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ENGINEERING CHANGE NOTICE

1. ECN 609982

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12. Description of Change

Complete revision of document. Criteria for fuel and moisture concentrations were changed. The source of decision inputs was expanded, and the decision rules were expanded and rewritten. The number of required analyses was reduced and the uncertainty requirements were relaxed. Confidence limits for the decision rules were changed. Appendix B, describing the selection of tanks that bound ferrocyanide aging, was added.

13a. Justification (mark one)

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

13b. Justification Details

Changes affect which tanks will be sampled, the number and type of analyses conducted, and the analytical uncertainties required by the laboratories.

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

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

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

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

20. Approvals

Signature	Date	Signature	Date
OPERATIONS AND ENGINEERING		ARCHITECT-ENGINEER	
Cog. Eng. J. E. Meacham *J. E. Meacham*	4/19/95	PE	
Cog. Mgr. R. J. Cash *R. J. Cash*	4/27/95	QA	
QA		Safety	
Safety		Design	
Environ.		Environ.	
Other		Other	
		DEPARTMENT OF ENERGY	
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RELEASE AUTHORIZATION

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

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7. Abstract

This document provides the requirements for obtaining tank characterization information to support resolution of the Ferrocyanide Safety Issue at the Hanford Site by applying the data quality objectives (DQO) process. A strategy describing the overall approach to safe storage and disposal of the waste in the ferrocyanide tanks identifies the problems and decisions that require characterization data. The DQO process is applied to each decision or group of related decisions to specify data requirements.

8. RELEASE STAMP

RECORD OF REVISION	(1) Document Number WHC-SD-WM-DQO-007, Rev. 1	Page 1

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CHANGE CONTROL RECORD

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

Westinghouse
Hanford Company Richland, Washington

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

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INTRODUCTION

Requirements for obtaining tank characterization information are developed through the Data Quality Objectives (DQO) process. A strategy describing the overall approach to safe storage and disposal of waste identifies the problems and decisions requiring characterization data. The DQO process is applied to each decision or group of related decisions to specify data requirements.

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

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

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PART

I

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SUMMARY

This document records the data quality objectives (DQO) process applied to the Ferrocyanide Safety Issue at the Hanford Site. Three important outputs of this particular DQO application were the following: (1) decision rules addressing historical data, fuel degradation (aging), and categorization of Ferrocyanide Watch List tanks; (2) recommendations for which tanks should be sampled and the number of tank cores or samples to be taken; and (3) analytical requirements that feed into the tank-specific characterization plans.

The decision rules developed in this DQO allow the ferrocyanide tanks to be categorized as *safe*, *conditionally safe*, and *unsafe* based on fuel and moisture concentrations. The decision rules also allow historical data and aging models to be corroborated by measuring fuel, moisture, nickel, total organic carbon, and nickel concentrations.

The number of core samples required to characterize a ferrocyanide tank is a function of variability and the desired confidence to make a correct decision. Assuming variability estimated from the tanks sampled thus far are representative, two cores are sufficient to characterize a ferrocyanide tank.

The analytical requirements from this DQO process fall into two groups, primary and secondary. The primary data requirements are always applied, while the secondary requirements are only necessary on those quarter segments with measured fuel concentrations greater than 600 Joules per gram (J/g) or that violate the moisture decision threshold.

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LIST OF TERMS

DOE	U.S. Department of Energy
DQO	Data Quality Objectives
DSC	Differential Scanning Calorimetry
EIS	Environmental Impact Statement
EPA	U.S. Environmental Protection Agency
GAO	U.S. General Accounting Office
ΔH	Heat of Reaction
RSD	Relative Standard Deviation
SAR	Safety Analysis Report
SST	Single-Shell Tank
TOC	Total Organic Carbon
TRAC	Track Radioactive Components
TWAP	Tank Waste Analysis Plan
TWRS	Tank Waste Remediation System
USQ	Unreviewed Safety Question

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1.0 SCOPE OF THE FERROCYANIDE DQO PROCESS

The primary scope of the Ferrocyanide DQO process is to assist in determining the interim safe storage status of the Ferrocyanide Watch List tanks and to help corroborate the historical and aging data that will be used to resolve the ferrocyanide safety issue. Specifically, the Ferrocyanide DQO process defines the type, quantity, and quality of data required to categorize the ferrocyanide tanks (as *safe*, *conditionally safe*, or *unsafe*) and to resolve the safety issue.

All available sources of characterization information are used including the original process flowsheets, waste transfer histories, waste lay down models, simulant experiments, ferrocyanide degradation (aging) data, and sampling results. In addition, this DQO process provides linkage with other safety issues (i.e., transfer of key issues that are outside the scope of this DQO process to other DQO processes) and Tank Waste Remediation System functional elements.

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2.0 STATEMENT OF THE PROBLEM

Various high-level radioactive waste from defense operations has accumulated at the Hanford Site in underground storage tanks since the mid-1940s. During the 1950s, additional tank storage space was required to support the defense mission. To obtain this additional storage volume within a short time period, Hanford Site scientists developed a process to scavenge cesium-137 from tank waste liquids (Sloat 1954, 1955). In implementing this process, approximately 140 metric tons (154 tons) of ferrocyanide were added [as $Fe(CN)_6^{4-}$] to waste that was later routed to some Hanford Site single-shell tanks (SSTs).

The scavenging process precipitated ferrocyanide from solutions containing nitrate/nitrite, and an intimate mixture of ferrocyanides and nitrates/nitrites may exist in some SSTs. Ferrocyanide, in sufficiently high concentrations and mixed with oxidizing material such as sodium nitrate/nitrite, can be made to react exothermically by heating it to high temperatures (Epstein et al. 1994a). Therefore, it is desired to know if there exists a potential for a exothermic ferrocyanide reaction that could produce a radioactive release.

Reviews of process flowsheets and waste transfer records (Borsheim and Simpson 1991) indicated that eighteen tanks received ferrocyanide waste, and thus fall under the scope of this DQO. The Ferrocyanide Watch List is comprised of the following tanks:

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

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3.0 DECISIONS AND DECISION INPUTS

3.1 SAFETY CATEGORIES FOR FERROCYANIDE TANKS

The chemical reactivity of waste stored in Ferrocyanide Watch List tanks places the tanks into one of three categories: *safe*, *conditionally safe*, or *unsafe*. Numerical criteria for the three safety categories have been developed for ferrocyanide waste based on empirical data and theoretical calculations (Fauske 1995). Tanks categorized as *safe* contain waste that cannot support a propagating reaction. Tanks categorized as *conditionally safe* contain waste that cannot support a propagating reaction under current storage conditions, while *unsafe* tanks require monitoring and controls to avoid conditions that could lead to reaction ignition. Mitigation is required to remove a tank from the *unsafe* category.

3.2 DECISION LOGIC

The decision logic for placing ferrocyanide waste into one of the three categories is shown in Figure 3-1. The decisions are listed in a logical order such that some decisions only need to be addressed based on the outcome of previous decisions. The decisions are broken down into six distinct questions. The decision rules or action limits corresponding to these general questions are stated in Section 4.0.

1. Was ferrocyanide ever transferred to the tanks? This step was previously accomplished by the establishment of the present Ferrocyanide Watch List based on the review of tank histories by Borsheim and Simpson (1991), and is thus outside the scope of this DQO. It is shown here only to present the complete logic sequence.

