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Resolving the Ferrocyandide Safety Issue at the Hanford Site

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Part 1

RESOLVING THE FERROCYANIDE SAFETY ISSUE AT THE HANFORD SITE

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ABSTRACT

Considerable data have been obtained on the chemical and physical properties of ferrocyanide waste stored in Hanford Site single-shell tanks (SSTs). Theoretical analyses and ferrocyanide waste simulant studies have led to the development of fuel, moisture, and temperature criteria that define continued safe storage. Developing the criteria provides the technical basis for closing the Ferrocyanide Unreviewed Safety Question (USQ). Using the safety criteria, the ferrocyanide tanks have been ranked into one of three safety categories: SAFE, CONDITIONALLY SAFE, and UNSAFE. All the ferrocyanide tanks are currently ranked in either the SAFE or CONDITIONALLY SAFE categories.

Analyses of core samples taken from three ferrocyanide tanks have shown cyanide concentrations about a factor of ten lower than predicted by the original flowsheets. Hydrolytic and radiolytic destruction (aging) of the ferrocyanide matrix have occurred during the 35 plus years the waste has been stored at the Hanford Site. Because of waste aging, it is possible that all of the ferrocyanide tanks may now contain less than the 8 wt% sodium nickel ferrocyanide specified in the fuel criterion for the SAFE category.

Ferrocyanide tanks that remain in the CONDITIONALLY SAFE category may require monitoring and surveillance to verify that the waste remains in an unreactive state. Further characterization of the tanks by core sampling and analyses should lead to resolution of the Ferrocyanide Safety Issue by September 1997.

BACKGROUND

Various radioactive wastes from defense operations have accumulated at the Hanford Site in underground waste tanks since the early 1940s. 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 ^{137}Cs from tank waste liquids. In implementing this process, approximately 140 metric tons of ferrocyanide were added to waste that was later routed to some Hanford Site SSTs. In 1991, based on available information, 24 tanks were assigned to the Ferrocyanide Watch List based upon the criterion that they originally received inventories of at least 1,000 g-moles of ferrocyanide [as the $Fe(CN)_6^{4-}$ anion].

Ferrocyanide, in the presence of oxidizing material such as sodium nitrate and/or nitrite, can propagate and sometimes explode by heating it to high temperatures or by an electrical spark of sufficient energy. Under laboratory conditions deliberately created to enhance the potential for reactions, significant exothermic reactions can start as low as 220 °C, but the lowest explosion temperature observed is approximately 285 °C. The explosive nature of ferrocyanide in the presence of an oxidizer has been known for decades, but the conditions under which the compound can undergo exothermic reactions have not been thoroughly studied. Because the scavenging process precipitated ferrocyanide from solutions containing nitrate and nitrite, an intimate mixture of ferrocyanides and nitrates and/or nitrites is likely to exist in some regions of the ferrocyanide tanks.

Efforts have been underway since the mid-1980s to evaluate the potential for ferrocyanide reactions in Hanford Site SSTs (Burger 1989, Burger and Scheele 1988). The potential consequences of a postulated ferrocyanide burn or explosion were not evaluated in the safety analysis reports (SARs) applicable to the Hanford Site SSTs. The SARs historically have considered an explosion from fuel/nitrate reactions an incredible event and the consequences of incredible events are not required to be analyzed (WHC 1992).

Although not considered a part of the safety analysis for the storage of waste in the SSTs, the 1987 Environmental Impact Statement (EIS), *Final Environmental Impact Statement, Disposal of Hanford Defense High-Level Transuranic and Tank Waste, Hanford Site, Richland, Washington* (HDW-EIS) (DOE 1987) did include an environmental impact analysis of potential explosions involving ferrocyanide-nitrate mixtures. The EIS postulated that an explosion could occur during mechanical retrieval of saltcake or sludge from a ferrocyanide waste tank. The EIS concluded that this worst-case accident could create enough energy to release radioactive material to the atmosphere through ventilation openings, exposing persons offsite to a short-term radiation dose of approximately 200 mrem. A General Accounting Office (GAO) study (Peach 1990) postulated a greater worst-case accident, with independently calculated doses of one to two orders of magnitude greater than in the DOE EIS (DOE 1987).

