A STRATEGY FOR RESOLVING HIGH-PRIORITY HANFORD SITE RADIOACTIVE WASTE STORAGE TANK SAFETY ISSUES

Harry Babad, Cherri DeFigh-Price, and John C. Fulton
Westinghouse Hanford Company

ABSTRACT

High-activity radioactive waste has been stored in large underground storage tanks at the U.S. Department of Energy's (DOE) Hanford Site in Eastern Washington State since 1944. Since then, more than 227,000 m^3 (60 Mgal) of waste have been accumulated in 177 tanks. These caustic wastes consist of many different chemicals. The waste forms include liquids, slurries, salt cakes, and sludges. A number of safety issues have been raised about these wastes, and resolution of these issues is a top priority of DOE. A Waste Tank Safety Program has been established to resolve these high-priority safety issues. This paper will deal with three of these issues. The issues described are the release of flammable vapors from single- and double-shell tanks, the existence of organic chemicals, and/or ferrocyanide ion-containing fuel-rich mixtures of nitrate and nitrite salts in single-shell tanks.

Extensive management controls are employed to ensure that the tanks in question continue to be maintained in a safe manner through issue resolution. In addition, comprehensive monitoring, characterization, and applied and basic research efforts have been initiated to support resolution of issues and to prevent creation of future problems associated with potentially incompatible wastes. The safety efforts will also support actions related to the planned retrieval and disposal of the wastes in these storage tanks. Such efforts will also provide the basis for remediation of the safety issues associated with these tanks on an as-needed basis and define the envelope of safety to support the disposal of all high-level waste in Hanford Site tanks.

Safety studies and evaluations have been conducted periodically as new waste-producing processes were developed and waste conditions changed. However, delaying permanent waste disposal, continual pressure of waste generation on limited storage space, and aging facilities have resulted in several current safety issues (1). Efforts on identification of and external review of the safety issues can be found in WHC-SA-1328 (2), Kazimi (3), WHC-SA-1369-FP (4), WHC-SA-1364-FP (5), and WHC-EP-0531 (6).

RESOLUTION OF SAFETY ISSUES

Resolution of all the safety issues will take several years (refer to Fig. 1). As the tanks receive further evaluation, it is anticipated that other issues may be identified. A Waste Tank Safety Program has been established to conduct this work, and an overview plan for implementing mitigation and/or remediation of the highest priority waste tank safety issues was prepared (1). Detailed plans also have been developed for each of the major activities.

The following issues are discussed in this paper:

- Flammable gas generation in tank 241-SY-101 and other tanks--Twenty-four tanks generate hydrogen and other flammable gases and appear to release them in a periodic fashion.
- Potential explosive mixtures of ferrocyanide in tanks-Twenty-four tanks may contain insoluble ferrocyanide salts in quantities potentially greater than 1,000 gram-moles mixed in a sodium nitrate/sodium nitrite matrix.
- Potential organic-nitrate reactions in tanks--Eight tanks contain organic chemicals at concentrations believed to be greater than 10 mole percent sodium acetate equivalent mixed in a sodium nitrate/sodium nitrite matrix. Three of the hydrogen and ferrocyanide tanks also appear on the organic list.

The hazardous characteristics of the existing wastes, leading to their identification and control, were estimated on the basis of information from the chemical literature, expert peer judgment, and limited historical and actual sampling data. Mitigating factors such as moisture content, presence of inert diluents (e.g., sodium carbonate, sodium aluminate and/or sodium phosphate), and conditions that could lead to a lack of reactivity of the wastes were purposely understated.

Scenarios of significant concern associated with waste in tanks include the following:

- Potential for ignition of flammable gases such as hydrogen-air, hydrogen-nitrous oxide, and/or air-organic vapor mixtures
- Potential for ignition of organic-nitrate and/or ferrocyanide-nitrate mixtures, initiated by the radiolytic or chemical heating of dry salt cake or by localized heating
- Potential for secondary ignition of organic-air and/or organic-nitrate mixtures, initiated by the burning of flammable gases.

