Double-Shell Tanks Chemistry Control Data Quality Objectives

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Abstract: This document describes the data quality requirements needed to support the sampling and analyses required for corrosion mitigation of the double-shell tanks. The type, quantity, and quality of the data needed to make the decisions required to maintain the waste chemistry within the OSD requirements are specified.

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LIST OF TERMS

Abbreviations and Acronyms

CPP	cyclic potentiodynamic polarization
DQO	data quality objective
DST	double-shell tank
LCS	Laboratory Control Sample
MS	Matrix Spike
N/A	Not applicable
OSD	operating specification document
PLM	polarized light microscopy
POC	Point of contact
QA	quality assurance
QC	quality control
RPD	Relative Percent Difference
SEM	Scanning Electron Microscopy
SMD	Sauter Mean Diameter
SST	single-shell tank
TIC	total inorganic carbon
TOC	total organic carbon
XRD	X-ray diffraction

Units

M	molarity, moles per liter
wt%	weight percent
%	Percent
°F	degrees Fahrenheit
T	Temperature

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 and other supplemental treatment systems are ready to receive and process the waste. Waste from the older single-shell tanks (SST) 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 treatment processes. 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 OSD-T-151-00007, *Operating Specifications for the Double-Shell Storage Tanks*. In order to control the DST waste chemistry, the Corrosion Mitigation Program requires analyses of 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 TFC-ENG-CHEM-C-16, *Data Quality Objectives for Sampling and Analysis*, and the U.S. Environmental Protection Agency EPA QA/G4, *Guidance on Systematic Planning Using the Data Quality Objectives Process*, with some modifications to accommodate project or tank specific requirements and constraints.

Additional information on the Corrosion Mitigation Program can be found in RPP-7795, *Technical Basis for Chemistry Control Program*.

2.0 PROBLEM STATEMENT

As mentioned above, waste chemistry limits have been established to mitigate corrosion in DSTs. These limits are for the hydroxide ion (OH^-), pH, nitrite ion (NO_2^-), and nitrate ion (NO_3^-) and are found in OSD-T-151-00007. The concentrations of these analytes change over time, and when the Corrosion Mitigation Program was established in March 2001 it was known for some time that four of the DSTs did not meet the specified operating specification document (OSD) limits. An August 29, 2000, Defense Nuclear Facilities Safety Board letter (attached to the referenced letter 0004843/00-OSD-104) stated the practice of allowing tanks to remain outside the corrosion control specifications is inappropriate. The letter also indicated if the current specifications are too conservative, they should be changed and any alternative limits should be justified and enforced. Therefore, the overall objective of the Corrosion Mitigation Program related to tank chemistry control is to maintain the waste chemistry of the DSTs within the OSD limits. With this objective in mind, the problem statement can be written as follows:

> Protect the inner wall of 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 (supernate and solids) meet OSD waste chemistry limits?
2. Are additional waste chemistry criteria necessary?
3. How do the chemical and physical characteristics of waste components affect the OSD chemistry limit components (OH^-, pH, NO_2^-, and NO_3^-)?

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 (decision statement 1 shown below). However, the second and third study questions do not have associated alternative actions, and conventional decision statements cannot be developed (decision statements 2 and 3 shown below). 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 for the second and third decision statements will be made from the principles developed from the sampling data. If the situation changes for the second and third decision statements, this DQO will be revised to address the changes. The decision statements are listed below:

1. Determine whether the tank waste (supernate and solids) meets the OSD waste chemistry limits and requires no action or requires chemical adjustment followed by the identification of future sampling.
2. Determine if additional waste chemistry criteria are needed.
3. Determine how the chemical and physical characteristics of certain waste components affect the OSD chemistry limit components (OH^-, pH, NO_2^-, and NO_3^-).

To maintain the waste within the OSD limits and address the decision statements listed above, sampling and analyses is required in three situations. Initial sampling takes place when a tank has never been sampled or sampled according to the RPP-7795 schedule for tanks that have been in compliance with OSD limits. The analysis is required to determine if a tank still meets the OSD limits. Chemical adjustment sampling and analyses is required after tank waste chemistry adjustments are made to return non-compliant waste to OSD limits. For the purposes of this DQO, waste chemistry adjustments could be accomplished by adding chemicals to a tank, adding waste, mixing the waste (naturally or mechanically), or retrieving the waste. In addition to initial and chemical adjustment sampling, process control sampling is required during waste retrieval from SST to DSTs. In this case, samples of the waste in the receiving DST are required when 50 percent (%) of the SST has been retrieved and when 100% of the SST has been retrieved. In some instances the 50% sample can be eliminated if the waste volume transferred from the SST

is considered too small to warrant a sample of the DST waste. The decision will be made as described in RPP-7795.

Figure 3-1 shows the logic flow chart for the activities and decisions made when tank waste is sampled for initial and chemical adjustment sampling activities. Figure 3-2 shows the logic flow chart for the activities and decisions made for process control sampling. The sampling activities are discussed in Section 8.0.

