-1 provides a summary of the analytical requirements for Ferrocyanide Watch List tanks. For each analyte, the decision threshold and the desired analytical variability are provided. The desired analytical variability should be incorporated into the tank-specific characterization plans. Total cyanide, total nickel, total organic carbon, cesium-137, and strontium-90 analytes are included in the table because they provide valuable corroborating data even though they are not directly linked to a decision rule.

Recommendations

Recommendations from the Ferrocyanide DQO process are as follows:

- Core sample locations must be chosen to represent the spatial distribution of the important analytes in the tank. The samples will be limited by the location and availability of risers.
- Analytical measurements associated with the safety criteria parameters for Ferrocyanide Watch List tanks must be applied to quarter segments for sludge layers and half segments for saltcake layers.

Table S-1. Analytical Requirements for Ferrocyanide Watch List Tanks.

Analyte to be Measured	Analytical Method	Sample	Decision Threshold	Assumed (Desired) Analytical Uncertainty
Nickel Concentration	Inductivity Coupled Plasma-Acid Digestion and Fusion	Quarter Segment	Not Specified	$\leq 5\%$ ^a
Total Fuel Content	Differential Scanning Calorimetry/Adiabatic Calorimetry	Quarter Segment	To be Converted to Ferrocyanide Concentration	$\leq 3\%$
Total Cyanide Concentration in Quarter Segment	Direct Assay (Method is Procedure PNL-ALO-285)	Quarter Segment	8 wt% (zero free water)	$\leq 3\%$ ^b
Moisture Content in Quarter Segment	Thermogravimetric Analysis	Quarter Segment	4/3 [Fuel - 8]	$\leq 5\%$
Tank Temperature	Thermocouple	N/A	90 °C	$\leq 5\%$
Total Organic Carbon	Direct Persulfate Oxidation	Quarter Segment	3 wt%	$\leq 5\%$
Cesium-137	Gamma Energy Analysis-Water Digestion and Fusion	Quarter Segment	Not Specified	$\leq 5\%$
Strontium-90	Beta Radiochemistry	Quarter Segment	Not Specified	$\leq 5\%$

^aThe analytical uncertainty for nickel contains uncertainty from sample preparation and analytical variability.

^bThe analytical uncertainty for total cyanide contains uncertainty from sample preparation and analytical variability (excluding variations due to sample extrusion and homogenization).

- Platinum, rather than nickel, crucibles should be used for the inductively coupled plasma fusion analytical method. This practice will reduce a bias in the nickel concentration measurements.
- The relative standard deviations (RSDs) should be updated before a tank-specific characterization plan is developed for any Ferrocyanide Watch List tank. We have assumed RSDs of 22% for fuel and 12% for moisture (this includes spatial, sampling, and analytical variations) for decision rules based on information from Tanks 241-C-109 and 241-C-112. If the revised RSDs for any decision rule vary from these assumed values, then the required number of cores may need to be modified although there appears to be flexibility up to 33% RSD for ferrocyanide.
- DQO applications for each of the TWRS functional elements should consider the safety consequences and operating conditions associated with ferrocyanide waste.
- A method for determining the speciation of the ferrocyanide compounds must be completed. This method will contribute to the understanding of the ferrocyanide safety issues and provide information to the retrieval, pretreatment, and disposal TWRS functional elements.

Conclusions

In developing this report, the implementation process of the decision-rule logic and error tolerance steps of the DQO process became better defined. The decision-rule logic forced reexamination of some of the criteria and assumptions and documented the entire decision process required for Ferrocyanide Watch List tanks. Finally, this DQO process provided a feedback system to decision makers and resulted in more information on how their criteria affect the outcome of a tank-specific characterization plan.

Many of the justifications for decision thresholds and decision error tolerances are briefly described in this DQO document. More detailed descriptions are presented in other companion documents (e.g., the unreviewed safety question [USQ] closure document [Postma et al. 1993]).

This page intentionally left blank.

ACKNOWLEDGMENTS

The authors of this report would like to acknowledge the support from staff in the safety, characterization, and other functional element TWRS programs. Safety personnel who provided invaluable input to this report include: Bob Cash, Gary Dukelow, Arlin Postma, Harry Babad, Cherri Defigh-Price, and Joe Meacham. Characterization staff who provided indispensable guidance and support to this effort are as follows: Brett Simpson, Kevin Bell, Julian Hill, Karl Pool, and George Borsheim. Discussions with modelers and laboratory scientists like Mike Lilga, Jim McLaren, Randy Scheele, and Pete McGrail were very beneficial to the completion of the report. Staff from other TWRS functional elements who also provided input include: Bob Watrous, Duc Nguyen, Pushpa Bhaha, and Mike Klem.

Appreciation is also extended to PNL staff who provided support to this report: P. G. Heasler, Mark Bryan, T. W. Wood, J. L. Scott, Melissa Peffers, John Glissmeyer, Joan Young, Alan Brothers, Valeria Hunter, and Lynda Gordon. We would like to thank Gene Wattenburger of Boeing Graphics for his efforts on the decision rule diagram and to Joan Slavens for her text processing support. Finally, we express sincere appreciation to Nancy Stratton and Becky Conner for their editorial support.

This page intentionally left blank.

CONTENTS

1.0	INTRODUCTION	1-1
1.1	RELATIONSHIP BETWEEN TWRS, TWCP, AND DATA REQUIREMENTS PROJECTS	1-1
1.2	GENERAL PURPOSE OF DQO PROCESS AND ITS IMPLEMENTATION FOR TWRS	1-2
1.3	SCOPE OF FERROCYANIDE DQO PROCESS	1-2
1.4	REPORT OUTLINE	1-3
2.0	STATEMENT OF THE PROBLEM	2-1
2.1	HISTORY OF TANKS CONTAINING FERROCYANIDE	2-1
2.2	CONTEXT OF THE FERROCYANIDE SAFETY ISSUE	2-3
2.3	RELATIONSHIP OF THE FERROCYANIDE SAFETY ISSUE TO OTHER TWRS ISSUES	2-3
3.0	KEY DECISIONS, REQUIRED INPUT, AND BOUNDARIES	3-1
3.1	TANK SAFETY CLASSIFICATION STRATEGY	3-1
3.2	REQUIRED INPUTS FOR CLASSIFICATION	3-1
3.3	SECONDARY DATA REQUIREMENTS	3-2
3.4	BOUNDARIES	3-3
3.4.1	Sampling Methods	3-3
3.4.2	Sample Segment Requirements	3-4
3.4.3	Riser Location	3-4
3.4.4	Core Recovery	3-4
4.0	STATEMENT OF THE KEY QUESTIONS AND ANSWERS	4-1
4.1	DESCRIPTION OF DECISION RULES	4-1
4.2	SAFE VERSUS CONDITIONALLY SAFE OR UNSAFE DECISION RULE	4-1
4.3	CONDITIONALLY SAFE VERSUS UNSAFE DECISION RULE	4-1
5.0	ERROR TOLERANCES ASSOCIATED WITH MEASUREMENTS	5-1
5.1	DESCRIPTION OF DISCOMFORT CURVES	5-1
5.2	SAFE VERSUS CONDITIONALLY SAFE OR UNSAFE DECISION RULE	5-2
5.2.1	Rationale for Decision Error Tolerances	5-3
5.3	CONDITIONALLY SAFE VERSUS UNSAFE DECISION RULE	5-4
5.3.1	Rationale for Decision Error Tolerances	5-5
6.0	OPTIMAL SAMPLING DESIGN	6-1
6.1	FACTORS AFFECTING SAMPLING REQUIREMENTS	6-1
6.2	ESTIMATES OF UNCERTAINTY FROM PRIOR INFORMATION	6-1

CONTENTS (Continued)

6.3	NUMBER OF CORES REQUIRED	6-3
6.3.1	Achievable Probabilities of Making Incorrect Decisions	6-3
6.4	SENSITIVITIES OF SAMPLE SIZE CALCULATIONS	6-4
7.0	CONCLUSIONS	7-1
7.1	FINDINGS	7-1
7.2	CONCLUSIONS	7-3
8.0	REFERENCES	8-1
APPENDIXES		
A	DESCRIPTION OF DQO PROCESS	A-1
B	SAMPLE SIZE FORMULAS AND STATISTICAL ISSUES	B-1

LIST OF FIGURES

2-1 Schematic Diagram of Typical Single-Shell Tank	2-1
4-1 Moisture Decision Rule	4-2
4-2 Ferrocyanide DQO Decision Logic	4-4
4-3 Ferrocyanide DQO Decision Rules Logic	4-4
5-1 Discomfort Curve for Ferrocyanide Concentration Used to Show Decision Error Tolerance for Ferrocyanide Safety Issue Measurement	5-3
5-2 Moisture Diagram	5-6
5-3 Discomfort Curve	5-6

LIST OF TABLES

6-1 Achievable Probabilities for Decision Error for the Safe Versus Conditionally Safe or Unsafe Decision Rule	6-4
6-2 Achievable Probabilities for Decision Error for the Conditionally Safe Versus Unsafe Decision Rule	6-4
7-1 Analytical Requirements for Ferrocyanide Watch List Tanks	7-2

LIST OF ACRONYMS

AC	Adiabatic Calorimetry
DOE	U.S. Department of Energy
DQO	Data Quality Objectives
DSC	Differential Scanning Calorimetry
EPA	U.S. Environmental Protection Agency
ICP	Inductively Coupled Plasma
PNL	Pacific Northwest Laboratory
RSD	Relative Standard Deviation
SST	Single-Shell Tank
TOC	Total Organic Carbon
TPA	Tri-Party Agreement
TRAC	Track Radioactive Components
TWCP	Tank Waste Characterization Plan
TWRS	Tank Waste Remediation System
USQ	Unreviewed Safety Question
WHC	Westinghouse Hanford Company

1.0 INTRODUCTION

1.1 RELATIONSHIP BETWEEN TWRS, TWCP, AND DATA REQUIREMENTS PROJECTS

High-activity radioactive and nonradioactive waste has been stored in underground tanks at the Hanford Site since 1944. Currently, 177 underground tanks contain approximately 277,000 m³ (60 Mgal) of waste consisting of many different chemicals in several waste forms (liquid, slurry, saltcake, and sludge). A number of safety issues related to public and worker health have been recognized with these storage tanks (Babad 1992). The resolution of these safety issues is the number-one priority of the U.S. Department of Energy (DOE) at the Hanford Site. The Waste Tank Safety Program Office was created to resolve these high-priority potential safety issues, which are as follows:

- Flammable gases in tanks (24 tanks)
- Ferrocyanide waste in tanks (20 tanks)
- Organics in tanks (9 tanks)
- Noxious vapors (Tank Farms C, BX, and BY)
- High-heat tanks (11 tanks)
- Criticality (all tanks).

