

PROGRESS IN EVALUATING THE HAZARD OF FERROCYANIDE WASTE STORAGE TANKS

Harry Babad and Robert J. Cash
Westinghouse Hanford Company

Arlin Postma
Benton City Technology

ABSTRACT

There are 177 high-level waste tanks on the Hanford site. Twenty-four single-shell tanks are identified as potential safety issues. These tanks contain quantities of ferrocyanide, nitrate, and nitrite salts that potentially could explode under certain conditions. Efforts were initiated in September 1990 to determine the reactive properties of the ferrocyanide waste and to define the criteria necessary to ensure tank safety until mitigation or remediation actions, if required, could be implemented.

This paper describes the results of recent chemical and physical studies on synthetic ferrocyanide waste mixtures. Data obtained from monitoring, tank behavior modeling, and research studies on waste have provided sufficient understanding of the tank behavior. The Waste Tank Safety Program is exploring whether the waste in many of the ferrocyanide tanks actually represents an unreviewed safety question.

The General Accounting Office (GAO) in October 1990 (1) suggested that ferrocyanide tank accident scenarios exceed the bounds of the Hanford Environmental Impact Statement (2). Using the same assumptions Westinghouse Hanford Company (WHC) staff confirmed the consistency of the GAO report calculations. The hypothetical accident scenario in the GAO report, and in the EIS, are based on several assumptions that may, or may not reflect actual tank conditions. The Ferrocyanide Stabilization Program at Westinghouse Hanford (summarized in this paper) will provide updated and new data using scientific research with synthetic wastes and characterization of actual tank samples. This new information will replace the assumptions on tank waste chemical and physical properties allowing an improved recalculation of current safety and future risk associated with these tanks.

PURPOSE AND SCOPE

This paper documents the current understanding of continued in situ storage, in underground storage tanks located at the Hanford Site, of high-level radioactive wastes containing ferrocyanide compounds. In situ storage is required until either final disposal of the waste or remediation options (if necessary) can be implemented.

The primary assessment is: (1) whether it is possible for a significant exothermic chemical reaction could occur in the ferrocyanide tank wastes under existing conditions; (2) and, if so, would the reaction reach runaway conditions.

BACKGROUND

Currently, 24 single-shell waste tanks on the Hanford Site are classified as containing ferrocyanide compounds at levels of 1,000 gram-moles or more (3). Since the initial classification, a more detailed evaluation of waste transfer records indicates that 6 of the 24 tanks contain less than 1,000 g-moles of ferrocyanide (4). Thus, 18 tanks are now identified as containing more than 1,000 g-moles of ferrocyanide.

During the 1950s, additional waste storage space was required to support the defense mission. Between 1953 and 1957, sodium or potassium ferrocyanide and nickel sulfate were added to the waste remaining from the uranium recovery process to precipitate cesium from the supernatant liquid as cesium nickel ferrocyanide. The resultant supernatant liquid was then discharged to cribs or specific retention sites, thus making more tank storage space available. Other waste types were added to many of the SSTs containing ferrocyanide before their deactivation in 1980 (5).

The General Accounting Office (GAO) reviewed the safety of the ferrocyanide tanks (1). It was postulated that a potential accident scenario of a runaway temperature excursion

or explosion could result in consequences outside the safety envelope defined in the Hanford Defense Waste Environmental Impact Statement (2). Because this accident scenario may not be currently bounded by the HDW-EIS (2), the ferrocyanide issue was declared an unreviewed safety question (USQ).

Ferrocyanide Scavenging

Three scavenging flowsheets were used in separate facilities to treat three different types of wastes. The corresponding flow sheets are termed "U-Plant", "T-Plant," and "In-Farm" flow sheets (6). In general, the aqueous-based waste was pumped to process tanks where the precipitating agents were added. Typically sodium ferrocyanide $[\text{Na}_4\text{Fe}(\text{CN})_6]$ was added to acid waste, the pH of the solution was adjusted to a pH of 9 ± 1 , and then an equal molar amount of nickel sulfate was added to produce $\text{Cs}_2\text{NiFe}(\text{CN})_6$ and $\text{Na}_2\text{NiFe}(\text{CN})_6$ precipitates. Other chemicals added included $\text{Ca}(\text{NO}_3)_2$, $\text{Sr}(\text{NO}_3)_2$, and $\text{Na}_2\text{HP0}_4$ to improve strontium (^{90}Sr) precipitation.

Ferrocyanide sludges were last produced in 1957 and have remained in storage since then. In subsequent tank farm operations, other wastes including the original wastes transferred in and/or out of the tanks. For example, concentrated wastes produced by an in-tank solidification (ITS) process added to Tank BY-104 and other BY Farm tanks (5). The solidification of ITS evaporator bottoms in the BY-104 tank has formed a "salt cake" layer some 1.22 meters thick. No waste have been added to the single-shell tanks since November 1980.

Description of the Single-Shell Tanks

The ferrocyanide wastes are contained in large underground tanks. A typical ferrocyanide-containing, single-shell tank (SST) that has been stabilized (pumpable liquid removed) is shown schematically in Fig. 1. The tanks are 75-ft in diameter and 29.75 to 37 feet in height, with nominal capacities of 500,000 to 750,000 gal (7). The tanks are below ground with at least seven feet of soil cover. As indicated in Fig. 1, the tanks contain level and temperature measuring instruments. The tanks also contain a pump pit where installed pumps can be used to remove supernatant and/or interstitial liquid from the tank (for stabilization). A limited number of the tanks contain a liquid observation well (LOW).

Previous Assessments of Safety of Ferrocyanide Wastes

A 1985 evaluation of hazards associated with core drilling of ferrocyanide wastes concluded that drilling operations could not initiate explosive reactions between ferrocyanide and nitrates (8).

