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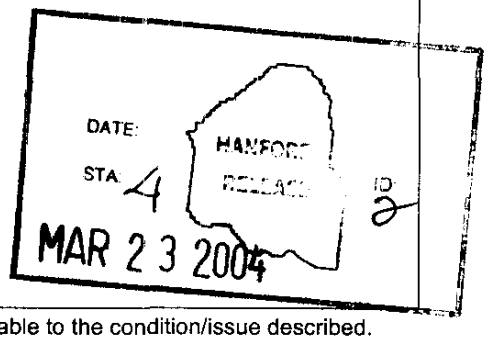

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Data Quality Objectives for Tank Farms Waste Compatibility Program

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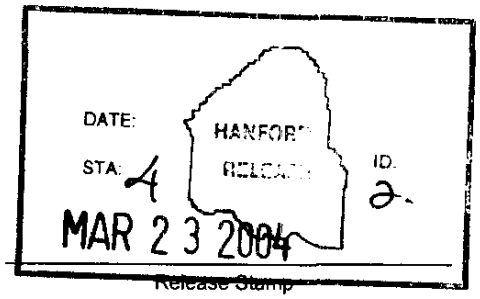

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DATA QUALITY OBJECTIVES FOR TANK FARMS WASTE COMPATIBILITY PROGRAM

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LIST OF TERMS

BDGRE	buoyant displacement gas release event
Bq	Becquerel
Bq/L	Becquerel per liter
Bq/μCi	Becquerel per microcurie
BTU/h	British thermal units per hour
CFR	*Code of Federal Regulations*
CI	confidence interval
cm	centimeters
CSR	criticality safety representative
DCRT	double contained receiver tank
df	degrees of freedom
DOE	U.S. Department of Energy
DQO	data quality objective
DST	double-shell tank
DSA	Documented Safety Analysis
Ecology	Washington State Department of Ecology
EPA	U.S. Environmental Protection Agency
FG	flammable gas
g	grams
g/L	grams per liter
g/mL	grams per milliliter
in.	inches
kg	kilograms
LCL	lower confidence level
LCS	laboratory control sample
LFL	lower flammability limit
LL	lower limit
M	molar or moles per liter
mg/m^3	milligrams per cubic meter
N/A	not applicable
NCRW	neutralized cladding removal waste
QA	quality assurance
QC	quality control
ORP	U.S. Department of Energy, Office of River Protection
PCB	polychlorinated biphenyl
ppm	parts per million
Pu-eq	Pu equivalent
RPD	relative percent difference
RSD	relative standard deviation
S.D.	standard deviation

LIST OF TERMS, Continued

SOFs	sum of fractions
SpG	specific gravity
SST	single-shell tank
Sv/Bq	Sieverts per Becquerel
Sv/L	Sieverts per liter
TOC	total organic carbon
TRU	Transuranic
TSR	Technical Safety Requirement
UCL	upper confidence level
UL	upper limit
ULD	unit liter dose
vol%	volume percent
WAC	*Washington Administrative Code*
wt%	weight percent
WTP	Waste Treatment and Immobilization Plant
X	neutron absorber
X/Pu	neutron absorber-to-plutonium mass ratio
%	percent
µCi/g	microcuries per gram
µCi/L	microcuries per liter
µCi/mL	microcuries per milliliter
µg/mL	micrograms per milliliter
°F	degrees Fahrenheit

1.0 INTRODUCTION

One of the main functions of the River Protection Project is to store Hanford Site waste until the Waste Treatment and Immobilization Plant (WTP) processes the waste and the tank farms are closed. Until the waste is processed and the tank farms are closed, the double-shell tank (DST) system will continue to receive waste and, as required, transfer waste within the DST system. These operations are under control of the Compatibility Program. The primary goal of the Compatibility Program is to ensure that sufficient controls are in place to prevent the formation of incompatible mixtures that could cause safety, regulatory, programmatic, or operational problems. In order to prevent these problems, analyses of waste samples are required.

The programmatic requirements in this DQO are established by the Compatibility Program document *Tank Farm Waste Transfer Compatibility Program*, HNF-SD-WM-OCD-015, (Knight 2004). These programmatic requirements are restated in this DQO to derive data collection requirements. Determinations to transfer waste are based on the criteria found in the program (Knight 2004). If the criteria in Knight (2004) changes, this DQO will be revised to reflect these changes.

This document describes the Data Quality Objective (DQO) process undertaken to ensure appropriate data (type, quantity, and quality) are collected to support Compatibility Program decisions, which prevent potential waste compatibility problems during waste transfers. The U.S. Department of Energy (DOE) requires the use of the DQO process prior to tank sampling activities. The process is implemented in accordance with *Data Quality Objectives for Sampling and Analyses,* TFC-ENG-CHEM-C-16, Rev A (Banning 2003) and the U.S. Environmental Protection Agency EPA QA/G4, *Guidance for the Data Quality Objectives Process* (EPA 2000). However, some process modifications from the EPA guidance are commonly made to accommodate project or tank specific sampling constraints.

Because of the multiple issues involved in waste transfers (see Section 4.0), each issue or potential problem will be discussed separately in Section 4.0. In addition, a more detailed decision statement and decision rule will be presented for that particular issue.

2.0 STATEMENT OF THE PROBLEM

As indicated above, the transfer of waste into or within the DST system typically involves the commingling of two or more waste streams. Mixing two or more waste types may cause physical and/or chemical reactions, some of which could result in safety or other problems. Therefore, the overall goal is to transfer waste in a safe manner and to prevent the creation of safety, regulatory, programmatic, or operational problems in the receiver tank or the source tank.

Considering the purpose of this DQO, the overall problem statement can be expressed as follows:

> Conduct waste transfers, including waste entering the DST system and waste transferred within the DST system, according to the Compatibility Program requirements that prevent waste incompatibilities that could cause safety, regulatory, programmatic, or operational problems.

Regulatory requirements for the treatment, storage, and disposal of waste are found in Dangerous Waste Regulations *Washington Administrative Code* (WAC) 173-303-395(1)(b), 40 *Code of Federal Regulations* (CFR) 264.17, and 40 CFR 265.17. The waste is managed so it does not:

- Generate extreme heat or pressure, fire or explosion, or violent reaction;
- Produce uncontrolled toxic mists, fumes, dusts, or gases in sufficient quantities to threaten human health or the environment;
- Produce uncontrolled flammable fumes or gases in sufficient quantities to pose a risk of fire or explosions;
- Damage the structural integrity of the device or facility containing the waste; and/or
- Through other like means, threaten human health or the environment.

Other potential problems covered by this DQO consider source term requirements, management of specific analytes (i.e., polychlorinated biphenyls [PCB]), and operational requirements (e.g., line plugging) within the DST system. The various potential problems, including safety items, are discussed under specific headings in Section 4.0.

The principal study question that addresses the compatibility problem statement is:

> Does a proposed waste transfer meet the requirements for transfers entering or for transfers within the DST system?

3.0 DECISION STATEMENTS

Decision statements are created by combining study questions with alternative actions. Using this formula, the decision statement for the study question shown above is:

> Determine whether or not the waste in a proposed transfer meets the Compatibility Program transfer requirements and allows for an unrestricted transfer, or must be transferred to a specific tank, altered to meet requirements, or the transfer disallowed.

Each type of issue or potential problem that requires analyses for waste to be transferred will be discussed in Section 4.0. This discussion will include specific decision statements and decision rules that address the particular issue or potential problem. For example, a reevaluation may be required in certain instances when an action level is exceeded with the alternative actions allowing a transfer by adjusting the waste or by justifying that in a specific transfer the potential problem will not occur.

A decision rule is developed as an "if----then" statement that incorporates the parameters of interest, the scale of decision making, the action level, and the action or actions that would result from the decision.

Commonly, an action level is a concentration at which point a predetermined action is taken depending on whether the results of the analyses are above or below the specified action level. To account for uncertainty in the data, analytical results are compared to the action level at a previously agreed upon statistical confidence interval. Because of the multiple issues addressed in this DQO, confidence intervals may vary for the different issues or, in some instances; uncertainty in the data may be handled by other means. Therefore, the discussion of each issue in Section 4.0 will contain a discussion on the error tolerance for that issue.

4.0 DATA INPUTS

This section contains the information required to address the problem statement and the decision statement listed in Section 3.0. In addition, each issue or potential problem requiring waste transfer data will be discussed along with the decisions to be made. Some reasons for sampling and analyzing for waste transfers address potential safety problems (e.g., criticality, etc.) while others address potential operational problems (e.g., line plugging, etc.).

The issues or potential problems, requiring waste samples and analyses for waste transfers are:

- Source term,
- Flammable gas (FG) (lower flammability limit [LFL] and buoyant displacement gas release event [BDGRE]),
- Tank bump,
- Corrosion,
- Criticality safety,
- Organic reactions (organic complexants and organic solvents),
- Waste stream profile,
- Chemical compatibility,
- PCB management,
- Waste feed delivery configuration control (feed control),
- Phosphate rule, and
- Line plugging,

The potential problems listed above are applied to one or more of five types of transfers. The five types of transfers are:

1. Within the DST system,
2. Tank farm generators and/or shippers (e.g., single-shell tanks [SSTs], some catch tanks, etc.) to DST,
3. Non tank farm generator and/or shippers (e.g., Plutonium Finishing Plant, 222-S Laboratory, inactive facilities, etc.) to DST,
4. 242-A Evaporator, and
5. Bulk chemical additions >10,000 gallons (including >10,000 gallons of water).

4.1 REQUIRED ANALYTES

Not all of the analytes are required for each issue listed in Section 4.0 or for each type of waste transfer. Table 4-1 shows the data inputs required by this DQO, the issue or potential problem addressed by the specific data, and the type of transfer requiring the data.

As with any DQO process, existing data may be used if it reflects the current conditions of the receiving tank and the waste being transferred. However, some time restrictions do exist for this DQO (see Section 5.2).

Currently waste can be transferred with a maximum insoluble solids content of 25% by volume. If the insoluble solids content is >25%, the transfer is prohibited unless an evaluation is performed to determine that the proposed transfer is within the analyzed safety basis. Therefore, when insoluble solids are present in concentrations >1% by weight, they must be analyzed. There is one exception in the issues discussed in this DQO. The exception is for the analyses for PCBs. Separate analyses for PCBs in solids are required when the solids are $\geq$0.5 percent by weight.

