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Characterization Strategy Report for the Organic Safety Issues

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Characterization Strategy Report for the Ogranic Safety Issues

Hanford Tank Characterization and Safety Issue Resolution Project

August 1997

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Summary

This report describes a logical approach to resolving potential safety issues resulting from the presence of organic components in Hanford tank wastes. The approach uses a structured logic diagram (SLD) to provide a pathway for quantifying organic safety issue risk. The scope of the report is limited to selected organics (i.e., solvents and complexants) that were added to the tanks and their degradation products. The greatest concern is the potential exothermic reactions that can occur between these components and oxidants, such as sodium nitrate, that are present in the waste tanks. The organic safety issue is described in a conceptual model that depicts key modes of failure-event reaction processes in tank systems and phase domains (domains are regions of the tank that have similar contents) that are depicted with the SLD.

Applying this approach to quantify risk requires knowing the composition and distribution of the organic and inorganic components to determine 1) how much energy the waste would release in the various domains, 2) the toxicity of the region associated with a disruptive event, and 3) the probability of an initiating reaction. Five different characterization options are described, each providing a different level of quality in calculating the risks involved with organic safety issues. Recommendations include processing existing data through the SLD to estimate risk, developing models needed to link more complex characterization information for the purpose of estimating risk, and examining correlations between the characterization approaches for optimizing information quality while minimizing cost in estimating risk.

Glossary

DBBP	dibutylbutylphosphonate
DBP	dibutyl phosphate
DOE	U.S. Department of Energy
DSC	differential scanning calorimetry
DTPA	diethylenetriaminepentaacetic acid
EDTA	ethylenediaminetetraacetate
HEDTA	hydroxyacetateethylenediaminetriacetate
HEPA	high efficiency particulate air (filter)
HLW	high-level (radioactive) waste
MBP	monobutyl phosphate
MIBK	methyl isobutyl ketone
NPH	normal paraffin hydrocarbon
NTA	nitrilotriacetic acid
OBDD	ordered binary decision diagram
PNNL	Pacific Northwest National Laboratory
PUREX	plutonium uranium extraction (process)
REDOX	oxidation-reduction
SLD	structured logic diagram
TBP	tributylphosphate
USTs	underground storage tanks
TWRS	Tank Waste Remediation System
WHC	Westinghouse Hanford Company

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1.0 Introduction

1.1 Scope

The purpose of this document is to describe a structured logic diagram (SLD) and associated support information (e.g., characterization and modeling needs) to resolve organic safety issues associated with high-level waste (HLW) in Hanford tanks. Staff at Pacific Northwest National Laboratory (a) have prepared this study. The SLD provides a logical approach for the evolution of risk resulting from various event scenarios. Event scenarios considered involve organic solvents and complexants and associated dry radiation products in mixed waste. Also considered is the possibility of rapid and energetic reactions with oxidants that are present. To support the SLD, the report also 1) defines a conceptual model for solvent/complexant disruptive events, 2) identifies the critical parameters requiring measurement to quantify the magnitude of solvent/complexant-driven disruptive events, and 3) identifies scenarios for critical parameter determinations. Emphasis was placed on disruptive events (e.g., explosions and fires) that could lead to an unacceptable risk. Events that result in lesser disruption (e.g., subsurface leaks, "burping") were also considered, but not emphasized in describing the SLD. Other events that are commonly handled through the U.S. Department of Energy (DOE) and DOE contractor administrative control and operations processes were considered outside the scope of this task.

The Hanford Tank Characterization and Safety Issue Resolution Project examined several safety issues (criticality, flammable gases, organic solvents, organic complexants, and ferrocyanide) to determine whether they could contribute to an unacceptable safety hazard risk. Information within this report involving the safety issues surrounding organic solvents and complexants has been integrated with the findings reported for the other three issues to assess overall tank safety.

1.2 Background

At the DOE Hanford Site, many years of producing nuclear defense materials, decontaminating facilities, and managing wastes from chemical recovery operations have generated radioactive HLWs containing organics. This waste, which could contain organic solvents, organic complexants, organic radiolytic alkaline hydrolysis degradation products, and the inorganic oxidants nitrate and nitrite, are stored in underground storage tanks (USTs). The potential chemical reaction hazards associated with these organic-bearing radioactive wastes have been recognized as priority safety issues, and plans have been developed to resolve the safety issues for continued storage of these wastes (Wilson and Reep 1991; Wodrich and Deichman 1992; Babad et al. 1993a; Babad et al. 1993b; Postma et al. 1994a) and to develop safe-storage criteria similar to those developed for waste containing high levels of ferrocyanide (Postma et al. 1994b, Webb et al. 1995).

Table 1.1 provides a summary of some of the solvents and complexants that were most commonly used in producing and reprocessing nuclear fuels at Hanford (Klem 1990). The compositions of the Hanford organic-bearing wastes in the USTs are quite diverse (Strachan et al. 1993; Klem 1990). Predominant organic materials contributing to the waste include 1) the plutonium uranium extraction (PUREX) solvent and diluent (30 vol% tributylphosphate [TBP] in normal paraffin hydrocarbon [NPH]), 2) TBP radiolytic degradation products dibutyl phosphate

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(DBP, also added as a complexant), monobutyl phosphate (MBP), butanol, and phosphoric acid, and 3) organic complexants such as ethylenediamine-tetraacetic acid (EDTA), N-(2-hydroxyethyl) ethylenediminetriacetic acid (HEDTA), hydroxyacetate, citrate, and tartrate. Also, nitribtriacetic (NTA), acetate, oxalate, sulfamate, and a wide range of inorganic species are known to have been either deposited in tanks, observed in samples, or both. The waste is becoming more complex as different aging processes change the organic composition. Various combinations of high pH, inorganic oxidants such as nitrate and nitrite, and radiation are driving the aging processes. The HLW possibly includes inorganic constituents such as hydroxide that was added to neutralize the acidic wastes and to make the wastes chemically compatible with the carbon-steel USTs. Fission products may also be in the waste, as are other process additives such as iron, hexavalent chromium, calcium, strontium, barium, lanthanum, fluoride, and nitrate. Nitrite, which either resulted from radiolysis of nitrate or was added as a corrosion inhibitor, is also present.

Since many of these materials are classified as fuels, strong oxidants, or heat-producing (e.g., radionuclides), the potential exists for an explosion to occur similar to that which occurred in Kyshtym, U.S.S.R in 1957 (Medvedev 1979). The Kyshtym explosion resulted from a tank cooling-system failure. The radioactive decay processes raised the temperature of a radioactive waste mixture to the point at which a thermal-runaway reaction occurred involving acetate and sodium nitrate. Fisher (1990) assessed available data for Hanford tank wastes and other available data with respect to the Kyshtym event and concluded that the temperature of wastes stored in Hanford's USTs was at that time well below those required to initiate reactions between sodium acetate and sodium nitrate and/or nitrite. The results of the Fisher report, however, were quite limited in assessing the potential safety hazard and risk associated with stored organic-bearing HLW in Hanford tanks.

Table 1.1. Examples of Solvents/Complexants Commonly Used in Nuclear Fuels Reprocessing at Hanford

Class/Chemical	**Plant/Process**				
Solvents	**B Plant**	**Z Plant[a]**	**REDOX (S Plant)**	**PUREX (A Plant)**	**Semi-Works**
Normal Paraffin Hydrocarbons	X		X	X[b]	X
Tributylphosphate	X	X	X	X[c]	X
Dibutybutylphosphonate		X		X	
Methylisobutylketone			X		
Carbon Tetrachloride		X			
Complexants					
EDTA[d]	X				X
HEDTA[e]	X				X
DTPA = diethylene-triaminepentaacetic acid					X
NTA					X
Oxalate	X	X	X	X	X
Citrate[f]	X				X
Acetate				X	X
Di-2-ethylhexylphosphoric Acid	X				X

(a) Z-Plant wastes are believed to have been disposed of outside and away from Hanford tanks. The absence of CCl_4 in vapor samples appears to confirm this. It has been estimated that (b)1.3×10^6 Kg of NPH; (c)7.2×10^5 Kg of TBP (Sederberg and Reddick, 1994) were placed in Hanford tanks from the PUREX process alone. It has also been estimated that (d)2.2×10^5 Kg of EDTA, (e)8.3×10^5 Kg of HEDTA, and (f)8.5×10^5 Kg of citric acid were placed in Hanford waste tanks (Allen 1976).

2.0 Approach

2.1. General Overview

Two activities were performed in parallel to address the organic solvent/complexant issue. In one activity, a team of scientists (these are the authors of this report, but also see Appendix A for the list of team participants and their associated expertise) developed a conceptual model on which to base the SLD structure. In the second activity, the team developed the SLD using the elements of the conceptual model as guidance.

A glossary of terms used in developing the conceptual model and the SLD can be found in Appendix B. The team of scientists also prepared selected pieces of technical information that would support a user's understanding of the conceptual model and elements of the SLD. Along this line, Appendix C summarizes information on probabilities of frequencies of external operations that could initiate an event involving organic-bearing waste. Appendices D through G provide information on specific reactions or reaction combinations that govern organic events, and Appendix H describes the various types of models that can be employed in using the SLD to estimate risk.

2.2. Conceptual Model

In the conceptual model (Figure 2.1), a disruptive event is depicted as a violent or sudden occurrence (e.g., fire, explosion, or their combination) that results in failure at one or more points in the tank system leading to leaks. The team considered dome failure, a breach of the tank ventilation system, release of waste material through a breach of the floor/wall, and failure of piping systems associated with inter-tank waste transfer as sources of leaks. The team identified pressure and heat generated by chemical reactivity (e.g., solvents/salt reactions) and the effects of organics on structural integrity (e.g., corrosion) as key parameters contributing to the onset of these identified failure scenarios. Table 2.1 summarizes the team's considerations of the inter-relationships between the sources of leaks and the processes responsible for failures.

Table 2.1. Tank Failure Type/Process Inter-Relationships

Source of Loss of Containment	**Parameter Responsible for Initiating Failure**		
	Pressure/Heat (Explosion)[(a)]	**Corrosion (Leak)**	**Pressure/Heat (Fire)**[(a)]
Wall break	X	X	
Dome collapse	X		X
Intertank pipe system break	X	X	
Ventilation system break	X	X	X

(a) Solvent fueled.

Next, the team defined an event volume as the volume of waste in the tank that would be affected by the disruptive event. In this volume, sources and quantities of materials (i.e., fuels, oxidants, and catalysts, etc.) are identified for initiating and sustaining an event along with those materials that could act as energy sinks (e.g., water, chlorinated solvents, other inert materials). Based on an event volume with known chemistry, calculations can be performed to determine net change in key parameters (e.g., net pressure or heat change).

