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WASTE TANK SAFETY SCREENING MODULE: AN ASPECT OF HANFORD SITE TANK WASTE CHARACTERIZATION

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J. G. Hill
T. W. Wood
H. Babad[a]
K. S. Redus[b]

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Pacific Northwest Laboratory
Richland, Washington 99352

(a) Westinghouse Hanford Company
Richland, Washington
(b) MACTEC, Richland Washington

WASTE TANK SAFETY SCREENING MODULE:
An Aspect of Hanford Site Tank Waste Characterization

J. G. Hill, T. W. Wood
Pacific Northwest Laboratory*
Richland, Washington

Dr. H. Babad
Westinghouse Hanford Company
Richland, Washington

K. S. Redus
MACTEC
Richland, Washington

ABSTRACT

Forty-five (45) of the 149 Hanford single-shell tanks have been designated as Watch-List tanks for one or more high-priority safety issues, which include significant concentrations of organic materials, ferrocyanide salts, potential generation of flammable gases, high heat generation, criticality, and noxious vapor generation. While limited waste characterization data have been acquired on these wastes under the original Tri-Party Agreement,[1] to date all of the tank-by-tank assessments involved in these safety issue designations have been based on historical data rather than waste characterization data. In response to guidance from the Defense Nuclear Facilities Safety Board (DNFSB finding 93-05)[2] and related direction from the U.S. Department of Energy (DOE), Westinghouse Hanford Company, assisted by Pacific Northwest Laboratory, designed a measurements-based screening program to screen all single-shell tanks for all of these issues. This program, designated the Tank Safety Screening Module (TSSM), consists of a regime of core, supernatant, and auger samples and associated analytical measurements intended to make first-order discriminations of the safety status on a tank-by-tank basis. The TSSM combines limited tank sampling and analysis with monitoring and tank history to provide an enhanced measurement-based categorization of the tanks relative to the safety issues. This program will be implemented beginning in fiscal year (FY) 1994 and supplemented by more detailed characterization studies designed to support safety issue resolution.

INTRODUCTION

The Tank Safety Screening Module (TSSM) was developed to assist in the characterization of the approximately 65 million gallons of high-level radioactive wastes that are currently stored in underground tanks at the Hanford Site. Of this, about 37 million gallons are stored in 149 single-shell tanks (SSTs), while the remainder are stored in 28 double-shell tanks.

This waste is residual material from a variety of chemical separations processes applied to extract plutonium, uranium, and, to a lesser extent, neptunium from the spent fuel generated at the Hanford production reactors over almost fifty years of operation. Several separation processes, including bismuth phosphate, reduction oxidation (REDOX), and plutonium-uranium extraction (PUREX) were employed in these separations campaigns at various times. All of these separations processes began with the HNO_3 dissolution of the irradiated uranium fuel elements that were encased in several types of metallic cladding material. These processes used a wide variety of complexants and solvents, which remain in significant quantities in the wastes.

In addition to the separations processes employed for Pu, U, and Np extraction, fission product extraction (primarily Cs and Sr) and other waste management operations were accomplished. Several waste volume reduction campaigns were also employed, including ferrocyanide (FeCN) scavenging of liquid wastes for Cs, evaporator operations to concentrate wastes by removing excess water, in-tank solidification using air sparging and steam coils, and salt-well pumping to remove drainable liquids from SSTs. With the exception of this Cs and Sr inventory, some of which was purified and is now stored separately in steel canisters, most of the decayed fission product inventory from Hanford production can be found in the tank wastes. In some cases the fission products are sufficiently concentrated to generate significant heat. Although a high fraction of the Pu was extracted, a significant amount remains in the tanks.

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The waste is physically composed of almost equal volumes of supernatant (liquids), saltcake (residual from evaporated supernatant), and sludges, composed principally of metal oxides. These waste forms are often mixed within individual tanks. The in-tank waste geometry is often complex, with multiple layers of several distinct materials in a tank.

In addition to the variety of processes and chemicals employed in site operations, a number of other factors also contribute to a wide variety of waste compositions among tanks and a lack of certainty regarding specific tank waste chemical and radiochemical inventories. These include an exceedingly complex and incompletely documented set of waste transfers between tanks and processing plants, the use of evaporator campaigns to concentrate wastes, and the reaction or radiolysis of chemical compounds in the tanks.

All of these factors together pose a significant challenge in ensuring safe storage of this material until it can be retrieved, treated, and disposed of in an environmentally acceptable fashion. The presence of potential fuels (organics and ferrocyanide) with oxidizers (nitrate and nitrite salts) poses risks of exothermic reactions. Both radiolytic and chemical degradation of organics can give rise to the generation of flammable and/or noxious gases. Low but unknown concentrations of fissile materials pose difficult criticality issues. Selective concentration of remaining fission product inventory leads to heat concerns for some tanks. Several tanks have indications of more than one safety issue, compounding the assessment and prioritization of tanks and issues. For a more complete description of the wastes contained in the Hanford Site waste tanks, see the *Waste Characterization Plan for Hanford Site Single-Shell Tanks.*[3]

OBJECTIVES OF THE TANK SAFETY SCREENING MODULE

The overall basis for tank safety classification at the Hanford Site is a scheme in which each tank is designated "safe," "conditionally safe," or "unsafe" for interim storage with respect to each potential safety issue. In this scheme, "safe" implies inherently or passively safe by virtue of inventory. The "conditionally safe" designation applies to tanks that require certain levels of moisture and control of waste temperature to ensure safety even in the presence of significant inventory factors. The "unsafe" designation is reserved for tanks in which neither safety nor conditional safety can be established.

