# Hanford Site Waste Tank Characterization

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#### HANFORD SITE WASTE TANK CHARACTERIZATION

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#### **ABSTRACT**

This paper describes the on-going work in the characterization of the Hanford-Site high-level waste tanks. The waste in these tanks was produced as part of the nuclear weapons materials processing mission that occupied the Hanford Site for the first 40 years of its existence. Detailed and defensible characterization of the tank wastes is required to guide retrieval, pretreatment, and disposal technology development, to address waste stability and reactivity concerns, and to satisfy the compliance criteria for the various regulatory agencies overseeing activities at the Hanford Site. The resulting Tank Characterization Reports fulfill these needs, as well as satisfy the tank waste characterization milestones in the Hanford Federal Facility Agreement and Consent Order.

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#### 1.0 INTRODUCTION

The U.S. Department of Energy (DOE) operates the Hanford Site on approximately 1,450 km² (560 square miles) of arid steppe in the southeastern part of Washington State. As one of the original facilities from the Manhattan Project, the Hanford Site produced defense related materials resulting in the large-scale generation of solid and liquid radioactive wastes. Since 1944, the chemical processing of irradiated uranium fuels has generated alkaline slurries containing heavy metals, organic and inorganic salts, uranium, plutonium, and mixed fission products (Anderson 1990). These radioactive wastes have been placed in 177 underground single-shell and double-shell tanks for temporary storage. No wastes have been added to the 149 single-shell tanks since November 1980, although water is added to two tanks for evaporative cooling purposes. As a result of leakage at the single-shell tank farms, double-shell tank construction was started in the late 1960's. The 28 double-shell tanks, placed into service starting in 1970, are Resource Conservation and Recovery Act of 1976 (RCRA) permitted facilities that are still in active service. The current Hanford Site tank waste inventory is approximately 234 million L (61.7 million gallons) (Hanlon 1994).

The current direction for the operation of the Hanford Site is the eventual retrieval, treatment, and disposal of the contents of the high-level waste tanks, and the remediation and restoration of the surrounding lands. The present objectives of the DOE and its contractors have changed significantly, from the weapons production and testing missions of the past, to waste management, environmental remediation, and energy and environmental research. These new missions require accurate knowledge of stored wastes to guide technology development and to satisfy the compliance criteria for the various regulatory agencies that oversee activities at the nation's DOE sites.

#### 2.0 DRIVERS FOR WASTE CHARACTERIZATION

At the Hanford Site, as well as at other DOE complexes, legally binding agreements have been made between the DOE and the applicable state and federal regulatory agencies. The Washington State Department of Ecology, the U.S. Environmental Protection Agency, and the DOE have entered into the Hanford Federal Facility Agreement and Consent Order, also known as the Tri-Party Agreement (Ecology et al. 1989; Ecology et al. 1993). The Tri-Party Agreement provides the framework, including both tasks and schedules, for the entire Site cleanup, and sets interim and final milestones necessary for the satisfactory completion of these tasks. Milestones have been set for mutually agreed-to deliverables that fulfill the letter and intent of the Tri-Party Agreement. Specifically, the Tri-Party Agreement establishes the criteria for final closure of the high-level waste tanks, for the transformation of the high-level and low-level wastes into forms that are satisfactory for final disposal, and for the eventual remediation and restoration of the Hanford Site.

The selection of waste removal, treatment, and final disposal options; the need to safely store the wastes; and the resolution of safety issues require accurate knowledge of the tank contents to satisfy the myriad technical and regulatory information needs of the data users. Under the originally negotiated terms of Tri-Party Agreement Milestone M-10 (Ecology et al. 1989), each single-shell waste tank would be sampled and characterized so that final waste disposal decisions could be made. Characterization of the contents of the single-shell tanks would then support a decision either to leave the tank waste in place, or to retrieve and process the waste into a glass or grout form (this is referred to as the leave/retrieve decision). To satisfy this task, sampling and analysis of two core samples from each single-shell tank was planned to provide a database upon which to select either the leave or retrieve option (Winters et al. 1990).

The two vertical, full-depth samples were intended to identify single-shell tanks that could potentially be disposed in place; it was assumed at this time that these tanks would then require more extensive characterization to support their classification. Retrieval of the wastes in the double-shell tanks for further processing has always been the anticipated final disposal option.