Figure 3-1. Chemistry Control Initial and Chemistry Adjustment Sampling Logic Flow Chart

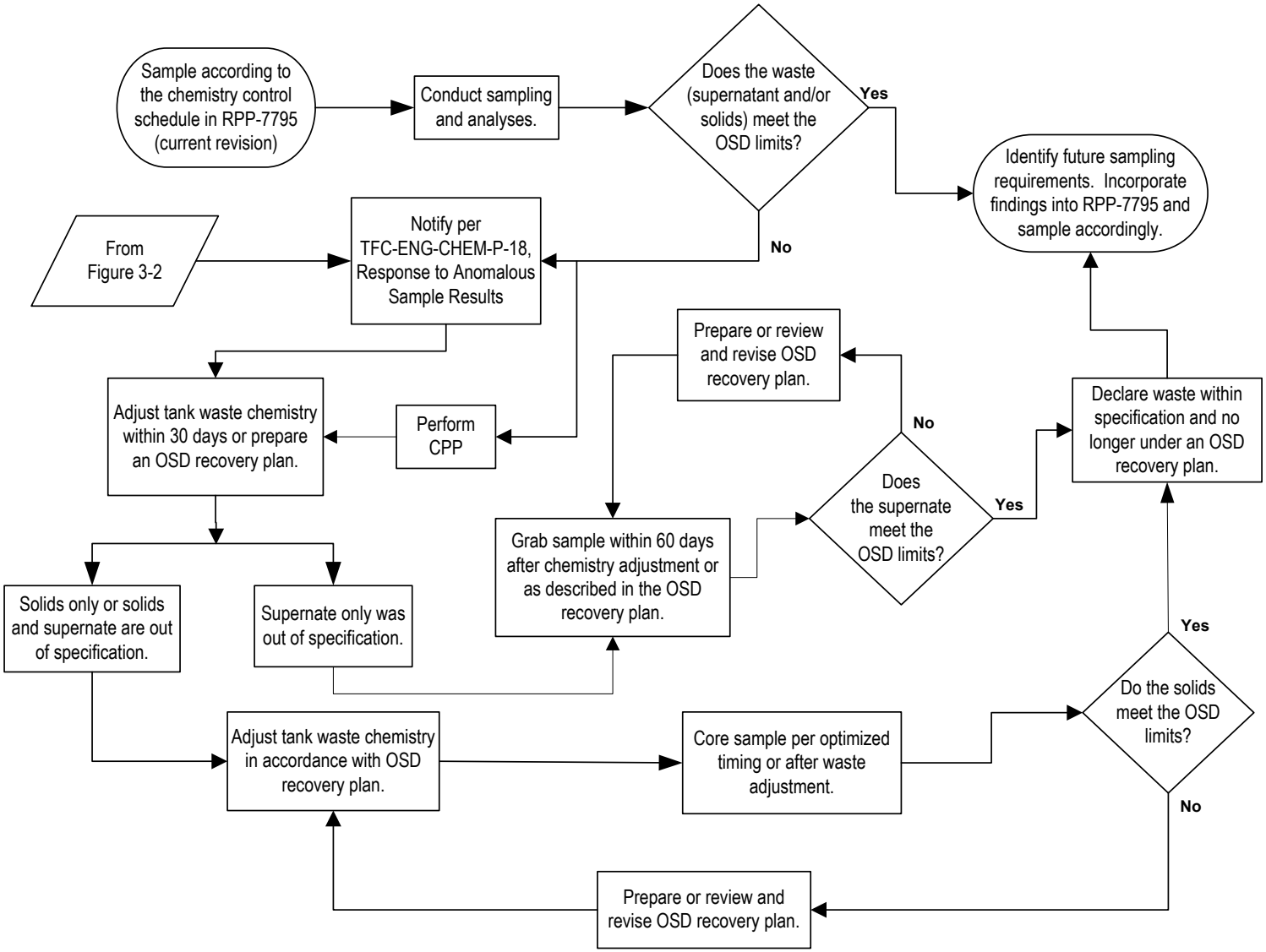
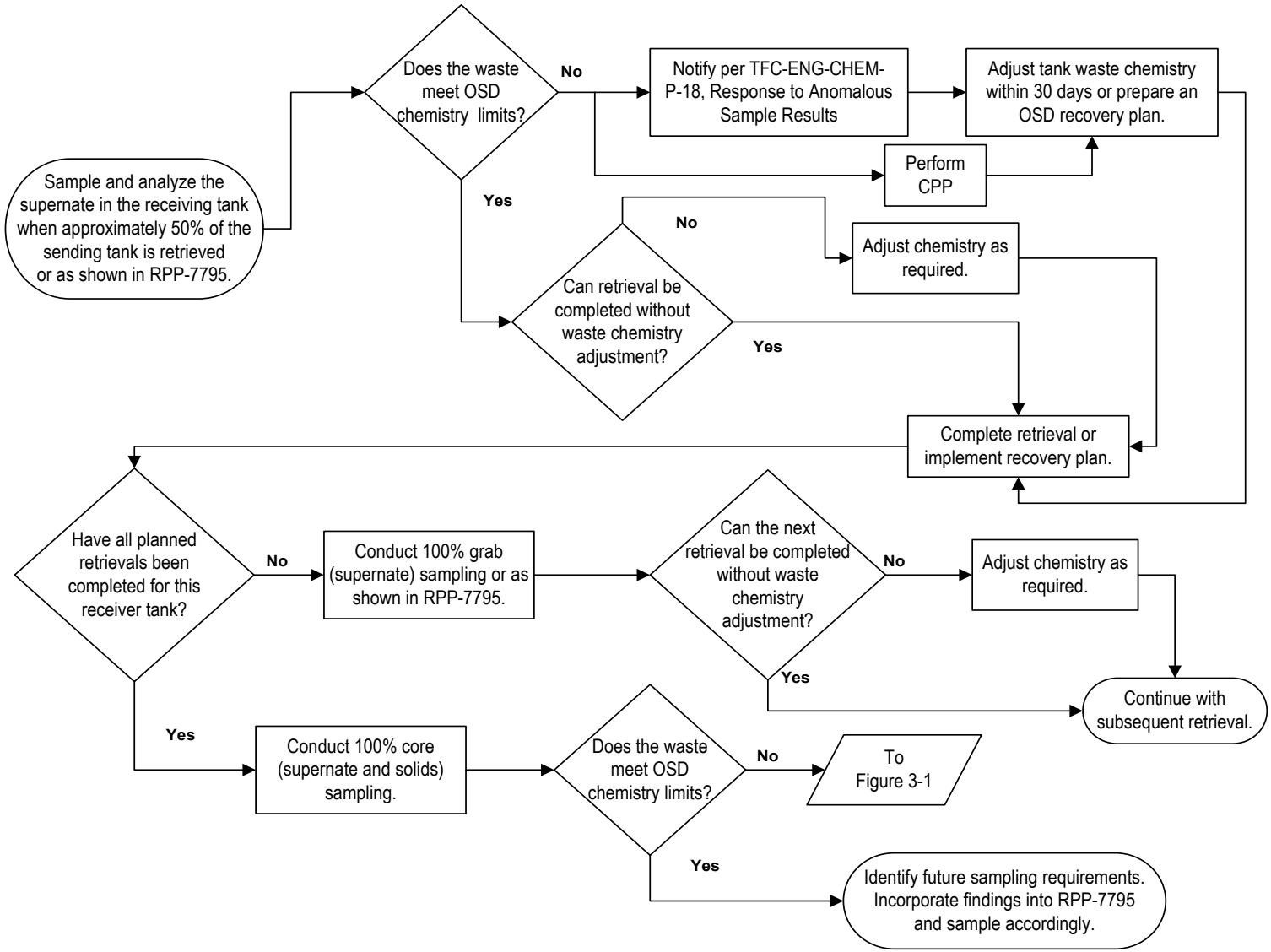


