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Resolution of the Ferrocyanide Safety Issue for the Hanford Site High-Level Waste Tanks

R. J. Cash
H. Babad
J. E. Meacham
Westinghouse Hanford Company

W. F. Hendrickson
U.S. Department of Energy

M. A. Lilga
Pacific Northwest National Laboratory

J. M. Grigsby
G & P Consulting, Inc.

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Assistant Secretary for Environmental Management

Westinghouse Hanford Company
P.O Box 1970
Richland, Washington

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RESOLUTION OF THE FERROCYANIDE SAFETY ISSUE FOR THE HANFORD SITE HIGH-LEVEL WASTE TANKS

R. J. Cash
Westinghouse Hanford Company
P. O. Box 1970
Richland, Washington 99352
(509) 373-3132

H. Babad
Westinghouse Hanford Company
P. O. Box 1970
Richland, Washington 99352
(509) 373-2897

J. E. Meacham
Westinghouse Hanford Company
P. O. Box 1970
Richland, Washington 99352
(509) 373-1961

J. M. Grigsby
G & P Consulting, Inc.
3640 Ballard Road
Dallas, Oregon 97338
(509) 376-5862

M. A. Lilga
Pacific Northwest National Laboratory
P. O. Box 999
Richland, Washington 99352
(503) 623-2608

W. F. Hendrickson
U.S. Department of Energy
P. O. Box 550
Richland, Washington 99352
(509) 376-8452

ABSTRACT

This paper describes the approach used to resolve the Ferrocyanide Safety Issue, a process that began in 1990 after heightened concern was expressed by various government agencies about the safety of Hanford Site high-level waste tanks. At the time, little was known about ferrocyanide-nitrate/nitrite reactions and the potential for offsite releases of radioactivity from the Hanford Site.

Recent studies have shown that the combined effects of temperature, radiation, and pH during more than 38 years of storage have destroyed most of the ferrocyanide originally added to tanks. This has been proven in the laboratory using flowsheet-derived waste simulants and confirmed by waste samples obtained from the ferrocyanide tanks. The resulting tank waste sludges are too dilute to support a sustained exothermic reaction, even if dried out and heated to temperatures of at least 250 °C. The U.S. Department of Energy (DOE) has been requested to close the Ferrocyanide Safety Issue.

I. INTRODUCTION AND BACKGROUND

High-level radioactive waste from defense operations has been stored in Hanford Site waste storage tanks from the early 1940s. During the 1950s, production of plutonium for defense created an urgent need for additional waste storage space. To obtain this space and minimize the construction of additional tanks, scientists developed a process to remove (scavenge) radiocesium (^{137}Cs) and other soluble radionuclides from tank waste liquids through precipitation processes. After adjusting the pH of the waste, sodium ferrocyanide, then nickel sulfate were added to create a nickel ferrocyanide precipitate that carried down radiocesium. A slurry containing the precipitated solids was transferred to single-shell, high-level radioactive waste tanks. After seven to 10 days of settling, the radionuclide content of the supernatant was measured; if the concentrations were below limits applicable at the time, the liquids were decanted to the ground through cribs and trenches.

From 1953 until early 1958, approximately 140 metric tons (154 tons) of ferrocyanide were added to waste now residing in a number of single-shell tanks. Ferrocyanide was added in great excess so that the predominant species that precipitated was sodium nickel ferrocyanide [$Na_2NiFe(CN)_6$]. Ferrocyanide, in sufficiently high concentrations and mixed with oxidizing material such as sodium nitrate/nitrate also in the tanks, can be made to react exothermically by heating it to high temperatures. The release of energy comes from oxidation of the carbon-nitrogen triple bond; therefore the form of the ferrocyanide (or cyanide) species present makes little difference in the energy that could be released. A unique feature of the scavenging process was the addition of nickel, a distinctive analyte that identifies whether the correct locations in the tank were sampled. No other significant source of nickel was added to the waste streams at the Hanford Site.

In March 1989, based on process records, transfer histories, and logbooks, 22 Hanford Site tanks were identified as potentially containing a ferrocyanide inventory of 1,000 gram-moles (g-moles) (211 kg [465 lb]) or more as the $Fe(CN)_6^{-4}$ anion. The 1,000 g-moles criterion has since been replaced with a fuel concentration criterion of 115 calories per gram (cal/g)[1]. Two additional ferrocyanide tanks were identified in January 1991, increasing the number of ferrocyanide tanks to 24. To avert possible injury to personnel and damage to the facility or environment, strict controls were identified for these and other safety issue tanks.