#### 2.1 THE REGULATORY ENVIRONMENT

The leave/retrieve decision for the single-shell tanks was to be based on comprehensive federal regulations regarding the characterization of sites contaminated with hazardous materials, and also on regulations concerning the treatment and handling of radioactive wastes. An appropriate adaptation to the more difficult case involving mixed wastes (wastes both chemically hazardous and radioactive) was perceived to be achievable with minor adjustments or amendments to very extensive existing regulations (10 CFR 1990, 40 CFR 1990). In 1989, for the first characterization efforts under Milestone M-10, the constituents and waste properties to be analyzed were selected based on the following considerations (Winters et al. 1990):

- A review of potentially applicable state and federal regulations [including RCRA and the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA)].
- Performance assessments of the waste matrices and the final waste forms.
- Development of technologies such as retrieval, vitrification, and grout.

The regulatory and risk based analytes were later refined using analyte prioritization and concentration threshold work. Long and short term risk scenarios were evaluated, and the Washington Administrative Code and 40 CFR were used to identify the analytes that were the greatest contributors to risk and waste classification.

The present regulatory guidelines (EPA 1986), however, regarding sample handling and the analysis of conventionally hazardous materials at contaminated industrial sites are often inadequate for the sampling conditions and requirements imposed by wastes produced from the manufacture and purification of plutonium, which is the case at the Hanford Site. These process wastes are highly corrosive, highly radioactive materials that are also laced with toxic heavy metals, organic constituents, and reactive components. There are few laboratory facilities in the world that are properly equipped to handle such materials without prior dilution and sample preparation. The transportation of these types of samples is also highly regulated (49 CFR 1990), restricting the shipment of the samples to other facilities should resource constraints begin to impact the timetable set by the Tri-Party Agreement. The regulations dealing with the analytical treatment, handling, and final disposal of radioactive materials are governed by a different set of criteria (10 CFR 1990), some of which are contradictory in nature to the handling of hazardous chemical wastes. Reconciliation of the discrepancies in sample handling and analytical treatment between the two sets of rules has not yet been achieved; many times the assays specified by the regulations are found to be inappropriate with regard to the eventual disposition of the wastes.

#### 2.2 TANK CHARACTERIZATION STRATEGY

To meet the sometimes conflicting regulatory and process design information needs, competition arose among different sampling and analysis alternatives. Competition also arose about how to interpret and report the results. There was the initial desire to follow a "regulatory" approach: comply with existing regulations regarding sampling and analysis of mixed waste and report the results in a regulatory format. Adherence to regulation was understood to be necessary for the eventual disposal of the wastes *in situ*, and proceeding on that basis would provide strict compliance with the law and established, legally binding agreements. The degree of analytical rigor, traceability, and defensibility that these procedures establish for the data was also strongly desired.

The other view regarding the treatment of samples and reporting of data was that the characterization was to be viewed as preliminary, and necessarily nonexhaustive. The initial results would be considered an engineering study, and would be intended to provide input to other programs for design and cost calculations, risk and performance assessments and safety issue definition. Retrieval, pretreatment, and chemical separation processes could then be designed conservatively to cope with the full range of expected waste properties and tank conditions. The relevant regulatory characterization, needed to comply with waste treatment and disposal operations, would not be required until the wastes were transferred from the original single-shell tanks to the double-shell tanks, for blending of the wastes in preparation for pretreatment and separation into high-level and low-level fractions. In cases where the wastes would remain in the tanks for permanent disposal, further characterization to meet land disposal restrictions would also be required. At the time of the signing of the Tri-Party Agreement in 1989, the regulatory approach was the favored interpretation.

Since 1989, there have been several changes in the philosophy and overall direction of the characterization effort. Most significantly, the leave/retrieve option has given way to the decision to fully retrieve all tank wastes. In addition, treatment of the wastes to a final grout form has been rejected in favor of high-level and low-level glass fractions; process development continues for vitrification options. Furthermore, concerns raised by the Defense Nuclear Facilities Safety Board (Conway 1993) about the stability and reactivity of the tank wastes have driven the need for resolution of the unreviewed safety questions and other safety issues pertaining to the Hanford Site waste tanks and tank farms.

