Progress in Resolving Hanford Site High-Level Waste Tank Safety Issues

Prepared for the U.S. Department of Energy
Office of Environmental Restoration and Waste Management

Westinghouse Hanford Company Richland, Washington

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PROGRESS IN RESOLVING HANFORD SITE HIGH-LEVEL WASTE TANK SAFETY ISSUES

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ABSTRACT

This paper summarizes recent progress toward resolving Hanford Site high-level radioactive waste tank safety issues, including modeling and analyses, laboratory experiments, monitoring upgrades, mitigation equipment, and developing a strategy to screen tanks for safety issues.

BACKGROUND

Interim storage of alkaline, high-level radioactive waste, from two generations of spent fuel reprocessing and waste management activities, has resulted in the accumulation of 238 million liters (63 million gallons) of waste in Hanford Site single- and double-shell tanks. Before the 1990’s, the stored waste was believed to be: 1) chemically unreactive under its existing storage conditions and plausible accident scenarios; and 2) chemically stable. This paradigm was proven incorrect when detailed evaluation of tank contents and behavior revealed a number of safety issues and that the waste was generating flammable and noxious gases.

In 1990, the Waste Tank Safety Program was formed to focus on identifying safety issues and resolving the ferrocyanide, flammable gas, organic, high heat, noxious vapor, and criticality issues. The tanks of concern were placed on Watch Lists by safety issue.

To ensure continued safety until needed data were collected and interpreted, the tanks associated with safety concerns were placed under stringent operating controls.
Data from extensive work done in the last few years (Babad et al. 1993a) have reduced uncertainties and allowed closure of several unreviewed safety questions. Technical findings, which resulted from laboratory studies on waste simulants and actual waste, accomplished the following: 1) identified and bounded the energetics of the fuel-rich materials added to the tanks; and 2) determined that waste aging processes over the last 30 to 40 years due to waste chemistry and tank physics reduced the potential risk. Waste aging processes have led to dispersion or degradation of these fuel-rich species (Babad et al. 1993b).

RECENT PROGRESS AND PLANS TO RESOLVE SAFETY ISSUES

Ferrocyanide. The ferrocyanide safety issue involves the potential for uncontrolled exothermic reactions of ferrocyanide and nitrate/nitrite mixtures (Postma et al. 1994a). Laboratory studies show that temperatures must exceed 250 °C for a reaction to propagate. The hottest tank’s temperature is currently 54 °C and decreasing.

Moisture levels above 20% will prevent reactions from propagating regardless of fuel concentrations. Current plans were to take two core samples from each of 18 tanks to determine ferrocyanide levels and moisture content. However, recent laboratory work with simulants confirmed that ferrocyanide fuel content decreases over time in intense radiation fields (Lilga et al. 1993, Lilga et al. 1994). Core sampling will be used to confirm aging in the tanks projected to have the highest ferrocyanide concentrations and exposed to the lowest radiation field and/or alkali concentrations. The sampling results are expected to show that the ferrocyanide has aged to levels low enough to resolve the safety issue. Six of the original Ferrocyanide Watch List tanks have been removed from the Watch List based on records that showed no ferrocyanide had been added to these tanks.

Organic Tanks. The organic tanks safety issue involves the potential for uncontrolled exothermic reactions of organic chemicals and nitrates/nitrites and for vapors from semi-volatile organics entrained in waste to exceed the flammability limits (Sederburg and Reddick 1994). Recent laboratory tests showed that fuel concentrations and temperatures required to support propagating exothermic reactions are comparable to those for ferrocyanide. In addition, moisture levels above 20% will prevent reactions from propagating regardless of fuel concentrations.

In prior years, work controls were implemented to prevent introduction of ignition sources to these tanks. Vapor sampling and safety analyses were completed and formed the basis for closing the Unreviewed Safety Question concerning flammability of the floating organic layer in tank 103-C (Postma et al. 1994b). Ten tanks that received organic complexants were added to the Organic Tanks Watch List following a review of sampling data and waste transfer records (Toth et al. 1994, Hanlon 1994).

Aging processes have destroyed or significantly lowered the energy content of the organic tanks. Recent laboratory work (Ashby et al. 1994) demonstrates that in the presence of alkaline aluminum salts and radiation, complexants such as hydroxyethylhexanediomine triacetic acid (HEDTA), ethylenediamine triacetic acid, and glycolic acid decompose to form.
less reactive fragments, ultimately creating a mixture of sodium formate and sodium oxalate. During this aging process, hydrogen, nitrogen, nitrous oxide and ammonia are evolved. This finding has been confirmed by studies on tank 101-SY waste (Campbell et al. 1994) that found the HEDTA had almost disappeared. Other complexants had partially degraded to sodium oxalate and formate and a complex mixture of degradation products such as the sodium salts of ethylenediamine diacetic acid and nitrilodiacetic acid.

