Understanding Waste Phenomenology to Reduce the Amount of Sampling and Analysis Required to Resolve Hanford Waste Tank Safety Issues

Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management.

Westinghouse Hanford Company Richland, Washington
Management and Operations Contractor for the U.S. Department of Energy under Contract DE-AC06-87RL10930

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DISCLM-2.CHP (1-91)
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Date Published
February 1996

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UNDERSTANDING WASTE PHENOMENOLOGY TO REDUCE THE
AMOUNT OF SAMPLING AND ANALYSIS REQUIRED TO RESOLVE
HANFORD WASTE TANK SAFETY ISSUES

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ABSTRACT

Safety issues associated with Hanford Site waste tanks arose because of inadequate safety analyses and high levels of uncertainty over the release of radioactivity resulting from condensed phase exothermic chemical reactions (organic solvent fires, organic complexant-nitrate reactions, and ferrocyanide-nitrate reactions). The approach to resolving the Organic Complexant, Organic Solvent, and Ferrocyanide safety issues has changed considerably since 1990. The approach formerly utilized core sampling and extensive analysis of the samples with the expectation the data would provide insight into the hazard. This resulted in high costs and the generation of a large amount of data that was of limited value in resolving the safety issues. The new approach relies on an understanding of the hazard phenomenology to focus sampling and analysis on those analytes that are key to ensuring safe storage of the waste.

INTRODUCTION

Safety issues arose for the 177 (149 single-shell and 28 double-shell) Hanford Site underground storage tanks because of uncertainty over the release of radioactivity resulting from condensed phase exothermic chemical reactions. There are three distinct safety issues that involve condensed phase exothermic chemical reactions: organic solvent fires, organic complexant-nitrate reactions, and ferrocyanide nitrate reactions.

A comprehensive safety program was begun in 1990 to examine and resolve these safety issues. Only limited understanding of the hazards existed; consequently, sampling and analysis activities were directed towards sampling the condensed phase and performing complete suites of analyses. The large number of analyses conducted on each waste sample resulted in few tanks being sampled and a large quantity of data that had only limited use in resolving the safety issues.

Much progress has been made on understanding the waste phenomenology and the safety hazards. This understanding has focused sampling effort and narrowed the suite of analyses to those contributing to resolution of the safety issues. The following sections review the background and current understanding of the waste phenomenology, as well as characterization needs based on the current understanding of the safety issues.
ORGANIC SOLVENT SAFETY ISSUE

Background

Various separation processes involving organic solvents have been used at the Hanford Site. These organic solvents were sent to the underground storage tanks, and subsequent waste transfer operations might have distributed organic solvent among several of the 177 high-level waste tanks (Sederburg and Reddick 1994). Given a sufficient ignition source, there are two potential hazards associated with organic solvent, an organic solvent pool fire, and ignition of organic solvent that is entrained in waste solids (a wick fire). A solvent fire would generate and heat headspace gases, pressurizing the tank. This pressurization might be significant enough to collapse the tank dome, releasing radioactive material to the environs.

Hazard Phenomenology

The organic solvent used at Hanford contains semivolatiles compounds (e.g., dodecane, tridecane, and tributyl phosphate); therefore, there is a direct relationship between liquid organic solvent in a tank and the organic solvent vapors found in the headspace. Tanks containing organic solvent can be identified by vapor sampling the tank headspaces. The mass transfer of semi-volatile species in an organic liquid to the headspace vapor is determined by several parameters, including the mass transfer coefficient, gas-liquid contact area, ventilation flow rate, and solvent volatility.

If organic solvent is present, organic solvent vapors should be detectable in a tank headspace, even if the tank is actively ventilated. Most single-shell tanks are only passively ventilated (i.e., the ventilation flow rate is quite small); thus the organic solvent vapors should be present at roughly equilibrium concentrations. Indeed, this was the case for tank 241-C-103, which contains a floating organic solvent pool. Analyses of the liquid organic solvent pool and the vapors in the headspace suggest that semivolatile concentrations are present at close-to-equilibrium concentrations in the tank headspace.