Table 4-1. Required Information and Reason for Inclusion. (3 Sheets)

Data Input	Transfer Type	Problem Addressed	Comments
$^{239/240}Pu$	3, 4	Criticality safety	Type 4 transfers include evaporator staging within the DST system.
^{233}U	1, 2, 3, 4, 5	Criticality safety Feed control	Type 4 transfers include evaporator staging within the DST system. Criticality safety only applied to type 3 and 4 transfers. Feed control tanks group 2[(a)]. Applied to type 1, 2, 3, and 5 transfers.
^{235}U	3, 4	Criticality safety	Type 4 transfers include evaporator staging within the DST system.
^{238}U	3	Criticality safety	Required if the Pu equivalent is >0.001 g/L
Cr	1, 2, 3, 5	Criticality safety FG	Criticality safety criteria applied to type 3 transfers only and if the Pu equivalent is >0.001 g/L. FG criteria applied to supernatant only.
Fe	1, 2, 3, 5	Criticality safety FG	Criticality safety criteria applied to type 3 transfers only and if the Pu equivalent is >0.001 g/L. FG criteria applied to supernatant only.
Mn	3	Criticality safety	Required if the Pu equivalent is > 0.001 g/L
Ni	1, 2, 3, 5	Criticality safety FG	Criticality safety criteria applied to type 3 transfers only and if the Pu equivalent is >0.001 g/L. FG criteria applied to supernatant only.
pH	1, 2, 3, 4, 5	Criticality safety Corrosion	Criticality safety criteria applied to type 3 transfers only.
Al	1, 2, 3, 5	Source Term FG	Source term applied to type 3 transfers only. FG criteria applied to supernatant and interstitial liquids only.
$\%H_2O$	1, 2, 3, 5	FG PCB	Wt % H_2O for the PCB issue is needed to report PCB concentrations in solids on a dry weight basis.
^{90}Sr	1, 2, 3, 5	FG Tank bump Source term Feed control	Source term applied to type 3 transfers only. ^{90}Y is obtained with the ^{90}Sr analysis, however, ^{90}Y is only required for source term. FG criteria applied to supernatant and solids only. Tanks in feed control group 5[(a)]
^{137}Cs	1, 2, 3, 5	FG Tank bump Source term Feed control	Source term applied to type 3 transfers only. FG criteria applied to supernatant and solids only. Tanks in feed control group 7[(a)]
TOC	1, 2, 3, 5	Source term FG	For source term applied to type 3 transfers and solids only. FG criteria applied to supernatant and interstitial liquids only.
TIC	1, 2, 3, 5	FG	Supernatant only.

Table 4-1. Required Information and Reason for Inclusion. (3 Sheets)

Data Input	Transfer Type	Problem Addressed	Comments
NO_2^-	1, 2, 3, 4, 5	Corrosion Source Term FG	For source term applied to type 3 transfers and liquids only. FG criteria applied to supernatant and interstitial liquids only.
NO_3^-	1, 2, 3, 4, 5	Corrosion Source Term FG	Source term applied to type 3 transfers only. FG criteria applied to supernatant and interstitial liquids only.
Tank Temperature: dome space and waste	1, 2, 3, 4,5	FG Corrosion	Temperature required in the receiver tank.
Tank Volume: supernatant and sludge	1, 2, 3, 5	FG Tank bump	
Specific Gravity (SpG)	1, 2, 3, 5	FG Line plugging	Supernatant and interstitial liquids.
Density	1, 2, 3, 5	Source term Tank bump FG	Source term applied to type 3 transfers only.
Na	1, 2, 3, 5	Source term FG Feed control	Source term applied to type 3 transfers and liquids only. FG criteria applied to supernatant only. Tanks in feed control groups 1, 3, 5, and 7[(a)].
OH^-	1, 2, 3, 4, 5	Corrosion Source term FG	Source term applied to type 3 transfers only. Liquids. FG criteria applied to supernatant only.
NH_3	1, 2, 3, 5	FG	Supernatant and interstitial liquids only.
Cl^-	1, 2, 3, 5	FG	Supernatant only.
SO_4^{2-}	1, 2, 3, 5	FG Feed control	Supernatant only. Tanks in feed control group 1[(a)].
PO_4^{3-}	1, 2, 3, 5	Phosphate rule FG	FG criteria applied to supernatant only.
Pb	3	Source term	Solids only
La	3	Source term	Solids only
Zr	3	Source term	Solids only
F^-	1, 2, 3, 5	Source term FG	Solids only for source term. FG criteria applied to supernatant only.
Se	3	Source term	Solids only
U	3	Source term	Solids only
Separable organics	1, 2, 3, 4	Organic reactions	
Caustic demand test	2, 5	Corrosion	Tests will be conducted as needed when waste analyses show TSR chemistry limits are not met.
Energetics	3	Organic reactions	
Total alpha	3	Source term	Source term applied to type 3 transfers only.
PCB	1, 2, 3, 4	PCB management	
TRU	1, 2, 3, 5	Feed control	Tanks in feed control group 5[(a)].
Envelope A	1, 2, 3, 5	Feed control	Tanks in feed control group 3[(a)].

Table 4-1. Required Information and Reason for Inclusion. (3 Sheets)

Data Input	Transfer Type	Problem Addressed	Comments

Notes:

LFL = Lower flammability limit
PCB = Polychlorinated biphenyl
TOC = Total organic carbon
TSR = Technical safety requirement
TRU = Transuranic

[a] Feed control tank groups are found in Knight (2004) Appendix A.

For the source term issue, analyses of additional constituents for a particular waste stream may be required. If the generator has knowledge of any constituent that is greater than 1% by weight of the waste stream, these constituents must be analyzed as well as those shown in Table 4-1.

4.2 SOURCE TERM

Source term requirements are applied to waste entering the DST system from outside generators or shippers (type 3 transfers). The source term requirements are divided into radiological and toxicological groups. The basis for the source term analytical requirements is found in *Tank Farms Operations Administrative Controls* (CH2M HILL 2003c).

4.2.1 Source Term Specific Decision Statements

The specific study question for the source term issue during waste transfers can be stated as follows:

> Is the waste in a proposed waste transfer bounded by the source term assumptions used in the Documented Safety Analysis (DSA)?

Considering the study question, the decision statement for the source term issue can be stated as:

> Determine whether or not the waste in a proposed waste transfer is below the source term action levels and allows the waste to be transferred as planned, or requires a reevaluation using additional evidence to allow the transfer, chemical adjustment of the waste to meet requirements, or disallows the transfer.

4.2.2 Required Data Inputs and Action Levels

Several types of data are required to determine if the waste to be transferred into the DST system will meet the source term requirements for safely transferring the waste. The data needed for the radiological source term requirements are ^{90}Sr, ^{137}Cs, total alpha, and density. The data needed for the toxicological source term requirements are shown in Table 4-2. As can be seen in Table 4-2, the toxicological data input requirements are different for liquids and solids. In addition, as indicated in Table 4-2, analyses must be performed for any constituent that the generator has knowledge of that is greater than 1% by weight of the waste stream.

Table 4-2. Toxicological Data Input Requirements

Liquids	Solids
Al	Al
Na	Na
NO_3^-	NO_3^-
OH^-	OH^-
NO_2^-	
	F^-
	La
	Pb
	Se
	U
	Zr
	TOC
Any constituent >1% of the waste stream by weight.	Any constituent >1% of the waste stream by weight.

Note: TOC = total organic carbon

The action levels for the radiological analytes ^{90}Sr, ^{137}Cs, and total alpha are a set of interrelated conditions in the form of unit liter dose (ULD) values for onsite and offsite receptors. Table 4-3 for liquids and Table 4-4 for solids show the action levels and are set up to aid in determining if the proposed transfer meets the action levels. Instructions for comparing the analyte concentrations to the action levels are provided below each table. When solids are analyzed separately, density is required to calculate μCi/mL.

Table 4-3. Action Levels and Calculation Matrix for Liquids

(A) Isotope	(B) Concen. µCi/mL	(C) Concen. µCi/L	(D) Conversion Bq/µCi	(E) Concen. Bq/L	(F) Onsite Dose Conversion Sv/Bq	(G) Offsite Dose Conversion Sv/Bq	(H) Onsite ULD Sv/L	(I) Offsite ULD Sv/L
^{90}Sr			3.70E+04		3.00E-08	3.6E-08		
^{137}Cs			3.70E+04		6.70E-09	4.6E-09		
Total Alpha			3.70E+04		4.50E-05	4.95E-05		
Calculated total on-site and off-site ULD in the waste to be transferred								
Maximum allowable on-site and off-site ULD (action levels)							1.0E+03	1.5E+03

Note: Concen. = concentration

Instructions for Table 4-3:

1. Enter data in µCi/mL in the appropriate row of column (B).
2. Multiply column (B) concentration values by 1,000 and enter each product in the appropriate row of column (C).
3. Multiply column (C) by the conversion factor in column (D) and enter each product in the appropriate row of column (E).
4. Multiply the concentration in column (E) by the dose conversion in column (F) and enter each product in the appropriate row of column (H).
5. Multiply the concentration in column (E) by the dose conversion in column (G) and enter each product in the appropriate row of column (I).
6. The sum of the values in column (H) and the sum of the values in column (I) are compared to the allowable onsite ULD and offsite ULD, respectively.

Table 4-4. Action Levels and Calculation Matrix for Solids

(A) Isotope	(B) Concen. µCi/g	(C) Density g/mL	(D) Concen. µCi/mL	(E) Concen. µCi/L	(F) Conversion Bq/µCi	(G) Concen. Bq/L	(H) Onsite Dose Conversion Sv/Bq	(I) Offsite Dose Conversion Sv/Bq	(J) On-Site ULD Sv/L	(K) Off-Site ULD Sv/
^{90}Sr					3.70E+04		3.00E-08	3.6E-08		
^{137}Cs					3.70E+04		6.70E-09	4.6E-09		
Total Alpha					3.70E+04		4.50E-05	4.95E-05		
Calculated total on-site and off-site ULD in the waste to be transferred										
Maximum allowable on-site and off-site ULD (action levels)									1.90E+05	2.90E+0

Note: Concen. = concentration

Instructions for Table 4-4:

1. Enter data in µCi/g in the appropriate row of column (B).
2. Enter density in g/mL in the appropriate row of column (C).
3. Multiply column (B) concentration values by column (C) values and enter each product in the appropriate row of column (D).
4. Multiply column (D) concentration values by 1,000 and enter each product in the appropriate row of column (E).
5. Multiply column (E) by the conversion factor in column (F) and enter each product in the appropriate row of column (G).
6. Multiply the concentration in column (G) by the dose conversion in column (H) and enter each product in the appropriate row of column (J).
7. Multiply the concentration in column (G) by the dose conversion in column (I) and enter each product in the appropriate row of column (K).
8. The sum the values in column (I) and the sum of the values in column (J) are compared to the allowable on-site ULD and off-site ULD, respectively.

The action levels for the toxic chemical constituents (see Table 4-2) are the sum of fractions (SOFs). The action level for liquids is SOFs 1.16E+07 and for solids SOFs 8.06 +07. The process to determine if the waste to be transferred is above or below these action levels is described in *Chemical Source Terms for Tank Farms Safety Analyses* (Cowley et al. 2003). The process is outlined in the bullets below.

- Convert the analyte concentrations provided by the generator to equivalent compounds expressed in mg/m^3.
- Divide the concentration (in mg/m^3) of each compound by the temporary emergency exposure limit three (TEEL-3) value of the compound (see Cowley et al. 2003, Appendix B) to obtain the unitless SOFs. TEEL-3 is used because the waste transfer leak accident unmitigated onsite toxicological consequences are "high," that is, they exceed TEEL-3.
- Once the SOFs are calculated for each compound, add the compound-specific SOFs together to obtain the total SOFs for the solid and liquid phases of the waste stream.

It is not necessary to recalculate the SOFs for the receiving tank. Because all existing tanks meet the source term requirements, it is not possible for the incoming waste to create a tank that exceeds the source term action levels.