The team also recognized the complex chemistry (radionuclides, organics, and inorganics), physical form (gases, liquids, and solids), and stratification (e.g., number and sequence of domains and their homogeneity) of the tank wastes. The team considered the effects of these diverse factors on initiating and/or sustaining event types when they defined the composition and reactivity of an event volume. The density and flammability of solvents are important properties influencing the composition and reactivity, respectively, of event volumes. Paraffinic hydrocarbons, alkylphosphates, alkylphosphonates, and ketones are less dense than water and therefore can constitute components of an organic-rich layer that could reside on the top of an aqueous liquid layer in a tank. At the other extreme are the chlorinated solvents (e.g., carbon tetrachloride) that are significantly denser than water and would tend to migrate toward the bottoms of tanks. However, unless in great excess, it is likely that chlorinated solvents will dissolve in the other solvent solution if given the opportunity. The former classes of chemicals are largely combustible whereas the latter class of compounds are generally not combustible. Organic complexants tend to be highly water soluble, and their viability as a combustion source is related to the moisture content of their surrounding environment. In a very simplified example of an event volume, a tank may contain an organic liquid surface layer with underlying aqueous and solid layers. The organic surface layer could ignite and start a fire. A heat sink (underlying aqueous layer) and energetic materials in the solid layer underlying the aqueous layer, which may or may not be available for contributing to sustaining the original event, would moderate the event's magnitude.

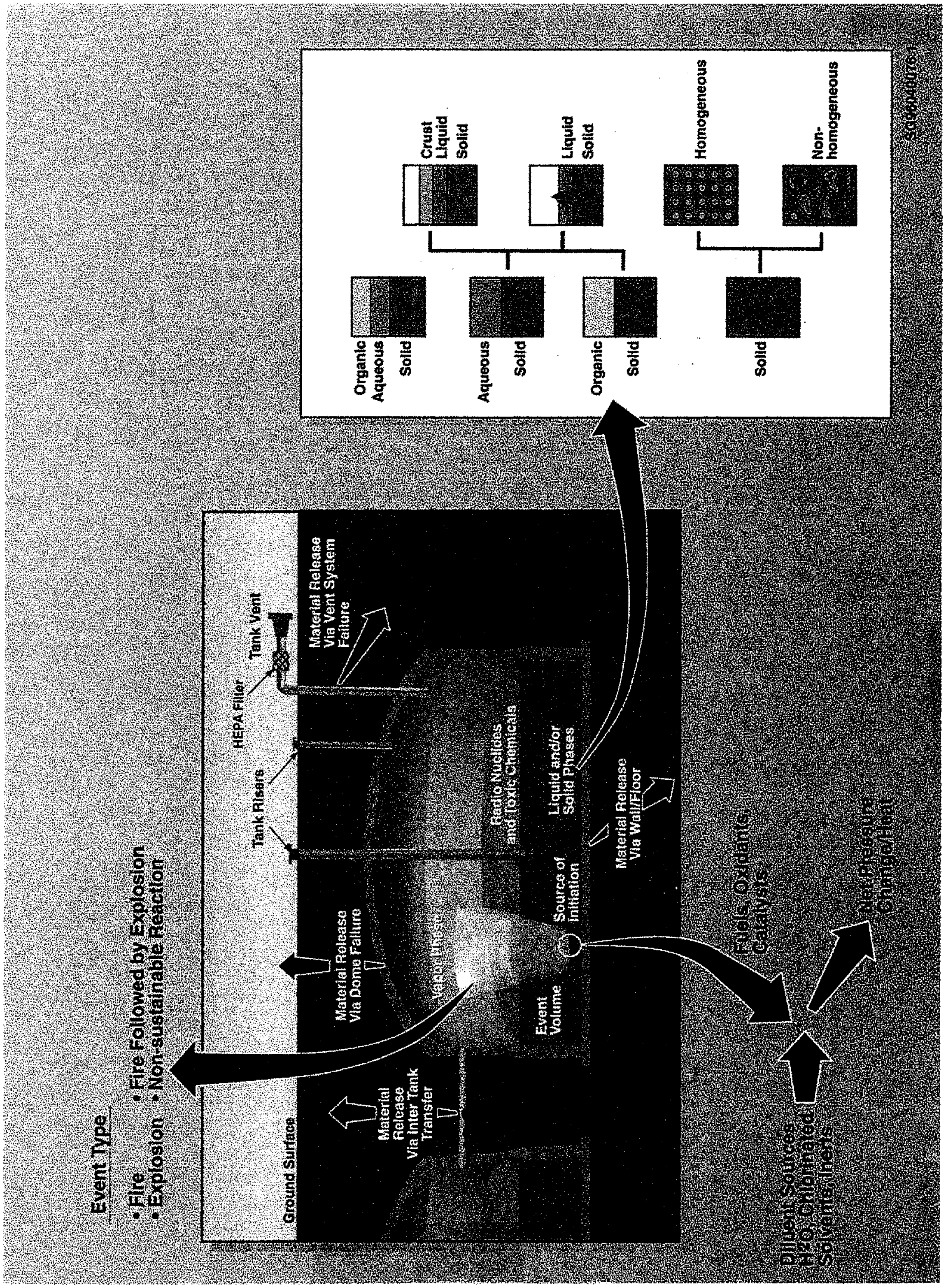


Figure 2.1. Conceptual Model of an Event Involving Organic-Bearing Waste

2.3. Estimating Risk Using Structured Logic Diagram

2.3.1. Quality of Risk Estimate Versus Cost of Characterization

Since risk can be calculated from data through this SLD, it can be represented as a data point with error bars. Figure 2.2 shows four possible risk situations that a user of the SLD may encounter. If risk is determined to be below acceptable limits, no action is necessary. If risk is determined to be above acceptable limits, intervention is necessary. If, however, it is not known whether the risk is above or below acceptable limits, then either intervention or additional characterization is necessary, as determined through further application of the logic diagram. Better characterization data would reduce the uncertainty in determining risk in two of the examples in Figure 2.2, such that "no action" or "intervention required" decisions could be made.

Data needs can generally be satisfied using any one of at least three of the following approaches (see Figure 2.3).

- measure the data from tank samples
- measure the data from simulated tank samples
- estimate the data from a model.

Each of those options has subsets, but the SLD for organics only identified the data that were needed, not the approach to obtaining these data. Each of these three options would have an associated uncertainty, and data uncertainty eventually translates to risk uncertainty in the SLD. Therefore, typically the least expensive (and probably least precise) option should be tried first.

2.3.2. Overview of Structured Logic Diagram

A simplified version of the SLD is depicted in Figure 2.3 (the detailed version of the SLD, along with written descriptions of individual elements of the SLD, is provided in Appendix I). Output at the top of the SLD is information that can be used to determine whether the solvent/complexant contents of a specific tank pose an unacceptable safety risk as a result of an event. Risk in this case is risk probably agreed upon by regulators and managers or the general public, which is acceptable. The user will evaluate the quality of the estimate of risk by considering the accuracy and precision of the data, taking into account the uncertainty of data used at different tier levels in the SLD and error propagation versus the cost incurred. The user might determine that the risk is unacceptable or that it cannot sufficiently be determined based on the uncertainty in applied data accuracy and precision. If so, he/she can use the SLD to identify places where the type and level of sophistication of additional characterization work or model development may be needed to provide sufficient improvement in the quality of the risk estimate

The decision whether to intervene or characterize should be related to cost (fiscal or safety). Figure 2.4 summarizes the cost/uncertainty interrelationships for different tank waste characterization approaches to satisfy the needs of the SLD. None of these methods can provide zero uncertainty, and 100% uncertainty costs nothing. Characterization strategies that do not address the data needs of the SLD give high uncertainty (in relation to the question of risk) and are likely to be the most expensive in the long-term (i.e., circle with asterisk in Figure 2.4). In general, characterization strategies with the least cost will have the most uncertainty and vice versa. Also, more or less rigor can be applied to each strategy leading to variation in the quality of accuracy and precision of individual data sets (i.e., reflected by size of circles in Figure 2.4).