The root cause of the ferrocyanide problem results from a combination of factors, beginning with the safety studies performed as precursors to using the ferrocyanide scavenging flowsheets. These studies did not include ultimate disposal of the ferrocyanide solids, and were not performed to the conservative standards used today, because the studies did not discuss the risk of adding ferrocyanide to waste tanks. In addition, no rigorous inventory was kept of the ferrocyanide or other chemicals added to the tanks. Subsequent safety studies either were not performed, or were performed to less conservative standards, to demonstrate that other chemicals would not increase the level of risk. Monitoring systems for designated SSTs, such as temperature measurement instrumentation, were allowed to be disconnected and fall into disrepair because the potential hazard was not highlighted.

In October 1990 (Deaton 1990), the Ferrocyanide Issue was declared an USQ* because the safety envelope for the waste tanks containing ferrocyanide was no longer bounded by the existing SAR.

In 1991, using process knowledge, process records, transfer records, and log books, 24 tanks were identified at the Hanford Site as potentially containing 1,000 g-mole (465 lb) or more of ferrocyanide [as the $Fe(CN)_6^{4-}$ anion]. These tanks were placed on a Ferrocyanide Watch List. The Ferrocyanide Watch List currently contains 20 tanks. Re-examination of the historical records (Borsheim and Simpson 1991) indicated that 6 of the 24 tanks do not contain the requisite 1,000 g-moles of ferrocyanide and should not have been included on the Watch List. Four of the 6 tanks were removed from the Watch List in June 1993 (Meacham et al. 1993) and removal of the other two tanks is pending (Borsheim et al. 1993).

STRATEGY FOR CLOSING THE USQ AND RESOLVING THE FERROCYANIDE SAFETY ISSUE

Work in and around any of the ferrocyanide tanks requires detailed planning, including preparation of supporting safety and environmental documentation and approval by DOE top management. These restrictions are imposed to ensure that appropriate precautions are taken to minimize the potential safety and environmental impacts associated with the USQ hazard. The need to evaluate the hazards and ensure that appropriate controls are implemented has increased the time required to complete work or install equipment in the ferrocyanide tanks. Closure of the USQ delegates authorization of activities dealing with ferrocyanide tanks to Westinghouse Hanford Company (WHC), which will expedite the clean up effort.

A strategy for closing the USQ and resolving the Safety Issue surrounding the ferrocyanide wastes was developed by DOE and WHC and presented to the DNFSB in August 1993 (Grumbly 1993). A summary of the strategy is presented in Fig. 1.

The strategy uncoupled USQ closure from resolution of the Safety Issue and calls for closure of the USQ before resolution of the Safety Issue. The USQ is closed by developing criteria