A recent evaluation of storage stability of ferrocyanide wastes concluded that the risk of an uncontrolled ferrocyanide-nitrate reaction was low because tank temperatures were far below the temperature required to initiate such a reaction (4). Borsheim and Kirch (4) recommended improvements in temperature measurements and studies to determine if undetected hot spots could exist in the tanks.

The 1987 Hanford Defense Waste Environmental Impact Statement (2) contained accident evaluations based on a hypothetical explosion caused by a runaway exothermic reaction in a ferrocyanide waste tank. The initiator for such a reaction was postulated to be a waste retrieval operation. The runaway chemical reaction was postulated to occur in a relatively thin layer of dried sludge that contains much of the ferrocyanide inventory of the tank. Also postulated was a reaction (assuming an initiating event) rapidly propagating through this layer. It appears that the concentrated optimally reactive layer was postulated as a means for describing an upper bound accident. Recent evidence indicates that although the ferrocyanide sludge was laid down in layers, diluents also present prevented formation of concentrated optimally reactive layers. Dose consequences of the hypothetical accident analyzed in the HDW-EIS (2) were low because the fractional release of key dose-contributing nuclides (^{137}Cs and ^{90}Sr) was predicted to be low (5×10^{-6}).

A review of the ferrocyanide-nitrate explosion postulated in the HDW-EIS (2) by the GAO (1) concluded that nuclide release fractions were significantly underestimated. The GAO consultant who reviewed the postulated ferrocyanide-nitrate reaction pointed out that if a concentrated ferrocyanide layer existed, cesium would be concentrated in that layer. Thus cesium would be vaporized by a burn, resulting in a higher release fraction than had been identified in the HDW-EIS.

In response to the GAO report and concerns expressed by the State of Washington (9) that the consequences of a ferrocyanide explosion could exceed those analyzed, Westinghouse Hanford Company (WHC) in October 1990 declared the safety issue of the ferrocyanide-containing tanks and its potential consequences to be an USQ (10).

A broad spectrum of research efforts augmented by independent reviews were initiated in order to provide informa-

tion necessary to resolve the safety issues related to safe storage of ferrocyanide wastes and to define an approach to close the USQ. Research programs are being conducted at WHC, Pacific Northwest Laboratory (PNL), Los Alamos National Laboratory (LANL), and by Fauske and Associates, Inc. (FAI). Independent reviews of the ferrocyanide safety issue were conducted by LANL (Spore 1991) and by the DOE High-Level Waste Tank Advisory Panel (11).

TECHNICAL ASSESSMENT OF THE POTENTIAL FOR A RUNAWAY CHEMICAL REACTION IN A FERROCYANIDE WASTE TANK

Approach

Two related types of exothermic chemical reactions are of concern. A runaway reaction can occur without an external initiator when the heat generation rate in a region exceeds the heat loss rate. A propagating reaction is one that is able to rapidly move through unreacted material after being initiated by any mechanism.

The key safety issue is whether propagating or runaway reactions can occur in wastes, therefore, the work effort is focused on such reactions. For the purposes of this report, these reactions are evaluated as follows:

- Identify important parameters
- Identify available data
- Perform technical analyses to see what the data mean with regard to propagating and runaway reactions
- Identify areas where more information is needed to resolve the issue.

Identification of Key Parameters for Ferrocyanide Wastes

Runaway chemical reactions can occur when the heat generated within a volume exceeds the rate at which it is lost (12,13,14). Key parameters of the waste that would affect heat production rates, heat absorption rates, and the degree of waste heatup are the following:

- Inventory of ferrocyanide
- Radionuclide decay heating rate
- Concentration of reactants
- Thermal properties of waste
- Moisture concentration
- Size and shape of sludge mass

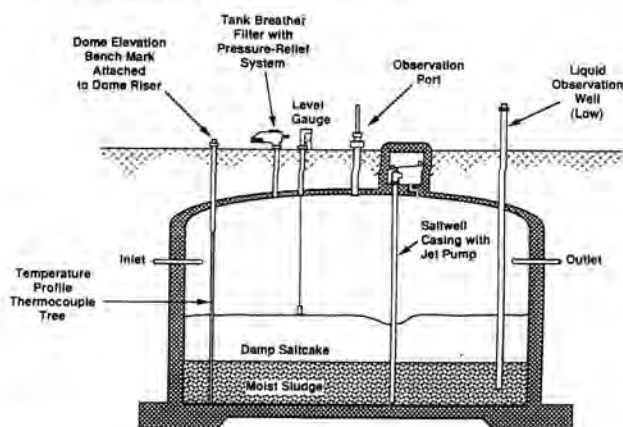


Fig. 1. Cross-sectional view of a typical ferrocyanide waste tank.

- Reaction kinetics
- Boundary conditions
- Reaction energetics
- Ignition temperature.

Summary of Information Known About Ferrocyanide Wastes

This section summarizes data on ferrocyanide waste characteristics. There are four sources of data on the wastes:

- Plant operating records
- Measurements performed on real waste (in situ and on samples)
- Laboratory tests on simulated wastes
- Modeling and engineering studies.

Information available from these four sources and important waste parameters are briefly discussed below.

Waste Quantities and Storage Conditions--Waste quantities and storage conditions are listed in Table I for each of the tanks on the Ferrocyanide Watchlist (3). As indicated by Table I data, most (70 percent) of the ferrocyanide is contained in the BY and T Tank Farms and was produced by the U-Plant flowsheet; 20 percent was produced by the In-Farm flowsheet and is stored in C-Farm tanks; the remaining 10 percent was produced by the T-Plant flowsheet and is stored in the TY-Tank Farm.