In 1990, little was known about the potential hazards of a ferrocyanide-nitrate/nitrite reaction in Hanford Site tanks. Consequently, a special Ferrocyanide Task Team was commissioned in September 1990 to address all issues involving the ferrocyanide tanks, including the consequences of a potential accident. Because the safety envelope was not adequately defined by existing analyses, an inadequacy existed in the authorization basis and an unreviewed safety question was declared in October. In the same month, the Defense Nuclear Facilities Safety Board issued Recommendation 90-7, which recommended the following: enhanced temperature monitoring of ferrocyanide tanks, continuous temperature monitoring with alarms and 24-hour surveillance, domespace monitoring for possible flammable gases, sampling tank waste to determine whether it could react, chemical reactivity studies to evaluate the properties of ferrocyanide reactions, and emergency planning in case an event were to occur. Also in October 1990, a General Accounting Office study[2] postulated a greater "worst-case" accident with independently-calculated doses one to two orders of magnitude greater than the 1987 environmental impact statement[3].

In November 1990, the Wyden Amendment (Public Law 101-510, Section 3137) was enacted. It required identifying Hanford Site "Watch List" tanks that might have a serious potential for release of high-level waste. The 24 ferrocyanide tanks were among the Watch List tanks identified. Later, detailed studies of the historical records indicated that six tanks originally listed had never received ferrocyanide waste, and the DOE reduced to 18 the tanks of concern in 1993 and 1994.

A. Potential Hazards Associated with Ferrocyanide Waste

Ferrocyanide is a complex of ferrous and cyanide ions that is considered stable in aqueous solutions. However, *Sax's Dangerous Properties of Industrial Materials* indicates that "fusion of mixtures of metal cyanides with metal chlorates, perchlorates, nitrates, or nitrites may cause violent explosions." The hazard of concern for Hanford Site ferrocyanide tanks was a sustainable, rapid exothermic reaction between ferrocyanide and nitrate/nitrite compounds contained in the waste sludge. 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; it excludes the slow aging (degradation) reactions shown to occur over a period of years.[10] A sustainable rapid exothermic reaction could produce sufficient heat and evolved gases to pressurize the tank headspace, releasing aerosolized waste from tank vents and potentially damaging the tanks structure.

Laboratory tests have demonstrated that these chemicals can react violently if they are present in stoichiometric proportion, dry, and heated to temperatures above 250 °C. However, information gathered over the past six years indicates that ferrocyanide waste sludge is composed mainly of inert chemicals and has a high water content; therefore, the waste cannot support self-sustaining reaction and cannot undergo the explosion scenarios postulated earlier.

Conservative testing of ferrocyanide-bearing waste simulants has not shown evidence of explosive waste behavior. However, one of the waste simulants (In-Farm) will support exothermic propagating reactions under special laboratory conditions. Laboratory studies of ferrocyanide waste simulants have been used to define conditions that could cause energetic reactions and conditions for which such reactions are not possible.[4] Conditions necessary to support rapid, sustained exothermic reactions include sufficient fuel concentration, sufficient oxidizer concentration (usually an excess is present in the tanks), relatively dry material, and an initiator that can heat a portion of the material above the ignition temperature.

II. WASTE CONDITIONS

The potential for an exothermic reaction in stored waste depends on the relative concentrations of the reactants, inert solid diluents, water, and potential initiators present. Process knowledge from historical records and from waste simulants produced from ferrocyanide scavenging process flowsheets, has been used to predict the major constituents and some general physical properties of the waste matrix.

A. Historical Records

The ferrocyanide scavenging processes were well documented, and campaign records are still available.[5,6,7] Two models, developed from historical records, were used to determine the inventory, concentration, and depth of ferrocyanide sludge originally stored in each of the 18 ferrocyanide tanks.

The first model estimates concentrations based on process records and is derived on the basis of material balance calculations that traced waste transfers in the tank farms. Details are provided in Borsheim and Simpson (1991).[8] A second model predicts sludge volumes in the 18 tanks based on data derived from simulant studies. This model predicts average concentrations in the sludge by dividing the ferrocyanide mass (material balance calculations) in a tank by the mass of the sludge in the tank. Key model parameters are described below.