The Tank Waste Remediation System (TWRS), as part of the Hanford Site Mission, provides an integrated approach to characterization by combining all functions associated with tank waste. The scope of the Tank Waste Characterization Plan (TWCP), as part of the TWRS, is to provide the characterization activities necessary for safely storing, retrieving, treating, and disposing of all tank waste. The highest near-term priority is the sampling and analysis of those tanks with unreviewed safety questions (USQs). Ultimately, the TWCP is required to characterize all 177 underground tanks (149 are single-shell tanks [SSTs] and 28 are double-shell tanks); to support the design of retrieval, pretreatment, and final disposal systems; and to comply with Tri-Party Agreement (TPA) milestone M-44 (Ecology 1989).

The data requirements project is a joint activity of Westinghouse Hanford Company (WHC) and Pacific Northwest Laboratory (PNL). The data requirements project was developed to provide a definition of data requirements in support of TWRS. This project assesses, in detail, the type, quantity, and quality of data required to support decisions regarding the storage, retrieval, treatment, and disposal of tank waste in a time-phased approach. A major component of the data requirements project is the data quality objectives (DQOs) effort, which is a process that assists in identifying and defining the data required to characterize a tank for each element of the TWRS. The sensitivity of decision outcomes to the quality, specificity, and accuracy of data and the extent to which large volumes of historical and routine tank monitoring data can be exploited are also to be assessed.

1.2 GENERAL PURPOSE OF DQO PROCESS AND ITS IMPLEMENTATION FOR TWRS

The DQO process was developed by the U.S. Environmental Protection Agency (EPA 1987, 1993; Neptune et al. 1990) to provide decision makers with a tool for determining data requirements and their acceptable levels of confidence before sampling occurs. The DQO process also assists in documenting the procedure used to determine the data requirements, thereby making them more defensible. The DQO process can be applied to problems involving the collection and use of data and has been extended to the different issues associated with Hanford Site tank waste.

There are several approaches to organizing and implementing the DQO process for the Hanford Site tanks. The simplest method is to develop DQOs for each of the 177 tanks on a tank-by-tank basis. A better, technical approach is to group the tanks by waste type and safety issue. This issue-based approach develops a template that can adapt the general DQO to a specific tank. An issue-based DQO approach guarantees a consistent application of the DQOs for that set of tanks and ensures the transfer of information for all tanks associated with that issue.

The initial DQO applications are based on the safety issues because of their high priority. A pilot DQO application was conducted on the high-heat safety issue (Tank 241-C-106). The recommendations from that DQO application are reported in the Tank 241-C-106 revised sampling and analysis document (Anderson et al. 1993). The next issue-based DQO application is associated with the Ferrocyanide¹ Safety Issue and is the subject of this report.

1.3 SCOPE OF FERROCYANIDE DQO PROCESS

The primary scope of the Ferrocyanide DQO process is to assist in defining the interim storage safety status of the Ferrocyanide Watch List tanks. In addition, this DQO process will provide linkage with other safety issues (i.e., transfer of key issues that are outside this scope of the DQO process to other DQO processes to ensure smooth transitions) and TWRS functional elements.

Although the Ferrocyanide DQO process deals primarily with core sampling, it is not limited only to that characterization technique. Historical information, simulant waste studies, and theoretical analyses are also considered part of the scope of this DQO process.

¹Ferrocyanide is used throughout the text of this report to represent all ferrocyanide compounds associated with the tank safety issue, e.g., NaCsNiFe(CN)_6 and $\text{Na}_2\text{NiFe(CN)}_6$. Fe(CN)_6 is used to represent generic ferrocyanide compounds in all equations.

This application of the DQO process addresses only the Ferrocyanide Safety Issue. All other tanks are considered in the safety screening module being developed by the Waste Tank Safety Program Office.

1.4 REPORT OUTLINE

This report is divided into eight chapters and two appendixes, which are described below.

- Chapter 1.0 provides background information regarding the Hanford Site high-level waste tanks and the different programs involved in characterizing and remediating them. It also gives an overview of the general DQO process and the specific scope of the Ferrocyanide DQO process.
- Chapter 2.0 describes the statement of the ferrocyanide waste problem including the history of the tanks, the specific safety issues, and the linkages to other TWRS issues (Step 1 of the DQO process).
- Chapter 3.0 summarizes the key decisions, required inputs, and boundaries that are associated with the ferrocyanide waste problem (Steps 2-4 of the DQO process).
- Chapter 4.0 describes decision rules of the Ferrocyanide DQO process and provides the decision logic (Step 5 of the DQO process).
- Chapter 5.0 documents the decision error tolerances with a general description of the discomfort curves. Next, the chapter provides specific tank characterization (*safe*, *conditionally safe*, and *unsafe*) discomfort curves and the justifications for error tolerances (Step 6 of the DQO process).
- Chapter 6.0 discusses the optimal sampling design including the factors affecting sampling requirements, the estimates of uncertainty from prior information, the number of core samples required, and the related sensitivities associated with assumed uncertainties (Step 7 of the DQO process).
- Chapter 7.0 gives a summary of the Ferrocyanide DQO process and includes a list of findings and recommendations.
- Chapter 8.0 presents the references for this report.
- Appendix A offers a step-by-step description of the basic DQO process.
- Appendix B provides sample size formulas.

This page intentionally left blank.

2.0 STATEMENT OF THE PROBLEM

2.1 HISTORY OF TANKS CONTAINING FERROCYANIDE

During the 1950s additional waste tank storage capacity was needed to support defense production activities. Figure 2-1 is a schematic typical of an SST waste storage tank. To obtain additional storage volume within a short period of time and to minimize construction of additional tanks, a process was developed to scavenge the cesium-137 and other soluble radionuclides from the tank waste liquids (Sloat 1954, Abrams 1956) using ferrocyanide compounds in a carrier-precipitation process. In implementing this process, approximately 140 metric tons of ferrocyanide were added to selected tank waste. The radionuclides then settled in the waste tanks in layers, and the supernate was discharged to the soil column (cribs and trenches).

Figure 2-1. Schematic Diagram of Typical Single-Shell Tank.

28905008.2

This treatment was used on U Plant waste effluent (U Plant ferrocyanide scavenging process) and selected waste previously discharged to tanks (in-farm ferrocyanide scavenging process). The U Plant ferrocyanide waste in the 241-BY Farm is expected to contain hard saltcake and to have lower concentrations of ferrocyanide in the sludge than the in-farm ferrocyanide waste, which is expected to contain relatively soft sludge.

In the Hanford Defense Waste Environmental Impact Statement (DOE 1987), the worst case (upper-boundary) scenario analyzed for radiation doses to the public from operational accidents was an explosion of SST waste during retrieval or handling operations. It was hypothesized that a waste layer containing ferrocyanide precipitates might react explosively with nitrates present in the waste under certain conditions. The consequences of this scenario were challenged by the General Accounting Office (Peach 1990), which led to the declaration of a USQ on the Ferrocyanide Safety Issue tanks in October 1990. In addition, 24 tanks were suspected to have ferrocyanide waste exceeding an initially established safety threshold of 1000 g-moles based on operating records and Track Radioactive Components (TRAC) (Jungfleisch 1984) inventory estimates of ferrocyanide waste transfer records. As a result, these tanks were placed on a Ferrocyanide Watch List.

In 1991, the Borsheim and Simpson (1991) study reviewed the available ferrocyanide scavenging records thoroughly. The studies concluded that Tanks 241-T-101, 241-BX-102, 241-BX-106, 241-BX-110, 241-BX-111, and 241-BY-101 do not contain the 1000 g-moles or more of ferrocyanide sludge required to place them on the Ferrocyanide Watch List. This study was instrumental in removing four of these (Tanks 241-T-101, 241-BX-110, 241-BX-111, and 241-BY-101) from the Ferrocyanide Watch List and USQ (Anttonen 1993). Therefore, as of the writing of this report, there are 20 Ferrocyanide Watch List tanks. Removal of the other two tanks (Tanks 241-BX-102 and 241-BX-106) is pending at DOE. The following is a list of the 20 tanks on the Ferrocyanide Watch List:

- 241-BX-102, -106
- 241-BY-103, -104, -105, -106, -107, -108, -110, -111, -112
- 241-C-108, -109, -111, -112
- 241-T-107
- 241-TX-118
- 241-TY-101, -103, -104.

2.2 CONTEXT OF THE FERROCYANIDE SAFETY ISSUE

It has been hypothesized that a ferrocyanide layer could undergo an exothermic reaction with nitrates present in the waste to potentially trigger a propagating reaction (DOE 1987). Fauske (1992) has shown that under the worst conditions expected (maximum fuel, 0% free water), the ferrocyanide would burn at a slow rate of 5 to 10 cm/min at 1 atm absolute pressure. This type of burn could generate aerosols that might plug and rupture the high-efficiency particulate air filter and release radioactive material into the environment. The ingredients for this reaction are known to exist in the Ferrocyanide Watch List tanks: fuel (ferrocyanide), oxidizer (nitrates), and heat (from radioactive decay). The main question is at what quantities do these ingredients need to exist in combination to create a potential for an exothermic reaction (thus the USQ).

In addition, it has been postulated that heat-generating radionuclides might somehow concentrate into a local hotspot, creating sufficient heat to cause local-heating of the sludge and possibly vaporization and removal of water (Dickinson et al. 1993, McLaren 1991). These hot spots would have to be sufficiently concentrated to cause waste temperatures to exceed the boiling point. If all other conditions were satisfied, a reaction might then be possible (although very improbable).

2.3 RELATIONSHIP OF THE FERROCYANIDE SAFETY ISSUE TO OTHER TWRS ISSUES

Although the primary component of this safety issue is associated with the Waste Tank Safety Technology element of TWRS and how it can be supported by the TWCP, other elements are considered. The retrieval, pretreatment, disposal and waste tank operations and maintenance elements also have been considered, but only in relation to safety issues associated with ferrocyanide waste. Any linkage with other DQO processes is to be identified to ensure smooth transition between the processes.

As the DQO processes for each of the other TWRS functional elements are conducted, a question of ferrocyanide waste compatibility with the selected tank transfers and processes will need to be addressed. For example, if the conditions defined for safe or conditionally safe interim storage classification are compromised during characterization, retrieval, pretreatment, or high-level waste/low-level waste immobilization, then the safety consequences and operating conditions will need to be defined.

Safety screening modules are being developed separate from, but associated with, the DQO process to evaluate all safety issues for each tank. Therefore, a Ferrocyanide Watch List tank will also be evaluated for other safety issues. Chapter 4.0 briefly discusses these safety screening modules.

This page intentionally left blank.

3.0 KEY DECISIONS, REQUIRED INPUT, AND BOUNDARIES

3.1 TANK SAFETY CLASSIFICATION STRATEGY

DOE's current strategy for determining the safety status of Ferrocyanide Watch List tanks places them into one of three classifications: *safe*, *conditionally safe*, and *unsafe*. Numerical criteria for the three safety classifications have been developed and selected for Ferrocyanide Watch List tanks based on experimental and theoretical information. Conservative values were selected to provide a margin of safety between the tank conditions and the conditions where a significant reaction could potentially occur.