These distinctions are illustrated by the interim criteria for organic-nitrate reactions, under which the "safe" designation applies only to tanks in which total organic carbon (TOC) (e.g., fuel) concentrations are below 5 wt% (dry basis), but "conditional safety" designations apply to even high TOC tanks for which there is assurance that minimum moisture content (greater than 17%) is sufficient to prevent a propagating reaction.[4] Tanks failing both tests would be designated unsafe and subjected to mitigative action. While the criteria defining the thresholds for safety and conditional safety are currently evolving for the priority-one safety issues, the basic logic of safety and conditional safety applies to all.

Thus the principal objective of the screening module is to provide a measurement-based initial classification of all tanks as safe, conditionally safe, or unsafe for each of the priority-one safety issues. This objective implies that all tanks will be screened (sampled and analyzed) for the relevant analytes for all issues.

An additional objective is to provide data supporting a "relative" hazard ranking for tanks designated as conditionally safe or unsafe within each of the safety issues. Supporting this objective benefits both the prioritization of scientific and engineering studies within the various tank safety programs and the prioritization of more detailed characterization studies.

Although not stated explicitly as an objective of the TSSM, an additional benefit will be realized in terms of supplementing the technical basis for tank characterization generally. This benefit will be gained by greatly strengthening and broadening the knowledge base with respect to in-tank spatial variability and between-tank waste characteristics similarity. This knowledge is pivotal in planning the overall tank waste characterization program in support of ultimate safety issue resolution and waste treatment planning.

CRITICAL QUESTIONS ADDRESSED BY THE TANK SAFETY SCREENING MODULE

Several critical questions are addressed by the TSSM. The questions are

- What are the <u>decision variables</u> used to place a tank on a safety issue watch list or consider the tank an unreviewed safety question (USQ)?

- What <u>data</u> are required (e.g., analytes of concern) to support the safety classification of tanks or the identification of a USQ?

- What are the decision rules, or the rationale, that use the safe storage decision variables and associated data to place a tank on a safety issue Watch List or consider the tank an USQ?

- Are tanks that are currently not on a safety issue Watch List or considered an USQ correctly classified as "safe"?

- Are tanks the are currently on a safety issue Watch List or considered an USQ classified in the correct safety issue Watch List or USQ?

- Are the tanks correctly classified as "conditionally safe" or "unsafe" within the safety issue Watch List or USQ?

- If a tank is presently on a safety issue Watch List or considered a USQ, should it be added to another safety issue Watch List or considered another USQ?

CHARACTERIZATION PROGRAM CONTEXT FOR THE TANK SAFETY SCREENING MODULE

To fully appreciate the utility of the TSSM, its context within a larger integrated characterization program must be discussed. Clearly, the highest near-term priority for the characterization effort is supporting resolution of the tank safety issues. Safety issue resolution requires a complete and prioritized list of tanks with safety issues. Uncertainty concerning the interim safe storage of tank wastes can be reduced by an appropriate screening of all of the tanks relative to the existing safety issues. Therefore, two types of interrelated characterization activities are required. One type supports resolution of the safety issues associated with tanks already identified on the Watch List; the second screens all tanks relative to the existing safety criteria and ensures all tanks with associated safety concerns are identified and placed on the Watch List. However, characterization in support of the development of retrieval, pretreatment, and immobilization systems for the tank wastes cannot be ignored. A third type of characterization support, with different requirements and objectives, is required to support these activities.

All of these characterization requirements do not have to be satisfied simultaneously for all tanks. There is a natural time phasing of these requirements relative to the life cycle of the tank farms (Fig. 1).

The four main phases of this approach are

- Phase I — Define Present Conditions
- Phase II — Ensure Interim Safe Storage
- Phase III — Disposal Feed Characterization
- Phase IV — Final Waste Form Qualification

This phased approach recognizes downstream characterization opportunities where more accurate characterization data can be obtained; it also utilizes a variety of sampling techniques and analytical methods to most appropriately characterize the waste media of interest. The phased approach also takes advantage of grouping tanks that are similar in chemical and physical characteristics. For a more detailed description of this phased characterization approach, see *TWRS Data Quality Objectives (DQO) Strategy*.[5]

Characterization using a screening module approach provides data supplementing historical information to ensure all Watch List tanks are identified. The screening module evaluates all tanks relative to the existing safety criteria with a short list of analytes of safety concern. Characterization data collected from the screening module will provide some of the needed input for issue resolution. The data collected as part of the TSSM will also shed needed insight on the general contents of the waste tanks to further the development of DQOs in support of safety issue resolution and waste disposal programs.

Implementation of the screening module must balance allocation of characterization resources between screening for Watch List tanks and detailed characterization in support of resolution of the safety issues and retrieval, pretreatment, and immobilization system development. Safety screening does not preclude performing additional analyses on those samples.