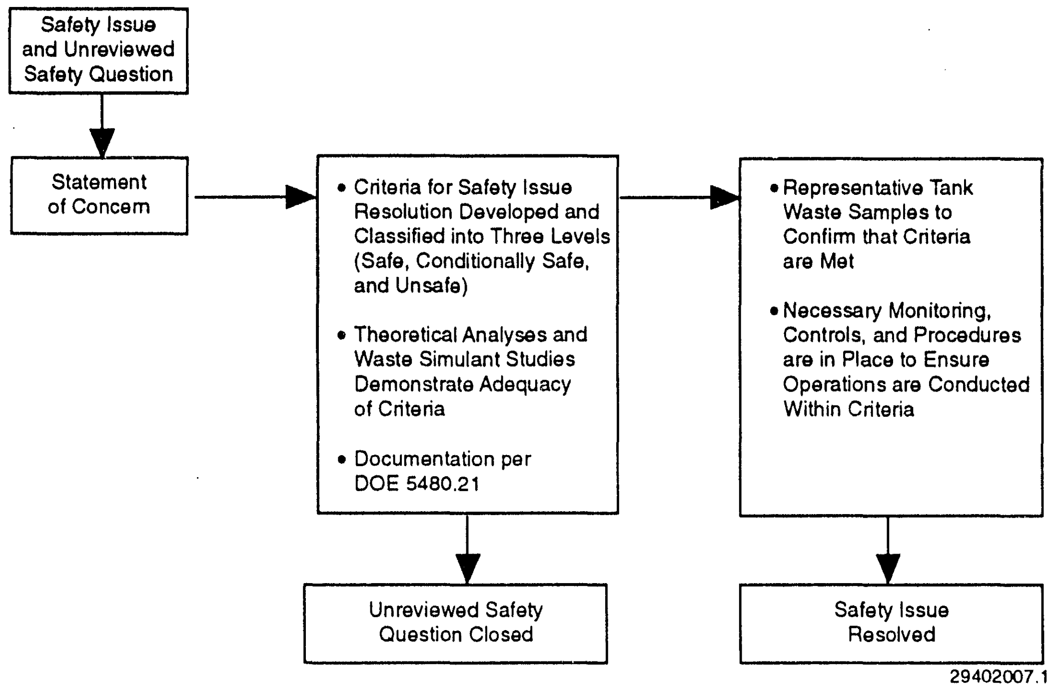
*An Unreviewed Safety Question, as defined by DOE Orders 5480.5 and 5480.21, is determined as follows. "A proposed change, test or experiment shall be deemed to involve an USQ if the following apply:

a. The probability of occurrence or the consequences of an accident or malfunction of equipment important to safety, evaluated previously by safety analysis will be significantly increased, or

b. A possibility for an accident or malfunction of a different type than any evaluated previously by safety analysis will be created which could result in significant safety consequences."

that define safe storage and by demonstrating the adequacy of the criteria through theoretical analyses and studies on ferrocyanide waste simulants.

Figure 1. Strategy for Closure of the USQ and Resolution of the Safety Issue



Resolution of the Safety Issue can be accomplished when sufficient data are obtained through core sampling to assure that ferrocyanide tanks meet the criteria and when controls and procedures are in place to assure that the waste will remain within the criteria.

FERROCYANIDE WASTE SIMULANT STUDIES AND THEORETICAL ANALYSES

Three types of waste (In Farm, U Plant, and T Plant) were scavenged to produce ferrocyanide sludges stored in the Hanford Site SSTs. The compositions of each of these waste types were significantly different. Scavenging treatments varied as a function of feed composition, process development, and chemicals available for treatment at a given time. This resulted in sludges with different compositions.

Four tanks received In Farm material; 14 tanks received U Plant material; and three tanks received T Plant material (note: one tank received material from both U Plant and T Plant flowsheets). Analyses of the ferrocyanide sludge were not made when the precipitation occurred. However, waste simulants replicating the original flowsheets have been prepared and analyzed. When the simulants were prepared, the sludge settled into distinct layers. The In Farm simulant contained the highest fuel content, with a peak concentration layer of 25.5 wt% sodium nickel ferrocyanide [$Na_2NiFe(CN)_6$]. The U Plant and T Plant simulants contained peak concentration layers of 8.3 and 8.8 wt% $Na_2NiFe(CN)_6$, respectively.

Adiabatic calorimetry tests on dried simulants have shown that U Plant and T Plant material do not contain enough fuel to support propagating reactions. Even when subjected to a strong ignition source, a reaction front did not move through the simulants. However, dried and well mixed In Farm simulant did propagate. Experiments conducted with dried In Farm simulant diluted with alumina or sodium nitrate revealed that at least 15 wt% $Na_2NiFe(CN)_6$ is required to support a propagating reaction (Postma et al. 1994).

To provide a safety factor from the empirical results, theoretical calculations using an experimentally derived heat of reaction of 6.0 MJ/kg have shown that an initiation temperature of 270 °C cannot be reached by releasing the chemical energy available in waste containing less than 8.0 wt% $Na_2NiFe(CN)_6$. This 8.0 wt% fuel concentration represents an extremely conservative value, and gives a safety factor of about 1.9 when compared to the experimental 15 wt% value.