#### 3.0 CHALLENGES TO CHARACTERIZATION

Based on the limited and conflicting regulatory guidance, the needs of retrieval and process development, and the storage tank permitting requirements, laboratory assays have been specified for tank waste samples (Bell 1994). The analytical data packages generated from these extensive physical, chemical, and radiochemical analyses are documents that are cumbersome, bulky, and of limited utility. While the data packages contain tremendous amounts of material data, providing a broad range of information regarding the physical and chemical composition of the wastes in a particular tank, there is limited data summary or interpretation provided. Given the complicated process history of the waste tanks, large amounts of historical data, both contextual and analytical, are necessary to properly interpret the results of tank sampling and to provide an adequate characterization of the wastes in the tank.

#### 3.1 LABORATORY DATA PACKAGES

The exercise of generating and delivering a validated core sampling data package had become a classic case of complying with the letter of the law and not its intent. The data packages, ranging from 4,000 to 6,000 pages in length, are highly detailed in content; unfortunately, they are unwieldy to use and possess no consistent format. Although the data packages contain all instrument results, including all of the quality assurance and quality control assays, such as spikes, blanks, carriers, standards, etc., they contain neither a process history to develop a context for understanding these sample results, nor any conclusions based on of the analysis. Such data assessment is required by the engineers and scientists working toward the eventual retrieval, pretreatment, and disposal of the tank wastes.

The large volume of prescriptive analytical data contained in the data packages does not lend itself to simple, repeatable, and defensible waste characterization. Difficulties are often encountered while attempting to interpret the analytical results without placing the data into a historical context. In addition, the sheer size and arcane content of the data packages discourage even the most persistent investigators from any but the most cursory inspection. Since little precedent has been established concerning the requirements of mixed waste

characterization documentation, no criteria exist to specify what the content or organization of such a characterization document should be. While they satisfy Tri-Party Agreement characterization milestones, by themselves the data packages do little else. (Only recently have the data started to become available electronically; documentation of the effort to date has been largely done on paper with little access or organization via electronic means.)

#### 3.2 WASTE MATRIX CHALLENGES

The tank waste matrix is a challenging media to sample accurately and to effectively analyze. Past waste management operations at the Hanford-Site tank farms have resulted in a complex and intermingled mixture of waste types. Knowledge of the chemical and radionuclide compositions of the waste streams from the different waste processing and extraction operations are not always well known. Furthermore, there are inherent difficulties in the core sampling concept in general, and there are specific limitations resulting from programmatic and safety requirements and unique tank and waste properties. The following difficulties are associated with the current tank sampling and analysis strategy.

- Cost of tank sampling and analysis—Taking core samples from each waste tank and conducting the full scope of laboratory analyses is an expensive proposition, costing several hundred thousand dollars for each set of core sample analyses. With 177 waste tanks on the Hanford Site, this analytical work may become prohibitively expensive.
- Risk of exposure—Operating and laboratory personnel may be exposed to radioactive and hazardous constituents present in the tank waste. To minimize this risk, samples are optimized with regard to the amount of information obtained, overall sampling is minimized, and sample volumes are typically small with respect to the amount of analytical work requested. For example, the volume of the core sample receiver is 187 mL, and the volume of liquid grab samples is only 120 mL.
- Representativeness of tank core samples—Depending upon waste type and fill history, some tank wastes have been shown through laboratory analysis to be heterogeneous over the volume of the tank. Sampling points are limited by the numbers of available risers, and the locations of the risers do not lend themselves to random and representative sampling. Therefore, there is a concern about whether limited tank sampling can accurately characterize the contents of an entire tank (Arvizu 1993). There is no consistent method to assess the degree to which two or three vertical core samples represent the waste characteristics and properties of a tank as a whole.
- <u>In-Tank Aging Effects</u>--Natural processes that occurred inside the tanks while they were in active service, such as segregation, settling, and precipitation, complicate the physical configuration of the waste in the tanks. In addition,

on-going chemical and radiolytic reactions associated with in-tank aging have caused unknown changes to the chemical composition of the waste matrices.