The sludge volume fractions are based on plant records and observed properties of flowsheet simulants. Three main scavenging flowsheets and their variations were used during the 1950s. The ratios of sludge volumes to treated waste volumes were assigned the following values[9]:

U-Plant Flowsheet:	4.25 volume percent (vol%)
In-Farm Flowsheet:	1.0 to 1.5 vol%
T-Plant Flowsheet:	3.7 vol%

Sludge densities in grams/milliliter (g/ml) were assigned values on the basis of values measured for the centrifuged sludges:

U-Plant Sludge:	1.27 g/ml
In-Farm Sludge:	1.45 g/ml
T-Plant Sludge:	1.29 g/ml.

Water concentrations in weight percent (wt%) were determined by centrifuging the flowsheet simulants and drying them in an oven at 105 °C for 24 hours or under vacuum at 60 °C. Results are listed below:

U Plant:	65 wt%
In Farm:	50 wt%
T Plant:	69 wt%.

The model does not account for the degradation[10] of ferrocyanide over 35 years of storage, and it does not account for dilution by mixing with other wastes added after the scavenging campaign was completed. For these reasons, the model was expected to overpredict current ferrocyanide concentrations.

Table 1 lists data on the 18 ferrocyanide tanks along with process record estimates of ferrocyanide concentrations and other key information.

B. Energetics

The theoretical approach, which was used to identify compositions capable of supporting a propagating reaction, was based on an energy balance where the potential reaction energy is equated to endotherms occurring when heating of waste from ambient temperature to a reaction threshold temperature. By this means, a ferrocyanide concentration criterion level was calculated as a function of waste moisture content.

The oxidation of ferrocyanide by nitrate and/or nitrite can result in a variety of reaction products with different reaction energies. The most energetic, for a given amount of fuel, is one that produces nitrogen and carbon dioxide (or carbonate salt if there is sufficient hydroxide available to form it). A representative equation with nitrate is

$$Na_2NiFe(CN)_6 + 6\ NaNO_3 \dashrightarrow FeO + NiO + 4\ Na_2CO_3 + 6\ N_2 + 2\ CO_2. \qquad (1)$$

The calculated energy (ΔH) for this reaction is approximately -9.52 megajoules (exothermic) per kilogram (MJ/kg) of ferrocyanide at 25 °C (298 °K).

Observations indicate that oxides of nitrogen are formed in slow, low-temperature reactions between ferrocyanide and nitrate-nitrite mixes. Calculated reaction energies are much lower for reactions that produce nitrogen oxides. The energy available from the reaction decreases to -6.6 MJ/kg when N_2O is the product. If NO is produced, a reaction endotherm of 0.73 MJ/kg is calculated. The wide variation in calculated reaction energies illustrates the need for experimental measurements to quantify reaction energy.

The reaction energy was assigned a value of -6 MJ/kg of $Na_2NiFe(CN)_6$ on the basis of three independent experimental determinations carried out with simulated waste.[1] This amounts to 63% of the theoretical value given above for Equation (1) and 90% of the calculated energy with N_2O as the product gas.

Adiabatic Calorimetry Tests. In these tests, sizable samples (10 g and 70 g) are heated under very low heat-loss conditions. As the sample is heated to the reaction onset temperature and above, the thermal energy produced by the reaction causes the sample to self-heat. The rate and extent of this self-heating provides direct evidence of the character of the reaction that has taken place.

A number of compositions containing ferrocyanide and $NaNO_3/NaNO_2$ were tested in the reactive system screening tool (RSST).[4] The RSST cannot measure the effect of water on reactivity because all samples are heated to dryness[a] before reaching the ignition temperature. It was found that all of the materials containing 15.6 wt% $Na_2NiFe(CN)_6$ or more can undergo a propagating reaction while those with 12 wt% or less cannot. However, tests using a tube propagation apparatus[4] have demonstrated that propagating reactions even for ferrocyanide-rich mixtures are inhibited by small amounts of water.

Tube Propagation Rate Tests. The test apparatus for measuring the velocity of propagation of a chemical reaction through sludge consists of a thin, insulated, stainless-steel cylinder, 25 mm in diameter and 100 mm tall, filled with the test material. The reaction was ignited at the top by a BaO_2-Al mixture. The progress of the reaction, if any, is monitored by four thermocouples spaced 20 to 30 mm apart. These show sharp temperature rises as the reaction front passes. Again, one of two distinct behaviors is noticed. A reaction that proceeds to the bottom of the cylinder in samples is capable of supporting a propagation reaction. If the reaction is not ignited, or if it fizzles out in a short distance, the sample cannot support a propagating reaction. Several compositions were tested by this method. Both ferrocyanide and water concentrations were varied.