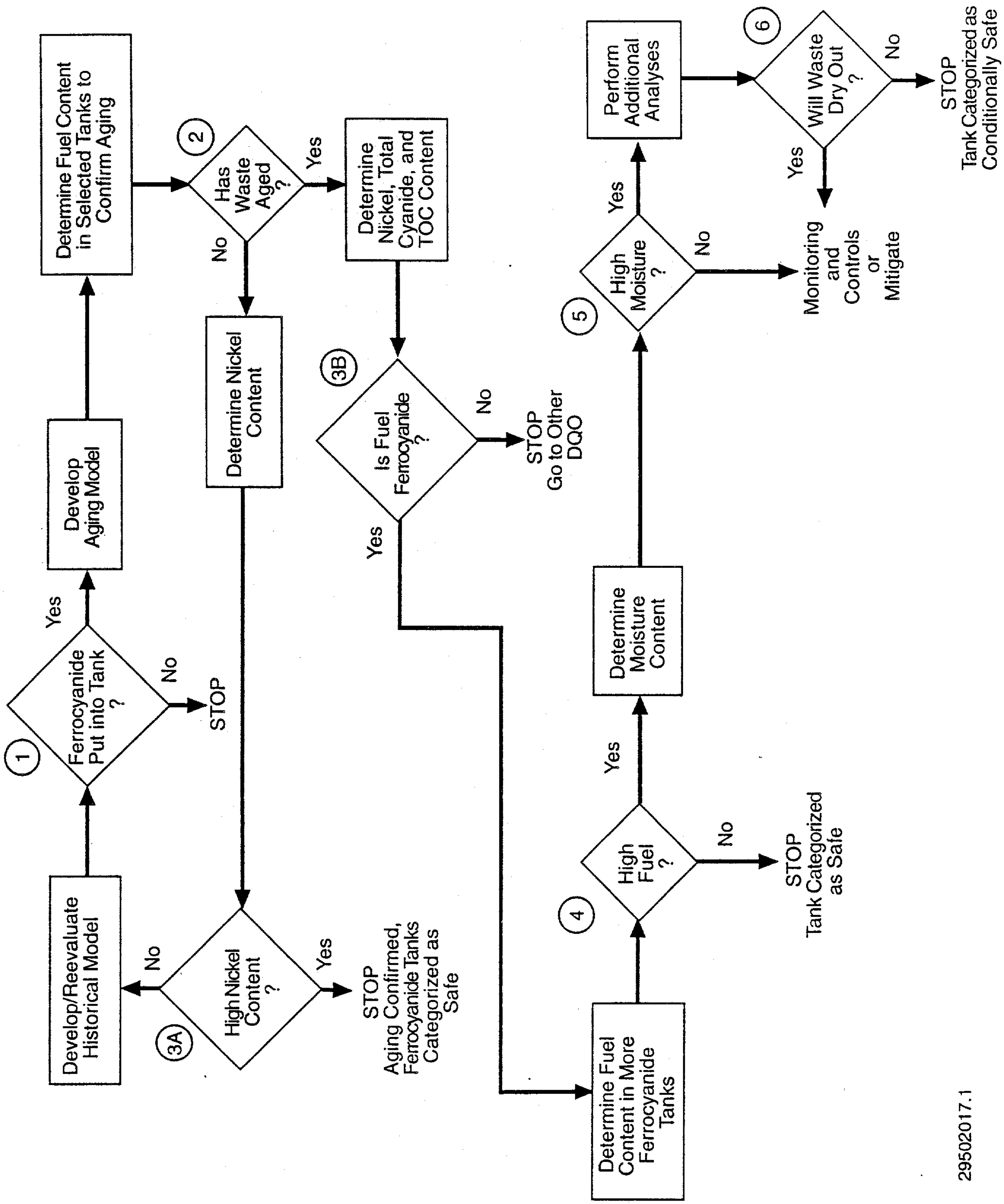
2. Does the waste contain a fuel concentration less than predicted by the repetition of the process flowsheets as reported by Jeppson and Wong (1993)? If so, then proceed to nickel analyses to confirm the historical and aging models (3A). If the fuel concentration is equal or greater than predicted, then additional analyses will be performed (3B).

3A. Does the waste have a sufficiently high nickel concentration to conclude that it originally did contain ferrocyanide sludge? If so, waste aging is confirmed and additional sampling of ferrocyanide waste is not required. The ferrocyanide tanks are categorized as *safe* and the decision process ends here. If the waste has a low nickel concentration, then the tank has been erroneously identified as containing ferrocyanide waste, and the historical model will require reevaluation.

3B. Is the fuel in the waste ferrocyanide? If the fuel is mostly composed of something other than ferrocyanide, then a different DQO (e.g., the Organic DQO) will address this waste.

4. Does the waste have enough fuel to support a propagating reaction when completely dried? If not, the waste is categorized as *safe* and the decision process ends here.

Figure 3-1. Decision Logic for Ferrocyanide Waste



5. Is enough moisture present in the waste to prevent a propagating reaction? If not, the waste is categorized as *unsafe* and the decision process ends here.

6. Does the waste have the potential to dry during interim storage? If not, then the tank is categorized as *conditionally safe* and the decision process ends here. If the moisture concentration could decrease to below safe levels during interim storage, then the tank is categorized as *unsafe*.

3.3 DECISION INPUTS

Decision inputs may consist of any piece of information or data that can help answer the decision. The decision inputs required to make the decisions are summarized in Table 3-1. The decision input is listed along with the reason it is needed. Each of the decision inputs are connected to one of the six decisions listed in Section 3.2.

3.4 BASES FOR DECISION INPUTS

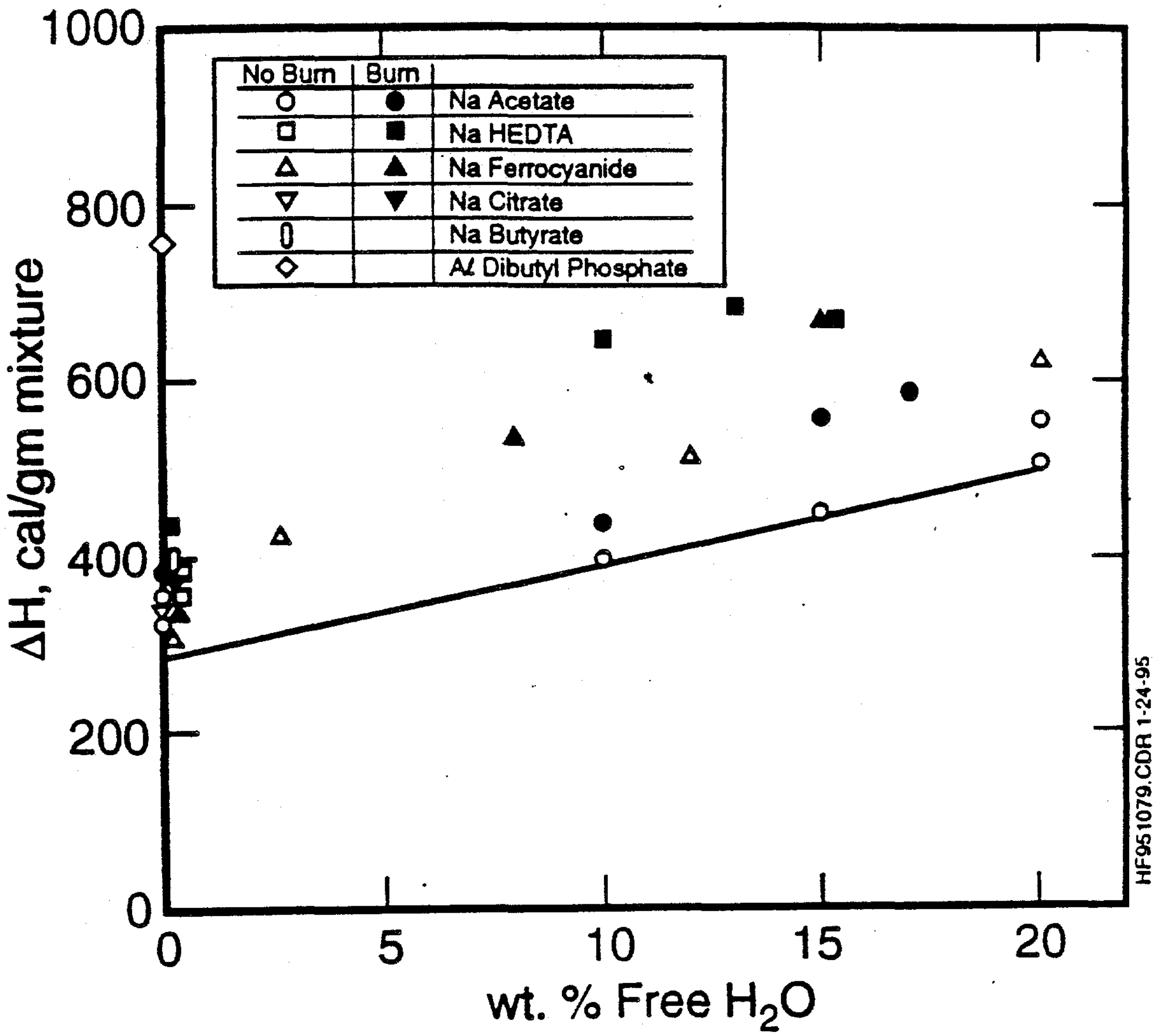
Data on fuel and moisture concentration are necessary to categorize a ferrocyanide tank as *safe*, *conditionally safe*, or *unsafe*. The waste must exceed a minimum fuel concentration to support a propagating reaction. This minimum fuel concentration, based on empirical data and theoretical calculations (Fauske 1995), is 1200 J/g on a dry weight basis. To judge whether waste exceeds this minimum, the fuel concentration (i.e., the exothermic energy in J/g) must be determined experimentally. Differential Scanning Calorimetry (DSC) can be used to quantify the exothermic energy concentration of samples.

Moisture can prevent an exothermic reaction and moisture concentration must be below a certain value for a propagating reaction to occur. Adiabatic calorimetry (AC) and reaction rate tests on ferrocyanide waste simulants have shown that propagating ferrocyanide reactions cannot occur if the wt% moisture exceeds 0.022 [fuel (in J/g) - 1200]. Moisture concentration should be measured by thermogravimetric analysis (TGA).

The limits on fuel and moisture concentration that define the range of possibly reactive waste, as used in the two preceding paragraphs, are based on a theoretical model verified by experimental data (Fauske 1995). These data, which include not only sodium nickel ferrocyanide but also several organic compounds of interest, are shown in Figure 3-2. Not that all reactive compositions as well as many nonreactive compositions in Figure 3-2 fall above the solid line that represents the fuel and moisture limits stated above. Thus, the limits used here are a conservative bound on the reactive compositions.

