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Ferrocyanide Safety Program: Safety Criteria for Ferrocyanide Watch List Tanks

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

Westinghouse
Hanford Company Richland, Washington

Hanford Operations and Engineering Contractor for the
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Ferrocyanide Safety Program: Safety Criteria for Ferrocyanide Watch List Tanks

A. K. Postma
J. E. Meacham
G. S. Barney
G. L. Borsheim
R. J. Cash
M. D. Crippen
D. R. Dickinson
J. M. Grigsby
D. W. Jeppson
M. Kummerer
J. M. McLaren
C. S. Simmons
B. C. Simpson

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Office of Environmental Restoration
and Waste Management

Westinghouse Hanford Company
P.O. Box 1970
Richland, Washington 99352

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A. K. Postma A.K. Postma 1-5-94

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LIST OF TERMS

DNFSB	Defense Nuclear Facilities Safety Board
DOE	U.S. Department of Energy
DSC	differential scanning calorimetry
LOW	liquid observation well
SST	single-shell tank
TAP	Tanks Advisory Panel
TGA	Thermogravimetric Analysis
USQ	Unreviewed Safety Question

DEFINITIONS

Bound water content: Bound water in waste is water remaining in waste after free water is removed. Bound water has been calculated to amount to 4.6 molecules of H_2O per molecule of sodium nickel ferrocyanide [$Na_2NiFe(CN)_6$] on the basis of tests described in Appendix B, Section B.3.2.

Free water content: Free water is water in ferrocyanide waste that can be removed from samples using standard drying methods by drying at 120 °C for 18 hr or by an equivalent laboratory process. As an example, if a 10.0 g sample of waste lost 5.0 g of water after drying at 120 °C for 18 hr, the free water content of the waste would be assigned a value of 50 wt%.

Total water content: Total water content is the sum of free and bound water contents

Dry sodium nickel ferrocyanide: Dry sodium nickel ferrocyanide [$Na_2NiFe(CN)_6$] is the ferrocyanide compound alone, with no bound water.

Ferrocyanide concentration on an energy equivalent basis: Theoretical analyses described herein indicate that the criterion for reaction propagation is closely related to exothermic reaction energy per unit mass of waste. The energy equivalent concentration of ferrocyanide is a value computed from a measured exotherm in a waste sample using a specific reaction energy of 6 MJ/kg of sodium nickel ferrocyanide. For example, if a waste sample exhibited a reaction exotherm of 0.6 MJ/kg of waste on a zero free water basis, the energy equivalent ferrocyanide concentration would be calculated as:

$$\frac{0.6MJ}{kg\ waste} x \frac{1\ kg\ Na_2NiFe(CN)_6}{6\ MJ}\ x\ 100 = 10\%\ Na_2NiFe(CN)_6$$

on a zero free water basis. The technical basis for this definition of ferrocyanide concentration on an energy equivalent basis is descried in Appendix B.

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CRITERIA FOR FERROCYANIDE WATCH LIST TANKS

1.0 SUMMARY AND CONCLUSIONS

1.1 SUMMARY

This report provides a technical basis for closing the ferrocyanide Unreviewed Safety Question (USQ) at the Hanford Site. Three work efforts were performed in developing this technical basis. The efforts described herein are:

1. The formulation of criteria for ranking the relative safety of waste in each ferrocyanide tank

2. The current classification of tanks into safety categories by comparing available information on tank contents with the safety criteria

3. The identification of additional information required to resolve the ferrocyanide safety issue.

Three safety categories were formulated on the basis of answers to two safety questions (1) Is a significant exothermic reaction possible during interim storage? and (2) Is a significant exothermic reaction possible under present conditions of waste moisture content? The word significant in these two questions is defined by reference to a safety objective which can be met only by limiting radiological and toxicological consequences to those specified in applicable guidelines (WHC 1992).

Numerical criteria for the three safety categories (SAFE, CONDITIONALLY SAFE, and UNSAFE) 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 criteria described herein pertain to the hazard posed by sustained, rapid exothermic reactions between ferrocyanide and nitrate/nitrite salts in stored waste. As such, these criteria do not replace or eliminate safety criteria that have been formulated to address other hazards of tank operations. Adoption of these criteria would not reduce the need for prudent monitoring and management of ferrocyanide waste tanks. A specific example of the latter is temperature monitoring and the action plan for response to unexpected increases in waste temperature (Cash and Thurman 1991). Unexpected temperature increases would continue as a trigger for emergency response even if measured waste temperatures were well below the temperature criterion for safe storage as specified herein.

1.2 CONCLUSIONS

Safety categories and applicable criteria were developed that define safe storage of ferrocyanide waste. These provide the technical basis for closing the ferrocyanide USQ at the Hanford Site. The hazard potential for exothermic reactions in the ferrocyanide waste were classified by:

Level 1 - SAFE

Concentration of fuel $\leq$ 8 wt% sodium nickel ferrocyanide*

Concentration of water - not limiting
Concentration of oxidizers - not limiting
Temperature of waste - not limiting

Level 2 - CONDITIONALLY SAFE

Concentration of fuel > 8 wt% sodium nickel ferrocyanide
Concentration of water $\geq$ 0 to 24 wt%**
Concentration of oxidizers - not limiting
Temperature of waste $\leq$ 90 °C***

Level 3 - 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 on minimum retained moisture and maximum waste temperature is required. For tanks that are assigned to the UNSAFE category, monitoring and controls are required to avoid conditions that could lead to reaction initiation. A modification in the waste state is required to remove a tank from the UNSAFE category.

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*$Na_2NiFe(CN)_6$ on an energy equivalent basis, calculated on a zero free water basis.

**Free water content. The moisture criterion increases linearly from 0 percent at 8 wt% fuel to 24 wt% at 26 wt% fuel.

***Temperature is not an independent criterion; it is implicit in the moisture criterion as discussed in Section 6.2.

The criteria specified for the three levels described above were selected to provide a significant safety margin compared to empirical limits, as illustrated below.

Criterion	Safety limit	Empirical safety limit
Fuel content, wt%	8	15 to 18
Free water content, wt%	24	12
Temperature, °C	90	250

The technical bases for the numerical values listed above are provided in Sections 5.0 and 6.0 of this report.

Based on a comparison of current knowledge of tank contents with the safety criteria, two ferrocyanide tanks were put into the SAFE category and the remainder were put into the CONDITIONALLY SAFE category. No tanks fit the UNSAFE category. The current ranking was done on the basis of a conservative interpretation of available data.

It is noteworthy that the two tanks (241-C-109 and 241-C-112) put into the SAFE category on the basis of sample data, contained so-called In Farm waste. The In Farm process flowsheets produced ferrocyanide waste that had much higher ferrocyanide concentrations than waste produced by other flowsheets used at the Hanford Site. Significant degradation of the ferrocyanide by radiolytic and other chemical reactions has apparently occurred during the 35+ years that have elapsed since the waste was put into the tanks. It is anticipated that degradation of ferrocyanide will be confirmed and that all of the tanks will be reclassified into the SAFE category after confirmatory waste characterization data are obtained.

Studies of heat dissipation and moisture retention (see Appendices C and D for details) led to two important conclusions regarding the safety of continued storage:

- Radioactive decay heat loads are low (3 kw or less), allowing heat dissipation by passive processes; no active cooling equipment is needed to prevent waste heatup during storage.

- Physico-chemical properties and storage conditions both foster the retention of moisture in ferrocyanide sludge; no active control is required to maintain moisture above required levels during continued storage.

The above data are sufficient to close the ferrocyanide USQ. The additional information needed to resolve the ferrocyanide safety issue is described as follows.

- Tank Characterization--Additional sampling is needed to characterize the waste in as-yet unsampled tanks.

- Resolution of Hypothetical Hot Spot Issue--A documented analysis of hypothetical hot spots that accounts for all relevant factors is needed to resolve this issue.

2.0 INTRODUCTION

2.1 OBJECTIVE

The objective of this report is to provide a technical basis for closing the ferrocyanide USQ. In accordance with DOE Order No. 5480.21 (DOE 1991), the following information is presented:

- A description of the hazard
- Criteria for assessing the significance of the hazard
- A review of the hazard in light of available information
- The identification of additional information needed to resolve the safety issue.

2.2 SCOPE

This report embraces the exothermic reaction hazard posed by Ferrocyanide Watch List Tanks at the Hanford Site and does not address other safety issues which may be associated with these tanks. It is limited to interim storage conditions and does not consider potential hazards associated with processes that will be used to either remove waste from the tank or convert it to a safe form for final, long-term storage.

2.3 HAZARD BACKGROUND

The ferrocyanide hazard in waste tanks at the Hanford Site has been under intensive study for the past several years. An interim hazards assessment report (Grigsby et al. 1992) and a review of current understanding of the hazard (Postma 1992) have been completed. The present report uses the earlier reports as points of departure and incorporates information gathered since their issuance.

Radioactive waste from defense operations has 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 Hanford Site defense mission. To obtain this additional storage volume in a short time period, while minimizing the construction of additional storage tanks, Hanford Site scientists developed a process to scavenge radiocesium and other soluble radionuclides from tank waste liquids. As a result of implementing this process,

approximately 140 metric tons of ferrocyanide were added to waste now residing in a number of single-shell tanks (SSTs). Using process knowledge and historical records, 20* tanks at the Hanford Site are currently estimated to contain 1,000 g-moles or more of ferrocyanide as the $Fe(CN)_6^{4-}$ radical (Borsheim and Simpson 1991).

Ferrocyanide is a complex of ferrous and cyanide ions that is considered nontoxic because it is stable in aqueous solutions. However, in the presence of oxidizing materials, such as nitrates and nitrites, near-stoichiometric mixes of ferrocyanide have been shown to undergo energetic reactions under special conditions in the laboratory by (1) heating to high temperatures (above 270 °C); or (2) by an electrical spark of sufficient energy to heat the mixture. The exothermic reaction of ferrocyanide in the presence of nitrates has been known for decades, but the conditions under which impure mixtures can undergo propagating reactions have not been thoroughly studied. Because the scavenging process involved precipitating ferrocyanide from solutions containing nitrate, it is likely that an intimate mixture of ferrocyanide with nitrates and nitrites** and inert diluents exists in parts of some of the SSTs.

Efforts have been underway since the mid-1980s to evaluate the potential for a ferrocyanide reaction in the Hanford SSTs (Burger 1989, Burger and Scheele 1988). In 1987, an environmental impact statement for disposal of Hanford Site waste farms was issued (DOE 1987). The environmental impact statement projected that the bounding worst-case accident in a ferrocyanide tank would be an exothermic reaction that could cause the release of radioactive waste to the environment.

A General Accounting Office (GAO) study (Peach 1990) postulated a worst-case accident, with calculated doses greater than the 1987 DOE environmental impact statement. The higher consequences postulated in the GAO study (Peach 1990) resulted from higher postulated cesium releases as compared to those postulated in the environmental impact statement (DOE 1987). A special Hanford Site Ferrocyanide Task Team was commissioned in September 1990 to address all issues involving the ferrocyanide tanks.

In October 1990, the hazard posed by potential reactions between ferrocyanide and oxidizers was declared an USQ*** (Deaton 1990), because the safety envelope for these tanks may

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*The ferrocyanide Watch List formerly contained 24 tanks (Hanlon 1993). However, four tanks were removed from the Watch List in July 1993 and two more tanks are pending removal (Cash et al. 1993, Borsheim 1993).

**Nitrate has been partially converted to nitrite as a result of radiolysis during storage. Recent samples indicate a nitrate:nitrite ratio of roughly 3:1.

***The USQ designation is a formal procedure required under specific orders from DOE (DOE 1986; DOE 1991). The USQ orders state, "A proposed change, test or experiment shall be deemed to involve an unreviewed safety question if:

no longer be bounded by the existing safety analysis report (Bergmann 1986) and the 1987 DOE environmental impact statement (DOE 1987). In response to the USQ designation, work in the ferrocyanide tanks requires detailed planning, together with the preparation of supporting safety and environmental documentation, and approval by DOE management. An early closure of the USQ would shorten review schedules currently required for each characterization activity and could therefore speed efforts required to resolve the ferrocyanide safety issue.

This report is prepared as one of the work efforts within an integrated program being carried out by DOE contractors (Cash 1991, Borsheim et al. 1992) designed to resolve the ferrocyanide safety issue.

2.4 APPROACH

A strategy for closure of the USQ and resolution of the safety issue surrounding the ferrocyanide waste was recently crafted by DOE (DOE 1993) and WHC. A summary of the strategy is presented in Figure 2-1. The strategy calls for closure of the USQ before resolution of the safety issue. Information required to close the USQ includes the following:

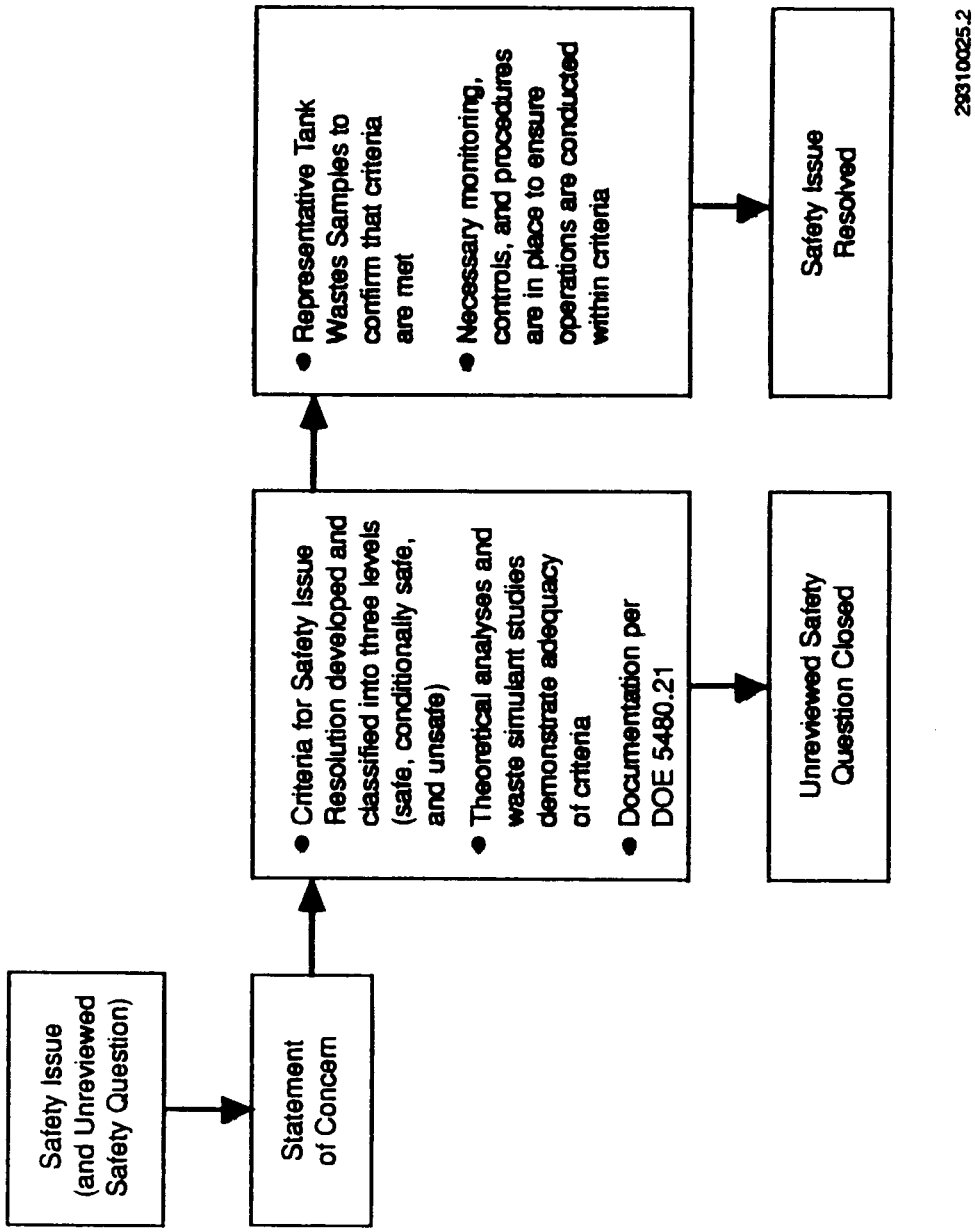
- Development of safety criteria
- Demonstration of the adequacy of the criteria
- Review of tank safety in accordance with DOE Order No. 5480.21 (DOE 1991).

Resolution of the safety issue can be accomplished when sufficient data are obtained to assure that tanks meet the criteria and that operations, with required controls, do not cause waste conditions to fall outside the envelope defined by the criteria.

- 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

- 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.

Figure 2-1. Strategy for Resolution of the Ferrocyanide Safety Issue (DOE 1993).



The safety criteria presented in this report were established on the basis of a five-step process: (1) defining the safety objective, (2) determining appropriate safety evaluations, (3) reviewing hazard phenomenology, (4) identifying key parameters that define the safety envelope for each safety category, and (5) selecting numerical values of key safety parameters on the basis of theoretical analyses and experimental studies on waste simulants. A sixth work step, a review of tank safety, was quantified by comparing information on tank contents with the criteria. This led to the current ranking of the tanks into safety categories. The remainder of this report is organized to document the bases for the criteria and the current categorization.

3.0 SAFETY OBJECTIVE

The primary safety objective is to maintain waste in a state that prevents chemical reactions that have the potential for

1. Radiation doses or toxic exposure either onsite or offsite more than applicable limits or guidelines (WHC 1992)

2. Damage to the tank so as to compromise its ability to store high-level waste safely.

   (Safety issues of the SSTs not related to the presence of ferrocyanide are outside the scope of this document.)

The primary safety objective stated above will be met by imposing a more stringent secondary objective that no sustainable rapid exothermic ferrocyanide reaction (propagating 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 aging (degradation) reactions believed to be occurring over a period of years.

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4.0 SAFETY CATEGORIES FOR CLASSIFYING FERROCYANIDE WASTE

4.1 PURPOSE OF SAFETY CATEGORIES

Categorizing the ferrocyanide waste hazard into safety categories helps define levels of assurance and controls required to meet the safety objective stated in Section 3.0. Using safety categories permits ranking relative risk posed by the 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.

4.2 KEY SAFETY QUESTIONS

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, and guidance contained in a report of the Tanks Advisory Panel (TAP) (Kazimi 1992).

Question 1

Is a significant exothermic reaction possible during interim storage?

The word *significant* in this question is defined by reference to the effects noted in 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 possible but unlikely events such 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 as follows.

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 a 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 lead to the definition of three safety categories which are described as follows.

4.3 SAFETY CATEGORIES

Three safety categories selected on the basis of answers to the key safety questions are defined as SAFE, CONDITIONALLY SAFE, and UNSAFE. The categories are described as follows.

SAFE

This 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.

In reaction phenomenology, the requirement is that reactions be self-extinguishing, (i.e., that they could not continue to propagate at a measurable rate as the result of a localized initiator). Another key requirement is that radioactive decay heat can be dissipated passively without inducing a runaway reaction. Both requirements must be satisfied at all free moisture concentrations that could occur during a hypothetical unattended operational mode.

CONDITIONALLY SAFE

This category corresponds to a yes answer to key safety questions 1 followed by a no answer to key safety question 2. The waste in this category is 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, runaway and propagating reactions can be ruled out for this safety category.

UNSAFE

This category corresponds to yes answers to both key safety questions. For waste 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 waste 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.

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5.0 SUMMARY OF HAZARD PHENOMENOLOGY

This section presents a summary of the phenomena that are key to understanding and quantifying the ferrocyanide hazard. Additional information on hazard phenomenology is presented in Appendices A, B, C, and D of this report.

5.1 WASTE COMPOSITION

The potential for an exothermic reaction in stored waste depends on the relative concentrations of the reactants, inert solid diluents, and water. Process knowledge obtained from historical records and waste simulants produced from scavenging process flow sheets can be used to predict the major constituents and some general physical properties of the waste matrix. A comparison of historical data with analytical results from samples taken from two tanks (241-C-109 and 241-C-112) provides evidence of ferrocyanide degradation in these two tanks. The following information is a summary of information presented in Appendix A.

5.1.1 Process Flowsheets

Three treatment processes were conducted in separate facilities to treat three different types of waste. The corresponding flowsheets are termed U Plant, T Plant, and In Farm flowsheets (Borsheim and Simpson 1991). In general, the aqueous waste was pumped to process tanks where precipitating agents were added. The slurry was then transferred to an underground storage tank for settling of the solids and disposal of the supernatant liquid to the ground. The precipitated solids formed a sludge that constitutes the ferrocyanide waste.

U Plant and T Plant flowsheets produced precipitates that contained relatively large percentages of inert diluents and thus produced sludge that contained relatively low concentrations of ferrocyanide. Some 74 percent (by mass) of ferrocyanide consumed at the Hanford Site was used by these two flowsheets.

The In Farm flowsheets contained lower concentrations of inert diluents, and therefore resulted in sludge that contained relatively higher concentrations of ferrocyanide. Roughly 26 percent of the total ferrocyanide consumed was used in the in-farm flowsheet.

5.1.2 Waste Simulant Properties

Simulants were prepared with nonradioactive chemicals using the three flowsheets used at Hanford (Jeppson and Wong 1993). Typically, two or three layers of precipitates (discernable by color) were formed at the bottom of the settling and centrifuging containers. These layers were sampled and separated from each other. The bottom layer of the U Plant

and In Farm simulants and the top layer of the T Plant simulant contained the higher ferrocyanide concentration. Compositions of the more concentrated layers of sludge produced by three flowsheets are listed in Table 5-1.

Table 5-1. Composition of the More Concentrated Layers of Three Simulant Sludges.

	Wt% for Stated Sludge		
Constituent	Dried U Plant 2	Dried In Farm 1	Dried T Plant
Bound water	2.5	5.8	~3
Sodium nitrate	45.2	39.8	27.1
Sodium nitrite	10.9	11.4	6.1
$Na_2NiFe(CN)_6$	8.3	25.5	~8.8
Nickel sulfide	0.0	2.7	0.0
Inert solids	~33	~15	~55
Free water*	64	48	69

*This value applies to the as-prepared, centrifuged sludge before drying.