Recent laboratory findings (Barney 1994) indicate that the more energetic complexants and the primary degradation products of tributyl phosphate (TBP) are water soluble in saturated nitrate-nitrite salt solutions and would a large percentage have been removed from the single-shell tanks when they were saltwell pumped.

In conclusion, the combination of waste aging, waste dissolution and dispersion appears to bound the inherent risk in fuel-rich nitrate-nitrite systems. When work on waste surrogates and simulants is completed, limited core sampling in bounding tanks will be used to verify the conclusions derived from these conceptual models of waste behavior.

Flammable Gas Tanks. The flammable gas tanks safety issue involves the potential release of flammable gases in concentrations above the lower flammability limit. In prior years, work controls were instituted to prevent introduction of spark sources, and evaluations were completed to ensure that attached equipment was intrinsically safe.

The worst tank, 101-SY, has been successfully mitigated with a mixing pump. The pump is operated up to three times a week to mix the waste and release gas.

Hydrogen monitors are being installed on all 25 flammable gas tanks. The Standard Hydrogen Monitoring System consists of a cabinet equipped with piping and instrumentation that support an on-line hydrogen detector and a "grab sampler." The cabinet isolates the equipment from the environment. The hydrogen detector is presently a Whittaker electrochemical cell, but other detectors can also be installed into these cabinets. The grab sampler allows gas samples, captured during a gas release event, to be removed from the tank for highly detailed analyses using state-of-the-art gas chromatograph and mass spectral analysis techniques. A better understanding of the physical properties of the tanks will be gained using a retained gas sampler, a viscometer, and void fraction devices. The void fraction test instrument has been successfully demonstrated in tank 101-SY. This monitoring data will be used, along with knowledge acquired during the process, to determine if any tanks other than 101-SY require active mitigation for safe storage. Documentation to close the Unreviewed Safety Question in SY tank farm was submitted earlier this year.

High-Heat Tanks. The high-heat tanks safety issue concerns tank 106-C, a single-shell tank that requires water additions for evaporative cooling. Without the water additions, which would be discontinued in the event of a tank leak, the tank could exceed structural temperature limits, resulting in potential tank collapse.
Tank 106-C is on an accelerated program for early retrieval to a double-shell tank. Double-shell tanks handle heat-bearing materials better than single-shell tanks, thus lowering the potential hazard from a structural failure if, in the event of a tank leak, cooling water additions to the tank are discontinued. Tank 106-C retrieval is scheduled to begin in late 1996. A process test and considerable thermal analyses were completed on tank 106-C to evaluate alternate cooling approaches. The studies concluded that the tank could be adequately cooled using an air chiller.

**Criticality.** The criticality safety issue involves the potential for criticality in tanks. Tank criticality prevention controls have been strengthened by improved administrative procedures and training, and the Unreviewed Safety Question was closed (Braun and Szendre 1994) using analyses that showed criticality during storage was highly unlikely. All the single- and double-shell tanks at the Hanford Site contain sufficient neutron absorbers to ensure safe storage; however, additional sampling or controls will be required for retrieval and pretreatment-related activities.

**Noxious Vapor Concerns.** The noxious vapor safety issue involves potential health and safety issues related to toxic vapors that may be present in some of the high-level waste tanks. The issues stem from an insufficient understanding of the causes of reported exposures of tank farm personnel to unacceptable levels of noxious vapors, and the concern that until the vapors in the waste tanks are well characterized, the risks to worker health and safety cannot be determined or controlled (Osborne 1994, Huckaby and Babad 1994). In prior years, worker protection controls were instituted to prevent worker exposures, and a program was implemented for routine workspace air monitoring and periodic personnel dosimetry.

In-tank vapor sampling equipment has been developed and tested. Two methods are used to collect vapor samples from the waste tanks (Huckaby 1994). The primary method employs: heated transfer tubing; a heated sampling manifold; temperature, flow control, and valving technology; and an air pump to draw air, gases, and vapors out of the waste tanks. This method currently requires that a customized vapor sampling probe be installed by crane into a tank riser. This integrated equipment is referred to as the vapor sampling system (VSS). The VSS was specifically designed to collect representative samples from warm, moist tanks, even if a fog exists in the tank headspace.