A *safe* Ferrocyanide Watch List tank is defined as having a concentration of fuel less than 8 wt% as sodium nickel ferrocyanide on an energy equivalent basis, calculated on a zero free water basis¹ (Postma et al. 1993). Under this condition, the concentration of water and oxidizers and the temperature of the waste are not expected to be limiting. Neither monitoring nor controls are required to address the ferrocyanide hazard during interim storage.

A *conditionally safe* Ferrocyanide Watch List tank is defined as having a fuel concentration greater than 8 wt% as sodium nickel ferrocyanide on an energy equivalent (zero free water basis) and moisture content greater than 4/3 [Fuel - 8] wt%. Under these conditions, the concentration of oxidizers is not limiting. Monitoring and controls are required to limit the loss of moisture and to ensure that waste temperature does not exceed 90 °C.

An *unsafe* Ferrocyanide Watch List tank is defined as not meeting the criteria for *safe* or *conditionally safe* classifications. For tanks in the *unsafe* safety classification, monitoring and controls are required to avoid conditions that could lead to reaction ignition. Modifications in waste state are required to remove a tank from the *unsafe* safety classification.

3.2 REQUIRED INPUTS FOR CLASSIFICATION

Simulant waste laboratory studies (Jeppson and Wong 1993; Fauske 1992) thermal modeling (McLaren 1991, 1992) of Ferrocyanide Watch List tanks have provided an understanding of the conditions under which an exothermic reaction could occur. From these studies, it was

¹Free water is defined as water in ferrocyanide waste that can be removed from samples by drying at 120 °C for 18 hr.

determined that the following core sampling measurements were critical to determining the safe storage requirements for this waste:

- Average ferrocyanide concentration in any quarter segment (approximately 4.75 in. longer)²
- The moisture content of any quarter segment.

The method of estimating the ferrocyanide concentration in any subsegment is based on the conversion from the total energy measured from Differential Scanning Calorimetry (DSC) or Adiabatic Calorimetry (AC) techniques. The measurement of moisture content is taken using thermogravimetric analysis.

3.3 SECONDARY DATA REQUIREMENTS

There are several data requirements for the Ferrocyanide DQO process listed below that are secondary to the key data needs (i.e., ferrocyanide concentration and moisture content). These secondary data requirements are not directly involved in the decision rule logic for ferrocyanide waste but add information to the process of determining the ferrocyanide safety issues.

- Temperature of the waste is an important data requirement that is used in support of the decision whether a tank is *conditionally safe* or *unsafe*. If the waste temperature is greater than 90 °C, the fuel concentration is greater than 8 wt% (zero free water), and the moisture content is less than 4/3 [Fuel - 8] wt%, then the tank is classified as *unsafe* for storage and mitigation procedures are required. Temperature is not a core sample data value but is obtained from instrument tree measurements. As stated in Postma et al. (1993), any validated tank temperature found to be increasing would require actions as mandated by the Ferrocyanide Action Plan (Cash and Thurman 1991).
- The strontium-90 and cesium-137 concentrations in the waste are secondary measurements that are used to inform the decision makers on the status of the waste tanks. The temperature of the waste and the strontium-90 and cesium-137 concentrations are closely linked because these analytes are the main source of heat in the tanks.

²Generically, when discussing decision criteria, this report will be referring to quarter segment samples where most ferrocyanide compounds, if not all, are expected to be found. For thoroughness, saltcake sample analyses will only be made on half segments.

-
-
- The Total Organic Carbon (TOC) in the waste is also a secondary measurement that provides more information on the fuel content of the waste. Together, the TOC measurement and the ferrocyanide concentration provide a complete set of data on the fuel content of the waste. In addition, the TOC measurement is a key decision measurement of the organic safety issue.
 - The total cyanide content, determined by argentometric titration, can be converted to a ferrocyanide concentration and compared with the ferrocyanide concentration derived from the DSC or AC measurement.
 - The nickel concentration measurement is associated with the aging of the ferrocyanide waste. The aging process of ferrocyanide waste is an important consideration because it helps explain why ferrocyanide concentrations in Tanks 241-C-109 and 241-C-112 are much lower than expected and suggests that the Ferrocyanide Watch List tanks are becoming safer with time (Lilga et al. 1993). The nickel concentration is a signature analyte of the nickel ferrocyanide scavenging process and indicates how much ferrocyanide was originally present in the waste. Comparison of the original values with current total cyanide measurements gives an answer for the degree of aging that has occurred during storage. These values can also be compared to those found using historical data.

3.4 BOUNDARIES

When defining key decisions and data requirements, the populations that will be characterized through sampling must be specified, and decision rules will be applied to each of these defined populations. Several tank content and configuration characteristics are important in defining the populations to be characterized, including sampling methods, sample segment requirements, riser location considerations, and core recovery issues, as discussed below.

3.4.1 Sampling Methods

Although other sampling methods, such as auger samples, could be applied to characterize the ferrocyanide tanks, it was determined that the most reliable information is obtained from core samples. General sampling information is documented in a report by Bell (1993). Specific ferrocyanide sampling data are available as published by Simpson et al. (1993a, 1993b). Historical information is valuable, but the detailed data required to confidently classify the tanks are generally not available without obtaining samples from the tanks. The one exception to using core sample information is in measuring temperature. Temperatures are measured using data from instrument trees placed inside the tanks.

3.4.2 Sample Segment Requirements

The thickness of the ferrocyanide waste layer(s) is an important parameter for determining the proper volume of sample for analysis. To have enough material to perform an adequate assay, the smallest possible segment subdivision is four quarter segments (approximately 4 3/4 in.). A quarter segment is also the approximate thickness of the ferrocyanide waste laid down per campaign. For U Plant, several ferrocyanide campaigns were performed in succession, providing a layer of ferrocyanide projected to be 10 in. thick. In addition, the composition of waste for each ferrocyanide campaign (ferrocyanide concentration) was very consistent between campaigns. Therefore, homogenized quarter segments will be the primary units to be characterized for the sludge layers (half segments will be used for saltcake layers). The decision criteria will be applied to the concentrations determined for each quarter segment of the same vertical cross section. Concentrations among subsequent and across the same vertical cross section will be compared.

3.4.3 Riser Location

Investigation of the current use and location of the risers associated with each tank can determine if current available risers are adequate or if other risers would need to be cleared of equipment to allow sampling. It may also be determined that new risers would have to be created (an extreme case). An analysis of the available risers for the 20 tanks currently on the Ferrocyanide Watch List indicates that some of the tanks may require special operations to prepare them for sampling depending on the number of cores required. For this DQO application, it was assumed that the core samples would be obtained from locations that would adequately represent the true, or conservative, nature of the spatial variations within a tank.

3.4.4 Core Recovery

Characterization of any population requires that samples obtained be representative of the population. The recovery volume of a core will help determine representativeness. If core samples are taken from two spatially different risers (from opposite ends of the tank) in a tank but the recovery of the cores is poor, then the cores are not comparable, and the vertical stratum of the tank waste are not well known. If poor recovery of a core is discovered during sampling, another core should be taken. If poor recovery is discovered later and it affects the quality of the data, another core sample may be required. This is not a trivial decision, and the severity of the problem must be considered before another core is taken.

All sampling requirements outlined in this document assume a representative core is available. Therefore, if core recovery is poor, all results are jeopardized. In this report, we assume that the issues regarding core recovery, the location and availability of risers, and the effect of core acquisition techniques will be resolved and that core samples can be considered to be representative.

In summary, cores will be obtained from each tank. Material within each quarter segment of sludge (half segments for saltcake layers) will be homogenized, and a sample will be obtained from each homogenized quarter segment. These quarter segment samples will be analyzed for the analytes specified in Section 7.0. Analytical results for quarter segments will be compared against the decision rule criteria. Sample recovery and the spatial distribution of sampling locations must be sufficient to assume representative sampling.

This page intentionally left blank.

4.0 STATEMENT OF THE KEY QUESTIONS AND ANSWERS

4.1 DESCRIPTION OF DECISION RULES

In the previous sections, the first four steps of the DQO process have been documented. Specifically, the primary measurements of concern and the important questions to be addressed have been delineated. In Step 5 of the DQO process, a decision rule is formulated. The decision makers are momentarily allowed to assume that perfect information will be available, i.e., the tank characteristics are known. Under this assumption of no uncertainty, the decision makers integrate the outputs from the previous DQO steps into an unambiguous "If...then..." statement that outlines the conditions under which alternative actions will be chosen. Two decision rules were developed for the ferrocyanide tank safety issue: (1) *safe* versus *conditionally safe* or *unsafe* and (2) *conditionally safe* versus *unsafe*.

4.2 SAFE VERSUS CONDITIONALLY SAFE OR UNSAFE DECISION RULE

The ferrocyanide concentration, on an individual subsegment basis, was chosen to distinguish between the *safe* and either *conditionally safe* or *unsafe* categories. The decision rule states:

- If the fuel concentration for all quarter segments in sludge layers is less than 8 wt% sodium nickel ferrocyanide (zero free water) on an energy equivalent basis, then the tank is considered *safe*. Otherwise, the tank is considered either *conditionally safe* or *unsafe*.

The rationale for this decision rule and the particular threshold of 8 wt% fuel is detailed in a separate report (Postma et al. 1993). It was determined that if the ferrocyanide concentration (based on an energy equivalent concentration) is less than 8 wt% (zero free water), then insufficient fuel would be present to sustain a propagating reaction. The 8 wt% fuel criterion was based on conservative theoretical calculations. Experimental results on waste simulants have shown that roughly twice this fuel concentration (greater than 15 wt% sodium nickel ferrocyanide) is necessary to sustain a propagating reaction. The conservatism of this decision rule as it affects decision error tolerances is further considered in Section 5.0 of this report.

4.3 CONDITIONALLY SAFE VERSUS UNSAFE DECISION RULE

If sufficient ferrocyanide concentration is present in the tank, other parameters must be considered to determine whether the tank can be classified as *conditionally safe* or must be

treated as *unsafe*, which would require mitigation actions. The parameter of concern for this decision rule is moisture content. The decision rule states the following:

- If the fuel concentration in any quarter segment layer is greater than or equal to 8 wt% sodium nickel ferrocyanide (zero free water) on an energy equivalent basis and if the wt% moisture content for that quarter-segment layer is greater than $4/3 [\text{Fuel} - 8]$, then the tank is considered *conditionally safe*. Otherwise, it is classified as *unsafe* for interim storage.