The simulant sludges were composed of small particles and had rheological properties similar to those of clay, mayonnaise, or toothpaste. Stoichiometric calculations based on the ferrocyanide and nitrate/nitrite concentrations shown in Table 5-1 indicate that nitrate and nitrite concentrations were in excess as compared to the ferrocyanide. Also, the total water content (bound plus free) of the simulant sludge was high, ranging from 53.8 percent (48 + 5.8) to 72 percent (69 + 3).

5.1.3 Properties of Sludge Removed From Tanks

Core samples have recently been removed from two tanks (241-C-112 and 241-C-109) that received waste generated by the In Farm flowsheet (Simpson et al. 1993a, Simpson et al. 1993b). These results provide a first glimpse of what is currently in the tanks.

Key properties of the retrieved waste are summarized as follows.

- The consistency of the sludge samples varied from a thin slurry to thick, chunky sludge; they appeared to be saturated with liquid.

- Free moisture contents varied from 28 percent to 57 percent on a mass basis.*

- Cyanide concentrations varied with vertical position as expected and ranged from 0.6 percent to 2.9 percent [reported as $Na_2NiFe(CN)_6$ on a zero free water basis]. These values are less than 12 percent of values expected on the basis of the simulants (see Table 5-1 for comparison).

- Reaction exotherms were consistently small (less than 13 cal/g on a zero free water basis), and correspond reasonably to those calculated on the basis of the measured cyanide concentrations.

The rheology and high moisture content of the sampled waste were as-expected using simulants as a guide. The observed low (as compared to flowsheet information) cyanide concentrations and reaction exotherms is evidence that substantial degradation of ferrocyanide has occurred during the 35 years of storage. The agreement of other analyte concentrations (^{137}Cs, ^{90}Sr, and Ni) with values expected from independent estimates of tank contents (Babad et al. 1993, Simpson et al. 1993a, Simpson et al. 1993b) supports the validity of the samples.

5.2 FERROCYANIDE-NITRATE/NITRITE REACTIONS

The potential for uncontrolled, exothermic reactions between ferrocyanide salts and salts of sodium nitrate and sodium nitrite represents the hazard of focus here. Each compound is stable under ordinary conditions, and can undergo rapid reactions only under a restrictive set of conditions. In this section, the phenomenology of ferrocyanide-nitrate/nitrite reactions is briefly reviewed to illustrate the conditions of concentration, temperature, and moisture content where rapid, exothermic reactions are possible. Sampled waste and waste simulants were examined to judge whether hazardous reactions in stored waste are possible, and if so, under what conditions. Appendix B contains a more detailed discussion of ferrocyanide-nitrate/nitrite reactions.

5.2.1 Theoretical Considerations

For a chemical reaction in solid materials to be self-sustaining, the reaction must produce enough energy to heat adjacent unreacted solids to a temperature where the reaction occurs at a rate fast enough that heat cannot be removed as fast as it is generated. Otherwise, a reaction initiated at a local region will die out.

*Moisture determined in hot cell operations are low by an indeterminate percentage because of evaporative losses into the relatively dry hot cell atmosphere.

The energy produced by oxidation-reduction reactions can be estimated by thermochemical analyses. For example, the following reaction has a calculated heat of reaction of -9.5 MJ/kg (2280 cal/g) of sodium nickel ferrocyanide (Burger 1993):

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

In general, the calculated energy of a reaction depends on which reaction products are specified. Experiments generally are required to obtain accurate estimates of heats of reaction for the conditions that apply. As described in Appendix B, heats of reaction measured in simulated waste solids yield an energy estimate of approximately -6 MJ/kg (1430 cal/g) of dry sodium nickel ferrocyanide.

Energy balance calculations can be made to identify the ferrocyanide concentration where the reaction energy is just sufficient to heat the unreacted material to the threshold temperature where the reaction can take place at an appreciable rate. The threshold temperature for waste simulants has been measured to be in the range of 220 °C to 270 °C.

Based on the measured reaction energy of -6 MJ/kg (1430 cal/g), an initial temperature of 30 °C and a reaction threshold temperature of 250 °C, energy balance calculations detailed in Appendix B have identified values of the minimum concentration (which could cause a reaction to propagate) of ferrocyanide as a function of moisture content of solid waste. Key results are the following.

- For waste with 0 percent free water, the minimum ferrocyanide concentration to sustain a reaction is computed to be 7.7 percent by weight of dry sodium nickel ferrocyanide.

- For the simulant waste with the highest ferrocyanide concentration (In Farm containing 25.5 percent on a dry basis) a moisture content of 24 wt% is computed to be required to limit the calculated temperature to 250 °C.

These criteria levels based on energy balance calculations are expected to be conservative because kinetic factors, (i.e., the reactions are not instantaneous) have been ignored. A more realistic model, described in Appendix B, yields a propagation limit of ~ 15 percent dry sodium nickel ferrocyanide.

At the 7.7 percent concentration level, the exothermic energy potential per unit mass of waste is calculated to be 0.46 MJ/kg (110 cal/g). This reaction energy is roughly a factor of 10 below the energy yield of 4.2 MJ/kg (1000 cal/g) that typifies explosives (Kirk-Othmer 1978). The reaction energy at the 7.7 percent level is roughly half the value determined experimentally for a propagating reaction (~ 1 MJ/kg) in dry ferrocyanide waste simulants (see Appendix B).

5.2.2 Experimental Studies on Simulants

Two types of experimental procedures have been used to study the propagation characteristics of waste simulants: adiabatic calorimetry and propagation rate tests. These tests and key results are discussed briefly in this section. More detailed information is presented in Appendix B.

ADIABATIC CALORIMETRY TESTS

In these tests, sizeable samples (10g and 70g) are heated under low-heat loss conditions. As the sample is heated to above the reaction onset temperature, 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. Two distinct types of behavior can be seen depending on sample reactivity.

1. A relatively slow heat-up rate that is typical of an Arrhenius or runaway reaction. Any material that contains chemicals that react exothermically will exhibit this behavior.

2. A sharp spike in temperature that typifies the passing of a reaction front. For materials which exhibit this behavior, a propagating reaction front is possible, given an appropriate initiator.

Based on adiabatic calorimetry tests (Jeppson and Wong 1993, Fauske 1992, Fauske 1993a) it was found that propagating reactions were not observed for sodium nickel ferrocyanide concentrations below 15 wt% on a zero free water basis (0.9 MJ/kg or 215 cal/g of waste). This number is approximately double the 7.7 percent number arrived at on the basis of the energy balance calculation described in Section 5.2.1. 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.

PROPAGATION RATE TESTS

In these tests, a confined cylinder of waste was ignited at the open upper end and the rate of propagation was measured by noting the time when the reaction front passed imbedded thermocouples. Cylinder size, ambient pressure, moisture content, initial waste temperature,

and ferrocyanide concentration were parameters in the set of propagation tests that was done (see Table B-4 of Appendix B for details). Key results are as follows.

1. Propagation rates varied from 5.3 to 32 cm/min* for relatively dry mixes containing 25.5 wt% ferrocyanide (zero free water basis).

2. Propagation ceased when the free moisture content was 12 wt% or more. This result applies for the simulants containing the highest concentration of ferrocyanide (25.5 wt%).

The 12 wt% moisture threshold determined experimentally is only 43 percent as much as indicated by the thermodynamic calculations presented in Section 5.1. The difference is as-expected because the thermodynamic calculations are inherently conservative.

5.2.3 Experimental Measurements on Waste Samples

As noted in Section 5.1.3, the analysis of recent waste samples provides a first indication of what is in the tanks. The exothermic energy potential of the samples was less than 13 cal/g on a zero free water basis. This amounts to less than 12 percent of the propagation energy level based on thermodynamic calculations and less than 6 percent of that based on the experimentally derived propagation limit. The energy content of sampled waste falls far below the criterion for a propagating reaction.

5.3 MOISTURE RETENTION CHARACTERISTICS OF FERROCYANIDE SLUDGE

Physico-chemical properties and storage conditions both foster the retention of moisture in ferrocyanide sludge. Because moisture is also an effective diluent in preventing reaction propagation, it is important to know current levels of moisture in waste tanks and to understand how this moisture could be lost. Additional information on moisture retention is provided in Appendix C.

*This was the fastest propagation rate observed at 51 atmospheres of pressure. At 1 atmosphere, the fastest propagation rate observed was 10 cm/sec.

5.3.1 Theoretical Considerations

Ferrocyanide sludge is formed by the precipitation of small particles in aqueous solution. After settling and consolidation into a sludge layer, moisture would be retained by the following mechanisms.

- Interstitial liquid held by capillary forces
- Water held as hydrates in waste salts and caustic in waste
- Water held in zeolytic form on solid $Na_2NiFe(CN)_6$
- Water bound in metal oxides found in sludge.

Experiments and theoretical calculations that help quantify the moisture content of stored waste are discussed as follows.

5.3.2 Moisture Contents of Waste Simulants

The water contents (free water plus bound water) of ferrocyanide sludge simulants prepared by the three flowsheets were greater than 50 percent by mass (see Table 5-1). Experiments have been carried out to determine how much water could be lost by liquid outflow, in the postulated event of a leaking tank or one which was saltwell pumped.

DRAINING TESTS

A moisture draining test has been underway for approximately 1 year. The test column is 8 inches in height and uses the In Farm simulant sludge with an initial free water content of 53 percent. Observed moisture loss rates are used to determine capillary constants that can be used in a theoretical model. The theoretical model can then be used to predict drainage losses for ferrocyanide sludge layers in the waste tanks. Results of work underway indicate that moisture content in an 8-ft deep sludge layer would remain above 40 percent after 300 years of drainage. The 40 percent value referred to applies to the upper surface of the layer. Higher moisture levels are predicted for lower positions in the layer.

CENTRIFUGE TESTS

In Farm simulant sludge has been centrifuged on a glass fritted disk to measure liquid drain rates under enhanced gravity forces. Centrifuge speed was selected to impose a force of 10, 20, and 50 g's. As indicated in Figure C-1 of Appendix C, moisture levels have remained above 45 wt% free water in all samples.

Taken together, the draining and centrifuge tests indicate that the moisture loss by draining is limited, and by itself, would not lead to waste dryout.

BOUND WATER CONTENT

Drying tests on simulants have shown the presence of a significant quantity of tightly bound water. This is evidenced by moisture evolved at temperatures up to 240 °C in simultaneous differential scanning calorimetry (DSC), thermogravimetric (TGA) and mass spectrometric analysis of offgas tests performed on samples that had previously been dried. The initial drying methods included heating for 18 hours at 120 °C, heating for 24 hours at 105 °C, and vacuum drying at 60 °C for 24 hours. The bound water was found to amount to an average of 4.6 molecules of H_2O per molecule of $Na_2NiFe(CN)_6$ (see Table B-1 in Appendix B for detailed test results).

5.3.3 Moisture Contents of Ferrocyanide Sludges in Tanks

While a full discussion of the moisture content of what is in the tanks is beyond the scope of this document, several observations that help put moisture content into perspective are the following.

MOISTURE IN WASTE SAMPLES

The moisture contents of retrieved samples from tanks 241-C-112 and 241-C-109 varied from 28 wt% to 64 wt%. These high values are consistent with expectations based on the simulant studies.

LIQUID LEVEL MEASUREMENTS

Interstitial liquid levels measured by neutron scans in liquid observation wells (LOW) installed in 10 ferrocyanide tanks indicate the liquid level to be close to the top of the sludge layer. Liquid level measurements are not available in ferrocyanide tanks that do not have installed LOWs.

EVAPORATION RATE CALCULATIONS

All ferrocyanide tanks are passively ventilated. This severely limits the exchange of air between tank headspace and the atmosphere and evaporation is negligible. If forced ventilation were to be instituted, higher evaporation rates would be possible. In the BY tanks, diffusion of water vapor through the overlying saltcake would limit water loss to ~ 1 percent per year even at very high ventilation rates. Losses could be higher in other tanks without a saltcake layer, but still acceptable for limited periods of forced ventilation. The minimum moisture level which could occur by ventilation is the equilibrium value as discussed in Appendix C.

5.4 DECAY HEAT DISSIPATION

The natural decay of radioactive isotopes in the waste generates thermal energy called decay heat. An effect of decay heat is to cause waste temperatures to be higher than ambient temperatures. At thermal equilibrium, steady state temperature gradients within the waste cause heat to flow into surrounding soil. Temperature gradients in soil cause most of the heat to flow to the above ground atmosphere; a small fraction flows downward to the water table. In ferrocyanide tanks, decay heat is produced mainly by ^{137}Cs and ^{90}Sr. These nuclides have a half-life of approximately 30 years so decay heat loads are now less than 50 percent of that when waste was put into the tanks.

From a safety standpoint, it is important to know if decay heat could raise waste temperature to reaction threshold temperatures. Pertinent information on this issue is summarized in this section; more detailed information is presented in Appendix D.

5.4.1 Decay Heat Loads in Ferrocyanide Tanks

The magnitudes of temperature gradients required to dissipate decay heat are proportional to the heat generation rates within the tank. Decay heat loads, waste depths, and current maximum measured temperatures are listed in Table 5-2.

As indicated by the data of Table 5-2, estimated heat loads are 3.0 kw or less. This energy production rate is spread throughout the waste in a tank 75 ft in diameter. These very small heat loads are currently being dissipated by the passive mechanisms of conduction through the sludge and soil and natural convection and radiation through the gas space.

Heat loads also can be estimated from nuclide contents measured on samples of waste removed from the tanks. Nuclide concentrations measured in tank 241-C-112 samples led to a calculated heat load for the tank of 2.3 kw (Simpson et al. 1993a). This value agrees well with the value listed in Table 5-2 (2.2 kw) that was based on measured headspace air temperatures.

A similar comparison for tank 241-C-109 indicates heat loads of 2.8 kw vs 2.1 kw (Simpson et al. 1993b). The good agreement of heat loads based on independent data sets is evidence that the heat loads are reasonably well known and that the samples are representative of average waste compositions.

5.4.2 Potential for Loss of Cooling

Attempts have been made to identify changes in storage condition that could significantly diminish natural heat dissipation in stored waste. No credible loss of cooling scenario is apparent. Major modifications of the storage configuration apparently would be required to significantly impair natural heat dissipation. Examples are: (1) filling of tank headspaces

Table 5-2. Thermal Characteristics of Ferrocyanide Tanks.

Tank	Depth of solids (m)[a]	Maximum temp (°C)[a]	Estimated heat load (kw)[b]
BY-103	3.9	28	1.6
BY-104	3.9	54	2.6
BY-105	4.8	50	2.6
BY-106	6.1	54	3.0
BY-107	2.7	35	2.6
BY-108	2.3	43	2.7
BY-110	3.9	48	2.0
BY-111	4.4	30	1.6
BY-112	2.9	32	1.9
C-108	0.8	22	1.7
C-109	0.8	26	2.1
C-111	0.7	21	1.9
C-112	1.2	26	2.2
T-107	1.8	20	0.9
TX-118	3.4	18	1.3
TY-101	1.3	25	0.9
TY-103	1.7	18	1.2
TY-104	0.6	16	0.9

[a]Solids depth calculated from Hanlon 1993.
[b]Crowe et al. 1993, based on measured headspace air temperature.

with rock aggregate (Campbell 1981) or (2) adding of large thicknesses of soil overburden on top of the tanks. Both changes represent major changes in storage configuration and are beyond the scope of this report.

5.4.3 Conclusions Regarding Decay Heat Dissipation

The following statements summarize current understanding of heat dissipation from ferrocyanide tanks.

- Decay heat loads are estimated to be 3.0 kw or less for the 75-ft diameter tanks. Estimates based on headspace air temperatures and on the nuclide contents of samples (for the two ferrocyanide tanks analyzed for nuclide content) are in good agreement.

- Decay heat loads have been dissipated passively during four decades of storage history, during which temperatures have trended downward or remained flat.

- Heat loss occurs by conduction, convection, and radiation. There are no active systems that can fail. Heat dissipation does not depend on evaporation of water.

- Significant changes in waste storage configuration (the filling of headspace with insulating materials or increasing soil overburden) would be required to significantly diminish heat dissipation capabilities. Such changes would not be permitted without additional study and are beyond the scope of this report.

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6.0 CRITERIA FOR SAFETY CATEGORIES

Limiting values of waste parameters that define the boundaries for each safety category are specified in this section. The values specified are based on hazard phenomenology information discussed in Section 5.0, the definition of safety categories given in Section 4.0, and the safety objective stated in Section 3.0. A proposed protocol for applying the criteria to specific tanks also is summarized at the end of this section.

Based on the phenomenology of ferrocyanide-nitrate/nitrite reactions, four parameters can be used to quantify the hazard:

1. Fuel concentration
2. Oxidizers concentration
3. Water concentration
4. Waste temperature.

Values for each of these parameters will be specified as criteria that define the boundaries of each safety category.

6.1 SAFE CATEGORY

CONCENTRATION OF FUEL

For this case, it is required that significant* reactions be impossible under conditions which could develop under a hypothetical unattended operational mode. To identify the fuel concentration criterion, a worst-case assumption of zero free water has been made. Only bound water, amounting to 4.6 molecules per molecule of sodium nickel ferrocyanide has been assumed to be present.

A conservative upper limit for the average ferrocyanide concentration in the sludge layer was selected as 8 wt%, energy equivalent sodium nickel ferrocyanide, expressed on a zero free water basis. This value is close to a limit deduced by thermodynamic calculations ($\sim$7.7 wt%) that are inherently conservative. Therefore, the criterion is:

$$\text{Fuel concentration} \leq 8 \text{ wt\% } Na_2NiFe(CN)_6$$

This value has a safety margin of approximately two as compared to the experimentally derived limit (Fauske 1993b) of approximately 15 wt% for propagating reactions.

*A "significant" reaction in this context is defined in Section 4.2.

CONCENTRATION OF OXIDIZERS

Oxidizers (NO_3/NO_2) have been assumed to be present in excess of stoichiometric concentrations. Any excess concentration of nitrates and nitrites will act as an inert diluent. Therefore no limits are specified for oxidizers.

CONCENTRATION OF WATER

The fuel concentration limit has been set on the basis of loss of all free water. This represents a limiting condition, hence no limits on water content are specified.

TEMPERATURE OF WASTE

The SAFE category applies to tanks for which temperature monitoring and controls are unnecessary. While no specific temperature criterion is required, an analysis of heat dissipation would be required to demonstrate that significant waste heatup could not occur during a hypothetical unattended operational mode. It is noted that temperature monitoring is a current requirement on all ferrocyanide tanks, and that an action plan for response to abnormal conditions is in place (Cash and Thurman 1991). The absence of a temperature criterion for the SAFE category does not remove the need for prudent monitoring of ferrocyanide tanks.

DISCUSSION OF MINIMUM FREE MOISTURE ASSUMPTION

The fuel concentration limit for the SAFE category (8 wt%) has been specified on the basis of zero free water in the waste. This assumption is probably overly conservative because moisture levels can only approach equilibrium values by evaporation into ambient air. The equilibrium moisture level depends on temperature and relative humidity in the tank headspace air (see Appendix C for data on one waste simulant). If equilibrium data for waste were available, one could identify a lower limit to moisture content that was higher than zero.

A realistic accounting for equilibrium free water is potentially important. For example, if it could be shown that an equilibrium moisture concentration of 10 wt% was applicable, the fuel concentration limit for the SAFE category could be increased from 8 percent to 14 percent on a zero free water basis. This value (14 percent) is calculated from the criteria line depicted in Figure B-1 in Appendix B.

The conservatism introduced by the zero free water assumption could be relaxed on the basis of relatively simple tests conducted with waste samples. Such tests will likely be recommended if future tank samples have fuel concentrations close to the 8 wt% criterion.

6.2 CONDITIONALLY SAFE CATEGORY

CONCENTRATION OF FUEL

For this category, fuel concentrations would have to be greater than 8 wt%, the criterion limit for the SAFE category.

CONCENTRATION OF OXIDIZERS

Oxidizers have been assumed to be present in excess. Therefore no specific limits are specified for oxidizers.

CONCENTRATION OF WATER

The thermodynamic calculations described in Section 5.2 and quantified in Appendix B showed that 24 wt% water would prevent the propagation of reactions in the In Farm simulant which contained 26 wt% $Na_2NiFe(CN)_6$ on a 0 free water basis.

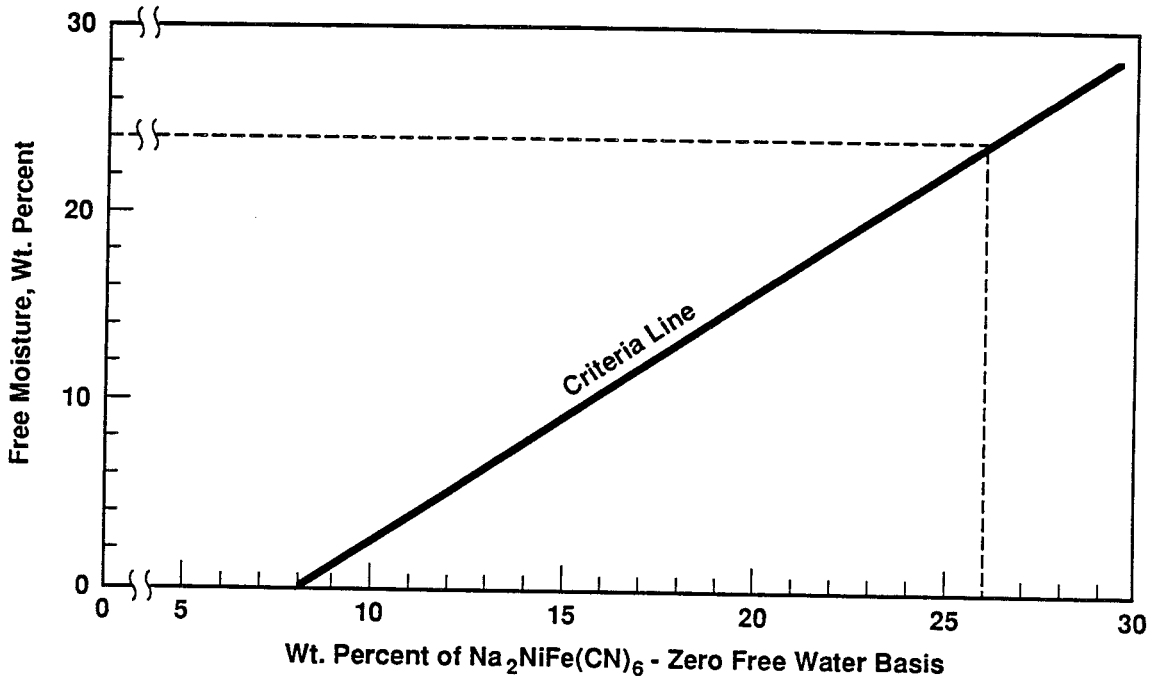
Experiments (Fauske 1992) showed that 12 wt% water was sufficient to quench propagating reactions in In Farm simulant waste. A conservative moisture criterion equal to the rounded theoretical value (24 percent) and equal to twice the experimental value, 2(12%) = 24 wt% is specified for sludge having ferrocyanide concentrations of 26 wt% on a dry basis. Thus the moisture criterion applicable to 26 wt% $Na_2NiFe(CN)_6$ on an energy equivalent basis is:

Moisture criterion = 24 wt% free water.