TANK SAFETY PROGRAM CHARACTERIZATION NEEDS

The characterization data needs for tank safety issue resolution will be provided by four sources of information, as shown in Figure 2. These sources are historical records analysis, new sampling and analysis, field instrumentation, and theoretic modeling/simulant studies. The total quantity and quality of the characterization information needed to resolve the tank safety issues will be identified and documented through the DQO process being implemented for each safety issue. The safety criteria for assessing the safety status of the tanks and analytes of concern for the TSSM are detailed in this section.

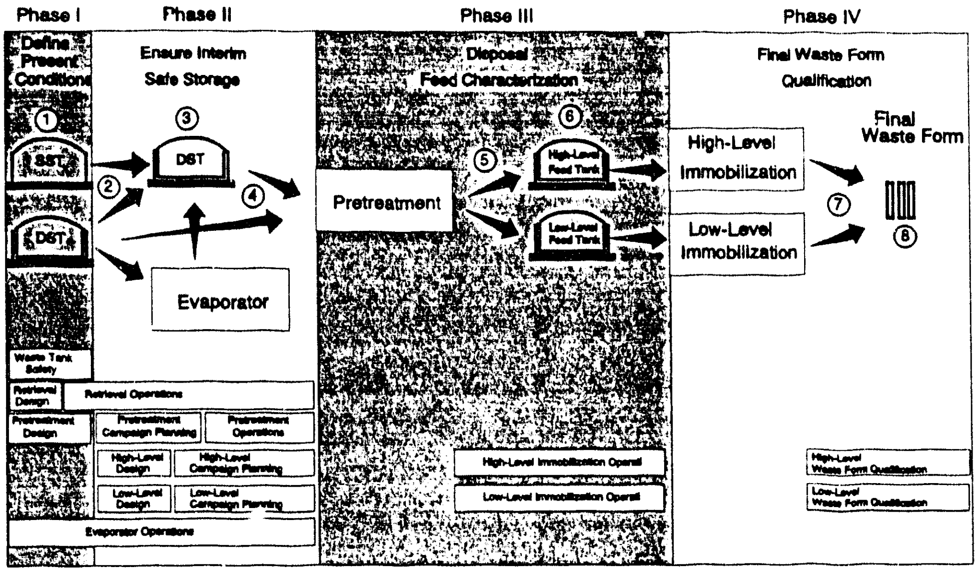

Fig. 1. Phased Tank Waste Characterization Strategy

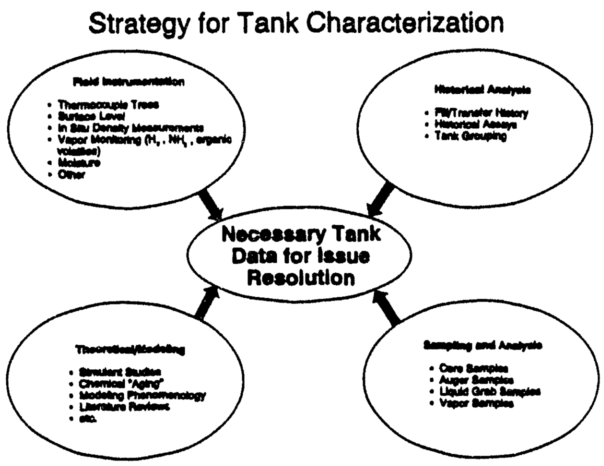

Fig. 2. Safety Issue Resolution Data Needs

Tank Waste Safety Criteria

Table I identifies the safety criteria threshold for evaluating the status of tanks relative to the existing safety issues.[4,6,7,8] Tanks that exceed these criteria are designated as Watch List tanks and have enhanced monitoring protocols.

Analytes of Concern for Tank Waste Safety

Analytes of concern were identified for each of the priority-one safety issues. These analytes of concern were developed through detailed interfacing with the individual safety programs and provide the basis for the analyses found in the TSSM. The analytes of concern are presented for each of the priority-one safety issues. Not all analytes of concern can be addressed with sampling and analysis; some require field instrumentation and/or historical evaluations. For illustrative purposes. the analytes of concern for the ferrocyanide safety issue are shown in Table II.[7]

Table I. Tank Waste Safety Criteria

Issue	Primary Criteria	Secondary Criteria
Ferrocyanide	FeCN < 8% dry wt	> 4/3 [Fuel - 8% moisture < 120 °C < 75 cal/g
Organics	5% TOC	> 17% moisture < 75 cal/g
Flammable Gas	< 25% LFL	N/A
High Heat	$T_{Concrete}$ < 300 °F	< 40,000 BTU/Hr
Criticality	^{239}Pu < 1 g/L	Pu/Metal Ratio
Vapors	OSHA/NIOSH Standards	N/A

Base Requirements for Tank Safety Screening

The base requirements for the TSSM are an integration of the individual requirements for each of the priority-one safety issues. These requirements will serve as baseline activities that will be conducted on all tanks. The base requirements for tank safety screening are as follows:

- Historical data evaluation--A thorough review and analysis of available historical records including waste transfers, waste type compositions, and historical sample analysis data.

- Field Instrumentation/Monitors--Enhanced instrumentation and monitors will be implemented in the field to support resolution of the priority-one safety issues.