Data on nickel concentration are necessary to confirm historical information and ferrocyanide aging models. Nickel is a signature analyte of the nickel ferrocyanide scavenging campaigns, the only source of high nickel concentrations. Experiments that replicated the original process flowsheets (Jeppson and Wong 1993) showed nickel contents of the sludges of 1.2 to

Figure 3-2. Measured Reactivity Limits. Comparison between surrogate data (measured fuel concentration times theoretical heat of reaction) and the proposed criterion for safety (represented by solid line), $\Delta H < 1200$ J/g + (wt% water)/0.022. Note that 1200 J/g = 290 cal/g.



4.8 wt% Ni on a dry weight basis. A lower bound of 1 wt% or 10,000 µg/g (dry weight basis) is selected as a minimum for any tank that contained ferrocyanide sludge. Nickel concentrations should be determined by inductively coupled plasma analysis (ICP) by either acid digestion or fusion preparations (whichever is more accurate). Non-nickel crucibles (e.g., platinum, zirconium, etc.) must be used during this analysis to reduce analytical bias.

Data on fuel and nickel concentrations can also be used as evidence of ferrocyanide waste aging (Babad et al. 1993, Lilga et al. 1993, 1994). Experiments replicating the original process flowsheets (Jeppson and Wong 1993) showed dry-basis fuel concentrations in sludges from 6.3 to 25.5 wt% $Na_2NiFe(CN)_6$. Using the lowest of these values and a calculated heat of reaction (ΔH) of 9,600 J/g of $Na_2NiFe(CN)_6$ (Fauske 1995), the fuel concentration should exceed 600 J/g in the ferrocyanide waste if no aging has occurred.

Table 3-1. Summary of Decision Inputs

Decision Input	Decision	Reason for Required Decision Input
1. Identification of ferrocyanide tanks	Did tank receive ferrocyanide?	Identification of tanks that contained ferrocyanide focuses analyses and sampling efforts.
2. Fuel	Does ferrocyanide still exist?	Determines whether the reaction hazard has been mitigated via degradation of the ferrocyanide fuel.
3A. Nickel	Did the ferrocyanide age?	Nickel is an indicator analyte that confirms that the tank once contained ferrocyanide waste and that the waste has aged.
3B. Nickel, cyanide, and total organic carbon	Is the fuel ferrocyanide?	Determines whether the fuel source is something other than ferrocyanide.
4. Fuel	Is there enough fuel to support a propagating reaction?	Determines if the waste can support an exothermic propagating reaction.
5. Fuel and moisture	Will moisture prevent a propagating reaction?	Even if sufficient fuel is present, a propagating reaction cannot occur if enough moisture is present.
6. Total carbon, cation, particle size, and waste dry out analyses	Will the waste dry out?	Evaluates whether the waste will dry out, possibly moving the waste to the *unsafe* category.

Cyanide and total organic carbon (TOC) analyses provide information on fuel characterization. These measurements are necessary to determine whether a waste tank should be covered by this DQO or the organic DQO and whether it belongs on the Ferrocyanide or Organic Watch List (possibly both). Total cyanide should be measured by dissolving the waste sample in an ethylenediaminetetraacetic acid/ethylenediamine solution, followed by argentometric titration or other suitable detection technique. Direct persulfate oxidation is recommended to determine TOC; however, other techniques that meet the desired analytical uncertainty are also acceptable.

Analyses for total carbon, particle size, and aluminum, bismuth, calcium, iron, phosphorus, sodium, and other cations help corroborate waste lay down and waste dryout (moisture retention and hot spot) models. These analyses are important to confirm that actual waste is bounded by waste simulant experiments (Jeppson and Wong 1993, Epstein et al. 1994b), and that the conclusions from these experiment apply to actual waste.

4.0 DECISION RULES

To formulate the decision rules, it is necessary to assume that the tank characteristics are known. Under this assumption of no uncertainty, the outputs from the previous DQO steps are integrated into an unambiguous "If...then..." statement that outlines the conditions under which alternative actions will be chosen. Action limits or decision thresholds have been defined to produce the decision rules shown in Table 4-1.

Table 4-1. Decision Rules

Decision	IF (Decision Threshold)	THEN
1.	No ferrocyanide waste was transferred to tank	Tank does not belong on Ferrocyanide Watch List. Stop.
2.	Fuel concentration < 600 J/g	Measure nickel concentration to confirm aging and historical models (3A).
	Fuel concentration ≥ 600 J/g	Measure nickel, total cyanide, and TOC to determine fuel source (3B).
3A.	Nickel ≥ 10,000 ppm	Ferrocyanide has degraded. Waste categorized as *safe*, stop.
3B.	Nickel < 10,000 ppm and CN^- < 3.1 wt% and TOC > 5.0 wt%	Fuel is non-ferrocyanide. Go to other DQO, stop.
4.	Fuel concentration < 1200 J/g	Waste cannot support a propagating reaction. Waste categorized as *safe*, stop.
5.	Moisture concentration > 0.022 [fuel (J/g) - 1200]	Measure temperature, examine dry out models, and collect cation, particle size, and total carbon data.
	Moisture concentration ≤ 0.022 [fuel (J/g) - 1200]	Waste categorized as *unsafe*, stop.
6.	Waste will not dry out during interim storage	Waste categorized as *conditionally safe*, stop.
	Waste can dry out during interim storage	Waste categorized as *unsafe*, stop.

The first decision threshold, whether a tank contains ferrocyanide, is a qualitative input from detailed examinations of waste transfer records (Borsheim and Simpson 1991). That is, based on historical records, a tank either received ferrocyanide waste or not. This is significant because tanks have been added and removed from the Ferrocyanide Watch List (Meacham et al. 1993) based on these examinations.

The second decision threshold, whether the waste has aged, is based on the fuel values predicted in the lowest concentration flowsheet material (Jeppson and Wong 1993, Sloat 1954, 1955). The nickel threshold of 10,000 ppm is based on the minimum nickel concentrations expected in ferrocyanide sludges (Jeppson and Wong 1993).

The total cyanide threshold of 3.1 wt% is based on the cyanide concentration that would produce an exotherm of 600 J/g, and the TOC threshold is based on the TOC fuel concentration criterion for identifying organic tanks (Webb et al. 1995). Fuel and moisture decision thresholds (thresholds four and five, respectively) are based on the conditions necessary to support a propagating reaction (Fauske 1995).

The final decision threshold, whether the ferrocyanide waste can dry out, is a function of the waste temperature, heat load, tank breathing rate, and the chemical, physical, and rheological properties of the waste. A study that examined the available data (Epstein et al. 1994b) concluded that ferrocyanide waste will not dry to unsafe levels under current storage conditions (i.e., no active ventilation and no external heating). Cation, particle size, and total carbon analyses may be required to confirm that the actual waste parameters are bounded by the waste simulants tested.

5.0 BOUNDARIES AND CONFIDENCE LIMITS FOR DECISION INPUTS

In Section 4.0, the decision thresholds were summarized. Because the decision threshold values determine the logic path in the DQO, acceptable boundary and confidence levels must be defined to determine whether the decision input meets the threshold value. A summary of the boundaries and confidence levels for the Ferrocyanide DQO effort is presented in Table 5-1. In some cases, the determination of the decision input and its comparison to the decision threshold limit may be based on a qualitative interpretation of the data or information source as compared to a statistical determination of the confidence.

Table 5-1. Decision Boundaries and Confidence Limits

Decision Boundary	Decision Threshold	Confidence Limit*
Tank	1. No ferrocyanide waste was transferred to tank	High (Best Engineering Judgement)
12 cm ferrocyanide sludge layers (all ¼ segments)	2. Fuel concentration < 600 J/g	80%
12 cm ferrocyanide sludge layers (measured on one central ¼ segment per core)	3A. Nickel ≥ 10,000 ppm	80%
12 cm ferrocyanide sludge layers (measured on all ¼ segments with fuel concentration > 600 J/g)	3B. Nickel < 10,000 ppm and CN^- < 2.9 wt% and TOC > 5 wt%	80%
12 cm ferrocyanide sludge layers (all ¼ segments) and 24 cm saltcake layers (all ½ segments)	4. Fuel concentration < 1200 J/g	95%
12 cm ferrocyanide sludge layers (all ¼ segments) and 24 cm saltcake layers (all ½ segments)	5. Moisture concentration > 0.022 [fuel (J/g) - 1200]	99.7%
Tank	6. Waste will not dry out during interim storage	High (Best Engineering Judgement)

* Confidence limit that the decision threshold is satisfied for the sample defined by the decision boundary.

The fuel and moisture decision thresholds are applied to each quarter segment (12-cm) of sludge waste and half segment (24-cm) of saltcake waste (Postma et al. 1994). The nickel decision threshold (3A) is applied to quarter segments of sludge and is measure on only one centrally located quarter segment per core sample. Nickel is not measured on saltcake waste. Nickel, total cyanide, and TOC decision thresholds (3B) are applied to any quarter segment of sludge (half segment of saltcake) whose measured fuel concentration is greater than 600 J/g.

When determining the acceptable confidence limit on a tank measurement to be used for making a decision, the consequences of an incorrect decision must be assessed. It is tempting to ignore statistical uncertainties and state that whenever a decision threshold is exceeded, that the correct decision will be made with 100% confidence. However, statistical uncertainties cannot be ignored. Thus, acceptable confidence limits must be specified considering the consequences of incorrect decisions.