Administrative and technical controls are in place to restrict activities that could cause undesirable exothermic reactions. For example, pumping of interstitial liquid from ferrocyanide tanks was stopped to maintain present moisture levels (e.g., to maintain present *thermal conductivity and heat* capacities) until data are gathered about the required moisture levels to maintain safety. Nonsparking tools and use of electrical bonding techniques are used around flammable gas tanks to prevent accidental ignition. "Normal" activities for tanks of concern are limited to surveillance. Special safety and environmental analysis documents are prepared for all work inside the tanks; these are extensively peer reviewed and are scheduled for periods when the vapor concentrations are well below the lower flammability limits.

Of the 53 tank safety issues, 4 have been selected for accelerated evaluation. Tank 241-SY-101 is of the greatest concern because of episodic releases of flammable gas that

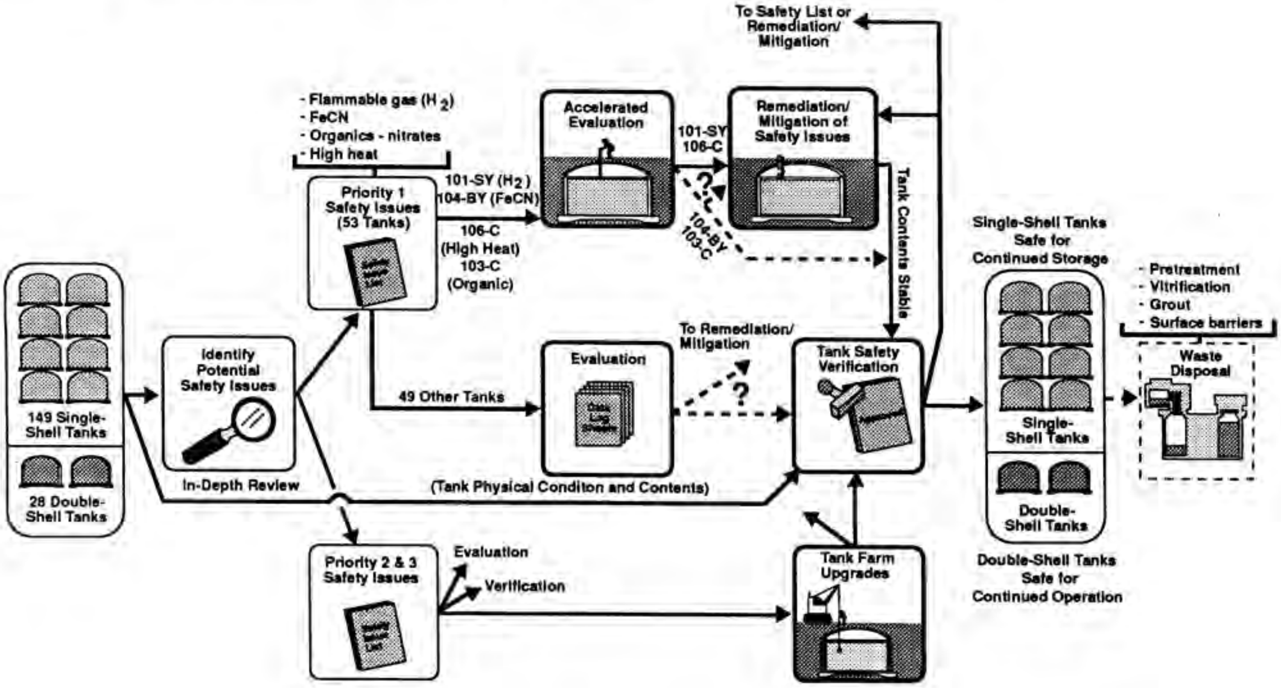

Fig. 1. Waste tank safety program overview.

exceed the lower flammability limits for short periods of time. Tanks 241-C-109 and 241-C-112 appear to have the largest concentration of ferrocyanide. Tank 241-C-103 has a separable organic layer floating on top of the aqueous waste and is a primary source of potentially flammable vapors. Although the ferrocyanide and organic tanks are handled as two separate programs for management convenience, they both can be classed as fuel-rich tanks.