#### 4.0 INTERPRETIVE WASTE CHARACTERIZATION

Faced with the physical, informational, and resource constraints inherent in characterizing the waste tanks, the uncertain (and in some cases, the ill-defined or even competing) nature of the user requirements, and the formidable complexity posed by the waste matrices themselves, rationality is necessarily bounded. Rational, deductive reasoning methods/frameworks, wherein an estimate regarding the composition of the tank waste is formed through completely logical processes, are not sufficient to accomplish the task by themselves (Arthur 1994). Furthermore, perfect characterization information about the tanks is neither necessary, achievable, nor economically viable with current means. To address these characterization shortcomings, which could not be resolved by the existing data collection and reporting system, validated RCRA-type data packages have been replaced as a final Tri-Party Agreement deliverable. Prescriptive, regulatory-defined data gathering and analysis was determined to be ill-equipped to handle the Hanford-Site tank wastes. An effort to provide the missing functions (i.e. contextual and interpretive) in the current characterization effort has since been undertaken for the DOE by the Westinghouse Hanford Company, with the assistance of Los Alamos Technical Associates, Inc.

The interpretive characterization effort initially had been intended to provide a resource to support facility and process design for the in-house engineering teams, which were tasked with the retrieval, pretreatment, and final disposal of the tank wastes. This interpretative function, however, rapidly evolved into a major focus of the Hanford-Site characterization program, as the extreme utility of contextual information and clear, defensible estimates became apparent. To deal with the characterization of the tank wastes, a synthesis was developed between inductive and deductive reasoning processes.

In the complex domain of the tank wastes, inductive reasoning provides a method of simplifying the intricate and sometimes contradictory nature of the data. By looking for patterns among different data sources and recognizing possibly spurious information, models or hypotheses can be formed concerning the tank conditions and constituent concentrations. In the case of the waste tanks on the Hanford Site, where full problem definition is by default incomplete, simplified models are used to fill gaps in understanding. A process of hypothesis formation, deductively tested expectations, and replacement of outmoded hypotheses is applied. Continued use of this inductive/deductive process causes the tank hypotheses, or models, that have the greatest correspondence with experience to be favored and selected. The vast quantity of historical information regarding the separation processes and tank transfers, both in general and in particular, is broadly applied to the tank wastes, and used to fill in gaps left in the model by a limited data set. Finally, a practical synthesis between historical and currently generated characterization data is possible (Figure 1).

#### 5.0 THE TANK CHARACTERIZATION REPORT

The tank characterization report is the end product of this reasoning process. Specific to each tank, a tank characterization report provides a brief summary of the process history of one tank during its active service life; a description of the tank's present inventory and general waste configuration; and a preliminary determination regarding the continued safety, stability, and integrity of the tank (De Lorenzo 1993). The main body of each tank characterization report is approximately 80-120 pages in length, a nearly 50-fold reduction in size from the data package. Taken together, all of the reports will provide an overall waste inventory of chemicals and radionuclides for the tank farms on the Hanford Site. In addition, examination of all of the tank data will allow studies in bounding waste properties, physical partition models, and qualitative descriptions regarding the physical characteristics of the various waste phases (sludge, salt cake, and liquid) present in the waste tanks.

These tank characterization reports have become an important and highly visible milestone in the latest revision of the Tri-Party Agreement (Ecology et. al. 1993). Information and conclusions contained in the tank characterization reports will support decisions regarding the resolution of safety issues, selection of retrieval and pretreatment options, and definition of waste feed characteristics. The ultimate objective in tank waste characterization is to develop a consistent, technically defensible model for the conditions, constituents, and radionuclides present in the waste tanks. The following specific objectives are reached by the sampling and characterization of the waste in each tank.

- Contribute toward the fulfillment of the Hanford Federal Facility Agreement and Consent Order Milestone M-44 concerning the characterization of Hanford-Site high-level radioactive waste tanks (Ecology et al. 1993).
- Complete safety screening of the contents of each waste tank to meet the characterization requirements of the Defense Nuclear Facilities Safety Board Recommendation 93-5 (Conway 1993).
- Provide tank-waste characterization to the Tank Waste Remediation System (TWRS) program elements, in accordance with the TWRS Tank Waste Analysis Plan (Bell 1994) and the tank specific tank characterization plans.

#### 5.1 TANK CHARACTERIZATION REPORT DEVELOPMENT DESCRIPTION

Tank characterization, as it is currently applied, relies on many sources of information. Historical data in the form of process knowledge, effluent discharges, and waste tank transfers form an initial basis. The amount of historical data, although imposing, is rather narrowly defined. Since there were only a select type and number of chemical separations processes used on the Hanford Site, for most tanks a handful of processes contributed the majority of the waste contents. This process information is coupled with several general

assumptions regarding the physical behavior of the slurries discharged to the tanks and the on-going processes occurring inside the tanks. The result of this historical review is to allow a detailed estimation of the contents of each waste tank based on historical process information and detailed transaction records.