Based on RSST tests and tube propagation tests,[4] it was found that propagating reactions were not observed for sodium nickel ferrocyanide concentrations below 15 wt% on a dry (0 free water) basis (0.9 MJ/kg [215 cal/g] of waste). This number is approximately double the 8 wt% number derived on the basis of the energy balance calculation. The 2:1 ratio of experiment and theory illustrates the degree to which the conservative theory under predicts the experimentally observed minimum ferrocyanide concentration required for a propagating reaction. With 25.5 wt% ferrocyanide (In-Farm-1 sludge, the most concentrated of the flowsheet simulants), propagation was observed with 8 wt% free water but not with 12 wt% free water. The 8 wt% $Na_2NiFe(CN)_6$ on a 0 free water basis was chosen as the upper limit for safe mixtures.

It is concluded from these tests that propagation was prevented when the free water content was 12 wt% or more. This applies to simulants containing the highest concentration of ferrocyanide (25.5 wt%). The 12 wt% moisture threshold determined experimentally is only 43% of the threshold indicated by the thermodynamic calculations. The difference is expected because thermodynamic calculations are inherently conservative.

C. Waste Safety Categories

The potential for a rapid exothermic ferrocyanide waste reaction was analyzed using the following: process knowledge obtained from historical records, experiments performed with waste simulants, and analyses of chemical and physical processes that might exacerbate or decrease the ferrocyanide hazard. The conditions required for a ferrocyanide accident to occur were determined through theoretical analysis and experiments. The results were used to define conservative criteria for *SAFE, CONDITIONALLY SAFE* and *UNSAFE* waste storage.

Criteria were selected on the basis of experimental and theoretical information. Conservative values were chosen to provide a safety margin between safe tank conditions and conditions where significant reactions could occur. The approved criteria are as follows:

SAFE

Concentration of fuel ≤ 8 wt% sodium nickel ferrocyanide
Concentration of water - not limiting
Concentration of oxidizers - not limiting
Temperature of waste - not limiting

CONDITIONALLY SAFE

Concentration of fuel > 8 wt% sodium nickel ferrocyanide
Concentration of water ≥ 0 to 24 wt%

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[a] The ferrocyanide simulants contain bound (hydrated) and free water. Free water can be removed using standard drying methods; for example, in an oven at 105 °C for 24 hours or under vacuum at 60 °C for 18 hours. Sodium nickel ferrocyanide [$Na_2NiFe(CN)_6$] contains approximately 4.6 moles of bound water. Bound water is not released until the sample approaches 160 °C and higher.

Concentration of oxidizers - not limiting
Temperature of waste ≤ 90 °C

UNSAFE

Criteria for SAFE and CONDITIONALLY SAFE are not met.

For tanks that fall into the *SAFE* category, assurance of low fuel content is sufficient to address the ferrocyanide hazard during interim storage. For *CONDITIONALLY SAFE* tanks, assurance of minimum retained moisture and maximum waste temperature is required. For unsafe tanks, monitoring and controls are required to avoid conditions that could lead to reaction initiation.

D. Waste Aging Processes

The aging of ferrocyanide waste, defined as thermal or radiolytic degradation of ferrocyanide, destroys the ferrocyanide and changes it into non-propagating compounds.[10] Insoluble sodium nickel ferrocyanide, the major component of ferrocyanide sludges formed during the scavenging campaign, will dissolve in a caustic solution containing 0.01 M or higher hydroxide. Dissolution of sodium nickel ferrocyanide results in soluble sodium ferrocyanide and a nickel hydroxide precipitate via Equation 2.

$$Na_2NiFe(CN)_6(s) + 2\ NaOH \longrightarrow Na_4Fe(CN)_6 + Ni(OH)_2. \qquad (2)$$

Under tank waste conditions, the ferrocyanide complex will hydrolyze to form formate, ferric oxide, and ammonia (see Equation 3).

$$6\ Fe(CN)_6^{-4} + 12\ OH^- + 66\ H_2O + O_2 \longrightarrow 36\ HCOO^- + 2\ Fe_3O_4 + 36\ NH_3. \qquad (3)$$

The available literature[11,12,13,14,15] and recent experiments at the Pacific Northwest National Laboratory (PNNL) on ferrocyanide waste simulants[10] indicate that the rate of aging is strongly affected by three parameters: temperature, radiation dose rate, and pH.