Ferrocyanide Inventory--The main source of information on the ferrocyanide inventory comes from material balances based on plant operating records. Inventories predicted from process records (4) are listed in Table I. Note that inventories less than 1,000 g-moles are indicated for tanks BX-102, BX-106, BX-110, BX-111 and BY-101, and T-101. These tanks are on the watchlist on the basis of earlier material balances (15) that are now believed to have overestimated their inventories. These tanks are candidates for removal from the list.

Core samples from tanks TY-101 and TY-103 in 1985 were analyzed for cyanide content (16,17). The average measured concentrations were 0.36 percent and 0.27 percent by weight for the two tanks, respectively. These measured cyanide concentrations translate (based on the assumption that the average applies to all of the sludge) into inventories of 17,200 g-moles and 18,200 g-moles for the two tanks, respectively. These inventories based on samples amount to 75 percent and 65 percent of the inventories listed in Table I. Considering uncertainties in both estimates, this is judged to be good agreement. The differences could also be an indication that some of the ferrocyanide was pumped out during stabilization or was destroyed by hydrolysis.

Cesium-137 and Strontium-90 Inventories--The principal heat-generating nuclides that could heat the wastes above ambient temperatures are ^{137}Cs and ^{90}Sr . In addition to the inventories based on material balances (Table I), in-tank spectral scans made with a collimated detector have given estimates of ^{137}Cs inventories (18). These two independent estimates are compared in Table II.

A comparison of the two estimates of ^{137}Cs inventory shows the scan-based estimate averaged 71 percent of the estimate based on flowsheet calculations. Considering uncertainties in both methods, this is judged to be good agreement.

Ferrocyanide Concentration--An important parameter in assessing the reactivity of ferrocyanide-nitrate mixtures is

the concentration of the two reactants. While confirmatory data on this question will have to await the results of core sampling of real waste, information presented below indicates that ferrocyanides may be distributed throughout the sludge layers rather than highly concentrated in thin layers. If concentrated layers do exist, the presence of diluents and excess sodium nitrate/nitrite (which also acts as a diluent) should preclude propagating reactions.

First, the ferrocyanide concentration in sludge layers, if present, is believed to be dilute, ranging from less than 2 wt% for BY tanks up to 20 wt% for the C-Farm tanks (6). Second, simulated sludge, prepared according to the U-Plant flowsheet, was estimated to contain only 1.8 wt% of $\text{Na}_2\text{NiFe}(\text{CN})_6$ (6). The stable sludge height found after centrifugation implies that further compaction with time (with attendant increase in concentration) would be limited. Third, vertical profiles of ^{137}Cs were obtained by means of calibrated collimated spectral gamma scans in a number of tanks (18). These scans indicate that ^{137}Cs is distributed throughout the sludge as opposed to being mostly located in a thin band. Two representative scans are reproduced in Figs. 2 and 3. The scan for Tank BY-104 (Fig. 2), selected here because historical records indicate this tank has the highest ferrocyanide inventory, shows that cesium is more or less uniformly distributed over the bottom six feet of the sludge. The scan for Tank BY-106 (Fig. 3) indicates the presence of a maximum concentration of 270 $\mu\text{Ci/g}$ near the bottom. This scan showed the most abrupt peak in ^{137}Cs of the 12 ferrocyanide tanks scanned. The peak is roughly three times the average for this tank.

A study of ^{137}Cs and ferrocyanide distributions showed that, at most, ferrocyanide would be concentrated no more than cesium (6). Therefore, the vertical ^{137}Cs profiles indicate that ferrocyanide is distributed throughout the sludge, with a peak-to-mean concentration of approximately three or less.

Moisture Content of Ferrocyanide Waste--The moisture content of stored waste is important because it is an inert diluent, and because its vaporization represents a large endotherm in postulated runaway reactions. Information on moisture content is available from tank samples, from synthetic sludge, and from a study of moisture retention by ferrocyanide sludge. Based on studies to date (6) it was concluded that moisture is held in capillaries, in gel form, and as chemical hydrates within the ferrocyanide waste. The capillary height of water in the sludges is predicted to be higher than the sludge depths for all tanks, so capillary action is predicted to be effective in keeping the waste moist even if a leak should drain the tank of excess liquid. A minimum moisture content of 40 percent by weight was predicted (6).

Core samples of ferrocyanide sludge obtained from Tanks TY-101, TY-103, and TY-104 in 1985 had moisture contents ranging from 43.5 percent to 62.7 percent (16,17). The moisture content in synthetic sludge was measured to be 66 percent by weight after it had been centrifuged into a stable sludge layer (6). This synthetic sludge was prepared to simulate the U-Plant flowsheet. Moisture measurements are planned on synthetic In-Farm and T-Plant flowsheet materials which are just now being produced.