Currently, one tank (241-C-103) is known to contain an organic solvent pool. Additional tanks that might contain an organic solvent pool will be identified through vapor sampling of the tank headspaces. Criteria for organic solvent headspace concentrations have been developed using theoretical analyses and organic solvent sample data from tank 241-C-103. All 149 single-shell tanks will be vapor sampled and screened against the criteria to identify potential organic solvent tanks.

The 28 double-shell tanks do not require headspace sampling for organic solvent. Double-shell tank design will accommodate a substantially larger pressure transient than single-shell tanks. An organic pool or wick fire could not build enough pressure to collapse the double-shell tank dome. Therefore, this safety issue only applies to single-shell tanks.

Organic solvent pool fires are difficult to ignite (Meacham et al. 1995a). Sparks, impacts, shocks, and friction sources lack sufficient energy to ignite pool fires, and credible ignition sources have been narrowed to robust and/or sustained energy sources. Experiments with a waste simulant (dodecane) required exposure to a propane torch for 10 - 15 seconds (>{1000 Watts) to ignite a 5 cm puddle.

Even if a pool fire could be ignited, consequences from such a fire would be very low (within risk acceptance guidelines) if an adequate vent path area exists. A pool fire would heat headspace gases pressurizing the tank. The fire would burn until the oxygen was depleted. The pressurization from a
postulated pool fire would increase with the fire spread rate. Calculations indicate that a puddle would have to be larger than 2 m² to create enough pressure to collapse the tank dome. If adequate vent path area was available, the tank dome would not collapse and any radioactive release would be minor. Of the 43 tanks recently vapor sampled, only one has a floating organic solvent pool (241-C-103) and adequate venting is available in this tank (Meacham et al. 1995a).

Entrained organic solvent is also difficult to ignite. Hot steel spheres (greater than 270 Joules) and an electronic match (about 138 Joules) failed to ignite entrained organic solvent (dodecane) during ignition experiments. Sparks, impacts, shocks, and friction sources could not ignite entrained organic solvent either.

The consequences from an entrained organic solvent fire are less than an organic pool fire. Open literature and preliminary calculations show that the spread rate for an entrained solvent fire is about an order of magnitude lower then that for a pool fire and would not result in tank over-pressurization. Therefore, the safety issue is bounded by the organic solvent pool fire hazard.

Resolution of the organic solvent safety issue requires two steps a) identification of tanks containing significant quantities of organic solvent (i.e., greater than a 2 m² puddle), and b) ensuring adequate vent path in those tanks that contain significant organic solvent.

Characterization Needs

By understanding hazard phenomenology, the characterization needs can be reduced to vapor sampling of single-shell tanks. Core sampling of the tanks is not required to resolve this safety issue. Only the 149 single-shell tanks need to be vapor sampled for the presence of organic solvent and this will be completed by the end of FY 1998.

ORGANIC COMPLEXANT SAFETY ISSUE

Background

Organic complexants were sent to the high-level waste tanks during the defense mission at the Hanford Site. These compounds and their decomposition products have the potential to react exothermically when combined with an oxidizer. The waste tanks also contain high quantities of sodium nitrate, a strong oxidizer. The organic complexant hazard is represented by two distinct types of reactions, spontaneous chemical runaway (self heating) reactions, and propagating chemical reactions typified by a passing reaction front. These reactions could produce gases that pressurize the tank and cause failure of the tank dome. The aerosols produced would carry radioactive materials to the environs, resulting in unacceptable onsite and offsite doses.

Hazard Phenomenology

Spontaneous chemical runaway reactions are not possible under current storage conditions. This conclusion was reached by evaluating the energy balance for the tanks. For a spontaneous chemical runaway reaction to occur, the chemical heating rate must exceed the tank cooling rate (Frank-Kamenetskii 1969). This can be evaluated by comparing the tank cooling response time (i.e., the time required to reach a new equilibrium temperature following an instantaneous change in the heating rate) with the waste storage time. Calculations show that the tank cooling response times
range from a few hours to 3.1 years. Some waste has been stored for more than 40 years, and there has been no transfer of waste into the single-shell tanks for about 15 years. Several cooling response times have passed over the last 15 years of storage; consequently, it can be concluded that bulk runaway reactions are not a hazard under current storage conditions. In addition, no credible mechanisms have been identified that would increase tank temperatures and cause a chemical runaway reaction.