#### 5.2 OTHER CHARACTERIZATION EFFORTS

Proceeding in conjunction with this tank-by-tank historical review is an on-going comprehensive computer modeling effort being undertaken by Los Alamos National Laboratory (LANL). As part of their characterization effort, LANL is deriving detailed composition estimates for the various waste streams sent to the Hanford-Site tank farms. By coupling this data with spreadsheet-based transaction records, an accounting of the waste present in each tank, as a function of time, is produced (Agnew 1994). Initial indications are that these model estimates, in their current form, are moderately successful in predicting certain bulk waste properties and constituent inventories (De Lorenzo et al. 1994). Further verification of the computer model and cross-checking of the data with other historical sources is continuing at this time. Expectations are that this historical characterization will provide reasonable presampling waste estimates to be used in developing tank sampling schedules, selecting appropriate analytical protocols, and defining data quality objectives.

#### 5.3 CHARACTERIZATION REPORT CONCLUSIONS

Once the historical characterization estimates are presented in a tank characterization report, the results of the sampling and analysis effort are summarized and interpreted both qualitatively and statistically. Several strategies are used to arrive at a final estimate of the tank contents, given the historical and analytical data. The framework provided by the historical information is used to assess and interpret the analytical findings, with discrepancies between the expected results and the analytical findings discussed and, it is hoped, reconciled upon closer investigation. Statistical techniques are employed to assess waste homogeneity, analytical error, and spatial variability. Precipitation models are applied to predict the species present in the solid and liquid phases. Biases identified from the analytical determinations are also used to reconcile differences between expected and actual results. Particularly useful as predictive tools are mass and charge balances of the historical and analytically derived results. By setting the charge balance equal to zero, for example, either nonanalyzed constituents or suspect data results can be examined and resolved.

#### 6.0 TANK CHARACTERIZATION DATA USERS

Tank characterization reports supply analytical data and contextual information used in the continued safe operation of the Hanford-Site tank farms. The data needs of the various Tank

Waste Remediation System program elements are currently being documented through the data quality objectives process (Babad et al. 1994). This ongoing effort to define the required analytes and detection limits, analytical rigor, and data traceability have resulted in a series of program specific data quality objective documents. Using these as reference sources, individual tank characterization plans are prepared to cover each intended sampling event. The plans describe the type, number, and location of samples; the requested analyses and attendant data validation; and the reporting limits for certain key determinations. Each tank characterization report then represents the final step in the process instituted by the tank waste analysis plan and the tank characterization plans. The general document and informational hierarchy is represented in Figure 2.

#### **6.1 RESOLUTION OF SAFETY ISSUES**

Concentration and inventory estimates derived in the tank characterization reports are used to address safety concerns associated with the tank wastes. Unresolved safety questions and ongoing safety issues that exist for the Hanford-Site waste tanks include concerns over ferrocyanide (Fe(CN)<sub>6</sub>-4) content from previous cesium scavenging campaigns, organic layers or high total organics concentration, excessive heat generation from radioactive decay, flammable or noxious vapors in the tank headspace, and potential criticality in the bottom layers of waste sludges. The full range of available sampling and analysis methods are employed to provide data to address these safety issues. Information is also derived through reviews of the process and transfer history of each waste tank. From this review, waste simulants are sometimes developed and tested; waste simulants are considered to represent bounding conditions for the tank waste.

The criticality safety issue, for example, was predicated on the possibility of a critical mass of uranium or plutonium settling and collecting at the bottom of a tank. Information and analyses that were determined to be needed to resolve this issue included uranium and plutonium isotopic analyses on samples from the bottom-most waste layers; total alpha activity, also as a function of depth; and the concentration of chain-reaction poisons and elements that displace actinides in the sludge matrix (Babad 1994). Samples necessary to support these analyses consisted of at least two vertical, full-depth samples of the waste material. Incidentally, the criticality unresolved safety question was closed recently after study of the available sampling data. In addition, the ferrocyanide unresolved safety question was closed after review of the historical data, the testing of simulants, and analytical information all pointed to the conclusion that no exothermic reaction was plausible in the waste under the present tank conditions.