Waste Temperature Histories--Temperatures inside the waste tanks have been recorded over their operating histories. In Fig. 4, the temperature history for one of the higher temperature tanks (Tank BY-104) is presented. While the data

TABLE I
Ferrocyanide Tank Data Summary

Tank	Waste processing source	Ferrocyanide content 1,000 g-moles	¹³⁷ Cs Ci decayed to 1/91	⁹⁰ Sr Ci decayed to 1/91	Solids volume/height kgal/ft		Max. temp as of 7/91 °F
		(1)	(1)	(1)	Total	Ferrocyanide sludge	°C (°F)
					(2)	(1)	
BX-102	U Plant	<1	-	-	96/3.5	0	18 (64)
BX-106	U Plant	<1	-	-	31/1.6	0	18 (64)
BX-110	U Plant	<1	-	-	198/6.6	0	19 (66)
BX-111	U Plant	<1	-	-	211/7.0	0	19 (67)
BY-101	U Plant	<1	-	-	387/12.3	0	23 (74)
BY-103	U Plant	66	1.6 E +05	2.3 E +05	400/12.7	212/7.0	31 (88) (LOW)
BY-104	U Plant	83	2.0 E +05	3.0 E +05	406/12.9	260/8.5	54 (130)
BY-105	U Plant	36	8.8 E +04	1.3 E +05	503/15.9	96/3.5	44 (112)
BY-106	U Plant	70	2.2 E +05	3.3 E +05	642/20.1	228/7.5	54 (130)
BY-107	U Plant	42	1.3 E +05	2.2 E +05	266/8.7	158/5.4	27 (80)
BY-108	U Plant	58	2.1 E +05	2.6 E +05	228/7.5	208/6.9	36 (97)
BY-110	U Plant	71	1.9 E +05	3.2 E +05	398/12.7	225/7.4	49 (120)
BY-111	U Plant	6	1.1 E +04	1.9 E +04	459/14.5	14/1.1	29 (84) (LOW)
BY-112	U Plant	2	5.1 E +03	8.1 E +03	291/9.4	7/0.7	27 (81) (LOW)
C-108	In-Farm	25	6.5 E +04	5.9 E +02	66/2.6	77/3.0	24 (75)
C-109	In-Farm	30	1.1 E +05	3.8 E +03	62/2.5	109/3.9	25 (77)
C-111	In-Farm	33	1.4 E +04	8.1 E +02	57/2.3	98/3.6	27 (80)
C-112	In-Farm	31	1.3 E +05	1.4 E +03	104/3.8	84/3.2	27 (80)
T-101	U Plant	<1	-	-	103/3.7	0	19 (67)
T-107	U Plant	5	7.8 E +03	1.3 E +04	171/5.8	212/7.0	20 (68)
TX-118	U/T Plant	<3	-	-	347/11.1	-	22 (71)
TY-101	T Plant	23	4.2 E +04	3.7 E +04	118/4.2	151/5.2	20 (68)
TY-103	T Plant	28	5.2 E +04	4.5 E +04	162/5.5	179/6.0	18 (65) (LOW)
TY-104	T Plant	12	2.1 E +04	1.9 E +04	43/1.9	75/2.9	20 (68)

Sources: (1) (6)
(2) (3).

LOW = TC in liquid observation well

TABLE II

¹³⁷Cs Inventories Based on Collimated Spectral Gamma Scans

Tank Number	¹³⁷ Cs Inventory, Ci ^a		Ratio of Cs scan to Material Balance
	Spectral Scan ^b	Material Balance ^c	
BY-103	7.1 E4	1.6 E5	0.44
BY-104	1.5 E5	2.0 E5	0.75
BY-105	6.0 E4	8.8 E4	0.68
BY-106	1.2 E5	2.2 E5	0.55
BY-107	9.8 E4	1.3 E5	0.75
BY-110	1.8 E5	1.9 E5	0.95
TY-103	3.8 E4	5.2 E4	0.73
		Average:	0.71

NOTE: ^aDecayed to January 1991

^b(18)

^cTable I values from Borsheim and Simpson (6).

are scattered, it is evident that waste temperatures have fallen considerably since 1975. The cooling of wastes with time, Fig. 4, is not solely the result of declining decay heat loads. The high temperature in 1975 stems mainly from tank heat-up in the 1970s caused by the addition of hot saturated solutions produced by in-tank solidification (ITS) processes. These

tanks were in the ITS loop for times ranging from 2 to 7 years starting about 1970 (5). Thus, the BY tanks, which contain 70 percent of the ferrocyanide, were subjected to a significant heating cycle. Yet no runaway reactions were observed in any of the heated tanks.

Onset Temperatures for Ferrocyanide Nitrate/Nitrite Reactions--A number of laboratory studies are being conducted to define a temperature where ferrocyanide-nitrate/nitrite reactions occur fast enough to be of concern.

Laboratory studies at PNL used three experimental methods to study the onset temperature: (1) differential scanning calorimetry (DSC); (2) scanning thermogravimetry (STG); and, (3) time-to-explosion tests (TTX) (19). The DSC and STG tests indicated reaction starting temperatures of 220 to 280°C depending on the nitrate and/or nitrite ratio and the composition of catalysts/initiators added. The TTX tests identified a minimum critical temperature (T_c) of 280 ± 5°C for an explosive reaction. The value of T_c was found to vary from 280 to 370°C depending on the oxidant/fuel ratio, the ratio of nitrite to nitrate, and the presence of the organic substance ethylenediaminetetraacetic acid (EDTA) (19).

In tests with an adiabatic calorimeter, propagating reactions were first noticed at about 280°C with mixtures of Cs₂NiFe(CN)₆, NaNO₃ and NaNO₂. The presence of EDTA,

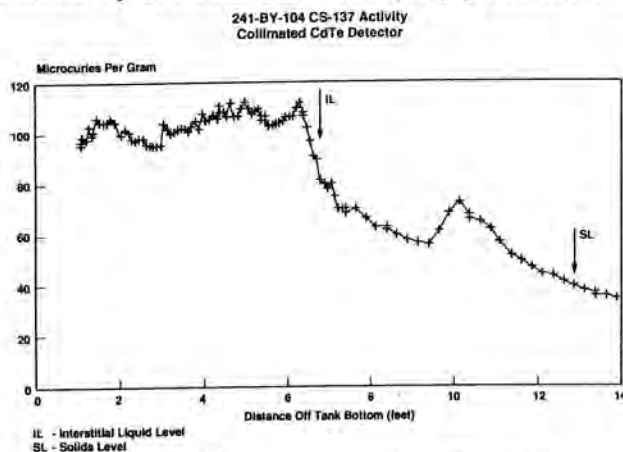


Fig. 2. Profiles of ¹³⁷Cs as measured by collimated spectral gamma scans for tank BY-104.