Because this minimum required water content was based on the In Farm simulant sludge (26 percent ferrocyanide), it will be overly conservative for sludge that has ferrocyanide concentrations close to the SAFE fuel criterion, 8 percent. To more realistically account for the lower exothermic energy potential of sludge that contains less than the maximum fuel concentration, the water criterion can be relaxed for tanks known to contain less than 26 percent of ferrocyanide. The thermodynamic calculations (Appendix B) indicate that the mass of free water (g water/g dry waste) required to quench reactions increases linearly with ferrocyanide concentration. This relationship can be approximated by a moisture concentration that increases linearly from zero at 8 wt% $Na_2NiFe(CN)_6$ to 24 wt% water at a ferrocyanide concentration of 26 wt% (zero free water basis).

The 24 wt% free water criterion cited above is applicable to the In Farm simulant, which contained the highest concentration of $Na_2NiFe(CN)_6$ found in any waste simulant. It is recognized that higher ferrocyanide concentrations are theoretically possible, and as illustrated in Figure 6-1, the criteria line extends beyond 26 wt% $Na_2NiFe(CN)_6$. While it is unlikely that waste will be found to contain ferrocyanide concentrations higher than 26 wt%,

Figure 6-1. Moisture Criterion for Conditional Safety Category as a Function of Ferrocyanide Concentration.



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the moisture criteria line allows for this possibility. For example, for a stoichiometric mixture of $Na_2NiFe(CN)_6 \bullet 4.6H_20 + 6NaN0_3$, the ferrocyanide concentration is 34.8 wt% (0 free water basis). Based on the criteria line of Figure 6-1, required free moisture concentration is computed to be 35.7 wt% for this mixture of pure reactants.

The water contents referred to in this criterion are free water. This is water in excess of bound water, which is assumed to amount to 4.6 molecules per molecule of $Na_2NiFe(CN)_6$. At 8 wt% $Na_2NiFe(CN)_6$, this bound water amounts to 2.1 wt% of total waste.

The linear approximation described above is shown graphically in Figure 6-1, where the water criterion is plotted as a function of ferrocyanide concentration.

TEMPERATURE OF WASTE

Waste temperature is potentially important in relation to two phenomena: (1) retained moisture concentration and (2) reaction onset temperature. The first of these is the more limiting because the boiling point of saturated nitrate solutions (~120 °C) is well below the reaction onset temperature (~250 °C). Because temperature limits are implicit in the moisture criterion described above, it is apparent that waste temperature is not a parameter that can be specified independently. The moisture criterion is controlling and temperature is a dependent criterion.

Although temperature per se is not an independent gauge of waste storage safety, an unexpected increase in temperature could be a signal of unexpected exothermic activity in the waste. Thus, prudent management of the waste requires that temperature be monitored. Such monitoring, and a response plan for abnormal conditions is currently in place for ferrocyanide tanks (Cash and Thurman 1991).

A secondary criterion of 90 °C is specified as the upper limit for ferrocyanide waste for the following reasons. (1) A 90 °C temperature criterion is consistent with the 200 °F (93.3 °C) criterion specified in the action plan for response to abnormal conditions in ferrocyanide waste tanks (Cash and Thurman 1991). According to the action plan (Cash and Thurman 1991) water would be added to a tank if other cooling methods failed to control waste temperatures to below 200 °F (93.3 °C). It is anticipated that the 200 °F (93.3 °C) criterion currently specified in the action plan (Cash and Thurman 1991) would be changed to 90 °C upon DOE approval of the 90 °C criterion proposed herein. (2) The 90 °C limit for safe storage provides a safety margin of ~30 °C between peak waste temperature and the boiling temperature of interstitial liquid where relatively rapid moisture loss could occur.

6.3 UNSAFE CATEGORY

Any tank that failed to meet criteria for SAFE or CONDITIONALLY SAFE categories automatically would be classified as UNSAFE.

6.4 PROTOCOL FOR APPLYING CRITERIA TO TANKS OR GROUPS OF TANKS

The numerical value of the ferrocyanide concentration criterion was calculated on the basis of energy content, MJ/kg of waste. To judge whether waste meets the concentration criterion, the exothermic energy, MJ/kg, must be determined experimentally. The equivalent ferrocyanide concentration would then be calculated using a reaction energy of 6 MJ/kg of dry sodium nickel ferrocyanide, the value used to derive the criterion.

The energy basis permits accounting for all reactants that might be present. Examples of potential reactants not explicitly identified in the concentration criteria are sodium sulfide and numerous organic substances that may be present at low concentrations in ferrocyanide waste.

Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) are tools that can be used to quantify the exothermic energy content of samples. For samples whose energy content approaches the 8 wt% $Na_2NiFe(CN)_6$ criterion, (0.48 MJ/kg), additional testing by adiabatic calorimetry is recommended. Reasons for this recommendation are twofold. First, relatively large samples (10 g or more) are tested. This provides assurance that the sample tested is representative of the bulk of the sampled material. Second, the observed self-heating behavior is direct evidence of the kinetics and energetics of the

reactions in dried waste. This information would allow for a more accurate comparison of energy content with the SAFE criterion; also, it would provide input to studies designed to confirm the validity of the criteria that are presently based on simulants.

The ferrocyanide concentration criterion is deemed to apply to relatively thin layers of ferrocyanide waste. The highest measured concentration (or concentrations deduced from other reliable characterization data) in quarter-segments, [a 12-cm (4.8-in.) high cylinder of waste removed in a core sample] would be used to rank the tank. It is recognized that the mixed quarter-segment samples would not permit the detection of thinner layers which could have higher-than-average concentration. The safety implications of not detecting peak concentrations in layers thinner than 12 cm (4.8 in.) are discounted for the following reasons.

- Studies of historical process information (Simpson et al. 1993a, 1993b, and Borsheim and Simpson 1991) indicate that individual batches produced layers thicker than 12 cm (4.8 in.) for U Plant and T Plant flowsheets. Therefore, for this waste (74 percent of total) 12 cm (4.8 in.) segments should detect the highest concentration layers.

- For the more concentrated In Farm sludge, individual batches could have deposited sludge layers of an estimated 3.6 to 6.1 cm (1.4 to 2.4 in.) in thickness (Simpson et al. 1993a). Thus a quarter segment (12 cm high) would theoretically intercept two to four layers. Homogenization of the quarter segment sample would average ferrocyanide concentrations for two to four batches. Based on simulants, the In Farm 1 and In Farm 2 sludges had maximum concentrations of 25.5 and 22.6 percent sodium nickel ferrocyanide, respectively (see Appendix A, Table A-2). The maximum (25.5 percent) is only 6 percent larger than the average (24.05 percent), so an analysis of two mixed layers (In Farm 1 and In Farm 2) would not differ significantly from that of the richer layer. Processes that would reduce concentration gradients during storage are the following:

  - Convection mixing in receiver tanks caused by the momentum of inflowing sludge making up each batch.

  - Diffusion during 35 yr of storage.

  - Degradation by chemical reactions that proceeds fastest in the highest concentration sludge.

Based on the foregoing discussion, large concentration gradients are not expected to exist within quarter segments removed from sludge comprised of two to four layers. However, it should be noted that a significant safety margin exists between the 8% ferrocyanide

concentration criterion and the experimentally-determined threshold for propagation (~ 15 percent). Therefore, relatively large gradients in concentration could be tolerated without posing a safety hazard.

The moisture criterion, like the ferrocyanide concentration criterion, would be applied on a layer-by-layer basis. Each layer would be identified by quarter-segment analysis or other reliable characterization data. The minimum required moisture in a given segment (or layer) would be related to that segment's ferrocyanide concentration using the criteria line in Figure 6-1.

The temperature criterion of 90 °C would be applied to the maximum value measured in a vertical profile. Instrumentation to measure the vertical temperature distribution in at least one location would be required in all tanks. A measured profile at one location, along with technical analyses of heat transport, is judged to be sufficient to verify conformance with the 90 °C criterion. Hypothetical concentrations of decay heat which could theoretically cause a local hot spot represents an issue that will be resolved in a future work effort.

Unexpected increases in temperature would be dealt with by the current action plan (Cash and Thurman 1991). It is recommended that headspace air temperature be included in the temperature data analyzed for unexpected changes. The reason is that headspace temperatures are relatable to heat generation in the whole tank (Crowe et al. 1993). Unexpected increases could provide evidence of exothermic activity at locations too far from the thermocouple tree to be detected by temperatures measured below the waste surface.

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7.0 COMPARISON OF FERROCYANIDE WATCH LIST TANKS WITH SAFETY CRITERIA

In this section, available information on waste in each of the ferrocyanide Watch List tanks is used to provisionally classify tanks into one of the three safety categories. Objectives of this current placement of tanks into safety categories are the following.

1. Provide a review of the ferrocyanide safety hazard and provide documentation as required in DOE Order 5480.21 (DOE 1991).

2. Illustrate how the criteria can be used to categorize the tanks.

3. Identify remaining issues that must be addressed in order to resolve the ferrocyanide safety issue.

7.1 SUMMARY OF CURRENT INFORMATION ON TANK CONTENTS

Information that pertains to the concentration of ferrocyanide in the Watch List tanks is listed in Table 7-1. Information presented in Table 7-1 is described as follows.

WASTE FLOWSHEET

The listed flowsheets represent the source of the sludge now stored in the tanks. Details of these flowsheets are described in Appendix A and in Section 5.1.

PROCESS RECORDS CONCENTRATION

Best estimate concentrations based on process records were derived on the basis of material balance calculations that traced waste transfers in the tank farms. Details of this model are provided in Appendix A and by Borsheim and Simpson (1991). Note that the model does <u>not</u> account for the degradation (Lilga et al. 1993, Babad et al. 1993) of ferrocyanide over the 35 years of storage; nor does it account for dilution by mixing with other waste. For these reasons the model is expected to over predict current ferrocyanide concentrations.

MAXIMUM SIMULANT CONCENTRATION

Simulant ferrocyanide waste has been prepared using the several flowsheet recipes originally used to prepare ferrocyanide sludge. As discussed in Appendix A, the simulant sludge was divided into top and bottom layers and the layer that contained the highest ferrocyanide concentration was selected for testing. The maximum simulant concentration cited here

Table 7-1. Comparison of Tank Contents with Criteria.

Tank	Waste flowsheet	Concentration of $Na_2NiFe(CN)_6$[a]			Current safety category
		Process records	Maximum simulant	Tank sample	
BX-102	--	b	n/a	No data	SAFE
BX-106	--	b	n/a	No data	SAFE
BY-103	U Plant	6.0	8.3	No data	CONDITIONALLY SAFE
BY-104	U Plant	6.0	8.3	No data	CONDITIONALLY SAFE
BY-105	U Plant	7.4	8.3	No data	CONDITIONALLY SAFE
BY-106	U Plant	5.2 - 5.5	8.3	No data	CONDITIONALLY SAFE
BY-107	U Plant	5.0 - 5.9	8.3	No data	CONDITIONALLY SAFE
BY-108	U Plant	5.0 - 5.8	8.3	No data	CONDITIONALLY SAFE
BY-110	U Plant	5.7 - 6.2	8.3	No data	CONDITIONALLY SAFE
BY-111	U Plant	6.6	8.3	No data	CONDITIONALLY SAFE
BY-112	U Plant	3.5	8.3	No data	CONDITIONALLY SAFE
C-108	In Farm 2	10.4 - 15.6	22.6	No data	CONDITIONALLY SAFE
C-109	In Farm 2	14.0 - 20.9	22.6	0.6 - 2.9	SAFE
C-111	In Farm 2	8.9 - 12.1	22.6	No data	CONDITIONALLY SAFE
C-112	In Farm 1	16.1 - 24.2	25.5	0.8 - 2.0	SAFE
T-107	U Plant	7.3	8.3	No data	CONDITIONALLY SAFE
TX-118	U Plant	b	8.3	No data	CONDITIONALLY SAFE
TY-101	T Plant	7.6	8.8	c	CONDITIONALLY SAFE
TY-103	T Plant	6.9	8.8	d	CONDITIONALLY SAFE
TY-104	T Plant	10.7	8.8	No data	CONDITIONALLY SAFE

[a]Wt%, on a zero free water basis

[b]Process records do not show that a significant quantity of ferrocyanide sludge is stored in these tanks (Borsheim and Simpson 1991). The tanks were erroneously placed on the Watch List because of earlier TRAC calculations (Jungfleisch 1984).

[c]Composited sample yielded concentrations of 1.2 - 1.4 wt%. Data are insufficient to rank tank (Winters 1988).

[d]Composited sample yielded concentration of 1.0 - 1.3 wt%. Data are insufficient to rank tank (Winters 1988).

represents the ferrocyanide concentration in the highest concentration layer for the flowsheet used to prepare waste now residing in the subject tank. The applicable concentrations are taken from Appendix A, Table A-2.

TANK SAMPLE CONCENTRATION

For the tanks that have been sampled, measured cyanide concentrations are reported here as $Na_2NiFe(CN)_6$ on a dry (zero free water) basis. The sample data are more fully discussed in Section A.4.0 of Appendix A.

7.2 CURRENT SAFETY CATEGORIZATION OF FERROCYANIDE TANKS

The bases and assumptions used to categorize the tanks, as listed in Table 7-1, are discussed as follows. A conservative approach has been used in this current categorization. As will be shown, there is a high probability that all ferrocyanide tanks can be put into the SAFE category, when sufficient data on contents become available.

TANKS CONTAINING U PLANT SLUDGE

All of the tanks with U Plant sludge were deemed to potentially contain ferrocyanide at concentrations greater than 8.0 wt%. This judgment is based on the U Plant 2 bottom fraction simulant sludge which, as indicated in Table 7-1, contained 8.3 wt% $Na_2NiFe(CN)_6$.

For ferrocyanide sludge with concentrations > 8 wt%, temperature and water content criteria must also be met. The highest measured temperature in any ferrocyanide tank is 54 °C (Table 5-2). This is well below the temperature criterion of 90 °C.

Although moisture concentrations in most U Plant tanks have not been measured, a substantial database leads to the conclusion that ferrocyanide sludge has a moisture content greater than the 24 wt% criterion. Information on moisture content is described in Section 5.3 and in Appendix C.

The conservatively estimated 8.3 wt% ferrocyanide would require minimal moisture to remain CONDITIONALLY SAFE. Based on the protocol described in Section 6.4, the free moisture content required at the 8.3 wt% level is:

$$\text{moisture limit} = \frac{(8.3 - 8.0)(24)}{(26 - 8)} = 0.4 \text{ wt\%}$$

This moisture concentration is small compared to values that are expected to be in equilibrium with ambient air (see Attachment C to Appendix C) and it is concluded that actual moisture levels will exceed this low requirement.

Note that the concentrations based on process records are all lower than the 8 wt% criterion. While these estimated concentrations are judged to over-estimate actual concentrations, confirmatory data from tank samples are needed to put the tanks into the SAFE category.

The samples taken from tank T-107 yielded a negligible ferrocyanide analysis. While this sample data represents actual ferrocyanide concentration, the numbers are considered preliminary pending the publication of a peer-reviewed report.

TANKS CONTAINING IN FARM SLUDGE

Two of the four tanks that contain In Farm sludge (C-108 and C-111) have not yet been sampled and for this reason have been put into the CONDITIONALLY SAFE category. Minimum moisture content and temperature limits are deemed to meet the criteria for the reasons noted above for tanks containing U Plant Sludge.

Note that both tanks were recommended for removal from the Watch List in a recent LANL study (Agnew 1993). This recommendation was based on estimates of ferrocyanide inventory and the results of sampling of tanks C-109 and C-112, which are described below.

The two tanks containing the highest projected ferrocyanide concentration (C-109 and C-112) are put into the SAFE category on the basis of sample data. Multiple core samples, taken from opposite tank quadrants, were divided into vertical subsegments. Both cyanide analyses and measured exotherms (see Table A-4 in Appendix A) in all samples indicate a ferrocyanide concentration well below the 8 wt% criterion. The ferrocyanide concentration on an energy equivalent basis, based on the largest DSC measured exotherm, is calculated to be 0.9 wt%. This value is small compared to the 8 wt% criterion level.

In addition to the 8 wt% criterion, a SAFE category requirement (see Section 6.1) is that an analysis of heat dissipation would be required to demonstrate that significant temperature rise could not occur during a hypothetical unattended operational mode. For these two tanks, simple calculations (which equate reaction exotherms to increases in sensible heat) show that the maximum adiabatic temperature rise due to a runaway reaction would be <40 °C. This fact, along with the small waste depths and low heat loads (Table D-1 of Appendix D) effectively eliminate this concern for tanks C-109 and C-112. Therefore we conclude that significant temperature increases could not occur in these two tanks during a hypothetical unattended operational mode.

TANKS CONTAINING T PLANT SLUDGE

The three tanks containing T Plant sludge have been put into the CONDITIONALLY SAFE category. Reasons for this assignment parallel those discussed above for U Plant sludge, and are briefly restated as follows.

- The maximum simulant ferrocyanide concentration is higher than the 8 wt% criterion so the SAFE category is not applicable.

- A moisture concentration of only 1.1 wt% is required at the 8.8 wt% $Na_2NiFe(CN)_6$ level to meet the moisture criterion. A substantial database on moisture retention provides a high level of confidence that actual moisture concentrations are well above the 1.1 wt% criterion.

- Ferrocyanide concentrations measured in samples taken from two tanks (TY-101 and TY-103) fall in the range 1.0 to 1.4 wt%. These values apply to composited samples of entire cores, and therefore may not represent maximum concentrations in the sludge layer. The sample data do not meet the quarter-segment analysis called for in the protocol discussed in Section 6.4, and therefore are insufficient to categorize the tanks as SAFE.

- The low measured concentrations of ferrocyanide in sampled tanks provides evidence that the tanks can be put into the SAFE category after confirmatory sample data are obtained.

7.3 ADDITIONAL INFORMATION NEEDED TO RESOLVE THE FERROCYANIDE SAFETY ISSUE

The following discussion highlights key areas where current information is insufficient to resolve the ferrocyanide safety issue.

TANK CHARACTERIZATION

A realistic comparison of tank contents against the safety criteria will require additional tank sampling. An important aspect of a sampling program is the strategy for obtaining representative samples. Both sample data and the technical basis for showing that the samples adequately represent the tank waste are needed to resolve the safety issue. Sampling and characterization programs are currently underway at WHC. A data quality objective (DQO) study of sampling requirements is underway at PNL.

HOT-SPOT ISSUE RESOLUTION

Regions of waste containing higher-than-average concentrations of heat producing nuclides have been postulated in some safety studies. While a draft study of hot-spot dryout indicates dryout to be incredible, a more comprehensive study is needed to tackle all of the issues. A study of hot-spot phenomenology is currently underway at WHC.

SAFETY EVALUATION OF TANK OPERATIONS

Tank operations (operations, maintenance, tests, experiments) will be evaluated against the criteria. Controls on the operations will be specified, if required, to maintain waste within the envelope defined by the criteria.

8.0 REFERENCES

Agnew, S. F., 1993, *Analysis of the History of 241-C Farm*, LAUR-93-3605, Los Alamos National Laboratory, Los Alamos, New Mexico.

Babad, H., C. DeFigh-Price, and J. C. Fulton, 1993, *A Strategy for Resolving High Priority Hanford Site Radioactive Waste Storage Tank Safety Issues*, WHC-SA-1661-FP, Westinghouse Hanford Company, Richland, Washington.

Babad, H., J. E. Meacham, B. C. Simpson, and R. J. Cash, 1993, *The Role of Aging in Resolving the Ferrocyanide Safety Issue*, WHC-EP-0599, Westinghouse Hanford Company, Richland, Washington.

Bergmann, L. M., 1986, *Single-Shell Tank Isolation Safety Analysis Report*, WHC-SD-WM-SAR-006, Rev. 2, Westinghouse Hanford Company, Richland, Washington.

Borsheim, G. L., and B. C. Simpson, 1991, *An Assessment of the Inventories of the Ferrocyanide Watch List Tanks*, WHC-SD-WM-ER-133, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Borsheim, G. L., R. J. Cash, and G. T. Dukelow, 1992, *Implementation Plan for the Defense Nuclear Facilities Safety Board Recommendation 90-7*, WHC-EP-0415, Rev. 1, Westinghouse Hanford Company, Richland, Washington.

Borsheim, G. L., 1993, *Ferrocyanide Safety Program Rationale for Removing Six Tanks from the Safety Watch List*, WHC-MR-0429, Westinghouse Hanford Company, Richland, Washington.

Boyles, V. C., 1990, *Single-Shell Tank Stabilization Record*, WHC-SD-RE-178, Rev. 2, Westinghouse Hanford Company, Richland, Washington.

Burger, L. L., 1989, *Complexant Stability Investigation, Task 1-Ferrocyanide Solids*, PNL-5441, Pacific Northwest Laboratory, Richland, Washington.

Burger, L. L., and R. D. Scheele, 1988, *Interim Report - Cyanide Safety Studies*, PNL-7175, Pacific Northwest Laboratory, Richland, Washington.

Burger, L. L., 1993, "Calculation of Reaction Energies and Adiabatic Temperatures for Waste Tank Reactions," PNL-8557, Richland, Washington.

Campbell, G. D., 1981, *Heat Transfer Analysis for In Situ Disposal of Nuclear Wastes in Single- and Double-Shell Underground Storage Tanks*, RHO-LD-171, Rockwell Hanford Operations, Richland, Washington.