A second method for collecting vapor samples from the waste tanks is referred to as in situ sampling (ISS). Rather than transferring the air, gases, and vapors to be sampled to a remote location, the sampling devices themselves (specifically sorbent traps) are lowered into the tank headspace. This minimizes the loss of constituents by adsorption on transfer tubing walls, and circumvents the need for heated probes, heated transfer tubing and a heated sampling manifold. Currently, the ISS equipment consists of a simple manifold and air pump mounted on a two-wheeled hand cart. Small bundles of about eight sorbent traps are lowered into the tank headspace, each sorbent trap having its own 0.64-cm (0.25-in.) plastic tube connection to the sampling manifold. The current sampling manifold is capable of collecting four samples simultaneously, and uses needle valves to control flow rates and a rotameter to monitor flow rates. In the ISS method, constituents that are not amenable to
sorbent trap sampling (e.g., gases such as H₂, N₂O, and CH₄), are sampled using an unheated plastic tube that transfers sample from the headspace to whole-air sampling devices (e.g., SUMMA¹ canisters) located outside the tank. By the end of 1994, 18 high-level waste tanks had been vapor sampled.

UPGRADED APPROACH TO WASTE TANK SAFETY SCREENING

In 1990, all Hanford Site high-level waste tanks were segregated into four different categories based primarily on historical and monitoring information. These tanks were placed on "Watch Lists" to ensure increased attention and monitoring. In mid-1993, a program was initiated to screen all single- and double-shell tanks using core sample data. This program is being updated to take advantage of recent improvements in vapor sampling capability and an improved understanding of conditions necessary for selected chemical reactions.

Key changes in the revised safety screening strategy will include placing flammability controls on all tanks until associated sampling is complete, and using vapor sampling to help determine tank contents. Rather than initially sampling the waste to determine fuel content, as was the past strategy, evaluation and/or checking of moisture levels will be performed. If moisture levels are above 20%, fuel-rich propagating reactions will not occur.

Figure 1 shows the logic chart for the proposed safety screening. Key steps include:

- Perform tank-by-tank evaluations of historical records (including past sampling results, laboratory waste testing, tank-specific modeling, and monitoring records), assessment of the adequacy of present monitoring systems, and tank-specific safety bases.

- Vapor samples will be used to check for flammable or explosive gases. Headspace samples will be evaluated for hydrogen, organic gases and vapors, including ammonia, and nitrous oxide levels. If concentrations exceed pre-determined requirements, additional monitoring, waste or vapor sampling, or mitigation using enhanced ventilation or inserting, may be required.

- Vapor samples will also be used to help identify the presence of volatile reactive materials and might be used to identify changes in waste chemistry resulting in significant changes in overhead gas compositions.

- Vapor samples will be further used to check for noxious vapor sources. Treatment systems may be required if vapors are detected in the tank headspace above levels immediately dangerous to life or health.

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¹ SUMMA is a registered trademark of Molecricts, Inc., Cleveland, Ohio.
Finalize Requirements for Safe Storage of Waste

1. Use History & Monitoring Data to Prioritize Tanks
   - Tank Parameters within Safety Envelope and Worker Protection Guidelines
     - Develop and Implement Mitigation or Controls

2. Vapor Sample in Tank for Flammability, Toxic Vapors & Volatiles
   - No
     - Condition 3

2A. Flammable Gas (25% Limit)
   - Yes
     - Done
   - No

2B. Noxious Vapors ≤IDLH Limit
   - Yes
     - Implement Appropriate Safety Controls & Precautions OR Mitigate to Reduce to Safe Levels
   - No

2C. Separable Organic Layer Entrained in Waste?
   - Yes
     - Implement Appropriate Safety Controls & Precautions OR Mitigate to Reduce to Safe Levels
   - No

Conditions being Evaluated:
1. Flammable gases (greater than 25% lower flammability limit)
2. Tanks with contents that immediately dangerous to life and health
3. Tanks with contents that could immediately cause severe injury
4. Waste with sufficient heat and oxidizer, but not temperature above ignition limit
5. Waste with liquid organic phase