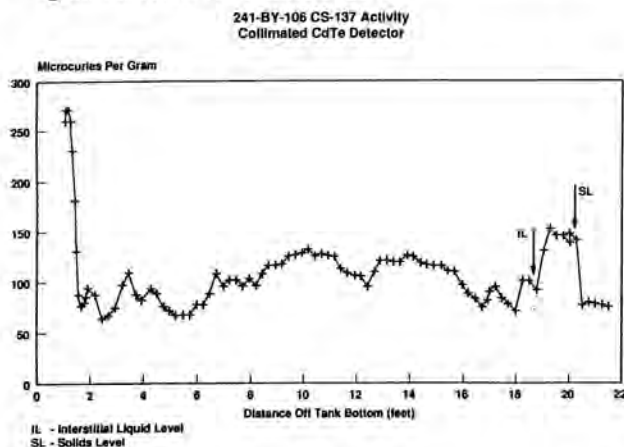


Fig. 3. Profiles of ¹³⁷Cs as Measured by Collimated Spectral Gamma Scans for Tank BY-106.

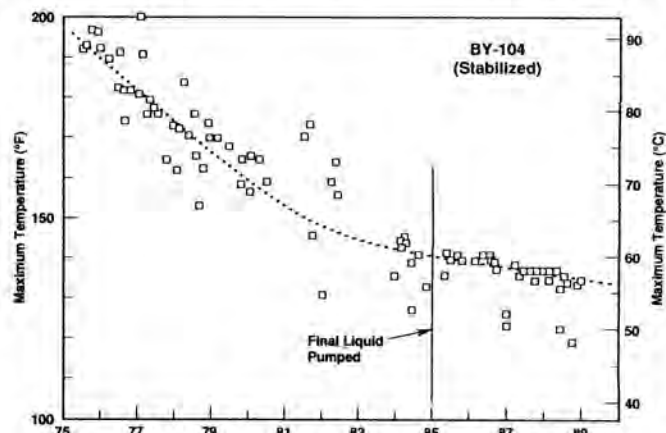


Fig. 4. Temperature history for tank BY-104.

however, appeared to lower the onset temperatures to about 220°C (20). These tests were done with pure reactants $\text{Cs}_2\text{NiFe}(\text{CN})_6$, NaNO_3 , NaNO_2 , and EDTA and the results did not imply that propagating reactions are possible in real wastes, which are considerably more dilute.

Reaction Propagation Velocity--Scouting tests to measure propagation velocities are being carried out using ferrocyanide-nitrate/nitrite mixtures (21). From the studies completed the main conclusion is that pure, dry reactants can support a propagating reaction. Anhydrous mixtures propagate faster than those containing waters of hydration.

Tests were also conducted with simulated waste (U-Plant flowsheet) in an adiabatic calorimeter (22). Results showed no evidence of a propagation reaction. Additional tests are planned as synthetic In-Farm and T-Plant flowsheet materials become available.

Assessment of Runaway Potential Based on Storage History

In this section the potential for a runaway reaction will be examined by comparing heat loss rates with heat generation rates. This approach is commonly used in the chemical industry to assess the safety of storing potentially reactive materials (12,13,14).

Criterion for Safety--The storage safety of a reactive substance can be judged on the basis of a heat balance. If heat is generated faster than it can be dissipated, the stored substance will increase in temperature at ever-increasing rates (i.e., it will experience a runaway reaction). On the other hand, if heat is dissipated faster than it is generated, no runaway reaction will occur and the material can be stored safely. The criterion for safety with respect to runaway reactions is that heat must be dissipated as rapidly as it is generated. One way of expressing this is by requiring the heat loss rate to be equal to or greater than the rate at which heat is generated. The criterion must be met at all points within the waste.

In most storage safety evaluations, the heat generation rate in the material to be stored is measured as a function of temperature. This generation rate can be used as an input to heat transfer calculations to identify the conditions under which the material can be safely stored. For the present case, the storage history becomes an integral experiment where it is demonstrated that the heat generated (decay heat and chemical reaction heat) was dissipated. If heat had not been dissipated as fast as generated, then the wastes would have increased in temperature and possibly experienced a runaway reaction during the past 34 years.

Heat Dissipation By Passive Dry Processes--The decay heat generation rates in ferrocyanide tanks are modest (<3.8 kw), and modeling code calculations have been carried out to put heat dissipation requirements into perspective.

Steady-state heat transfer analyses indicate that most of the decay heat in waste tanks is transferred upward through the waste, through the tank head space, through the overburden, and into the atmosphere (23). It is important to know that decay heat could be transferred through the tank head space in the event that heat transfer were not augmented by either moisture evaporation or condensation in the head space. Simple heat transfer calculations indicate that radiation and natural convection without evaporation or condensation of moisture can, with small temperature differences, transfer decay heat through the tank head space.

Conclusions From Storage History--The absence of either runaway reactions or significant temperature increases over the past 34 years is evidence that heat dissipation rates are equal to or larger than heat generation rates. Two conclusions from storage history are:

- The safe storage history demonstrates that, under past storage conditions, heat generated could be safely dissipated.
- If a change in waste or storage conditions occurs that caused the safety criterion to fail, it would be reflected in temperature increases in the waste. Therefore, waste temperatures should be monitored to allow detection of unexpected rises and implementation of mitigating actions, if required.