Cash, R. J., 1991, *Implementation Plan for the Defense Nuclear Facilities Safety Board Recommendation 90-7*, WHC-EP-0415, Westinghouse Hanford Company, Richland, Washington.

Cash, R. J. and J. Thurman, 1991, *Action Plan for Response to Abnormal Conditions in Hanford Site Radioactive Tanks Containing Ferrocyanide*, WHC-EP-0407, Rev. 1, Westinghouse Hanford Company, Richland, Washington.

Cash, R. J., G. T. Dukelow, C. J. Forbes, and J. E. Meacham, 1993, *Quarterly Report on Defense Nuclear Facilities Safety Board Recommendation 90-7 for Period Ending June 30, 1992*, WHC-EP-0474-9, Westinghouse Hanford Company, Richland, Washington.

Crowe, R. D., M. Kummerer, and A. K. Postma, 1993, *Ferrocyanide Safety Program: Estimate of Heat Load in Waste Tanks Using Average Vapor Space Temperature*, WHC-EP-0709, Westinghouse Hanford Company, Richland, Washington.

Deaton, D. E., 1990, *Unusual Occurrence-Unreviewed Safety Questions Regarding Tanks Containing Ferrocyanide*, WHC-90-B003-R1, Update 10-22-90, Westinghouse Hanford Company, Richland, Washington.

DOE, 1986, *Safety of Nuclear Facilities*, DOE Order 5480.5, U.S. Department of Energy, Washington, D.C.

DOE, 1987, *Final Environmental Impact Statement - Disposal of Hanford Defense High-Level, Transuranic, and Tank Wastes*, Vols. 1-5, DOE/EIS-0113, U.S. Department of Energy, Washington, D.C.

DOE, 1991, *Unreviewed Safety Questions*, DOE Order 5480.21, U.S. Department of Energy, Washington, D.C.

DOE, 1993, "Strategy for [Ferrocyanide] Safety Issue Resolution," Letter from T. P. Grumbly, DOE, to J. T. Conway, Chairman, Defense Nuclear Facilities Safety Board, dated August 25, 1993.

Fauske, H. K., 1992, *Adiabatic Calorimetry and Reaction Propagation Tests with Synthetic Ferrocyanide Materials Including U Plant 1, U Plant 2, In Farm 1, In Farm 2, and Vendor-Procured Sodium Nickel Ferrocyanide*, WHC-SD-WM-RDT-054, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Fauske, H. K., 1993a, "Fuel Concentration Required for Deflagration of Ferrocyanide Mixtures," Memo to R. J. Cash, Westinghouse Hanford Company, dated September 14, 1993. This memo is reproduced as Attachment B-3 of Appendix B.

Fauske, H. K., 1993b, "Propagation Tests With In Farm 1 Bottom Half Flow Sheet Material [~26 wt% $Na_2NiFe(CN)_6$ - Dry Basis] Using Al_2O_3 as a Diluent," Memo to R. J. Cash, Westinghouse Hanford Company, dated September 23, 1993. This memo is reproduced as Attachment B-4 of Appendix B.

Grigsby, J. M., D. B. Bechtold, G. L. Borsheim, M. D. Crippen, D. R. Dickinson, G. L. Fox, D. W. Jeppson, M. Kummerer, J. M. McLaren, J. D. McCormack, A. Padilla, B. C. Simpson, and D. D. Stepnewski, 1992, *Ferrocyanide Waste Tank Hazard Assessment - Interim Report*, WHC-SD-WM-RPT-032, Rev. 1, Westinghouse Hanford Company, Richland, Washington.

Hanlon, B. M., 1993, *Tank Farm Surveillance and Waste Tank Summary Report for June 1993*, WHC-EP-0182-63, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Jeppson, D. W., and J. J. Wong, 1993, *Ferrocyanide Waste Simulant Characterization*, WHC-EP-0631, Westinghouse Hanford Company, Richland, Washington.

Jungfleisch, F. M., 1984, *TRAC: A Preliminary Estimation of the Waste Inventories in Hanford Tanks Through 1980*, SD-WM-TI-057, Rockwell Hanford Operations, Richland, Washington.

Kazimi, M. S., C. S. Abrams, D. O. Campbell, F. N. Carlson, M. W. First, C. W. Forsberg, B C. Hudson, T. S. Kress, T. E. Larson, D. T. Oakley, G. E. Schmauch, S. E. Slezak, and A. S. Veletsos, 1992, *Approach to Resolution of Safety Issues Associated with Ferrocyanides in the Hanford Waste Tanks*, High-Level Waste Tanks Advisory Panel, U.S. Department of Energy, Washington, D.C.

Kirk-Othmer, 1978, "Encyclopedia of Chemical Technology," Third Edition, Vol. 9, p. 561 - 618, Wiley Interscience, New York, New York.

Lilga, M. A., M. R. Lumetta, and G. F. Schiefelbein, 1993, *Ferrocyanide Safety Project, Task 3 Aging Studies, FY 1993 Annual Report*, PNL-8888, Pacific Northwest Laboratory, Richland, Washington.

Peach, J. D., 1990, "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.

Postma, A. K., H. Babad, R. J. Cash, and J. L. Deichman, 1992, *Current Understanding of the Safety of Storing High-Level Waste Containing Ferrocyanide at the Hanford Site*, WHC-EP-0531, Rev. 1, Westinghouse Hanford Company, Richland, Washington.

Simpson, B. C., G. L. Borsheim, and L. Jensen, 1993a, *Tank Characterization Data Report: Tank 241-C-112*, WHC-EP-0640, Rev. 1, Westinghouse Hanford Company, Richland, Washington.

Simpson, B. C., G. L. Borsheim, and L. Jensen, 1993b, *Tank Characterization Report: Tank 241-C-109*, WHC-EP-0668, Westinghouse Hanford Company, Richland, Washington.

WHC, 1992, *Nonreactor Facility Safety Analysis Manual*, Rev. 2, WHC-CM-4-46, Westinghouse Hanford Company, Richland, Washington.

Winters, W. I., 1988, "Analysis of Archive Samples from Tanks 241-TY-101 and 241-TY-103 for Total Cyanide," memo 12715-ASL88-067 to D. M. Nguyen, dated December 29, 1988.

Wong, J. J., 1992, *Test Report on Characterization of Hydraulic and Thermal Properties of Synthetic Ferrocyanide Sludges*, WHC-SD-WM-TRP-102, Westinghouse Hanford Company, Richland, Washington.

APPENDIX A

WASTE COMPOSITION

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APPENDIX A

TANK WASTE COMPOSITION

A.1.0 INTRODUCTION

Physico-chemical properties of ferrocyanide waste that are important to storage safety have been the subject of several recent studies. Information is available from the following sources:

- Plant processing records
- Studies of waste simulants
- Samples of stored waste.

In this appendix, available information is briefly reviewed in order to identify sludge compositions put into the tanks, the compositions of simulants prepared by flowsheet recipes, and how the properties of tank samples compare with properties expected on the basis of process records and flowsheet simulants.

A.2.0 PROCESS FLOWSHEETS

Three different flowsheets were used to decontaminate aqueous waste solutions during the 1950s at the Hanford Site (Borsheim and Simpson 1991, Jeppson and Wong 1993). While all of these flowsheets used ferrocyanide and nickel salts as precipitating agents, differences in the waste streams and treatment chemicals led to sludges having different concentrations of ferrocyanide, and therefore potentially different exothermic energy content.

A.2.1 U PLANT FLOWSHEET

The following description is summarized from the reports of Jeppson and Wong (1993) and Borsheim and Simpson (1991); the reader is referred to these reports for a more detailed description of the processes used in the U Plant scavenging campaign.

The aqueous feed, consisting mainly of uranium recovery waste, was pumped to process tanks at the U Plant where the precipitation process was carried out. The precipitating agents were sodium or potassium ferrocyanide, calcium, or strontium nitrate, and nickel sulfate. After mixing the dissolved ferrocyanide and nitrate salts with the aqueous waste, sodium hydroxide was added to raise the pH to 9 ± 1. Nickel sulfate was then added, and

the cesium and strontium formed insoluble precipitates. The treated waste was then pumped to one of the large BY Farm tanks where the ferrocyanide-bearing particles settled out by gravity forces. After a minimum settling time of 7 days, the supernatant liquid was sampled, and if it contained sufficiently low levels of radionuclides, it was discharged to the soil column. Settled sludge was pumped to two other storage tanks in the BY farm for long term storage when the sludge level in the settling tank became high enough to impact the receiving batch size.

Two different concentration levels of ferrocyanide were used: 0.0025 M and 0.005 M. Experience (obtained from earlier plant runs) indicated similar results could be obtained when the lower concentration was used, so most U Plant processing used ferrocyanide at 0.0025 M. The flowsheet that used 0.0025 M ferrocyanide has been termed "U Plant 1" and the flowsheet that used 0.005 M ferrocyanide is called "U Plant 2." This delineation is potentially important from a safety standpoint because the U Plant 2 sludge would be expected to contain roughly double the concentration of ferrocyanide as compared to U Plant 1 sludge.

Most U Plant sludge was prepared by the U Plant 1 flowsheet (~70 percent). Approximately 66 percent of the total ferrocyanide used for scavenging waste at the Hanford Site was used to treat U Plant waste. This waste is stored in the BY Farm in tanks BY-103, -104, -105, -106, -107, -108, -110, -111 and BY-112, and in the T Farm tank T-107.

A.2.2 IN FARM FLOWSHEET

The In Farm scavenging process was used to decontaminate a variety of supernatant waste stored in the large underground storage tanks. These supernatant liquids contained relatively low concentrations of inert salts and suspended solids, and therefore the ferrocyanide sludge produced by this flowsheet was comparatively rich in ferrocyanide.

Twenty nine batches of In Farm waste were processed. The scavenging chemical addition was performed in the 241-CR vault tanks. Each batch was evaluated and a specific admixture was developed to treat the waste on a batch-by-batch basis. The source of feed solution, feed solution composition, treatment received, and quantity of solution processed are listed in Table A-1 of Appendix A of the Jeppson and Wong (1993) report. Six of the 29 batches were scavenged for strontium and cobalt only, and did not receive any ferrocyanide. One batch and part of another batch were scavenged with ferrocyanide at 0.0075 M. One batch and parts of two other batches were scavenged with 0.0025 M ferrocyanide. The remaining batches or fraction of batches were scavenged with 0.005 M ferrocyanide. Approximately one-half of the batches were treated with sodium sulfide (up to 0.006 M) for ^{60}Co decontamination. The sulfide formed precipitate that could act as a fuel (like ferrocyanide) in the sludge. Most of the batches were treated with calcium nitrate (up to 0.03 M) for ^{90}Sr decontamination. The calcium formed a phosphate and/or sulfate precipitate which acts as inert solid diluent in the sludge.

One batch and part of a second batch (out of 29 total) that used 0.0075 M ferrocyanide have been termed the In Farm 1 flowsheet. It represents the flowsheet that produced sludge with the highest fuel (ferrocyanide + sulfide) concentration at the Hanford Site. An estimated 5 percent of ferrocyanide used at the Hanford Site went into the In Farm 1 flowsheet. The larger volume of sludge (~80 percent of ferrocyanide used in In Farm flowsheet) was produced using 0.005 M ferrocyanide; this formulation is termed the In Farm 2 flowsheet. An estimated 26 percent of total ferrocyanide used in scavenging campaigns was used in 29 In Farm batches. The In Farm sludges are stored in tanks C-108, -109, -111, and C-112.

A.2.3 T PLANT FLOWSHEETS

Aqueous waste from the T Plant bismuth phosphate process first decontamination cycle was scavenged in T Plant by a process similar to that used in the U Plant flowsheet. The ferrocyanide concentration used was 0.005 M, the same as used in the U Plant 2 flowsheet (see Section 2.1 of this appendix). It is estimated that 8 percent of the ferrocyanide used in scavenging campaigns at the Hanford Site was used in the T Plant flowsheet. This sludge is stored in tanks TY-101, -103, and -104.

A.3.0 SIMULANT SLUDGE

Simulants were prepared to represent ferrocyanide waste produced by the three flowsheets described above. The amount of ferrocyanide and other scavenging chemicals used for the U Plant and In Farm processes varied depending upon the requirements for a particular batch. Simulant variations were prepared for these two wastes to represent: (1) waste which would have the highest ferrocyanide concentration (U Plant 2 and In Farm 1) and (2) waste which would have a typical ferrocyanide waste concentration (U Plant 1 and In Farm 2). No attempt was made to prepare simulants of batches which would be expected to form waste with lesser concentrations of ferrocyanide. These simulants and variation (except U Plant 1) were further divided into a top and bottom fraction for analysis and reactivity testing.

Three main departures from the actual processes used in the 1950s were made in preparing the test simulants thought to more nearly represent ferrocyanide waste stored in SSTs today and to provide simulants that were not radioactive. These adjustments were (1) the processes for producing the simulants were modified to produce simulants which contained 3:1 mole ratio of nitrate to nitrite (nitrite is presently in the waste due to the partial radiolysis of the nitrate over the 35 years of storage), (2) no uranium or fission products were included in the simulants because of the increased difficulty in working with radioactive materials, and (3) the ferrocyanide waste prepared (settled for 10 days) in the laboratory was further concentrated by centrifuging to an equivalent 30 gravity year settling period using a centrifugal force of approximately 2,000 g's to consolidate the simulant sludge. Centrifuging of the 10-day-settled solids reduced the suspended solids volume to about one

fifth of the settled solids volume. This reduction in sludge volume occurred during the initial equivalent 4 gravity year time period* (Jeppson and Wong 1993) and appeared to be an end point. The simulant formed by centrifuging is expected to contain the same or greater ferrocyanide concentration than the waste formed in the waste tanks and stored for 35 years. No attempt was made in simulant preparations to account for any degradation of the ferrocyanide which may have occurred over the 30 plus years of storage. If uranium were included in the simulants, it would act as an inert diluent and would be expected to reduce the ferrocyanide concentrations to a value less than that of the U Plant and T Plant simulants as prepared.

The volume fraction of simulant produced from the respective feed solution volumes are listed in Table A-1 with the simulant densities. The fraction of ferrocyanide used at the Hanford Site for processing the various wastes and the simulant ferrocyanide and water concentrations are listed in Table A-2.

Table A-1. Simulant Sludge Volume Fraction and Density After Centrifuging for a 30 Gravity-Year Product. (Jeppson and Wong 1993).

Simulant	Fraction of sludge per volume of feed solution	Sludge density (g/mL)
U Plant 1	0.036	1.40
U Plant 2	0.043	1.27
T Plant	0.038[a]	1.29[a]
In Farm 1	0.013	1.49
In Farm 2	0.010	1.39

[a]This is a recent value made available by one of the authors (D. W. Jeppson)

*It has been assumed that sludge compaction is a function of the product of gravitational force and time.

Table A-2. Comparison of Simulant Ferrocyanide and Water Concentrations (Jeppson and Wong 1993).

Simulant	Fraction of Total Ferrocyanide Used at Hanford	Weight percent		
		Simulant ferrocyanide concentration (wet)	Simulant free water content	Simulant ferrocyanide concentration (dried)
U Plant 1	0.46	1.57	66	4.62
U Plant 2	0.20[a]			
Top (50%)		2.09	67	6.33
Bottom (50%)		2.97	64	8.25
T Plant[b]	0.08			
Top (90%)		2.72	69	8.8
Bottom (10%)		1.08	35	1.6
In Farm 1	0.05			
Top (40%)		8.94	51	18.2
Bottom (60%)		13.3	48	25.5
In Farm 2	0.21			
Top (50%)		8.92	52	18.6
Bottom (50%)		11.3	50	22.6

[a]Calcium nitrate was used with about half (about 0.10 fraction of total of the ferrocyanide used for this U Plant 2 related waste which resulted in a precipitated waste with a considerably lower ferrocyanide concentration than listed here for U Plant 2. No attempt was made to prepare a simulant with the lower ferrocyanide concentration because it was considered less reactive than the U Plant 2 simulant. This fraction of 0.20 includes 9 batches without calcium nitrate and 9 batches with calcium nitrate.

[b]Values for T Plant simulant are recent values made available by one of the authors (D. W. Jeppson).

A.4.0 TANK SAMPLES

Core samples have recently been taken from tanks C-112, C-109, and T-107. Core samples were taken in 1985 from tanks TY-101 and TY-103. Detailed results for the C-112 and C-109 cores are provided in the reports of Simpson et al. (1993a) and Simpson et al. (1993b). Results for samples from tanks TY-101 and TY-103 are summarized by Grigsby et al. (1992). Detailed results for the sample recently taken from tank T-107 have yet to be reported; a preliminary value is reported herein.

Key results obtained from the analysis of tank samples are listed in Table A-3. The most notable features of the data obtained from tank samples are:

- Ferrocyanide concentrations are low
- Exotherms are very small
- Water contents are relatively high.

These features are important to safety because they provide a basis for comparison with the properties of freshly prepared simulants that were used in reaction propagation studies.

Table A-3. Analysis Results from Tank Samples.

Tank	Cyanide[a] concentration wt%	DSC[b] exotherm cal/g	Free water wt%
C-109	0.6 - 2.9	0 - 12.4	28[e] - 48
C-112	0.8 - 2.0	4 - 9	39 - 57
T-107	NA	None[c]	NA
TY-101	1.0 - 1.3	Slight	43.5
TY-103	1.2 - 1.4	33[d]	52.5

[a]Cyanide reported as $Na_2NiFe(CN)_6$, zero free water basis.

[b]Result from differential scanning calorimetry, zero free water basis.

[c]Preliminary value.

[d]Value based on sample data reported on February 1, 1980. Recent analyses on archived samples show no exotherms.

[e]The 28 wt% water content value was observed in the upper portion of tank 241-C-109 and should not be considered representative of ferrocyanide waste. The process history of the tank indicates that a layer, consisting primarily of coating wastes and strontium semiworks waste, exists at the top of the tank. The extremely high aluminum and ^{90}Sr levels observed in the upper subsegments corroborate this process history. In addition, the water content values reported should be considered minimums, since water content can be lost during storage and sample handling in the hot cell.

NA - Results not yet available.

A.5.0 COMPARISON OF TANK SAMPLE DATA WITH ESTIMATES BASED ON PROCESS INFORMATION

Ferrocyanide concentration and, in turn, exothermic activity are key safety parameters in regards to uncontrolled oxidation-reduction reactions in ferrocyanide waste. A comparison of tank sample data with estimates based on process information is made in Table A-4.

The bases for the numbers given in Table A-4 are described as follows. The sample data values are taken directly from Table A-3. The best-estimate model prediction is based on process records and sludge volume data derived from simulant studies. This model predicts average concentration in the sludge by dividing the ferrocyanide mass (material balance calculations) in a tank by the mass of the sludge in the tank. The model itself is described in detail by Borsheim and Simpson (1991). Key parameters used in the model are the following.

SLUDGE VOLUME FRACTIONS

Based on plant records and the observed properties of flowsheet simulants, the ratio of sludge volume to treated waste volume were assigned the following values:

- U Plant: 4.25 volume percent
- In Farm: 1.0 to 1.5 volume percent
- T Plant: 3.7 volume percent.

SLUDGE DENSITY

Sludge densities were assigned values on the basis of values for simulants:

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

WATER CONCENTRATION

Water concentration, derived again from tank sample data and values measured for simulants, were assigned the following values:

- U Plant: 65 wt%
- In Farm: 50 wt%
- T Plant: 69 wt% (Fauske 1992).

The two values listed in Table A-4 for flowsheet simulants are based on analyses performed on top and bottom fractions of the respective simulants. The concentration data are taken from Table A-2 and the reaction energy is calculated by multiplying percent $Na_2NiFe(CN)_6$ by 6 MJ/kg (1,435 cal/g).

The most important conclusion to be reached from the comparisons made in Table A-4 is that ferrocyanide concentrations and exothermic activity are generally less than 10 percent of the values expected on the basis of what was put into the tanks 35 year ago. In all cases the exothermic energy is small, 33 cal/g or less. Ferrocyanide has apparently been partially destroyed by radiolysis and hydrolysis reactions (Babad et al. 1993) during the 4 decades of storage time. In addition to chemical degradation, the ferrocyanide sludge may have mixed with inert waste, a process that would diminish the energy potential per unit mass of waste. For the In Farm and T Plant flowsheets, it appears that freshly prepared simulants are conservative with respect to energetics as compared to actual waste. No actual tank sample data are yet available for the U Plant flowsheet materials.

Table A-4. Comparison of Ferrocyanide Concentration

Tank	Ferrocyanide concentration wt%[a]			Exothermic activity, cal/g[b]		
	Sample data	Process records model	Flowsheet simulant	Sample data	Process records model	Flowsheet simulant
C-109	0.6 - 2.9	14.0 - 20.9	18.2 - 25.5	0 - 12.4	200 - 300	261 - 366
C-112	0.8 - 2.0	16.1 - 24.2	18.2 - 25.5	4 - 9	231 - 347	261 - 366
T-107	--	7.0	4.6 - 8.3	None	100	66 - 120
TY-101	1.0 - 1.3	7.6	1.6 - 8.8	Slight	109	23 - 127
TY-103	1.2 - 1.4	6.9	1.6 - 8.8	33	99	23 - 127

[a]$Na_2NiFe(CN)_6$ on a zero free water basis.

[b]Model and simulant values calculated from concentration of $Na_2NiFe(CN)_6$ using a reaction energy of 6 MJ/kg--zero free water basis.

[c]Value based on sample data reported on February 1, 1990. Recent analyses on archived samples show no exotherms.

A.6.0 REFERENCES

Babad, H., J. E. Meacham, B. C. Simpson, and R. J. Cash, 1993, *The Role of Aging in Resolving the Ferrocyanide Safety Issue*, WHC-EP-0599, Westinghouse Hanford Company, Richland, Washington.

Borsheim, G. L., and B. C. Simpson, 1991, *An Assessment of the Inventories of the Ferrocyanide Watch List Tanks*, WHC-SD-WM-ER-133, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Fauske, H. K., 1992, *Adiabatic Calorimetry and Reaction Propagation Tests with Synthetic Ferrocyanide Materials Including U Plant 1, U Plant 2, In Farm 1, In Farm 2, and Vendor-Procured Sodium Nickel Ferrocyanide*, WHC-SD-WM-RDT-054, Rev. 0, July 1992, Westinghouse Hanford Company, Richland, Washington.