- Sampling and analysis (core and auger)
  - % H_2O
  - Energetics
  - Total cyanide
  - Total organic carbon (TOC)
  - Heat generation (^{137}Cs, ^{90}Sr)
  - Fissile material (^{239}Pu)
  - Separable organic phase (visual)

Table II. Analytes of Concern for the Ferrocyanide Safety Issue

WASTE CHARACTERISTIC	SAMPLING METHOD(S)	MEASUREMENT METHOD
Ferrocyanide Concentration	Full Core Auger	Total Cyanide Assay
Total % Organic Carbon	Full Core Auger	Direct Persulfate Oxidation
Energetics	Full Core Auger	DSC/TGA validated by adiabatic calorimetry if >75 cal/g
Total % Nickel [1]	Full Core Auger	ICP on caustic fused waste
% Moisture	Full Core Auger LOW In-Tank Monitor Penetrometer	Gravimetric Analysis TGA Neutron Probe Activation Foils in Drill Stem Under Development at CPAC
Temperature	Thermocouple Trees	Thermocouples/RTD

Notes [1] Nickel on composites only. Presence of appropriate concentrations of nickel is a signature of ferrocyanide waste

Discussion of Tank Safety Screening

Closure of some of the USQs will require gathering additional core sample data to determine relative hazard and establish necessary controls to ensure safety. This supplemental sampling and analysis required for issue closure will be detailed in safety issue-specific DQO studies currently underway or planned in the near future.[5,7] The characterization activities in support of safety issue resolution can be built on top of the foundation established by the TSSM. Complete resolution of safety issues will require historical evaluations; field instrument; sampling and analysis data; and theoretical/simulant studies. Core sample data will be necessary, in most cases, to determine if a tank is "conditionally" safe and/or to support interim mitigation steps prior to retrieval.

TECHNICAL BASIS FOR TANK SAFETY SCREENING MODULE

The technical basis for the TSSM has three parts. The first part is the development of safety screening logic diagrams to show how the information collected during the implementation of the module will be used to categorize the tanks relative to their safety status. This will be followed with a discussion of the dilemma in screening. Finally, the risk management approach being used for the screening module will be detailed.

Tank Safety Screening Logic

A series of TSSM decision logic flow diagrams was developed in conjunction with the Waste Tank Safety Program. These logic diagrams show how the information being gathered as a result of the implementation of the TSSM will be used to make decisions regarding the safety status of all tanks relative to the existing safety issues. As an example, the safety screening logic diagram for the ferrocyanide safety issue is presented as Fig. 3.

This logic diagram starts with using tank history to conduct grouping analysis around the physical characteristics expected to be drivers of analyte variability. This grouping analysis is discussed in detail later in this paper under implementation of the TSSM. Once a tank has been placed in a group, it is determined whether the spatial variability of that group of tanks is already known. If the spatial variability is not sufficiently known, then some reference phase characterization studies are conducted to develop a group variability estimate. (These reference phase studies are also further discussed later under implementation). If the spatial model for the tank has already been sufficiently defined, then only a single sample needs to be obtained from that tank for the purposes of safety screening. Once sampling and analysis has been accomplished for a given tank, the pertinent analytical data for the ferrocyanide safety issue will be compared to the safety criteria threshold presented in Table I and classified into one of the three safety categories. The safety classification will be made using the risk management approach described below. Required actions for each tank depends on the safety classification. If a tank is deemed to be in the "safe" category, a routine monitoring regime will be continued. If the tank is determined to be either "conditionally safe" or "unsafe," these tanks will be placed on the Watch

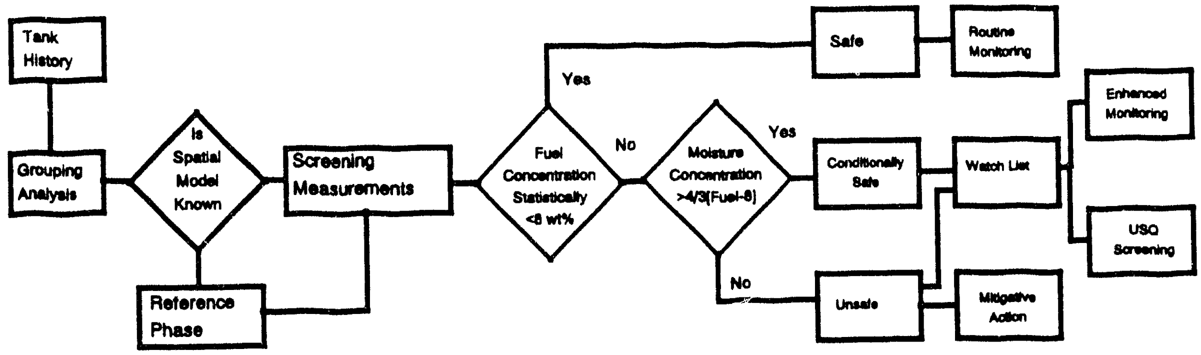

Fig. 3. Safety Screening Logic Diagram for FeCN

List for the associated safety issue. Watch List status triggers an enhanced monitoring protocol and a USQ screening. Tanks that are placed in the "unsafe" category will require some mitigative action to place the tank in either a "safe" or "conditionally safe" category.

Dilemma in Screening

To accelerate the screening of all tanks relative to the existing safety issue, the number of samples taken per tank must be minimized. However, a single sample (or no samples) implies a high risk of misclassification of tanks (Watch List or Non-Watch List). Conservatism will dictate a bias toward placing questionable tanks on the Watch List. A trade-off must be made between minimizing the time and resources required to perform adequate screening and the accuracy of Watch List/Non-Watch List decisions.