APPROACHES TO ASCERTAINING THE RISK FROM FUEL-RICH OR FLAMMABLE GAS TANKS

General Considerations

Proof of the conditions in any given tank will rarely be absolute. Rather, the preponderance of the evidence must

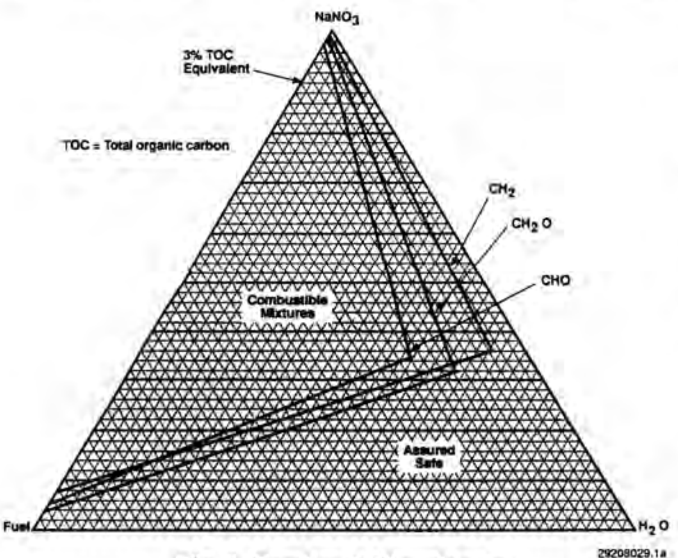

Fig. 2. Combustibility triangle.

substantiate that the potential for an exothermic reaction in a fuel-rich tank (e.g., a ferrocyanide salt-containing tank) is very low. Evidence for demonstrating these safety classes is not mutually exclusive. Information on the potential safety of a fuel-rich tank can and will be obtained from a variety of activities.

The conventional "fire" safety triangle sets the stage for the analysis. For an exothermic reaction to occur, the system must contain appropriate concentrations of fuel, oxidizer, and heat or other initiator (refer to Fig. 2). Conservative deterministic safety assessments require assuming the presence of a spark, heat, or other initiator. Because sodium nitrate and nitrite exist in high concentrations in almost all of the single- and double-shell tanks, the strategy for issue resolution will focus on the fuel.

Three long-term alternatives bound evaluating the safety condition in any given tank. To safely store waste in a tank until final disposal is accomplished, the waste must be kept in a safe form. It must be demonstrated on a tank-by-tank basis that the contents of the tank are either intrinsically safe (low fuel inventory), passively safe (low fuel concentration), or in a state of controlled safety (effective monitoring and corrective system in place) (refer to Fig. 3). Otherwise, the contents of that tank may be subject to in situ mitigation or early remediation.

A listing of these factors affecting a judgement of safety (e.g., inventory, concentration limits) will be presented. In addition, this presentation will identify the associated information needed to prove the credibility of the evaluation. However, existing and new data are unlikely to provide absolute proof of safety for any given tank other than those tanks that either received no inventory of fuel or were completely emptied of the suspect materials. Rather, a case will have to be made that the preponderance of the data and analysis results clearly suggest that continued storage of the waste is safe under the specified operating safety requirements control found in Table I.

GENERAL ISSUE RESOLUTION CONSIDERATIONS

Proof of the conditions in any given tank will rarely be absolute, but demonstrating a safe inventory and/or concentration of fuel in the condensed phase of a 1/2 to 1-million gallon single-shell tank poses special difficulties. Rather than "absolute proof," the preponderance of the evidence must convince external peer reviewers that the potential for an exothermic reaction in a fuel-rich single-shell tank, such as a ferrocyanide salt-containing tank, is considered extremely low. Also, evidence is mounting that maintaining sufficient moisture content to prevent propagation of any exothermic reaction will not be difficult. Information on the potential safety of a fuel-rich tank can and will be obtained from a variety of activities. Evidence for demonstrating a tank meets a specific safety class is not mutually exclusive. Rather, the data obtained by the program will create a consensus of peer opinion that individual or grouped tanks are safe. That process will close the safety issue(s) related to that tank.