Another important parameter evaluated during tests with simulants is the effect of water on propagating behavior. Experiments showed that 12 wt% water was sufficient to quench propagating reactions in In Farm simulant (Fauske 1992). Thermodynamic calculations have shown 24 wt% water would contain sufficient latent and sensible heat to absorb the chemical energy produced by the most concentrated In Farm simulant (Postma et al. 1994).

Moisture retention experiments on waste simulants have demonstrated that the waste retains considerable water. The moisture content of ferrocyanide waste simulants centrifuged to 30 equivalent gravity years ranged from 48 to 67 wt%. Moisture is held in the waste by capillary action, in gel form, and as chemical hydrates.

SAFETY CATEGORIES AND CRITERIA FOR INTERIM SAFE STORAGE

Based on the knowledge gained from simulant studies and theoretical analyses, safety categories and safety criteria have been delineated to meet the interim safe storage safety objective. The primary safety objective is to maintain waste in a state that prevents chemical reactions that have the potential for radiation doses or toxic exposure (either onsite or offsite) more than applicable limits or guidelines (WHC 1992), and damage to the tank that compromises its ability to store high-level waste safely. The primary safety objective is met by imposing a more stringent secondary objective; that is, no sustainable rapid exothermic ferrocyanide reaction be possible, regardless of the severity of its consequences. A sustainable reaction is one that can spread beyond a local ignition source. A rapid reaction is one that generates heat faster than it can be removed by conduction; it excludes the slow degradation reactions believed to be occurring over a period of years.

Categorizing the ferrocyanide waste hazard into safety categories helps define levels of assurance and the controls required to meet the safety objective. Using safety categories also permits ranking relative risks posed by the ferrocyanide tanks. At one extreme, where waste is non-reactive, no ferrocyanide related monitoring or controls would be required to meet the safety objective. At the other extreme, reactive waste (if any exists) would require modification to meet the safety objective.

Two key safety questions can be used to identify three safety categories. These questions were developed on the basis of the current understanding of the ferrocyanide waste hazard.

Question 1: *Is a significant exothermic reaction possible during interim storage?*

The word *significant* in this question is defined by reference to the safety objective. A *significant* reaction would have consequences greater than permitted by the safety objective. The phrase *possible during interim storage* in Question 1 means conditions that could theoretically occur if no controls were placed on tank operations. This no control stipulation allows for such possible but unlikely events as dryout and the introduction of local initiators. The no control stipulation does not cover processes and operations that could be imposed in future efforts directed at final disposal of the waste.

If the answer to Question 1 is no, then the waste can be safely stored without human intervention. If the answer to Question 1 is yes, then a second key question is posed.

Question 2: *Is a significant exothermic reaction possible under present conditions of waste moisture content?*

If the answer to this question is no, then the safety objective can be met by assuring that the waste maintains moisture content above a level that prevents significant exothermic reactions. If the answer to this question is yes, then the primary safety objective can be met only by imposing controls that avoid conditions that could initiate a reaction. The more stringent secondary objective cannot be met if the answer to Question 2 is yes.

Answers to these two key safety questions led to the definition of three safety categories: SAFE, CONDITIONALLY SAFE, and UNSAFE. The SAFE category corresponds to a "no" answer to key safety Question 1 (i.e., that a significant reaction is not possible during interim storage). The safety objective can be met by a hypothetical unattended operational mode; no special requirements for monitoring and controls are imposed by the presence of ferrocyanide.

The CONDITIONALLY SAFE category corresponds to a yes answer to key safety Question 1, followed by a no answer to key safety Question 2. The wastes in this category are safe on the condition that moisture content be maintained at or above a definable critical level. In reaction phenomenology, the requirements are the same as for the SAFE category, except that a waste moisture level above a critical value applies. Therefore, propagating reactions can be ruled out for this safety class.

The UNSAFE category corresponds to yes answers to both key safety questions. For wastes in this category, a reaction initiated at a local site could propagate through a significant quantity of waste. Accidents would be prevented by imposing controls that avoid conditions that could initiate a reaction. Storage of wastes in this category is inconsistent with the more stringent secondary safety objective, because significant reactions cannot be ruled out. A change in waste state would be required to ensure that waste storage met the level of safety required by the secondary safety objective.