Figure 3-2. Chemistry Control Process Control Sampling Logic Flow Chart



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 supernate, centrifuged and uncentrifuged 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, after chemical adjustment, or process control) 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	Supernate, interstitial (centrifuged) liquid, and centrifuged solids. Each core segment or grab.
NO_2^-	1, 2, and 3	Supernate, interstitial (centrifuged) liquid, and centrifuged solids. Each core segment or grab.
OH^-	1, 2, and 3	Supernate and interstitial (centrifuged) liquid. Each core segment or grab.
pH	1, 2, and 3	Supernate and interstitial (centrifuged) liquid. Each core segment or grab.
Na^+	See comment column.	Needed to evaluate pH data. Supernate and interstitial (centrifuged) liquid. Each core segment or grab.
Cl^-	2	Supernate, interstitial (centrifuged) liquid, and centrifuged solids. Each core segment or grab.
F^-	2	Supernate, interstitial (centrifuged) liquid, and centrifuged solids. Each core segment or grab.
SO_4^{2-}	2	Supernate, interstitial (centrifuged) liquid, and centrifuged solids. Each core segment or grab.
PO_4^{3-}	2	Supernate, interstitial (centrifuged) liquid, and centrifuged solids. Each core segment or grab.
Al	3	Supernate, interstitial (centrifuged) liquid, and centrifuged solids. Each core segment or grab.
TIC	3	Supernate, interstitial (centrifuged) liquid, and centrifuged solids. Each core segment or grab.
TOC	3	Supernate, interstitial (centrifuged) liquid, and centrifuged solids. Each core segment or grab. Analyzed by two methods (furnace combustion and/or persulfate ultra-violet or heated persulfate oxidation).
$\%H_2O$	3	Supernate, interstitial (centrifuged) liquid, and centrifuged solids. Each core segment or grab.
Density	3	Supernate and interstitial (centrifuged) liquid. Each core segment or grab. Needed to determine supernatant layering.
Weight	3	Decanted (settled) solids, interstitial (centrifuged) liquid and centrifuged solids. Each core segment.
Volume	3	Decanted (settled) solids, interstitial (centrifuged) liquid, and centrifuged solids. Each core segment.
Particle Size	3	Solids when first extruded. The test may be conducted when particle size distribution data are unavailable for the tank waste and the waste does not meet OSD chemistry limits or is near the limits. A test plan will be prepared to control the tests.