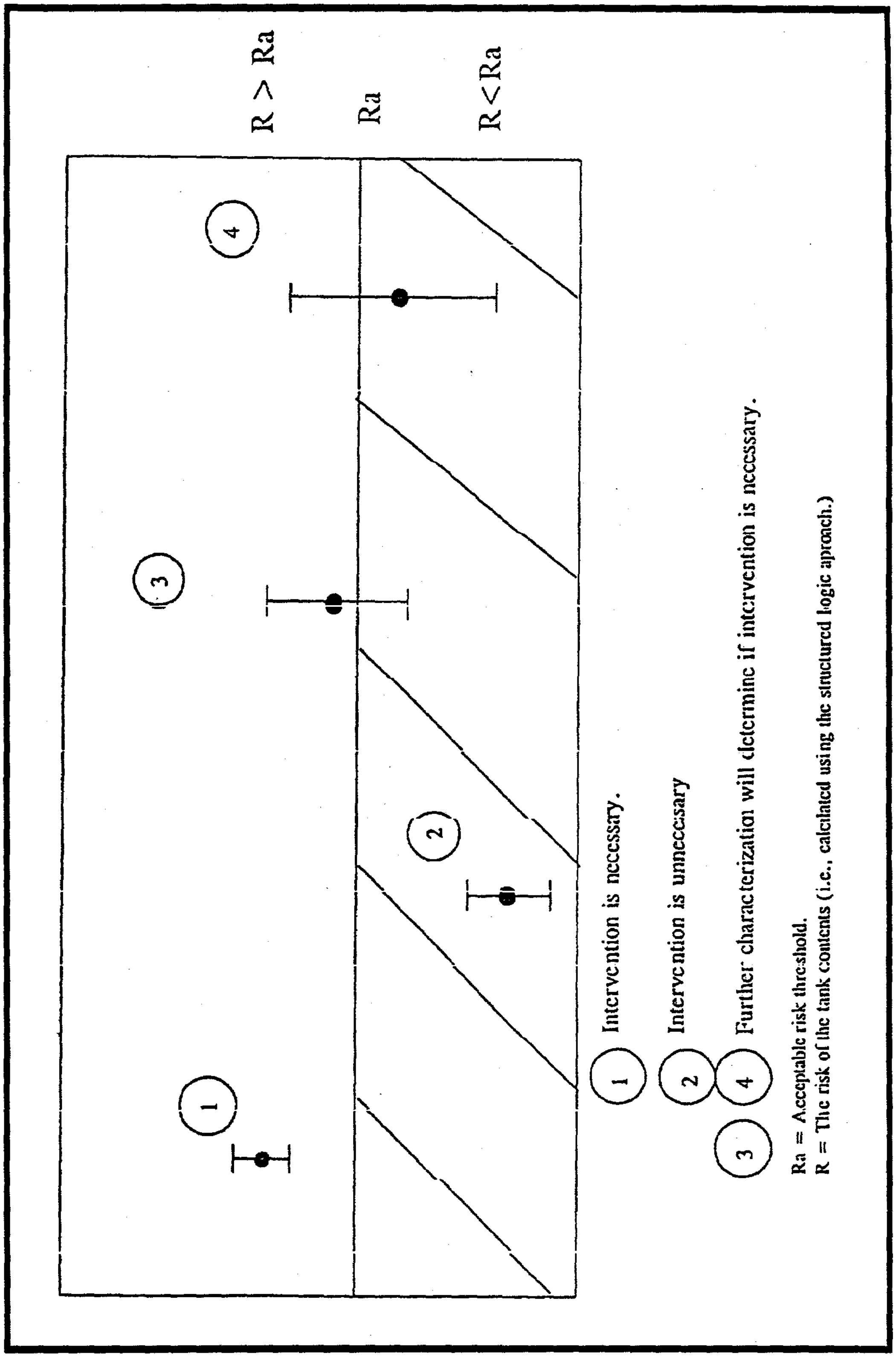


Figure 2.2. Risk Uncertainty Situations

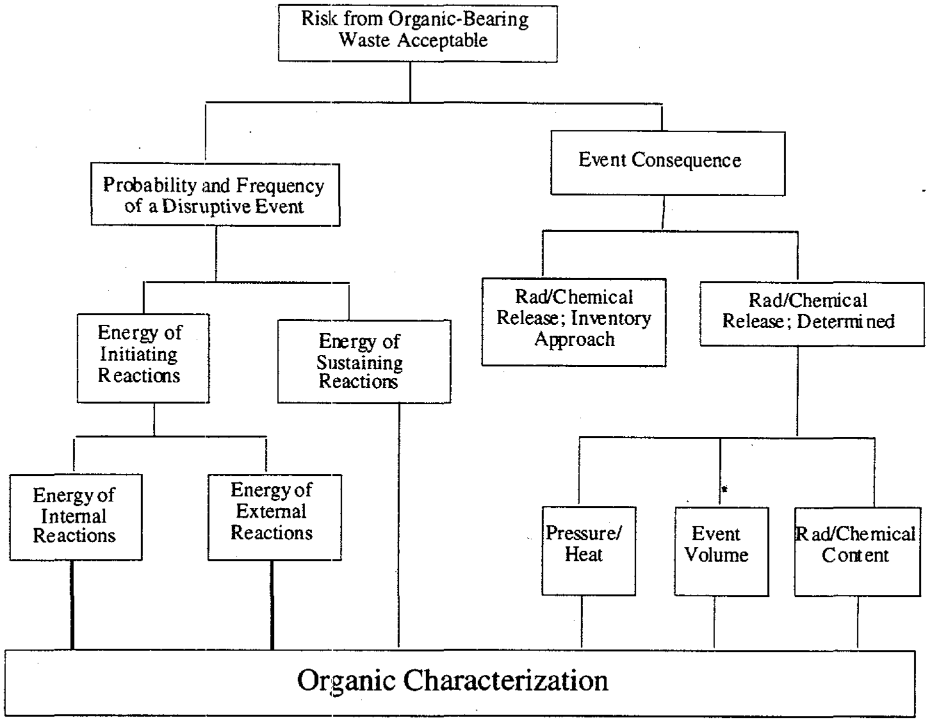
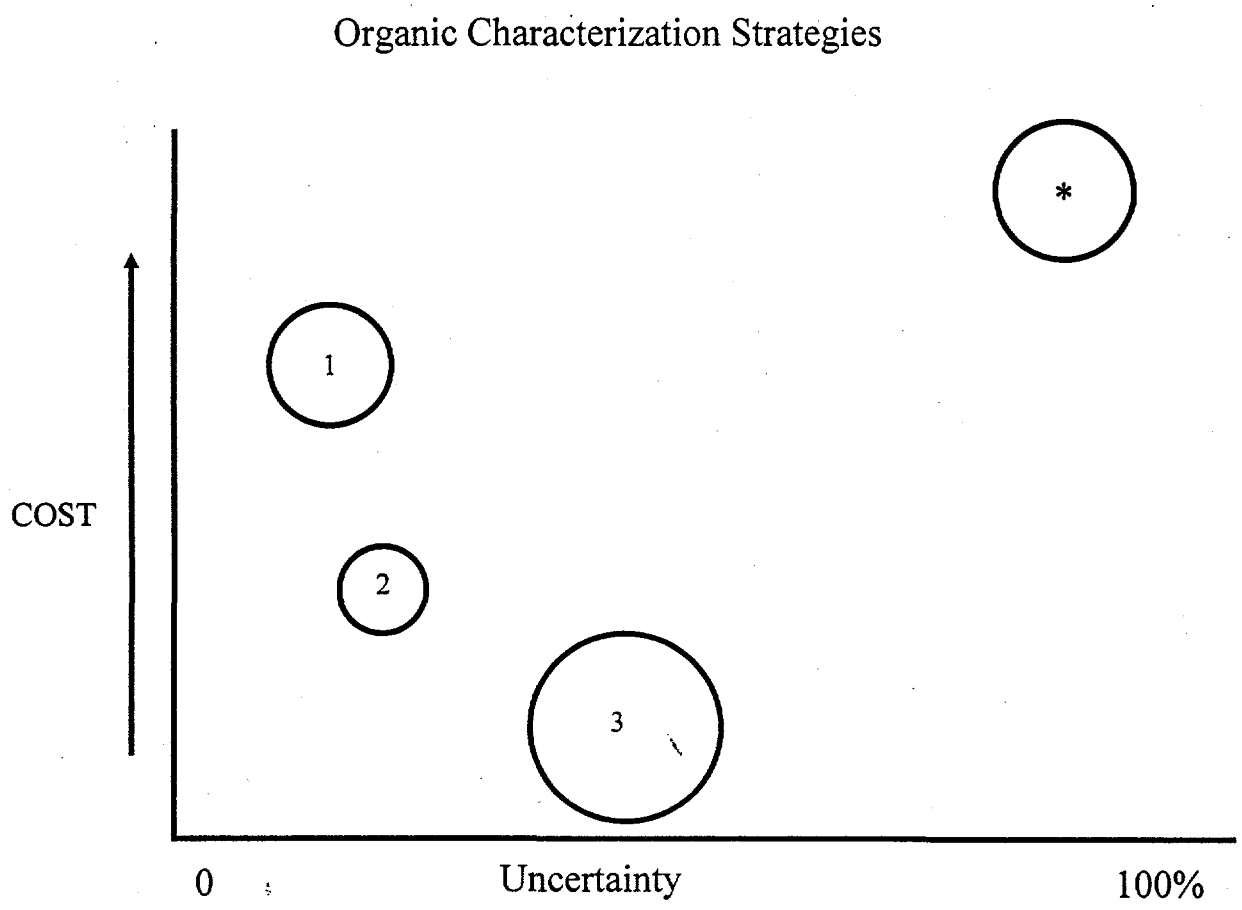


Figure 2.3. Simplified Organic Structured Logic Diagram



* Characterization activities outside the Structured Logic Diagram.
1 Measure data from tank samples.
2 Measure data from simulated tank samples.
3 Estimate the data from a model.

Size of the circle reflects the quality in the accuracy and precision of individual data sets (large reflecting poorer quality).

Figure 2.4. Inter-relationships of Cost and Uncertainty for Different Organic Characterization Strategies

Information on risk is derived by applying a risk model that considers the consequences of an event (radionuclide/chemical dose to humans and the environment). It also considers the probability/frequency of external events (e.g., lightning) and other internal events (e.g., ferrocyanide, initiating reactions) playing a role in initiating the solvent/complexant-containing disruptive (sustaining) event. The probability and frequency of events is determined by comparing the summation of energies of all initiating and sustaining reactions against reaction thresholds. Energies and thresholds are determined from organic characterization and experimentation. Initiating reactions could either be internal or spontaneous, or they could originate from external sources, such as lightning or human error (Appendix C). Energies released by non-organic reactions in the tank were incorporated into the internal initiating reactions.

The radionuclide/chemical dose information under event consequence is derived from exercising a model (see Appendix H) using radionuclide chemical-event release data.

Similar logic is associated with both radionuclide and chemical releases. That is, the risks may be different, but the chances of either one being released are related to critical factors requiring measurement (i.e., pressure, volume, radionuclide/chemical content). The team envisioned two possible sources of radionuclide/chemical event release data. The first source, and the most conservative, assumes that the radionuclide and chemical contents of a tank were completely known and would be used to calculate a total release from a tank (inventory approach). A second source of release information uses radionuclide/chemical data derived from a theoretically calculated event volume (determined). Source-term data from the latter approach are then applied within an ejection model to determine radionuclide/chemical release data. The latter approach is necessary to address some of the excessively conservative elements of the first and most conservative approach.

Information from the latter approach to deriving radionuclide/chemical source-term information is then combined and applied within a model that contains important containment-failure parameters to predict radionuclide/chemical releases for different tank failure scenarios identified by the team. Unlike the inventory approach, this approach takes into account 1) the different types and magnitudes of disruptive events (e.g., explosion and fire), 2) different failure modes (dome, wall and floor, inter-tank, and ventilation system), and 3) different levels of scientific investigation (e.g., thermodynamic and kinetic data acquisition and assessment for initiated and sustained reactions and effects of diluents; waste form, and configuration).

The team determined that changes in pressure (number of moles of gas) and heat of reaction for organic chemical reactions tied to disruptive events were critical parameters to be determined in predicting the type, magnitude, and mode of event failure. Four scenarios for determining these parameters were developed under the element of organic characterization. In case 1, known as the bounding case, total fuel content is assumed to be known, and a model is applied that provides for instantaneous combustion of all the fuel. A second case (intermediate case 1) is the same as the first case except that the model accounts for the effects of fuel distribution. In the third case (intermediate case 2), data for calculating pressure and heat are derived from calorimetry experiments on various waste-material domains. The fourth case is the most rigorous where data for pressure and heat are derived from the thermodynamics and kinetics of all important initiating and sustaining reactions.

3.0 Conclusions

The SLD for organic-bearing waste provides a number of paths of varied levels of sophistication that can be used to determine if the organics in the Hanford tanks pose an acceptable risk. One path is intervention, which is considered early on, before paths involving different levels of waste characterization are considered. Another path to consider early on assumes the probability of an initiating event occurring is equal to one. Both paths are conservative in their estimation of acceptable risk. The presence of these options at high levels within the SLD ensures that options that lead to an estimation of lower risk are not used unless good evidence exists to support our lower risk estimates.

The SLD indicates that four reasons exist to perform an analysis of reactive or toxic species in any waste tank at Hanford: 1) determine whether the probability of an initiating event is high enough to be a risk, 2) determine whether an event would create enough pressure to damage the tank system, 3) determine how much material would be released in an event, and 4) determine the toxicity of the event volume.