Assessment of Runaway Potential Based on Thermodynamic Analysis

In this analysis the energy given off by the oxidation-reduction reaction (ferrocyanide-nitrate/nitrite) is compared to the energy required to heat waste to a critical reaction temperature. The reaction can propagate if the reaction energy is sufficient to heat unreacted waste to the threshold reaction temperature. An energy balance based on this temperature rise allows a threshold composition limit to be determined. Once a threshold limit has been determined, waste compositions may be judged to be reactive or nonreactive according to whether they fall above or below the limit.

Threshold Limits for Propagating Reactions--The energy given off by ferrocyanide-nitrate and/or nitrite reactions depends greatly on the specific reaction products that are formed (19,24). This is illustrated by the heats of reaction listed in Table III.

Reaction energy will be absorbed by the waste, causing it to heat up. Key parameters that were used in constructing the propagation limit for a ferrocyanide-nitrate reaction are the following:

- Initial waste temperature = 55°C
- Ignition temperature = 275°C
- Reaction energy = 80 percent of 3025 kJ/mol ferrocyanide
- Moisture evaporates prior to ignition.

The reaction threshold limit can be shown as a line on a triangular diagram, as illustrated in Fig. 5. Compositions that lie above the limit line are reactive, while those that fall below the line are nonreactive.

Comparison of Waste Composition with Propagation Limit Line--Available estimates of waste compositions are plotted on Fig. 5, and as is evident by inspection, all compositions fall well below the limit line. The calculated range for ferrocyanide sludge compositions was obtained from flowsheet calculations (6) and is believed to represent the range for all ferrocyanide tanks. The water content, 40 percent, was chosen as the minimum value identified in a recent review of moisture content. Actual samples from Tanks TY-101 and TY-103 also fall well below the limit line. It should be noted that these samples were from composite core samples and would not reflect variations in concentration with height. Vertical profiles of ^{137}Cs showed variations in concentrations, with peak and/or average ratios as high as 3.1 (for Tank BY-106). The peak ferrocyanide concentration is estimated to be

TABLE III

Heats of Reaction for Different Oxidation Reactions (19).

Reactants	Products	Enthalpy (kJ/mol)
NaNO ₃ and Na ₂ NiFe(CN) ₆	FeO, NiO, CO ₂ , N ₂ , Na, Cs hydroxides	-2490
NaNO ₃ and Na ₂ NiFe(CN) ₆	FeO, NiO, CO ₂ , N ₂ , Na, Cs Carbonates	-3025
NaNO ₃ and Na ₂ NiFe(CN) ₆	FeO, NiO, CO ₂ , N ₂ , Na, Cs oxides	-1566
NaNO ₃ and Na ₂ NiFe(CN) ₆	FeO, NiO, CO ₂ , N ₂ , Na, Cs hydroxides	-2925
NaNO ₃ and Na ₂ NiFe(CN) ₆	FeO, NiO, CO ₂ , N ₂ , Na, Cs Carbonates	-3720
NaNO ₃ and Na ₂ NiFe(CN) ₆	FeO, NiO, CO ₂ , N ₂ , Na, Cs oxides	-1705
NaNO ₃ and Na ₂ NiFe(CN) ₆	FeO, NiO, CO, N ₂ , Na, Cs hydroxides	-1180
NaNO ₃ and Na ₂ NiFe(CN) ₆	FeO, NiO, CO, N, Na, Cs hydroxides	+ 620

0.25 M or less for this tank (6). Assuming that stoichiometric sodium nitrate is present, the reactant concentration is computed to be 13 percent. This composition falls well below the propagation limit line at a 40 percent water content. Synthetic sludge made by the U-Plant flowsheet (22) also falls well below the limit line. Notably missing from this plot are concentrations that apply to the In-Farm flowsheet. The In-Farm sludges are much richer in ferrocyanide with relatively lower impurity levels. In the extreme limit with no inerts present, the In-Farm composition would lie on the zero percent inert line (the side of the triangle labeled "Weight Percent Reactants"). Compositions along this line would be nonreactive if they contained 50 percent or more water but reactive if they contained less than 50 percent water by weight.

Work is in progress at Hanford to produce and characterize synthetic sludges with the In-Farm and T-Plant flowsheets. Once concentration data are available, the compositions can be located on the triangular diagram. It is expected that the water content, as a minimum, will be 40 wt% for these two flowsheet materials.

Effect of Hypothetical Waste Dryout on Waste Reactivity--The removal of moisture from waste moves the composition towards the reactive limit, as illustrated by a dryout line drawn in Fig. 5. The dryout line is located by connecting an initial composition to the 100 percent water apex. The synthetic sludge crosses the propagation limit line (Fig. 5) at a water content of approximately 1 percent. The other sample compositions (Fig. 5) remain below the limit line even when their moisture content is reduced to zero.

Studies of moisture transport in ferrocyanide tanks by others led to three important conclusions (23):

- Evaporation by atmospheric breathing leads to negligible losses.
- Wastes will retain a moisture content of 40 percent or more, even if the tanks leak or are saltwell pumped.
- Forced or unrestricted natural convection could, over time, significantly dry the wastes.

If these conclusions are valid, then waste dryout is impossible unless large quantities of dry air flow through the tank vapor space for extended time periods. Tank farm management actions can (and should) preclude this from happening and, therefore, dryout is considered a hypothetical occurrence.