The parameters important for exothermic oxidation/reduction reactions involving ferrocyanide are fuel, oxidant, and moisture concentrations, and temperature. Criteria have been established on fuel concentration, moisture content, and temperature that allow the tanks to be ranked into the three safety categories.

I. **LEVEL 1 - SAFE**

Concentration of fuel:	≤ 8 wt% sodium nickel ferrocyanide on an energy equivalent basis (i.e., ≤480 J/g)
Concentration of water:	Not limiting
Concentration of oxidizers:	Not limiting
Temperature of waste:	Not limiting

II. **LEVEL 2 - CONDITIONALLY SAFE**

Concentration of fuel:	> 8 wt% sodium nickel ferrocyanide on an energy equivalent basis
Concentration of water:	≥ 0 to 24 wt%
Concentration of oxidizers:	Not limiting
Temperature of waste:	≤ 90 °C

III. **LEVEL 3 - UNSAFE**

Criteria for SAFE and CONDITIONALLY SAFE are not met; a modification in waste state is required to remove a tank from the UNSAFE class.

It is important to note three features of the criteria. The fuel criterion is determined on an energy equivalent basis that accounts for possible contributions from other potential fuel sources, such as sulfide or organics. The moisture criterion is not fixed at one value, but increases linearly from 0 at 8 wt% fuel, to 24 wt% at 26 wt% fuel. Waste that contains, for example, 8.3 wt% fuel is not required to have 24 wt% water; it requires only 0.4 wt% water. Temperature is not a primary criterion, and is set at 90 °C to preclude rapid moisture loss in the waste. Actions to cool the waste would be taken long before temperatures in the tank increased to 90 °C (Cash and Thurman 1991).

Using information from the waste simulants and core sample analyses, all of the ferrocyanide tanks are currently placed in either the SAFE or CONDITIONALLY SAFE categories (Postma et al. 1994).

ANALYSES FROM FERROCYANIDE TANKS TO DATE

Core samples obtained from ferrocyanide tanks 241-C-109, -112, and 241-T-107 have been analyzed. Tanks 241-C-109 and -112 received waste from the In Farm flowsheet (the highest concentration of ferrocyanide), and 241-T-107 received waste from the U Plant flowsheet. Analyses were performed on quarter segments (12.1 cm [4.75 in.] slices) so that the effect of layering could be evaluated. A brief comparison between characteristics of quarter segment samples extruded and simulant material is presented in Table I. With the noted exception of total cyanide and energetics, there was good agreement between simulant sludge properties and those observed for actual waste material (Jeppson and Wong 1993; Simpson et al. 1993a; Simpson et al. 1993b).

Table 1. Comparison of Tank Samples With Flowsheet Simulants

Sample Description	Heat of Reaction* (J/g)	$Na_2NiFe(CN)_6$ Energy Equiv* (Wt%)	Water (wt%)	Total CN^-* (wt%)
241-C-109	-115	1.9	18 to 64	0.30 to 1.10
241-C-112	-36	0.6	42 to 58	0.40 to 0.97
In Farm Simulant	-1500	25.5	48 to 52	12.6
241-T-107	No Exotherm	——	18 to 60	0.00 to 0.01
U Plant Simulant	-500	8.3	64 to 67	4.1

*Highest values reported. Values on a dry basis with all free water removed. Samples still contained approximately 2 to 3 wt% bound water.

Low total cyanide and energetic values are significant. Core sampling offers the best evidence to date that degradation has occurred in the ferrocyanide tanks. Total cyanide and energetic values are approximately an order of magnitude lower than predicted by ferrocyanide sludge simulants and flowsheet mass balances. However, measurements of nickel concentration suggest that the ferrocyanide sludge was not transferred to other tanks and was once in the tanks. Aging offers an explanation for the low energetics and cyanide values. Verification of low energetics by core sampling may lead to all of the tanks being placed in the SAFE category.