If any one of the four characterization results demonstrates that the risk is acceptable, the tank poses no immediate safety concern. However, if the toxicity and radioactivity of released materials were within acceptable limits, a disruptive event would probably still be unacceptable, but the overall risk from an event would be relatively low. If, however, all issues are found to be of concern, the risk of leaving the tank in its current condition would be unacceptable. For example, if the tank contains enough energy to cause damage to the tank, but the probability of an initiating reaction is close to zero, the risk would also be very small. Also, if the probability of an event is high, and the pressure generated by an event could damage the tank, but the amount of toxic or radioactive material was within risk limits, then leaving the tank alone may be an acceptable practice.

4.0 Recommendations

This report provided three reasons for characterizing the organics in tank wastes: 1)to determine the probability of an initiating event, 2) to determine the pressure generated by a sustaining event, and 3) to evaluate how much toxic and radioactive material would be released in an event. All three of these require substantial knowledge of the organic components in the waste. However, estimates can be made based on gross measurements with a high uncertainty. Evaluating the uncertainty through the SLD will determine whether these estimates are adequate to determine whether the risk is greater or less than acceptable limits.

The next level of sophistication in characterizing the organic components could be in measuring organic content and composition from a limited number of regions within the tank. These measurements will also contain certain inherent uncertainties, which taken together with the measured values will help evaluate whether the risk of the waste is acceptable. The advantage of speciation is the clearer picture it provides in determining whether one of the several scenarios is likely.

The concentration of water or other diluents in the organic waste is an important consideration in evaluating reactivity. Some simplifying calculations can be made based on two pieces of information: the total fuel and its dilution (concentration) in the waste. The simplest model assumes no dilution, but the next model takes dilution effects into account. One should be cautioned in oversimplifying tank wastes since generally heterogenous and highly reactive domains may be hidden in the tanks. These domains can either be very small (for initiating reactions) or large (e.g., the floating organic layer in Tank 241-C-103). An alternative to determining the chemical composition of the tank waste, at least for pressure determinations, is to measure the energy of the waste as by adiabatic calorimetry. Measurements like these are being made, but differential scanning calorimetry (DSC) is being used. If DSC[a] could be shown to contain the information needed to calculate the energy and number of moles of gas generated in waste, then these DSC data could be used to help evaluate this branch of the SLD. As more and more domains are evaluated in a tank, the probability that the existing data will represent the remaining waste increases. Staff should be able to apply statistics to decide when they have enough data to determine the risks of the waste.

Nearly all of the characterization strategies described in this report could be used in some manner to estimate the risk of leaving the organic material in the tanks. For example, adiabatic data could be used to estimate whether initiation reactions are likely to occur, the pressure likely to be generated from the tank, or the event volume. Likewise, exhaustive organic analysis could provide adequate information to determine pressure, the probability of initiating reactions, and the event volume. The exception is in the radioactivity and toxicity of the event volume. For these, organic, inorganic, and radionuclide speciation is necessary.

Many of the Hanford tanks have already been categorized into several different areas, including, but not limited to, organic tanks. Placing tanks in categories can be useful, especially in relation to their determined risk. It would be useful, for example, to calculate the risk of leaving the organic materials in each tank based on existing data. The risk could then be used to generate a grading system for each tank. Those with the highest (or lowest) grade could have the greatest risk as determined by the SLD. Existing watchlists could be a starting point for developing these ratings.

(a) DSC normal increases temperature changes as heat is exchanged. Pressure changes are typically not included in the measurement. Therefore, classical DSC measurement would not provide the information needed here.

New and existing organic data should be carefully examined with the SLD in mind. Much of the data generated to date may or may not achieve the goals identified in this SLD. Each tank should be evaluated separately to examine how well the existing data meet the needs defined in the SLD. As an example, research on the correlation between DSC data and bomb calorimetry is recommended to define whether these data can be used to estimate the pressure generated by an event.

This report leaves the reader with a risk-based approach to characterization. At the top of the SLD is a goal: to have acceptable risk. At the bottom of the SLD are characterization needs. These characterization needs are generic rather than specific. For example, the organic reactants may need to be known to satisfy a characterization need. The specific method of obtaining these data has been left to the reader. Identifying that method is a worthy next step. Such a need may be satisfied in numerous ways. These may include analytical chemistry, such as gas chromatography, or estimates from process data or other models. The reader is encouraged to use more than one characterization method to calculate each risk.

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Appendix A

Contributors

Appendix A:Contributors

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J. A. Campbell, Ph.D. analytical chemistry, Montana State University, 1983. Dr. Campbell is a staff scientist at PNNL with 18 years industrial experience. He has developed analytical techniques for the determination of organic components in mixed hazardous wastes from Hanford tanks. He has also organized several symposia on the characterization of DOE tank waste for the American Chemical Society. He is the author of over 100 journal articles, progress reports, symposium proceeding articles, or invited presentations.

G. E. Fryxell, Ph.D., organic chemistry, University of North Carolina, 1986. He then spent 2 years as a postdoctoral fellow at Emory University (Atlanta, Georgia) before coming to PNNL in 1988. Dr. Fryxell is a Senior Research Scientist at PNNL. He has 16 years professional experience as an organic chemist. He has contributed to approximately 60 journal articles, book chapters, invited presentations, and technical reports in the field of organic reaction mechanisms, many addressing mechanisms of molecules associated with surfaces. Dr. Fryxell participated in the "Technical Review of the Pacific Northwest Laboratory Tank Waste Remediation System Safety Projects" (WTSPM:080195) August 1995, and the "Independent Technical Review of the Report "*Hanford Tank Waste is Stored Safely*" by Hans K. Fauske," January 1996.

L. L. Burger,Ph.D., University of Washington, 1948. Dr. Burger is a staff scientist at PNNL (part time). He has over 50 years of research experience in chemistry with approximately 100 publications, mostly in physical chemistry. Recently, he has studied several Hanford tank issues, some of which are sources of tank wastes, including ferrocyanide and organic compounds and associated processes used, a laboratory study of energetic reactions including nitrate-nitrite-NO_x chemistry. He has explored thermodynamic calculations for potential in-tank reactions and high temperature and incineration of wastes. He has also studied iodine and tritium behavior and control in waste-management processes.

R. T. Hallen,MS degree, organic chemistry, Oregon State University, 1981. Mr. Hallen is the project manager for the Tank Waste Remediation System (TWRS) Organic Safety and Ferrocyanide Safety Projects at PNNL. He has 15 years of research experience at Hanford and has been involved with tank-waste chemistry associated with characterization, pretreatment, and disposal. He has published over 50 reports and articles in this field. He has participated in numerous committees/workshops addressing various aspects of Hanford tank waste characterization and disposal.

T. Jones, Ph.D., chemistry, Washington State University, 1974. In his research, he examined the kinetics and thermodynamics of electron-transfer and metal ion complexation reactions. While a postdoctoral research associate at Wayne State University, he investigated heavy metal ion/macrocyclic thiaether complexation reactions. Dr. Jones taught analytical chemistry at the University of New Mexico from 1975 to 1980. Since arriving at the Hanford Site in 1980, he organized and managed an analytical laboratory supporting geohydrological characterization of the

Site as part of the Basalt Waste Isolation Project and conducted material characterization studies of waste package materials in support of the high-level waste repository program. In 1989, he developed and managed an interdisciplinary team providing chemical and physical characterization of highly radioactive materials taken from Hanford's single- and double-shell tanks. In 1992, he became a program manager in the Office of Hanford Environment. For the past year, he has supported DOE's TWRS Privatization in the area of environmental regulatory compliance.

G. S. Klinger, senior research scientist of the Organic Analytical Group of the Analytical Chemistry Laboratory at PNNL. He has analyzed many of the tank core samples from Hanford over the past several years.

B. P. McGrail, Technical Task Leader, participated in meetings and provided an interface with other task activities.

L. Morgan, Ph.D., physical chemistry, Oregon State University, 1978. Project Manager, participated in some key meetings to help keep the group focus in line with the mission of the project.

L. R. Pederson, Ph.D., chemistry, University of Wisconsin-Milwaukee, 1978. Dr. Pederson, a senior staff scientist, is the technical leader of the Materials Synthesis and Modification Group, Materials and Chemical Sciences Department, at PNNL. For the past 5 years, he has studied gas generation and retention in Hanford double shell wastes in support of the Flammable Gas Safety project. He has studied thermal and radiolytic gas-generating reactions and rates of reactions between product gases in the gas phase, evaluated physical properties of wastes such as surface tension and heat capacity, and determined gas solubilities.

R. G. Riley, Ph.D., environmental science and chemistry, Syracuse University, 1974, and Ph.D., chemistry, State University of New York's College of Environmental Science and Forestry, 1974. Dr. Riley is a staff scientist at PNNL. He has 22 years of research, project, and line management experience in using chemistry to solve environmental cleanup and waste management problems. He has over 80 publications in the environmental arena. As a subtask leader, he was recently responsible for compiling and synthesizing environmental data for facility siting in support of the U.S. Department of Energy's TWRS Privatization Phase I Program.

D. S. Sklarew, Ph.D., organic geochemistry, University of Arizona, 1978. Dr. Sklarew is a senior research scientist at PNNL. Her primary interest is in the application of analytical organic chemistry to environmental and geological problems. She has been the editor for organic methods in the DOE Methods Compendium project, which includes methods for analyzing tank wastes, and has contributed to the Tank Vapor database project.

Appendix B

Glossary of Terms

Appendix B: Glossary of Terms

Complexants	Organic species that were initially used to complex with radionuclides during separation processes at Hanford. Wastes from the reprocessing activities were deposited into the tanks. Examples include sodium butyrate, citric acid, acetic acid, oxalic acid, di-2-ethyl hexyl phosphoric acid, and chelators such as EDTA and HEDTA. Degradation products that are complexants are also included in the tank wastes. For more details, see Appendix E.
Disruptive	Violent (sudden) damage to containment (tank walls, dome collapse, etc.).
Domain	Regions of the tank with similar contents.
Event	Either a non-disruptive or disruptive occurrence. A non-disruptive event may be slow and continuous, sudden, or episodic (e.g., corrosion resulting in a leak or a sudden toxic gas release resulting in worker exposure). A disruptive event could potentially cause violent damage to the container (tank) and would typically be associated with an explosion or fire.
Event volume	The volume of material impacted by an event.
Failure	Loss of containment.
Non-disruptive	May include releases of substances on a continuous, periodic, or occasional basis, but not associated with an explosion or fire.
Release	Failure of the tank components resulting in radioactive and/or toxic material escaping outside the confines of the tank boundary.
Secondary Event	An event caused by another event. It may include an explosion (secondary event) caused by loss of ventilation from a high-efficiency particulate air (HEPA) system failure, creating an increase in tank temperature (primary event) or soil erosion resulting in additional leakage.
Solvents	Organic liquids that were initially used at Hanford in reprocessing nuclear fuels. Wastes containing these materials were disposed to the tanks. Example liquids include dibutylbutylphosphonate (DBBP), normal paraffin hydrocarbons (NPH), and tributylphosphate (TBP) (Table 1.1). Degradation products of these solvents are also included.