CONCLUSIONS: WHAT THE AVAILABLE INFORMATION MEANS ABOUT FERROCYANIDE TANK SAFETY

Key conclusions from the review of available information on ferrocyanide wastes are:

1. Contents are different for each tank. The tanks must be analyzed on an individual basis.
2. Expected compositions in most tanks are below the propagation limit line (Fig. 5), and hence would not support propagating reactions.
3. The wastes apparently retain high moisture levels (> 40 wt%) even when subjected to saltwell pumping or leakage. Significant dryout could only occur by evaporation into dry air flowing through tank head spaces.
4. Vertical scans of the tanks studied show that ¹³⁷Cs is distributed over the entire sludge layer, with peak-to-mean ratios as high as three. This indicates that ferrocyanides are not concentrated in a thin band.
5. Thermodynamic analysis provides a means for developing criteria for controlling waste temperature and water content to ensure that wastes remain nonreactive.

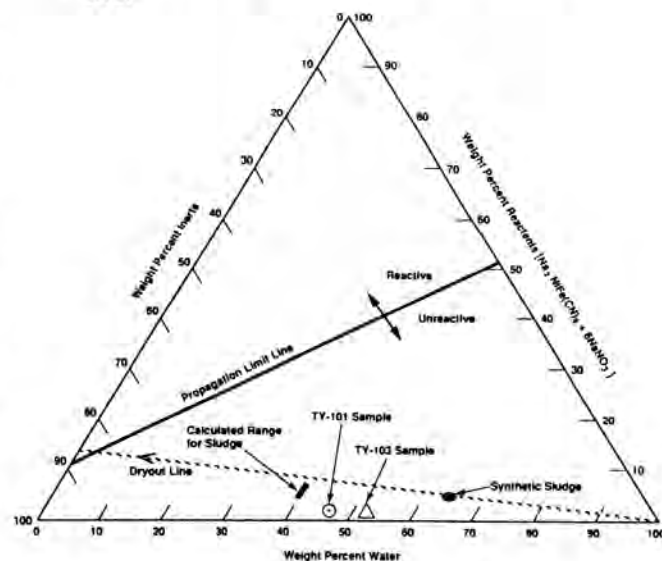


Fig. 5. Composition limits for reactive mixtures.

What Available Information Means With Respect to Continued In Situ Storage

Prevent Dryout of Stored Wastes--Each tank should be reexamined to verify that dry air flowing through the head space cannot remove a significant quantity of water by evaporation. What is "significant" should be judged by changes in reactivity (as a result of water loss) as indicated by thermodynamic analyses (Fig. 5).

Develop Criteria for Safe Storage--Criteria are needed to guide tank management and surveillance operations. Of particular importance are criteria for the following parameters:

- Moisture content
- Temperature increases
- Ferrocyanide waste concentration and composition compared to the reactivity limit.

Monitor Tanks to Confirm Safe Conditions--Wastes must be monitored to verify that conditions for safe storage do not deteriorate with time. Obvious parameters to be measured include moisture content and temperature.

Install Control Equipment--Prudent management requires that control systems be developed to mitigate unexpected changes. Examples would be significant temperature increases or significant drying of waste. The controls, at a minimum, should allow for the addition of the water or the removal of heat from a tank that exhibits unexpected behavior.

What Additional Information is Needed to Understand Storage of Ferrocyanide Wastes

Ferrocyanide/Oxidant Concentrations--While available information indicates that ferrocyanide concentrations are below levels that could support a propagating reaction, data confirmation is needed. Tank sampling, flowsheet calculations, and simulant preparation will be needed to identify the concentrations of fuels (including organic materials) and oxidants that actually exist in the tanks. Tests on solubility and hydrolysis of ferrocyanide species under tank conditions should be continued.

Moisture Retention by Wastes--Work needs to be continued on the retention of moisture by the waste. Additional technical analyses and experiments are needed to confirm that sufficient water is retained (in leaking tanks and in tanks that have been saltwell pumped) to maintain compositions below the propagation limit line.

Reactivity Limits--Realistic composition limits are needed to judge the safety of compositions in the tanks. Further study, and possibly experiments, will be needed to confirm presently proposed composition limits for self-propagating reactions.

Hot Spots--Hypothetical hot spots provide a possible means for drying wastes, perhaps causing the dried volume to become reactive. Such hot spots represent pockets of potentially reactive material. Understanding is needed on: (1) what kinds (volumes, shapes, and concentrations) of hot spots could be formed; (2) how long it would take them to reach peak temperatures; and, (3) whether the peak temperature would be high enough to initiate a runaway reaction in dried material. Studies, including experimental work, are needed to gain an adequate understanding of hot spots.

Reaction Propagation Rates--While it has been tentatively concluded that most waste can be kept moist and non-reactive, it is likely that uncertainties related to peak

concentrations and hot spots represent a perceived residual risk. In order to obtain realistic estimates of the consequences of reactions in limited waste volumes, data are needed on how fast a reaction could propagate through these volumes. Experimental representative wastes, dried to varying degrees of moisture content, are needed. This would provide a basis for predicting how much waste could become airborne if exothermic reactions were to occur within limited waste volumes.

Chemical Changes in Waste with Time--Chemical changes over the past 34 years could affect waste reactivity. Studies, including laboratory tests on simulants and actual waste, are needed to quantify the significance of changes that could occur. Information is needed to evaluate how chemical changes would affect fuel concentrations, propagation rates, and ignition temperatures.

In the interim period, while collecting the data to support closure of the safety issue, administrative and technical controls remain in place to restrict activities that could cause undesirable exothermic reactions. While the probability of an excursion in the ferrocyanide tank waste is probably very low, the consequences of such an event are unacceptable. Characterization efforts are being complemented using studies that define the envelope of risk associated with ferrocyanide tanks. Risk to the operating staff, the Hanford Site environment, and the general public appears to be low, but it is being reevaluated. Work to quantify the risk and provide for mitigation, if necessary for the short term, is continuing at the Hanford Site on a priority schedule. Results will factor into the longer term final disposal of waste from Hanford's double-shell and single-shell tanks.