This decision rule (see Figure 4-1) is dependent on two parameters, namely moisture content and fuel concentration (based on an energy equivalent to $\text{Na}_2\text{NiFe}(\text{CN})_6$ with zero free water). The rationale for this decision rule is detailed in a separate report (Postma et al. 1993). As the fuel concentration increases above 8 wt% (zero free water), the required moisture content also increases to ensure no propagating reaction occurs. There is conservatism inherent in this decision rule. For example, at 26 wt% ferrocyanide equivalent, the corresponding moisture criterion is 24 wt%. However, experiments have shown that 12 wt% moisture will prevent propagating reactions at 26 wt% sodium nickel ferrocyanide (Fauske 1992, Jeppson and Wong 1993). This conservatism is considered in determining appropriate decision error tolerances as outlined in Section 5.0 of this report.

Note that the temperature of the waste is a secondary data requirement.

Figure 4-1. Moisture Decision Rule.

4.4 DECISION LOGIC

To fully understand the Ferrocyanide DQO decision logic, one must understand how it relates to the general tank characterization DQO strategy. Figure 4-2 outlines the general tank characterization DQO logic and defines the relationships between the several safety issue DQOs, TWRS functional element DQOs, and the safety screening module.

Based on historical data and/or data available from safety screening module campaigns to date, tanks will be classified as tanks with or without significant safety issues. For those tanks that violate safety issue screening criteria, characterization requirements will be defined by the appropriate safety data requirements as outlined in a report documenting the DQOs for that specific safety issue. For example, 20 tanks are on the Ferrocyanide Watch List based on historical data. Other tanks could potentially be added to this list if the screening module criteria for ferrocyanide waste were violated. For these tanks on the Ferrocyanide Watch List, waste characterization requirements are outlined in this DQO report. If some of these tanks are suspect of other safety issues, the data requirements outlined through the DQO process for those safety issues would also be essential for developing tank sampling and analysis plans. Finally, depending on time and resource considerations, data requirements from other TWRS functional elements (i.e., retrieval, pretreatment, and disposal) would also be considered.

As the data from the characterization campaign for each tank become available, the appropriate decision rule logic for each applicable safety issue and/or TWRS functional element would be applied as outlined in each safety issue or TWRS functional element DQO report.

The Ferrocyanide Safety Issue decision rule logic is shown in Figure 4-3. Each of the decision rules are shown for classifying a tank as *safe*, *conditionally safe*, or *unsafe*. Note that the decision rules require a statistical demonstration that the decision criteria are met. Spatial, sampling, and analytical uncertainties must be considered to confidently demonstrate that a tank is either *safe* or *conditionally safe*.

Figure 4-2. Ferrocyanide DQO Decision Logic.

S9311061.6

Figure 4-3. Ferrocyanide DQO Decision Rules Logic.

S9311061.5

5.0 ERROR TOLERANCES ASSOCIATED WITH MEASUREMENTS

The error tolerances for the decisions identified in this report represent a balance between the need for precise analytical results and the impact of making an incorrect decision based on the sample results. The decision error tolerances must be provided by the decision makers and are often based on specific assumptions, prior knowledge, and/or expert opinion. The discomfort curves, the mechanisms used to obtain this information from the decision makers (EPA 1993), are described in this section.

5.1 DESCRIPTION OF DISCOMFORT CURVES

A discomfort curve is a visual way for the decision makers to describe the acceptable probability of making a decision error. The theory behind these curves is based on statistical hypothesis testing, in which the data are used to decide between one condition of the environment (the null hypothesis, H_0) and an alternative condition (the alternative hypothesis, H_1). The null hypothesis is assumed to be true in the absence of strong evidence to the contrary. A decision error occurs when the decision makers are led to believe in one hypothesis when the other is true.

There are two types of decision errors that must be considered. The first type of decision error occurs when the decision makers conclude, based on the data, that H_1 is true when, in fact, H_0 is true. This error is sometimes referred to as a false positive, or a Type I, error. The second error occurs when the decision makers conclude, based on available data, that H_0 is true when, in fact, H_1 is true. This error is sometimes referred to as false negative, or Type II, error.

The desired probabilities of making both types of decision errors are represented in a discomfort curve. The curve is produced by first determining the possible range of the parameter of interest and setting that to be the bottom axis of the curve. Next, a decision, or action, threshold (T_0) is set at the level where action will be required. For example, for the decision that the fuel concentration in a quarter segment is greater than or equal to 8 wt% for $\text{Na}_2\text{NiFe}(\text{CN})_6$ (zero free water) on an energy equivalent basis, the bottom axis would represent the range of possible fuel concentrations and the decision threshold, T_0 , would be 8 wt% for the discomfort curve.

To develop the discomfort curve, the decision makers are asked to define the acceptable probability of making an incorrect decision if the true value of the parameter of interest is a particular value on the bottom axis. The probability of making an incorrect decision defines the vertical axis of the discomfort curve. For fuel concentration in a quarter segment, two of those desired probabilities have been defined to be 20% at the decision threshold (8 wt% fuel) and 20% at 4 wt% fuel. The first probability is equivalent to making the statement that if the true fuel concentration in a quarter segment is 8 wt%, then it is acceptable to have up to a 20% chance of deciding that the fuel concentration is less than 8 wt% (or concluding

that the tank is *safe*). The 20% is a Type I error rate, or false positive (α). By choosing 20% probability at 4 wt% fuel, the decision makers are making the statement that if the true fuel concentration in a quarter segment is 4 wt%, then it is acceptable to have up to a 20% chance of deciding that the fuel concentration is greater than or equal to 8 wt%. The 20% is a Type II error rate, or false negative (β).

Discomfort curves have been produced for each of the decision rules in this report and are provided in the following sections. These discomfort curves were developed by the primary decision makers with assistance from statisticians. Justification for the specified thresholds and decision error tolerances will be provided in the sections that follow.

5.2 SAFE VERSUS CONDITIONALLY SAFE OR UNSAFE DECISION RULE

It has been determined that if the true average fuel (as energy equivalent ferrocyanide) concentration in each quarter segment is less than 8 wt% then the tank can be classified as *safe*. The decision rule was described and justified in Section 4.2. In this section, the hypothesis statement that corresponds to that decision rule will be provided, the discomfort curve will be described, and justification for the decision error tolerances will be given.

In Section 4.2, the decision rule was stated as the following: If the concentration of fuel (as energy equivalent ferrocyanide) in all quarter segments is less than 8 wt% (zero free water), then the tank can be classified as *safe*; otherwise, it must be classified as conditionally *safe* or *unsafe*. This decision rule corresponds to a null hypothesis, H_0 , and alternative hypothesis, H_1 , as follows:

H_0 : Fuel Equivalent in Quarter Segment (μ) $\geq 8\%$ wt% (zero free water) as $\text{Na}_2\text{NiFe}(\text{CN})_6$ [*Conditionally Safe* or *Unsafe*]

H_1 : Fuel in Quarter Segment (μ) $< 8\%$ wt% [*Safe*]

Note that the burden of proof is on those trying to show that the tank is *safe*; i.e., we assume H_0 is true unless sufficient evidence exists to conclude otherwise that H_1 is safe. The desired discomfort curve for this decision rule is illustrated in Figure 5-1 and represents the following threshold and error tolerance specifications:

Decision Threshold (T_0) = 8 wt% (zero free water) as $\text{Na}_2\text{NiFe}(\text{CN})_6$

Type I Error Rate (α_1) $\leq 20\%$ (at $\mu = 8\%$ wt% Fuel)

Type I Error Rate (α_2) $\leq 5\%$ (at $\mu = 12\%$ wt% Fuel)

Type I Error Rate (α_3) $\leq 1\%$ (at $\mu = 15\%$ wt% Fuel)

Type II Error Rate (β) = 20% (at $\mu = 4\%$ wt% Fuel)

Figure 5-1. Discomfort Curve for Ferrocyanide Concentration Used to Show Decision Error Tolerance for Ferrocyanide Safety Issue Measurement.

S9311061.4

5.2.1 Rationale for Decision Error Tolerances

When determining the acceptable probability of making an incorrect decision, the consequences of that decision error must be assessed. It would be tempting to ignore statistical uncertainties and state that whenever the fuel concentration is greater than 8 wt%, we will conclude with 100% confidence that the tank is either *conditionally safe* or *unsafe* regardless of whether or not the true value is close to 8 wt%. However, statistical uncertainties cannot be ignored. Thus, acceptable probabilities of making decision errors must be specified considering the consequences of those decision errors.

The consequence of misclassifying a tank with slightly greater than 8 wt% zero free water fuel (for any one subsegment) is very small because of the large amount of conservatism factored into the 8 wt% fuel decision criterion. The 8 wt% fuel criterion was based on conservative theoretical calculations. Experiments on waste simulants have shown that roughly twice this fuel concentration [greater than 15 wt% sodium nickel ferrocyanide (zero free water)] is necessary to sustain a propagating reaction (Postma et al. 1993). Therefore, it was deemed acceptable to have a 20% probability of concluding that a tank is *safe* if the true percent fuel is 8 wt%.

The consequence of misclassifying a tank increases as the percent zero free water fuel value approaches 15 wt%. It was considered appropriate to require only a 1% chance of classifying a tank as *safe* if the true percent fuel is 15 wt% and to require only a 5% chance of classifying a tank as *safe* if the true percent fuel is 12 wt%. These probabilities were considered to provide adequate protection given that other secondary data will be available to corroborate, or refute, the appropriateness of the decision and that continued prudent monitoring of the tanks is planned.

The consequence of misclassifying a tank as *conditionally safe* or *unsafe* when it is, in fact, *safe* is primarily driven by the need for prudent use of resources and the desire to avoid unnecessary safety concerns. There exists a strong precedence for expecting fuel concentrations to be far below the 8 wt% criterion because of destruction of ferrocyanide by aging (Babad et al. 1993). Analyses from Tanks 241-C-109 and 241-C-112, two of the four Ferrocyanide Watch List tanks expected to have the highest concentration (up to 26% dry weight), revealed concentrations that were about a factor of 10 less (1 to 2.9% zero free water) than predicted from flow sheet simulants (Jeppson and Wong 1993, Simpson et al. 1993a, 1993b). Therefore, it was deemed acceptable to have up to a 20% chance of concluding that a tank is *unsafe* or *conditionally safe* when the true fuel value is 4 wt% (zero free water) because we expect the ferrocyanide concentrations to be less than 4 wt% for all of the remaining tanks.

Note that these desired probabilities of decision errors are used to define the sampling requirements. Once the sampling requirements are defined, the achieved decision error probabilities may be improved (see Section 6.0).

5.3 CONDITIONALLY SAFE VERSUS UNSAFE DECISION RULE

The decision rule to distinguish between a tank that must be classified as *conditionally safe* from a tank that must be classified as *unsafe* was described in Section 4.3. In this section, the corresponding hypothesis statement to that decision rule will be provided, the discomfort curve will be described, and justification for the decision error tolerances will be given.

