S

ENGINEERING CHANGE NOTICE

Page 1 of 2

1. ECN 669250

Proj. ECN

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☒ No	Savings ☐	$	Savings ☐	$	Delay ☐	

19. 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 13. Enter the affected document number in Block 20.

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	☐		☐

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

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Design Authority			Design Agent		
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Cog. Mgr.	J.W. Hunt	10/8/01	QA		
QA	L.P. Markel	10/8/01	Safety		
Safety			Design		
Environ.			Environ.		
Other			Other		
	M.A. Knight M.A. Knight	10/4/01			

DEPARTMENT OF ENERGY

Signature or a Control Number that tracks the Approval Signature

ADDITIONAL

DISTRIBUTION SHEET

To	From	Page 1 of 2
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Name	MSIN	Text With All Attach.	Text Only	Attach./ Appendix Only	EDT/ECN Only
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D. L. Banning (5)	R2-12	H			
K. G. Carothers	R2-11	X			
C. DeFigh-Price	R2-58	X			
J. G. Field	R2-12	X			
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T. C. Oten	S5-05	X			
D. A. Reynolds	R2-11	X			
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Double-Shell Tanks Chemistry Control Data Quality Objectives

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DOUBLE-SHELL TANKS CHEMISTRY CONTROL DATA QUALITY OBJECTIVES

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LIST OF TERMS

DQO	Data quality objective
DST	double-shell tank
M	molarity of moles per liter
QC	quality control
TSR	technical safety requirement
WTP	Waste Treatment Plant
%	percent
°F	degrees Fahrenheit

1.0 INTRODUCTION

One of the main functions of the River Protection Project is to store the Hanford Site tank waste until the Waste Treatment Plant (WTP) is ready to receive and process the waste. Waste from the older single-shell tanks is being transferred to the newer double-shell tanks (DSTs). Therefore, the integrity of the DSTs must be maintained until the waste from all tanks has been retrieved and transferred to the WTP. To help maintain the integrity of the DSTs over the life of the project, specific chemistry limits have been established to control corrosion of the DSTs. These waste chemistry limits are presented in the Technical Safety Requirements (TSR) document HNF-SD-WM-TSR-006, Sec. 5.15, Rev 2B (CHG 2001). In order to control the chemistry in the DSTs, the Chemistry Control Program will require analyses of the tank waste.

This document describes the Data Quality Objective (DQO) process undertaken to ensure appropriate data will be collected to control the waste chemistry in the DSTs. The DQO process was implemented in accordance with *Data Quality Objectives for Sampling and Analyses*, HNF-IP-0842, Rev. 1b, Vol. IV, Section 4.16, (Banning 2001) and the U.S. Environmental Protection Agency EPA QA/G4, *Guidance for the Data Quality Objectives Process* (EPA 1994), with some modifications to accommodate project or tank specific requirements and constraints.

Additional information on the Chemistry Control Program can be found in the documents *Technical Basis for Chemistry Control Program*, RPP-7795, Rev. 1 (Fort et al. 2001) and *Technical Basis for Caustic Additions to Tanks 241-AY-101, 241-AY-102, and 241-AN-102*, RPP-8173, Rev. 0 (Jo et al. 2001).

2.0 PROBLEM STATEMENT

As mentioned above, waste chemistry limits have been established to help control the corrosion in DSTs. These limits are for the hydroxide ion (OH^-), nitrite ion (NO_2^-), and nitrate ion (NO_3^-) and can be found in the TSR document HNF-SD-WM-TSR-006, Sec. 5.15, Rev 2B (CHG 2001). The concentrations of these analytes change over time, and it has been known for some time that four of the DSTs do not meet the limits specified in the TSR. An August 29, 2000, Defense Nuclear Facilities Safety Board letter (Conway 2000) stated the practice of allowing tanks to remain outside the corrosion specifications is inappropriate. The letter also indicates that if the present corrosion specifications are too conservative, they should be changed. Therefore, the overall problem is to maintain the waste chemistry of the DSTs within the TSR limits.

Consensus on the overall problem statement was reached in a DQO process meeting. The problem statement is:

> Protect the double-shell tank primary vessels from excessive corrosion by controlling the waste chemistry.