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
SMD	3	Each core segment or initial grab. Centrifuged and uncentrifuged solids. Core solids when first extruded and prior to any homogenization, centrifugation, etc. This test is conducted when particle diameter data are required to support modeling of waste component physical characteristics. A test plan will be prepared to control the tests.
PLM, SEM, XRD	3	Each core segment and each initial grab when solids are apparent. Centrifuged and uncentrifuged solids. These tests will be conducted when mineralogy data are required to support modeling and will be performed by technical procedures.
Viscosity	3	Supernate. The test may be conducted when viscosity data are unavailable for the tank waste. A test plan will be prepared to control the tests.
Caustic Demand Test	3	Supernate, centrifuged solids, and uncentrifuged solids. The test may be conducted when analyses show the waste does not meet OSD chemistry limits or is near the limits. A test plan will be prepared to control the tests.
Corrosion Potential	2	Supernate, solids, and interstitial (centrifuged) liquid. The test is commonly conducted when waste analyses show the waste does not meet OSD chemistry limits or is near the limits. A test plan will be prepared to control the tests.
Tank Supernate and Solids Level (Volume)	3	From existing data.
Tank Vapor Space, Supernate, and Solids temperatures	3	From existing data.
Waste heat load	3	From existing data or calculated energy balance.
Ventilation Rate	3	From existing data.

Notes:

PLM = polarized light microscopy
SEM = scanning electron microscopy
SMD = Sauter Mean Diameter
TIC = Total inorganic carbon
TOC = Total organic carbon
XRD = X-ray diffraction

As discussed in Section 3.0, this DQO covers data collection under three situations (initial, chemical adjustment, or process control). The analytes shown in Table 4-1, which address decision statement 1, are needed to determine if the waste in a tank meets the OSD chemistry limit requirements shown in Tables 4-2 and 4-3. The sampling scheme for each situation is discussed in Section 8.0 and shown in Figures 3-1 and 3-2.

Free OH^- concentration is normally determined by an approved 222-S Laboratory analytical titration method. However, titration results at low OH^- concentrations [<0.03 molar (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 OH^- concentration is normally determined by the analytical titration method. Sodium and buffer [aluminum, phosphate, TOC, and carbonate] concentrations as well as the shape and quality of the potentiometric titration curve are used in the evaluation of OH^- and pH data at low OH^- concentrations.

The analytes in Table 4-1 that address decision statement 2 are not part of the OSD chemistry limits, but they are known to influence corrosion rates. These analytes are collected to help determine if additional waste chemistry criteria are needed.

The data requested in Table 4-1, which address decision statement 3, apply when determining how certain waste components and parameters (e.g., waste physical characteristics) affect OH^-, NO_2^-, and NO_3^- waste concentrations. Included are data that allow predictions of when waste in a particular tank will no longer meet the OSD chemistry limits (RPP-7795). SMD testing and solids mineralogy (SEM, PLM, and XRD) shall be conducted during initial grab sampling when solids are readily visible (e.g., greater than 10% solids) and for all core sampling. SMD supports modeling of waste component physical characteristics and will be conducted by test plan. Solids mineralogy testing supports modeling of interstitial liquid porous flow and will be conducted using laboratory technical procedures.

Caustic demand tests (see Table 4-1) may be conducted on the supernate and solid wastes (normally not centrifuged) that are outside the OSD chemistry limits. Some constituents (e.g., Al, PO_4^{3-} and organics) tend to consume more hydroxide. The caustic demand test provides a better understanding of constituent interactions with the caustic and helps determine the amount of caustic to be added to waste not in compliance with the OSD chemistry limits. A test plan will be prepared to direct any caustic demand tests.

The corrosion potential test is conducted by making cyclic potentiodynamic polarization (CPP) measurements on a carbon steel coupon immersed in supernate, saltcake, sludge, or interstitial liquid obtained from centrifuged solid waste. Testing actual waste under conditions that, to the extent practical, reflect those in the tank at the location of the sampling gives achievable, representative results. Electrochemical corrosion measurements, which utilize the electrochemical nature of metallic corrosion, are used to determine corrosion behavior of metal-electrolyte systems and estimate corrosion resistance (Tait 1994). The information resulting from the CPP test can be used to characterize corrosion behavior, i.e., estimate general corrosion rates, investigate the tendency towards localized corrosion of a material in a given environment, and identify electrochemical potential regions where susceptibility to stress corrosion cracking may occur (Stansbury and Buchanan 2000). Corrosion potential tests shall be conducted according to applicable technical procedures.