4.2.3 Decision Rules

The decision logic addressing the source term issue is shown in Figure 4-1. As can be seen in Figure 4-1, several different action levels must be met before waste can be transferred. Although there are several different action levels, all must be met before waste can be transferred without reevaluating the transfer. Therefore, they are all included in one decision in Figure 4-1. Although the decision rule below is divided into two parts (radiological and toxic), both parts must be met before the waste can be transferred without a review.

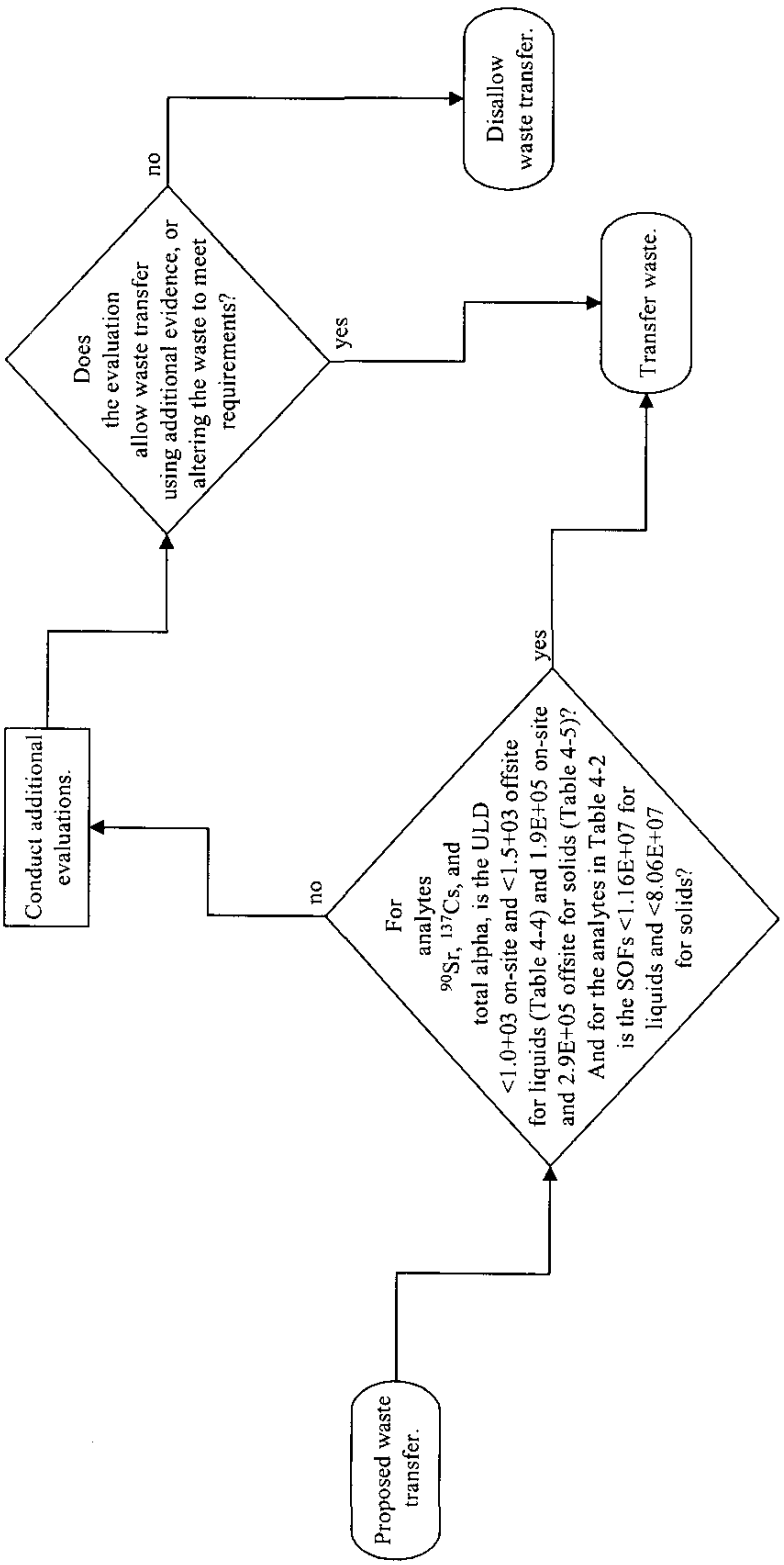
1a. If the 95% UCL of the calculated ULD for ^{90}Sr, ^{137}Cs, and total alpha is <1.0E+03 onsite and <1.5E+03 offsite for liquids (Table 4-3) and 1.9E+05 onsite and 2.9E+05 offsite for solids (Table 4-4), then the waste can be transferred as planned; otherwise, the transfer must be reevaluated or disallowed.

1b. If the SOFs for the constituents for liquids and for solids (see Table 4-2) is <1.16E+07 and <8.06 +07 respectively, then the waste can be transferred as planned; otherwise, the transfer must be reevaluated or disallowed.

If required, the reevaluation is conducted by Nuclear Safety and Licensing organization and is subjective. A transfer may take place after the reevaluation if it is determined the waste will not significantly affect the receiving tank or violate the DSA. Waste may also be adjusted to meet the action level requirements.

Determination of the 95% UCL for this data set is shown in Section 4.3.4.

Figure 4-1. Source Term Decision Logic Flow Chart



4.2.4 Error Tolerance

It is assumed that analyte concentration data for the radiological analytes (^{90}Sr, ^{137}Cs, and Total Alpha) are obtained from at least two samples. It is also assumed that there are primary and duplicate observations from sample one and a single primary observation from sample two. This type of arrangement is called an unbalanced data set.

For the radiological analytes, the ULD (Sv/L) is a linear combination of the observations for ^{90}Sr, ^{137}Cs, and Total Alpha. That is,

$$\text{ULD (Sv/L)} = C_1{}^{90}\text{Sr} \times C_2{}^{137}\text{Cs} \times C_3 \text{ (Total Alpha)},$$

where C_1, C_2, and C_3 are constants. They are used to convert analyte concentration, in μCi/mL, into Sv/L. The conversions or constants are given in Table 4-3 (columns D, F, and G) for liquid samples and Table 4-4 (columns F, H, and I) for solid samples. There are two ways ULD can be compared to an action level. The first is to fit a one-way analysis of variance model to the unbalanced data for each of four analytes. The classification variable is the "sample." The one-way analysis of variance is used to give an estimate of the mean concentration and the standard deviation of the mean for each of the analytes. For each analyte, the mean and standard deviation of the mean in Sv/L is obtained by multiplying by the appropriate constant C_1, C_2, or C_3. The estimate of the mean ULD (Sv/L) and standard deviation of the mean ULD (Sv/L) is the sum of the four means and the square root of the sum of squares of the individual standard deviations. This method is based on the assumption that the three analytes, ^{90}Sr, ^{137}Cs, and Total Alpha, are uncorrelated with each other.

The preferred method is to combine the individual, ^{90}Sr, ^{137}Cs, and Total Alpha observations by sample. They are combined, using the constants C_1, C_2, C_3, and C_4 given in Table 4-3 or Table 4-4 into a primary duplicate pair for sample one and primary for sample two. The units of the three numbers are now ULD (Sv/L). If, ^{90}Sr, ^{137}Cs, and Total Alpha, are correlated with each other, then this method automatically incorporates the correlations. Since the data are unbalanced, a one-way analysis of variance model is fit to the ULD (Sv/L) data to provide an estimate of the mean ULD, $\overline{ULD}$, and standard deviation of the mean ULD, S.D.($\overline{ULD}$). The upper limit to the one-sided 95% confidence interval on the mean is then compared to the action level. That is,

$$\text{UCL}(95\%) = \overline{ULD} + t_{(0.05,\, df)} \times \text{S.D.}(\overline{ULD})$$

where $t_{(0.05,\, df)}$ is the appropriate quantile from Student's t distribution with df degrees of freedom. The degrees of freedom are the number of samples minus one. If UCL(95%) is less than the action level for liquid samples, then the hypothesis that ULD for liquid samples is greater than the action level (greater than 1.0E+03 Sv/L or greater than 1.5E+03 Sv/L) is rejected at the 0.05 level of significance. If the observations are for solid samples, the hypothesis that

ULD is greater than the action level (greater than 1.9E+05 Sv/L or greater than 2.9E+05 Sv/L) is rejected at the 0.05 level of significance.

For the toxicological analytes (Table 4-2), the error tolerance is a simple comparison of the determined SOFs of the waste stream to the SOFs action levels for liquids and solids (see decision rule 1b).

4.3 FLAMMABLE GAS

All tank wastes generate FG. Generation rates differ among tanks depending on the composition, temperature, and radiation level of the waste in each tank. In order for FG to be a safety problem, a mixture of gaseous fuel and oxidizer at concentrations greater than the LFL of the mixture must be present in the tank dome space (LFL issue) or gas must be retained below the waste surface in a manner that the gas can be released spontaneously (BDGRE issue).

In DSTs, active ventilation prevents buildup of FG in the headspace during steady-state operations.

When transferring waste, sampling and analyses are required to prevent flammable gas conditions from developing in the receiver tank and source tank.

4.3.1 Flammable Gas Specific Decision Statements

The flammable gas focus in this DQO is to predict waste transfers that could cause gas generation that would cause an excess of gas in the headspace greater than the action level or gas retention that could cause a BDGRE. Therefore, the specific study question for the FG issue can be stated as follows:

> Will a proposed waste transfer cause an unacceptable FG buildup in the headspace of the receiving tank or retention of the gas beneath the waste surface that could cause a BDGRE?

Considering the study question, the decision statement for the FG issue can be stated as:

> Determine whether or not waste from a proposed transfer will cause unacceptable gas buildup in the receiving tank and requires the waste transfer to be disallowed, additional evaluation prior to transfer, or allows the waste transfer as planned.

4.3.2 Required Data Inputs and Action Levels

Different data inputs are required from supernatant, solids, and interstitial liquids. The required data inputs for the supernatant are ^{137}Cs, ^{90}Sr, TOC, total inorganic carbon (TIC), NO_2^-, NO_3^-, OH^-, NH_3, Al, Na, Fe, Cr, Ni, PO_4^{3-}, SO_4^{2-}, F^-, Cl^-, % water, SpG, density in g/mL, waste volume, and waste temperature.

Data inputs for solids are ^{137}Cs, ^{90}Sr, solids volume, % water, and density in g/mL.

Data inputs for interstitial liquids are TOC, NO_2^-, NO_3^-, NH_3, % water, and SpG.

In addition to the data requirements listed above, dome space temperature of the tank is required.

The model used to determine FG generation is developed in *Steady-State Flammable Gas Release Rate Calculation and Lower Flammability Level Evaluation for Hanford Tank Waste* (Hu and Zach 2003). Since the data obtained from the analytes for FG generation are used as input to a model, none of the analytes has an independent action level. The actual action level is a combination of the rate of flammable gas generation using the model described in Hu and Zach (2003). The action levels are determined assuming loss of the primary tank ventilation. The action levels (discussed in *Tank Farms Operations Administrative Controls* (CH2M HILL 2003d) can be stated as the minimum time for the FG to increase by 25 percent of the LFL in the tank headspace remains ≥13 days (≥8 days for tanks 241-AY-101 and 241-AY-102).