Appendix C

External Operations that Could Initiate an Organic "Event"

Appendix C: External Operations that Could Initiate an Organic "Event"

A number of external operations or accidents, such as the following, could initiate an organic event: filling, emptying, monitoring (surveillance), pumping, mixing, sluicing, sampling/characterization (core, auger, etc.), materials addition (i.e., more caustic to prevent corrosion), equipment installation, equipment maintenance, replacement, and repair, equipment failure, emergency operations, etc. (see Table C.1).

Accidental initiators can be separated into two categories:

- natural phenomena (lightning, earthquake, volcano, flood)
- human accidents (vehicle fuel, flammable gas burn).

Table C.1. Example Reaction Initiators, With Preliminary Annual Frequencies*

Type of Initiator	Occurrence Probability per Demand	Uncontrolled Frequency	Controlled Frequency
1. Electrical Arcs	1.0E-2	3.0E-2	3.0E-3
2. Grinding	1.0E-3	5.0E-3	5.0E-4
3. Welding	1.0E-3	5.0E-3	5.0E-4
4. Vehicle Fire	3.3E-6	2.3E-4	2.3E-6
5. Core Drilling	1.0E-0	3.4E-0	2.3E-4
6. Lightning	1.0E-0	4.5E-4	4.5E-5
7. Flammable Gas	1.0E-0	1.0E-4	2.0E-7
8. Combustion Gas	1.0E-0	?	?
9. Solvent	1.0E-1	1.0E-2	?
10. Bulk Heatup	Not probabilistic; applicable only to Tank C-106.		

*Provided by Westinghouse Hanford Company (WHC).

Hazard Analysis is defined in DOE-STD-3009-94, "Preparation Guide for US DOE Nonreactor Nuclear Facility Safety Analysis Reports."

WHC specifies risk acceptance guidelines in WHC-CM-4-46.

Appendix D
Organic Fuel-Salt Reactions

Appendix D: Organic Fuel-Salt Reactions

Most organic compounds can be burned in air, releasing considerable energy (see Appendix G). The same compounds may react with oxidizing inorganic salts such as nitrates and nitrites if the temperature is raised above a critical point, commonly in the vicinity of 200 to 300°C. Since the Hanford waste tanks contain a variety of organic materials such as solvents, diluents, and complexing agents, and large amounts of sodium nitrate and sodium nitrite, potentially hazardous exothermic reactions are possible under some conditions.

The most simple example might be the reaction of sodium nitrate with a hydrocarbon such as decane

$$C_{10}H_{22} + 12.4 NaNO_3 = 6.2\ Na_2CO_3 + 3.8\ CO_2 + 11\ H_2O + 6.2\ N_2 \qquad \Delta H = -5063\ kJ \qquad (D.1)$$

indicating formation of sodium carbonate, carbon dioxide and water with the liberation of 5063 k J of heat per mol of decane, or 35.6 kJ per gram. Actually, this particular reaction does not proceed efficiently as the decane is not sufficiently reactive, and unless the reactants are confined, most of the decane just volatilizes as the temperature is raised. More likely reactions are seen in the following examples (Burger 1995):

$$NaCH_3COO + 1.6\ NaNO_3 = 1.3\ Na_2CO_3 + 0.7\ CO_2 + 1.5\ H_2O + 0.8\ N_2 \qquad \Delta H = -651\ kJ \qquad (D.2)$$

$$Na_3C_6H_5O_7 + 3.6\ NaNO_3 = 3.3\ Na_2CO_3 + 2.7\ CO_2 + 2.5\ H_2O + 1.8\ N_2 \qquad \Delta H = -1460\ kJ \qquad (D.3)$$

$$NaCH_2OHCOO + 1.2\ NaNO_3 = 1.1\ Na_2CO_3 + 0.9\ CO_2 + 1.5\ H_2O + 0.6\ N_2 \qquad \Delta H = -498\ kJ \qquad (D.4)$$

$$NaCHOO + 0.4\ NaNO_3 = 0.833\ Na_2CO_3 + 0.3\ CO_2 + 0.5\ H_2O + 0.2\ N_2 \qquad \Delta H = -176\ kJ \qquad (D.5)$$

Similar reactions will occur with sodium nitrite as oxidant, for example, for sodium acetate

$$NaCH_3COO + 2.67\ NaNO_2 = 1.83\ Na_2CO_3 + 0.17\ CO_2 + 1.5\ H_2O + 1.3\ N_2 \qquad \Delta H = -840\ kJ \qquad (D.6)$$

The reaction may proceed by a different path, for example, producing nitrous oxide in place of nitrogen. This reduces the energy produced; for sodium acetate reacting with sodium nitrate, ΔH becomes -530 kJ in place of -651. Other potential products are nitric oxide and carbon monoxide. On the other hand, only part of the organic compound may be oxidized.

For the Hanford tanks, it is generally more realistic to assume an excess of caustic, (NaOH), in which case any excess CO_2 is converted to Na_2CO_3.

Other compounds contain both fuel and oxidant, e.g.,

$$NH_4NO_3 = N_2O + 2H_2O \qquad \Delta H = -200\ kJ \qquad (D.7)$$

Since these reactions are exothermic, the reaction rate will theoretically continue to increase until an explosion occurs. This has been demonstrated for some of the compounds (Kozlowski and Bartholomew 1968; Fisher 1990). On the other hand, if the system is not adiabatic (heat is lost from the reaction mixture), or if the reaction mixture has enough inert material to absorb the heat produced, then the reaction may never proceed. These inert materials can differ widely in their heat capacities. Thus it is important to know the composition of the tank waste, not only the fuel and oxidant, but also the diluent materials such as water, sodium aluminate, sodium carbonate, sodium hydroxide, etc. The distribution within the tank also becomes significant.

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Appendix E

Formation of High Energy Metal Complexes as Potential Initiators

Appendix E: Formation of High Energy Metal Complexes as Potential Initiators

Over the 50 years of operations at Hanford, significant quantities of organic and inorganic complexing agents were used during various separations processes. Much of this material is assumed to be incorporated in the waste materials stored in high-level waste tanks. It is also assumed that many of the complexing agents, particularly the aminopolycarboxylic acids such as ethylenediaminetetraacetate (EDTA), N-(2-hydroxyethyl) ethylenediaminetriacetic acid (HEDTA), NTA, etc., used in the processes will have decomposed to other species. Finally, it is assumed that in the metal ion-rich waste tank environment, most of the complexing reagents will be associated with metal ions.

A major impact of having complexing agents incorporated in the waste tank material is the possibility of direct exothermic oxidation by nitrate/nitrite salts described in Appendix D. A second impact is the formation of metal complexes themselves and the effect on metal solubility. For example, the concentrations of some metal ions could be much higher in the aqueous phase than would be predicted based on metal solubility data. Thus, complexation of radioactive metal ions could impact the consequences of a tank leak or predicted sorption behavior in the soil column. Also, complexation will have an effect on the oxidation-reduction (redox) chemistry for metal ion couples.

It is known from both tank analysis data and historical records that the tanks contain a broad spectrum of metal ions. For example, mercury was added during separation processes. Additionally, silver nitrate filters were used at Hanford reprocessing plants during the plutonium production campaigns. The silver iodine adsorber or silver reactor (Burger 1991) consisted of a column of Berl saddles that were coated with silver nitrate and supported by wire mesh. The reactor trapped iodine by forming silver iodate and silver iodide. The reactor was regenerated by adding fresh silver nitrate solution. It is uncertain whether the spent silver nitrate and excess rinse solutions were deposited in cribs or in tanks. For the purposes of this discussion, it is reasonable to assume that some of this material found its way into tanks. Other chemical compounds that could form potentially unstable complexes are also found in tanks (Gerber et al. 1994).

If silver were deposited in the tanks, some interesting reactions could occur. Silver will form ammoniacal silver complexes in the presence of hydroxide ion, ammonia, and some simple amines (Jenkins 1987; Mellor 1967a; Mellor 1967b; Bailar 1973; Bjerrum 1942).

$$AgNO_3(a) + 2NH_4OH(aq) \text{ -> } Ag(NH_3)_2NO_3(aq) + 2H_2O \qquad \Delta H = -15.3 \text{ kJ} \qquad (E.1)$$

Likewise, mercury also forms ammoniacal complexes such as $Hg(NH_3)_2^{2+}$, $Hg(NH_3)_3^{2+}$, and $Hg(NH_3)_4^{2+}$ under similar conditions (King 1994).

The ammoniacal silver ion is the basis for the Tollens' reagent test for aldehydes. Tollens' reagent is typically prepared by dissolving silver nitrate in a solution of sodium hydroxide and then adding ammonium hydroxide. Aged Tollens' reagent is known to form silver nitride (Ag_3N) and it is speculated that silver imide (Ag_2NH) also forms (Jenkins 1987) both of which are unstable and release considerable energy on decomposition. The pathway or the mechanism by which the $Ag(NH_3)_2^+$ ion converts to the metal nitride or imide could not be found in the brief literature survey conducted. We could speculate that silver amide is first formed and that further condensation leads to the formation of the nitride. However, it is unlikely that in the alkaline matrix of tank waste that any silver azide (AgN_3) is formed.

During a brief literature search, no references to amines larger than CH_3NH_2 forming these complexes with Ag and Hg could be found, but it could be presumed that larger amines also have the potential to form these energetic complexes. Other so called "fulminating" metals include gold and platinum nitrides. It is not unlikely that palladium, which is a fission product and a decay product of ruthenium, might also form an unstable nitride.

Formation of these metal nitrides cannot be ruled out under conditions in tanks that contain excess hydroxyl ion, ammonia, and small amines, and this should be investigated.

A number of metal oxalate complexes are known to be thermally unstable and shock sensitive (Bretherick 1990). These include the oxalate complexes of Ag, Hg, and Fe. In the aqueous environment, these materials are generally benign. However, in the absence of water, the oxalate metal complexes are both thermodynamically and kinetically unstable, leading to cause for concern when a fuel/oxidant mixture containing certain metal complexes becomes dehydrated. Thus, saltcake could be saturated with organic solvents, and this could be done at a temperature great enough to remove remaining water. Given the lack of understanding of tank chemistry, one cannot speculate on the chances that this situation might exist in any of the Hanford tanks.