Dependence on Temperature. PNNL experiments on the aging of ferrocyanide waste simulants were conducted at 50, 70, 80, 90, and 100 °C in 2 M NaOH solutions. Solutions were exposed to ^{60}Co gamma radiation at a dose rate of about 1 x 10^5 rad per hour (rad/h). The control solutions were not irradiated but were otherwise prepared and treated identically. The concentrations of ammonia, formate ion, and other species produced by hydrolysis of the ferrocyanide ion in the dissolved simulant were measured over a three-week period of reaction.

Overall, the ammonia concentration at each temperature increased approximately linearly with hydrolysis time, and the rate of hydrolysis increased with temperature. As an approach toward a mathematical model, the increase in ammonia concentration was assumed to be linear, and global rate constants were calculated from the slopes. The Eyring plot of these rate data was linear, and an activation energy of $\Delta H = 32.5$ kilocalories per mole was calculated. Rate constants for ammonia production at a given temperature (°K) at a gamma dose rate of 1 x 10^5 rad/h may be calculated with Equation (4). The calculated rate constants do not directly represent but approximate the rate of ferrocyanide hydrolysis because the rate of ammonia radiolysis is included. Rate constants predicted from this equation are generally within a factor of about 2 of the observed rate constants.

$$\ln(k_T/T) = 33.1 - 1.64 \times 10^4 \cdot 1/T. \qquad (4)$$

Historical records for the 18 ferrocyanide tanks show that all of the tanks except the three in TY Farm and possibly TX-118 were operated at temperatures as high as or higher than 75 °C. The BY Farm tanks were part of the "In Tank Solidification" program conducted from 1966 to 1976 where wastes were purposely heated in tanks BY-101, BY-102, and BY-112 to drive off excess water and condense the waste into saltcake. The waste was heated to high temperatures, some to 125 °C, and then pumped at various times to the rest of the BY Farm tanks (12 total) for cooling to crystalize out the saltcake. Based on PNNL aging experiments with the ferrocyanide simulants, the BY-Farm temperatures were high enough to degrade the concentration of ferrocyanide to about 0 in a few years time. Four of the BY tanks were sampled, and all showed very low concentrations of cyanide, but significant levels of the nickel thereby indicating that the ferrocyanide was present at one time. Tank BY-108 temperatures were the lowest of the ferrocyanide tanks in that farm; this tank was also sampled. It is the bounding tank and based on its results, the BY ferrocyanide tanks are categorized as *SAFE*.

Waste temperatures in the TY tanks may never have exceeded 55 °C, although there is an operating record showing that tank TY-104 received 100+°C waste in 1969 and 1970. Only tank TY-104 was sampled, and results show that an insignificant amount of cyanide remains. Because temperatures in TY-104 were lower or about the same as TY-101 and TY-103 and the three TY tanks received the same ferrocyanide flowsheet waste, it is concluded that the ferrocyanide in TY-101 and TY-103 also degraded; therefore, these tanks can be categorized as *SAFE*.

Temperature data for tank TX-118 have not been found for the 1960s and 1970s. Transfer records show that no ferrocyanide solids were ever transferred to tank TX-118, but it was on the list of ferrocyanide tanks in 1989 because it was erroneously identified as containing ferrocyanide in the Tracking Radioactive Components document.[16] Anderson (1990)[14] shows the tank received evaporator bottoms from the 242-T evaporator from 1969 until 1977. This waste would have had high enough temperatures to degrade any ferrocyanide present. The present status[18] shows the tank contains all saltcake waste with no sludge. This tank is also categorized as *SAFE*.

Tanks C-109, C-111, and C-112 also experienced high enough temperatures to enhance ferrocyanide degradation. Temperatures recorded in the 1960s were in the 70 °C to the 80 °C range. Available temperature data for C-108 do not extend back to the time when these tanks were warmer. However, a review of the operating history indicates that tank C-108 should have experienced temperatures similar to tank C-109. The temperatures in these tanks were sufficient to carry out the ferrocyanide aging discussed above. All these tanks have been sampled, and all show degradation of ferrocyanide by a factor of 10 or more. These tanks are categorized as *SAFE*.

The remaining ferrocyanide tank, T-107, was sampled, and results show insignificant amounts of total cyanide. This tank is categorized as *SAFE*.

Dependence on Gamma Dose Rate and Integrated Dose. The same PNNL experiments on ferrocyanide waste simulants[10] show that gamma radiation promotes ferrocyanide aging. Simulants that were not irradiated aged up to one order of magnitude less than irradiated samples under similar conditions of time, pH, and temperature.