As described in *Methodology and Calculations for the Assignment of Waste Groups for the Large Underground Waste Storage Tanks at the Hanford Site,* (Hedengren and Barker 2003), the waste tanks are assigned to one of three waste groups (A, B, or C). The tank is assigned to a waste group according to the propensity for the tank to retain flammable gas and the potential of the waste to release retained gas by a BDGRE, which is determined using several criteria (see Hedengren and Barker 2003). Therefore, the basic action level for the BDGRE issue is to prevent the tanks in a waste transfer from becoming a waste group A tank without prior written approval from the U.S. Department of Energy, Office of River Protection (ORP). Waste transfers into waste group A tanks are prohibited without prior written approval from ORP. In addition, if a receiver tank changes from one group to another (including B and C tanks), appropriate ignition controls must be applied. A list of tanks with the waste group designation is in CH2M HILL (2003d).

4.3.3 Decision Rules

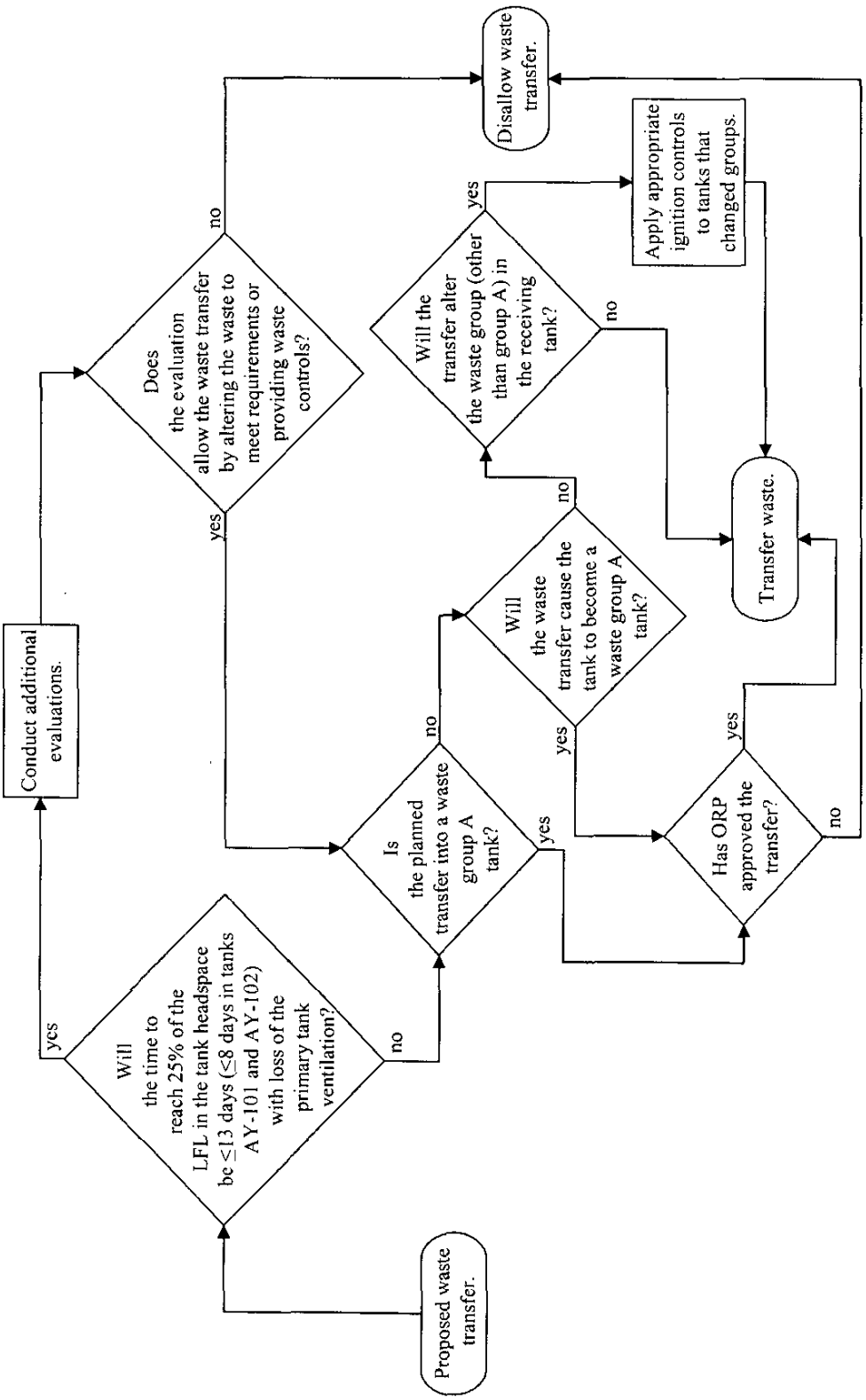
The decision logic addressing the FG issue is shown in Figure 4-2. As can be seen in Figure 4-2, there are three decisions; one addressing time to LFL and two addressing waste group designation of the tank. All decision rules shown below must be met to transfer waste.

1. If after a transfer the FG generation rate allows the headspace in the receiver tank to reach 25% of the LFL within 13 days (8 days for AY-101 and AY-102), then the transfer is reevaluated; otherwise, the transfer can be completed as planned.

2. If a transfer is planned for a waste group A tank or the transfer will cause a waste group A tank, then ORP approval is required to transfer the waste; otherwise, the transfer can be completed as planned.

3. If a transfer is planned for a waste group B or C tank and the transfer will cause the tank to change waste groups, then appropriate ignition controls must be applied; otherwise, the transfer can be completed as planned

Figure 4-2. Flammable Gas Decision Logic Flow Chart



4.3.4 Error Tolerance

The flammable gas requirement addressing the time to reach 25 percent of the LFL in the tank headspace was developed based on an empirical flammable gas model developed in Hu and Zach (2003). Consequently, no additional statistical analysis will be applied to the data. The action level of 25 percent of the LFL is conservative. Similarly, the categorization of the tanks into specific waste groups (A, B, or C) is developed in Hedengren and Barker (2003). Therefore, no additional statistical analysis will be applied to the decision addressing the creation of a waste group A tank resulting from a proposed transfer.

4.4 TANK BUMP

There is a potential for a tank bump under certain conditions of waste depth, heat load, and buoyancy ratio. However, the DSA concludes that a tank bump is not a credible accident if certain controls are maintained (Tomaszewski 2003a and Tomaszewski 2003b). Therefore, prior to a proposed waste transfer, the end state of the receiving tank must be assessed to avoid creating the conditions that would cause a tank bump (CH2M HILL 2003e).

4.4.1 Tank Bump Specific Decision Statements

The end state of the receiving tank waste must meet only one of four conditions (total tank heat load $\leq$38,000Btu/h, non-convective layer thickness $\leq$12 inches, supernatant layer $\leq$40 inches, or a ratio of the vertical void fraction profile to the neutral buoyant void fraction of $<$1.0 [Tomaszewski 2003a]) to meet the requirements to accept transferred waste. Therefore, the decision statement could be written as follows:

> Determine whether or not the waste to be transferred will cause the receiver tank to exceed all four conditions; non-convective layer is $\leq$12 inches, supernatant layer is $\leq$40 inches, total tank heat load is $\leq$38,000BTU/h, and the ratio of the vertical void fraction profile to the neutral buoyant void fraction is $<$1.0 and requires the waste transfer to be disallowed, transferred to an alternate tank, or requires no action.

4.4.2 Required Data Inputs and Action Levels

The input required to assess the four conditions affecting a tank bump are the depth of solids, depth of the liquids, heat load, and buoyancy ratio.

Because the only constituents used from the compatibility waste sampling to determine these inputs are the density of solids and liquids (one of the criteria used in the determination of the buoyancy ratio [Hedengren and Barker 2003]) and the concentrations of ^{90}Sr and ^{137}Cs used to calculate heat load, these data inputs do not have independent action levels.

4.4.3 Decision Rules

As can be seen in Figure 4-3, only one of the four criteria used to address the tank bump issue must be met to transfer waste. The four criteria are commonly addressed in the order presented in the Figure 4-3. The decision rule can be written as follows:

> If the supernatant layer is ≤40 inches or the non-convective layer is ≤12 inches or the total tank heat load is ≤38,000BTU/h or there is a buoyancy ratio of <1.0, then no action is necessary; otherwise, the waste transfer must be disallowed or transferred to a different tank.

4.4.4 Error Tolerance

The only data input addressing the tank bump issue that can be used to determine a confidence limit is heat load. The heat generation rate is determined by taking the mean concentration of ^{90}Sr and ^{137}Cs in the supernatant and the solids separately. A weighted average of the amount (volume) of the solids and supernatant is used to determine the contribution of each phase to the heat generation rate for the waste in a tank and the waste being transferred to the tank. The ^{90}Sr concentrations are multiplied by 2.28E-02 BTU/(Ci-h) to determine ^{90}Sr contribution to heat generation rate. The ^{137}Cs concentrations are multiplied by 1.61E-02 BTU/(Ci-h) to determine the ^{137}Cs contribution to the heat generation rate. If the tank bump decision for the transfer is based on the heat load, a 95% confidence limit can be calculated as shown below

Based on liquid and solid samples, let the estimates of the mean and standard deviation (S.D.) of the mean for ^{90}Sr and ^{137}Cs be denoted by

$$^{90}Sr : \overline{X}_L, \text{S.D.}(\overline{X}_L) \text{ and } \overline{X}_S, \text{S.D.}(\overline{X}_S)$$
$$^{137}Cs : \overline{Y}_L, \text{S.D.}(\overline{Y}_L) \text{ and } \overline{Y}_S, \text{S.D.}(\overline{Y}_S)$$

These means and standard deviations may be estimates obtained for a one-way analysis of variance model fit to the data. It is assumed that the concentration data has been multiplied by the appropriate factors so that the units for the means and standard deviations are BTUs per hour.

Let W_L and W_S be the proportions of liquids and solids in the waste. Let the total amount of heat, and its standard deviation, generated by ^{90}Sr and ^{137}Cs be

$$^{90}Sr : \overline{X}_T = W_L\overline{X}_L + W_S\overline{X}_S, \text{S.D.}(\overline{X}_T) = \sqrt{[W_L\text{S.D.}(\overline{X}_L)]^2 + [W_S\text{S.D.}(\overline{X}_S)]^2}$$
$$^{137}Cs : \overline{Y}_T = W_L\overline{Y}_L + W_S\overline{Y}_L, \text{S.D.}(\overline{Y}_T) = \sqrt{[W_L\text{S.D.}(\overline{Y}_L)]^2 + [W_S\text{S.D.}(\overline{Y}_S)]^2}$$

An estimate of the total amount of heat and its standard deviation is

$$T = \overline{X}_T + \overline{Y}_T, \text{S.D.}(T) = \sqrt{\text{S.D.}(\overline{X}_T)^2 + \text{S.D.}(\overline{Y}_T)^2}$$

The upper limit to a one-sided 95% confidence interval on the total amount of heat is

$$\text{UCL}(95\%) = T + t_{(0.05,df)} \times \text{S.D.}(T)$$

where $t_{(0.05, df)}$ is the appropriate quantile from Student's t distribution with df degrees of freedom. The degrees of freedom are approximate. They are determined using Satterwaithe's approximation (Snedecor and Cochran 1982). If UCL(95%) is greater than the action level for maximum amount of heat, then the hypothesis of being greater that the action limit is rejected at the 0.05 level of significance.