The consequences of concluding that a waste has aged when the true fuel concentration is actually slightly greater than 600 J/g are very small because this waste could still not support a propagating reaction (a fuel concentration greater than 1200 J/g would be required). If a high confidence limit (e.g., 95% or 99%) were specified for the aging decision rule, the result would be more stringent and costly sampling requirements that do not reflect the actual ferrocyanide risk. Therefore, it was deemed acceptable to have a 20% probability of concluding that a tank has aged when the true fuel concentration is 600 J/g. This same argument holds true for the nickel, total cyanide, and TOC decision rules (3A and 3B).

However, the consequence of making an incorrect decision increases as the fuel value increases and the moisture value decreases. To reflect this, the acceptable probability of miscategorizing a tank decreases as the fuel value increases. Only a 5% chance is acceptable for concluding that a tank with a fuel concentration greater than 1200 J/g is less than this value (decision rule 4). The worst error is to conclude that a waste has sufficient moisture when in fact it actually contains high fuel and low moisture (decision rule 5). Therefore, the acceptable probability of this error is only 0.27%.

6.0 DECISION INPUT SOURCES

Decision input sources come from numerous data sources. The sources used for the Ferrocyanide DQO are summarized in Table 6-1. The input sources for each of the decision inputs are presented.

Table 6-1. Information Sources for Decision Inputs

Decision Input	Input Sources
1. Identification of ferrocyanide tanks	Process flowsheets and waste transfer histories.
2. Fuel	Waste lay down model, aging model, and core sample data from tanks that bound aging.
3A. Nickel	Process flowsheets and waste sampling data.
3B. Nickel, cyanide, and TOC	Waste sampling data.
4. Fuel	Process flowsheets, waste lay down model, simulant experiments, chemical reaction theory, and sampling data.
5. Moisture	Observation of waste surface, moisture monitoring data, waste dry out model, and sampling data.
6. Total carbon, cation, particle size, and waste dry out analyses	Surveillance data, heat load models, tank breathing rates, and sampling data.

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7.0 OPTIMIZATION OF THE DQO PROCESS

The available data on aging, variability, uncertainties, and the desired confidence levels all affect the selection of ferrocyanide tanks to be sampled to bound aging and the analytical requirements for these tanks. This section summarizes the results of optimization; additional details on the methods used for optimization are provided in the appendices of this document.

7.1 TANKS THAT BOUND AGING

Three parameters strongly affect the rate of aging, temperature, exposure to high pH, and radiation dose (Lilga et al. 1993, 1994). The current fuel concentration is a function of the starting ferrocyanide concentration and the amount of aging that has occurred. Historical data show that all the ferrocyanide tanks have been exposed to enough caustic to promote aging (i.e., had pH values higher than 10). However, there is some question whether the caustic solutions would penetrate more then a meter into ferrocyanide sludge (McGrail 1994) and the ferrocyanide at greater depths may not have been exposed to high pH solutions. Therefore, sludge depth has been factored into the selection of tanks that bound aging.

Tanks with high concentrations and sludge depths, and low temperature and radiation dose histories have been selected for core sampling to bound aging (see Appendix B). If the ferrocyanide has aged in these tanks, then as much or more aging should have occurred in the remaining ferrocyanide tanks. Table 7-1 reviews the tanks selected for sampling to bound aging, and the reason for selection.

Table 7-1. Tanks That Bound Aging

Tank	Primary Reasons for Selection
BY-103	High sludge depth (the ferrocyanide inventory from BY-105 was transferred to this tank).
BY-104	High sludge depth and low integrated dose.
BY-108	High sludge depth and low integrated dose.
BY-110	High sludge depth.
C-108	High concentration flowsheet.
C-109	High concentration flowsheet.
C-111	High concentration flowsheet.
C-112	High concentration flowsheet.
TY-103	Low temperature.
TY-104	Low temperature.

Two core samples will be taken from each of the ten tanks listed in Table 7-1. If the fuel and nickel analyses of each of the quarter segments taken from the ferrocyanide layer of each of these ten tanks are consistent with the ferrocyanide aging model, as defined by Decisions 2, 3A, and 3B of Tables 4.1 and 5.1, then the model will be considered to be verified. All ferrocyanide sludge will then be considered to have aged to fuel concentrations below the level of possible reactivity, and all ferrocyanide tanks will be categorized as *safe* with no need for further sampling.

7.2 ANALYTICAL REQUIREMENTS

The decisions rules defined in Section 4.0 allow the data requirements to be separated into two groups, primary and secondary data requirements. The primary data requirements are always addressed, while the secondary data requirements are only necessary if specific limits are exceeded. Table 7-2 reviews the primary data requirements and lists the analytical uncertainties required to meet the desired confidence levels specified in Section 6.0.

Table 7-2. Primary Data Requirements for Ferrocyanide Tanks

Analyte	Analytical Method[1]	Sample[2]	Decision Threshold	Required Analytical Uncertainty
Fuel	DSC/AC[3]	¼ Segment	1200 J/g	≤ 15%[4]
Moisture	TGA	¼ Segment	0.022 [Fuel (in J/g) - 1200]	≤ 15%[5]
Nickel	ICP[6]	¼ Segment (Sludge Only)	10,000 μg/g	≤ 30%[7]
Fuel and Nickel	DSC/AC ICP	¼ Segment (Sludge Only)	Fuel < 600 J/g and Nickel > 10,000 μg/g	≤ 30% ≤ 30%

1 Other techniques that meet the required uncertainty are also acceptable.
2 Analyses are conducted on homogenized quarter segments for sludge and homogenized half segments for saltcake.
3 Adiabatic calorimetry is conducted on one homogenized sludge quarter segment per tank.
4 The uncertainty required to meet the desired confidence in the decision rules varies with fuel concentration. The uncertainties required for fuel values (on a dry basis) are the following: (1) less than 15% for fuel values greater than 900 J/g, (2) less than 30% for fuel values between 400 and 900 J/g, and (3) less than 90% for fuel values between 100 and 400 J/g.
5 Values less than 5 or greater than 20 wt% moisture do not require the specified uncertainty.
6 Non-nickel crucibles must be used for nickel analyses to reduce the potential for analytical bias.
7 Nickel values less than 5,000 or greater than 13,000 μg/g do not require the specified uncertainty.

Two core samples will be taken from each of the ten tanks listed in Table 7-1. If the fuel and nickel analyses of each of the quarter segments taken from the ferrocyanide layer of each of these ten tanks are consistent with the ferrocyanide aging model, as defined by decisions 2, 3A, and 3B of Tables 4.1 and 5.1, then the model will be considered to be verified, all ferrocyanide sludge will be considered to have aged to fuel concentrations below the level of possible reactivity, and all ferrocyanide tanks will be classed as safety with no need of further sampling.

Table 7-3 provides a summary of the secondary data requirements for the Ferrocyanide Watch List tanks. The secondary data requirements are necessary on those quarter segments with measured fuel concentrations greater than 600 J/g or that violate the moisture decision threshold (see Section 4.0 for decision rules).

Table 7-3. Secondary Data Requirements for Ferrocyanide Tanks

Analyte	Analytical Method[1]	Sample[2]	Required Sensitivity	Required[3] Analytical Uncertainty
Cations (Al, Bi, Ca, Fe, P, Na)	ICP	¼ Segment & Liquid	5,000 μg/g	≤ 30%
Total Cyanide	Direct Analyses	¼ Segment & Liquid	1000 μg/g	≤ 30%
Total Organic Carbon	Persulfate Oxidation	¼ Segment & Liquid	10,000 μg/g	≤ 30%
Total Carbon	Coulometric Detection	¼ Segment & Liquid	10,000 μg/g	≤ 30%
Particle Size	Laser	¼ Segment	2 μm[4]	≤ 30%

1 Other techniques that meet the required uncertainty are also acceptable.
2 Analyses are conducted on homogenized quarter segments for sludge, homogenized half segments for saltcake, and composited liquid samples.
3 Uncertainty not required for values lower than the specified sensitivity.
4 An estimate of the total number and mass of particles under 2 μm in diameter is required. Determination of particle sizes under 2 μm is not necessary.

7.3 NUMBER OF SAMPLES REQUIRED

Estimates of the expected spatial, sampling, and analytical variations were derived from available core sample data for two tanks on the Ferrocyanide Watch List (tanks 241-C-109 and 241-C-112). Based on the desired confidence levels and assuming the variability estimated from the two sampled tanks are representative, two cores are sufficient to characterize a ferrocyanide tank (see Appendix A). Where possible, sampling locations should be chosen to increase the likelihood of obtaining samples that represent the true spatial variations within a tank (e.g., opposite sides or side-center for two cores, side-center-side for three cores).

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APPENDIX A

STATISTICAL ISSUES

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APPENDIX A

FORMULAS AND STATISTICAL ISSUES

The underlying statistical procedures and formulas used to generate the results summarized in Section 7.0 are provided in this appendix. Specifically, this appendix describes the statistical hypothesis test for the population mean, provides the procedure for calculating the number of core samples required, discusses the non-central t-distribution used for sample size probability calculations, and describes the analysis of variance method for estimating uncertainties.