Experiments to investigate the influence of incident gamma dose rate on the rate of hydrolysis of ferrocyanide simulants were conducted at 90 °C in 2 M NaOH solutions. Ammonia production is again approximately linear; the slopes of the lines give rate constants at each applied dose rate. The rate of ammonia production increases with increasing dose rate. The rate constant for ammonia production is linearly related to the applied dose rate. The C-Farm tanks have experienced a relatively high integrated gamma dose of between 2.4×10^8 rad to 5.3×10^8 rad. In aging experiments, the maximum incident integrated dose is about 5×10^7 rad, less than that experienced by C-Farm tank waste by up to one order of magnitude. Based on the PNNL aging experiments, the radiation exposure in the tanks was more than sufficient to significantly age the ferrocyanide waste.

Dependence on Alkalinity. Aging of ferrocyanide waste by a dissolution and hydrolysis process is most effective under highly alkaline conditions because the ferrocyanide becomes soluble from dissolution of sodium nickel ferrocyanide at high pH. Experiments also show that hydrolysis occurs at pH $\approx$ 10, where sodium nickel ferrocyanide has low solubility.

In cesium scavenging operations, precipitation of sodium nickel ferrocyanide was done at slightly alkaline conditions (pH $\approx$ 9 - 10). Later, the ferrocyanide tanks were used for a variety of waste management operations that introduced highly alkaline waste to the tanks.[14] Samples from all of the 11 ferrocyanide tanks tested had pH values above 10 and many of the samples were > pH = 12, especially the BY-Farm tanks that received highly alkaline saltcake waste.

Values for pH are only estimates because the solutions tested had a high ionic strength. (Most samples exceeded 4 M, making a direct correlation between hydrogen ion activity and concentration difficult.) Therefore, measurements of the hydroxide concentrations are a more reliable measure of alkalinity. Hydroxide concentrations were measured by direct potentiometric titration of the solutions with a standardized acid. Many ferrocyanide tank samples were not titrated for hydroxide concentration. This is not critical to the argument that the ferrocyanide has aged because PNNL[10] has shown that aging still occurs, although at a slower rate, in the solid phase as well.

Historical pH and hydroxide data show that all the ferrocyanide tanks contained enough caustic to promote aging, subsequent to the ferrocyanide campaigns. Tank BY-111 had no data later than June 1956 when the pH was 9.6, but this tank was used for the same operations that transferred high-pH waste into the other BY farm ferrocyanide tanks. Consequently, waste pH was not expected to be a limiting factor for ferrocyanide waste aging in Hanford Site tanks. Although modeling indicated that caustic waste added after the initial scavenging campaigns could penetrate sludge at a rate of 3 meters per year,[19] it was questioned whether ferrocyanide sludge would age at greater depths, if it does not otherwise come into contact with high pH waste. Therefore, aging under less alkaline conditions was studied.

Aging of In-Farm simulant was investigated at 60 °C in a gamma-irradiated pH 10 solution. The concentration in the 161-day sample indicates an apparent cyanide conversion of about 18 mole %, based on the amount of ammonia present at the end of the test. The actual conversion is higher because ammonia is also destroyed by radiolysis. If it is assumed that ammonia production is linear with time, a global rate constant for ammonia production of 8.0×10^{-5} M/day is calculated. The fit of the data to the linear model is not very good, but this rate constant is similar to the rate constant determined for the 70 °C experiment conducted in 2 M NaOH. Considering the low solubility of In-Farm simulant in pH 10 solution, the magnitude of this rate is remarkable. It is possible that direct gamma radiolysis of ferrocyanide in the solid phase forms ferricyanide, which may have a higher solubility, thereby promoting aging. The difference in pH may not greatly affect the hydrolysis reaction itself because it is reported that thermal hydrolysis is unaffected by pH above pH 9.[20] These results show that even ferrocyanide sludge that did not come into direct contact with highly basic waste may also have aged significantly over the decades of storage.

Based on tank histories and laboratory experiments with simulated ferrocyanide flowsheet materials, conditions existed within the tanks that would promote ferrocyanide aging. Caustic solutions, high temperature, and the presence of gamma radiation contribute to the hydrolysis of ferrocyanide ion. It is likely that ferrocyanide was dissolved from sludge that contacted high pH evaporator or cladding waste and was subsequently hydrolyzed. Modeling predicts that sludges not initially exposed could eventually contact caustic waste through convection, thereby causing dissolution and aging. Other experiments indicate that aging also could occur in sludges that were never exposed to high pH waste. These experimental results are consistent with analytical results from actual tank samples which show the expected amount of nickel but very low cyanide and energy content, thereby proving that aging occurred.