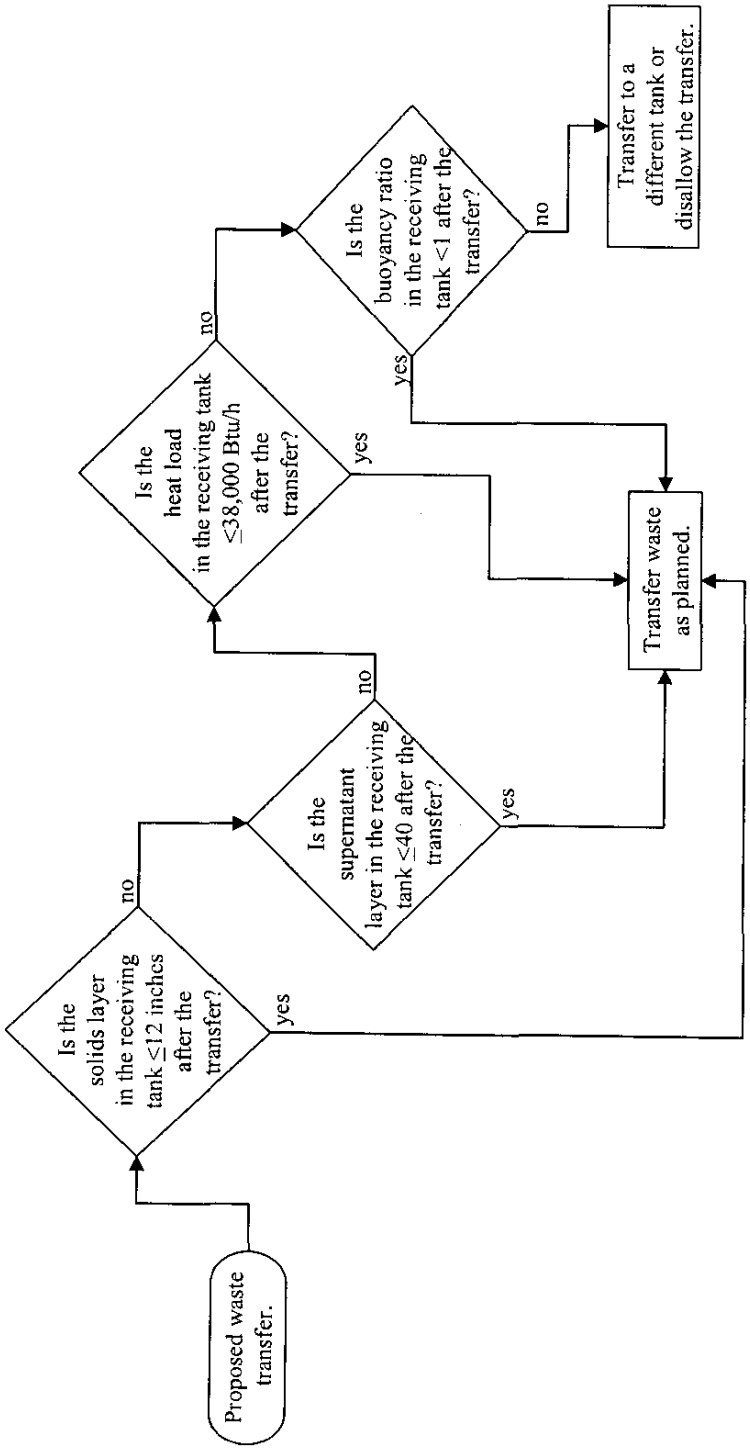


Figure 4-3. Tank Bump Decision Logic Flow Chart

4.5 CORROSION

The overall sampling and analytical requirements for the chemistry control portion of the Tank Integrity Program is governed by *Double-Shell Tanks Chemistry Control Data Quality Objectives* (Banning 2002a). Part of Banning (2002a) describes the requirement of preserving tank integrity by maintaining the chemistry (hydroxide ion [OH^-], nitrite ion [NO_2^-], and nitrate ion [NO_3^-]) at specified concentration levels documented in CH2M HILL (2003a). This requirement is also applicable during all waste transfers as part of the Compatibility Program requirements.

The corrosion requirements apply to all transfer types (see Section 4.0). However, for the DST 241-SY-102 exceptions are allowed (Schepens 2003) (see Sections 4.5.2 and 4.5.3).

4.5.1 Corrosion Specific Decision Statement

The specific waste transfer study question for the corrosion issue can be stated as follows:

> Will a proposed waste transfer cause unacceptable corrosion in pipes and tanks?

Considering the study question, the decision statement for corrosion concerns can be stated as:

> Determine whether or not a proposed waste transfer will cause unacceptable corrosion in pipes or tanks and requires chemical adjustment of the waste, transfer to a different tank, or can be transferred as planned.

4.5.2 Required Data Inputs and Action Levels

The established inputs to evaluate corrosion potential due to a waste transfer are the hydroxide ion [OH^-], nitrate ion [NO_3^-], and nitrite ion [NO_2^-]. The action levels for OH^-, NO_2^-, and NO_3^- are a set of interrelated conditions presented in the Technical Safety Requirements (TSR) document HNF-SD-WM-TSR-006, Section 5.16, Rev 3 (CH2M HILL 2003a) and shown in Table 4-5. All of the conditions that must be met under each scenario are considered the action level for that particular scenario. Waste temperature is also required to determine the scenario and, therefore, the action levels (see Table 4-5).

In addition to the analytes mentioned above, for the tank 241-SY-102 exception (see Sections 4.5 and 4.5.3) pH and the depth of solids in the tank 241-SY-102 are required.

Caustic demand tests are required in one transfer situation; for SST waste that does not meet tank farm chemistry control requirements. The caustic demand tests are performed to determine the chemistry adjustments required to bring the waste into compliance or maintain the waste within the corrosion control specifications.

4.5.3 Decision Rules

Criteria for type 1, 2, and 4 waste transfers differ from type 3 and 5 transfers. The decision logic for transferring waste, when considering chemistry control for corrosion, is shown in Figure 4-4.

The decision rule for waste transfers other than type 1, 2, and 4 can be stated as:

> If the limits to the 95% confidence interval satisfy the TSR chemistry limits for OH^-, NO_2^-, and NO_3^- (Table 4-5) in the receiving DST after a transfer, then the waste can be transferred as planned; otherwise, another receiver tank must be selected for the waste transfer or the waste adjusted to meet the requirements.

As can be seen in Figure 4-4, an exception to the decision rule above can occur under specific conditions. If a waste transfer is planned for tank 241-SY-102 the transfer may take place even if the waste in tank 241-SY-102 does not meet the corrosion control requirements after the transfer as long as other criteria are met. In this case, the transfer may take place if, after the transfer, the supernatant in tank 241-SY-102 has a pH $\geq$11, the supernatant has a temperature of $\leq 122^{\circ}$ F, and the solids in the tank are $\leq$146 inches. This decision rule can be written as follows:

> If a waste transfer into tank 241-SY-102 does not meet the corrosion criteria (Table 4-5) but the supernatant pH is $\geq$11 and the supernatant temperature is $\leq 122^{\circ}$ F and the solids in the tank are $\leq$146 inches, then the waste can be transferred as planned; otherwise the transfer is disallowed.

The decision rule for a type 3 and 5 transfer can be stated as:

> If the limits to the 95% confidence interval satisfy the TSR chemistry limits for OH^-, NO_2^-, and NO_3^- (Table 4-5) in the waste scheduled for transfer, then the waste can be transferred as planned if the receiving DST meets the TSR chemistry limits after the transfer; otherwise, the waste chemistry must be adjusted to meet the limits prior to transfer or the transfer disallowed.

Table 4-5. Technical Safety Requirements (TSR) Waste Chemistry Limits

FOR $[NO_3^-]$ RANGE	VARIABLE	FOR WASTE TEMPERATURE (T) RANGE		
		T < 167 °F	167 °F ≤ T ≤ 212 °F	T > 212 °F
$[NO_3^-] \leq 1.0$ M	$[OH^-]$	0.010 M ≤ $[OH^-]$ ≤ 8.0 M	0.010 M ≤ $[OH^-]$ ≤ 5.0 M	0.010 M ≤ $[OH^-]$ < 4.0 M
	$[NO_2^-]$	0.011 M ≤ $[NO_2^-]$ ≤ 5.5 M	0.011 M ≤ $[NO_2^-]$ ≤ 5.5 M	0.011 M ≤ $[NO_2^-]$ ≤ 5.50 M
	$[NO_3^-] / ([OH^-] + [NO_2^-])$	< 2.5	< 2.5	< 2.5
1.0 M < $[NO_3^-]$ ≤ 3.0 M	$[OH^-]$	0.1 ($[NO_3^-]$) ≤ $[OH^-]$ < 10 M	0.1 ($[NO_3^-]$) ≤ $[OH^-]$ < 10 M	0.1 ($[NO_3^-]$) ≤ $[OH^-]$ < 4.0 M
	$[OH^-] + [NO_2^-]$	≥ 0.4 ($[NO_3^-]$)	≥ 0.4 ($[NO_3^-]$)	≥ 0.4 ($[NO_3^-]$)
$[NO_3^-]$ > 3.0 M	$[OH^-]$	0.3 M ≤ $[OH^-]$ < 10 M	0.3 M ≤ $[OH^-]$ < 10 M	0.3 M ≤ $[OH^-]$ < 4.0 M
	$[OH^-] + [NO_2^-]$	≥ 1.2 M	≥ 1.2 M	≥ 1.2 M
	$[NO_3^-]$	≤ 5.5 M	≤ 5.5 M	≤ 5.5 M