Table 4-2. OSD Waste Chemistry Limits Except For Interstitial Liquids In Tanks 241-AN-102, 241-AN-106, 141-AN-107, 241-AY-101, and 241-AY-102

For $[NO_3^-]$ Range	Variable	For Waste Temperature Range		
		T < 167 ºF	167 ºF ≤ T ≤ 212 ºF	T > 212 ºF
$[NO_3^-] \leq 1.0$ 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 ≤ $[NO_2^-]$ ≤ 5.5 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

Notes:

ºF = degrees Fahrenheit

T = temperature

Table 4-3. OSD Waste Chemistry Limits For Interstitial Liquids In Tanks 241-AN-102, 241-AN-106, 241-AN-107, 241-AY-101, and 241-AY-102

Temperature	Variable	Limit
≤122 degrees Fahrenheit	$[NO_2^-]/[NO_3^-]$	≥ 0.32[a]
	pH	≥ 10
>122 degrees Fahrenheit	Limits in Table 4-2[b]	

Notes:

[a]The NO_2^-/ NO_3^- limit does not apply to tank 241-AY-102.

[b]241-AY-102 – Table 4-3 chemistry limits apply for ≤ 170 degrees Fahrenheit; otherwise, Table 4-2 chemistry limits apply.

4.2 QUALITY CONTROL

ATL-MP-1011, *ATL Quality Assurance Project Plan for 222-S Laboratory*, and ATS-MP-1032, *222-S Laboratory Quality Assurance Project Plan*, specify the requirements to ensure the quality of the analyses conducted at the 222-S Laboratory. The requirements shall meet DOE/RL-96-68, *Hanford Analytical Services Quality Assurance Requirements Documents*, 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 (QA) and quality control (QC) procedures. At a minimum, field blanks will be utilized for new samples. Analyses of the field blanks will consist of ion chromatography for anions, inductively coupled plasma/atomic emission spectroscopy for metals, and pH only (see Table 4-4). 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 is required for each preparation batch. In addition, a duplicate analysis of the supernatant surface sample is required and satisfies the requirement for a duplicate analysis for that particular preparation batch. Other laboratory QC will be conducted according to the criteria outlined in Table 4-4. Table 4-4 identifies project-specific QC requirements. Where project-specific QC requirements are more stringent than requirements in the laboratory QA program, the tank sampling and analysis plan will ensure that the project-specific criteria are met.

Required detection limits are discussed in Section 4.3.

A technical report documenting the results of all the analyses and QC data shall be released in accordance with TFC-ENG-DESIGN-C-25, *Technical Document Control*, with the assistance of the WRPS Integration Control Organization. The report will be a format VI and will require a QA review of the final report. The Laboratory shall append any characterization change notice that changes the tank sampling and analysis plan to the data report. Notifications will be made per TFC-ENG-CHEM-P-18, “Response to Anomalous Sample Results”.

The Format VI report shall be issued within 60 days of the receipt of the samples at the laboratory loading dock or, for non-compliant tanks, as required by the governing tank sampling and analysis plan, or as specified in an approved OSD recovery action plan. The raw data, sample photographs, and extrusion video shall be accessible to the program in accordance with the laboratory’s Records Inventory and Disposition Schedule.

A Format II report shall be provided consisting of an interim report for selected analytical results. This report will assist in determining if the tank is out of specification in a timely manner and will guide the development of test plans. The deliverables will consist of data summary tables from the Laboratory Information Management System which are transmitted to the chemistry control point of contact and the tank sampling and analysis plan author via electronic mail or facsimile. Interim QA-reviewed results for pH, OH^-, density, NO_2^-, and NO_3^- shall be transmitted within seven working days after receipt of the last sample at the 222-S

Laboratory. An Excel®[1] spreadsheet containing preliminary data results shall be provided to the Corrosion Mitigation technical point of contact (POC) to more timely determine if the tank is out of specification.

Results for particle size distribution, SMD, viscosity measurements, caustic demand test, solids mineralogy testing (PLM, SEM, and XRD) and corrosion potential tests are documented as specified in a controlling test plan or applicable technical procedures.

Table 4-4. Quality Control Parameters

Analytes	QC Acceptance Criteria		
	LCS % Recovery[(a)]	MS % Recovery[(b)]	Duplicate RPD[(c)]
Al, Na^+	80 – 120%	75 – 125%	≤20%
Cl^-, F^-, PO_4^{3-}, SO_4^{2-}	80 – 120%	75 – 125%	≤20%
NO_3^-, NO_2^-	80 – 115%	75 – 125%	≤10%[(d)]
TIC	80 – 120%	75 – 125%	≤20%
TOC	80 – 120%	75 – 125%	≤20%
OH^-	90 – 110%	75 – 125%	≤5%[(d)]
pH	± 0.1 pH Units	N/A	N/A
Wt% H_2O	80 – 120%	N/A	≤20%
Density	95 – 105%	N/A	≤1%[(d)]

Notes:
LCS = laboratory control sample
MS = matrix spike
N/A = not applicable
RPD = relative percent difference

(a) LCS: This sample is generally carried through the preparation and analytical process. The accuracy of a method is usually expressed as the percent recovery of the LCS. The LCS contains a known concentration of analytes that are processed with each preparation and analyses batch. The LCS is expressed as a percent recovery; i.e., the amount measured, divided by the known concentration, times 100.