In Section 4.3, the moisture portion of the decision rule was stated as the following: If moisture in a quarter segment is greater than $4/3$ multiplied by (fuel concentration in a quarter segment - 8), then the tank can be classified as *conditionally safe*; otherwise it must be classified as *unsafe*. This decision rule corresponds to a null hypothesis, H_0 , and an alternative hypothesis, H_1 , as follows:

$$\begin{aligned} H_0: & \text{Moisture} \leq 4/3 \bullet [\text{Fuel} - 8] & [\text{Unsafe}] \\ H_1: & \text{Moisture} > 4/3 \bullet [\text{Fuel} - 8] & [\text{Conditionally Safe}] \end{aligned}$$

Again, the burden of proof is on those trying to show that the tank is *conditionally safe*; we assume H_0 (*unsafe*) unless there are sufficient data to conclude H_1 is true. In order to make these hypotheses more compatible with the discomfort curve terminology, the equations can be algebraically manipulated to the following statements:

$$H_0: \text{Fuel} - 3/4 \bullet \text{Moisture wt\%} \geq 8 \text{ wt\%} \text{ or } H_0: K^1 \geq 8 \text{ wt\%}$$

$$H_1: \text{Fuel} - 3/4 \bullet \text{Moisture wt\%} < 8 \text{ wt\%} \text{ or } H_1: K < 8 \text{ wt\%}$$

Figure 4-1 in Section 4.3 illustrates this decision rule. This same diagram was used to specify the decision error tolerances (shown in Figure 5-2). For example, if the true ferrocyanide or fuel concentration (zero free water) is 26 wt% and the true moisture content is 20 wt% ($K = 11$), the tank should be considered *unsafe*. For this case, the decision makers only wanted a 5% chance of concluding that it was *conditionally safe*. By using K on the horizontal axis, we constructed the desired discomfort curve shown in Figure 5-3. The corresponding error tolerance specifications are as follows:

Decision Threshold (T_0): $K = 8 \text{ wt\%}$

Type I Error Rate (α_1) = 10% (at $K = 8 \text{ wt\%}$ or when Fuel = 26 wt% and Moisture = 24 wt%)

Type I Error Rate (α_2) = 5% (at $K = 11 \text{ wt\%}$ or when Fuel = 26 wt% and Moisture = 20 wt%)

Type I Error Rate (α_3) = 1% (at $K = 17 \text{ wt\%}$ or when Fuel = 26 wt% and Moisture = 12 wt%)

Type II Error Rate (β_1) = 5% (at $K = -3 \text{ wt\%}$ or when Fuel = 15 wt% and Moisture = 24 wt%)

Type II Error Rate (β_2) = 1% (at $K = -10 \text{ wt\%}$ or when Fuel = 8 wt% and Moisture = 24 wt%)

5.3.1 Rationale for Decision Error Tolerances

The justification for the desired decision error probabilities for the moisture-based decision rule is similar to the argument presented for the ferrocyanide-based decision rule. There is significant conservatism inherent in the moisture criteria. For example, at 26 wt% zero free water fuel, the corresponding moisture criterion is 24 wt% (Postma et al. 1993). However, experiments have shown that 12 wt% moisture will prevent propagating reactions at 26 wt% fuel (Jeppson and Wong 1993). Thus, a safety factor of two is built into the criterion.

¹where $K = \text{Fuel} - 3/4 \bullet \text{Moisture wt\%}$.

Figure 5-2. Moisture Diagram.

Figure 5-3. Discomfort Curve.

Given this conservatism, a 10% chance of concluding that a tank is *conditionally safe* when the fuel concentration is 26 wt% and the moisture is 24 wt% was deemed acceptable.

As the ratio of moisture to fuel decreases, the consequence of making an incorrect decision increases. Because experiments have shown that 12 wt% moisture will prevent propagating reactions at 26 wt% zero free water fuel, a 1% chance of concluding that a tank was *conditionally safe* if $K = 17$ [fuel = 26 wt%, moisture = 12 wt%] was deemed acceptable. Likewise, a 5% chance of concluding that a tank was *conditionally safe* if $K = 11$ [fuel = 26 wt%, moisture = 20 wt%] was deemed acceptable.

Adequate protection is also desired against concluding that the tank is *unsafe* when, in fact, it is *conditionally safe*. Unnecessary expense and concern would be the result of this misclassification. In the extreme case that fuel concentration was 8 wt% (marginally *safe*) and moisture content was 24 wt%, the decision makers wanted to have at most a 1% chance of concluding the tank was *unsafe*. If the fuel concentration were 15 wt% and the moisture content were 24 wt%, the decision makers desired to have at most a 5% chance of concluding the tank was *unsafe*.

This page intentionally left blank.

6.0 OPTIMAL SAMPLING DESIGN

Optimal sampling requirements are determined by combining the information illustrated in the discomfort curves with estimates of uncertainty that incorporate all relevant sources of variability. Sources of variability that are applicable to the ferrocyanide safety issue include tank-to-tank variability, core-to-core variability, quarter segment-to-quarter segment variability, sample preparation variability, and analytical variability. In this section, the factors that affect sample requirements will be discussed, the estimates of uncertainty for the ferrocyanide safety issue will be presented, and requirements for the number of core samples will be provided.

6.1 FACTORS AFFECTING SAMPLING REQUIREMENTS

The primary sampling method for the Ferrocyanide Watch List tanks is the core sampling method¹. However, in the near future neutron diffusion and near-infrared technology may become primary sources for moisture measurements. Requirements for the number of cores are affected directly by the physical constraints of the sampling process as related to the questions of interest, the inherent sample variabilities, and the decision error tolerances.

Analyses for decision rules that relate to quarter segments will be made on samples from homogenized quarter segments. The important sources of variability are core-to-core differences within a segment and analytical variants. These estimates are provided in Section 6.2.

Statistical distributional assumptions are also key in determining sampling requirements. Normality was assumed for all sample requirement calculations. Based on previously available core sample results from other tanks containing ferrocyanide, normality appears to be an appropriate assumption.

6.2 ESTIMATES OF UNCERTAINTY FROM PRIOR INFORMATION

The information illustrated in the discomfort curves is an important factor affecting sample requirements. It is the pertinent information regarding the decision makers' tolerance to making Type I and Type II errors. This information also relates to the estimates of uncertainty. If the uncertainty is large and the consequences of making an incorrect decision

¹Core sampling data cannot, and will not, be used to address temperature and "hot-spot" concerns, although strontium and cesium measurements from core samples are used to address these issues.

are significant for relatively small differences between the true and threshold values, more samples would be required. Consequently, estimates of uncertainty are required to develop an optimal sampling scheme (Heasler et al., 1993a).

Estimates of uncertainty, called relative standard deviations (RSDs), were obtained (where possible) from analyses of samples obtained from 5 cores from Ferrocyanide Watch List Tanks 241-C-109 and 241-C-112. The spatial, sampling, and analytical variations observed are assumed to be representative of most Ferrocyanide Watch List tanks. The data available for analysis and applicable to the decision rules and/or secondary questions include ferrocyanide concentrations on quarter segments, moisture content on quarter segments, and nickel concentrations on core composites.

Analysis of variance techniques were used to estimate the variance for each of the sources of variability (or variance components). The results for ferrocyanide and nickel concentrations indicated that the tank-to-tank variability is not significantly different from zero. The core-to-core RSDs and the analytical RSDs showed good agreement for ferrocyanide and nickel concentrations. The overall estimate of uncertainty (RSD) is approximately 22% of the mean for both ferrocyanide and nickel concentrations. This estimate accounts for both core-to-core and analytical uncertainty.

The tank-to-tank variability for moisture content was significantly different from zero, although this estimate was based on a small number of data points. The overall estimate of uncertainty (RSD) is approximately 12% of the mean for moisture. This estimate accounts for tank-to-tank, core-to-core, and analytical uncertainty. Therefore, because tank-to-tank variations are included, the estimate is a conservative value for the RSD of interest. However, this value is not the appropriate uncertainty estimate to use for the decision rule that gives moisture content as a function of ferrocyanide concentration. For that decision rule, we used a combined estimate of uncertainty that incorporates both ferrocyanide and moisture variations. The estimate of RSD for the *conditionally safe* versus *unsafe* decision rule is 22%, dominated by the ferrocyanide concentration variability.

Core sample data from two other SSTs (Tanks 241-B-110 and 241-U-110) have been analyzed and are sufficient for estimation of spatial, sampling, and analytical uncertainties (Heasler et al. 1993b). The statistical analysis of these tanks indicated that the overall RSD could range from 10% to 100%. The RSDs of this report are very specific because they were calculated using only cyanide, nickel, and moisture data from two Ferrocyanide Watch List tanks and were based on five cores. The RSD estimate should be updated as additional samples become available. In Section 6.4, we will address the sensitivities of the sample size calculations to the estimate of RSD.

6.3 NUMBER OF CORES REQUIRED

Two cores are required for the *safe* versus *conditionally safe* or *unsafe* decision rule. The inputs to the sample size calculations are provided with the discomfort curves in Section 5.2. An RSD of 22% is used for the calculation. A formula for calculating the required sample size is provided in Appendix B.

Two cores are also required for the *conditionally safe* versus *unsafe* decision rule. The inputs to the sample size calculations are provided with the discomfort curves in Section 5.3, and an RSD of 22% is used for the calculation.

6.3.1 Achievable Probabilities of Making Incorrect Decisions

Assuming that two cores will be taken from a Ferrocyanide Watch List tank and assuming that the tank has an overall estimate of variability (RSD) of 22%, the achievable probabilities of making incorrect decisions can be estimated. If the discomfort curve represents the desired probabilities for decision error, these calculations represent the actual probabilities for decision error under these assumptions.

For the *safe* versus *conditionally safe* or *unsafe* decision rule, the estimate of standard deviation is calculated by assuming that the standard deviation is accurate at a mean of 8%. The standard deviation for the mean fuel concentration is calculated by taking the RSD times eight divided by the square root of two. For this decision rule, the standard deviation for the mean is estimated to be 1.2445 wt% (zero free water). This value was used to calculate all probabilities. At 8 wt% zero free water fuel, the achievable probability for decision error with 2 cores is 0.20; at 4 wt% fuel, the achievable probability for decision error is 0.0588; at 12 wt% the achievable probability for decision error is 0.0001, and at 15 wt% fuel the achievable probability for decision error is less than 0.0001. Except for the 0.20 probability for decision error, which was fixed, all other achievable probabilities are well below the desired values. Table 6-1 summarizes these values along with the desired decision error probabilities.

For the *conditionally safe* versus *unsafe* decision rule, the estimate of standard deviation is calculated by assuming that the standard deviation is accurate at a mean of 8 wt%. The standard deviation for the mean value of K is calculated the same as above; the value is 1.2445 wt%. At K = 8 wt% zero free water fuel, the achievable probability for decision error with two cores is 0.10; at K = -3 wt% the achievable probability for decision error is 0.0063, and at -10 wt% fuel, the achievable probability for decision error is less than 0.0001; at 11 wt%, the achievable probability for decision error is 0.0001, and at K = 17 wt%, the achievable probability for decision error is less than 0.0001. Except for the 0.10 probability for decision error, which is fixed, all other achievable probabilities are well below the specified values. Table 6-2 summarizes these values along with the desired decision error probabilities.