A.1 STATISTICAL TEST FOR THE POPULATION MEAN

Hypothesis tests are based on a statistical test procedure for population means. The generalized form of the hypothesis test is

H_0: True population mean (μ) > μ_0
H_1: True population mean (μ) $\leq$ μ_0

where μ_0 = the decision threshold.

There are two types of decision errors that can occur. The first type of decision error occurs when it is concluded that H_1 is true, when in fact H_0 is true. This error is referred to as a false positive or a Type I error. The second error occurs when it is concluded that H_0 is true, when in fact H_1 is true. This error is referred to as false negative or a Type II error.

Assuming the underlying population is normally distributed with a mean μ and standard deviation σ, an appropriate statistical procedure for determining which hypothesis is most likely correct is the traditional t-test. This statistical test procedure concludes that the null hypothesis (H_0) is false if

$$T = \frac{\overline{x} - \mu_0}{s/\sqrt{n}} < t_{\alpha,n-1} \qquad \text{(A-1)}$$

where $\bar{x}$ = mean
s = standard deviation
n = random sample of size taken from the population
$t_{\alpha,n-1}$ = α-th percentile of a central t-distribution with n-1 degrees of freedom.

When the true population mean is equal to μ_0, the statistic T has a central t-distribution with n-1 degrees of freedom. The constant $t_{\alpha,n-1}$ in the above formula, normally referred to as the critical value of the test, is affected both by the sample size n and by α, the desired Type I error rate at $\mu = \mu_0$. The value of $t_{\alpha,n-1}$ can be obtained from a table of the central t-distribution.

A.2 DETERMINING THE NUMBER OF CORES REQUIRED

Let n denote the sample size (number of cores) required to carry out a statistical test for the population mean. This n should be chosen to satisfy constraints on the Type I and Type II error rates of the test. These error rates are functions of μ, the unknown true value of the parameter of interest. To calculate n, at least two constraints must be specified. A Type I error rate is specified for $\mu = \mu_0$ (where μ_0 is the decision threshold), and a Type II error rate is specified at some μ value, μ_1, which is within the range of H_1. Such constraints can be written as

$$\text{Type I error rate (when } \mu = \mu_0) \leq \alpha$$

and

$$\text{Type II error rate (when } \mu = \mu_1 < \mu_0) \leq \beta$$

The latter error rate can be written as

$$Pr_{\mu=\mu_1}\,(T > t_{\alpha,\,n-1}) \leq \beta$$

or equivalently,

$$Pr_{\mu=\mu_1}(T \leq t_{\alpha,\,n-1}) > 1-\beta \qquad \text{(A-2)}$$

Notice that for a fixed Type I error rate α, the critical value $t_{\alpha,n-1}$ is a function of n. Therefore, the sample size n can be determined based on this inequality.

When the true population mean is μ_1, $\mu_1 \neq \mu_0$, the distribution of T is no longer a central t-distribution. According to statistical theory (Johnson and Kotz 1970), T has a non-central t-distribution with n-1 degrees of freedom and non-centrality parameter δ, where

$$\delta = \frac{\mu_1 - \mu_0}{\sigma/\sqrt{n}} \qquad \text{(A-3)}$$

and σ is the population standard deviation. To satisfy the Equation A-2, the (1-ß)-th percentile of this non-central t-distribution, denoted by $t_{1-\beta,n-1,\delta}$, must be greater than the critical value of the test, $t_{\alpha,n-1}$. That is

$$t_{1-\beta,\,n-1,\,\delta} > t_{\alpha,\,n-1} \qquad \text{(A-4)}$$

These percentile values can be found in tables of the non-central t-distribution or by using functions available in many mathematical and statistical packages. The minimum value of n for which Equation A-4 holds is the number of samples required to satisfy the constraints on the Type I and Type II error rates.

Unfortunately, there is no explicit formula for determining n from inequality shown in Equation A-4. One way to obtain this value is to overlap the curves of $t_{1-\beta,n-1,\delta}$ and $t_{\alpha,n-1}$ versus n for a reasonably wide range of n. The range should start with the minimum possible value of n, n = 2. Then the smallest value of n for which $t_{1-\beta,n-1,\delta}$ lies above $t_{\alpha,n-1}$ is the required sample size.

The two constraints on Type I and Type II error rates were specified for the fuel and moisture concentration decision rules are 95 and 99.7%, respectively (see Section 5.0). The achievable probabilities for decision error discussed are the probabilities of rejecting the null hypothesis, H_0, when the true population mean μ is within the range of H_0, and are the probabilities of accepting the H_0 when μ is within the range of H_1. For the tests, H_0 is rejected if $T < t_{\alpha,n-1}$, the quantity appearing on the left side of Equation A-2 is the achievable probability at $\mu = \mu_1$, where $\mu_1 > \mu_0$. Knowing the values of α, n, μ_1, and σ, this quantity can be found in tables of the non-central t-distribution or by using functions available in many statistical packages. The probability of accepting H_0 is the probability of $T > t_{\alpha,n-1}$, which can be obtained in the similar way.

A.3 ESTIMATING RELATIVE STANDARD DEVIATION (RSD)

To calculate required sample size and achievable probabilities for decision errors, the uncertainty in the underlying distribution must be known. One measure of this uncertainty is the relative standard deviation (RSD), defined as the ratio of the standard deviation to the mean of this distribution:

$$RSD \equiv \frac{\sigma}{\mu} \qquad \text{(A-5)}$$

The RSDs of ferrocyanide and moisture concentrations were estimated through analysis of variance procedures based on core sampling data from tanks C-109 and C-112. A random effects model was fitted to the ferrocyanide data and moisture data:

response = overall mean + tank effect + core (tank) effect + segment (tank, core) effect + analytical error

Each of the effects (including analytical error) appearing on the right side of this model are random effects. Associated with each random effect is a variance component, which is the contribution of this random effect to overall uncertainty in the response. The variance components of the random effects were estimated by the restricted maximum likelihood method. The RSD of each effect was then evaluated by the ratio of the corresponding estimated standard deviation to the estimated overall mean of the model. The overall RSDs for fuel concentration and moisture were obtained by combining the RSDs of the random effects.

The analysis for ferrocyanide concentration indicated that the tank-to-tank variation for fuel concentration was not statistically different from zero. Therefore, the sources of the overall variation of ferrocyanide concentration at a quarter segment layer of a tank include only core-to-core (spatial) variation and analytical variation. The overall RSD for ferrocyanide concentration was calculated by the following formula

$$RSD_{overall} = \sqrt{(RSD_{spatial})^2 + (RSD_{analytical})^2}$$

The variance component estimation yielded the spatial RSD estimate of 21% and the analytical RSD estimate of 5%. The combined uncertainties resulted in a 22% overall RSD. This RSD estimate was used to calculate the number of cores required for the ***safe*** versus ***conditionally safe*** or ***unsafe*** decision rule.

For moisture concentration, the tank-to-tank variation was statistically different from zero, implying that the concentration of moisture varied significantly from tank to tank. To obtain a conservative RSD estimate for moistüre concentration for all tanks, the tank-to-tank variation was also included in the overall RSD. The formula used to calculate the overall RSD estimate was

$$RSD_{overall} = \sqrt{(RSD_{tank})^2 + (RSD_{spatial})^2 + (RSD_{analytical})^2}$$

The estimates of the tank RSD, spatial RSD, and analytical RSD are 6.6%, 10%, and 2.5%, respectively. The combined uncertainties resulted in a 12% overall RSD. For the *conditionally safe* versus *unsafe* decision rule, the RSD of K [where K = Fuel (in J/g) - 45 moisture (in wt%)] is needed. The variance of ferrocyanide and moisture can be calculated by using the corresponding $RSD_{overall}$ and estimated overall mean. The $RSD_{overall}$ for K is equal to the ratio of the variance of K to the estimated mean value of K. The estimate of overall RSD for K is 22%.

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APPENDIX B

SELECTION OF TANKS THAT BOUND AGING

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SELECTION OF TANKS THAT BOUND AGING

Aging of ferrocyanide waste is broadly defined as degradation processes that result in a lower potential for ferrocyanide reactions (Babad et al. 1993). The available literature (MacDiarmid and Hall 1953, Masri and Haissinsky, Hughes and Willis 1961, Ohno and Tsuchihasi 1965, Robuck and Luthy 1979) and recent experiments on ferrocyanide waste simulants (Lilga et al. 1992, 1993, 1994) indicate that three parameters strongly affect the rate of aging, temperature, exposure to high pH solutions, and radiation dose.

The extent of aging is a function of the starting ferrocyanide concentration (i.e., the higher the original ferrocyanide concentration, the more ferrocyanide that might remain) and the rate of aging. Therefore, tanks with high concentrations and low temperature, pH, and radiation dose histories should be candidates for sampling. The following sections review the available data on initial ferrocyanide concentrations (and inventories), temperature, pH, and radiation dose for the ferrocyanide tanks.

B.1 FERROCYANIDE CONCENTRATION

Several different flowsheets were used to precipitate ferrocyanide in Hanford Site tanks and the flowsheets can be separated into three main groups, U Plant, In Farm, and T Plant. Table B-1 presents estimates of the original ferrocyanide inventory, depth of ferrocyanide sludge, anticipated maximum ferrocyanide concentration (from flowsheet simulants), and maximum actual concentration (obtained from waste sampling).