Three principal study questions identify the key unknown conditions or issues that address the waste chemistry control problem (see above). The three study questions developed by the DQO team are listed below.

1. Does the tank waste chemistry (supernatant and solids) meet TSR waste chemistry limits?
2. Are additional waste chemistry criteria necessary?
3. How do waste components affect the TSR chemistry components?

3.0 DECISION STATEMENTS

Decision statements are created by combining the study questions with alternative actions. The first study question has alternative actions associated with it, and a conventional decision statement can be developed. However, the second and third study questions do not have associated alternative actions, and conventional decision statements cannot be developed. Alternative actions are not appropriate in the second and third decision statements because the data collection results will not be used to make decisions directly. Decisions will be made from the principles developed from the data.

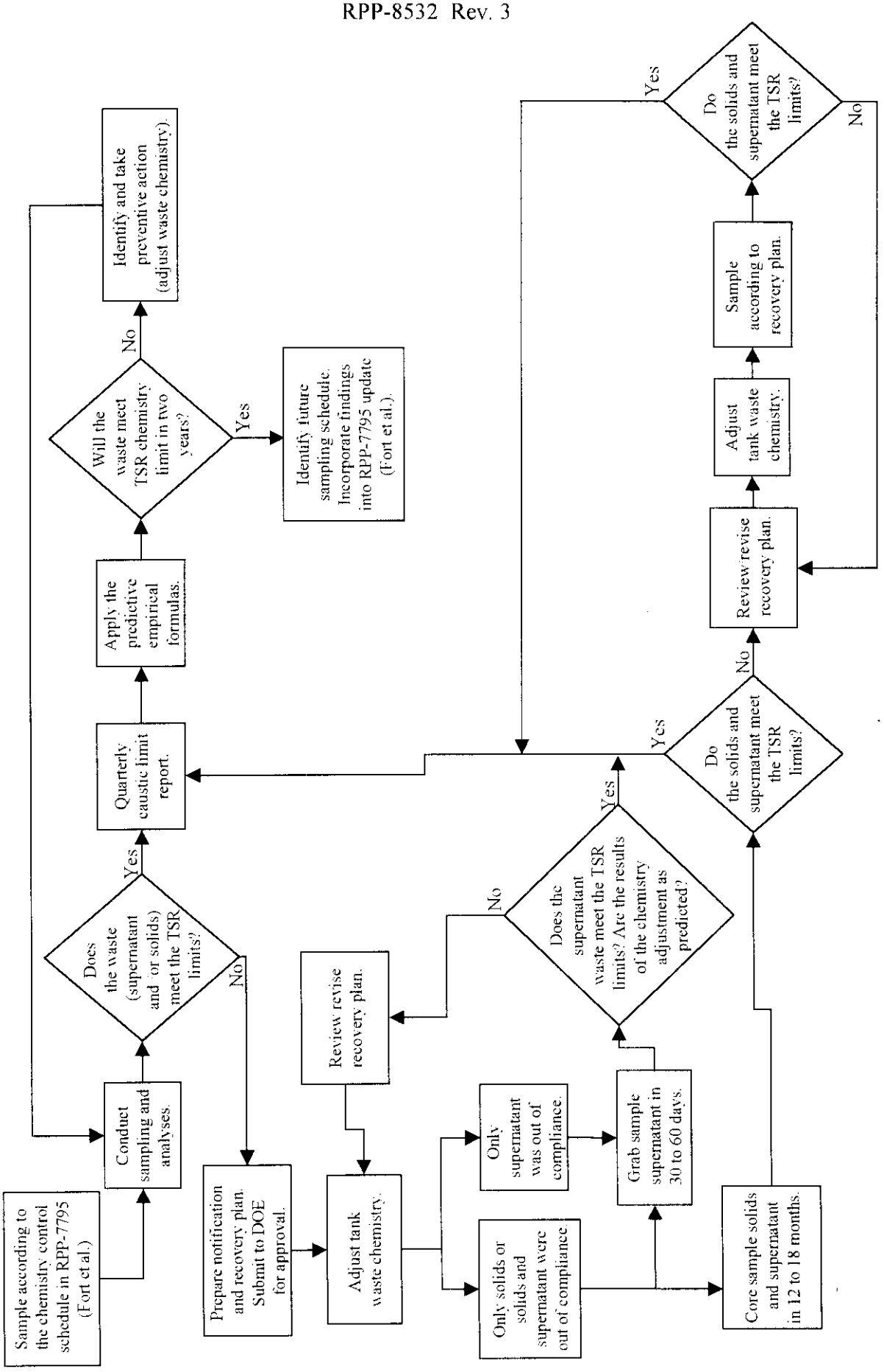
The decision statements are listed below:

1. Determine whether or not the tank waste chemistry (supernatant and solids) meets the TSR waste chemistry limits and requires chemical adjustment, or the application of the predictive empirical equations followed by the identification of future sampling or preventive actions.
2. Determine if additional waste chemistry criteria are needed.
3. Determine how certain waste components affect the TSR chemistry limit components (OH^-, NO_2^-, and NO_3^-).

To maintain the waste within the TSR limits and address the decision statements listed above, sampling and analyses will be required in two situations. The first situation is the sampling and analyses to determine if a tank meets the TSR limits (called initial sampling). The second is the sampling and analyses required after tank waste chemistry adjustments are made. Waste chemistry adjustments could be accomplished by adding chemicals to a tank, adding waste that is in compliance, mixing the waste (naturally or mechanically), or retrieving the waste.

Figure 3-1 shows the logic flow chart for the chemistry control of tank waste. The flow chart shows the activities and decisions that are made when tank waste is sampled to determine if it meets the TSR chemistry limits. Sampling will be conducted according to the schedule in Fort et al. (2001). If a tank is found to be out of compliance, a recovery plan will be prepared and submitted to the U.S. Department of Energy, Office of River Protection for approval. If a recovery plan already exists for that tank, the existing recovery plan will be reviewed to determine if it covers planned recovery actions or should be revised to add additional recovery actions.

Figure 3-1. Chemistry Control Flow Chart



4.0 DATA INPUTS

This section contains the information required to address the problem statement and the decision statements listed in Section 3.0.

4.1 ANALYTES

Table 4-1 lists the information and data input needed to address the decision statements listed in Section 3.0. The data needs are listed along with the reason for inclusion (which decision statement is addressed), the type of waste analyzed, and any additional requirements or clarifications.

Analyses will be performed on supernatant, solids, and interstitial liquids from centrifuged solids. However, not all data inputs are required for each waste type and not all waste types will be obtained in each sampling event. The information needed depends on the sampling situation (initial or after chemical adjustments) and the decision to be addressed by a specific analysis. The sampling design is discussed in Section 8.0.

Table 4-1. Required Information and Reason for Inclusion. (2 Sheets)

Data Input	Reason for Inclusion (Number = Decision Statement Addressed)	Type of Material Analyzed and Comments
NO_3^-	1, 2, and 3	Supernatant and Interstitial (centrifuged) liquids. Each segment or grab.
NO_2^-	1, 2, and 3	Supernatant and Interstitial (centrifuged) liquids. Each segment or grab.
OH^-	1, 2, and 3	Supernatant and Interstitial (centrifuged) liquids. Each segment or grab.
pH	1, 2, and 3	Supernatant and Interstitial (centrifuged) liquids. Each segment or grab.
Na	See comment column.	Needed to evaluate pH data. Supernatant and Interstitial (centrifuged) liquids. Each segment or grab.
Cl^-	2	Supernatant and Interstitial (centrifuged) liquids. Each segment or grab.