III. TANK WASTE SAMPLE RESULTS

Nine ferrocyanide tanks (BY-104, BY-108, BY-110, C-108, C-109, C-111, C-112, T-107, and TY-104) have been sampled that meet the sampling requirements specified in the Ferrocyanide Data Quality Objectives document.[21] Tank BY-106 was sampled also, but sludge was only obtained from one riser. The ranges of ferrocyanide contents measured for the tanks samples are shown in column 5 of Table 1.

A. Aging Confirmed by Sample Results

The characterization approach for ferrocyanide described in the Meacham et al. (1995)[21] also allows the historical data and aging models to be corroborated by measuring fuel and nickel concentrations.

The logic used to evaluate the effects of aging first considers the fuel concentration. If the waste contains a fuel concentration less than predicted by the process flowsheets, then aging may be the reason. This aging hypothesis was evaluated by considering the nickel content of the waste.

Data on nickel concentrations were used to confirm historical information and ferrocyanide aging models because nickel is a signature analyte of the nickel ferrocyanide scavenging campaigns, the only source of high nickel concentrations. Experiments that replicated the original process flowsheets showed nickel concentrations ranging between 0.87 to 4.8 wt% on a dry-weight basis. A lower bound of 0.8 wt% or 8,000 μg/g (dry-weight basis) was selected as the minimum value needed to confirm that the tank originally contained ferrocyanide sludge.

Did the waste have a sufficiently high nickel concentration to conclude that it originally contained ferrocyanide sludge? If so, waste aging was confirmed, and additional sampling of ferrocyanide waste was not required. If the waste had a low nickel concentration, then the tank might have been identified erroneously as containing ferrocyanide waste; or another explanation may apply. For example, many of the ferrocyanide tanks received saltcake waste that should show little or no nickel present, while others received just sludges. None of this added waste would have contained nickel. Additional mixing, which undoubtedly occurred under some of the risers, would have diluted the nickel results.

B. Aging in the Worst-Case Tanks

The four C-Farm tanks (C-108, C-109, C-111, and C-112) received the richest concentration of ferrocyanide (In-Farm flowsheet) because the scavenging campaigns for these tanks involved supernatant only and not the solids as was done using the U-Plant and T-Plant flowsheets. These four tanks, and especially tank C-112 which received the most concentrated ferrocyanide, are considered the worst-case tanks because tests showed this material could propagate if dry and heated to a temperature of 250 °C. The Ferrocyanide Safety Program focused on these tanks from early on. The first tanks to be sampled were tanks C-112 and C-109. However, total cyanide, energetics, and nickel analyses of the waste samples confirm that the ferrocyanide in these tanks has aged.

Table 2 compares the concentrations from sampling with the original concentrations indicated by process flowsheets and experiments.[9] These data have been treated statistically to provide an upper 95% confidence limit. (Data for the other sampled tanks were still being analyzed at the time this paper was prepared and will be presented at the conference.) Table 2 shows the average ferrocyanide concentrations were at least a factor of ten less than the original concentrations, and the nickel analyses indicate that ferrocyanide once was present. The differences between the current measured waste energetics and cyanide and the original concentrations are explained by aging. Because an insufficient amount of fuel is present in these tanks, they are categorized as *SAFE*.

IV. CONCLUSIONS

Approximately 74% of the ferrocyanide waste added to the tanks (U-Plant and T-Plant flowsheets) was sufficiently dilute in ferrocyanide when formed that it could not support a propagating reaction even if dry (0 free water). The other 26% of the waste, however, was significantly higher in ferrocyanide concentration. These sludges were stored in four C-Farm tanks. Nine of the ferrocyanide tanks have been sampled and analyzed including all four C-Farm tanks. The results show that all of the sludges are now low enough in ferrocyanide concentration and have insufficient potential for a propagating reaction. This is attributable to chemical aging that has occurred over the years of storage.