(b) MS: This sample is generally carried through the preparation and analytical process. Since it is performed on an actual field sample it can be used to evaluate both accuracy and sample matrix effect. It is expressed as the percent recovery of a spiked analyte, 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.

(c) RPD: The RPD is the difference between the sample and its analytical duplicate. The sample duplicate can be used to assess method precision. Since it is performed using an actual field sample, the sample matrix homogeneity can also be assessed. Duplicates are taken through the same preparation and analysis as the sample. Acceptable sample precision is usually ≤20% RPD. .If the sample result is below the quantitation limit, or estimated quantitation limit, the precision criterion does not apply.

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

(d) If the RPD or LCS requirements are not met, the laboratory will make only one rerun. If the RPD or LCS is not met after the second run, the laboratory will contact the tank sampling and analysis plan author. This information will be reported and discussed in the data report.

[1] Excel® is a registered trademark of the Microsoft Corporation, Redmond, Washington.

4.3 DETECTION LIMITS

The current OSD chemistry limits are shown in Table 4-2 and 4-3. As can be seen in Table 4-2, waste remains within the chemistry limits at an OH^- concentration as low as 0.01 molar and a NO_2^- concentration as low as 0.011 molar. Data reproducibility is commonly poor near the detection limits; therefore, the detection limits for OH^- and NO_2^- are set an order of magnitude below the threshold values (i.e., 0.001 molar $OH^-$and 0.0011 molar NO_2^-). The hydroxide detection limit of 0.001 M. Hydroxide concentration will be measured using both potentiometric titration and pH meter. The specified hydroxide detection limit cannot be achieved by potentiometric titration. When hydroxide concentrations are near that level, pH results will be used.

The threshold limit for NO_3^-, the other analyte required to determine OSD chemistry limits, is set at 0.05 molar. This is determined from the NO_3^- to total inhibitor (OH^- + NO_2^-) ratio requirement for the lowest in-specification OH^- and NO_2^- concentrations. For this case, the NO_3^- has to be less than 0.0525 molar in order for the ratio to be less than 2.5. Using a concentration of 0.05 molar, the ratio will be below 2.5; therefore, 0.05 molar would be the lowest NO_3^- concentration required to be quantified. As a result, the detection limit for NO_3^- is set an order of magnitude lower, at 0.005 molar. These detection limits are adequate to determine if the waste meets the OSD 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 4-2, NO_2^- can be negligible or not present at all and the waste will still meet the OSD 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 molar (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 molar.

In the scenario where NO_3^- is less than or equal to 1.0 molar, the indication is that NO_3^- can be negligible or not present at all. However, 0.0525 molar NO_3^- is the lowest value at which the waste could potentially be out of compliance. In this scenario, any values of NO_3^- below 0.0525 molar would comply with the OSD 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.

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 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.

As discussed in Section 3.0, there are three sampling situations that require different sampling times and frequencies. The first, initial sampling, requires tanks to be sampled when a tank has never been sampled or sampled according to the RPP-7795 schedule for tanks that have been in compliance with OSD limits and to determine if that tank still meets the OSD limits. The second, chemistry adjustment sampling, requires samples to be taken within 60 days of making a chemistry adjustment intended to bring a tank back into compliance with OSD chemistry limits or as specified in the OSD recovery plan. The third, process control sampling, requires sampling to be conducted in a DST when 50% of an SST has been retrieved into the DST (except in some instances when the waste volume transferred from the SST is considered too small to warrant sampling of the DST waste, see Section 8.0) and when 100% of the SST has been retrieved or as specified in RPP-7795.

Waste chemistry control is tank specific; 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 the Corrosion Mitigation Program 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 analytical data collected from the chemistry control samples.

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 limit.

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 each analysis is compared to the OSD chemistry limit at the sample location (depth in the tank waste). Therefore, one data point at each location is used to determine whether the tank waste meets the OSD chemistry limits. If any of the analysis does not meet the chemistry limits, the tank is determined to be out of specification with the OSD limits. Multiple supernatant samples are used to determine if there is stratification in the supernatant waste and how well and how quickly added chemicals are dispersing after chemical adjustment.

For this DQO, the action levels for OH^-, NO_2^-, NO_3^- and pH are a set of interrelated conditions (see Tables 4-2 and 4-3). All of the conditions that must be met under each scenario are considered the action level for that particular scenario.