Table 6-1. Achievable Probabilities for Decision Error for the Safe Versus Conditionally Safe or Unsafe Decision Rule.

Fuel as Equivalent $\text{Na}_2\text{NiFe}(\text{CN})_6$ (0% free water)	Desired Probability for Decision Error	Achievable Probability for Decision Error	
		RSD=22 %	RSD=33 %
4	0.20	0.0588	0.2047
8	0.20	0.20	0.20
12	0.05	0.0001	0.0032
15	0.01	<0.0001	<0.0001

Table 6-2. Achievable Probabilities for Decision Error for the Conditionally Safe Versus Unsafe Decision Rule.

Fuel as Equivalent $\text{Na}_2\text{NiFe}(\text{CN})_6$ (0% free water) wt %	Moisture (wt %)	K = Fuel - 3/4 • wt % Moisture	Desired Probability for Decision Error	Achievable Probability for Decision Error	
				RSD = 22 %	RSD = 30 %
8	24	-10	0.01	<0.0001	0.0011
15	24	-3	0.05	0.0063	0.045
26	24	8	0.10	0.10	0.10
26	20	11	0.05	0.0007	0.0040
26	12	17	0.01	<0.0001	<0.0001

6.4 SENSITIVITIES OF SAMPLE SIZE CALCULATIONS

Since the sample size results that are given above are based on certain assumptions (the most notable being the estimate of RSD at 22% was assumed at a mean of 8 wt% fuel), it is reasonable to ask what would happen if that assumption was wrong. To address this question, the RSD has been increased successively and the achievable decision errors calculated until at least one of the desired decision error probabilities is not met. This is an attempt to quantify the sensitivity of the sample size to the estimate of RSD that is built into the sample size of two.

For the *safe* versus *conditionally safe* or *unsafe* decision rule, the RSD can be as high as 33% with the desired decision error tolerances still achievable. At an RSD of 33%, the standard deviation of the mean at 8 wt% fuel is 2.4890 wt%. At 8 wt% fuel, the achievable probability for decision error with 2 cores is 0.20; at 4 wt% fuel, the achievable probability is 0.2047; at 12 wt% fuel, the achievable probability is 0.0032; and at 15 wt% fuel, it is less

than 0.0001. Consequently, the RSD can be as high as 33%, and the desired decision error tolerances will be met (the limiting factor is the decision error probability at 4 wt% fuel). These values are summarized in Table 6-1.

For the *conditionally safe* versus *unsafe* decision rule, the RSD can be as high as 30% with the desired decision error tolerances still achievable. At an RSD of 30%, the standard deviation of the mean at $K = 8$ wt% is 3.7335 wt%. At $K = 8$ wt%, the achievable probability for decision error with 2 cores is 0.10; at $K = -3$ wt%, the achievable probability is 0.045; at $K = -10$ wt%, the achievable probability is 0.0011; at $K = 11$ wt%, it is 0.0040; and at $K = 17$ wt%, the achievable probability is less than 0.0001. Consequently, the RSD can be as high as 30%, and the desired decision error tolerances will be met (the limiting factor is the decision error probability at $K = -3$ wt%). These values are summarized in Table 6-2.

This page intentionally left blank.

7.0 CONCLUSIONS

The DQO process has been applied to the ferrocyanide safety issue to determine data requirements and develop an appropriate sampling scheme that would enable decision makers to confidently make decisions. Sampling requirements also were defined to ensure adequate protection against making incorrect decisions.

7.1 FINDINGS

The major findings of this process are as follows:

- Two spatially distributed cores are required from each Ferrocyanide Watch List tank to increase the chances that desired levels of protection against making incorrect decisions are obtained.
- Analytical measurements must be applied to each homogenized quarter segment of sludge within the core sample. Key analytes for the decisions are fuel concentrations as energy equivalent $\text{Na}_2\text{NiFe}(\text{CN})_6$, determined through energetics measurements (DSC or AC measurements of calories per gram), and wt% moisture content. Secondary measurements include total cyanide, nickel, cesium-137, strontium-90, and TOC (see Table 7-1).
- Desired decision error tolerances are still achieved with two core samples even if the fuel RSD increases from the current best estimate of 22% up to 33%.

When analytical results for each Ferrocyanide Watch List tank are received, a statistical evaluation should be conducted (to assess the design performance by comparing desired error tolerances to the achieved values) to determine whether one can confidently conclude a tank is *safe* or *conditionally safe*.

Other direct outputs of this DQO process are given below:

- Core sample locations must be chosen to represent the spatial distribution of the important analytes in the tank.
- DQO applications for each of the TWRS functional elements should consider the safety consequences and operating conditions associated with ferrocyanide waste.
- Platinum, rather than nickel, crucibles should be used for the inductively coupled plasma (ICP) fusion analytical method, thereby reducing the potential for a bias in the nickel concentration measurements.

Table 7-1. Analytical Requirements for Ferrocyanide Watch List Tanks.

Analyte to be Measured	Analytical Method	Sample	Decision Threshold	Assumed (Desired) Analytical Uncertainty
Nickel Concentration	Inductively Coupled Plasma-Acid Digestion and Fusion	Quarter Segment	Not Specified	$\leq 5\%$ ^a
Total Fuel Content	Differential Scanning Calorimetry/Adiabatic Calorimetry	Quarter Segment	To be Converted to Equivalent $\text{Na}_2\text{NiFe}(\text{CN})_6 \bullet 4.6 \text{ H}_2\text{O}$ wt%	$\leq 3\%$
Total Cyanide Concentration in Quarter Segment	Direct Assay (Method is PNL-ALO-285)	Quarter Segment	8 wt% $\text{Na}_2\text{NiFe}(\text{CN})_6 \bullet 4.6 \text{ H}_2\text{O}$	$\leq 3\%$ ^b
Moisture Content in Quarter Segment	Thermogravimetric Analysis	Quarter Segment	4/3 [fuel - 8] wt%	$\leq 3\%$
Tank Temperature	Thermocouple	N/A	90 °C	$\leq 5\%$
Total Organic Carbon	Direct Persulfate Oxidation	Quarter Segment	3 wt% (zero free water)	$\leq 5\%$
Cesium-137	Gamma Energy Analysis-Water Digestion and Fusion	Quarter Segment	Not Specified	$\leq 5\%$
Strontium-90	Beta Radiochemistry	Quarter Segment	Not Specified	$\leq 5\%$

^aThe analytical uncertainty for nickel contains uncertainty from sample preparation and analytical variability.

^bThe analytical uncertainty for total cyanide contains uncertainty from sample preparation and analytical variability (excluding variations due to sample extrusion and homogenization).

-
-
- The RSD estimates should be updated as more data become available. An RSD of 22% for ferrocyanide and 12% for moisture based on data from Tanks 241-C-109 and 241-C-112 have been used to develop the sampling requirements. If the revised RSDs vary significantly from these assumed values, the required number of cores may need to be modified.
 - A method for determining the specifications of the ferrocyanide compounds should be completed. This method will contribute to the understanding of the ferrocyanide safety issues and will provide information to the retrieval, pretreatment, and disposal TWRS functional elements.

7.2 CONCLUSIONS

Key successes resulting from the application of the DQO process to the Ferrocyanide Safety Issue include the following:

- Developed and documented a logical, defensible approach to defining core sampling requirements while explicitly recognizing inherent spatial, sampling, and analytical uncertainties
- Caused a reexamination of, and narrowed the decision criteria down to, two key decision rules for classifying a Ferrocyanide Watch List tank as *safe*, *conditionally safe*, or *unsafe* for interim storage
- Developed an innovative approach to developing the joint decision rule and decision error tolerances for the moisture criteria, which accounted for the dependence on the ferrocyanide concentration
- Demonstrated that decision errors can be controlled to desired levels with a minimum sampling requirement.

In summary, the application of the DQO process to the Ferrocyanide Safety Issue has resulted in a well-documented, logical approach to defining characterization requirements. Uncertainties also have been explicitly addressed and managed to acceptable levels. Finally, this process provided a mechanism for communicating the integral relationships between sampling requirements and desired levels of protection against making incorrect decisions.

This page intentionally left blank.

8.0 REFERENCES

- Anderson, C. M., K. E. Bell, S. M. Blacker, D. Goodman, M. S. Peffers, B. A. Pulsipher, J. L. Scott, O. S. Wang, 1993, *Tank 241-C-106 Revised Sampling and Analysis Plan Through a Data Quality Objectives Study*, WHC-EP-0723, Westinghouse Hanford Company, Richland, Washington.
- Abrams, R. B., 1956, *History: Metal Recovery Waste Scavenging Program*, HW-43066, General Electric Company, Richland, Washington.
- Anttonen, J. H., 1993, *Resolution of Unreviewed Safety Question (USQ) for Four Ferrocyanide Tanks*, 93-CAB-223, (DOE Letter 9304645B, to T. M. Anderson, Westinghouse Hanford Company), July 9, 1993.
- Babad, H., 1992, *An Overview of Progress Made Toward Resolving Priority One Safety Issues: Fiscal Year 1992*, WHC-EP 0606, Westinghouse Hanford Company, Richland, Washington.
- Babad, H., J. E. Meacham, B. C. Simpson, and R. J. Cash, 1993, *The Role of Aging in Resolving the Ferrocyanide Safety Issue*, WHC-EP-0599, Westinghouse Hanford Company, Richland, Washington.
- Bell, K. E., 1993, *Tank Waste Remediation System Tank Waste Characterization Plan*, WHC-SD-WM-PLN-047, Rev. 1, Westinghouse Hanford Company, Richland, Washington.
- Borsheim, G. L., and B. C. Simpson, 1991, *An Assessment of the Inventories of the Ferrocyanide Watchlist Tanks*, WHC-SD-WM-ER-133, Rev. 0, Westinghouse Hanford Company, Richland, Washington.
- Cash, R. J., and J. Thurman, 1991, *Action Plan for Response to Abnormal Conditions in Hanford Site Radioactive Waste Tanks Containing Ferrocyanide*, WHC-EP-0407, Rev. 1, Westinghouse Hanford Company, Richland, Washington.
- Dickinson, D. R., J. M. McLaren, G. L. Borsheim, and M. D. Crippen, 1993, *Credibility of Drying Out Ferrocyanide Tank Waste Sludges by Hot Spots*, WHC-EP-0648, Westinghouse Hanford Company, Richland, Washington.
- DOE, 1987, *Final Environmental Impact Statement, Disposal of Hanford Defense High-Level Transuranic Wastes, Hanford Site, Richland, Washington*, DOE/EIS-0113, vols. 1 through 5, U.S. Department of Energy, Washington, D.C.