The minimum fuel concentration required to support a propagating reaction is 1200 J/g (Fauske 1995). Reviewing Table B-1, only the tanks the received In Farm flowsheet material (i.e., tanks C-108, C-109, C-111, and C-112) would have once contained ferrocyanide concentrations greater than 1200 J/g. Therefore, the four tanks that received In Farm material either have been or will be sampled. Additional sampling will also be conducted on the tanks that originally contained a substantial inventory of ferrocyanide.

From Table B-1, the tanks that contained high inventories of ferrocyanide include BY-103, BY-104, BY-106, BY-108, and BY-110. Therefore, sampling will include at least one tank from this group. The tanks to be sampled from this group will be selected once other factors, such as temperature and pH histories, are weighed.

B.2 WASTE pH

Although the precipitation of sodium nickel ferrocyanide was done at slightly alkaline conditions (pH = 8.5 - 10), the ferrocyanide tanks were used for a variety of waste management operations that exposed the tanks to alkaline waste (Anderson 1990). Table B-2 presents a summary of the available historical pH and hydroxide data collected for the eighteen ferrocyanide tanks (Wodrich et al. 1992).

Table B-1. Summary of Estimated Original Ferrocyanide Inventory, Sludge Depth, and Available Sample Data

Tank	Waste Flowsheet	Original Inventory[a] (kg)	Sludge Depth[a] (m)	Ferrocyanide Concentration (J/g)	
				Maximum Simulant	Maximum Sample
BY-103	U Plant	20,900[b]	2.1	800 [8.3][c]	No data
BY-104	U Plant	26,300	2.6	800 [8.3]	No data
BY-105	U Plant	11,400[b]	1.1	800 [8.3]	No data
BY-106	U Plant	22,200	2.3	800 [8.3]	No data
BY-107	U Plant	13,300	1.6	800 [8.3]	No data
BY-108	U Plant	18,400	2.1	800 [8.3]	No data
BY-110	U Plant	24,500	2.3	800 [8.3]	No data
BY-111	U Plant	1,900	0.3	800 [8.3]	No data
BY-112	U Plant	630	0.2	800 [8.3]	No data
C-108	In Farm	7,900	0.9	2,200 [23]	110[d] [1.2]
C-109	In Farm	9,500	1.2	2,200 [23]	30[e] [0.3]
C-111	In Farm	10,400	1.1	2,200 [23]	No data
C-112	In Farm	9,800	1.0	2,400 [26]	36[f] [0.4]
T-107	U Plant	1,600	2.1	800 [8.3]	0[g] [0.0]
TX-118	U Plant	<500[h]	<0.1	800 [8.3]	No data
TY-101	T Plant	7,300	1.6	840 [8.8]	13[i] [0.1]
TY-103	T Plant	8,900	1.8	840 [8.8]	0[i] [0.0]
TY-104	T Plant	3,800	0.9	840 [8.8]	0[j] [0.0]

[a] Data from Borsheim and Simpson (1991)
[b] Waste transfer records indicate that the inventory in tank BY-105 was transferred to tank BY-103 in 1966 (Brevick et al. 1994).
[c] Equivalent concentration of $Na_2NiFe(CN)_6$ in dry wt% in brackets.
[d] Data from WHC (1995a).
[e] Data from Simpson et al. (1993a).
[f] Data from Simpson et al. (1993b).
[g] Differential scanning calorimetry analyses for tank T-107 samples indicated no exothermic results except for what appeared to be a small (about 2 mm in diameter) piece of plastic (Valenzuela et al. 1994).
[h] Process records indicate that no appreciable quantity of ferrocyanide was transferred to tank TX-118 (Borsheim and Simpson 1991).
[i] Analyses for homogenized core sample (Beck 1993).
[j] Data from WHC (1995b)

Table B-2. Summary of Available pH and Hydroxide Data for the Ferrocyanide Watch List Tanks

Tank	pH	OH^- (Molar)	Date(s) (mo/yr)	Tank	pH	OH^- (Molar)	Date(s) (mo/yr)
BY-103	9.3 13.3 13.5	--- 2.6 2.6	05/55 11/90 06/91	C-108	9.8 11.8 11.8	--- --- 0.5	05/56 12/71 09/75
BY-104	9.3 >14	--- 3.7	11/55 03/76	C-109	11.9 12.5 13.7	--- 0.8 0.5	12/71 06/75 11/90
BY-105	9.3 13.2 13.3	--- 0.8 0.8	07/56 11/90 06/91	C-111	12.2 8.6 13.9	--- --- 0.8	05/55 10/57 02/75
BY-106	9.4 >14 13.5	--- 3.9 2.9	03/55 04/72 11/90	C-112	10.1 11.7 11.9	--- --- 0.5	01/56 12/71 06/75
BY-107	9.3 12.3 >14	--- --- 5.2	11/54 04/57 07/79	T-107	13.2 12.3 11.1	0.2 0.1 0.03	03/65 09/75 09/89
BY-108	9.0 13.2 13.4	--- 2.5 2.4	11/54 11/90 06/91	TX-118	13.8 >14 >14	0.6 3.0 3.2	03/65 05/72 01/80
BY-110	9.8 11.9 >14	--- --- 3.1	10/54 06/57 06/76	TY-101	9.1 12.5 12.7	--- 0.03 0.05	11/56 03/65 12/82
BY-111	9.6	---	06/56	TY-103	9.7 12.0 11.7	--- 0.24 ---	06/55 03/65 02/72
BY-112	>14 >14	6.6 3.2	01/72 06/76	TY-104	12.0 12.1	0.32 ---	03/65 02/72

Values for pH presented in Table B-2 are only estimates, because of the solutions tested had a high ionic strength (most of the samples exceeded 4.0 *N* making a direct correlation between hydrogen ion activity and concentration difficult). Therefore, the hydroxide concentration measurements presented are a more reliable measure of basicity. Hydroxide concentrations were measured by direct potentiometric titration of the solutions with a standardized acid.

Except for tank BY-111 (which had no data later than June 1956), historical pH and hydroxide data show that all the ferrocyanide tanks have contained enough caustic to promote aging (i.e., had pH values higher than 10) since the ferrocyanide scavenging campaigns were completed. Tank BY-111 was used for the same operations that transferred high pH waste into the other BY ferrocyanide tanks. Consequently, waste pH is not expected to be a limiting factor for ferrocyanide waste aging in Hanford Site tanks. However, there is some question whether the caustic solutions would penetrate more then a meter into ferrocyanide sludge and the ferrocyanide at greater depths may not have been exposed to high pH solutions (McGrail 1994). Therefore, sludge depth will be factored into the selection of tanks that bound aging.

B.3 INTEGRATED DOSE

Experiments on ferrocyanide waste simulants (Lilga et al. 1992, 1993, 1994) indicate that gamma radiation strongly affects ferrocyanide aging. Simulants that were not irradiated aged one to two orders of magnitude less than irradiated samples under similar conditions of time, pH, and temperature. Integrated beta and gamma doses have been estimated for the ferrocyanide waste tanks (Parra 1994), and the results are presented in Table B-3.

Table B-3. Average Estimated Integrated Beta and Gamma Radiation Dose for the Ferrocyanide Watch List Tanks

Tank	Total Beta (Rad*10^{-8})	Total Gamma (Rad*10^{-8})	Tank	Total Beta (Rad*10^{-8})	Total Gamma (Rad*10^{-8})
BY-103	0.4	0.9	C-108	2.6	4.3
BY-104	0.4	0.9	C-109	2.9	5.3
BY-105	0.2	0.6	C-111	2.3	4.4
BY-106	0.5	1.0	C-112	0.1	2.4
BY-107	0.9	1.8	T-107	0.8	1.8
BY-108	0.4	0.9	TX-118	0.1	0.3
BY-110	0.4	0.9	TY-101	1.0	2.0
BY-111	0.2	0.4	TY-103	0.5	1.0
BY-112	0.3	0.5	TY-104	4.9	8.5

From Table B-3, the ferrocyanide tanks with the lowest estimated integrated beta and gamma doses are TX-118, BY-111, BY-112, BY-105, BY-103, BY-104, BY-108, and BY-110. Tanks TX-118, BY-111, and BY-112 had low original inventories, and waste transfer records (Brevick et al. 1994) indicate that the ferrocyanide waste in BY-105 was transferred to BY-103. Therefore, sampling will be conducted on BY-103, BY-104, and BY-108.

B.4 WASTE TEMPERATURES

Another important parameter in the aging process is temperature. Higher temperatures lead to faster dissolution and hydrolysis. The current bulk temperature of the ferrocyanide tanks ranges between 20 to 55 °C (Hanlon 1995). Temperatures in the tanks have dropped steadily since the scavenging campaign ended and the highest current temperature is in tank BY-104, approximately 55 °C. However, temperatures have historically been much higher. The available historical temperature data is reviewed in Table B-4.