Grigsby, J. M., D. B. Bechtold, G. L. Borsheim, M. D. Crippen, D. R. Dickinson, G. L. Fox, D. W. Jeppson, M. Kummerer, J. M. McLaren, J. D. McCormack, A. Padilla, B. C. Simpson, and D. D. Stepnewski, 1992, *Ferrocyanide Waste Tank Hazard Assessment - Interim Report*, WHC-SD-WM-RPT-032, Rev. 1, Westinghouse Hanford Company, Richland, Washington.

Jeppson, D. W., and J. J. Wong, 1993, *Ferrocyanide Waste Simulant Characterization*, WHC-EP-0631, Westinghouse Hanford Company, Richland, Washington.

Simpson, B. C., G. L. Borsheim, and L. Jensen, 1993a, *Tank Characterization Data Report: Tank 241-C-112*, WHC-EP-0640, Rev. 1, Westinghouse Hanford Company, Richland, Washington.

Simpson, B. C., G. L. Borsheim, and L. Jensen, 1993b, *Tank Characterization Report: Tank 241-C-109*, WHC-EP-0668, Westinghouse Hanford Company, Richland, Washington.

APPENDIX B

REACTION PHENOMENOLOGY

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APPENDIX B

REACTION PHENOMENOLOGY

B.1.0 INTRODUCTION

The hazard of concern in this report is the uncontrolled oxidation-reduction reaction between ferrocyanide and nitrate/nitrite in stored waste. As noted in the Safety Objective (Section 3.0 in the main report) the hazard is acceptable if physio-chemical conditions are such that a reaction cannot propagate. Theoretical and experimental information that is pertinent in defining the line between waste states that can support a propagating reaction and those that cannot is presented in this appendix.

B.2.0 THEORETICAL CONSIDERATIONS

This section presents simple theoretical concepts that help interpret experiments performed to characterize exothermic reactions in waste simulants and help to set criteria that will define conditions in stored waste where propagating reactions are impossible.

B.2.1 EXOTHERMIC REACTIONS

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 sodium available to form it). A representative equation with nitrate is:

$$Na_2NiFe(CN)_6 + 6NaNO_3 \rightarrow FeO + NiO + 4\ Na_2CO_3 + 6N_2 + 2CO_2 \qquad \text{(B-1)}$$

The calculated energy (ΔH) for this reaction is ~ 9.52 MJ/kg of ferrocyanide at 298 °K (Burger 1993).

Observations (Scheele et al. 1992; Burger and Scheele 1991) 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. Calculations presented by Burger (1993) show that reaction energy decreases to -6.6 MJ/kg when N_20 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. As discussed in Section B.3.0 of this appendix, three independent measurements of reaction energy yield values close to 6 MJ/kg of $Na_2NiFe(CN)_6$. This amounts to 63 percent of the theoretical value given above for equation (B-1) and 90 percent of the calculated energy with N_2O as the product gas.

B.2.2 ENERGY CONTENT FOR PROPAGATING REACTIONS

Conservative estimates of exothermic energy density required for propagating reactions can be made on the basis of a simplistic model that largely ignores kinetic factors. The model (Colby and Crippen 1992) may be described in terms of an energy balance expressed as:

$$\Delta H_M + \Delta H_R \geq 0 \qquad \text{(B-2)}$$

Where:

ΔH_M = Change in enthalpy of waste upon heating from initial temperature to reaction onset temperature

ΔH_R = Reaction enthalpy.

In words, the energy balance represented by equation (B-2), says that propagation is impossible if the reaction energy is insufficient to heat unreacted material to the reaction onset temperature.

A similar model that applies reaction heat to reaction products rather than to unreacted material is discussed by Burger (1993). Both models are expected to yield conservative results because in both it is assumed that the reaction goes to completion at temperatures below the threshold temperature, and that the reaction takes place adiabatically.

A more realistic estimate of minimum reaction energy may be made by accounting for heat transfer between reacted and unreacted material. The concept, by H. K. Fauske (see Attachment B-1 to this appendix), estimates the interface temperature between solid slabs initially at different temperatures. The criterion for propagation is that the interface temperature must be heated to the reaction threshold temperature. Because interface temperature is approximated by the average between unreacted and reacted material, the threshold can be reached only when the temperature of reacted material is appreciably higher than the threshold temperature. A rough estimate of required energy density (cal/g) for this model is a factor of 2 greater than that expressed in equation (B-2).

As will be shown in Section B.3.0 of this appendix, experiments on waste simulants support the validity of the realistic model as well as the factor of 2 conservatism inherent in the model expressed in equation (B-2).

B.2.3 NUMERICAL EVALUATION OF PROPAGATION LIMITS

The propagation limits can be evaluated from Equation B-2 by summing exotherms and endotherms to zero. Methods used for evaluating exotherms and endotherms are described as follows.

Exotherms--The reaction exotherm in a unit mass of unreacted material is taken as the weight fraction of fuel, $Na_2NiFe(CN)_6$, multiplied by the reaction enthalpy per unit mass of fuel (6 MJ/kg).

Endotherms--Endotherms are associated with changes of state and gains in sensible heat as the materials are heated from an initial temperature to a reaction threshold temperature. Initial temperature was taken as 30 °C, an average for ferrocyanide waste. The reaction threshold temperature was taken as 250 °C, an average value obtained from adiabatic calorimetry tests performed on waste simulants (Jeppson and Wong 1993).

The composition of the unreacted material was approximated by the U Plant 2 simulant with a free water content of zero. Free water is defined as all water in excess of bound water. Bound water was assumed to represent 4.6 molecules of H_2O per molecule of $Na_2NiFe(CN)_6$ on the basis of drying tests described in Section B.3.0 of this appendix.

The heat capacity of $Na_2NiFe(CN)_6 \bullet 4.6\ H_2O$ was assigned a value of 0.34 cal/g °C on the basis of Burger's (1993) estimate for the dry compound. For nitrates and nitrites, heat capacity was assigned a value of 0.32 cal/g °C, an average (Perry 1950) for the temperature range of interest. The heat capacity of molten nitrates and nitrites was assigned value of 0.43 cal/g °C (Burger 1993). For the remainder of inert solids, a heat capacity of 0.25 cal/g °C was used.

Phase transitions were assigned enthalpies as follows. The bound water vaporization was assumed to absorb 875 cal/g of water, an average of a range (750 to 1,000 cal/g) cited by Burger (1993). Bound water was assumed to be released at 170 °C on the basis of DSC experimental results. The melting of nitrates and nitrites was assumed to occur at 220 °C and absorb 45 cal/g (a weighted average of fusion enthalpies listed by Burger (1993).

Conservative Estimate of Propagation Limit in Dry Waste

The concentration of $Na_2NiFe(CN)_6$ in a mix containing zero free water is calculated from the parameters and assumptions described in the foregoing, to be 7.7 wt%. As noted in Section B.2.2, this conservative value is expected to be roughly 50 percent of the more realistic estimate that accounts for heat transfer effects.

Water Needed to Prevent Propagation in Mixtures Containing Higher Ferrocyanide Concentrations

Equation B-2 was used to predict the concentration of free water that would prevent propagation in a waste mix that contained 26 wt% $Na_2NiFe(CN)_6$ on a zero free water basis. This mix was patterned after the sludge simulant that contained the highest ferrocyanide concentration. The composition of this material, called In Farm 1 Bottom Fraction, is described more fully in Section B.3 of this appendix.

The endotherms associated with free water were quantified by assigning heat capacities of liquid and vapor, the values of 1.0 and 0.47 cal/g °C, respectively. Vaporization enthalpy was taken as 540 cal/g. Other endotherms were quantified in the same manner as described above for the dry case.

The minimum required moisture concentration was calculated to be 24 wt%. This value is roughly double the value that would be predicted by the more realistic model developed by H. K. Fauske, which is presented in Attachment B-2 to this appendix.

B.2.4 SUMMARY OF THEORETICAL PROPAGATION LIMITS

An inherently conservative energy balance calculation identified the propagation limit in dry waste (zero free water) to be the energy equivalent of 7.7 wt% $Na_2NiFe(CN)_6$ using a reaction energy of 6 MJ/kg. For the most concentrated waste simulant (26 wt% $Na_2NiFe(CN)_6$) a moisture concentration of 24 wt% was predicted to prevent propagation.

The free water concentration required to prevent propagation of mixes with intermediate ferrocyanide concentrations can be approximated linear interpolation between 0 at 7.7 wt% ferrocyanide and 24 wt% water at 26 wt% ferrocyanide.

These conservatively calculated limits are expected to have a safety factor of roughly 2 compared to realistic limits.

B.3.0 EXPERIMENTAL MEASUREMENTS

Experimental studies of the reaction between ferrocyanide and nitrates and nitrites have been carried out at LANL (Cady 1992) at FAI (Jeppson and Wong 1993) at PNL (Burger and Scheele 1991) and at WHC. The focus of this report is the dividing line between mixtures that can sustain a propagating reaction and those that cannot, and for this reason attention will be focussed on tests that bear directly on propagation.

B.3.1 REACTION ENERGY

Three independent experiments provide information that can be used to quantify the heat of reaction in waste-like simulants. First, adiabatic calorimetry tests (Fauske 1992, Jeppson and Wong 1993) with dried U Plant 1 and 2 (bottom fraction) ferrocyanide waste simulants (approximately 70 g samples) yield a measured sample temperature rise from which a heat of reaction can be calculated. Using thermal properties listed in Section B.2.3 of this appendix, a reaction energy of 6.0 MJ/kg was calculated. Second, an exotherm measured by a DSC apparatus (calibrated against potassium nitrate) for In Farm 1 (bottom fraction) simulant that contained sulfide yielded an energy of 6.1 MJ/kg of $Na_2NiFe(CN)_6$. This test was performed at WHC by one of the authors of this report (G. S. Barney). Third, an ARC test performed at LANL (Cady 1992) on In-Farm 1 (bottom fraction) waste simulant yielded an energy that was calculated to amount to 4.8 MJ/kg of $Na_2NiFe(CN)_6$. Based on the results of these three independent tests, it is concluded that the oxidation of ferrocyanide by nitrate/nitrite mixtures in waste-like simulants yields an exotherm of approximately 6 MJ/kg of $Na_2NiFe(CN)_6$.

B.3.2 BOUND WATER IN FERROCYANIDE WASTE SIMULANTS

Water held as hydrates and in zeolytic form is not susceptible to loss by drying at ambient temperatures. This tightly held, or bound water, is important to safety because endotherms associated with its loss at higher temperatures can play a role in preventing propagating reactions.

One of the authors of this report (G. S. Barney) has carried out a series of tests with waste simulants to quantify bound water content. The tests were performed in two steps.

1. Drying samples by standard procedures

2. Measuring residual water content of dried samples by simultaneous DSC, TGA, and MASS spectrometry analysis.

Results from five sets of tests are listed in Table B-1.

Table B-1. Bound Water Content of Simulants by Various Drying Methods.

Drying method	Simulant	Bound water (wt%)	Mole bound water/mole $Na_2NiFe(CN)_6$
120 °C, 18 hrs	In Farm 2 top	4.4	4.2
105 °C, 24 hrs	In Farm 2 top	4.3	4.1
Vac. 60 °C, 18 hrs	In Farm 2 top	5.6	5.3
Vac. 60 °C, 18 hrs (FAI)	In Farm 1 top	5.8	5.6
Vac. 60 °C, 18 hrs (FAI)	In Farm 1 bottom	5.4	3.7

The data in Table B-1 show bound water varied from 3.7 to 5.6 molecules per molecule of $Na_2NiFe(CN)_6$, with an average of 4.6.

An examination of the TGA curve showed that there are two definite temperature ranges in which water is evolved from the dried samples. A relatively small release occurs in the range of 80 to 150 °C and a larger one occurs in the range of 190 to 240 °C. The relatively high temperatures required to drive off the bound water indicates the relative strength of the bonds that hold the water in the waste matrix.

A bound water content of 4.6 molecules of water per molecule of $Na_2NiFe(CN)_6$ has been assumed to be a worst case for analysis in regards to propagating reactions in waste. Realistic analyses of moisture contents would show much higher moisture concentrations even for the case of no controls on tank headspace ventilation. A minimum free moisture content would correspond to the equilibrium value, which, based on data contained in Attachment C to Appendix C, would amount to free water in the range of 4 to 12 wt%.

B.3.3 PROPAGATION TEST IN SIMULANTS

Two kinds of tests were performed with waste simulants to determine compositions that would support a propagating reaction (1) adiabatic calorimetry, and (2) propagation rate tests. These test were performed at Fauske and Associates Inc. (Fauske 1992), and results are described by Jeppson and Wong (1993).

Waste simulants used in the propagation tests are identified and characterized in Table B-2. The simulant mixes listed in Table B-2 were vacuum dried at 60 °C for 18 hours.

Table B-2. Hanford Ferrocyanide Sludges.

Simulant/fraction of Hanford CN	U Plant/66%	In Farm/26%	T Plant/8%
Simulant of greatest on concentration	Dried U Plant 2 bottom	Dried In Farm 1 bottom	Dried T Plant Top
Constituent	Weight Percent		
Bound water	2.5	5.8	3
Sodium nitrate	45.2	39.8	27.1
Sodium nitrite	10.9	11.4	6.1
$Na_2NiFe(CN)_6$	8.3	25.6	8.8
Nickel sulfide	0.0	2.7	0.0
Inert solids	~33	~15	~55
Total organic carbon	0.0	0.0	0.0

B.3.3.1 Adiabatic Calorimetry Tests

In these tests, relatively large (10 g and 70 g) samples are heated in thin-walled flasks (Fauske 1992, Jeppson and Wong 1993). Initial heatup is done by electrical heaters. After the reaction onset temperature is reached, sample heatup rate is responsive to the energy production rate from the chemical reaction in the sample. The measured response of a thermocouple imbedded in the sample is indicative of the character of the reaction that has occurred.

For reactions that are propagating, a reaction front develops and moves past the thermocouple. This results in an almost step change in measured temperature. Therefore, for materials where an abrupt rise in temperature is observed (typically $>10^4$ °K/min), it is concluded that the material sustains a propagating reaction.

Self-heating rates that start low (~ 1 °K/min) and then increase with temperature at a rate consistent with the Arrhenius law, are typical of reactive mixtures which experience runaway reactions. Any reactive mixture that produces heat will exhibit this behavior. The rate and extent of self-heating of runaway reactions determines their significance in a particular case. Self-heating curves for a number of tests are provided by Jeppson and Wong (1993).

Results for three adiabatic calorimetry tests on waste simulants are listed in Table B-3.

Table B-3. Results of Adiabatic Calorimetry Tests.
(Fauske 1993a, Fauske 1993b, Jeppson and Wong 1993)

Simulant	Ferrocyanide concentration	Propagation
Dried U Plant 2 bottom	8.3 (VSP)*	No
Dried and nitrite diluted In Farm 1 bottom	15 (RSST)**	No
Dried and nitrite diluted In Farm 1 bottom	18 (RSST)**	Yes

*VSP tests use sample mass of ~ 70 g. The VSP apparatus is described by Fauske (1992).

**RSST tests use sample mass of ~ 10 g. The RSST apparatus is described by Fauske (1992).

The results in Table B-3 show the concentration limit for propagation was between 15 and 18 wt%. This applies for samples that had free water removed, but contained bound water amounting to ~ 4.6 molecules H_2O per molecule of $Na_2NiFe(CN)_6$.

B.3.3.2 Propagation Rate Tests

In these tests, a confined cylinder of waste is ignited at the upper open end by means of a thermite-like igniter. The rate of propagation is measured by noting the time when a reaction front passes imbedded thermocouples (Fauske 1992). The apparatus and results are discussed by Jeppson and Wong (1993). Propagation rate tests results are summarized in Table B-4.

The most important result shown in Table B-4 is that the simulant containing the highest ferrocyanide concentration (26 wt%) will not sustain a propagating reaction when free-moisture content is greater than 12 wt%.

Table B-4. Propagation Properties of In Farm Bottom Fraction Simulant as a Function of Free Water Content, Pressure, and Initial Temperature (Fauske 1992).

Simulant	Diameter (mm)	Free water content (wt%)	Pressure (atm absolute)	Initial temperature (°C)	Maximum temperature (°C)	Propagation rate (cm/min)
In Farm 1 bottom	50	48	1	26	---	0
In Farm 1 bottom	25	14.6	1	26	---	0
In Farm 1 bottom	25	12	1	26	---	Ignited* but stopped
In Farm 1 bottom	25	8.0	1	26	900	5.3
In Farm 1 bottom	25	0	1	26	1150	10
In Farm 1 bottom	25	0	10	60	>1200	16
In Farm 1 bottom	25	0	53	60	>1200	32
In Farm 1 bottom	25	1	3	60	1150	13
In Farm 1 bottom	25	1	3	120	1200	20

B.4.0 COMPARISON OF THEORY AND EXPERIMENTS

Propagation limits derived from theory can be compared with those obtained experimentally on a triangular composition diagram. The triangular diagram is convenient because the sum of the normal distances to each side from any point on the diagram is a constant. This allows mass fractions of mixes formed by adding or subtracting any one component to be represented by a straight line.

Experimental and theoretically derived propagation limits are exhibited in Figure B-1. The three corners of the diagram represent compositions where only one of the three components is present. The lower right-hand apex corresponds to a mix containing only free liquid water. The top corresponds to a stoichiometric mix of ferrocyanide and nitrate:

$$Na_2NiFe(CN)_6 \bullet 4.6H_2O + 6NaNO_3$$

The lower left-hand apex represent non-reactive diluents such as excess oxidizer and other inorganic salts.

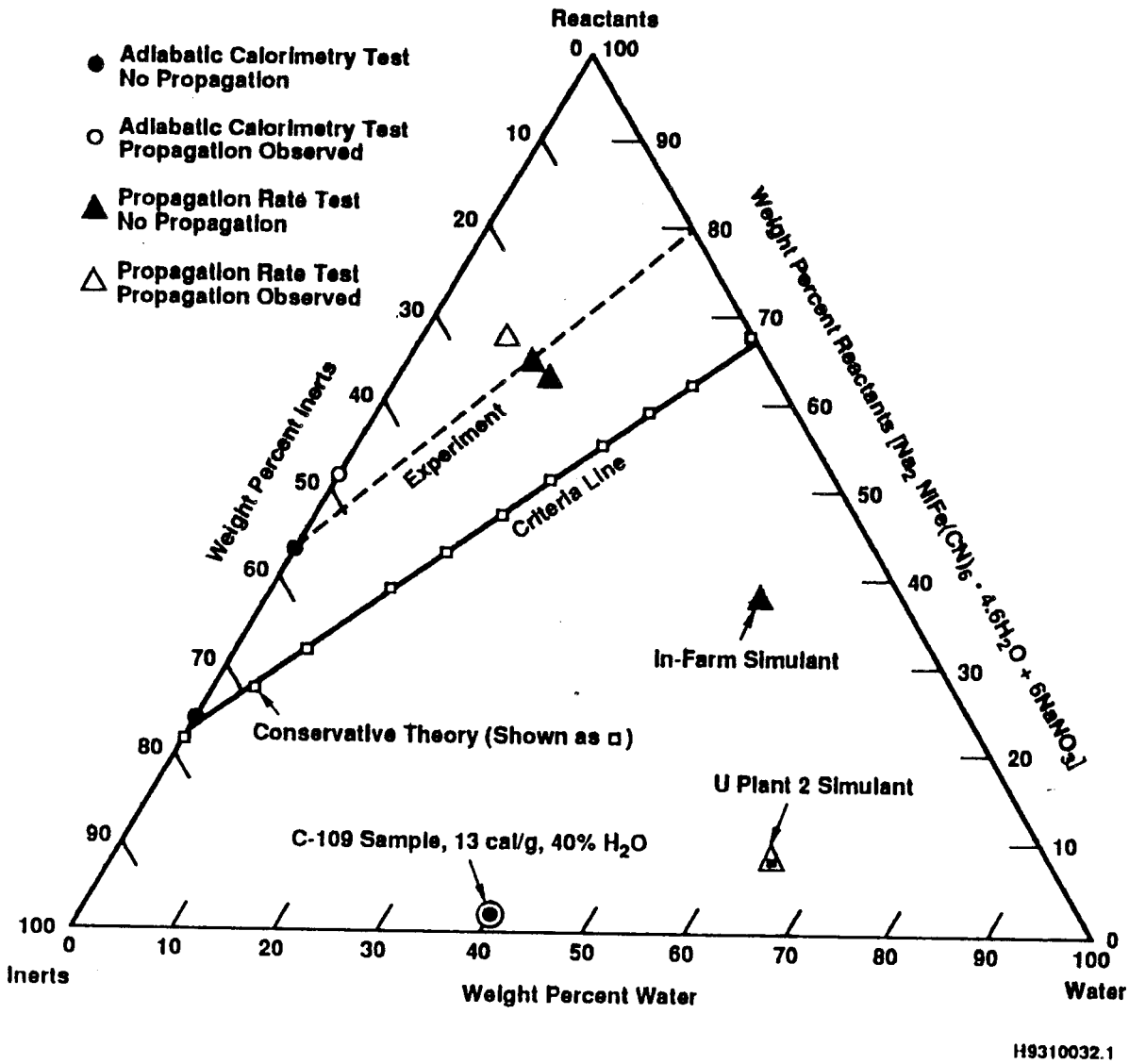
Based on stoichiometric calculations, each unit mass of reactants contains 34.8 wt% $Na_2NiFe(CN)_6$, 9.1 wt% bound water and 56.1 wt% $NaNO_3$. Therefore a dry (zero free water) sludge containing 7.7 wt% $Na_2NiFe(CN)_6$ would be represented on Figure B-1 as 7.7/0.348 = 22.1 wt% "Fuel Mix" and 100 - 22.1 = 77.9 wt% inerts.

The dots identified as "Conservative Theory" are positioned on the basis of theoretical limits of 7.7 wt% $Na_2NiFe(CN)_6$ at zero free water and 24 wt% free water for a waste containing 26 wt% $Na_2NiFe(CN)_6$ on a zero free water basis. The line delineates concentrations of fuel, water, and inerts where the simplistic energy balance (Equation B-2) is satisfied.