The TSSM presents an approach to manage the risk of using a relatively small (one to three samples per tank) number of samples to screen tanks against existing safety criteria. The rationale for this approach will be detailed in the next section.

Risk Management Approach for Tank Safety Screening

The TSSM will evaluate the safety status of tanks using a statistical model employing group-based spatial variability estimates to allow the use of single samples for many tanks. This risk management approach is illustrated in Figure 4. Once a group-based spatial model has been developed, the mean concentration (M) for the parameter of concern will be determined from the analytical results from a single-sample event. Uncertainty in that mean concentration will be represented by the standard deviation (σ) derived from the group-based spatial variability model. The mean concentration plus (n) standard deviations will be compared to the threshold of concern. Care must be given in establishing (n) to ensure a high probability of placing Watch List tanks on the Watch List but also minimizing the number of safe tanks that are designated as Watch List tanks. The appropriate values for (n) will be determined in the near future based upon discussions among the affected programs.

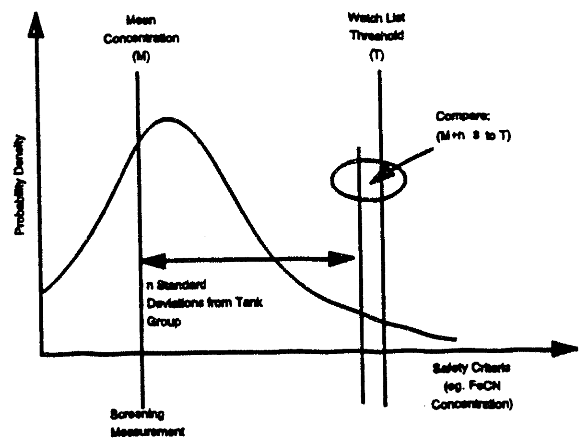

Fig. 4. Application of the Risk Management Approach for Safety Screening

IMPLEMENTATION PLAN FOR THE TANK SAFETY SCREENING MODULE

The previous sections of this paper presented the theoretical and programmatic considerations upon which the TSSM was developed. This section will provide the detail on how this screening approach will be implemented for the Hanford Site waste tanks. The implementation of the TSSM hinges on five main pieces: (1) relevant population groups, (2) the reference phase of the TSSM, (3) multiple sampling techniques, (4) analytical plan, and (5) the resources required for the TSSM.

Relevant Population Groups

The implementation of the TSSM relies heavily on dividing the 177 high-level waste storage tanks into *relevant population groups* (RPGs). An RPG is defined as a group of tanks that are expected to have similar physical characteristics around which grouped-based analytical variability will be estimated. These group-based variability estimates will be applied to single-sample events within a given RPG to provide an estimate of tank inventory/concentration and the associated uncertainty with that estimate. The TSSM utilizes three readily observable physical characteristics of the Hanford waste tanks to categorize them into eight RPGs. The three criteria are sluicing history, free supernatant volume, and presence of saltcake.

The sluicing history of a waste tank is considered a major driver for analyte variability. Sluicing is the process of removing sludge from waste tanks using a high-pressure, high-volume water jet. Most sludge-type wastes were placed in the tanks as highly diluted slurries that were allowed to settle in relatively flat pancake-like layers. Sluicing a tank would significantly disturb these layers and alter the variability model of the waste. A sluiced tank is thought to resemble a "donut," with a ring of older wastes near the perimeter of the tank surrounding newer wastes placed in the hole resulting from sluicing operations. In addition to the sluicing history, free liquid content is also thought to be a significant factor in determining waste variability. Tanks with a large volume of free liquid (supernatant) to assist in the distribution of analytes within a tank are expected to have different variabilities than relatively dry tanks. Finally, the presence of saltcake is a major contributor to waste variability. Saltcakes were placed in the tank as supersaturated liquids which solidified upon cooling. Saltcake is known to have substantially different physical and chemical characteristics than sludge-type wastes. A hierarchial view of the application of these criteria to the 177 waste tanks is illustrated in Figure 5. Other tank grouping models are currently evolving.

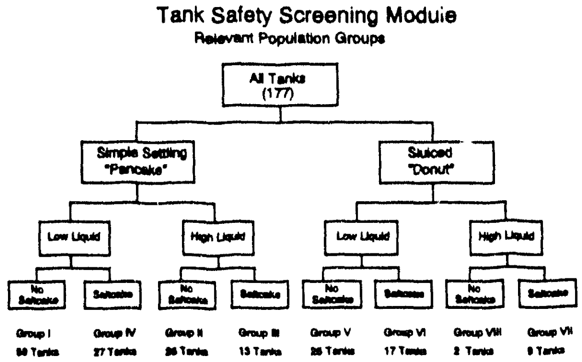

Fig. 5. Relevant Population Groups

Reference Phase of the Tank Safety Screening Module

A key aspect of the TSSM is the use of group-based variability estimates, which will be derived from multiple-sample-per-tank events in a selected number of tanks from each RPG. Once this group-based variability estimate has been determined, the remaining tanks within an RPG are sampled only once per tank. The process of gathering the group-based variability estimates is known as the reference phase. A summary of the reference phase is shown in Table III.