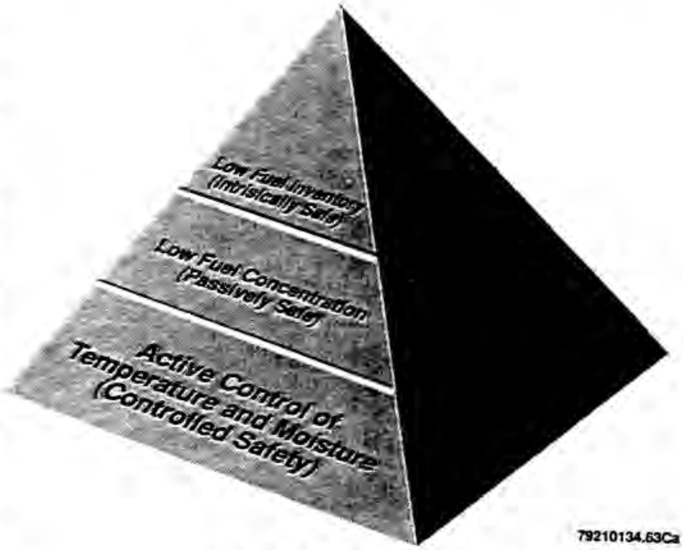

Fig. 3. Safety pyramid.

TABLE I
Information Sources Associated with Evaluation of Safety Factors

Safety Factor	Data Source	Information Needs
Inventory limit	• Historical information	• Inventory estimates from transfer records • Flow sheet projections
	• Characterization data	• Dome gas sample analysis • Tank sample analysis
	• Modeling	• Dome gas flow models • Transient maximal inventory of flammable gas • Thermodynamic energy estimates
Inventory limit	• Synthetic waste studies	• Gas generation, retention and release mechanisms • Large scale combustion data (e.g., Bureau of Mines) to define the energetics of a gas burn • Fuel degradation or decomposition
Concentration limit	• Historical information	• Flow sheet analysis • Concentration factors
	• Characterization data	• Multiple point dome gas measurements to define concentration profiles • Liquid and solid tank sample analyses
	• Modeling	• Thermodynamic energy estimates • Thermal modeling of tank responses
	• Synthetic waste studies	• Synthetic waste studies - Fuel dispersion mechanism - Degradation pathways - Fuel concentration pathways - Initiators and catalysts
Control limits	• Historical information	• Analysis of tank records
	• Characterization data	• Tank vapor sample analysis • Tank surface Sample analysis • Concentrations of key constituents
	• Monitoring data	• Enhanced dome space monitoring data • Enhanced moisture and temperature monitoring data
Control limits	• Energetics and reaction dynamics	• Thermodynamic energy estimates • Thermal and structural modeling of tank

The history of the single-shell tanks sheds light on difficulties in dealing with the safety issues associated with them. First, no wastes have been added to any of the single-shell tanks since November 1980. Half of the tanks, 67 of the 149, are classified as assumed leakers. To prevent or diminish impacts from future leaks from single-shell tanks, a program to remove pumpable liquids from these tanks was started and, *after* pumping, the tanks were isolated from their neighbors. A prohibition exists against adding waste to single-shell tanks (except for 241-C-105 and 241-C-106, our high-heat tanks), providing a means of preventing leakage to the environment in these singly contained vessels. There is also concern that any attempts to stir their contents would increase the risk of a leak, thus further limiting our mitigation options. Note that double-shell tanks pose no such intrinsic constraint because one can keep them wet and, if necessary, stir them as is planned for tank 241-SY-101.