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Appendix F

Unstable Organic Reactions

Appendix F: Unstable Organic Reactions

The organic components of the Hanford tank wastes are largely comprised of normal paraffinic hydrocarbons (NPH, C_{12}-C_{15}), tributylphosphate (TBP), and various organic complexants (e.g., ethylenediaminetetraacetate [EDTA]). The chemical conditions of the tanks include highly alkaline conditions (pH ≈ 12), high nitrite/nitrate concentrations, warm temperatures (50 to 60°C) and high radiation fluxes. This combination results in a unique set of conditions for chemically changing the organics in that the nitrite/nitrate provides for their oxidation, whereas radiolytic breakdown of the organics releases free electrons capable of reducing portions of the organic components.

The Hanford tank wastes have been slowly giving off heat and breaking down over a period of many years. The result of this is that the energy contents of the waste as a whole are steadily decreasing(Webb et al. 1995). However, the fact that total energy content is decreasing does not preclude a small portion of the components from being converted into high-energy species. Due to the high nitrate/nitrite content of the wastes, the species of obvious concern would be the nitroalkanes and nitrate esters. One viable mechanism for forming these compounds would involve trapping alkyl radicals by nitrite or nitrate in an $S_{RN}1$-like process (Bunnett 1978; Saveant 1980; Rossi 1982; Korblum et al. 1987).

$$R\cdot + NO_2^- \text{------>} [R\text{-}NO_2]^{-\cdot} \text{------>} R\text{-}NO_2 + e^- \qquad (F.1)$$

$$R\cdot + NO_3^- \text{------>} [R\text{-}ONO_2]^{-\cdot} \text{------>} R\text{-}ONO_2 + e^- \qquad (F.2)$$

It would also be possible to form potentially explosive diazoalkanes under these conditions. These compounds are not likely to accumulate as they are rather fragile and decompose by a variety of pathways (thermal, photochemical, and catalytic by Rh, Ag, Cu and Ni) (Gilchrist and Rees 1969); however, they could possibly serve as an exothermic initiator for other chemistry.

$$R_2CH\cdot + N_2O \text{------>} R_2CH - N = NO \qquad (F.3)$$

$$R_2CH - N = NO\cdot \quad H_2O + e^- \text{------>} R_2CH\text{-}N = N - OH + OH^- \qquad (F.4)$$

$$R_2CH - N = N - OH + OH^- \text{------>} R_2C = N = N + OH^- + H_2O \qquad (F.5)$$

In addition, the decomposition of the waste components can provide a chemical feedstock for the metallic components, which can combine to form other high-energy compounds. For example, inorganic cyanides and isocyanates have been found in the tanks. These are not directly cause for concern; however, related species would include mixed metallic oxide/cyanides (some of which are explosive, e.g., mercury [Weast 1980a]) and fulminates. Once again, these explosive compounds could serve as initiators for other exothermic chemistry.

If any primary acetylenes are formed as the organic components of the waste decompose, the silver that is known to be in the tanks could easily react to form the corresponding silver acetylide. These are known to be unstable compounds and explode easily.

Another decomposition product of the tank waste is oxalate. Certain metal complexes of oxalate are known to be explosive. Of particular interest to the current discussion is the unstable silver oxalate (Weast 1980b).

Taken as a whole, it seems reasonable that the Hanford tank wastes do indeed produce measurable quantities of high-energy compounds capable of initiating an exothermic reaction. However, due to the unusual reaction conditions of the tank waste (continual heating, high rad doses, nitrate/nitrite oxidation, free radicals and free electrons), the longevity of these energetic species is highly uncertain.

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Appendix G

Organic Oxidation Reactions

Appendix G: Organic Oxidation Reactions

Organic Fuel Burn

Organic compounds in Hanford waste tanks consist mainly of n-paraffin hydrocarbons (NPH), phosphate esters such as tributyl phosphate (TBP), methyl isobutyl ketone (MIBK), complexants, and their degradation products. The possibility that these compounds could be involved in an organic fuel burn is one scenario to be considered in the logic diagram.

An organic fuel burn requires both a source of organic fuel and oxygen for combustion. A burn could potentially occur if sufficient organic material can volatilize, thereby exceeding its flammability limit in the vapor phase. Lower and upper flammability limits for several compounds that may be in tank headspaces are given in Table G.1 (Johnson and Auth 1951; Gerber et al. 1992). Organics in a floating organic layer or in pore spaces in solids close to the surface (from which they can migrate to the surface) are the likely sources for a fuel burn. Oxygen is available in the tank headspace because the ventilation system is open to the atmosphere.

Table G.1. Flammability Limits[a,b]

Compound	Lower Limit	Upper Limit
Pentane	1.4	8.0
Butanol	1.6	8.5
MIBK	1.4	
Ethanol	3.7	13.7

(a) Percent by volume, given at 25°C and atmospheric pressure.

(b) Defined as the limiting composition of a combustible gas in air, beyond which the mixture will not ignite and continue to burn.

Mixtures of hydrocarbons and oxygen react very slowly at temperatures less than 200°C. Combustion is typically started at a single point by some external source of heat, and the heat developed by combustion serves to raise the rest of the mixture to the ignition temperature (Johnson and Auth 1951). External materials may facilitate combustion. For example, aldehydes (which are known degradation products of TBP and NPH) can catalyze the reaction (Glassman 1977); a piece of hot metal may transfer sufficient energy to the system to initiate combustion. However, for combustion to occur, the proportions of fuel and air must be within the limits of flammability. Large quantities of water vapor will raise the lower flammability limit (Gerber et al. 1992), whereas an increase in temperature tends to decrease the lower flammability limit (Johnson and Auth 1951). The concentration of oxygen may be diluted by carbon dioxide and water vapor in the headspace, decreasing the flammability of the fuel. See Gerber et al. (1992) for a more complete discussion and Postma et al. (1994) for a discussion of flammability issues in Tank 241-C-103.

Combustion reactions can potentially lead to pressure failures in the tank because they are highly exothermic and gas generating. Examples of possible combustion reactions are given with ΔH

found in the CRC Handbook (and modified for water vapor) or calculated from ΔH_f found in Burger (1995) or Glassman (1977).

$C_{10}H_{22}$ (l) + 15.5 O_2 = 10 CO_2 +11 H_2O (g) $\Delta H = -6294$ kJ $\Delta n_g = 5.5$ (G.1)

$C_{12}H_{26}$ (l) + 18.5 O_2 = 12 CO_2 + 13 H_2O (g) $\Delta H = -7518$ kJ $\Delta n_g = 6.5$ (G.2)

C_5H_{12} (l) + 8 O_2 = 5 CO_2 + 6 H_2O (g) $\Delta H = -3274$ kJ $\Delta n_g = 3$ (G.3)

$C_4H_{10}O$ (l) (butanol) + 6 O_2 = 4 CO_2 + 5 H_2O (g) $\Delta H = -2454$ kJ $\Delta n_g = 3$ (G.4)

$C_6H_{12}O$ (l) (MIBK) + 8.5 O_2 = 6 CO_2 + 6 H_2O (g) $\Delta H = -3483$ kJ $\Delta n_g = 3.5$ (G.5)

$C_{12}H_{27}PO_4$ (l) (TBP) + 18 O_2 = 12 CO_2 + 12 H_2O (g) + H_3PO_4 (l)(a) $\Delta H = -6473$ kJ $\Delta n_g = 6$ (G.6)

(a) P could be converted to H_3PO_4 if sufficient water is available; otherwise it could go to P_2O_5. H_3PO_4

$Na_4C_{10}H_{12}N_2O_8$ (EDTA)(b) + 10 O_2 = 8 CO_2 + 6 H_2O (g) + N_2 + 2Na_2CO_3 $\Delta H = -3015$ kJ $\Delta ng = 5$ (G.7)

(b) At the pH of the waste tanks, EDTA would be a Na+ salt or other metal complex, either in aqueous solution or as a solid. For EDTA to be available as a fuel, it would most likely be present as a solid.

Here, Δn_g is the change in the number of modes of gas produced; ΔH is the change in ehthralopy. The reactions above assume complete combustion. Lower temperature oxidation may form many compounds that are not as oxidized as CO_2 and H_2O; these reactions produce less energy. Also, degradation by partial oxidation of compounds in the tanks (to form ketones, aldehydes, alcohols, acids, etc.) lowers the potential total energy available for combustion reactions. Volatilization of moderately volatile compounds may be incomplete leading to less fuel available for combustion.

The exothermic reactions described above could be a source of heat to initiate other reactions if the heat is not dissipated in a timely fashion, e.g., an organic fuel-salt reaction (Appendix D), or if vaporized and combusted materials condensed on the dome of the tank. Heat may dissipate, however, because of inert materials, such as water, chlorinated solvents, aluminates, etc., which can absorb the heat generated and/or can be vaporized. For example, in the case of an organic floating layer overlying a water layer, the extent of heat dissipation would depend on the thickness of the water layer, the composition of the water layer, other physical and chemical properties of the water layer, and the heat generated by the burn.

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Appendix H

Model Descriptions

Appendix H: Model Descriptions

The structured logic diagram shown in Appendix J uses models in a number of places to generate data for making decisions and assessing data. The lower tiers of the diagram, (those closest to terminal data inputs) generally use chemical models, i.e., the rigorous approach (Appendix J, Org-13), the intermediate approaches (Appendix J, Org-11), the radioactive source-term determination (Appendix J, Org-3), and the initiating reactions (Appendix J, Org-14). Two common types of chemical models that are used are thermodynamic and kinetics computer models. Thermodynamic models can include software with a thermochemical database. This database may contain information on each chemical compound, such as enthalpy, entropy, and heat capacity. Software uses information from the database to apply mathematical equations to predict reaction products, equilibrium, and heat and material balance. Kinetics models function much the same as thermodynamics models. A database of rate constants can be used to predict reaction rates in a system as a function of various temperatures, pressures, composition, etc. When thermodynamic or kinetic data are not available, theoretical data can be developed to augment what is known.

More sophisticated models are employed when chemical reactions are not known or well understood. Such models calculate potential reactions, heats of formation, and thermodynamic properties, based on factors such as bond energy and geometry, charge, and other surface characteristics, including Van der Waals forces, water solvation, hydrogen bonding, dipole interactions, etc.

Fluid dynamics models are also used extensively. Generally, these are finite-element-analysis models that calculate hydrodynamic pressure as a function of space and time for a given geometry and flow situation. These models are used at various points in the logic diagram to calculate the forces produced for gas and/or heat generating reactions. Fluid dynamics models are found in the source-term determination branches (Appendix J, Org-3 and Org-4). They are often used in conjunction with structural models.

Structural models are generally finite element analysis models (or some derivative such as finite difference) that are used to model the effects of forces on solid materials. They are used in the event-consequence branch (Appendix J, Org-1) in conjunction with fluids models to calculate the event volume and the material ejected from the tank.