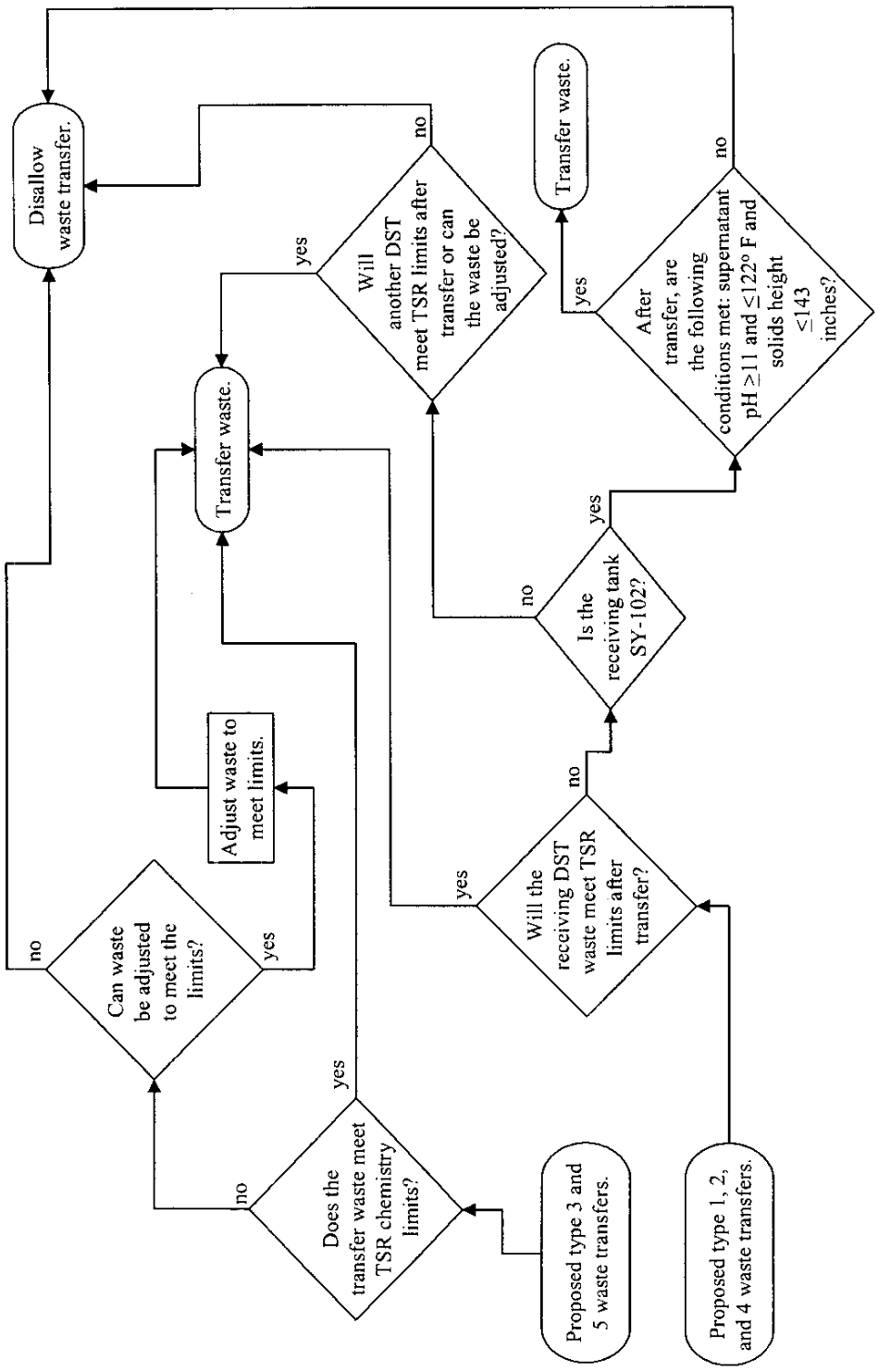


Figure 4-4. Corrosion Decision Logic Flow Chart

4.5.4 Error Tolerance

It is assumed that $[NO_3^-]$, $[NO_2^-]$, and [OH-] will be measured on multiple tank samples. It is also assumed that there is at least one set of duplicate measurements (primary and duplicate) per laboratory batch. Let the measured values of $[NO_3^-]$, $[NO_2^-]$, and [OH-] be denoted by X_{ij}, Y_{ij}, and Z_{ij}, respectively, where i=1, 2,..., a, and j=1,...,n_i denote the sample number and replicate value. Also, let

$$R_{ij} = \frac{X_{ij}}{Y_{ij} + Z_{ij}} = \frac{[NO_3]}{[OH] + [NO_2]}, \text{and}$$

$$S_{ij} = Y_{ij} + Z_{ij} = [OH] + [NO_2].$$

The following paragraphs outline the methods used to construct confidence intervals on the mean for the concentration of

$[NO_3^-]$, $[NO_2^-]$, $[OH^-]$, the ratio $[NO_3^-]$ / ($[OH^-]$ + $[NO_2^-]$), and the sum $[OH^-]$ + $[NO_2^-]$.

Each of X_{ij}, Y_{ij}, Z_{ij}, R_{ij}, and S_{ij} are replicate observations from multiple samples. Consequently, a one-way analysis of variance is used to estimate the means and standard deviations of the mean. If the observations are balanced (n_i=n), the analysis of variance estimates of the means are usually the arithmetic means of the observations. If the observations are unbalanced, the estimates of the means will be the restricted maximum likelihood estimates (REML). Let the estimates of the means and standard deviations of the means be denoted by

$\overline{X}, \overline{Y}, \overline{Z}, \overline{S}, \text{and} \overline{R}$ and by

$SD(\overline{X}), SD(\overline{Y}), SD(\overline{Z}), SD(\overline{S}), \text{and} SD(\overline{R})$,

respectively. The degrees of freedom (df) are usually the number of samples minus 1. The two sided 100(1-α)% confidence intervals (CIs) for each of $[NO_3^-]$, $[NO_2^-]$, $[OH^-]$, the ratio $[NO_3^-]$ / ($[OH^-]$ + $[NO_2^-]$), and the sum $[OH^-]$ + $[NO_2^-]$ are

$[NO_3^-]$: $\overline{X} - t_{(\alpha,df)} \times SD(\overline{X})$ and $\overline{X} + t_{(\alpha,df)} \times SD(\overline{X})$

$[NO_2^-]$: $\overline{Y} - t_{(\alpha,df)} \times SD(\overline{Y})$ and $\overline{Y} + t_{(\alpha,df)} \times SD(\overline{Y})$

$[OH^-]$: $\overline{Z} - t_{(\alpha,df)} \times SD(\overline{Z})$ and $\overline{Z} + t_{(\alpha,df)} \times SD(\overline{Z})$

$[NO_3^-]$ / ($[OH^-]$ + $[NO_2^-]$): $\overline{R} - t_{(\alpha,df)} \times SD(\overline{R})$ and $\overline{R} + t_{(\alpha,df)} \times SD(\overline{R})$

$[OH^-]$ + $[NO_2^-]$: $\overline{S} - t_{(\alpha,df)} \times SD(\overline{S})$ and $\overline{S} + t_{(\alpha,df)} \times SD(\overline{S})$

where $t_{(df, \alpha)}$ is the appropriate quantile from Student's t distribution with df degrees of freedom and 100(1-α)% confidence. If α=0.05, the intervals are 95% CIs. The symbol α is the percent for the 100(1-α)% confidence statement.

In Table 4-5, there are multiple CIs that must be satisfied. There are four intervals for the first and third [NO_3^-] range and three for the second range. If there is to be 100(1-α)% confidence associated with the combined three or four confidence intervals, then based on Bonferroni's inequality, the individual CIs should have 100(1-α/n)% confidence where n (the number of confidence intervals) is three or four (Snedecor and Cochran 1982, page 116). If n is three, the individual CIs should be 98 percent, and if n is four, the individual CIs should be 99 percent. The combined [NO_3^-] will jointly have 95 percent confidence, approximately.

For example, for the first range of [NO_3^-] and the first temperature range, four CIs are computed. Let LL and UL denote the lower limits and upper limits of the CIs. The intervals and their acceptance conditionals are shown in Table 4-6.

Table 4-6. Confidence Intervals and Acceptance Conditions

Confidence Interval	Conditions on Interval
One-sided upper 99% CI on [NO_3^-]	UL([NO_3^-])≤1.0
Two-sided 99% CI on [OH^-],	0.01≤LL([OH^-]) and UL([OH^-])≤8.0
Two-sided 99% CI on [NO_2^-]	0.011≤LL([NO_2^-]) and UL([NO_2^-])≤5.5
One-sided upper 99% CI on the ratio [NO_3^-] / ([OH^-] + [NO_2^-])	UL([NO_3^-] / ([OH^-] + [NO_2^-]))≤2.5

If these conditions are all true, then one is approximately 95 percent confident that the limits are satisfied. There are similar tables of LLs and ULs for the other range of limits on [NO_3^-] and temperature.

4.6 CRITICALITY SAFETY

The following factors affect the criticality safety of tank waste:

- Concentration of the fissile material in the waste,
- The proportion and proximity of the fissile material to neutron absorbers, and
- Waste chemistry, particularly pH.

The concentration of the fissile material is affected by its solubility at a given pH. The fissile material in the Hanford Site tank waste consists primarily of ^{239}Pu and ^{235}U, with small amounts of ^{233}U and ^{241}Pu. Fissile material concentrations are calculated as if all the material were ^{239}Pu on a gram for gram basis (one gram of ^{233}U, ^{235}U, or ^{240}Pu is considered equivalent to one gram

of ^{239}Pu) using the unit plutonium equivalents (Pu-eq). Although ^{240}Pu is not a fissile isotope, including it in the fissile material inventory is a conservative means of accounting for the presence of other Pu isotopes. The quantity of ^{235}U in the waste must be included in the fissile material quantity; however, ^{235}U may be excluded in accordance with the Criticality Prevention Specifications (CH2M HILL 2003b) on a case-by-case basis with approval of the tank farms criticality safety representative (CSR) or alternate. Americium 241 is not included because it cannot become critical in an over-moderated system. The quantity of water and other hydrogen-containing compounds in tank waste is greater than the required amount for optimum moderation; therefore, the waste is "over-moderated."

According to the Criticality Safety Evaluation Report (CSER) *Criticality Safety Evaluation Of Hanford Tank Farms Facility* (Kessler et al. 2002) Hanford Site tank waste has been analyzed and a criticality accident is not credible in its current condition. This is due to both the form and distribution of the fissile material. Therefore, analyses are not required for transfers within the DST system. As can be seen in Table 4-1, criticality analytical requirements are required only for type 3 and some constituents for type 4 transfers.

4.6.1 Criticality Specific Decision Statement

The specific study question for criticality can be written as follows:

> Will the addition of waste from a proposed transfer to a receiving tank alter the form and distribution of fissile material in the receiving tank such that a criticality hazard could be caused?

Considering the study question, the decision statement for criticality can be stated as:

> Determine whether or not the waste in a proposed transfer meets the criteria for the form and distribution of fissile material allowing an unrestricted transfer, or requires waste alteration prior to transfer, a reevaluation, or causes the transfer to be disallowed.

4.6.2 Required Data Inputs and Action Levels

Three criteria are used to control the form and distribution of the fissile material in a waste transfer entering the DST system. These criteria are pH, the concentration of the fissile material, and the relative concentration of fissile material versus insoluble neutron absorbers. The criteria require interdependent decisions be made when addressing criticality safety prior to waste transfers.

As can be seen in Table 4-1, the criticality data inputs are the concentrations of $^{239/240}$Pu, ^{233}U, ^{235}U, Cr, Fe, Mn, and Ni. In addition, a measurement or calculation of pH is required. Other than pH, the actual concentrations of these analytes are not action levels. Action levels are determined by combining concentrations of the analytes and by ratios of the concentrations (see below).

The total fissile material concentration is determined by summing the concentrations of $^{239/240}Pu$, ^{233}U, and ^{235}U. The concentration of fissile material, or Pu equivalent (Pu-eq), is used to determine the first two action levels (see Figure 4-5) for criticality transfer decisions. The analytes Cr, Fe, Mn, Ni, and ^{238}U are neutron absorbers and the concentrations are used to calculate subcritical mass ratios. The ratios are calculated by dividing the concentrations of Cr, Fe, Mn, Ni, and ^{238}U by the Pu-eq.