Specific points representing compositions tested are shown in Figure B-1. An "Experimental" line is drawn through the highest points where propagation was not observed. The experiments where propagation occurs all correspond to composition having calculated energy densities much higher than both the theory and criteria line. As indicated, the criteria line falls close to the theory line, and thus affords a significant degree of conservatism as compared to the experiments. As described in Section 6.0 of this report, the criteria limits are 8.0 wt% $Na_2NiFe(CN)_6$ for a mix containing zero free water and 24 wt% water for a mix containing 26 wt% $Na_2NiFe(CN)_6$ on a zero free water basis.

Compositions corresponding to the In Farm 1 and U Plant 2 simulants (see Table 5-1) and the most energetic of samples withdrawn from tanks C-112 and C-109 (13 cal/g) are also shown on Figure B-1. It is apparent that these compositions fall below the conservative criteria line, and therefore could not support propagating reactions.

Figure B-1. Comparison of Theoretical and Experimental Propagation Limits.



B.5.0 REFERENCES

Burger, L. L., and R. D. Scheele, 1991, *The Reactivity of Cesium Nickel Ferrocyanide Toward Nitrate and Nitrite Salts*, PNL-7550, Pacific Northwest Laboratory, Richland, Washington.

Burger, L. L., 1993, "Calculation of Reaction Energies and Adiabatic Temperatures for Waste Tank Reactions," PNL-8557, Pacific Northwest Laboratory, Richland, Washington.

Cady, H. H., 1992, "Evaluation of Ferrocyanide/Nitrate Explosion Hazard," LA-12589-MS, Los Alamos National Laboratory, Los Alamos, New Mexico.

Colby, S. A., and M. D. Crippen, 1992. In Grigsby, J. M., *Ferrocyanide Waste Tank Hazard Assessment -- Interim Report*, WHC-SD-WM-RPT-032, Westinghouse Hanford Company, Richland, Washington.

Fauske, H. K., 1992, *Adiabatic Calorimetry and Reaction Propagation Tests with Synthetic Ferrocyanide Materials Including U Plant-1, U Plant 2, In Farm 1, In Farm 2, and Vendor-Procured Sodium Nickel Ferrocyanide*, WHC-SD-WM-RDT-054, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Fauske, H. K., 1993a, "Fuel Concentration Required for Deflagration of Ferrocyanide Mixtures," Memo to R. J. Cash, Westinghouse Hanford Company, dated September 14, 1993. This memo is reproduced as Attachment B-3 of Appendix B.

Fauske, H. K., 1993b, "Propagation Tests With In Farm 1 Bottom Half Flow Sheet Material (~26 wt% $Na_2NiFe(CN)_6$ - Dry Basis) Using Al_2O_3 as a Diluent," Memo to R. J. Cash, Westinghouse Hanford Company, dated September 23, 1993. This memo is reproduced as Attachment B-4 of Appendix B.

Jeppson, D. W. and J. J. Wong, 1993, *Ferrocyanide Waste Simulant Characterization*, WHC-EP-0631, Westinghouse Hanford Company, Richland, Washington.

Perry, J. M., 1950, "Chemical Engineers Handbook," 4th Edition, 1950, McGraw-Hill Book Company, New York, New York.

Scheele, R. D., L. L. Burger, J. M. Tingey, R. T. Hallen, and M. A. Lilga, 1992, "Chemical Reactivity of Potential Ferrocyanide Precipitates in Hanford Tanks with Nitrate and/or Nitrite." In *Proceedings of the Symposium on Waste Management*, Tucson, Arizona, March 1-5, University of Arizona, 1992.

ATTACHMENT B-1

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Fauske & Associates, Inc.

FAX TRANSMITTAL

DATE: October 14, 1993

TO: Arlan Postma

FAX NO: (503) 623-0479

FROM: Hans Fauske, FAI for HKF

SUBJECT: The Lower Bound Value for the Fuel Concentration that will Sustain a Propagating Reaction for Dry Waste Tank Materials

TRANSMITTAL EQUALS A TOTAL OF 2 PAGE(S)

A very conservative value for the fuel concentration can be estimated where the reaction energy is just sufficient to heat the unreacted material to the critical temperature or onset temperature for a propagating reaction. The critical temperature for synthetic flow sheet materials involving ferrocyanide is about 250°C. Your estimated value using this procedure is about 8 w% sodium nickel ferrocyanide with 0 w% free water at typical waste temperatures.

Clearly, the above value of the fuel concentration will not support a reaction front moving through the cold unreacted material, i.e., the reacted material has no excess energy (above 250°C) to deliver to the unreacted cold material to satisfy the minimum requirement to sustain the reaction. A more realistic lower bound value (necessary but not sufficient) for a given waste temperature can be obtained by satisfying the requirement that the interface or the contact temperature, T_i (K), between the reacted and unreacted materials, must equal or exceed the critical temperature, T_c (K), in order to sustain the reaction front

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$$T_i \geq T_c \tag{1}$$

The interface temperature, T_i, can be estimated from

$$\frac{T_i - T_{UR}}{T_R - T_i} \approx \left[\frac{(kc\rho)_{UR}}{(kc\rho)_R}\right]^{1/2} \tag{2}$$

where T_{UR} (K) is the temperature of the unreacted material, T_R (K) is the adiabatic reaction temperature, k ($w\ m^{-1}\ K^{-1}$) is the thermal conductivity, c ($J\ kg^{-1}\ K^{-1}$) is the specific heat, ρ ($kg\ m^{-3}$) is the density, and subscripts R and UR represent reacted and unreacted materials, respectively.

If we assume that the product (ρck) is about the same for unreacted and reacted materials, we obtain

$$T_i \approx \frac{T_R + T_{UR}}{2} \tag{3}$$

The above approximation suggests that the lower bound value of the fuel concentration to sustain a propagating ferrocyanide reaction in dry waste (0 w% free water) is about twice the value necessary to just heat the unreacted material to the critical temperature, i.e., the lower bound value is estimated to be about 16 w% sodium nickel ferrocyanide.

The above lower bound value is consistent with our experimental observations, i.e., a 15 w% dry sodium nickel ferrocyanide mixture did not exhibit propagating characteristic at ambient waste temperature.

Finally, it should be emphasized again that satisfying Inequality (1) is believed to be a necessary but not a sufficient criterion for sustaining a propagating reaction. As such, the actual fuel concentrations required to sustain a propagating reaction for given waste temperatures including up to the critical temperature remains an impirical quantity and therefore requires experimental data. In other words, basing the fuel concentration value entirely upon satisfying Inequality (1), becomes increasingly conservative as the bulk waste temperature approaches the critical temperature.

HKF:jal

ATTACHMENT B-2

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Fauske & Associates, Inc.

FAX TRANSMITTAL

DATE: November 2, 1993

TO: Arlan Postma

FAX NO: (509) 376-8446
(503) 623-0479

FROM: Hans Fauske, P.E.

SUBJECT: Assessing Water Concentration that will Prevent Initiation of a Propagating Reaction

REFERENCE: "The Lower Bound Value for the Fuel Concentration that will Sustain a Propagating Reaction for Dry Waste Tank Materials", Memo from Hans Fauske to Arlan Postma dated October 14, 1993.

TRANSMITTAL EQUALS A TOTAL OF 4 PAGE(S)

The subject reference suggested that the interface or the contact temperature, T_i (K), between the reacted and unreacted materials, must equal or exceed the critical, T_c (K), in order to initiate a reaction front

$$T_i \geq T_c \tag{1}$$

In this memo the above criterion is extended to include the presence of water and its effect upon the contact temperature. Since the boiling temperature of water is usually well below the critical contact temperature, the phase change associated with the presence of water will lower the contact temperature for a given fuel concentration.

Figure 1 provides a numerical representation of the contact temperature as a function of the volume fraction of water (ϵ) present in the fuel-oxidizer mixture where

$$\theta_{ad} = \frac{T_{ad} - T_i}{T_{ad} - T_{bP}} \tag{2}$$

$$\theta = \frac{T_{bP} - T_o}{T_{ad} - T_{bP}} \tag{3}$$

$$H = \frac{\epsilon\lambda}{c\left(T_{ad} - T_{bP}\right)} \tag{4}$$

with T_{ad} (K) is the adiabatic reaction temperature of the mixture (including the effect of water). T_{bP} (K) is the boiling temperature of water, T_o (K) is the ambient waste temperature, λ (J kg^{-1}) is the latent heat of vaporization and c (J kg^{-1} K^{-1}) is the specific heat of the mixture. The numerical representation provided in Figure 1 assumes that the product (ρck) where ρ (kg m^{-3}) is the density, k (w m^{-1} K^{-1}) is the thermal conductivity, is about the same for unreacted and reacted material. In the absence of water (free and bound) this assumption leads to the simple result (see subject reference)

$$T_i = \frac{T_{ad} + T_o}{2} \tag{5}$$

Figure 1 can now be used to estimate the weight fraction of water required to prevent initiation of a propagating reaction for a given fuel fraction, assuming a suitable ignition source is available. In case of the In Farm flow sheet material with 26 wt $Na_2NiFe(CN)_6$ (on a dry basis), use of Figure 1 suggests that the presence of about 12 wt free water (in addition to 6.8 wt bound water) would violate Inequality (1). This observation is in good agreement with experimental data (FAI/92-81, July, 1992).

The above result was obtained by using the following parameter values: T_c = 523K, T_{ad} = 963K, T_o = 303K, T_{bP} = 393K, λ = 2.25 · 10^6 J kg^{-1}, c = 1000 J kg^{-1} K^{-1} and ϵ = 0.305. These values lead to

ϕ = 0.158

H = 1.20

ϕ_{ad} = 0.78

and results in T_i = 517K which is less than T_c = 523K.

Finally, we note that in absence of free water (but including bound water of 4.6 moles per mole of $Na_2NiFe(CN)_6$) we estimate a lower bound fuel concentration of about 14 w% in order to satisfy Inequality (1). We emphasize that satisfying Inequality (1) is a necessary but not a sufficient condition to initiate a propagating reaction. As such, we note that a 15.6 w% $Na_2NiFe(CN)_6$ diluted In Farm flow sheet material (no free water present) did not exhibit a propagating reaction at ambient waste temperature of 303K, while a 18.6% $Na_2NiFe(CN)_6$ diluted In Farm flow sheet material (no free water present) did. ["Propagation Tests with In Farm 1 Bottom Half Flow Sheet Material (-26 w% $Na_2NiFe(CN)_6$ - Dry Basis) Using Al_2O_3 as Diluent", Memo from H. K. Fauske to R. J. Cash dated September 23, 1993.]

HKF:jal
Attachment

cc: R. J. Cash, WHC
M. Epstein, FAI
M. Grigsby, WHC
D. Jeppson, WHC
J. Meacham, WHC
M. Plys, FAI
D. Turner, WHC

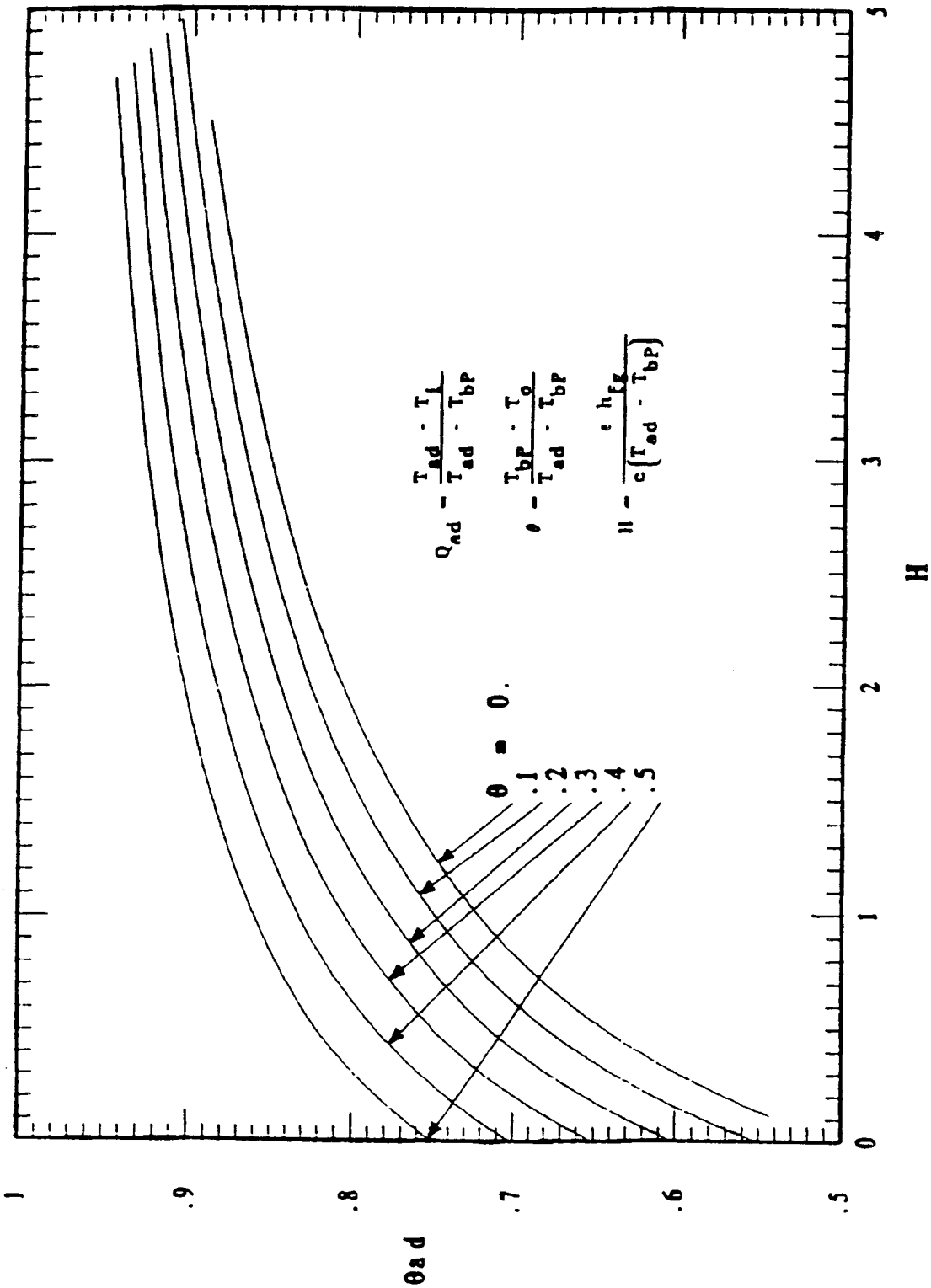

Figure 1 Relationship between contact temperature and volume fraction of water.

ATTACHMENT B-3

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Fauske & Associates, Inc.

FAX TRANSMITTAL

DATE: September 14, 1993

TO: R. J. Cash, WHC

FAX NO: (509) 373-2479

FROM: H. K. Fauske, FAI

SUBJECT: Fuel Concentration Required for Deflagration of Ferrocyanide Mixtures

TRANSMITTAL EQUALS A TOTAL OF 3 PAGE(S)

As is the case for gaseous mixtures (such as hydrocarbon-air mixtures), deflagration of solid or liquid mixtures such as ferrocyanide-nitrate mixtures requires a certain fuel concentration (equivalent to the lower flammability limit). While the lower flammability limit or fuel concentration required for deflagration or propagation* is an entirely empirical parameter it is nevertheless a well-defined property, i.e., the concentration limit is not dependent on system size, etc. This is in contrast to Arrhenius behavior, where the runaway reaction potential is highly system size dependent, i.e., the indication of measurable exothermic activity is dependent upon the type of calorimeter, etc.

The significant difference between a mixture that exhibits deflagration behavior versus one that exhibits Arrhenius behavior is that for the former credible initiators are difficult to rule out while for the latter credible initiators can clearly be ruled out for the ferrocyanide containing waste tanks. As an example, for the U Plant material which does not exhibit propagating characteristics, an unreasonably large heating source

*Deflagration or propagation refers to a reaction front moving through the mixture where the rate of temperature rise is extremely large (- 10^6°C/min) as compared to an Arrhenius reaction which occurs throughout the sample with a rate of temperature rise at the initiation temperature which is many orders of magnitude smaller.

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would be required in order for an Arrhenius reaction to spread throughout the waste.

Previously we have reported that a dry mixture of U Plant flow sheet material (~ 8.6 w% $Na_2NiFe(CN)_6$) does not exhibit propagating characteristics while a dry mixture of In Farm 1 flow sheet material (~ 26.0 w% $Na_2NiFe(CN)_6$) does exhibit propagating characteristics (see Reference 1). Also we have reported that a 12 w% moisture content in the In Farm 1 sample prevented propagation when subjected to a strong ignition source (see Reference 2).

If we take the heat of reaction to be 4 MJ per kg of $Na_2NiFe(CN)_6$, we can estimate the amount of fuel required to satisfy the sensible and latent heats associated with 12 w% water which results in about 8 w% fuel. From this observation we estimate that the fuel concentration in a dry mixture should be in excess of about 18 w% in order to satisfy deflagration from ambient waste temperature conditions given a credible ignition source.

In order to verify this estimate, we have carried out two additional deflagration tests with dry mixtures of In Farm 1 bottom half material (~ 26 w% $Na_2NiFe(CN)_6$) diluted with $NaNO_2$ resulting in fuel concentrations of 15.6 w% and 18.6 w% $Na_2NiFe(CN)_6$. Consistent with the above observation, the 18.6 w% fuel sample exhibits a deflagration with the sample temperature at about 50°C. In contrast, the 15.6 w% fuel sample, did not exhibit a deflagration at the ambient waste temperature of 50°C. The latter sample did deflagrate following extensive heatup of the sample as the thermocouple reading reached a value of about 300°C.

We conclude from the above observations that a best estimate of the fuel concentration to sustain a propagating reaction throughout a dry waste mixture at ambient temperature is about 18 w% $Na_2NiFe(CN)_6$. It is of interest to note that in our ongoing organic investigations, a 20 w% sodium acetate concentration is suggested in order to sustain a propagating reaction in ambient temperature dry organic waste material. Our current estimate of heat of reaction for this system is 3.7 MJ per kg of sodium acetate (see Reference 3), suggesting that the onset of deflagration would require an energy content such as ~ 700 KJ (~ 170 Kcal) per kg of dry mixture independent of the specific nature of the fuel. Clearly 100 Kcal per kg of dry waste mixture would be a very conservative safety criteria, but would nevertheless eliminate all flow sheet materials with the exception of the In Farm.

References

1. Fauske, H. K., "Screening for Propagation Using the RSST - In Farm 1 Bottom Half and U Plant 2-4 Bottom Half Flow Sheet Materials", Memo to R. J. Cash dated August 30, 1993.

2. Fauske, H. K., "Adiabatic Calorimetry and Reaction Propagation Rate Tests With Synthetic Ferrocyanide Materials Including U Plant-1, U Plant-2, In Farm-1, In Farm-2 and Vendor-Procured Sodium Nickel Ferrocyanide", FAI/92-81, July, 1992.

3. Fauske, H. K., "Adiabatic Calorimetry (RSST and VSP) Tests with Sodium Acetate", Memo to D. Turner dated August 17, 1993.

HKF:jal

cc: J. Meacham, WHC
D. Jeppson, WHC

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ATTACHMENT B-4

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Fauske & Associates, Inc.

FAX TRANSMITTAL

DATE: September 23, 1993

TO: R. J. Cash, WHC

FAX NO: (509) 373-2479

FROM: H. K. Fauske, FAI JL for HKF

SUBJECT: Propagation Tests With In Farm 1 Bottom Half Flow Sheet Material (~ 26 wt% $Na_2NiFe(CN)_6$-Dry Basis) Using $A\ell_2O_3$ as Diluent

* *

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* *

As requested by D. Jeppson on September 17, 1993, we have carried out two additional deflagration or propagation tests with dry mixtures of the subject flow sheet material diluted with $A\ell_2O_3$ resulting in fuel concentrations of 15.6 wt% and 18.6 wt% $Na_2NiFe(CN)_6$. These mixtures were screened for propagation characteristics by subjecting 10 gm samples to full heater power from the RSST test cell immersion heater (~ 10 w). The initial temperature was about 30°C and the containment pressure was set at about 28 psia.

Consistent with previous observations (see Reference 1), the 18.6 wt% fuel sample exhibited a deflagration with the sample temperature at about 60°C. In contrast, the 15.6 wt% fuel sample, did not exhibit a deflagration at this temperature. The latter sample required extensive heatup and exhibits a deflagration at a sample temperature of about 270°C. A comparison between the two sample tests are provided in Figures 1 through 3. These results are similar to the tests using $NaNO_2$ as diluent.

Reference

1. Fauske, H. K., "Fuel Concentration Required for Deflagration of Ferrocyanide Mixtures", Memo to R. J. Cash dated September 14, 1993.