The diagram has several places where a hybrid of one or more models is used, i.e., a chemical and fluid dynamics model or a fluid dynamics and structural model. Hybrid models reflect the state of the art in modeling. Examples of hybrid models are those used by industry to model internal combustion engines, explosions, and the effects of weather on building structures.

Atmospheric dispersion models have a database component that stores the physical properties of chemicals (e.g., vapor density, vapor pressure), as well as other kinds of information. These models predict gas phase and/or particle concentrations of chemicals as a function of space and time based upon atmospheric conditions such as wind, inversion height, solar radiation, ground roughness, etc. This model can be used to predict the chemical or radiological plume characteristics and depositional patterns resulting from a containment failure (Appendix J, Org-1).

Dose and environmental models are used at the same point in the diagram as the dispersion model (Appendix J, Org-1). These models use a chemical database that incorporates physical constants and partitioning coefficients (e.g., n-octanol/water distribution coefficient, Henry's law constants) and other chemical properties and output from, for example, an atmospheric dispersion model to determine the fate of the material released in a disruptive event to an environmental or human receptor.

Models for predicting aging mechanisms (of tank waste) and rates need to be developed; otherwise tanks would need to be characterized repeatedly. Aging models are not incorporated into the structured logic diagram (SLD) because the SLD only applies to an instant in time. The aging model would allow the SLD to be applicable (unmodified) over a longer period, but their application would also influence the uncertainty of (both data and risk. Another way of looking at it is that the SLD applies to all times, but aging or other perturbations influence the data and therefore the risk.

Appendix I

An Introduction to Structured Logic Diagrams

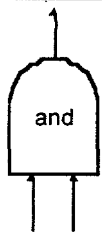
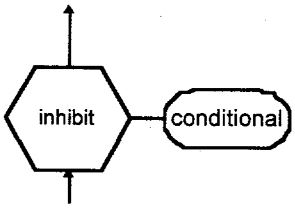
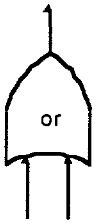
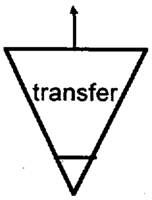
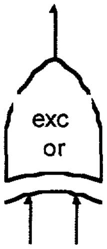
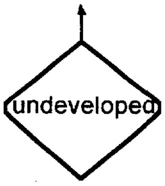
Appendix I: An Introduction to Structured Logic Diagrams

Logic diagrams are often used in business, science, and engineering to communicate interrelationships or sequences of facts or events that lead to an inevitable or predictable outcome. Many types of logic diagrams have been developed for different purposes. Flow charts are often used in computer science to represent the sequence of instructions that a computer program will execute. Gantt and PERT charts show inter-task dependencies and time required and percent complete of various tasks. Spider diagrams are excellent for representing functional area relationships. However, a key problem with using many of these types of diagrams is that formal rules for their construction and interpretation do not exist. Hence, for applications where system reliability or risk assessment is important, logic diagrams that impose a formalized structure for their construction and interpretation are preferred. Some examples of these types of diagrams include ordered binary decision diagrams (OBDDs) that have found widespread use in the formal verification, logic synthesis, and test generation of digital circuits, and fault trees that have been used extensively in the nuclear power industry for system reliability and failure analysis.

The structured logic diagram (SLD) is a construct developed by B. Peter McGrail that extends and expands the "fault" tree methodology so that it may be applied to complex problems that are not necessarily related to hardware system failures. First and foremost, the SLD method abandons the concept of defining a "system fault" as the top event in the tree. The SLD is a "success" oriented analysis method where the top event is defined as the *desired* objective. The diagram is then constructed using *deductive* reasoning and a set of standard logic gates that are defined in Table I.1. The key advantage of this approach is that it is holistic, i.e., *all* possible paths to achieve the top objective are considered. As a result, the SLD reveals the full scope of the problem domain. The second key distinction between a fault tree and the SLD is that the bottom of tree is no longer a failure mode for a particular hardware component. In the SLD, the bottom of the tree is defined as the *tree resolution*, normally corresponding to a parameter or data need. For example, a parameter in SLD might be the concentration of a particular chemical element or temperature. The selection of the tree resolution is arbitrary. However, it is possible to extend the SLD to very low resolutions, even to specifying measurement and data-analysis techniques.

After the SLD has been constructed, both qualitative and quantitative analysis techniques can be applied to extract additional information. For example, the SLD can be analyzed to develop a type of proof that guarantees the occurrence of the top event by generating *cut sets* for the top event. A cut set is a collection of basic parameters or data needs at the tree resolution that, when obtained, guarantee the occurrence of the top event through a specific path in the SLD. The union of all cut sets represents coverage of all possible paths through the SLD and, hence, represents a proof that the top event will occur. A secondary benefit of generating cut sets is that they effectively collapse a complex SLD to focus on the fundamental data needs that are required if the top objective is to be met.

Table I.1. SLD Logic Gates and Descriptions

	Two or more inputs must occur in any order to exit the gate.		The input value must meet the condition specified to exit the gate.
	Two or more inputs must occur in left-to-right order to exit the gate.		Parameter or information need that represents the resolution limit of the SLD.
	Any one of two or more inputs must occur to exit the gate.		Transfers to another branch if it is located on the same page.
	Any one, but not more than one, of the inputs must occur to exit the gate.		Transfers to another branch of the SLD that is located off the current page.
	A process or data need that is outside the scope of SLD or will be developed at a later date.		

Because fault trees represent binary failures of hardware components at the tree resolution, it is possible to apply Boolean algebraic rules to propagate reliability data through the tree. Because the tree resolution of a SLD has no such binary failure definition, the simple reliability-analysis techniques used for fault trees no longer apply. In principle, it is possible to propagate uncertainty and variability in the parameters at the tree resolution through a SLD, provided mathematical or statistical methods of error propagation can be applied to the processes represented at each level in the SLD. If so, the quantitative analysis of the SLD provides an extraordinarily powerful tool for conducting sensitivity and uncertainty analysis. It is this potential for assessing uncertainty associated with the top event that provides a link for using SLDs in risk-based decision analysis.

In summary, the SLD is a simple but powerful technique for analyzing complex technical problems. The SLD must be prepared by experts that thoroughly understand the underlying phenomenology. Once developed, the SLD makes it easy to assess the completeness and adequacy of the analysis to any expert peer. Omissions, incorrect assumptions, and incomplete logic pathways can be quickly discovered and corrected. If the SLD is made part of a stable technical basis, it can be expected to mature with rapid elimination of error, and it can include new scientific understanding as it becomes available.

Appendix J

Description of Detailed Structured Logic Diagram for the Organic Solvents/Complexants Safety Issue

Appendix J: Description of Detailed Structured Logic Diagram for the Organic Solvents/Complexants Safety Issue

Explanation of the Individual Elements of the Structured Logic Diagram (SLD)

Organic Risk

The statement "The risk associated with having organic solvents in tank waste is acceptable.." was the starting point of this task. The goal was to determine the data needed to be able to safely make this statement. After the SLD was completed, the team examined logic for organic complexants. The logic for both organic solvents and complexants was found to be nearly identical. The difference was in the types of reactions that may be responsible for either an initiating or a sustaining event. While solvents may be responsible for either an organic-fire (Appendix G) or an organic-salt (e.g., organic-nitrate) reaction (Appendix D), complexants could either produce violent reactions from unstable complexes (Appendix E), produce other reactions from unstable organics (Appendix F), or contribute to corrosion. Below the risk statement is a choice of two options. Either the risk is less than or equal to what is acceptable, or intervention is needed.

This SLD assumes that any organics placed in the tanks that fall outside these two categories (solvents and complexants) do not pose a significant safety hazard. An example of where this assumption may not hold is for the disposal of laboratory animals in the tanks. Much of the organic material from these animals will not all fall within the two categories that were selected.

Consequences and Probability

The risk gate ($R_F \leq R_a$) is connected to a "conditional and" statement. This suggests that three things need to take place in the listed order. First, the probability and frequency of an event must be determined, then the consequences of an event must be determined, and finally, a model that calculates risk must be applied.

An event includes both a disruptive reaction and a release of hazardous and/or toxic material to the environment. Examples of non-disruptive events include corrosion that may lead to a slow leak of toxic or radioactive material, failure of the ventilation system, or an organic burn that did not compromise the integrity of the tank. Operator errors were considered outside our scope because such events can cover a wide range of possibilities that may have little to do with tank chemistry. The disruptive event risks were the main focus of this task because they could be calculated from characterization data and could potentially result in severe safety hazards.

The probability and frequency of an event occurring is related to the energy released and frequency of an initiating reaction, the rate of energy release from other events, the rate at which the initiating energy is dissipated, and the energy required by a sustaining reaction. These determinations can be avoided by assuming that the probability of an initiation is unity. This may be a reasonable assumption for many of the USTs because the temperature of the tanks is above ambient, probably either due to the release of radiolytic energy, chemical energy, or both. The chemical energy is likely to be that released from reactions similar or identical to those that could cause an event. Initiating reactions can either be from internal or external sources. Examples of external sources include lighting and human factors. More examples of external initiating factors are listed in Appendix C along with their probabilities and frequencies of occurring.

The probability and frequency of an internal initiation reaction creating an event is related to whether that initial reaction event has enough energy to overcome the activation energy required to start the sustaining event (Org. 12). Internal initiating events can either be related to the presence of organic materials in the tank or can be caused by other reactions. Organic initiating events could include the rapid decomposition of unstable organics (Appendix F), organic fuel-salt reactions (Appendix D), unstable chelator/metal reactions (Appendix E), or other types. Nonorganic internal initiating reactions include those from ferrocyanide, flammable gas, and other tank reactions that are outside the scope of this task. Some typical organic sustaining reactions include an organic burn and organic/salt reactions (Table J.1). If an internal initiating reaction has enough energy to overcome the energy barrier of the sustaining reaction, then the sustaining reaction is more likely to occur. The risk of the sustaining reaction taking place, coupled with the risk of a release from that reaction, will determine whether intervention is necessary.

Consequences of an Event (Org-1)

The safety consequences of an event (Org-1) can be determined if the consequences of the toxic and radiolytic exposure are determined. The impact of an explosion is a safety concern, but this issue was considered outside the scope of this task. The greater concern was the exposure from releases of radioactive and toxic materials from an event. Exposure after an event can have longer lasting effects than impact alone. Other consequences of an event might include damage to nearby buildings or tanks that may or may not cause an immediate safety concern. These could be considered components of the overall risk of an event.

Exposure to radionuclides and exposure to toxic substances can largely be determined individually. However, synergistic effects are not easily evaluated. Yet, they can be significant. This logic diagram addresses synergistic effects as an undeveloped issue titled "Combined effects determined."