Examples of criteria that would likely be associated with a demonstration of safety for flammable gas and fuel rich tanks are proposed in Tables II and III.

CONCLUSIONS

The Hanford Site's Waste Tank Safety Program is large and complex and has high priority within the DOE. Evaluating the safety issues identified above and defining appropriate remedial action to correct these safety concerns are being actively pursued at the highest possible priority. Risk to the operating staff, the Hanford Site environment, and to the general public appears to be extremely low; this is being reaffirmed. Work is in progress to quantify the risk and to take appropriate corrective actions to support continued safe storage of the waste as well as the eventual permanent disposal of Hanford Site's single- and double-shell tanks. The road to resolving the safety issues has been mapped out, and although it will be a journey of several more years, significant progress is being made toward understanding the basic safety issues and applying effective interim controls.

REFERENCES

1. G. R. WILSON and I. E. REEP, "A Plan To Implement Remediation of Waste Tank Safety Issues at the Hanford Site," WHC-EP-0422, Revision 1, Westinghouse Hanford Company, Richland, Washington (1991).
2. D. D. WODRICH and J. L. DEICHMAN, "Hanford Site Radioactive Waste Storage Tank Safety Issues: The Path to Resolution," WHC-SA-1328, Westinghouse Hanford Company, Richland, Washington (1992).
3. M. S. KAZIMI, "Approach to Resolution of Safety Issues Associated with Ferrocyanides in the Hanford Waste Tanks," U.S. Department of Energy High-Level Waste Tank Advisory Panel, U.S. Department of Energy, Washington, D.C. (1992).
4. H. BABAD, R. J. CASH, and A. K. POSTMA, "Progress in Evaluating the Hazard of Ferrocyanide Waste Storage Tanks," WHC-SA-1369-FP, Westinghouse Hanford Company, Richland, Washington (1992).
5. H. BABAD, D. R. JOHNSON, D. A. REYNOLDS, and D. M. STRACHAN, "Understanding of Cyclic Venting Phenomena in Hanford Site High-Level Waste Tanks: The Evaluation of Tank 241-SY-101," WHC-SA-1364-FP, Westinghouse Hanford Company, Richland, Washington (1992).
6. A. K. POSTMA, H. BABAD, R. J. CASH, and J. L. DEICHMAN, "Current Understanding of the Safety of Storing High-Level Waste Containing Ferrocyanide at the Hanford Site," WHC-EP-0531, Rev. 1, Westinghouse Hanford Company, Richland, Washington (1992).

TABLE II
Preliminary Guidelines for Assuring Safety of Flammable Gas Producing Tanks

Safety Factor	Characteristic	Criteria	Notes
Inventory limit	• Cyclic tank pressurization • Anomalous unexplained increases in tank surface levels	None	Based on records of tank behavior (past selection criterion)
Concentration limits	Dome gas concentration	Gas concentration <25% of lower flammability limit (LFL)	Based on industrial protection standards (present safety criterion)
Control limits	Dome gas concentration	<25% lower flammability limit	Assumes that tank concentrations require mitigation to even out cyclic gas releases to below LFL criterion.
	Dome gas pressure	Maintain negative pressure in tank -4 to -10 inch water gauge pressure	May require ventilation upgrade to meet criteria

TABLE III
Preliminary Guidelines for Assuring Safety of Fuel-Rich Tanks

Safety Factor	Characteristic	Criteria	Notes
Inventory limit	Total waste quantity	3% TOC or 1,000 gram/mole FeCN salts per tank (present criterion)	Based on initial assessment of risk
Concentration limits	Waste concentration	<100 cal/gram (present preliminary guestimate)	Specific to actual chemical composition and waste energetics
Control limits			Assumes that data are insufficient to prove inventory or concentration based safety.
• Moisture	• Tank moisture content	• 20+% moisture	
• Temperature	• Tank temperature	• Lack of a fuel concentration mechanism and <TBD Btu/hr heat generation • A TBD temperature limit (<85°C)	

TBD = To be determined.
TOC = Total organic carbon.