HKF:jal
Attachments

cc: D. Jeppson, WHC
J. Meacham, WHC

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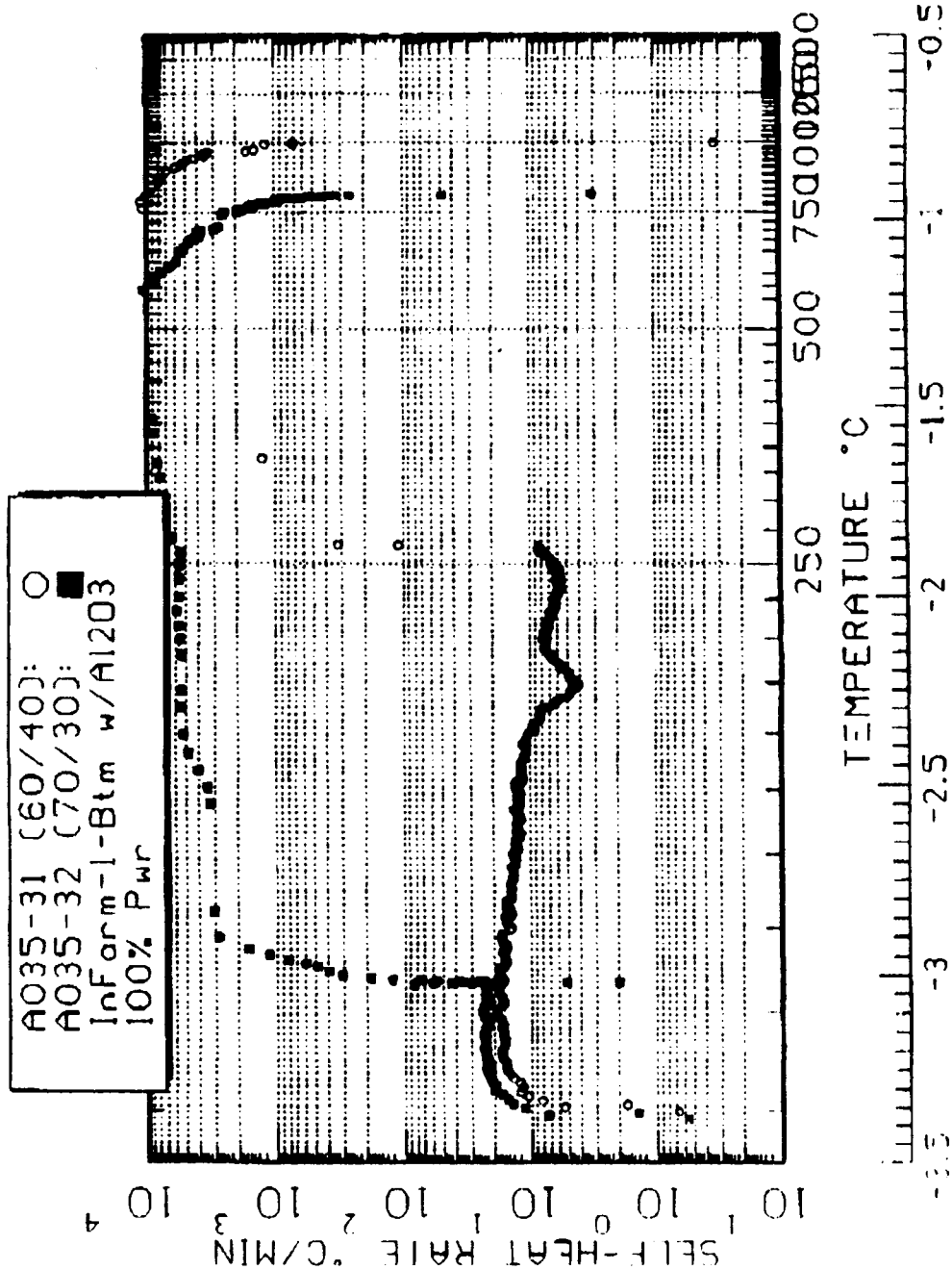

FIGURE 1 SELF-HEAT RATE DATA FROM A035-31,-32

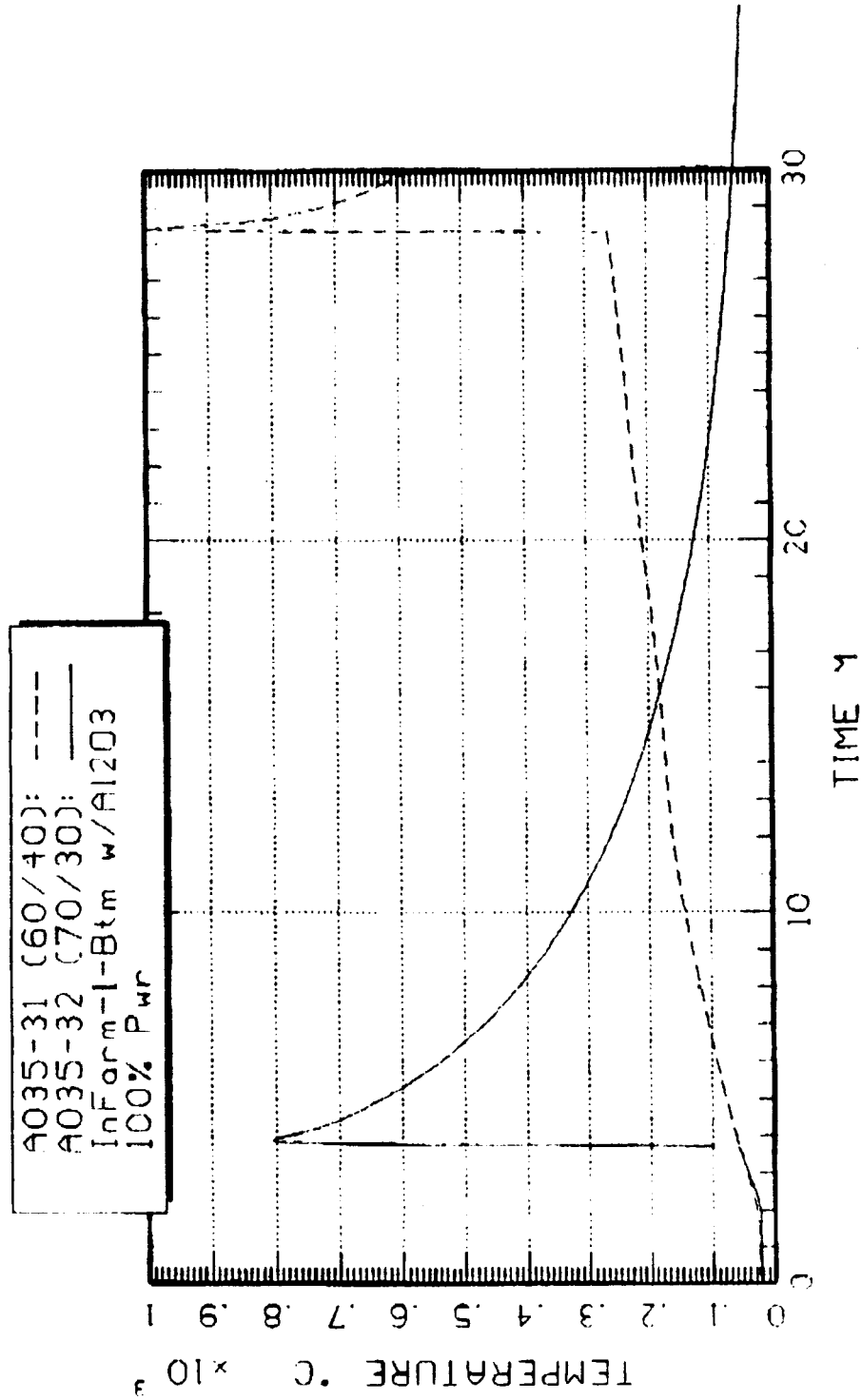

FIGURE 2 TEMPERATURE DATA FROM A035-31,-32

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APPENDIX C

MOISTURE RETENTION CHARACTERISTICS OF FERROCYANIDE SLUDGE

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APPENDIX C

MOISTURE RETENTION CHARACTERISTICS OF FERROCYANIDE SLUDGE

C.1.0 MOISTURE ENDOTHERMS

The presence of water in the ferrocyanide sludge is a potentially important factor in retarding propagation of an exothermic reaction. Energy released in the reaction would initially be consumed in raising the temperature of the material. Because the heat capacity of water is about four times that of dry salts, the presence of water significantly retards the ability of a material to experience a temperature rise in response to a given energy input. When the vaporization temperature is reached, no further temperature rise will occur until all the free water present is vaporized. In addition, release of water held in the sludge matrix by chemical bonding and physical forces will consume additional energy.

C.2.0 EVIDENCE OF WATER CONTENT IN FERROCYANIDE SLUDGE

Evidence of moisture content of ferrocyanide sludge is available from three kinds of measurements:

1. Moisture content measured from samples retrieved from tanks
2. Liquid level measurements obtained by neutron scans in a number of tanks equipped with liquid observation wells (LOW)
3. Moisture content of simulant wastes prepared according to the three flowsheets used at the Hanford Site.

C.2.1 TANK SAMPLE DATA

To date, data are available from sludge core samples taken from five ferrocyanide tanks. Core samples from tanks TY-101, TY-103 and TY-104 were analyzed in 1985, and sample results from C-112 and C-109 became available in 1993.

The ferrocyanide waste in the TY farm tanks was produced from the "T Plant" flowsheet. This flowsheet waste is similar in ferrocyanide content to the "U Plant" waste that represents most of the ferrocyanide waste in the farms. However, it differed somewhat in the various other precipitated species present as described in Appendix A. The samples included one core from tank TY-101, two from TY-103 and four from TY-104.

All of these sample data showed free moisture content greater than 43 wt% (Grigsby et al. 1992). Tanks TY-101 and TY-103 had been interim stabilized by saltwell jet pumping two years before the core samples were taken.

The two C farm tanks sampled in 1993 contain waste from the "In Farm" flow sheet process. Neither was jet pumped* to achieve interim stabilization. Gravimetric measurements of multiple subsegments of three cores taken from tank C-112, and three from tank C-109, indicate free water contents that ranged from 28 wt% to 64 wt% (Simpson et al. 1993a, Simpson et al. 1993b).

In summary, samples of ferrocyanide sludge retrieved from five different tanks (2 flowsheets) had water concentrations of 28 wt% or more. Two of the tanks had been saltwell pumped, and still showed free moisture contents of 43 wt% or more. These data are evidence that the pumping of drainable liquid from a tank does not result in "dry" sludge.

C.2.2 TANK LIQUID LEVEL MEASUREMENTS

Ten of the 20 ferrocyanide tanks have a liquid observation well (LOW) installed. In this well, neutron and gamma scans are routinely made to monitor interstitial liquid levels for leak indications. The interstitial liquid level can be taken as the elevation below which solids are saturated with liquid.

Table C-1 provides a comparison of the interstitial liquid levels and the estimated level of the ferrocyanide sludge. All of the tanks that have not had the drainable liquid removed by jet pumping show the sludge to be saturated. However, even some of those that have been jet pumped show interstitial liquid levels above the sludge level.

In all cases where the interstitial liquid level is below the estimated height of the ferrocyanide sludge, it is at a level of four feet or greater above tank bottom. This indicates that liquid is held up in the sludge by physical forces, probably capillarity, to a height of at least four feet.

*Jet pumping has been used to remove drainable liquid from tanks as part of an "interim stabilization" process at the Hanford Site.

Table C-1. Interstitial Liquid Level Measurements in Ferrocyanide Tanks (Grigsby 1992).

Tank	Ferrocyanide sludge height (ft)	Interstitial liquid level (ft)		Jet pumped
		neutron	gamma	
BY-103	7.0	11.9	11.3	No
BY-104	8.5	7.0	6.7	Yes
BY-105	3.5	13.6	14.8	No
BY-106	7.5	18.5	18.6	No
BY-107	5.4	5.1	5.6	Yes
BY-110	7.4	6.2	5.9	Yes
BY-111	1.1	6.8	4.0	Yes
BY-112	0.7	2.8	3.1	Yes
TY-103	6.0	4.9	4.1	Yes

The data on estimated sludge height and interstitial liquid height were converted to volumes by the method used by tank farms to calculate volumes (Boyles 1990).

$$V = 12{,}500 \text{ gal} + (h - 1 \text{ ft}) \times 33{,}000 \frac{gal}{ft}$$

where:

V = Volume of tank contents to height h (gal)
h = Height of tank contents from tank center (ft).

12,500 gal is the volume of the 1 ft dish at the tank bottom, and 33,000 gal/ft is the volume per foot of a 75 ft diameter tank.

The total volume of ferrocyanide sludge in all of the ferrocyanide Watch List tanks is estimated to be 2,400 kgal (Grigsby et al. 1992). The volume of this sludge that lies above the interstitial liquid level is 250 kgal.

From these data it is estimated that, at present, only about 10% of the volume of ferrocyanide sludge in the tanks is less than saturated with liquid. It should be noted that all of the tanks that contain "In Farm" sludge, (i.e., those in the C-Farm) have sludge levels at less than four feet. Therefore, the tanks that are expected to contain the most reactive waste are also likely to retain high moisture content because waste depths are less than the expected capillary height.

C.2.3 TESTING OF SIMULANT SLUDGE

C.2.3.1 Centrifuge Tests

Extensive testing has been done to measure the physical and chemical behavior of sludge simulants made up using the flowsheets from the original ferrocyanide campaigns. Simulants from all three flowsheets retained about 45 to 70 wt% free water after centrifuging in a closed tube to simulate 30 gravity years.

Further centrifuge tests have been performed to simulate sludge drainage. These tests used an open tube with a filter at the bottom to retain the solids. The results of four tests performed by one of the authors (G. S. Barney) at 10, 20, and 50 G's are shown in Figure C-1. For all the tests shown, the water content appears to reach an equilibrium level after about 200 hours. The tests have so far been continued for 700 hours. These tests will be continued at successively higher G's until no more liquid can be extracted by this means. The minimum water content to date for any of the tests was 45.8 wt%. The sum of gravity year products for the tests shown in Figure C-1 amounts to 2 gravity years.

C.2.3.2 Column Draining Tests

An 8 inch column of simulant sludge (In Farm 2, bottom fraction) was set up for observation of the drainage rate. Drainage has continued for more than a year. The data to date from the test were fitted to a mathematical model that uses the principles of unsaturated flow in porous media. The physical properties assumed for this model were the measured properties of the simulant (Wong 1992). The long term drainage behavior of an eight foot column was calculated by one of the authors (C. S. Simmons).

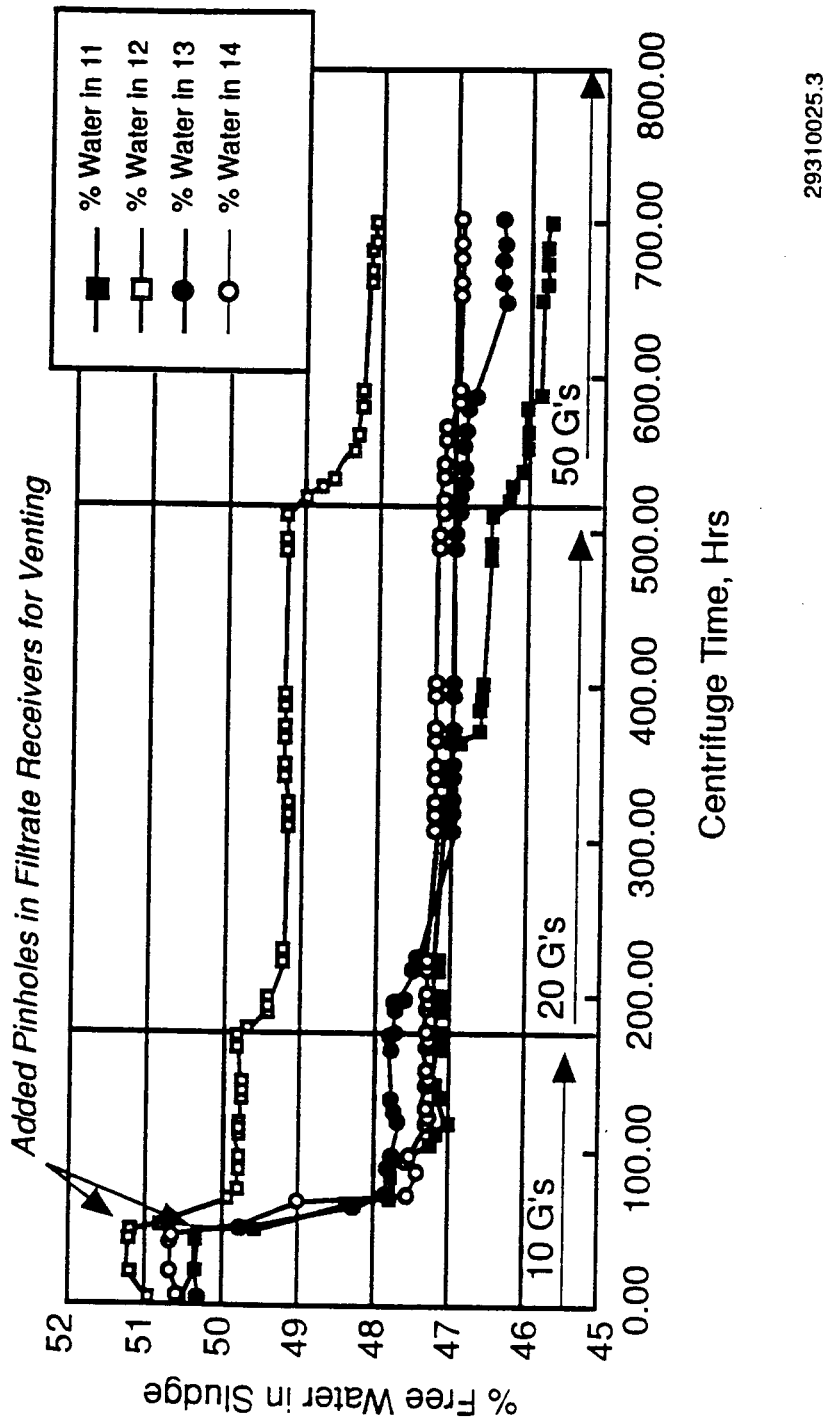
Figure C-2 shows the measured water content of the small column along with the model predictions. Figure C-3 shows the model's prediction of an eight foot column of sludge. It is predicted that the surface of the sludge profile cannot drain by gravity and capillary flow to less than 41 wt% water, when starting at 53 wt%, during about 300 years.

C.3.0 MECHANISMS FOR LOSS OF WATER FROM TANK SLUDGE

C.3.1 DRAINAGE FROM A TANK LEAK OR FLOW INTO SALTWELL

The process of interim stabilization by saltwell jet pumping involves allowing liquid to drain from the solids into a saltwell near the center of the tank. The liquid collected in the saltwell is then pumped out and transferred to another tank. This process is continued for a

Figure C-1. Water Content of Ferrocyanide Sludge Centrifuged in Tubes with Porous Bottoms.



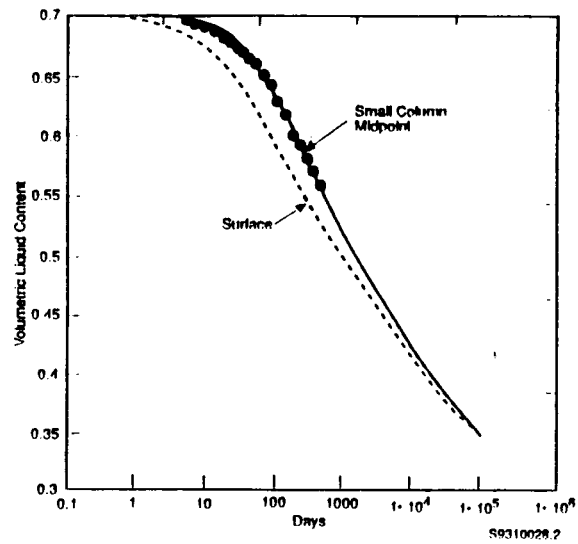


Figure C-2.

Predicted volumetric liquid content (average) for drainage from the small test column (Solid Curve) and measurements (● symbol). Dash curve is predicted liquid content at the column's surface for In Farm 2 sludge simulant.

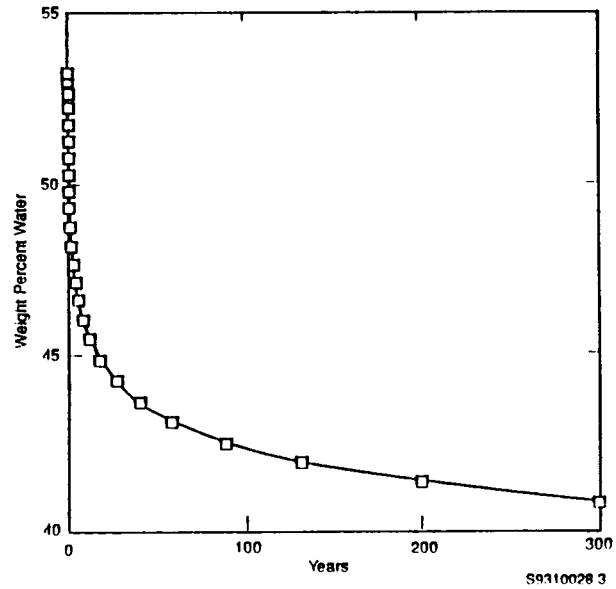


Figure C-3.

Predicted water content at the top surface of an 8 foot high ferrocyanide sludge profile. Based on initial 53 wt% water in sludge and 75 wt% water in the draining salt solution (supernate).

considerable period of time, as long as two years in some cases, to assure that the quantity of liquid available to drain through a breach in the tank will be minimized.

For the tanks that have already been interim stabilized by saltwell pumping, minimal liquid is available for loss through a leak. The tanks that have been declared administratively stabilized because they meet interim stabilization criteria for quantities of drainable liquid, and the tanks that are not yet interim stabilized, could lose water because of a leak. However, as discussed in Section 2.0, loss of moisture through draining by gravitational forces leaves a significant portion of the sludge still saturated with moisture, and the rest of it with a significant moisture content.

C.3.2 EVAPORATION

Evaporation of water from a waste surface in contact with the tank dome space is a potential means of decreasing the water content of ferrocyanide sludge. Potential for surface evaporation is of most concern in tanks where the ferrocyanide sludge is in direct contact with the vapor space. For tanks with overlying saltcake layers, evaporation is slowed due to diffusional resistance in the saltcake.

All the ferrocyanide tanks are currently ventilated passively, that is they exchange air with the outside by means of atmospheric pressure fluctuations through filtered vents. Annual moisture losses from tank breathing are conservatively estimated to be less than 50 gallons water per year (Grigsby et al. 1992). In some tanks, air is provided to the level gauges at a rate that approximates the breathing rate. For these tanks, moisture losses would be expected to be about double that from breathing alone, or about 100 gallons per year. Therefore, ferrocyanide sludge in contact with the tank vapor space will not lose significant moisture even over a long period of time while the tanks remain passively ventilated.

Circumstances may occur, however, that make active ventilation of a tank desirable for a limited time. For instance, during core sampling, in-tank photography or jet pumping, ventilating the tank may be used as a safety precaution.

A bound on the possible rate of evaporation of water from a well ventilated tank may be estimated from the following simplistic model.

- There is a layer of saltcake, which has dried out, above the ferrocyanide sludge.
- Water evaporates from the top of the sludge layer and the vapor migrates by diffusion through the pores in the saltcake. This diffusion controls the rate of evaporation.

- The ventilation rate is high enough to keep the humidity above the saltcake equal to that of the atmospheric air. The average wet and dry bulb temperatures of the air at Hanford are 48 °F and 54 °F, respectively. The corresponding relative humidity is 64% and the water vapor concentration is 6.9 g/m^3.