AGING OF FERROCYANIDE WASTES

It has been postulated that the low cyanide and energetic values are the result of aging (hydrolysis and radiolysis) of the ferrocyanide waste. Aging of ferrocyanide waste is broadly defined in terms of the processes that result in a lower potential for ferrocyanide reactions. This includes degradation of the ferrocyanide to a less energetic form by hydrolysis and/or radiolysis.

Review of the literature suggests that $Na_2NiFe(CN)_6$ will dissolve and hydrolyze to form ammonia and sodium formate in solutions with a pH greater than ten. Strong caustic (≥ 4 M hydroxide) solutions have been added to all of the ferrocyanide tanks from aluminum decladding waste or evaporator bottoms. Dissolution of $Na_2NiFe(CN)_6$ results in soluble sodium ferrocyanide and a nickel hydroxide precipitate via Equation 1.

$$Na_2NiFe(CN)_6(s) + 2\ NaOH \rightarrow Na_4Fe(CN)_6 + Ni(OH)_2\downarrow \qquad \text{(Eq. 1)}$$

Soluble ferrocyanide is a by-product of many industries, including aluminum manufacturing, iron and steel making, metal finishing, and chemical manufacturing. Because ferrocyanide wastes are not uncommon, several papers have been written on alkaline hydrolysis reactions involving ferrocyanide. Research (Robuck and Luthy) using spent potlining leachate demonstrated that ferrocyanide will hydrolyze to form formate, ferric oxide, and ammonia (see Eq. 2). The reaction was found to be first order with respect to cyanide, and zero-order with respect to hydroxide for pH values greater than ten. Similar reactions should be possible in the alkaline conditions found in the ferrocyanide SSTs.

$$6\ Fe(CN)_6^{4-} + 12\ OH^- + 66\ H_2O + O_2 \rightarrow 36\ HCOO^- + 2\ Fe_3O_4\downarrow + 36\ NH_3\uparrow \qquad \text{(Eq. 2)}$$

The effect of γ-radiation on ferrocyanide solutions has been investigated, but offers very complex chemistry. The decomposition of water by ionizing radiation yields radical and molecular products (see Eq. 3). In turn, these products can react to reduce or oxidize ferric or ferrous iron in solution. It has been demonstrated that, whereas ferrocyanide is oxidized in aerated acid solution, ferricyanide is reduced at pH greater than 11 (Hughes and Willis 1961). However, no mechanism was put forward to account for these observations.

$$H_2O \rightsquigarrow H\cdot,\ \cdot OH,\ H_2,\ H_2O_2,\ \text{etc.} \qquad \text{(Eq. 3)}$$

Recent experiments at Pacific Northwest Laboratory on waste simulants have shown rapid hydrolysis during gamma pit experiments. Over 42% of the cyanide groups was hydrolyzed in a three week period at 90 °C in a field of 1.65×10^5 Rad/hour (Lilga et al. 1993). Similar experiments conducted at pH 10 revealed that degradation still occurs at lower pH, albeit at a slower rate. However, considerable time (35 plus years) has passed since the waste was originally precipitated.

Data from aging experiments and results from core sampling support the concept that aging of ferrocyanide is taking place in the waste tanks. If all of the ferrocyanide tanks exhibit the extent of aging found in tanks 241-C-109, -112, and 241-T-107, then all would contain considerably less than 8 wt% $Na_2NiFe(CN)_6$.

CONCLUSIONS

Fuel, moisture, and temperature criteria that define continued safe storage have been developed from theoretical analyses and ferrocyanide waste simulants studies. By applying the criteria to ferrocyanide waste tanks at the Hanford Site, it has been shown that all of the ferrocyanide tanks are currently ranked in either the SAFE or CONDITIONALLY SAFE categories. Analyses of core samples taken from three ferrocyanide tanks have shown cyanide concentrations about a factor of ten lower than predicted by the original flowsheets. Aging of the ferrocyanide matrix has occurred during the 35 plus years the waste has been stored. Because of waste aging, it is possible that all of the ferrocyanide tanks may now contain less than the 8 wt% $Na_2NiFe(CN)_6$ specified in the fuel criterion for the SAFE category. Waste characterization, which includes tank core sampling, should lead to resolution of the safety issue by September 1996.

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