Notes:
1. Flammable gas tanks were previously identified by conducting tank leak checks.
2. Noxious/volatile tanks were previously identified by reviewing process records.
3. A tank with continuous aqueous layer which forms the aqueous layer due to leakage or internal contamination may be required to undergo rescreening starting at step 2.
Conditions being Evaluated:
1. Flammable vapors (greater than 25% lower flammability limit)
2. Toxic vapors (greater than immediately dangerous to life and health)
3. Wastes with sufficient fuel, temperature, and oxidizers to exceed safety
4. Wastes with sufficient fuel and oxidizers, but not temperature unless ignited externally
5. Wastes with liquid organic phases

Notes:
1. Flammable gas tanks were previously identified by evaluating tank level changes.
2. Peroxyacids tanks were previously identified by reviewing process records.
3. A tank with continuous aqueous layer which loses the aqueous layer due to leakage or interim stabilization may be required to undergo reprocessing starting at step 2.

Figure 1. Safety Screening Logic (Page 2 of 2)
Visual inspections will be used as an initial screening for moisture. For tanks with continuous aqueous layers (all double-shell and about five single-shell tanks), no additional sampling will be required. Other tanks will require either evaluation or near-surface samples to determine moisture content. If moisture levels are 20% or higher, no further safety screening sampling will be required.

If moisture levels are not adequate, fuel levels will be determined by near-surface sampling, or a low-cost mitigation process will be implemented to increase moisture levels.

This sampling program is expected to greatly accelerate tank safety screening, with considerable cost savings.

This new approach will require vapor sampling of all passively ventilated tanks (26 have already been completed) and near-surface moisture sampling of up to 70 tanks. Either auger samples or an in situ device will be used to determine moisture. An auger sampling device is like a drill bit that is rotated into the waste to obtain the sample. Auger samples are much easier to obtain than core samples; however, sample recovery may not be adequate. Commercially available devices such as an electromagnetic induction moisture monitor could be modified and used in a penetrometer. Some limited core sampling will be required to support the technical basis for the new strategy.

TECHNICAL BASIS FOR UPGRADED SCREENING STRATEGY

To provide greater assurance that all tanks with safety issues have been identified, a safety screening will be conducted to determine whether any other tanks generate flammable gases or noxious vapors above limits, or if conditions exist that would support exothermic propagating reactions due the fuel and oxidizers mixtures, or if surface combustion could occur due to entrained or pooled organic solvents.

Previous testing with vapor sampling has demonstrated that waste tank headspaces are essentially homogeneous (Huckaby and Story 1994). In addition, near-surface moisture levels are believed generally high enough to reduce the number of waste samples required for adequate moisture assessment to reasonably attainable levels, particularly for sludge-containing tanks.

Ferrocyanide and organic chemicals act as a fuel when combined with an oxidizer, and nitrate salts (an oxidizer) have been precipitated in the tanks. These compounds have the potential for propagating exothermic reactions between fuel and salts of sodium nitrate and sodium nitrite. Two types of propagating exothermic reactions are possible in fuel-rich wastes: 1) bulk runaway reactions, in which an entire tank’s contents reach a critical temperature and then self-heat; and 2) propagating reactions in which the reactive zone spreads at a measurable rate as the result of a localized initiator (Fauske 1994).
For a bulk runaway reaction to occur, a major fraction of the waste would have to be heated to above 250 °C (Fauske 1994). Heat loads in most of the Hanford Site tanks are low, and temperatures are declining with time. In addition, most single-shell tanks are passively cooled (Crowe et al. 1993). Bulk heating of waste to 250 °C is not credible.

For a propagating reaction to occur, a mixture of fuel-oxidizer must be heated to high temperatures or energized by applying an ignition source (Cady 1993). Because specific conditions of fuel, moisture, and temperature are all required to support a propagating reaction, screening criteria have been set based on extensive energetics studies on waste stimulants. For the ferrocyanide safety issue, these results have been confirmed on actual waste. Safety screening criteria for the propagating exothermic reactions in the condensed phases are listed in Table 1.

Table 1. Safety Screening Criteria For Condensed Phase Oxidizer-Fuel Reactions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Criteria</th>
<th>Units</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel concentration</td>
<td>290</td>
<td>cal/g</td>
<td>DSC^2</td>
</tr>
<tr>
<td>Moisture concentration</td>
<td>wt-% moisture &gt; 0.93 fuel - 27</td>
<td>wt%</td>
<td>TGA^3</td>
</tr>
<tr>
<td>Bulk temperature</td>
<td>≤ 90</td>
<td>°C</td>
<td>Thermal analysis^4</td>
</tr>
</tbody>
</table>

Notes:

1. Applicable to Hanford Site single-shell tanks.
2. Differential scanning calorimetry (DSC) measurement on a dry weight basis.
3. Thermogravimetric analysis (TGA).
4. Maximum waste temperature derived from thermal analysis using temperature readings from tank's thermocouple tree.