Table 4-1. Required Information and Reason for Inclusion. (2 Sheets)

Data Input	Reason for Inclusion (Number = Decision Statement Addressed)	Type of Material Analyzed and Comments
F^-	2	Supernatant and Interstitial (centrifuged) liquids. Each segment or grab.
SO_4^{2-}	2	Supernatant and Interstitial (centrifuged) liquids. Each segment or grab.
PO_4^{3-}	2	Supernatant and Interstitial (centrifuged) liquids. Each segment or grab.
Al	3	Supernatant, Interstitial (centrifuged) liquids, and centrifuged solids. Each segment or grab.
TIC	3	Supernatant, Interstitial (centrifuged) liquids, and centrifuged solids. Each segment or grab.
TOC	3	Supernatant, Interstitial (centrifuged) liquids, and centrifuged solids. Each segment or grab.
$\%H_2O$	1 and 3	Supernatant, Interstitial (centrifuged) liquids, and centrifuged solids. Each segment or grab.
Specific Gravity	1 and 3	Supernatant and Interstitial (centrifuged) liquids. Each segment.
Weight	1 and 3	Interstitial (centrifuged) liquids and centrifuged solids. Each segment.
Volume	1 and 3	Decanted (settled) solids, centrifuged solids, and centrifuged liquids. Each segment.
Caustic Demand Test	1	Supernatant and uncentrifuged solids. Will only be conducted when waste analyses show it does not meet TSR chemistry limits. A test plan will be prepared to control the tests.
Corrosion Potential	2	Interstitial (centrifuged) liquids or wet solids. A test plan will be prepared to control the tests.
Tank Supernatant and Solids Level (Volume)	1	From existing data.
Ventilation Rate	1	From existing data.

Notes:

TOC = Total organic carbon
TIC = Total inorganic carbon

As discussed in Section 3.0, this DQO covers data collection under two situations (initial or after chemical adjustments). The analytes shown in Table 4-1 that address decision statement 1 are needed to determine if the waste in a tank meets the TSR chemistry limit requirements (see Table 4-3). The sampling scheme for each situation is discussed in Section 8.0 and shown in Figure 3-1

Free hydroxide concentration is normally determined by an approved 222-S Laboratory analytical titration method. However, titration results at low OH^- concentrations (< 0.03 M) pose accuracy problems. As a general guideline, when the waste samples have a pH < 12.5, the free OH^- concentration is calculated from the analytical pH measurement. For waste samples with pH > 12.5, the free hydroxide concentration is normally determined by the analytical titration method. Sodium and buffer (aluminum, phosphate, TOC, and carbonate) concentrations and the shape and quality of the potentiometric titration curve are used in the evaluation of the hydroxide and pH data at low OH^- concentrations.

Discussions have occurred (Stewart 2001) concerning evaluation and perhaps changes to the present TSR chemistry limits. While the analytes in Table 4-1 that address decision statement 2 are not part of the TSR chemistry limits, they are known to influence corrosion rates. These analytes are required to help determine if additional waste chemistry criteria are needed. The information collected on these analytes will be used to support corrosion testing.

The data requested in Table 4-1 that address decision statement 3 apply to the prediction of when the waste in a particular tank will no longer meet the TSR chemistry limits. One of the goals of the chemistry control program is to increase the accuracy of predicting when the waste in a tank will no longer meet the TSR chemistry limits. With an accurate predictive tool, sampling requirements could be reduced, and planning for any required chemistry adjustments would be more efficient. Presently, two empirical equations are used to predict when the waste in a tank will no longer meet the chemistry limits (Fort et al. 2001). The information collected according to the requirements in this DQO will increase the accuracy of these equations and will be useful to build better predictive tools.

Caustic demand tests will be conducted on the supernatant waste and solid waste (not centrifuged) that do not meet the TSR chemistry limits. This test helps determine the amount of caustic needed to bring a tank into compliance with the TSR chemistry limits. A test plan will be prepared to govern any caustic demand tests.

The corrosion potential test is conducted by making potentiostatic and potentiodynamic anodic polarization measurements on a carbon steel coupon immersed in interstitial liquids obtained from centrifuged solid waste or wet sludge. This information helps determine if the carbon steel is susceptible to stress corrosion cracking in the solids environment. A test plan will be prepared to govern any corrosion potential tests. The corrosion potential test is second in priority to the other data needs listed in Table 4-1 and will be conducted if enough interstitial liquid or wet solids are available after the other analyses have been conducted.