In Table III, previous sampling refers to core samples already taken and analyzed since 1990 as part of current and ongoing characterization efforts. New sampling refers to additional cores that need to be taken as part of the reference phase, and the total reference is the sum of the previous and new sampling. The reference phase summary has been broken down by RPG. It is interesting to note that most of the previous sampling has been concentrated in Group I, and no new sampling of this group is required for the Reference Phase.

Multiple Sampling Techniques

The TSSM uses a variety of sampling techniques depending upon the media of interest. For soft, sludge-type wastes, the present push-mode core sampling system will be used. A rotary-mode system has been developed to sample hard saltcake wastes. Many of the 177 waste tanks contain relatively small volumes of wastes which can be as adequately sampled with an auger sampler as with the core sample trucks. For tanks with large volumes of supernatant liquid, a liquid grab sampler will be employed for the liquid fraction. Using a variety of sampling techniques allows the characterization program to tailor the performance of a particular technology to the characteristics of the media in

Table III. Summary of Reference Phase

Group No.	Total No. of Tanks	Previous Sampling		New Sampling		Total Reference	
		No. of Tanks	No. of Cores	No. of Tanks	No. of Cores	No. of Tanks	No. of Cores
I	59	12	34	0	0	12	34
II	25	3	3	5	7	5	10
III	13	1	2	2	4	3	6
IV	27	0	0	4	8	4	8
V	25	1*	7*	4	8	4	8
VI	17	0	0	3	6	3	6
VII	9	0	0	3	6	3	6
VIII	2	0	0	2	4	2	4
Total	177	16	39	23	43	36	82

question, and thus obtain a more representative sample. The use of multiple techniques also enables the characterization program to operate parallel crews, increase sampling capacity, and shorten sampling duration.

Analytical Plan for the Tank Safety Screening Module

This section will highlight the pertinent parts of the analytical plan for the TSSM, including the analyses that will be accomplished in support of screening, the segmentation and compositing scheme, and the analytical burden of conducting safety screening.

Sampling operations will collect core, auger, and liquid grab samples and transport the sample to one of the two Hanford Site analytical laboratories. Liquid grab samples and auger samples will be homogenized before analyses. Each 19-inch core sample will be extruded in hot cells and divided into subsegments according to the following segmentation scheme.

- Quarter-segments on all known ferrocyanide tanks. All known FeCN tanks will be divided into four 4¾ inch quarter-segments. Ferrocyanide waste was placed in the tanks in batches that could have deposited layers approximately 4-6 inches thick. The analytical horizon for screening FeCN wastes must be on the same size scale to distinguish between potentially reactive concentrations of FeCN within these layers and more dilute, non-reactive wastes.

- Full segments on 200 series (55 kgal) tanks. There are 16 of these relatively low-volume tanks. Although these tanks have a small inventory of waste, the small diameter (20 ft) results in a significantly larger number of segments. Subdividing core samples from these tanks is not warranted due to the small waste volumes.

- Semi-segments on all remaining tanks. All remaining tanks not covered above will be divided into two 9½ inch semi-segments.

The analytical portion of the TSSM consists of three different suites of analyses (Figs. 6, 7, and 8). The first suite will be implemented on a subsegment basis. This is the set of assays that is the heart of the TSSM. These analyses will be accomplished on an expedited basis and be available within 45 days of the date of sampling. The second set of analyses will be performed on liquid composites within a tank, and the final suite of analyses is for tank solids composites.

The safety screening assays in Figure 6 will be conducted on a homogenized subsegment sample. The major portion of the subsegment suite of safety screening analyses will be conducted on the direct waste sample with minimal sample preparation and will consist of a differential scanning calorimetry (DSC) and thermal gravimetry analysis (TGA) to measure the energetics of the sample. The sample energetics (fuel value) is thought to be a leading driver for several of the safety issues. If the energetics are below a threshold value, no reaction could occur within the waste. The percent of water in the sample will be measured by gravimetry (and confirmed with TGA). The water content is considered to be the major prohibitor for any potential reaction. If the waste can be demonstrated to be sufficiently wet, no reaction can occur even if sufficient fuel is present. Total CN^- will be measured as a screen for FeCN. Total organic carbon will be analyzed to compare against the organic Watch List threshold. Lithium will be analyzed by inductively coupled plasma (ICP) in the drainable liquids and a water leach preparation of the solids for a segments taken using a hydrostatic head fluid. Lithium-traced water will be used as the hydrostatic head fluid to keep waste out of the drill string during sampler change-out. The lithium assays will test for hydrostatic head fluid contamination and be subtracted from the water content measured by gravimetry. During the core sample extrusion, an observational determination will be made of the existence of a separable organic layer. Total α and $^{239\backslash240}$Pu assays will be performed on a fusion dissolution of the bottom-most subsegment from every core. It has been postulated that Pu may settle to the bottom of the waste tanks because of its greater density; these assays check for this phenomenon. If the $^{239\backslash240}$Pu assay is > 1.0 g/L, then an isotopic analysis by mass spectrometry will be performed.