Table B-4. Summary of Available Temperature Data for the Ferrocyanide Watch List Tanks

Tank	Temperature (°C)	Date(s) (mo/yr)	Tank	Temperature (°C)	Date(s) (mo/yr)
BY-103	49 29 27	12/74 12/82 03/90	C-108	32 24 21	01/75 01/84 03/90
BY-104	93 77 63	06/75 01/80 01/85	C-109	77 54 27	01/63 09/64 01/83
BY-105	55 40 39	01/75 01/85 01/90	C-111	88 27 27	09/64 01/77 01/83
BY-106	85 54 50	12/74 11/84 01/90	C-112	75 54 24	12/61 04/63 01/76
BY-107	30 90 90	01/75 06/75 10/89	T-107	28 22 18	08/76 02/82 01/91
BY-108	16 66 43	01/75 01/76 01/90	TX-118	46 29 21	01/76 01/83 12/89
BY-110	33 83 57	01/75 01/76 01/85	TY-101	28 21 18	01/72 01/82 01/90
BY-111	30 100 38	01/75 01/79 01/90	TY-103	29 18 18	09/77 01/83 01/90
BY-112	71 38 24	12/76 01/80 12/89	TY-104	18 21 18	09/70 01/77 03/91

Ferrocyanide tanks with the lowest temperature histories are the C Farm tanks, TY Farm tanks, and TX-118. All of the C-Farm tanks will be sampled because of originally high ferrocyanide concentrations. Tank TX-118 contains little or no ferrocyanide and the benefits of sampling this tank to confirm aging is small. Of the three TY tanks, only TY-103 and TY-104 had significant inventories.

B.5 SUMMARY OF FERROCYANIDE TANK SELECTIONS

With the data presented thus far, it is possible to choose tanks with the highest sludge depth, lowest integrated dose, and lowest temperature histories. However, when is unknown is the combined affects of sludge depth, integrated dose, and temperature. For example, can a low temperature be compensated by a high radiation dose or vise versa? Because these relationships are not yet known, the list of tanks will optimized by selecting tanks that are influenced by the whole combination of factors (i.e., high sludge depth, low temperature, and low radiation dose).

Table B-5 summarizes the tanks selected to bound aging and the reasons for selection.

Table B-5. Tanks Selected for Full Depth Core Sampling

Tank	Primary Reasons for Selection
BY-103	High sludge depth (ferrocyanide inventory from BY-105 was transferred to this tank). Also the lowest temperature history of the high sludge depth tanks.
BY-104	High sludge depth and low integrated dose.
BY-108	High sludge depth and low integrated dose.
BY-110	High sludge depth.
C-108	High concentration flowsheet.
C-109	High concentration flowsheet.
C-111	High concentration flowsheet.
C-112	Highest original concentration flowsheet.
TY-103	Low temperature and highest sludge depth of low temperature tanks.
TY-104	Lowest temperature history of the ferrocyanide tanks.

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PART

II

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SUMMARY OF CHANGES

This section describes the data quality objectives (DQO) process applied to the Ferrocyanide Safety Issue at the Hanford Site based on the new approach to safety characterization (Meacham et al. 1995). The major change in this second part is that fuel and moisture values from only the waste surface are adequate to categorize a tank as safe, conditionally safe, or unsafe. This section contains the material that will be inserted into part one of this report, after acceptance of the new approach to safety characterization.

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3.0 DECISIONS AND DECISION INPUTS

3.1 DECISION TO RESOLVE PROBLEM

The chemical reactivity of waste stored in Ferrocyanide Watch List tanks places the tanks into one of three categories: *safe*, *conditionally safe*, or *unsafe*. Numerical criteria for the three safety categories have been developed for ferrocyanide waste based on empirical data and theoretical calculations (Fauske 1995). Tanks categorized as *safe* contain waste that cannot support a propagating reaction. Tanks categorized as *conditionally safe* contain waste that is unlikely to support a propagating reaction, while *unsafe* tanks require monitoring and controls to avoid conditions that could lead to reaction ignition. Mitigation is required to remove a tank from the *unsafe* category.

3.2 DECISION LOGIC

The decision logic for placing ferrocyanide waste into one of the three categories is shown in Figure 3-1. The decisions are listed in a logical order such that some decisions only need to be addressed based on the outcome of previous decisions. The decisions are broken down into six distinct questions. The decision rules or action limits corresponding to these general questions are stated in Section 4.0.

1. Was ferrocyanide ever transferred to the tanks? This step was previously accomplished by the establishment of the present Ferrocyanide Watch List based on the review of tank histories by Borsheim and Simpson (1991), and is thus outside the scope of this DQO. It is shown here only to present the complete logic sequence.

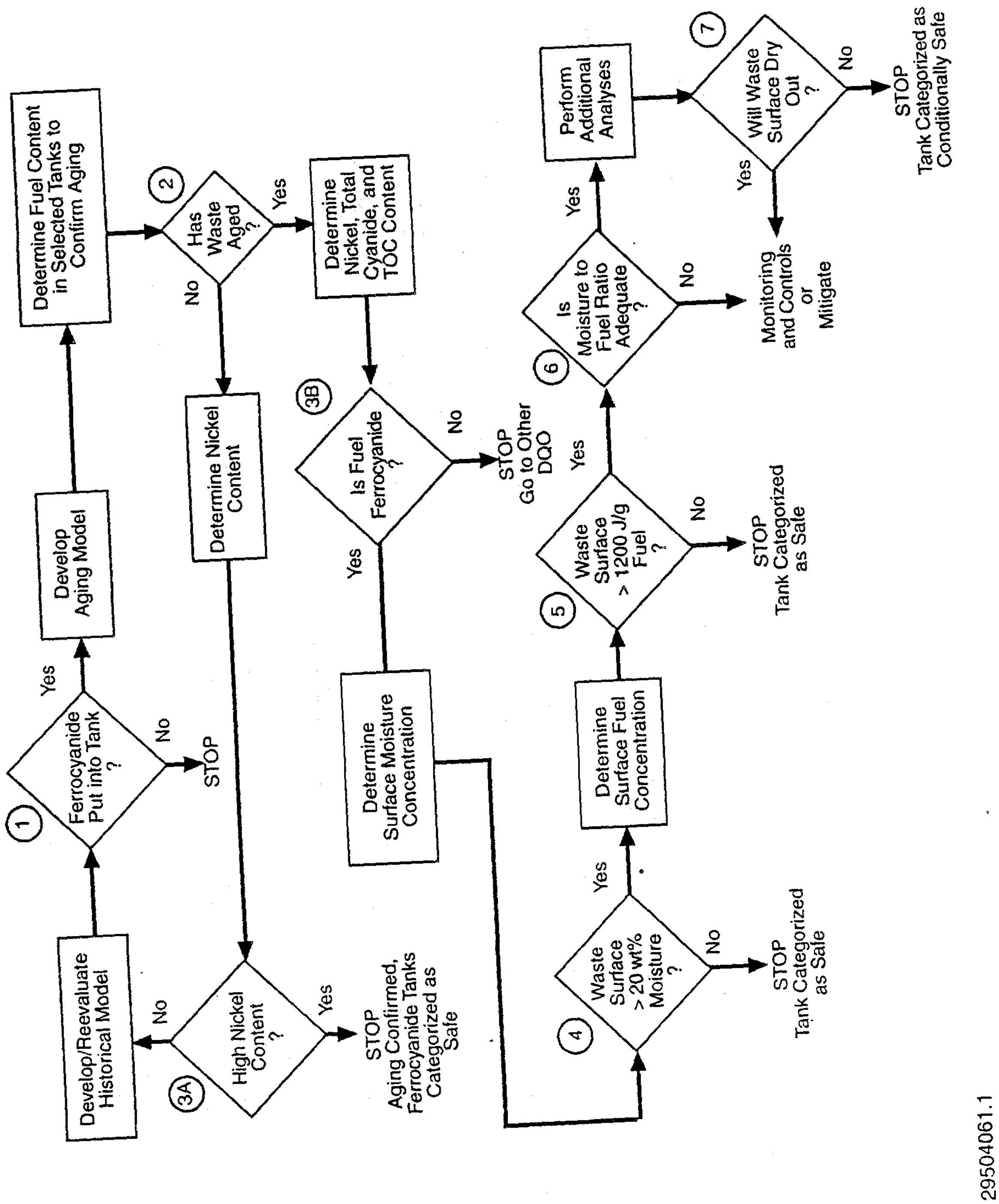
2. Does the waste contain a fuel concentration less than predicted by the repetition of the process flowsheets as reported by Jeppson and Wong (1993)? If so, then proceed to nickel analyses to confirm the historical and aging models (3A). If the fuel concentration is equal or greater than predicted, then additional analyses will be performed (3B).

3A. Does the waste have a sufficiently high nickel concentration to conclude that it originally did contain ferrocyanide sludge? If so, waste aging is confirmed and additional sampling of ferrocyanide waste is not required. The ferrocyanide tanks are categorized as *safe* and the decision process ends here. If the waste has a low nickel concentration, then the tank has been erroneously identified as containing ferrocyanide waste, and the historical model will require reevaluation.

3B. Is the fuel in the waste ferrocyanide? If the fuel is mostly composed of something other than ferrocyanide, then a different DQO (e.g., the Organic DQO) will address this waste.