4.2 QUALITY CONTROL

The *222-S Laboratory Quality Assurance Plan* (Clark 2001) specifies the requirements to ensure the quality of the analyses conducted at the 222-S Laboratory. The requirements shall meet the *Hanford Analytical Services Quality Assurance Requirements Documents* (DOE-RL 1998) baseline requirements for laboratory quality systems. All of the analyses conducted to support this document shall be performed in accordance with these requirements.

All sampling events will be conducted using established quality assurance and quality control (QC) procedures. At a minimum, field blanks will be utilized for new samples. Analyses of the blanks will consist of IC, ICP/AES, and pH only (see Table 4-2). The requirements for tank sampling and sample analyses will be detailed in the tank sampling and analysis plans prepared prior to the sampling events.

A duplicate analysis will be required for each sample batch. Other laboratory quality control will be conducted according to the criteria outlined in Table 4-2. Table 4-2 also lists the suggested analytical methods to be used for each analysis.

Required detection limits are discussed in Section 4.3.

Format II reporting will be used to report the analytical data. A QA-reviewed letter report documenting the results of the analyses shall be issued, at minimum, to the Process Control point of contact. The laboratory shall issue the letter report within 60 days of the receipt of the samples at the laboratory. In addition to the analytical QC results, this letter report shall contain the laboratory worklists for hydroxide analyses, including titration curves. The Format II report is not required to contain any other supporting raw data.

Table 4-2. Quality Control Parameters.

Analytes	Suggested Analytical Technique	QC Acceptance Criteria		
		LCS % Recovery[(a)]	Spike % Recovery[(b)]	Duplicate RPD[(c)]
Al, Na	ICP/AES	80 - 120%	75 - 125%	≤20%
Cl^-, F^-, NO_3^-, NO_2^-, PO_4^{3-}, SO_4^{2-}	IC	80 - 120%	75 - 125%	≤20%
TIC	Silver catalyzed persulfate oxidation	80 - 120%	75 - 125%	≤20%
TOC	Solids – Silver catalyzed persulfate oxidation Liquids – Combustion furnace without acid sparging and subtraction of TIC values from TC values	80 - 120% (for TC)	75 - 125% (for TC)	≤20% (for TC)
OH^-	Potentiometric titration	80 - 120%	N/A	≤20%
pH	$[H^+]$	± 0.1 pH Units	N/A	N/A
Volume	Visually	N/A	N/A	N/A
Weight	Gravimetric	N/A	N/A	N/A
Wt% H_2O	Themogravimetric	N/A	N/A	≤20%
Specific gravity	Gravimetric	80 - 120%	N/A	≤20%

Notes:

IC	Ion Chromatography
ICP/AES	Inductively Coupled Plasma / Atomic Emission Spectroscopy
LCS	Laboratory Control Sample
N/A	Not applicable
RPD	Relative Percent Difference
TIC	Total inorganic carbon
TOC	Total organic carbon
Wt%	Weight percent

(a) LCS = Laboratory Control Sample. This sample is carried through the entire method. The accuracy of a method is usually expressed as the percent recovery of the LCS. The LCS is a matrix with known concentration of analytes processed with each preparation and analyses batch. It is expressed as percent recovery; i.e., the amount measured, divided by the known concentration, times 100.

(b) For some methods, the sample accuracy is expressed as the percent recovery of a matrix spike sample. It is expressed as percent recovery; i.e., the amount measured, less the amount in the sample, divided by the spike added, times 100. One matrix spike is performed per analytical batch. Samples are batched with similar matrices. For other analytes, the accuracy is determined based on use of serial dilutions.

(c) RPD = Relative Percent Difference between the samples. Sample precision is estimated by analyzing duplicates taken separately through preparation and analysis. Instrument analysis duplicates cannot be substituted except gamma energy analysis (GEA), which requires no preparation. Acceptable sample precision is usually <20% RPD if the sample result is at least 10 times the instrument detection limit.