Propagating reactions require an ignition source and sufficient fuel and oxidizer. Tube propagation tests with waste surrogates and theoretical analyses have shown that ignition sources greater than 1 Joule (10,000 times more than that required to ignite flammable gas) are required to initiate organic complexant reactions in dry waste. Sparks and static electric shocks lack sufficient energy to initiate organic complexant propagating reactions.

It may be possible to show that no credible initiators exist that cannot be controlled. Laboratory experiments on simulants indicate about 5 weight percent (wt%) free water will prevent initiation of propagating reactions by 100 J ignition sources. Tests on actual waste samples will be conducted to determine a minimum moisture concentration under in-tank waste storage conditions. Confirmation that waste free water concentrations exceed approximately 5 wt%, would reduce the amount of sampling and analysis required to resolve the safety issue.

Safe storage criteria have been established through theoretical analysis and tests on waste surrogates. The minimum fuel concentration required to support a propagating reaction has been determined using a contact-temperature ignition model (Fauske et al. 1995). A necessary (but not sufficient) condition for a propagating reaction is that the fuel concentration be greater than 1200 J/g (4.5 wt% total organic carbon), on an energy equivalent basis (Fauske et al. 1995).

For fuel concentrations between 1200 and 2100 J/g, the waste moisture (free water) content required to prevent a propagating reaction varies linearly from 0 to 20 wt%. Above 20 wt%, the fuel-moisture linear relationship no longer holds because the mixture becomes liquid continuous and a stoichiometric fuel-oxidizer mixture will not support a propagating reaction (Fauske et al. 1995). All of the waste in the double-shell tanks have aqueous supernatants and the waste would be too wet to support a propagating reaction.

Experiments on waste simulants indicate that fuel concentrations in the tanks have been decreased by saltwell pumping and waste aging (i.e., decomposition of the high energy waste into low energy products). Experiments show that the reactive organic complexant salts (e.g., sodium acetate, EDTA, HEDTA) remain soluble in the tank solutions and are removed by saltwell pumping (Barney 1994). Most of the single-shell tanks have been saltwell pumped (113 out of the 149 total) and the liquid sent to the double-shell tanks. Hence, much of the fuel values in the single-shell tanks might have already been removed.

Experiments also indicate that organic compounds age to less energetic products (e.g., oxalate) (Camaioni et al. 1994). Laboratory experiments have shown that these organic salts will not support propagating reactions (Fauske et al. 1995). Therefore, any remaining fuel in the single-shell tanks might not be reactive enough to be a hazard.

It might be possible to show that the fuel concentrations in the single-shell tanks are too low to support propagating reactions. The solubility model indicates that energetic organic species are present principally as solutes in tank liquids. The aging model indicates that organic complexants age
over time to less energetic species, providing additional confidence regarding the stability of stored waste. Organic speciation analyses of actual waste will be conducted on selected tanks to confirm that the organic complexants remained soluble, and to confirm that any remaining fuel has aged.

It might be possible to show that tank waste contents meet the safe storage criteria. Information from the solubility and aging models and sample data from selected tanks will be used to assess the potential fuel and moisture concentrations in the tanks. In situ moisture monitoring capability is being developed in an attempt to provide representative measurements of waste moisture concentration in the single-shell tanks.

Characterization Needs

From an understanding of hazard phenomenology, the sampling needs can be focused and the number of analyses performed can be reduced. Only selected single-shell tanks require sampling to resolve the safety issue. Analyses have been reduced to include only measurement of energetics, total organic carbon, moisture, and some organic speciation to confirm organic solubility and organic aging. If tests on actual waste samples indicate that the waste will retain 5 wt% free water, the sampling and analysis needs will be reduced further.