#### 6.2 OPERATIONS AND MAINTENANCE

The tank characterization reports provide concentration and inventory estimates that assist in the continued safe storage of the tank wastes and allow the continuation of current waste management operations. As a result of the design of the single-shell and double-shell tanks,

design driven limits exist regarding several analytes (for example: waste pH; total heat generation; and the concentrations of nitrates, nitrites, and hydroxides). Waste compatibility determinations are necessary before tank-to-tank transfers, and before transfers to an evaporator. The volume of free liquid in the single-shell tanks is kept to a minimum. When possible, standing liquids are pumped off and/or interstitial liquids are salt-well pumped to the double-shell tanks in order to reduce the environmental release of wastes in the event of a single-shell tank leak. To conduct these and other intrusive pumping and transfer operations, previous knowledge of the tank contents and waste properties is required.

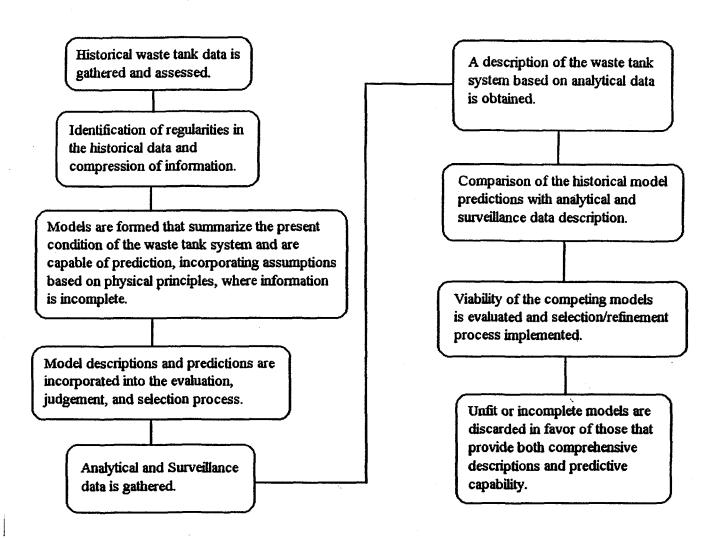
#### **6.3 FACILITY AND PROCESS DESIGN**

Because all wastes stored in the Hanford-Site underground storage tanks will be retrieved, treated, vitrified, and then disposed of in monitored retrievable storage facilities or geologic repositories, characterization estimates are required in order to design the retrieval equipment and the pretreatment, vitrification, and storage facilities. Retrieval planning and design requires information primarily about the physical properties of the waste, including viscosity, density, and critical flow rates. The pretreatment facilities are being designed to remove or separate species that hinder the operation of the vitrification operation or pose an environmental risk; therefore, minor waste constituents and trace elements are important. The design of the planned high-level and low-level vitrification plants is concerned primarily with the major waste constituents, which typically include the metals sodium, calcium, aluminum, and bismuth in abundance. The final waste form qualification for risk and performance assessment will focus on toxic metals and radionuclides. (Note that the initial round of tank characterization will not provide inventory estimates for permitting or closure of the tanks.)

#### 7.0 CONCLUSION

Accurate and defensible characterization of very complicated waste sites is only possible if comprehensive knowledge of the history and conditions at a site, actual sample data, and an understanding of the continuing natural and artificial processes in effect are combined. This paper describes the methods being used to characterize the hazardous and radioactive tank wastes at the Hanford Site. These techniques combine the historical knowledge, process knowledge, and empirical knowledge that can be developed for the wastes, interpret the data, and merge them into a coherent whole. The methods used to characterize the Hanford-Site tank wastes can be applied to other RCRA permitted treatment, storage, and disposal units and DOE mixed waste sites.

Figure 1. Description of the Tank Characterization Process.



Tri-Party Agreement Milestones Tank Waste Remediation System Defense Nuclear Facilities Safety Board Program Element Data Needs Characterization Requirements Data Quality Objective Documents Tank Characterization Reference Guide Tank Waste Analysis Plan Historical Tank Data Sample Prioritization Estimated Chemical Tank Characterization Plans Integrated Sampling Schedule Inventories Sampling Work Package Quality Assurance Project Plan Stastical Analysis Tank Sampling Data Validation Mass/Charge Balances Laboratory Analysis - Solid Core - Auger - Liquid Grab Tank Characterization Report Data Package Preparation - Vapor Space Concentration and Inventory Estimates

Figure 2. Tank Characterization Functional Hieracrchy

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