RPD = ((absolute difference between primary and duplicate)/mean) x 100

4.3 DETECTION LIMITS

The current TSR chemistry limits are shown in Table 4-3. As can be seen in Table 4-3, it is possible to be within the chemistry limits with an OH^- concentration as low as 0.01 molar and a NO_2^- concentration as low as 0.011 molar. Because data reproducibility is commonly poor near the detection limits, the detection limits for OH^- and NO_2^- are set at an order of magnitude below these threshold values (i.e., 0.001 molar and 0.0011 molar, respectively). The other analyte included in the TSR chemistry limits (NO_3^-) has a threshold limit of 0.05 molar. This is the lowest value of NO_3^- that is required to be quantified. Therefore, the detection limit for NO_3^- is set at 0.005 molar. These detection limits are adequate to determine if the waste meets the TSR chemistry limit requirements.

In two of the scenarios (NO_3^- concentrations of 1.0 molar to 3.0 molar and greater than 3.0 molar) in Table 4-3, NO_2^- can have a concentration 0.0 and still meet the TSR chemistry limits. However, when NO_3^- undergoes radiolysis, it converts to NO_2^-. Therefore, it is unlikely that NO_2 would be less than 0.011 (the threshold limit shown above) when NO_3^- is 1.0 molar or greater. This is also indicated from existing tank waste analyses. For this reason, the threshold limit for NO_2^- is set at 0.011 for this DQO.

In the scenario where NO_3^- is less than or equal to 1.0 molar, the indication is that NO_3^- can be 0.0 molar. However, 0.0525 molar NO_3^- is the lowest value where the waste could potentially be out of compliance. In this scenario, any values of NO_3^- below 0.0525 molar would comply with the TSR chemistry limits.

The rest of the analytes in Table 4-1 do not have specific action levels. Therefore, the laboratory will use the least possible dilution to obtain the lowest practical detection limits for all analyses.

Table 4-3. 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

5.0 STUDY BOUNDARIES

This step in the DQO process defines the spatial and temporal boundaries for the required sampling and analyses needed to make the necessary decisions. The spatial boundaries define the physical area to which the decisions will apply and where the samples should be taken. The temporal boundaries describe the timeframe that the data will represent and when the samples should be taken. In addition, this portion of the DQO addresses any sampling constraints.

5.1 SPATIAL AND TEMPORAL BOUNDARIES

The spatial boundaries for the sampling and analyses covered by this DQO include the waste in all DSTs. The maximum interval between chemistry control sampling events for any DST is planned to be five years. If the empirical equations used to predict caustic depletion indicate a tank will be out of compliance sooner than five years, the tank will be sampled one year before the tank is predicted to be out of compliance (Fort et al. 2001). Section 8.0 further discusses the sampling planned for the chemistry control program.

Chemistry control is applied on a tank-specific basis. Therefore, this DQO will be applied to all DSTs as long as waste is stored in any DST or until the tank is taken out of service.

5.2 SAMPLING CONSTRAINTS

Sampling events for chemistry control will contend with the usual sampling constraints encountered in sampling tank waste (e.g., operational constraints, resource limitations on the number of samples, sample location restrictions, etc.). The sampling plan is discussed in Section 8.0.

6.0 DECISION RULES

The DQO process includes development of decision rules, which define the actions to be taken as a result of exceeding an action level. Decision rules require action levels and alternative actions that will be taken if the action levels are exceeded. For this DQO, action levels only exist for the first decision rule. Therefore, a decision rule will be developed only for decision statement 1.

If information needed to develop decision rules for decision statements 2 and 3 becomes available through the evaluation of additional data, the DQO will be revised to incorporate these decision rules. Although no decision rules will be developed for decision statements 2 and 3, the decision statements shown in Section 3.0 will be addressed through the application of the data collected during the chemistry control sampling events.

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. However, for this DQO confidence intervals were not established because the determination of whether the tank waste meets the TSR chemistry limits will be made on the results of one analysis for supernatant and one or two analyses for the solids (see Section 7.0).

For this DQO, the action levels for OH^-, NO_2^-, and NO_3^- are a set of interrelated conditions (see Table 4-3). All of the conditions that must be met under each scenario are considered the action level for that particular scenario.