The logic associated with determining the radiation dose, and that of the toxic material dose were nearly identical. Therefore, this discussion will address one, not both, for the sake of providing an example case. The logic gate below "Radioactivity release determined" provides either of two options. Either the total tank contents can be assumed released, or the amount of release could be calculated. The easiest option is to assume released and then calculate whether this risk is acceptable in the logic diagram. However, the more realistic case is that only part is released, requiring a more detailed calculation.

When the radioactivity release is calculated, not only does the failure mode need to be determined, but so does the amount of radioactivity in the source term. These pieces of information can be entered into a fluid dynamics model to calculate how much material was released.

Containment Failure Modes (Org-2)

To determine the containment failure modes, each structural component of the tank should be considered separately. These are listed in Table 2.1.

In this section, only the dome failure is considered. Other tank failure modes are discussed in the sections defined in Table J.1. For a dome failure, either the dome will collapse completely, or it will be partially damaged because of a rapid change in pressure. These two choices assume that the waste is not in direct contact with the dome, negating other modes of failure, such as corrosion. A dome collapse could also involve a non-pressure-induced failure, such as corrosion/ erosion of the base of the dome and collapse from its own weight, or added weight as from heavy machinery. While such a collapse is possible, it was considered to have a low probability and was not developed further.

Table J.1. References to Report Sections for the Various Tank-Failure Modes

Tank Component Failure	Refer to Section
Ventilation system	Org-5
Dome	Org-2
Intra or Inter-tank connections	Org-6
Walls and floor	Org-7

The possibility of a pressure failure of the dome can be calculated if the mechanical properties, tank wall (dome) temperature, and dome pressure are determined. These pieces of information can be entered into a structural/mechanical failure model to identify whether a pressure failure will occur.

The position in the SLD, Org-8, is provided at this point in the logic diagram as a cross-reference.

Radioactivity Source-Term (Org-3)

To calculate the material that would be released in an event, the location of that event is important. If the reaction causing the event takes place below the surface, then not only the material involved in the reaction, but also that above the reaction, is part of the “event volume.” To be able to find out what is included in the event volume, the composition and physical properties of both the reactive and unreactive portions of the event volume need to be determined.

Toxic Chemical Source-Term (Org-4)

The logic for this section is essentially the same as for Radioactivity Source-Term (Org-3). Here, the toxicity of the event volume would be determined along with the other parameters identified in Org-3.

Ventilation System (Org-5)

Failure of the ventilation system depends on whether any of its components fail. This is possibly one of the weaker points in any of the tanks and one which could potentially allow materials to be released to the atmosphere. To predict failure, the mechanical properties of each component would need to be determined. This would include examining weakened regions such as from erosion, corrosion, or aging. Duct tape was listed because it may be one of the weakest parts of the ventilation system. Fans are not part of all the tank ventilation systems, but when they are, they may also be prone to failure. These mechanical properties together with the temperature and pressure of the system should be adequate information to calculate whether failure is likely to occur in this portion of the tank system.

Intra- or Inter-Tank Connections (Org-6)

The intra or inter tank failure can be calculated from the pressure caused by the event, the temperature, the strength of the connections, and the application of a model. Pressure can be calculated from the logic described in Org-8.

Connections between Hanford tanks are common, especially between single shell tanks. They were designed to allow liquid supernatant to flow from the top of one tank to the next tank in the cascade, thus promoting solids to settle in the first, but not the second or third tanks of the cascade. Tank farms usually cascade from 101 to 102 to 103, then from 104 to 105 to 106, and so on. Many of the connections were originally from 3 to 6 inches in diameter and the estimated drop from one tank to the next was about 1 foot. It is now known that many of these connections are clogged, probably either with solid waste or rust. It is believed they were constructed of the same soft steel that was used to build the tank liners. All connections were placed above the waste level. Therefore, clogged transfer lines could be filled with solid waste material that has had several years to dry. These dry wastes could be of concern not only for ignition sources, but also for disruptive events in the transfer lines that could damage the tanks themselves, especially if the disruptive event took place close enough to the tank wall.

Wall and Floor Failures (Org-7)

To determine whether the walls or floor of a tank will fail, not only does the pressure of an event need to be calculated (Org-8), so does the mechanical strength of the tank. Since this task involves the role of organics in potential safety issues, several scenarios could be imagined in that the organic species in the tank could influence the mechanical properties of the walls and floors. The most obvious of these was in promoting corrosion. Other concepts were in the potential influence of organic complexing agents on linear integrity. While this influence could be a subset of the tank mechanical properties, it could also be evaluated separately.

Dome Pressure (Org-8)

The dome pressure could be estimated in several ways in the case of an event. In this logic diagram, four are shown. The simplest approach (bounding case) is to determine the total fuel content of the tank and assume all of it is instantly converted to its lowest possible energy state by combustion. Tanks known to have very low organic content may be evaluated in this manner and determined to be safe from an organic event. Otherwise, pressure calculations based on this model are unrealistically high, and values determined by this method may exceed acceptable limits. In that case, three alternatives are described. One is a similar model to the bounding case in which the dilution of the organic fuel is taken into account (Org-11). Another is a more rigorous model in which all components are carefully evaluated, and the energy and moles of gas produced from each equation are entered into a model (Org-9). The third is possibly the most realistic model in which samples from each domain of the tank are placed into an adiabatic reaction chamber, and the pressure that is generated is measured as a function of temperature (Org-10).

Rigorous Approach (Org-9)

The most complex, but yet one of the most accurate methods for determining pressure in the tank is to follow the rigorous approach in which pressure is calculated based on extensive knowledge of the tank contents. Two rather large pieces of information are needed to calculate pressure using this model: the boundary or initial conditions and the reactions that will take place in the tank to lead to a pressure change. Boundary conditions involve not only tank geometry, temperature, and initial pressure, but also initial tank contents. Tank contents must include not only reactive, but also non-reactive, species. During an event, the composition of the contents will change, but the reactions that are likely to take place are calculated in the second portion of the logic diagram (Org-13).

Adiabatic Pressure Model (Org-10)

Another approach to calculating the amount of pressure that tank waste can release in an event is by using calorimetry. In this model, samples are taken from each domain of the tank and tested using adiabadic calorimetry (or other methods that give enthalpy and moles of gas released). This test determines the amount of energy given off by the waste as a function of temperature. If all domains are tested in this manner, and the size of each domain is known, then the total pressure given off in the tank under any given temperature can be calculated. This is possibly the most direct measurement for pressure, but it does not require that the chemical components of the tank be determined.

Intermediate Chemistry Model (Org-11)

The bounding case (Org-8) allowed the total fuel content of the tank to be determined with the assumption that all fuel would be immediately oxidized to completion. Such a model is harsh and may leave several tanks suspect. A slightly more realistic case is one in which the dilution of the waste is also taken into account. This would allow many of the reactions from the bounding case to be eliminated because the reactants may be too dilute to react violently. This model requires better knowledge of the waste than in the bounding case, but not the extensive knowledge required by the rigorous model (Org-9).

Reaction Characteristics (Org-12)

The pressure generated by an event was evaluated in Org-8. However, this section evaluates the amount of material that would be released in the case of an event. If a tank has fuel near the top of the tank, a disruptive event of that fuel may cause the release of a minimal volume of radioactive and/or toxic material. If however, the disruptive event takes place near the bottom of the tank, then all the material in the reaction, as well as the material above the explosion could be released to the environment. Therefore, the location and size of the reaction in the waste material is important in calculating the "event volume." This situation could be simplified if a high reactive model is applied. Such a model is similar to the intermediate case described in Org-11. That is, after the distribution of the organic material is determined, rather than determining all reactions that are likely to take place, all fuel could be assumed to be highly reactive. This would allow a conservative estimate of the reactive capability of the waste to be determined and would simplify characterization to only determining the concentration of organic material at any point in the waste rather than speciation.

An alternative to the highly reactive model is to determine the reaction characteristics of all the various phases (liquid, solid, gas) within the tank. While some organics may react with other organics to form an event, such a scenario is unlikely to cause significant damage. An example might be unstable oxygenated-organics generated via radiolytic degradation. These may or may not be high in concentration at any one place in the tank, and they have been discounted as a major contributor to a sustaining reaction for that reason. Likewise, this task does not evaluate the possibility of inorganic reactions. But, inorganic-organic reactions are much more likely to produce sustaining violent effects in any of the tanks and are within the scope of this task. Reactions were divided by phase for simplicity. Likewise, this logic emphasizes that not only do all phases need to be analyzed for reactants, but reactions between phases also need to be considered. Once all reactions between and within all phases have been determined, their stoichiometry, kinetics, and energetics can be determined, and a model can be applied that allows the event to be better defined.

In Org-8, various reactions were evaluated for the sake of producing pressure. The purpose of those calculations was to determine whether the tank would fail. The calculations in this section are to identify how much material would be involved in a release if such an event were to occur. While both branches of the tree would be activated simultaneously, slightly different information is needed to determine the two answers. These are pressure generated by a reaction to determine if the tank would fail (Org-8) and location, as well as pressure to determine what material is released. Yet, similar measurements would need to be made to go through the calculations.

Important Reactions (Org-13)

Important reactions to consider when calculating a pressure change for the rigorous case (Org-9) can either be heat or gas-generating. A similar event could be imagined in which an implosion occurred. There would be a net decrease in the number of moles of gas, and the enthalpy change could be negative or marginally positive. However, for simplicity, only the explosion case is described here. The two sides of this portion of the logic diagram indicate that chemical reactions must either generate heat or a net increase in the volume of gas. Not all reactants are likely to contribute to such a scenario for several reasons. First, they may not actually produce either heat or a net increase in the number of moles of gas. Second, the reaction may have such a high activation energy that the reaction is highly unlikely. Third, the reaction may be likely except that the reactants are so dilute that any reaction that takes place is slow. Other reasons may influence whether a postulated reaction can make it through the Δn, ΔH gates. Those that meet these criteria can be considered in the model shown under Org-9 to calculate the pressure inside the tank.

Initiating Reactions (Org-14)

Organic tank components would be involved in several possible initiating reactions. Many of these are described in more detail in appendices to this report. Others may also exist that are not described, but could be added later as they are discovered. Those that have been discussed include unstable metal/complexant reactions, electron transfer reactions, and the spontaneous decomposition of unstable organics. Initiating reactions are those that could occur quickly and give off considerable heat, but may or may not extend over a wide region of the tank. An initiator only needs to give off enough energy to start a secondary reaction. This could be significantly larger in some cases than others. For example, starting an organic burn could take more energy than starting a solvent/salt (e.g., acetate and sodium nitrate) event.

All possible initiating reactions need to be evaluated to determine if an event can start. In each case, the reactants, oxidants, and their concentrations need to be determined along with their reaction kinetics. Nonorganic initiating reactions are also considered in parallel, but the logic for determining these can be found in their respective sections of the task reports (e.g., ferrocyanide, high heat, criticality, etc.).

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