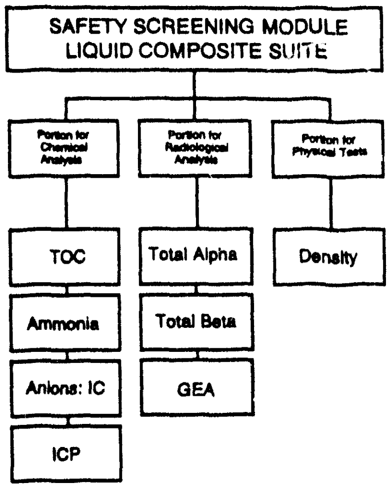

Fig. 7. Liquid Composite Suite of Analyses

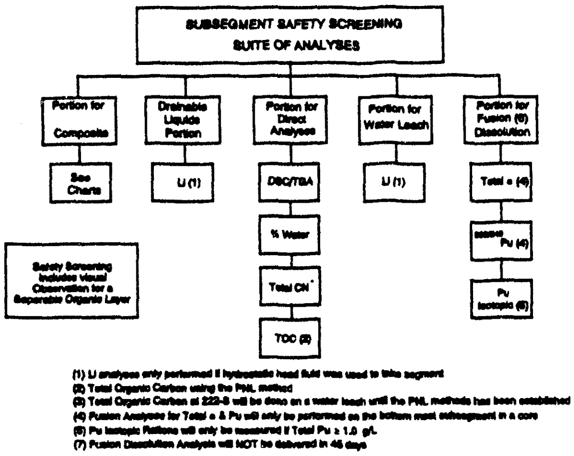

Fig. 6 Subsegment Suite of Analyses

The analyses for the liquid composite are presented in Figure 7. All of the drainable liquids will be composited into a single sample. This modest suite of analyses is intended to give a general composition of the drainable liquids in the waste tanks. Therefore, it measures cations (ICP), anions [ion chromatography (IC) and NH_3], TOC, and radionuclides [total α and ß, gamma energy analysis (GEA)]. This suite also provides for a density measurement.

Core composite samples will be generated for each core. At the present time, saltcake and sludge cannot be adequately homogenized; therefore, if both saltcake and sludge are present in a core, two separate composites will be generated. If only saltcake or only sludge is present, then only one composite will be formed and analyzed. Composites will be built by combining representative portions of each homogenized subsegment. The composites will be analyzed by the suite of assays shown in Figure 8.

This analysis is far more modest than previous composite analysis performed as part of this characterization program. The core composite suite provides more compositional information than the subsegment safety screening analyses. An adiabatic calorimetry assay will be run because this method is more accurate for determining fuel content of the waste. However, this method uses a large amount of sample and cannot be conducted on the subsegments because of limited available sample volumes. The core composite suite contains a homogenization test to check the adequacy of the homogenization techniques. The homogenization test will be accomplished by taking samples from the top and bottom of the homogenized composite and analyzing each, in duplicate, for cations by ICP. The more robust suite of assays being conducted on the fusion dissolution preparation will provide a total radionuclide content and a sample heat load. If the $^{239/240}$Pu assay is > 1.0 g/L an isotopic analysis will be accomplished using mass spectrometry. The core composite suite of analyses will also support prioritization of future characterization activities.

Analytical Burden

To facilitate long-term laboratory planning in support of a multitude of Hanford programs with diverse sampling and analytical requirements, a concept called analytical equivalent unit (AEU) has been developed to determine a common unit of analytical burden. All analytical requests are rated in terms of AEUs by the Hanford analytical services. For the TSSM, the subsegment suite of analyses (Fig. 6) has been rated as 0.03 AEUs every time the suite is performed. The composite (liquid and solids) has been given a rating of 0.07 AEUs. Generating a laboratory data package requires 0.1 AEUs of laboratory resources. By converting all analytical

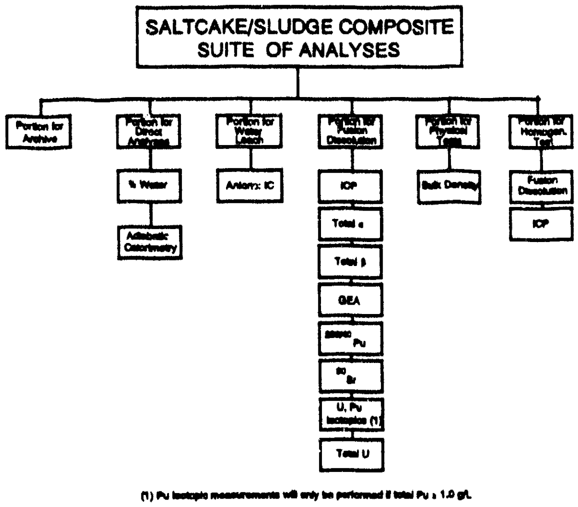

Fig. 8 Saltcake/Sludge Composite Suite of Analyses

activities into AEUs, the demand (number and types of samples requested) can be compared with the capacity of the laboratory to perform those activities. The following example demonstrates the application of this concept to a TSSM sampling event.

This same methodology was applied to all 177 waste tanks. A summary of the total numbers of samples and the associated analytical burden required to accomplish the goals of the TSSM is presented in Table IV. Table IV shows, for every RPG, the total number of tanks and the number of Watch List tanks in the entire group; the number of core samples previously taken and analyzed; and the number of additional push-mode, rotary-mode, and auger samples required for implementing of TSSM. The average AEU per sample was determined for each RPG. The average AEU per core is a function of depth of waste (number of segments and subsegments) and the number of composites that will be generated. The total analytical burden for each RPG is also provided. Implementing the TSSM will require 73 push-mode cores, 97 rotary-mode cores, 31 auger samples, and 96.5 AEUs. The resources required for the TSSM are substantially less than previously required under the Tri-Party Agreement (TPA). This reduction in required resources is illustrated in Figure 9.