Based on studies of ferrocyanide aging mechanisms and verification from waste samples from nine ferrocyanide tanks, it has been shown that the ferrocyanide concentration in all sludges has chemically degraded. Although not all ferrocyanide tanks were sampled, results from the nine sampled tanks bound the aging conditions for the unsampled tanks. The sludges in all 18 ferrocyanide tanks are categorized as *SAFE* with regard to the Ferrocyanide Safety Issue. They cannot support a propagating ferrocyanide reaction even if the waste was totally dry. Ferrocyanide propagating reaction accidents are concluded to be extremely unlikely events for these sludges. The DOE as been requested to remove all 18 ferrocyanide tanks from the Watch List and declare the Ferrocyanide Safety Issue closed. All program activities are scheduled to cease at the end of Fiscal Year 1996.

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Table 1. Comparison of Tank Contents with Criteria

Tank	Waste flowsheet	Concentration of $Na_2NiFe(CN)_6$ (wt%, on a 0 free water basis)			Safety category	Control requirements
		Process records	Maximum simulant[a]	Tank sample[b]		
BY-103	U Plant	6.0	8.3	Not Sampled	*SAFE*	None
BY-104	U Plant	6.0	8.3	<0.025	*SAFE*	None
BY-105	U Plant	7.4	8.3	Not Sampled	*SAFE*	None
BY-106	U Plant	5.2 - 5.5	8.3	<0.025[c]	*SAFE*	None
BY-107	U Plant	5.0 - 5.9	8.3	Not Sampled	*SAFE*	None
BY-108	U Plant	5.0 - 5.8	8.3	<0.47	*SAFE*	None
BY-110	U Plant	5.7 - 6.2	8.3	<0.12	*SAFE*	None
BY-111	U Plant	6.6	8.3	Not Sampled	*SAFE*	None
BY-112	U Plant	3.5	8.3	Not Sampled	*SAFE*	None
C-108	In Farm 2	10.4 - 15.6	22.6	1.1	*SAFE*	None
C-109	In Farm 2	14.0 - 20.9	22.6	1.6	*SAFE*	None
C-111	In Farm 2	8.9 - 12.1	22.6	0.02	*SAFE*	None
C-112	In Farm 1	16.1 - 24.2	25.5	1.5	*SAFE*	None
T-107	U Plant	7.3	8.3	<0.04	*SAFE*	None
TX-118	U Plant	n/a[d]	8.3	Not Sampled	*SAFE*	None
TY-101	T Plant	7.6	8.8	Not Sampled	*SAFE*	None
TY-103	T Plant	6.9	8.8	Not Sampled	*SAFE*	None
TY-104	T Plant	10.7	8.8	In Progress[e]	*SAFE*	None

Notes:

[a] Ferrocyanide concentration of the flowsheet simulant for the most concentrated waste added to the tank (does not account for aging).

[b] Tanks not sampled are bounded by sampled tanks where the ferrocyanide would be less likely to have aged.

[c] Only one sample of sludge (approximately 5 cm in length) was obtained from tank BY-106, however, analysis for nickel and cyanide show that the ferrocyanide had degraded.

[d] Process records do not show that a significant quantity of ferrocyanide sludge is stored in this tank.[8] Tank erroneously identified as ferrocyanide tanks because of earlier track radioactive components (TRAC) calculations.[16]

[e] Cyanide determinations not available at time paper was prepared. There were no exotherms for either of two auger samples obtained from this tank. The waste contained over 50 wt% water.

Table 2. Current Ferrocyanide and Nickel Concentrations Compared to Original Concentrations (Dry Basis)

Tank	Original $Na_2NiFe(CN)_6$ wt%, dry	Waste sludge layer	Average $Na_2NiFe(CN)_6$ wt%, dry	$Na_2NiFe(CN)_6$ upper 95% confidence limit wt%, dry	Original nickel wt%, dry	Average nickel wt%, dry
C-108	22.6	A	1.1	5.2	3.5 - 4.2	1.0
		B	0.3	1.0		2.9
C-109	22.6	A	1.4	1.9	3.5 - 4.2	1.0
		B	1.6	2.8		3.9
		C	0.7	1.0		3.2
C-111	22.6	A	0.04	<1	3.5 - 4.2	2.5
		B	0.05	<1		4.3
		C	0.02	<1		2.0
C-112	25.5	A	1.3	2.5	3.2 - 4.7	n/a[b]
		B	1.2	4.0		3.0
		C	1.2	3.2		5.1
		D	1.5	4.0		3.0
		E	1.5	n/a[a]		n/a[b]

Notes:

[a] Statistics were not performed for this layer because only one sample was available.

[b] Nickel analysis was originally performed with nickel crucibles. Reanalysis performed with non-nickel crucibles was only performed on layers B, C, and D.

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