FERROCYANIDE SAFETY ISSUE

Background

During the 1950s, additional tank storage space was required to support the defense mission. To obtain this additional storage volume within a short time period, and to minimize the need for constructing additional storage tanks, Hanford Site scientists developed a process to scavenge cesium-137 from tank waste liquids. In implementing this process, approximately 140 metric tons of ferrocyanide were added to waste that was later routed to eighteen Hanford Site single-shell tanks.

Ferrocyanide, in the presence of oxidizing material such as sodium nitrate, can propagate and sometimes be made to explode by heating it to high temperatures or by providing an electrical spark of sufficient energy. Because the scavenging process precipitated ferrocyanide from solutions containing nitrate, an intimate mixture of ferrocyanides and nitrates may have existed in some regions of the eighteen ferrocyanide tanks.

Hazard Phenomenology

Ferrocyanide ages (i.e., decomposes to lower energy products) when exposed to tank waste conditions. Three parameters strongly affect the rate of aging, temperature, exposure to high pH, and radiation dose (Lilga et al. 1995). The current fuel concentration is a function of the starting concentration and the amount of aging that has occurred. Historical data (Wodrich et al. 1992) show that all the ferrocyanide tanks have been exposed to enough caustic to promote aging (i.e., had pH values higher than 10). However, ferrocyanide sludge depths in the tanks range from 0.1 to 2.6 meters (Borsheim and Simpson 1991) and there is some question whether the caustic solutions would penetrate more than one meter into ferrocyanide sludge (McGrail 1994). Therefore, ferrocyanide at greater depths might not have been exposed to high pH solutions and might not have aged.
Tanks with high ferrocyanide concentrations and sludge depths, and low temperature and radiation dose histories, have been selected for core sampling to bound aging. If the ferrocyanide has aged in these tanks, then as much or more aging should have occurred in the remaining ferrocyanide tanks.

Nine ferrocyanide tanks have been selected for sampling and analysis to bound ferrocyanide aging. Sampling and analysis have been completed for six of these nine tanks and the data is reviewed in Table 1 (Meacham et al. 1995b). Results indicate that ferrocyanide has aged to concentrations more than a factor of ten lower than the original concentrations. The remaining ferrocyanide concentrations are substantially below the 1200 J/g minimum required to support a propagating reaction (Fauske et al. 1995).

Table 1. Summary of Original Ferrocyanide Concentrations and Current Ferrocyanide Concentrations

<table>
<thead>
<tr>
<th>Tank Number</th>
<th>Original Concentration, J/g</th>
<th>Current Concentration, J/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-108</td>
<td>2,200 [23]*</td>
<td>110 [1.2]</td>
</tr>
<tr>
<td>C-109</td>
<td>2,200 [23]</td>
<td>30 [0.3]</td>
</tr>
<tr>
<td>C-111</td>
<td>2,200 [23]</td>
<td>0 [0.0]</td>
</tr>
<tr>
<td>C-112</td>
<td>2,400 [26]</td>
<td>36 [0.4]</td>
</tr>
<tr>
<td>T-107</td>
<td>800 [8.3]</td>
<td>0 [0.0]</td>
</tr>
<tr>
<td>TY-104</td>
<td>840 [8.8]</td>
<td>0 [0.0]</td>
</tr>
</tbody>
</table>

*Numbers in brackets represent concentration in wt% Na₃NiFe(CN)₆.

Characterization Needs

Understanding the hazard phenomenology has reduced the number of ferrocyanide tanks that need to be sampled from all eighteen to the nine that bound aging. The analyses required to resolve the safety issue have been narrowed to energetics and ferrocyanide [Na₃NiFe(CN)₆]. Six of the nine tanks that bound ferrocyanide aging have been sampled and analyzed, and only three tanks remain to be sampled. If aging is confirmed in these final three tanks as expected, then no additional sampling is required to resolve the ferrocyanide safety issue.
REFERENCES