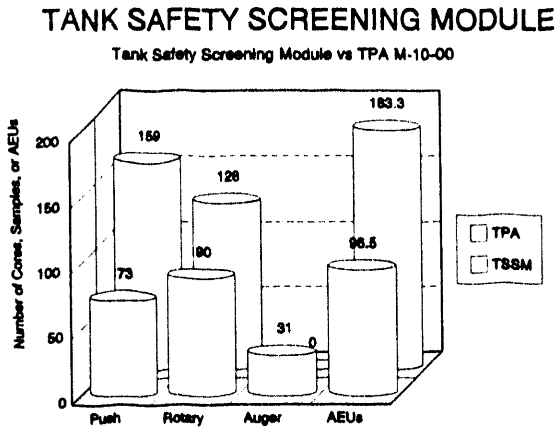

Fig. 9 Comparison of TSSM vs. TPA Milestone M-10

CONCLUSIONS

The uncertainty concerning interim safe storage can be reduced by an appropriate screening of all of the tanks relative to the existing safety criteria. The TSSM combines sampling and analysis, tank history, group-based variability estimates, and risk management to provide an enhanced classification of all tanks relative to the existing safety issues. Implementing the TSSM should balance allocation of characterization resources between screening and characterization in support of priority safety issue resolution. This module can serve as the foundation for an issue-driven characterization program as further defined by a formal DQO process and, using a small suite of measurements, can be applied using only one to three samples per tank and could be accomplished within three years.

In conclusion, the TSSM should be implemented for the Hanford Site underground storage tanks.

Example: Tank BY-110 has 103,000 gal of sludge and 295,000 gallons of saltcake. This tank is a FeCN tank. There will be approximately two segments of sludge and 6 segments of saltcake from this tank. Therefore the AEU calculation will be as follows:

2 segments FeCN sludge x 4 Qtr-Seg x 0.03 AEU/Qtr-Seg	= 0.24 AEUs
6 segments saltcake x 2 semi-seg x 0.03 AEU/Semi-seg	= 0.36 AEUs
(1 saltcake comp. + 1 sludge comp.) x 0.07 AEU/Comp.	= 0.14 AEUs
Reduced data Package	= 0.1 AEUs
Total AEU/Core	0.84 AEUs

Table IV Summary of Tank Safety Screening Module

RPG Group No.	No. of Tanks	No. of Previous Cores	No. of Watch List Tanks	No. of Push-Mode Cores	No. of Rotary Cores	No. of Augers	Average AEU/Core	Total AEUs
I	59	34	9	33	14	14	0.33	17.5
II	25	3	5	15	0	3	0.29	7.2
III	13	2	4	2	13	0	0.80	11.8
IV	27	0	12	0	35	0	0.77	26.5
V	25	7	1	21	0	9	0.31	9.2
VI	17	0	8	0	20	5	0.52	13.6
VII	9	0	8	0	13	0	0.74	9.3
VIII	2	0	2	2	2	0	0.32	1.3
Total	177	39	49	73	97	31	0.46	96.5

REFERENCES

1. ECOLOGY, EPA, and DOE, "Hanford Federal Facility Agreement and Consent Order (Tri-Party Agreement)," Washington State Department of Ecology, U.S. Environmental Protection Agency, U.S. Department of Energy, Olympia, WA (1989).

2. J. T. CONWAY, Letter to H. R. O'Leary, DOE, "DNFSB Recommendation 93-5 to the Secretary of Energy," 940070, Defense Nuclear Facilities Safety Board (July 19, 1993).

3. W. I. WINTERS, L. JENSEN, L. M. SASAKI, R. L. WEISS, J. F. KELLER, A. J. SCHMIDT, and M. G. WODDRUFF, "The Waste Characterization Plan for Hanford Site Single-Shell Tanks," WHC-EP-0210 Rev 1, Westinghouse Hanford Company, Richland, WA (1990).

4. H. BABAD, D. A. TURNER, "Interim Criteria for Organic Watch List Tanks at the Hanford Site," WHC-EP-0681, Westinghouse Hanford Company, Richland, WA (1993).

5. H. BABAD, S. D. BLACKER, K. S. REDUS, J. G. HILL, J. L. SCOTT, "TWRS Data Quality Objectives Strategy," WHC-EP-0732, Westinghouse Hanford Company, Richland, WA (1994).

6. V. C. BOYLES, "Operating Specifications for Single-Shell Waste Storage Tanks," OSD-T-151-00013 Rev D-1, Westinghouse Hanford Company, Richland, WA (1992).

7. R. J. CASH, et al., "Ferrocyanide Safety Program: Data Requirements for the Ferrocyanide Safety Issue Developed Through the Data Quality Objectives (DQO) Process," WHC-EP-0728, Westinghouse Hanford Company, Richland, WA (1993).

8. I. E. REEP, "Status Report on Resolution of Waste Tank Safey Issues at the Hanford Site," WHC-EP-0600, Westinghouse Hanford Company, Richland, WA (1992).

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