4. Does the waste surface contain greater than 20 wt% moisture? Is so, the waste is categorized as *safe* and the decision process ends here. Moisture concentration will be monitored during interim storage.

Figure 3-1. Decision Logic for Categorizing Ferrocyanide Waste



5. Does the waste surface have enough fuel to support a propagating reaction (i.e., fuel > 1200 J/g)? If not, the waste is categorized as *safe* and the decision process ends here.

6. Is enough moisture present in the waste surface to inhibit a propagating reaction [i.e., wt% moisture $\geq$ 0.022 [fuel (in J/g) - 1200]? If not, the waste is categorized as *unsafe* and the decision process ends here.

7. Does the waste surface have the potential to dry during interim storage? If not, then the tank is categorized as *conditionally safe* and the decision process ends here. If the moisture concentration (in wt%) could decrease to below 0.022 [fuel (in J/g) - 1200] during interim storage, then the tank is categorized as *unsafe*.

3.3 DECISION INPUTS

Decision inputs may consist of any piece of information or data that can help answer the decision. The decision inputs required to make the decisions are summarized in Table 3-1. The decision input is listed along with the reason the decision input is needed. Each of the decision inputs are connected to one of the six decisions listed in Section 3.2.

Table 3-1. Summary of Decision Inputs

Decision Input	Decision	Reason for Required Decision Input
1. Identification of ferrocyanide tanks	Did tank receive ferrocyanide?	Identification of tanks that contained ferrocyanide focuses analyses and sampling efforts.
2. Fuel	Does ferrocyanide still exist?	Determines whether the reaction hazard has been mitigated via degradation of the ferrocyanide fuel.
3A. Nickel	Did the ferrocyanide age?	Nickel is an indicator analyte that confirms that the tank once contained ferrocyanide waste and that the waste has aged.
3B. Nickel, cyanide, and total organic carbon	Is the fuel ferrocyanide?	Determines whether the fuel source is something other than ferrocyanide.
4. Moisture	Surface moisture concentration greater than 20 wt%?	Even if sufficient fuel is present, a propagating reaction cannot occur if enough moisture is present.
5. Fuel and moisture	Surface chemically reactive?	Determines if the waste can support an exothermic propagating reaction.
6. Waste dry out analysis	Will the waste dry out?	Determines whether the waste will dry out, possibly moving the waste to the *unsafe* category.

4.0 DECISION RULES

The decision logic (see Section 3.2) and decision inputs (see Section 3.3) have been delineated, and it is now necessary to define decision rules that allow categorization of the ferrocyanide waste. Action limits or decision thresholds have been defined to produce the IF - THEN decision rules shown in Table 4-1.

Table 4-1. Decision Rules

Decision	IF (Decision Threshold)	THEN
1.	No ferrocyanide waste was transferred to tank	Tank does not belong on Ferrocyanide Watch List. Stop.
2.	Fuel concentration in the waste is ≤ 600 J/g Fuel concentration in the waste is > 600 J/g	Measure nickel concentration to confirm aging and historical models (3A). Measure nickel, total cyanide, and TOC to determine fuel source (3B).
3A.	Nickel ≥ 10,000 ppm	Ferrocyanide has degraded. Waste categorized as *safe*, stop.
3B.	Nickel < 10,000 ppm and CN^- < 3.1 wt% and TOC > 5.0 wt%	Fuel is non-ferrocyanide. Go to other DQO, stop.
4.	Moisture concentration in the waste surface > 20 wt%	Waste cannot support a propagating reaction. Waste categorized as *safe*, stop.
5.	Moisture concentration in the waste surface ≥ 0.022 [fuel (J/g) - 1200] Moisture concentration in the waste surface < 0.022 [fuel (J/g) - 1200]	Measure temperature, examine dry out models, and collect sample data. Waste categorized as *unsafe*, stop.
6.	Waste will not dry out during interim storage Waste can dry out during interim storage	Waste categorized as *conditionally safe*, stop. Waste categorized as *unsafe*, stop.

The first decision threshold, whether a tank contains ferrocyanide, is a qualitative input from detailed examinations of waste transfer records (Borsheim and Simpson 1991). That is, based on historical records, a tank either received ferrocyanide waste or not. This is significant because tanks have been added and removed from the Ferrocyanide Watch List (Meacham et al. 1993) based on these examinations.

The second decision threshold, whether the waste has aged, is based on the fuel values predicted in the lowest concentration flowsheet material (Jeppson and Wong 1993, Sloat 1954, 1955, Postma et al. 1994). The nickel threshold of 10,000 ppm is based on the minimum nickel concentrations expected in ferrocyanide sludges (Jeppson and Wong 1993, Postma et al. 1994).

The total cyanide threshold is based on the cyanide concentration that would produce an exotherm of 600 J/g, and the TOC threshold is based on the TOC fuel concentration criterion for identifying organic tanks (Webb et al. 1995). Fuel and moisture decision thresholds (thresholds four and five, respectively) are based on the conditions necessary to support a propagating reaction (Fauske 1995).

The final decision threshold, whether the waste surface can dry out, is a function of the waste temperature, heat load, tank breathing rate, and the physical and rheological properties of the waste. A study that examined the available data (Epstein et al. 1994) concluded that ferrocyanide waste will not dry to unsafe levels under the current storage conditions (i.e., no active ventilation and no external heating). Therefore, no additional chemical or rheological analyses are required to determine if the ferrocyanide sludge will retain sufficient moisture during interim storage to remain *conditionally safe*.

5.0 CONFIDENCE LIMITS AND BOUNDARIES FOR DECISION INPUTS

In Section 4.0, the decision thresholds were summarized. Because the decision threshold values determine the logic path in the DQO, acceptable boundary and confidence levels must be defined to determine whether the decision input meets the threshold value. A summary of the boundaries and confidence levels for the Ferrocyanide DQO effort is presented in Table 5-1. In some cases, the determination of the decision input and its comparison to the decision threshold limit may be based on a qualitative interpretation of the data or information source as compared to a statistical determination of the confidence.

Table 5-1. Decision Boundaries and Confidence Limits

Decision Boundary	Decision Threshold	Confidence Limit*
Tank	1. No ferrocyanide waste was transferred to tank	High (Best Engineering Judgement)
12 cm ferrocyanide sludge layers (all ¼ Segments)	2. Fuel concentration < 600 J/g	80%
12 cm ferrocyanide sludge layers (measured on one central ¼ Segment per core)	3A. Nickel ≥ 10,000 ppm	80%
12 cm ferrocyanide sludge layers (measured on all ¼ Segments with fuel concentration > 600 J/g)	3B. Nickel < 10,000 ppm and CN^- < 3.1 wt% and TOC > 5 wt%	80%
Top 14 cm of waste	4. Moisture concentration > 20 wt%	95%
Top 14 cm of waste	5. Moisture concentration ≥ 0.022 [fuel (J/g) - 1200]	99.7%
Top 14 cm of waste	6. Waste will not dry out during interim storage	High (Best Engineering Judgement)

* Confidence limit that the decision threshold is satisfied for the sample defined by the decision boundary.

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6.0 DECISION INPUT SOURCES

Decision input sources come from numerous data sources. The sources used for the Ferrocyanide DQO are summarized in Table 6-1. The input sources for each of the decision inputs are presented.

Table 6-1. Information Sources for Decision Inputs

Decision Input	Input Sources
1. Identification of ferrocyanide tanks	Process flowsheets and waste transfer histories.
2. Fuel	Waste lay down model, aging model, and core sample data from tanks that bound aging.
3A. Nickel	Process flowsheets and waste sampling data.
3B. Nickel, cyanide, and TOC	Waste sampling data.
4. Moisture	Observation of waste surface, moisture monitoring data, waste dry out model, and sampling data.
5. Fuel and moisture	Process flowsheets, waste lay down model, simulant experiments, chemical reaction theory, moisture monitoring data, and sampling data.
6. Waste dry out analysis	Surveillance data, heat load models, tank breathing rates, and sampling data.

All the information available on ferrocyanide waste is used in determining the correct safety category. This includes the following: (1) a detailed review of process records and waste transfer histories (Borsheim and Simpson 1991); (2) waste lay down information (Jeppson and Wong 1993, Sloat 1953, 1954), aging experiments (Lilga et al. 1992, 1993, 1994), and core sample data from the tanks that bound aging (see Appendix B for discussion on tank selection), (3) data on nickel concentration (Jeppson and Wong 1993), (4) moisture monitoring, modeling, and sampling data (Watson 1993, Epstein et al. 1994, Simpson et al. 1993a, 1993b, Valenzuela and Jensen 1994, WHC 1995), (5) chemical reactivity data, moisture data, and sampling data (Fauske 1995), and (6) heat load and dry out models (Crowe et al. 1993, McLaren 1994a, 1994b, Epstein et al. 1994) that evaluate moisture retention of ferrocyanide waste.

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7.0 OPTIMIZATION OF THE DQO PROCESS

An important result from this DQO process is an understanding that not all information needs to be derived from core sampling, and that surface sampling or in situ moisture determination of the waste surface is sufficient to categorize a tank as *safe*, *conditionally safe*, or *unsafe*.

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