In addition to determining if the waste meets the TSR chemistry limits at the time of sampling, the concentrations for OH^- will be utilized in the empirical equations used to predict when the waste will no longer meet the TSR chemistry limits. If the predictive equations indicate the tank waste will not meet the limits within two years, corrective action will be taken and the waste chemically adjusted. Figure 3-1 shows the logic flow of the activities and the decision points.

The decision rule for decision statement 1 is:

> If the analysis of the tank waste shows the concentrations of OH^-, NO_2^-, and NO_3^- do not meet the TSR chemistry limits (see Table 4-3), a recovery plan will be prepared and the waste chemistry adjusted; otherwise, future sampling will be scheduled or preventive actions will be taken (see Figure 3-1).

7.0 ERROR TOLERANCE

The uncertainty in the DQO process provides an evaluation of the probability of decision error based on an estimation of the mean, variance, and number of samples. The uncertainty evaluation is used to assess the accuracy and precision specified for sample collection and analysis, the level of decision error, and the number of samples required to meet a given decision error rate. However, as mentioned above, no confidence interval can be determined because only one analysis for supernatant and one or two analyses for the solids will be obtained from any one sampling event.

Decisions can be made on the analysis from one sample because the waste samples are taken at tank locations where, if the tank waste is out of compliance, the out-of-compliance condition is most likely to occur. These areas can be considered as worst-case locations for tank waste compliance.

While the supernatant in a tank is expected to be fairly well mixed because of thermal and density convection mechanisms, the supernatant will be sampled at the surface (see Section 8.0). The surface area is at the greatest risk of being out of compliance with the TSR chemistry limits, particularly if mixing does not occur, because of three reasons. The first reason is the adsorption of CO_2, a weak acid, at the surface of supernatant reduces the OH^- concentration. The second reason is adsorption of O_2, which depletes the NO_2^- concentration. The CO_2 and O_2 are adsorbed from the ventilation air. The third reason is if the supernatant is not well mixed, the material with the least density will be at the surface and will have fewer chemicals present and, therefore,

less OH^-, NO_2^-, and NO_3^-. This assumes the chemicals from the less dense areas to the more dense areas are proportional. For these reasons, a sample at the supernatant surface would be the area most likely to be out of compliance and provide a worst-case analysis.

The discussion in the preceding paragraph is supported by analytical data. Samples from multiple depths for tanks 241-AN-101, 241-AN-102, 241-AP-101, 241-AP-103, 241-AP-105, 241-AP-108, 241-AW-103, 241-AW-104, 241-SA-102 were analyzed for OH^-, NO_2^-, Na, and pH. In all of these tanks the lowest concentrations of OH^-, NO_2^-, Na, and the lowest pH were found in the supernatant surface sample (one inch below the supernatant surface for grab samples or first segment for core samples).

As discussed in Section 8.0, solid samples will be obtained from the bottom of the solids layer. The bottom of the solids is the area with the least influence from the supernatant and will be the area most likely different from the supernatant. In addition, if the solids are greater than 60 inches deep, a sample will be taken just below the solids supernatant contact. This will provide an estimation of the range of waste compliance through the solids and provide better information to determine caustic consumption.

8.0 SAMPLING DESIGN

As discussed in Section 3.0, sampling and analyses for tank waste chemistry control will be conducted under two situations: initial sampling and sampling after waste chemistry adjustments are made. Both initial sampling and sampling after waste chemistry adjustments are made will be conducted according to Table 8-1 and are consistent with RPP-7795, Rev. 1 (Fort et al. 2001).

As shown in Figure 3-1, when an initial sampling event is conducted, both the supernatant and solids will be sampled and analyzed to determine if the waste in a tank complies with the TSR chemistry limits. Sampling after chemical adjustments are made will depend on the type of waste (solids or supernatant) found to be out compliance in the initial sampling. If only the supernatant was found to be out of compliance, subsequent sampling events would only sample the supernatant. However, if only the solids were found to be out of compliance or both the solids and supernatant were out of compliance, subsequent sampling events would sample both the solids and supernatant.