Two decision rules are required to address decision statement 1 for the activities and decisions for initial sampling and chemistry adjustment sampling shown in Figure 3-1. The decision rules shown below are sequential for the initial sampling and chemistry adjustment sampling.

1. If the analysis from initial sampling event shows the tank waste does not meet the OSD chemistry limits (see Tables 4-2 and 4-3), then declare the tank waste out of specification and adjust the waste chemistry within 30 days or issue an approved OSD recovery plan; otherwise, schedule future initial sampling.
2. If the analysis after chemistry adjustment sampling shows the tank waste does not meet the OSD chemistry limits (see Tables 4-2 and 4-3), then adjust the tank waste and plan for additional chemistry adjustment sampling; otherwise, schedule future initial sampling.

As stated in Section 3.0 and shown in Figure 3-2, process control sampling is conducted in the receiving DST when 50% of the SST has been retrieved and/or (see Section 8.0) when 100% of the SST has been retrieved. Decision rule 3 (shown below) addresses the 50 % process control sampling while decision rule 4 (shown below) addresses the 100% process control sampling. Decision rule 4a is used when no additional retrievals are planned for the DST being sampled, while decision rule 4b is used when additional retrievals into the DST are expected.

3. If the analysis of the 50% process control sample (see Figure 3-2) meets the OSD limits (see Tables 4-2 and 4-3) and confirms retrieval can be completed without chemistry adjustment, then continue retrieval; otherwise, adjust tank waste chemistry before completing retrieval.

4a. If the analysis of the 100% process control sample (see Figure 3-2) meets the OSD limits (see Tables 4-2 and 4-3) and no additional retrievals are expected, then schedule future initial sampling; otherwise, adjust tank waste chemistry and plan for chemistry adjustment sampling (see Figure 3-1).

4b. If the analysis of the 100% process control sample (see Figure 3-2) meets the OSD limits (see Tables 4-2 and 4-3) and additional retrievals are expected, then continue with subsequent retrievals (see Figure 3-2) if OSD limits can be met without adjusting tank waste chemistry; otherwise, adjust tank waste chemistry and plan for subsequent retrievals (see Figure 3-2).

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, confidence intervals are not determined because each analysis is compared to the OSD chemistry limit at the sample location (depth in the tank waste). Therefore, one data point at each location is used to determine whether the tank waste meets the OSD chemistry limits. If one analysis does not meet the chemistry limits, the tank is determined to be out of specification with the OSD limits. The multiple supernatant samples are used to determine if there is stratification in the supernatant waste and how well and how quickly added chemicals are dispersing after adjustment. In these cases, the analytical data from each individual sample is used independently.

8.0 SAMPLING DESIGN

As discussed in Section 3.0, sampling and analyses for tank waste chemistry control will be conducted under three situations: initial sampling, chemistry adjustment sampling, and process control sampling during retrieval. These sampling events are described in Table 8-1 and 8-2.

As shown in Figure 3-1 and Table 8-1, when an initial sampling event is conducted, the supernate and possibly the solids will be sampled and analyzed to determine if the waste in a tank complies with the OSD chemistry limits. Where only the supernate requires initial sampling, the solids will not have to be sampled. Sampling after chemical adjustments are made will depend on the type of waste (solids or supernate) found to be out-of-specification by the initial sampling. If the supernate was found to be out-of-specification, subsequent sampling events would sample the supernate. However, if the solids were found to be out-of-specification subsequent sampling events would be required after the tank was chemically adjusted to mitigate the out-of-specification condition. In this case both the solids and supernate would be sampled.

Table 8-1. Sampling Design For Initial and Chemistry Adjustment Sampling

Solids Depth	Initial Sampling Events, Number and Location of Samples[a]	Chemical Adjustment Sampling, Number and Location of Samples[a]
≤ 22 inches[b]	**Grab sampling**: Sampling will depend on the depth of the supernate. **Supernate less than 40 inches** – Two samples plus a duplicate: surface and approximately 10 inches above the liquid solid interface. **Supernate between 40 inches and 100 inches** – Four samples in the supernate plus a duplicate. The first sample at the supernatant surface, the second sample 10 inches below the surface and the fourth sample approximately 10 inches above the bottom of the supernate. The third sample will be equally spaced between the second and fourth sample. **Supernate greater than 100 inches** – Minimum of four samples equally spaced in the supernatant plus a duplicate. The first sample at the supernatant surface and the fourth sample approximately 10 inches above the bottom of the supernatant. Samples should be approximately 50 inches or less apart when waste layering in the supernatant is expected.	**Grab sampling:** Grab sampling within 60 days after a chemical adjustment. A minimum of three samples equally spaced in the supernate. The first sample at the supernatant surface and the third sample approximately 10 inches above the bottom of the supernate.
> 22 inches	**Core sampling**: Supernate samples obtained using the core sampler at the locations as described above for grab sampling; however, supernatant samples also may be obtained by grab sampling. A full depth core will be obtained for the solids. The first segment will start approximately 3 inches below the supernate solid interface. Additional core segments will be specified as described in the text, below.	**Grab sampling:** If supernate only was out of specification. Grab sampling within 60 days after a chemical adjustment: A minimum of three samples equally spaced in the supernate will be collected. The first sample at the supernatant surface and the third one approximately 10 inches above the bottom of the supernate. **Core sampling**: If only solids or supernate and solids were out of specification. Obtain a full depth solids core sample following completion of mitigating actions. The first segment will start approximately 3 inches below the supernate solid interface. Analyze each half segment at the bottom of the solids. Obtain supernatant samples using the core sampler at the locations discussed above; however, supernatant samples also may be obtained by grab sampling. Supernatant segments may be collected by the "syringe" method if layering is suspected and a sample is needed from a specific elevation. Additional segments may be required to obtain sufficient solids for testing as described in the text, below.