The action level of the pH measurement or calculation is eight. A transfer is not allowed if the pH measurement or calculation is less than eight.

Figure 4-5 shows the decision logic to determine if the waste in a proposed transfer (type 3) meets the criticality criteria. Each decision point shows the action levels for that decision.

The action levels for decisions 4 and 5 in Figure 4-5, determined by the ratios of the concentrations of the neutron absorbers (subcritical mass fraction) to the Pu-eq (Table 4-7), can be met (the waste transferred) if the following formulas are true:

Decision 4: $(Fe/Pu\text{-}eq)/160 + (Mn/Pu\text{-}eq)/32 + (Ni/Pu\text{-}eq)/105 + (Cr/Pu\text{-}eq)/135 + (^{238}U/Pu\text{-}eq)/770 > 1$

Decision 5: $(Fe/Pu\text{-}eq)/160 + (Mn/Pu\text{-}eq)/32 + (Ni/Pu\text{-}eq)/105 + (Cr/Pu\text{-}eq)/135 (^{238}U/Pu\text{-}eq)/770 \geq 2$

The action level for decision 4 in Figure 4-5 also can be met (the waste transferred) if any one of the actual ratios is > the minimum shown in Table 4-7 (e.g., Fe/Pu-eq is >160). In addition, the action level for decision 5 in Figure 4-5 also can be met if any one of the actual ratios is > twice the minimum shown in Table 4-7 (e.g., Fe/Pu-eq is >320)

Table 4-7. Minimum Neutron Absorber/Plutonium Subcritical Mass Ratio

Neutron Absorber (X)	Minimum Neutron Absorber/Plutonium Subcritical Mass Ratio (X/Pu-eq)
Iron (Fe)	160
Manganese (Mn)	32
Nickel (Ni)	105
Chromium (Cr)	135
Uranium (^{238}U)	770

Because the waste presently stored in the tanks cannot cause a criticality accident in its present form, the information requirements for waste compatibility is considered necessary only for waste entering the DST system (type 3 transfers). However, in addition to the requirements on waste entering the DST system (Figure 4-5), Pu-eq limits (CH2M HILL 2002b) are established for Hanford Site tanks. Therefore, when a tank is scheduled to receive waste from an outside

generator or shipper, it is evaluated prior to receiving the waste. Figure 4-6 shows the limits for DSTs and double contained receiver tanks (DCRTs) and the decision logic for accepting type 3 transfers. The limits shown in Figure 4-6 are a total limit (combined solids and supernatant) for a tank. Because solid samples are not commonly required in a receiver tank, the evaluation of the receiver tank is conducted using existing data.

In addition to the type 3 transfers, criticality information (Pu-eq only) is required for type 4 transfers. Waste staged for the evaporator (type 4 transfers) requires the Pu-eq concentration to be < 0.005 g/L.

4.6.3 Decision Rules

As stated above, three criteria are used to control the form and distribution of the fissile material in a waste transfer entering the DST system. These criteria are pH, the concentration of the fissile material, and the relative concentration of fissile material versus insoluble neutron absorbers. Therefore, there is more than one action level addressed by the concentration of fissile material (see Figure 4-5) for a type 3 transfer. These action levels are considered sequentially. If the concentration of fissile material is greater than the first action level, the second action level is considered. With this in mind, the decision rule is stated as follows:

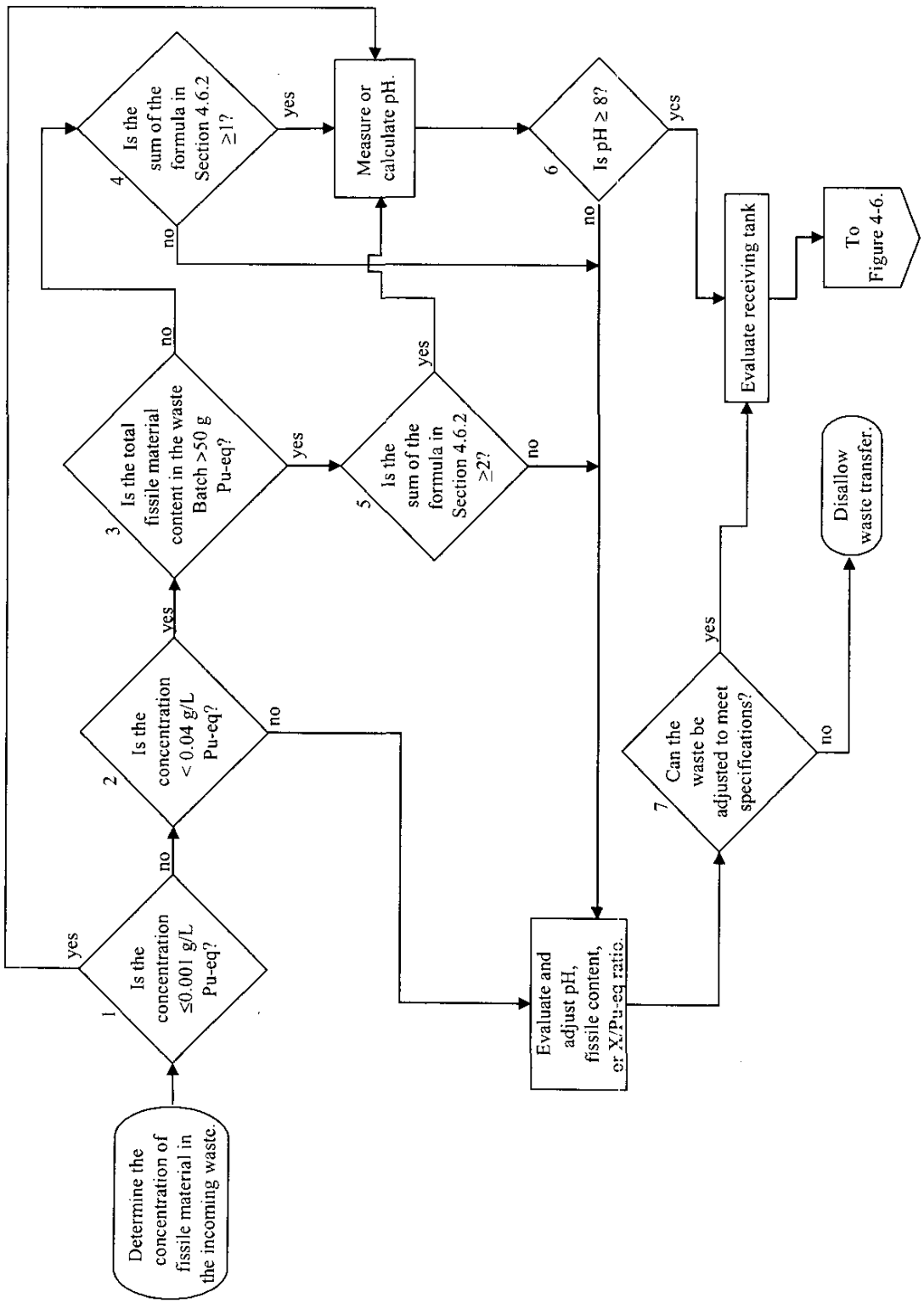
> If the 95% lower limit to a one-sided confidence interval (LCL) for pH is ≥ 8 and the 95% UCL for the concentration of the fissile material (Pu-eq) is ≤ to the action levels (Figure 4-5) in the waste of a proposed transfer, then the waste can be transferred [provided the receiving tank limits are not violated (Figure 4-6)]; otherwise, the waste must be adjusted to meet the requirements or the transfer disallowed.

A second decision rule for waste staged for the evaporator (type 4 transfer) can be written as follows:

> If the 95% UCL for the concentration of the fissile material is <0.005 Pu-eq in the waste of a proposed transfer to stage 242-A-Evaporator feed, then the waste can be transferred; otherwise, the waste must be adjusted to meet the requirements or the transfer disallowed.

Determination of the 95% confidence limit (CL) for this data set is shown in Section 4.6.4. Determination of the 95% UCL for second decision rule is calculated the same as the first two decisions shown in Figure 4-5 and Section 4.6.4.

Figure 4-5. Criticality Decision Logic Flow Chart for Incoming Waste



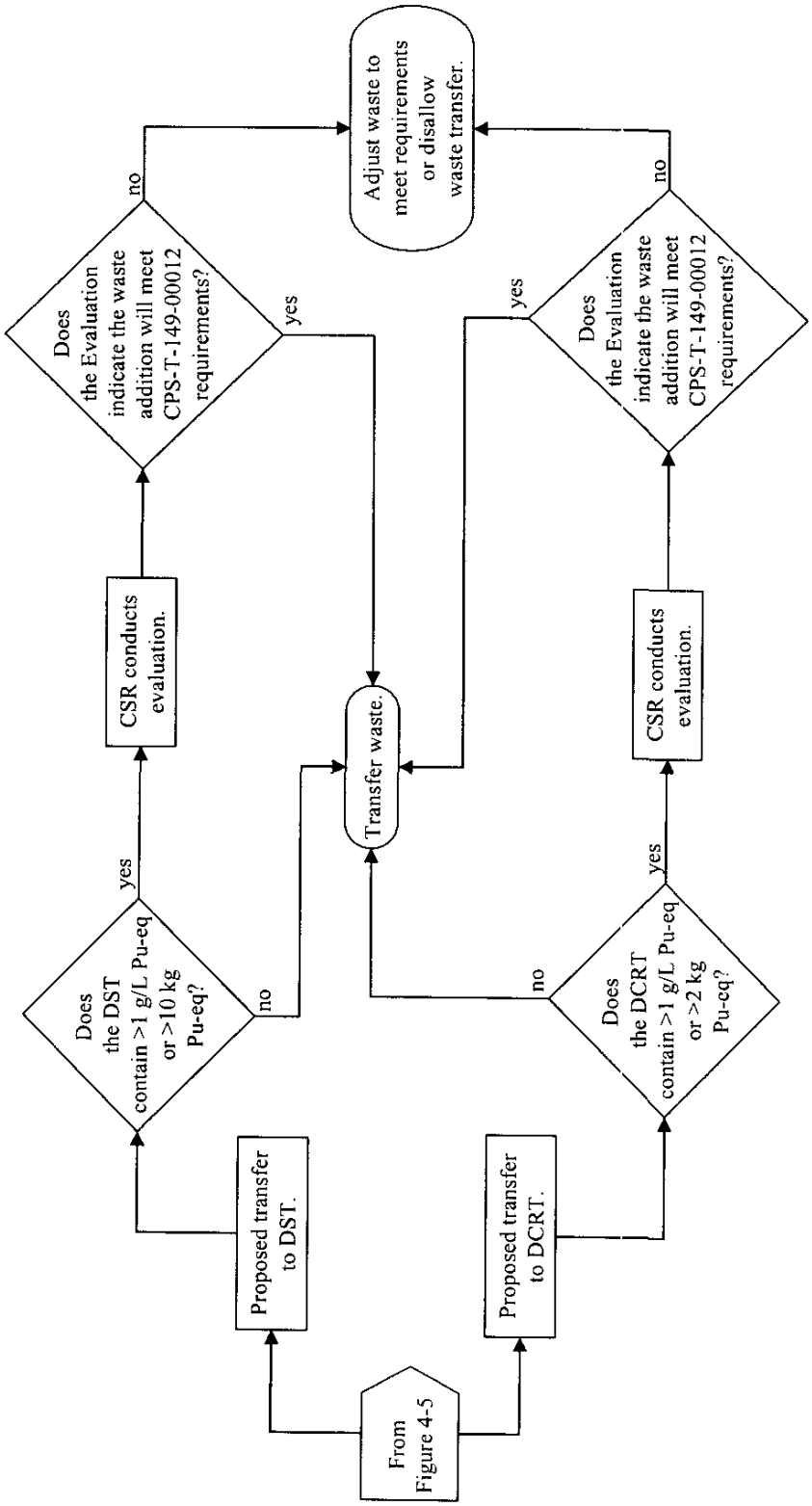


Figure 4-6. Criticality Decision Logic Flow Chart for Receiving Tanks

4.6.4 Error Tolerance

It is assumed that analyte concentration data is obtained from at least two samples. It is also assumed that there are primary and duplicate observations from sample one and a single primary observation from the other sample(s). This type of arrangement is called an unbalanced data set.