REFERENCES

1. J. D. PEACH, "Consequences of Explosion of Hanford's Single-Shell Tanks are Understated," (Letter B-241479 to C. M. Synar, Chairman of Environment, Energy and Natural Resources Subcommittee, Committee on Government Operations, House of Representatives), GAO/RCED-91-34, General Accounting Office, Washington, D.C. (1990).
2. U.S. DEPARTMENT OF ENERGY, *Final Environmental Impact Statement - Disposal of Hanford Defense High-Level, Transuranic and Tank Waste*, DOE/EIS-0113, U.S. Department of Energy, Washington, D.C. (1987).
3. B. M. HANLON, *Tank Farm Surveillance and Waste Status Report for October 1991*, WHC-EP-0182-43, Westinghouse Hanford Company, Richland, Washington (1991).
4. G. L. BORSHEIM and N. W. KIRCH, *Summary of Single-Shell Waste Stability*, WHC-EP-0347, Westinghouse Hanford Company, Richland, Washington (1991).
5. J. D. ANDERSON, *A History of the 200 Area Tank Farms*, WHC-MR-0132, Westinghouse Hanford Company, Richland, Washington (1990).
6. G. L. BORSHEIM and B. C. SIMPSON, *An Assessment of the Inventories of the Ferrocyanide Watch List Tanks*, WHC-SD-WM-ER-133, Rev. 0, Westinghouse Hanford Company, Richland, Washington (1991).
7. D. M. SMITH, "Single-Shell Tank Isolation Safety Analysis Report," SD-WM-SAR-006ENG, Rev. 2, Rockwell Hanford Operations, Richland, Washington (1986).

8. R. L. KOONTZ, *Hazards Identification and Evaluation for Waste Tank Core Sampling Equipment*, SD-WM-SAR-007, Rockwell Hanford Operations, Richland, Washington (1985).
9. ECOLOGY AND HEALTH, "Special Report: Ferrocyanide in Single-Shell High-Level Waste Tanks at Hanford," Washington State Department of Ecology and Washington State Department of Health, Olympia, Washington (1990).
10. D. E. DEATON, "Unusual Occurrence - Unreviewed Safety Questions Regarding Tanks Containing Ferrocyanide," WHC-90-B003-R1, Update, 10-22-91, Westinghouse Hanford Company, Richland, Washington (1990).
11. 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).
12. R. W. GYGAX, "Scaleup Principles for Assessing Thermal Runaway Risks," *Chem. Engr. Prog.*, pp 53-60 (February 1990).
13. F. L. LEES, *Loss Prevention in the Process Industries*, Vol. 1, pp 495-498, Butterworths, London, England (1989).
14. D. I. TOWNSEND and J. C. TOU, "Thermal Hazard Evaluation by an Accelerating Rate Calorimeter," *Thermochimica Acta*, 37: 1-30.
15. D. M. NGUYEN, "Data Analysis of Conditions in SST Suspected of Containing Ferrocyanide," (Internal Memo #11314-89-025) to N. W. Kirch, dated March 1989, Westinghouse Hanford Company, Richland, Washington (1989).
16. R. L. WEISS and B. M. MAUSS, *Data Transmittal Package for 241-TY-103 Waste Tank Characterization*, SD-RE-TI-184, Rockwell Hanford Company, Richland, Washington (1987).
17. R. L. WEISS and B. M. MAUSS, *Data Transmittal Package for 241-TY-101 Waste Tank Characterization*, SD-RE-TI-185, Rockwell Hanford Company, Richland, Washington (1987).
18. B. D. KEELE, ET AL., *Application of a CdTe Gamma-Ray Spectrometer to Remote Characterization of High-Level Radioactive Waste Tanks*, WHC-SA-1196-FP, Westinghouse Hanford Company, Richland, Washington (1991).
19. L. L. BURGER and R. D. SCHEELE, *The Reactivity of Cesium Nickel Ferrocyanide Toward Nitrate and Nitrite Salts--A Status Report*, PNL-7550, Pacific Northwest Laboratory, Richland, Washington (1991).
20. H. K. FAUSKE, *Potential for Runaway Ferrocyanide Reactions in Hanford Waste Tanks*, Presentation to U.S. Department of Energy High-Level Radioactive Waste Tank Task Force and Advisory Panel Meeting, Richland, Washington, January 10, 1991.
21. FAI, 1991, *Reaction Propagation Velocity Measurements for $K_4Fe(CN)_6$* , FAI/91-66, Fauske and Associates, Inc., Burr Ridge, Illinois (April 1991).
22. H. K. FAUSKE, *Assessment of the Ferrocyanide Issue*, Presentation to Waste Management External Advisory Committee, Fauske and Associates, Inc., Burr Ridge, Illinois (1991).
23. J. M. MCLAREN, *Single-Shell Tank 241-BY-104 Thermal-Hydraulic Analysis*, WHC-EP-0521, Westinghouse Hanford Company, Richland, Washington (1991).
24. S. A. COLBY and M. D. CRIPPEN, *Graphical Presentation of Ferrocyanide Tank Compositions*, WHC-SA-13404-FP, Westinghouse Hanford Company, Richland, Washington (1991).
25. J. SPORE, "Hanford High-Level Waste Tank Safety Reanalysis: Tank 241-104-BY," (Presentation to Advisory Committee on Nuclear Facility Safety in Denver, Colorado, July 1991), Los Alamos National Laboratory, Los Alamos, New Mexico (July 1991).