Notes:

[a] Additional samples may be requested by the Corrosion Mitigation technical POC to determine layering composition when waste stratification is expected with the number and location of additional samples based on the suspected stratification.

[b] As described below, core sampling of solids at less than 22 inches to obtain a partial segment may be requested.

The 22-inch minimum solids depth to obtain a core segment (Table 8-1) is based on obtaining a full segment (19 inches) with an approximate 3-inch contingency at the top of the segment to reduce the chance of commingling with the supernate. Core sampling of less than 22 inches of solids may be requested by the Corrosion Mitigation technical POC under special circumstances and where the partial segment will provide sufficient solids for testing.

Core samples may be re-taken at locations of interest within the solids layer in order to provide sufficient solids for testing. When samples are re-taken, care is required to prevent co-mingling of supernate and drill string fluids with the sludge to be sampled. Typically the drill string shall be raised to the starting elevation of the next segment to be re-taken and held in place for several hours prior to unseating the sampler to allow the waste to re-fill the cavity created when the drill string is raised. For chemical adjustment core sampling, samples may be re-taken at locations of interest within the solids layer in order to provide sufficient solids for testing. The retaken sample may consist of a full 19 inch push, a "syringe" sample from a given location, or a series of small pushes traversing the area of interest. When core sampling liquids, the drill string can collect "syringe" samples at closely spaced intervals near the waste surface to identify layering.

As shown in Figure 3-1, sampling of the supernate and solids can occur at different times after the chemistry of non-compliant waste is chemically adjusted.

When the initial sampling shows that only the supernate is out-of-specification sampling will be conducted as shown in Table 8-1 within 60 days (or as described in the OSD recovery plan) after the chemical adjustment, preferably, from the riser furthest from the chemical adjustment riser. If the supernate is still out-of-specification, or the adjustment does not provide the expected results, either prepare and submit an OSD recovery action plan for approval or, if the tank is under an existing recovery action plan, review the plan to determine if it covers planned recovery actions or should be revised to add supplementary recovery actions including chemical waste adjustment and sampling.

When the initial sampling show that only the solids or both the solids and supernate are out of compliance, multi-depth supernatant samples (chemical adjustment sampling) are obtained within 60 days after the chemical adjustment (or as described in the OSD recovery plan) as well as core samples (chemical adjustment sampling) after mitigative actions are completed to adjust the solids chemistry (Table 8-1). If these samples indicate the waste is still out of OSD specifications, the waste (supernate and solids) will be sampled (chemical adjustment sampling) again (Table 8-1) after additional waste adjustment. Each tank specific OSD recovery action plan describes all actions required to not corrode the tank.

As shown in Figure 3-2 and Table 8-2, process control sampling will take place in the DST when a SST is being retrieved. Samples will be obtained when approximately 50% of the waste from the SST has been retrieved to the DST and/or when 100% (bulk retrieval is declared complete) of the waste has been retrieved to the DST. The 50% sampling event may not be conducted if the process engineer for DST corrosion mitigation determines the 50% sample is not needed. An example is when the process engineer determines the volume of retrieved waste does not make a 50% sample useful. The Process Engineer may also choose to sample at a retrieval percentage

different than 50%. The actions taken after the sampling, which depend on the analytical results (the waste meet OSD requirements or found to be out of specifications), are shown in Figure 3-2.

Table 8-2. Process Control Sampling Events

Sample Timing	Number and Location of Samples[(a)]
50% retrieval	A minimum of three grab samples are obtained at three equally spaced locations in the supernate. The first sample at the supernatant surface and the third sample approximately 10 inches above the bottom of the supernate.
100% retrieval	A minimum of three grab samples are obtained at three equally spaced locations in the supernate. The first sample at the supernatant surface and the third sample approximately 10 inches above the bottom of the supernate.

[(a)] Additional samples may be requested by the Corrosion Mitigation technical POC to determine layering composition (e.g., for modeling) when waste stratification is expected. The number and location of additional samples will be determined based on the suspected stratification.

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