The maximum fissile material concentration (Pu-eq) is the sum of the observations for $^{239/240}Pu$, ^{233}U, and ^{235}U. That is,

$$\text{Pu-eq} = {}^{239/240}\text{Pu} + {}^{233}\text{U} + {}^{235}\text{U}$$

There are two ways Pu-eq can be compared to an action level. The first is to fit a one-way analysis of variance model to the unbalanced data for each of three analytes. The classification variable is the "sample." The one-way analysis of variance is used to give an estimate of the mean concentration and the standard deviation of the mean for each of the three analytes. The estimate of the mean Pu-eq and standard deviation of the mean is the sum of the three means and the square root of the sum of squares of the individual standard deviations. This method is based on the assumption that the three analytes, $^{239/240}Pu$, ^{233}U, and ^{235}U, are uncorrelated with each other.

The preferred method is to combine the individual $^{239/240}Pu$, ^{233}U, and ^{235}U observations by sample into a Pu-eq primary duplicate pair for sample one and primary for sample two. If $^{239/240}Pu$, ^{233}U, and ^{235}U are correlated with each other, then this method automatically incorporates the correlations. Since the data are unbalanced, a one-way analysis of variance model is fit to the Pu-eq data to provide an estimate of the mean (Pu-eq) and standard deviation of the mean S.D. (mean(Pu-eq)). The upper limit to the one-sided 95% confidence interval on the mean is then compared to the action level. That is,

$$\text{UCL}(95\%) = \text{mean(Pu-Eq)} + t_{(0.05,\,df)} \times \text{S.D.(mean(Pu-Eq))}$$

where: $t_{(0.05,\,df)}$ is the appropriate quantile from the Student's t distribution with df degrees of freedom. The degrees of freedom are the number of samples minus one. If UCL(95%) is less than the action level, then the hypothesis that Pu-eq is greater than the action level (greater than 0.001 g/L or greater than 0.04 g/L) is rejected at the 0.05 level of significance.

The upper limit to a one-sided 95% confidence limit on the total fissile material in a waste batch is the UCL(95%) on Pu-eq times the volume of the batch. If the product is greater than the action limit (50 g), then the hypothesis (fissile material < 50 g) is rejected at the 0.05 level of significance.

The lower limit to a one-sided 95% confidence limit on pH is computed using the following equation:

$$\text{LCL}(95\%) = \overline{X} - t_{(0.05,\,df)} \times \text{S.D}(\overline{X})$$

Where $\overline{X}$ and S.D.($\overline{X}$) are the mean and standard deviation of the mean of the pH values. The difficulty that may be encountered is the scale that should be used. The LCL can be computed on the pH scale or it can be computed on the anti-log scale and then the LCL transformed to the pH scale. In either case, if LCL(95%) on pH is ≥ the action limit, then the hypothesis (pH ≥8) is rejected at the 0.05 level of significance.

The lower limit to a one-sided 95% confidence interval on the ratio X/Pu-eq can be computed two ways (X stands for Fe, Mn, Ni, or Cr). The first is to use a one-way analysis of variance to estimate the mean and standard deviation of X and Pu-eq. These means and standard deviations are used to construct an approximated confidence limit. That is, if R is the ratio of means (X/Pu-eq), then the LCL(95%) is approximately

$$LCL(95\%, Ratio) = R(1 - t_{(0.05,df)} \times RSD(R))$$

where RSD(R) is the square root of the sum of squares of the individual RSDs squared, $t_{(0.05, df)}$ is the quantile from Student's t distribution with df degrees of freedom for a one-sided 95% CI. The df are the number of samples minus one. The RSD is the relative standard deviation; it is the standard deviation divided by the mean.

The preferred method is to form the ratio of the individual Fe, Mn, Ni, or Cr and Pu-eq observations by sample into the primary duplicate pair for sample one and primary for sample two. Since the data are unbalanced, a one-way analysis of variance model is fit to the ratios of observations to provide an estimate of the mean of ratios ($\bar{r}$) and standard deviation of the mean of ratios (S.D.($\bar{r}$)). The means and standard deviations are computed for each of the four ratios Fe/ Pu-eq, Mn/ Pu-eq, Ni/ Pu-eq, and Cr/ Pu-eq. Any correlations between Fe, Mn, Ni, or Cr and Pu-eq are automatically incorporated into the standard deviations. The lower limit to the one-sided 95% confidence interval on the ratio is then compared to the action level. That is,

$$LCL(95\%) = \bar{r} - t_{(0.05, df)} \times S.D.(\bar{r})$$

where $t_{(0.05, df)}$ is the appropriate quantile from the Student's t distribution with df degrees of freedom. The degrees of freedom are the number of samples minus one. If LCL(95%) is greater than the action level, then the hypothesis that the ratio Fe/ Pu-eq, Mn/ Pu-eq, Ni/ Pu-eq, or Cr/ Pu-eq is less than the action level is rejected at the 0.05 level of significance. The action levels for the ratios Fe/ Pu-eq, Mn/ Pu-eq, Ni/ Pu-eq, and Cr/ Pu-eq are given in Table 4-7.

The preferred method used to compare the sum of ratios to the numbers "1" and "2" decisions 4 and 5 in Figure 4-5 is as follows. First, form the ratio of the individual Fe, Mn, Ni, or Cr and Pu-eq observations, by sample, into the primary duplicate pair for sample one and primary for sample two. The primary duplicate pair for sample one and the primary for sample two, for each of the four ratios are then "normalized" by dividing by 160, 32, 105, and 135, respectively, and then summing them. Since the data are unbalanced, a one-way analysis of variance model is fit

to the normalized sum of ratios of observations to provide an estimate of the mean of ratios ($\bar{r}$) and standard deviation of the mean of ratios (S.D.($\bar{r}$)). Any correlations between the normalized ratios of Fe, Mn, Ni, and Cr to Pu-eq are automatically incorporated into the standard deviations.

The lower limit to a one-sided 95% confidence interval is then compared to the number "1" in decision 4 and to the number "2" in decision 5 of Figure 4-5. That is, the lower limit LCL(95%) is used, where

$$LCL(95\%) = \bar{r} - t_{(0.05,\,df)} \times S.D.(\bar{r})$$

The degrees of freedom are the number of samples minus one. If LCL(95%) is greater than the action level, then the hypothesis that the sum of normalized ratios (Fe/ Pu-eq/160), (Mn/ Pu-eq)/32, (Ni/ Pu-eq)/105, or (Cr/ Pu-eq)/135 is < the action level is rejected at the 0.05 level of significance.

4.7 ORGANIC REACTIONS

Two safety issues concerning reactions of organic material are considered for tank waste. The first issue (organic complexant) is discussed in the *Organic Complexant Topical Report* (Sandgren 2003). Sandgren (2003) summarizes the safety basis used to resolve the organic complexant safety issue. The second issue (organic solvent) is discussed in the *Organic Solvent Topical Report* (Cowley et al.2000), along with the justification to close the organic solvent safety issue.

Although both safety issues have been closed, it is necessary to collect data during waste transfers to maintain the tanks in a safe condition and avoid creating a problem in a receiving tank.

4.7.1 Organic Reactions Specific Decision Statement

The specific study question for the organic reactions during waste transfers can be stated as follows:

> Will a proposed waste transfer cause unacceptable storage conditions in the receiving tank from wastes containing organic complexants, organic solvents, or other reactive material?

Considering the study question, the decision statement for organic reactions can be stated as:

> Determine whether or not a proposed waste transfer will cause unacceptable storage conditions in the receiving tank from organic complexants, organic solvents, or other reactive material and requires the transfer to be disallowed; or allows the waste transfer after further assessment, altering the waste, or providing controls; or allows the waste transfer as planned.

4.7.2 Required Data Inputs and Action Levels

Only two data inputs (energetics and separable organics) are necessary to address the organic issue.

Type 1 and type 2 transfers only require visible separable organics observations, while type 3 and type 4 transfers require data on energetics as well as visible separable organics observations. This information is needed on the waste to be transferred.

In addition to the separable organics observations required in type 1 and 2 transfers, type 3 transfers requires the exotherm/endotherm ratio to be <1. Type 4 transfers require separable organic observations, exotherm/endotherm ratio to be <1, and no exotherms below 168 degrees Fahrenheit.

4.7.3 Decision Rules

As noted above, requirements differ for type 1 and 2, type 3 and type 4 transfers. Therefore, three decision rules are required. The decision logic for transferring waste, when considering organic reactions, is shown in Figure 4-7.

The decision rule for type 1 and 2 transfers can be expressed as:

> If no observable organics are present in the waste to be transferred, then the transfer is allowed; otherwise, the transfer is evaluated against safety concerns and will be allowed or disallowed depending on the outcome of the evaluation.

Type 3 transfers have two sequential decisions (see Figure 4-7), and the decision rules can be expressed as:

1. If the waste to be transferred contains observable separable organics, then the transfer is disallowed; otherwise, an evaluation of the ratio of exotherms/endotherms is made.

2. If the 95% UCL of the ratio for exotherms/endotherms is <1 for the incoming waste, then the waste can be accepted; otherwise, the waste is evaluated against safety concerns and will be allowed or disallowed depending on the outcome of the evaluation.

Type 4 transfers have three sequential decisions (see Figure 4-7) the decision rules can be expressed as:

1. If the waste to be transferred contains observable separable organics, then the transfer is disallowed; otherwise, an evaluation of the ratio of exotherms/endotherms is made.

2. If waste to be transferred contains exotherms below 168 degrees Fahrenheit, then the transfer is disallowed; otherwise, an evaluation of the ratio of exotherms/endotherms is made.

3. If the 95% UCL of the ratio for exotherms/endotherms is <1 for the incoming waste, then the waste can be accepted; otherwise, the transfer is disallowed.

The only data input addressing the organic issue that can be used to determine a confidence limit is exothermic/endothermic ratio. The method for computing the 95% confidence limits for the ratio for exotherms/endotherms is <1 is shown in Section 4.7.4.

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