-
- Ecology, EPA, and DOE, 1989, *Hanford Federal Facilities Agreement and Consent Order*, 2 vols., Washington State Department of Ecology, U.S. Environmental Protection Agency, U.S. Department of Energy, Olympia, Washington.
- EPA, 1987, *Data Quality Objectives for Remedial Response Activities - Example Scenario: RI/FS Activities at a Site with Contaminated Soils and Ground Water*, PB90-272634, U.S. Environmental Protection Agency, Washington D.C.
- EPA, 1993, *Guidance for Planning for Data Collection in Support of Environmental Decision Making Using the Data Quality Objectives Process*, EPA QA/G-4 (interim final), U.S. Environmental Protection Agency, Washington, D.C.
- Fauske, H. F., 1992, *Adiabatic Calorimetry and Reaction Propagation Tests with Synthetic Ferrocyanide Materials Including U Plant 1, U Plant 2, In Farm 1, In Farm 2, and Vendor Procured Sodium Nickel Ferrocyanide*, WHC-SD-WM-RPT-054, Rev. 0, Westinghouse Hanford Company, Richland, Washington.
- Heasler, P. G., C. M. Anderson, and D. B. Baird, 1993a, *Generic Tank Characterization Estimation and Sample Size Problems*, PNL draft, Pacific Northwest Laboratory, Richland, Washington.
- Heasler, P. G., C. M. Anderson, D. B. Baird, R. J. Serne, and P. D. Whitney, 1993b, *Statistical Evaluation of Core Samples From Hanford Tank B110*, PNL-8745, Pacific Northwest Laboratory, Richland, Washington.
- Jeppson, D. W., and J. J. Wong, 1993. *Ferrocyanide Waste Simulant Characterization*, WHC-EP-0631, Rev. 0, Westinghouse Hanford Company, Richland, Washington.
- Jungfleisch, F. M., 1984, *TRAC: A Preliminary Estimation of the Waste Inventories in Hanford Tanks Through 1980*, SD-WM-TI-057, Rockwell Hanford Operations, Richland, Washington.
- Lilga, M. A., M. R. Lumetta, and G. F. Schiefelbein, 1993, *Ferrocyanide Safety Project, Task 3 Aging Studies, FY 1993 Annual Report*, PNL-8888, Pacific Northwest Laboratory, Richland, Washington.
- McLaren, J. M., 1991, *Single-Shell Tank 104-BY Thermal Hydraulic Analysis*, WHC-EP-0521, Rev. 0, Westinghouse Hanford Company, Richland, Washington.
- McLaren, J. M., 1992, *Thermal Analysis of Tank 241-BY-106*, WHC-EP-0591, Rev. 0, Westinghouse Hanford Company, Richland, Washington.
- Neptune, D., E. P. Brantly, M. J. Messner, and D. I. Michael, 1990, "Quantitative Decision Making in Superfund: A Data Quality Objectives Case Study." *Hazardous Materials Control* 3(3):19-27.
-

-
-
- Peach, J. D., 1990, *Consequences of Explosion of Hanford's Single-Shell Tanks Are Understated*, (GAO Letter B-241479 to C. M. Synar, Chairman of Environment, Energy and National Resources Subcommittee, Committee on Government Operations, House of Representatives), GAO/RCED-91-34, General Accounting Office, Washington, D.C.
- Postma, A. K., J. E. Meacham, R. J. Cash, W. S. Barney, G. L. Borsheim, M. D. Crippen, D. R. Dickinson, D. W. Jeppson, M. Kummerer, J. L. McLaren, C. S. Simons, and B. C. Simpson, 1993, *Safety Criteria for Ferrocyanide Watch List Tanks*, WHC-EP-0691, Westinghouse Hanford Company, Richland, Washington.
- Simpson, B. C., G. L. Borsheim, and L. Jensen, 1993a, *Tank Characterization Report: Tank 241-C-109*, WHC-EP-0668, Rev. 1, Westinghouse Hanford Company, Richland, Washington.
- Simpson, B. C., G. L. Borsheim, and L. Jensen, 1993b, *Tank Characterization Data Report: Tank 241-C-112*, WHC-EP-0640, Rev. 1, Westinghouse Hanford Company, Richland, Washington.
- Sloat, R. J., 1954, *In Farm Scavenging Operating Procedure and Control Data*, HW-38955 Rev. 1, General Electric Company, Richland, Washington.

This page intentionally left blank.

APPENDIX A

DESCRIPTION OF DQO PROCESS

This page intentionally left blank.

APPENDIX A**DESCRIPTION OF DQO PROCESS**

The basic structure¹ of the DQO process consists of seven steps. The steps are sequential, and each step is dependent on the previous step. The same structure was used for the Ferrocyanide DQO, with one exception. Steps 5 and 6 were reversed based on the lessons learned from the Tank 241-C-106 DQO pilot study (WHC 1993b). The seven steps used for the Ferrocyanide DQO process are:

- Step 1: Understanding the context
- Step 2: Converging on a set of relevant questions
- Step 3: Defining the array of possible useful answers
- Step 4: Selecting the measurements that will estimate the answers
- Step 5: Arriving at a decision rule
- Step 6: Setting error tolerance for the measurements
- Step 7: Optimizing the design.

STEP 1: UNDERSTANDING THE CONTEXT

The primary method for understanding the context is through three decision elements: 1) key personnel and documents will be identified, 2) informal discussions will be held, and 3) documents will be reviewed. Documents reviewed will include summaries and assessments of the safety topic areas, relevant engineering studies, program plans, and any decision logic diagrams that exist. Relevant regulatory issues will also be reviewed. As a result of this effort, decisions will be documented and the relevant uncertainties and potential outcomes identified. (Decisions to be made by regulators are uncertainties from DOE's perspective and will be treated as such).

The relationship between these three decision elements will be tentatively developed. The result will be a document that provides a description of the context that will serve as a basis for all future work. This document will be made available for review by Tank Waste Remediation System (TWRS) managers and scientists. The review comments will then be formally incorporated into the context document, and this will be submitted to DOE.

STEP 2: CONVERGING ON A STATEMENT OF THE RELEVANT QUESTIONS

The context document provides the first step in converging on an understanding of the relevant questions. When applying the DQO process to situations as complex as TWRS,

¹Notes from a 1992 Hanford presentation by S. Blacker and D. Goodman.

there will always be more than one question that needs to be addressed. Some key questions may relate fuel as equivalent to the tank's state of nature. For example, one key question might be. "What is the concentration of fuel as equivalent ferrocyanide in a particular tank." There may be other questions that DOE asks itself such as, "Should a particular tank be removed from the Ferrocyanide Watch List?"

Due to the complexity of the issue, it may be that there are myriads of potential questions (as well as potential answers). Consequently, additional analysis will be undertaken, as needed, to determine those questions that are truly important for resolution of the topic area.

STEP 3: DEFINING THE ARRAY OF POSSIBLE USEFUL ANSWERS

Answers are useful to the extent that they differentiate between decision alternatives and increase the likelihood of satisfactory outcomes. Potentially useful answers will be explored initially as a consequence of understanding the context. The set of possible useful answers will be further refined as a result of converging on the important questions. Also, initial discussions with project managers, scientists, and engineers will focus on what are the consequences of possible findings for decisions and outcomes.

STEP 4: SELECTING THE MEASURES THAT WILL ESTIMATE THE ANSWERS

The process of quantifying the relationship between decisions and outcomes will require the development of appropriate metrics. The metrics chosen will be based upon discussions with project managers, scientists, and engineers and will also take into account the availability of existing historical and Track Radioactive Components (TRAC) data. In addition to measures for data uncertainties, it may also be necessary to develop performance measures for the possible outcomes. If the contest is complex, then there may be more than one measure of outcome performance. This may necessitate the development of utility measures for the outcomes and a multiattribute utility function. Such functions will be developed and checked for consistency with overall goals and objectives for TWRS. Consequently, TWRS decision documents will be reviewed (in particular, the rebaselining decision documents) for consistency with these higher-level objectives to the extent that they are discriminators for decisions within the chosen topic area.

STEP 5: ARRIVING AT A DECISION RULE

Decision rules relate the possible sampling results for the data estimates to decision alternatives. The analysis of the quantitative decision structure, developed in the previous steps, will be used to arrive at a decision rule. The decision structure will be expanded, as necessary, to calculate the expected value of sample information. The decision rule will consider all the information that has been obtained: the consequences of the

decision/outcome combinations, the values and costs of these consequences, the prior probability distributions for uncertain events, and the extent to which the sample information is diagnostic for in-tank conditions.

STEP 6: SETTING ERROR TOLERANCES FOR THE ESTIMATES

Error tolerances will be set based on the uncertainties associated with estimating the true answers. It may be possible to obtain these from expert judgement of discomfort curves. Analytes with error tolerances within the range of uncertainty for historical and TRAC data will not need to be further characterized. Quality measures, such as precision and accuracy, will be used to determine data quality and set error tolerances. A quantitative decision structure could be developed. This structure will make explicit the relationship between characterization uncertainties and potential outcomes/conditional alternatives. In particular, this structure will be used to refine error tolerances by determining the cost of errors. Sensitivity analysis can be used to further identify the significant questions and their resulting answers. The value of information may be used to further reduce the list of needed analytes.

STEP 7: OPTIMIZING THE DESIGN

The optimization of the design will supply the required information at the minimum sampling and analytical costs associated with error tolerances developed in Step 5.

CONCLUSION

The ultimate goal of this effort is to develop an optimized sampling and analytical plan. This plan will be a generic plan that provides a method for transforming the information that is known about a particular tank into a specific sampling and analytical plan for the tank. Historical data, TRAC estimates, and specific tank information (such as the riser configuration) will be used to apply the generic plan to specific tanks. The resulting sampling and analysis plan will describe the number of cores, sample preparation, analyte lists, and laboratory flow sheets. The current baseline sampling and analysis plan for ferrocyanide safety issue tanks is Module A of the Tank Waste Characterization Plan. Expected minimum information needs for ferrocyanide safety issue tanks are fuel concentration, water concentration, and temperature. Generation of the sampling and analytical plan will involve analytical laboratory personnel.

This page intentionally left blank.

APPENDIX B

SAMPLE SIZE FORMULAS AND STATISTICAL ISSUES

This page intentionally left blank.

APPENDIX B

SAMPLE SIZE FORMULAS AND STATISTICAL ISSUES

The underlying formulas and calculations that provided many of the results of this paper are provided in this appendix. This appendix will describe the sample size formulas, the analysis of variance calculations for estimates of uncertainty, and will provide an explanation of the non-central t-distribution which was used in the calculation of the achievable probabilities in Section 6.0.