Table 8-1. Sampling Criteria

Solids Depth	Type of Sampling	Number and Location of Samples
< 25 inches	One grab sampling event from one riser.	One sample (consisting of two 125 ml bottles) at the surface of the supernatant is required. One bottle will be analyzed, the second archived.
25 to 60 inches	One core sampling event from one riser.	One sample (segment) as close to the supernatant surface as possible and one sample (segment) at the bottom of the solids.
> 60 inches	One core sampling event from one riser.	One sample (segment) as close to the supernatant surface as possible and two samples (segments) in the solids. One solids sample (segment) approximately three inches below the solids surface and one solids sample (segment) at the bottom of the solids.

The 25-inch minimum depth for a core is based on obtaining a full segment (19 inches) with a 3-inch safety margin at the bottom of the tank and a 3-inch contingency at the top of the segment to reduce the chance of commingling with the supernatant.

As shown in Figure 3-1, sampling of the supernatant and solids will occur at different times after the chemistry of out-of-compliance waste is adjusted by adding chemicals, adding waste that is in compliance, mixing the waste (naturally or mechanically), or retrieving the waste.

When the initial sampling and analyses show that only the supernatant is out of compliance, a supernatant sample will be taken (Table 8-1, row 1) 30 to 60 days after the chemistry adjustment, preferably, from a riser furthest from the riser used for the chemical adjustment. If the supernatant is still out of compliance or the adjustment is not as predicted, the existing recovery plan will be reviewed to determine if it covers planned recovery actions or should be revised to add additional recovery actions and the waste adjusted accordingly.

When the initial sampling and analyses show that only the solids or both the solids and supernatant are out of compliance, supernatant samples (Table 8-1, row 1) are obtained 30 to 60 days after adjustments as well as core samples (Table 8-1, row 2 or 3), in 12 and 18 months. If these samples indicate the waste is still out of compliance, the waste (supernatant and solids) will be sampled again (Table 8-1, row1 and row 2 or 3) after additional chemical adjustment. The timing for this second sampling event will be determined from the results of the first sampling event after adjustment and based on the planned recovery actions. The recovery plan describes all actions required to bring a tank back into compliance with the TSR chemistry limits.

9.0 REFERENCES

Banning, D. L., 2001, *Data Quality Objectives for Sampling and Analyses*, HNF-IP-0842, Rev. 1b, Vol. IV, Section 4.16, CH2M HLL Hanford Group, Inc., Richland, Washington.

CHG, 2001, "Chemistry Control Program," *Tank Farms Technical Safety Requirements*, Section 5.15, HNF-SD-WM-TSR-006, Rev. 2B, CH2M HILL Hanford Group, Inc., Richland, Washington.

Clark, G. A., 2001, *222-S Laboratory Quality Assurance Plan*, HNF-SD-CP-QAPP-016, Rev. 5, Fluor Hanford, Inc., Richland, Washington.

Conway, J. T., 2000, Untitled, (letter to C. L. Huntoon, U.S. Department of Energy, August 29), Defense Nuclear Facilities Safety Board, Washington, D.C.

DOE-RL, 1998, *Hanford Analytical Services Quality Assurance Requirements Documents*, DOE/RL-96-68, Rev. 2, U.S. Department of Energy, Richland Operations Office, Richland, Washington.

EPA, 1994, *Guidance for the Data Quality Objectives Process*, EPA QA/G-4, U.S. Environmental Protection Agency Quality Assurance Management Staff, Washington, D.C.

Fort, L. A., D. A. Reynolds, K. G. Carothers, M. A. Knight, and M. J. Klem, 2001, *Technical Basis for Chemistry Control Program*, RPP-7795, Rev. 1, CH2M HILL Hanford Group, Inc., Richland, Washington.

Jo, J, R. P. Anantatmula, C. P. Shaw, H. Berman, D. M. Ogden, and M. J. Thurgood, 2001, *Technical Basis for Caustic Additions To Tanks 241-AY-102, 241-AY-101, and 241-AN-102*, RPP-8173, Rev. 0, CH2M HILL Hanford Group, Inc., Richland, Washington.

Stewart, C. W., 2001, *Expert Panel Recommendations for Hanford Double-Shell Tank Life Extension*, PNNL-13571, Pacific Northwest National Laboratory, Richland, Washington.