All double-shell tanks contain adequate moisture levels to prevent propagation. Ferrocyanide fuels are found only in sludges in single-shell tanks. Organic fuels may be in sludges or saltcakes and in double- or single-shell tanks. Most sludges, except for those in shallow tanks or high-heat tanks, contain adequate moisture to prevent propagating exothermic reactions and will remain adequately moist indefinitely unless temperatures increase above 90 °C. Considerable research work has shown that formation of dry regions due to local hot spots in sludges is not credible. In addition, no credible mechanisms exist to raise temperatures inside wastes to reaction levels. Therefore, only external initiators are credible. Several potential external initiators have been evaluated, including instrumentation, cameras, pumps, core samplers, vehicles, and lightning strikes.

The maximum waste temperature criterion of 90 °C reflects the need to preserve existing waste moisture contents. It is important to note that this is a bulk waste temperature, and that point source temperatures (e.g., from rotary core sampling) are allowed to be only as high as 150 °C, well below the critical ignition temperature for a propagating reaction (Fauske 1994, Webb 1995). Experimental work at Fauske and Associates (Fauske 1994) measured the actual energies released for a variety of bounding organic-nitrate-nitrite-
containing surrogates, and bounded the actual propagating energy ranges and conditions for a variety of mixtures containing organic complexants, TBP and related materials. Fauske and Associates is completing documentation of the quenching effects of moisture on such systems.

Evaporation of saturated salt solutions in the passively ventilated tanks is slow; therefore, extensive dryout of the tanks is an improbable event.

Operational upsets were considered by using a "what if" approach that focused on upset conditions that would significantly increase the amount of energy deposited in the tank or waste. Heating a small portion of dry, reactive waste to fuel-nitrate ignition temperatures could initiate a sustainable rapid exothermic fuel-nitrate reaction accident if the waste were reactive. The potential for tank farm equipment and operations to heat a portion of waste to ignition temperatures has been evaluated in Bajwa and Farley (1994). Energy from external initiators and natural events such as lightning strikes were also considered. Lightning was the most energetic, and therefore was used to bound the maximum depth that an external initiator would penetrate the waste surface.

Given that credible initiators transfer their energy to the waste surface, sufficient fuel and oxidizer must exist near the surface in order for a propagating chemical reaction to be induced. Conversely, if insufficient fuel and oxidizer exist in a surface layer that could be heated by an initiator, then it is physically impossible to initiate a propagating reaction. In addition, preliminary work by Camaioni and Samuels (1994) has confirmed the general findings on complexant decomposition and also demonstrated the facile destruction of TBP and its primary hydrolysis product sodium dibutyl phosphate. Only normal paraffinic hydrocarbon, which would evaporate or boil out of hot waste, was resistant to gamma-radiation-induced aging under initial test conditions.

Further insight into the distribution of organic material was gained from a series of solubility studies by Barney (1994). Accurate data have been obtained for solubilities of selected organic compounds in tank supernate solutions. Initial research resulted in development of a model for fuel distribution in saltcake that shows the more energetic species to be soluble in the aqueous-saturated waste solution and thus susceptible to removal when drainable liquid is removed from the single-shell tanks by saltwell pumping. Work is continuing to determine whether the salts of calcium, aluminum and/or iron form insoluble precipitates of complexants leading to their deposition in saltcake (creating localized concentrations of fuel). In the absence of localized insoluble salts, a case can be made that organic complexants are dispersed in the aqueous phase.

In summary, the presence of separable organic liquids can be quantified from concentration data obtained from headspace air. Because the energy required to ignite an entrained solvent is likely to be small, it is likely that mitigation efforts such as inerting the tank headspace (e.g., with nitrogen replacing air) may be necessary. Meanwhile, as mentioned earlier, flammability controls will be applied, not just to known Watch List tanks, but to all tanks.
CONCLUSIONS

Westinghouse Hanford Company and supporting organizations and laboratories have made remarkable progress toward resolving waste tank safety issues. Three unreviewed safety questions were closed in 1994, the worst tank was successfully mitigated, understanding chemical reactions limits has improved dramatically, instrumentation to enhance understanding of tank conditions is being installed on an accelerated schedule, and an innovative cost saving approach has been developed to screen all of the tanks.
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