SAMPLE SIZE FORMULA

The specifications that relate to the discomfort curves in Section 5 are the fundamental inputs to the sample size calculations. The hypotheses allow the decision maker to state that if the difference between the decision threshold, T_0 , and an alternate threshold, T_1 , is greater than or equal to a specified value, then the power of the test ($1-\beta$) must be greater than or equal to a specified level. The decision rule for ferrocyanide in a quarter segment specifies that $T_0 = 8$ wt%, $T_1 = 4$ wt%, $\alpha=0.20$, and $\beta=0.20$. For these specifications, the decision maker is stating that if the difference between 8 wt% and T_1 is greater than or equal to 4 wt%, then the power of the test must be greater than or equal to 80%.

The sample size formula which applies to the one-sided tests is given by

$$n = \frac{(z_{1-\alpha} + z_{1-\beta})^2 RSD^2}{\left(\frac{T_1 - T_0}{T_0}\right)^2}$$

where $z_{1-\alpha}$ and $z_{1-\beta}$ are obtained from the standard z table.

ANALYSIS OF VARIANCE CALCULATIONS

The RSD (relative standard deviation) in the above formula is the estimate of uncertainty that is addressed in Section 6.2 of this report. By definition, RSD is σ/μ where σ is the estimate of uncertainty and μ is the mean of the distribution of the null hypothesis, H_0 . The RSD accounts for the spatial and analytical uncertainties.

To obtain the RSD of 22% for the safe vs. conditionally safe or unsafe decision rule, variance components were computed for total CN data. The variance components procedure

resulted in estimates of spatial and analytical uncertainties for total cyanide. Data from DSC measurements, the measurements that will actually be used to determine ferrocyanide, were not available to estimate spatial uncertainties. The approach used to calculate total uncertainty was to use the analytical uncertainty from the DSC measurements, which was available from the labs, and the spatial uncertainty from the total cyanide measurements (the assumption is that the spatial uncertainty would not be affected by the method of measurement). This resulted in estimates of analytical uncertainty = 5% RSD, and estimates of core-to-core uncertainty (spatial) = 21%. The RSDs are combined by multiplying each RSD by the estimated mean, squaring the standard deviations to get a variance, adding the variances, taking the square root, and dividing by the mean. The combined uncertainties resulted in a 22% RSD.

To obtain the RSD of 22% for the conditionally safe vs. unsafe decision rule, similar techniques to the one described above were used. Moisture measurements were used to estimate analytical and spatial uncertainties for moisture. However, the moisture and ferrocyanide estimates of uncertainty needed to be combined to represent the decision rule. The variance for the equation $[\text{Fuel} - 3/4] \bullet \text{Moisture}$ is equal to the variance for ferrocyanide plus $(3/4)^2$ times the variance for Moisture. The square root of this variance divided by the combined mean resulted in an RSD of 22% for that decision rule.

NON-CENTRAL t-DISTRIBUTION

To calculate the achievable probabilities for decision error provided in Section 6, the assumption is made that the assumed uncertainties are the estimated uncertainties after two cores have been taken and the measurements in the laboratory have been completed. This assumption places the non-central t-distribution as the underlying distribution. The method of showing that the non-central t-distribution applies is given below.

For each sample event, compute the mean ($\bar{x}$), and the standard deviation (s) and construct

$$\bar{x} + t \bullet s/\sqrt{n}$$

Compare to u_0 . Then,

$$\Pr(\bar{x} + t \bullet s/\sqrt{n} \leq \mu_0) = \Pr\left(\frac{\bar{x} - \mu_0}{s/\sqrt{n}} \leq -t\right)$$

then, after algebraic manipulation we have

$$Pr \left(\frac{\frac{\bar{x} - \mu}{\sigma / \sqrt{n}} + \frac{\mu - \mu_0}{\sigma / \sqrt{n}}}{\sqrt{\frac{(n-1) s^2}{\sigma^2}} \sqrt{(n-1)}} \leq -t \right)$$

which equals

$$Pr \left(\frac{N(0,1) + \delta}{\sqrt{\frac{\chi_v^2}{v}}} \leq -t \right)$$

then, $Pr(T_{\delta, \nu} \leq -t)$

where $T_{\delta, \nu}$ is Non-Central t-Distribution with ν degrees of freedom and non-centrality parameter δ is

$$\delta = \frac{\mu - \mu_0}{\sigma / \sqrt{n}}$$

This page intentionally left blank.

DISTRIBUTION

Number of Copies

OFFSITE

6	<u>U.S. Department of Energy</u> EM-35, Trevion II Washington, D.C. 20585 John C. Tseng
1	<u>U.S. Department of Energy</u> Savannah River Operations Office P.O. Box A Aiken, South Carolina 29808 Thomas C. Temple
1	Charles S. Abrams 1987 Virginia Idaho Falls, ID 83404
1	David O. Campbell 102 Windham Road Oak Ridge, TN 37830
1	Fred N. Carlson 6965 North 5th West Idaho Falls, ID 83401
1	Donald T. Oakley 409 12th Street SW, Suite 310 Washington, DC 20024-2188
1	Arlin K. Postma 3640 Ballard Road Dallis, Oregon 97338
1	William R. Prindle 1556 Crestline Drive Santa Barbara, CA 93105

DISTRIBUTION (cont)

Number of copies

OFFSITE

1	Alfred Schneider 5005 Hidden Branches Drive Dunwoody, GA 30338
1	<u>Air Products & Chemicals, Inc.</u> 7201 Hamilton Blvd Allentown, PA 18195-1501 George E. Schmauch
1	<u>Battelle Columbus Laboratories</u> 505 King Avenue Columbus, OH 43201-2693 James A. Gieseke
1	<u>Brookhaven National Laboratory</u> Upton, NY 11973 Kamal K. Bandyopadhyay
1	<u>Design Science, Inc.</u> 163 Witherow Road Sewickley, PA 15143 Gary Powers
1	<u>Fauske and Associates, Inc.</u> 16W070 W. 83rd St. Burr Ridge, IL 60521 Hans K. Fauske
1	<u>Florida State University</u> Department of Chemistry B-164 Tallahassee, FL 32306 Greg R. Choppin

DISTRIBUTION (cont)

Number of copies

OFFSITE

1	<u>Harvard University</u> 295 Upland Avenue Newton Highlands, MA 02161 Melvin W. First
1	<u>Hazards Research Corporation</u> 200 Valley Road, Suite 301 Mt. Arlington, NJ 07856 Chester Grelecki
1	<u>Lawrence Livermore National Laboratory</u> P.O. Box 808, L-221 Livermore, CA 94550 Billy C. Hudson
4	<u>Los Alamos National Laboratory</u> P.O. Box 1663 Los Alamos, NM 87545 Steve F. Agnew Steve W. Eisenhower Thomas E. Larson L. Harold Sullivan
1	<u>MIT/Department of Nuclear Engineering</u> 77 Massachusetts Ave. Room 24-102 Cambridge, MA 02139 Mujid S. Kazimi

DISTRIBUTION (cont)

Number of copies

OFFSITE

1	<u>Nuclear Consulting Services, Inc.</u> P.O. Box 29151 Columbus, OH 43229 J. Louis Kovach
1	<u>Oak Ridge National Laboratory</u> Emory D. Collins P.O. Box 2008 7930, MS-6385 Oak Ridge, TN 37831-6385
1	Charles W. Forsberg P.O. Box 2008 MS-6495 Oak Ridge, TN 37831-6495
1	Thomas S. Kress P.O. Box 2009 9108, MS-8088 Oak Ridge, TN 37831-8088
1	<u>Rice University</u> 5211 Paisley Houston, TX 77096 Andrew S. Veletsos
1	<u>Sandia National Laboratory</u> P.O. Box 5800 Albuquerque, NM 87185 Scott E. Slezak

DISTRIBUTION (cont)

Number of copies

OFFSITE

3	<u>Science Applications International Corporation</u> 12850 Middlebrook Road Trevion I, Suite 300 Germantown, MD 20874 Ray S. Daniels (3)
1	<u>State of Washington</u> Department of Ecology P. O. Box 47600 Olympia, WA 98504-7600 Michael T. Gordon
1	<u>University of South Carolina</u> Department of Electrical and Computer Engineering Swearingen Engineering Center Columbia, SC 29208 Joseph S. Byrd
1	<u>University of Washington</u> Center for Process Analytical Chemistry Chemistry Department BG-10 Seattle, WA 98195 Bruce R. Kowalski
1	<u>Vanderbilt University</u> P.O. Box 1596, Station B Nashville, TN 37235 Frank L. Parker

DISTRIBUTION (cont)
Number of copiesONSITE

15

U.S. Department of Energy,
Richland Field Office

R. F. Christensen (4)	R3-72
R. E. Gerton (7)	R3-72
A. G. Krasopoulos	A4-81
Public Reading Room	H2-53
RL Docket File (2)	H5-36

17

Pacific Northwest Laboratory

R. T. Allemann	K7-15
C. M. Anderson	K7-34
S. A. Bryan	P7-25
J. W. Buck	K6-55
A. R. Felmy	K6-82
P. G. Heasler	K7-34
B. M. Johnson	K1-78
M. A. Lilga	P8-38
B. P. McGrail	K2-38
B. A. Pulsipher	K7-34
R. D. Scheele	P7-25
G. F. Schiefelbein	P8-38
J. L. Scott	P7-35
D. M. Strachan	K2-44
P. J. Turner	P7-35
J. J. Toth	K7-94
Hanford Technical Library	P8-55

46

Westinghouse Hanford Company

H. Babad	R2-78
G. A. Barnes	H5-09
J. B. Billetdeaux	R2-08
D. C. Board	S1-57
G. L. Borsheim	R2-11
S. R. Moreno	B3-06
R. J. Cash (2)	R2-78

DISTRIBUTION (cont)
Number of copiesONSITEWestinghouse Hanford Company (cont)

M. D. Crippen	L5-31
G. M. Christensen	H4-21
D. R. Dickinson	L5-31
G. T. Dukelow	R2-78
J. C. Fulton	R2-31
J. M. Grigsby	H4-62
H. D. Harmon	R2-52
D. A. Healey	T4-07
J. M. Held	R3-09
M. N. Islam	R3-08
D. W. Jeppson	L5-31
N. W. Kirch	R2-11
C. A. Kuhlman	B3-30
M. Kummerer	H4-62
J. D. McCormack	L5-31
J. M. McLaren	H0-34
J. E. Meacham	R2-78
N. J. Milliken	H4-62
T. L. Moore, Sr	H5-09
A. F. Noonan	R2-12
R. S. Popielarczyk	R1-30
R. W. Reed	R1-51
F. R. Reich	L5-63
C. P. Schroeder	L7-06
B. C. Simpson	R2-12
J. P. Summerhays	R2-85
H. Toffer	H0-38
W. T. Watson	H0-38
W. D. Winkelman	L5-55
D. D. Wodrich	H0-30
D. D. Wodrich	R2-85
W. F. Zuroff	R2-14
Central Files	L8-04
EDMC	H6-08
Information Release Administration (3)	R1-05
TFIC	R1-20

This page intentionally left blank.

**DATE
FILMED**

6/1/94

END