- The interstitial sludge liquid rapidly reaches saturation at the evaporation interface, and its vapor pressure is 72% of that of pure water at the same temperature on the basis of vapor pressure data for $NaNO_3$ solutions (International Critical Tables).

- The evaporation temperature was taken as the presently measured value at the top of the sludge. No credit was taken for reduction of this temperature by the postulated high ventilation rate or by evaporative cooling.

- The effective void fraction for diffusion through the saltcake was taken as 0.5.

The results of such calculations for several of the BY tanks are given in Table C-2. Evaporation Rates are of the order of 1% of the sludge water content per year. The ferrocyanide sludge has a very small particle size, so capillary forces will be strong and keep the remaining liquid distributed throughout the sludge volume. Therefore, a dried out layer will not form at the top of the sludge, although one may exist in the saltcake, which may drain more effectively.

A somewhat different model is appropriate for those tanks that have no layer of solids on top of the ferrocyanide. Assume that evaporation takes place from the top of the tank solids at a temperature equal to the air temperature (54 °F). The vapor pressure of the saturated evaporating salt solution is 72% of that of pure water, giving a saturated air concentration of 7.8 g/m^3. If a typical tank ventilation rate of 150 cfm (2.3 m^3/s) of air containing 6.9 g/m^3 of water is then brought to saturation, the evaporation rate will be limited to 2 g/s, or 2%/month for a typical sludge depth of 1.0 m. This would not cause excessive water loss over a limited period of time.

C.4.0 EQUILIBRIUM MOISTURE LEVELS

Sludge that is exposed to dry air would eventually come to an equilibrium moisture content. The equilibrium moisture level would depend on the sludge composition, and the temperature and relative humidity at the air-waste interface.

An experimental study conducted by Nuclear Consulting Services, Inc. (reproduced in Attachment 1 to this appendix) on a synthetic sludge yielded the equilibrium data listed in Table C-3.

Table C-2. Predicted Rate of Evaporation from Ferrocyanide Sludge with Hypothetical Active Ventilation.

Tank	Depth[a] (m)		Temperature (°C)	Diffusivity (cm^2/s)[b]	Evaporation rate (g/s)	(%/yr)[c]
	Saltcake	Sludge				
BY-104	1.3	2.6	47	.273	.18	1.0
BY-105	3.8	1.1	44	.268	.05	0.3
BY-106	3.8	2.3	52	.277	.08	0.5
BY-108	0.18	2.1	39	.267	.76	4.9
BY-110	1.6	2.3	48	.288	.18	1.0
BY-111	4.1	.34	28	.249	.02	0.7

[a]From Grigsby et al., 1992, Table 4-23
[b]At mean saltcake temperature
[c]Based on sludge water content of 570 kg/m^3 for U Plant sludge

Table C-3. Equilibrium Free Water Contents at 25 °C (Armstrong et al., Attachment 1).

Relative humidity percent	Equilibrium water content wt. percent
30	4.1
50	10.6
75	31.3
90	65.4

The equilibrium moisture levels shown in Table C-3 represent the minimum theoretical values that could be attained by evaporation. Even at a low relative humidity (30 percent) a potentially significant (4.1 percent) free moisture level is retained. It is noted that the annual average atmospheric relative humidity at the Hanford Site is 54%.

C.5.0 SUMMARY

This brief discussion of moisture retention by ferrocyanide sludge is intended only to provide perspective on this important property. Important aspects from a safety standpoint include the following.

1. Observed moisture contents in waste samples and in simulant sludges are high, ranging from 28 wt% to 70 wt%.

2. Moisture is held in a fine particle matrix as liquid that has a very limited mobility. Significant moisture levels will be retained even in tanks that leak or are saltwell pumped.

3. Moisture loss by evaporation is limited by a number of factors. Minimal controls apparently would be adequate to control evaporative losses to low rates.

C.6.0 REFERENCES

Armstrong, L. L., W. P. Freeman, and J. L. Kovach, 1993, *Ferrocyanide Simulant In-Farm-REV-25 Water Adsorption Isotherm*, NUCON 05NU189/01, Nuclear Consulting Services, Inc., Columbus, Ohio. [Attachment C]

Boyles, V. C., 1990, *Single-Shell Tank Stabilization Record*, WHC-SD-RE-178, Rev. 2, Westinghouse Hanford Company, Richland, Washington.

Grigsby, J. M., D. B. Bechtold, G. L. Borsheim, M. D. Crippen, D. R. Dickinson, G. L. Fox, D. W. Jeppson, M. Kummerer, J. M. McLaren, J. D. McCormack, A. Padilla, B. C. Simpson, and D. D. Stepnewski, 1992, *Ferrocyanide Waste Tank Hazard Assessment - Interim Report*, WHC-SD-WM-RPT-032, Rev. 1, Westinghouse Hanford Company, Richland, Washington.

Simpson, B. C., G. L. Borsheim, and L. Jensen, 1993, *Tank Characterization Data Report: Tank 241-C-112*, WHC-EP-0640, Rev. 1, Westinghouse Hanford Company, Richland, Washington.

Simpson, B. C., G. L. Borsheim, and L. Jensen, 1993, *Tank Characterization Report: Tank 241-C-109*, WHC-EP-0668, Westinghouse Hanford Company, Richland, Washington.

Wong, J. J., 1992, *Test Report on Characterization of Hydraulic and Thermal Properties of Synthetic Ferrocyanide Sludges*, WHC-SD-WM-TRP-102, Westinghouse Hanford Company, Richland, Washington.

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ATTACHMENT C

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Nuclear Consulting Services, Inc.
P.O. BOX 29151 7000 HUNTLEY ROAD
COLUMBUS, OHIO 43229 U.S.A.

TELEPHONE: (614) 846-5710
OUTSIDE OHIO: 1-800-992-5192
TELEX: 6974415
FAX: (614) 431-0858

FERROCYANIDE SIMULANT IN-FARM-REV-25

WATER ADSORPTION ISOTHERM

L. L. Armstrong
W. P. Freeman
J. L. Kovach

Issue Date: 7 October 1993

Performed By:

Nuclear Consulting Services, Inc.

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The following is the final report on the In-Farm-Rev-25 surrogate Ferrocyanide sample water adsorption/desorption experiments performed in the laboratories of Nuclear Consulting Services Inc. in Columbus OH. The tests were performed with as received sample.

DESCRIPTION OF THE EXPERIMENTS AND OBSERVATIONS.

Approximately 1 g samples of the as received material were weighed to 0.1 mg in tared weighing dishes, and uncovered in humidity chambers at 30 %, 50 %, 75 % and 90 % relative humidities. The % RH values are constant based on NIST derived control to +/- 2 %. The humidity chambers were maintained at 25 C +/- 1 C. The humidity chambers were periodically opened, the weighing dishes immediately covered and weighed to 0.1 mg. After weighing, the samples were returned into the humidity chambers and uncovered. The weighings continued until constant sample weights were obtained.

The samples exposed at 30 %, 50 % and 75 % RH all lost weight. The 90 % exposed sample gained weight. After obtaining constant weight on the 50 % and 75 % RH exposed samples, they were transferred to a drying oven for 18 hours at 120 +/- 2 C to determine the reference moisture content of the starting sample and to permit conversion of adsorption isotherm values to "dry" weight. (It is important to point out that both literature data and Hanford site related tests indicate that the 120 C dried sample still contains some "bound" water.)

Prior investigators often refer to "bound" water as crystal water, however the water is probably physically adsorbed in the ferrocyanide lattice, similar to adsorption in zeolitic structures. The 120 C, 18 hours test was selected based on WHC recommendation (to match the existing data base reference). The weight obtained after the 18 hours 120 C drying is used for calculational purposes as the base dry weight.

The 30 % RH and the 90 % RH samples, after reaching constant weight, were switched. The 30 % RH equilibrated sample was transferred into the 90 % RH chamber and the 90 % RH equilibrated sample was transferred into the 30 % RH chamber.

The test weighings continued until the samples were again at equilibrium weight with the appropriate RH. The thus re-wetted or re-dried samples reached the same weight as the original exposure at the same % RH. Therefore, in the ranges measured, there is no observable hysteresis in the water adsorption/desorption tests.

In both the original 90 % RH exposure and in the re-exposure of the 30 % RH equilibrated sample at 90 % RH deliquescence of the sample was observed near its equilibrium weight. The free solution observed was clear and not colored, indicating that only some of the sample components are deliquescent and the ferrocyanide component does not participate in the deliquescence.

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The desorption rates appear to be dependent on the original moisture content versus % RH of exposure difference, i. e. the as is sample exposed to 30 % RH reached moisture equilibrium the fastest, and the one exposed to 75 % RH the slowest. The weight gain at 90 % RH (adsorption rate) was in all cases slower than the weight loss, but the data are disturbed somewhat by the above mentioned deliquescence.

When the 30 % and 90 % RH re-exposed samples reached constant weight gain they were also dried at 120 C at 18 hours to obtain sample reference "dry" weight.

Additional observations during the various % RH exposures. The samples turned somewhat greener upon exposure to lower % RH and appeared grainier than the starting material. The originally 90 % RH exposed sample maintained a creamy bluish green appearance, however, the originally 30 % RH exposed sample when re-exposed to 90 % RH, stayed grainy in appearance, but a color change to bluish green developed, without the sample becoming creamy in appearance.

PRESENTATION OF THE RESULTS.

Original humidity exposure tests:
(Weights are expressed based on as received weights)

TABLE 1

Elapsed Time hours	Cumulative Weight Change, wt % at 30 % RH S-1	50 % RH S-2	75 % RH S-3	90 % RH S-4
7	-40.3	-23.0	-14.4	+ 2.5
24	-50.9	-44.7	-24.1	+10.3
31	-51.0	-46.8	-25.1	+11.3
72	-----	-----	-25.7	-----
96	-51.2	-47.8	-33.2	+27.1
120	-51.2	-47.8	-33.0	+29.8
144	-51.2	-47.8	-33.0	+33.8
168.3	-----	-----	-----	+35.3
196	-----	-----	-----	+35.5
216	-----	-----	-----	+36.1*
254	-----	-----	-----	+36.0*

The * indicates clearly observed deliquescence at 90 % RH. Deliquescence may have initiated earlier but was not observed.

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Hysteresis tests with preexposed material:
(Weights are expressed based on as received weights)

TABLE 2

Elapsed Time hours	Cumulative Weight Change, wt % at original 30 % RH re-exposed at 90 % RH S-1	original 90 % RH re-exposed at 30 % RH S-4
7	-35.2	-22.1
24	-10.9	-50.8
31	- 4.9	-50.9
48	+ 7.0	-51.0
72	+16.9	-51.0
96	+22.8	-51.2
168	+32.9	-51.2
196	+34.1	-----
220	+36.1*	-----

The * indicates clearly observed deliquescence of the 90 % RH exposed sample. Deliquescence may have initiated earlier but was not observed.

Oven drying (120 C for 18 hours) weight losses:

The samples which were used in the various experiments were dried at 120 C as described in the Experiments section. These % weight loss values also correspond to the moisture content of the as received sample on a total sample weight basis.

TABLE 3

Elapsed Time hours	Weight Loss from As Received Weight, wt %			
	S-1	S-2	S-3	S-4
18	-53.3	-53.3	-53.1	-53.0

On the basis of the oven drying tests the original as received sample dry weight basis moisture contents were calculated.

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TABLE 4

	S-1	S-2	S-3	S-4
Starting moisture wt. % of dry wt.	114.3	114.3	113.2	112.8

Adsorbed Water as a Function of % Relative Humidity:

The adsorption data are always described on a dry weight basis. It is important again to emphasize that the values used for dry weight here are not absolute dry weights but those obtained at 120 C, 18 hours oven drying.

TABLE 5

	Relative Humidity %			
	30	50	75	90
Water Adsorbed at Equilibrium, wt. %	4.3	11.9	42.8	189.4
Water Content at Equilibrium wt. % of Total wt.	4.1	10.6	31.3	65.4

The shape of the water adsorption isotherm, on the In-Farm-Rev-25 material follows the Brunauer S. et al. (1938) Type III adsorption isotherm shape with a possible deviation due to deliquescence. While the equations can be derived using the BET equation for the full RH spread of the water adsorption isotherm, and have been found valid for the concentrated salt water mixtures by others also, Braunstein J (1971), a simplified approach is satisfactory to describe the isotherm in a narrower range. The adsorption isotherm plot shown on Figure 1 at 25 C was developed from the water adsorbed at equilibrium obtained at the 30%, 50% and 75% RH corresponding adsorption values.

On the basis of the obtained the water adsorption (on a "dry" weight basis) isotherm, the following equation was developed to describe water adsorbed as a function of relative humidity, in the 30 to 75% range, for the In-Farm-Rev-25 sample:

$$\log(\text{wt.\% water adsorbed}) = 0.02218(\%RH) - 0.03246$$

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EVALUATION OF THE RESULTS AND CONCLUSIONS.

The Ferrocyanide surrogate, In-Farm-Rev-25 sample, exhibits an adsorbent type behavior and it is not a drainable to dry material. Its water content is strongly dependent on the relative humidity to which it is exposed. Even in tanks from which drainable water was removed, the residual saturated salt solution maintains a high % RH, which keeps the layers above it, exposed to the corresponding relative humidity.

As an example, a saturated potassium nitrate solution will exert an 85% RH above it at 50 C, a 90% RH at 30 C and a 93.2% RH at 25 C. In all cases, above saturated salt solutions, the relative humidity increases with decreasing temperature, thus the slow cooling of the tanks improves safe condition, not only by lowering the temperature, but also by increasing the relative humidity and the commensurate moisture content of the material represented by the surrogate tested.

If necessary to increase the moisture content of the stored sludge, it is satisfactory to introduce approximately 50 - 80% RH humid air into the tank to increase the moisture content of the stored solids and liquid water addition (which would have influence on leaks) is not needed. It is not worthwhile to introduce air at higher than approximately 85% RH into the tank due to possible deliquescence developing with the actual aged tank contents also, which could affect leakage from the tank.

The observed, Brunnauer Type III adsorption isotherm, typically describes systems where the heat of adsorption is equal to or slightly less than the heat of liquefaction of the pure adsorbate, in this case water. From this an approximation of the energy input required to desorb the water from the solids can also be estimated. However, the energy input required to desorb the water also has to be considered when evaluating the energetics of the material. This is a significantly higher energy input than, what would be the case if it was assumed that the water was removed solely by drainage.

It is important to understand also that even in neat sodium nitrate-water systems the heat of vaporization of water is also higher than for pure liquid water by approximately 10%.(Haug 1965),(Peleg 1967),(Tripp 1969).

The significant quantity of adsorbed water also ameliorates the conditions postulated by "hot spot" development. In subsurface, postulated heating the of the sludge, there would be a steam rather than a stable gas bubble developing, and the surrounding area would be exposed to higher than normal relative humidity, thus reducing the propagation mechanism.

It cannot be assured that the actual sludge contents would behave identically to the surrogate material on which the above experiments were performed and it is recommended that at least on one of the tank samples, preferably, from the one represented by the In-Farm-Rev-25 surrogate, water adsorption isotherms would also be developed.

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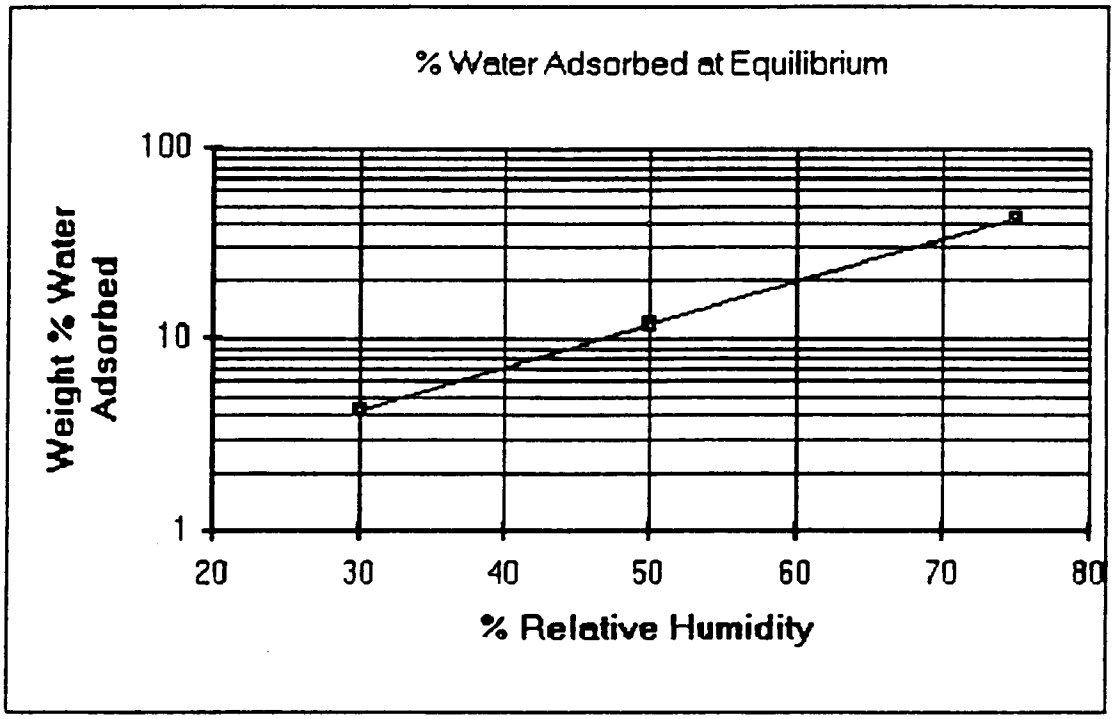
FIGURE 1
WATER ADSORPTION ISOTHERM ON IN-FARM-REV-25 SAMPLE AT 25 C
IN THE 30 - 75 % rh RANGE



Raw data for the experiments is maintained at NUCON in file 05NU189/01.
The NUCON chain of custody number for the sample is Log #0993-18
All measurements standards are NIST traceable.
The work was performed and reviewed by L.L.Armstrong, W.P Freeman and J.L.Kovach all ANSI Level III personnel.

REFERENCES

Brunauer,S.,Emmett,P.H.,and Teller,E.(1938) J.Am.Chem.Soc. 60,309

Braunstein,J.(1971)in IONIC INTERACTIONS,Vol 1,p195-8. Acad.Press Haug,H. & Albright,L.F.(1965) IEC Proc.Design.Dev. 4,241.

Peleg,M.(1967) J. Phys. Chem. 71, 4553.

Tripp,T.B. & Braunstein,J.(1969) J. Phys. Chem. 73.1984.

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APPENDIX D

DECAY HEAT DISSIPATION IN FERROCYANIDE TANKS

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APPENDIX D

DECAY HEAT DISSIPATION IN FERROCYANIDE TANKS

D.1.0 DESCRIPTION OF SAFETY ISSUE

The decay of radionuclides contained in ferrocyanide waste (primarily ^{137}Cs and ^{90}Sr) is accompanied by the production of heat energy. An effect of decay heat is to cause waste temperatures to be higher than ambient temperatures. At thermal equilibrium, steady state temperature gradients within the waste cause heat to flow to boundaries (tank wall or waste surface), and to the surrounding soil. Temperature gradients in soil cause most of the heat to flow to the above-ground atmosphere; a small fraction flows downward to the water table. ^{137}Cs and ^{90}Sr have half-lives of approximately 30 yr so decay heat loads are now less than 50% of that when waste was put into the tanks.

From a safety standpoint, it is important to know if decay heat could raise waste temperature to reaction threshold temperatures. Pertinent information on this issue is summarized in this appendix.

D.2.0 DECAY HEAT LOADS

Several methods can be employed to obtain estimates of decay heat loads in ferrocyanide tanks; estimates for four different methods are listed in Table D-1. Technical bases for these are described as follows.

Heatloads Based on Measured Headspace Air Temperatures

Steady-state heat flow is proportional to the temperature gradient across the soil overburden as described in Equation D-1.

$$Q = \frac{k\ A(T_a - T_s)}{F\ \Delta Z} \qquad \text{(D-1)}$$

Table D-1. Thermal Characteristics of Ferrocyanide Tanks.

Tank	Depth of Solids[a] (m)	Maximum Temperature[b] (°C)	Estimate of heat load (Kw)				
			McLaren[c]	Crowe[d]	TRAC[a]	Borsheim Simpson[a]	Hanlon[b]
BY-103	3.9	28		1.6	4.7	2.3	2.5
BY-104	3.9	54	2.3	2.6	4.1	2.9	1.6
BY-105	4.8	50	1.9	2.6	3.8	1.3	0.97
BY-106	6.1	54	2.6	3.0	4.7	3.2	0.97
BY-107	2.7	35		2.6	1.9	2.1	4.3
BY-108	2.3	43	2.1	2.7	1.6	2.7	6.7
BY-110	3.9	48	1.9	2.0	4.7	3.0	7.4
BY-111	4.4	30	1.1	1.6	4.7	0.2	10.0
BY-112	2.9	32		1.9	0.9	0.1	< 3.
C-108	0.8	22		1.7	0.2	0.3	< 3.
C-109	0.8	26	1.6	2.1	0.02	0.5	1.1
C-111	0.7	21		1.9	0.6	0.1	< 3.
C-112	1.2	26	1.7	2.2	0.3	0.6	< 3.
T-107	1.8	20		0.9	0.2	0.1	< 3.
TX-118	3.4	18		1.3	11.	---	1.4
TY-101	1.3	25		0.9	0.1	0.4	< 3.
TY-103	1.7	18		1.2	1.4	0.6	< 3.
TY-104	0.6	16		0.9	0.1	0.2	< 3.

[a]Grigsby et al. 1992, Table 4-34.
[b]Hanlon 1993
[c]McLaren 1992; Dickinson et al. 1993, Appendix A. Published values were corrected by multiplying by 1.6
[d]Crowe et al. 1993

Where:

Q = Heat flow, Btu/hr
k = Thermal conductivity of overburden, Btu/hr °F ft
A = Cross-sectional area of tank dome, ft^2
T_a = Temperature of air in tank headspace, °F
T_s = Temperature of overburden at ground level, °F
F = A constant
ΔZ = Average burial depth for tank dome, ft.

The factor F accounts for the fraction of total heat that flows upward through the tank dome as well as the small temperature difference between the headspace air and tank dome.

A parametric study done for the present document by one of the authors (J. M. McLaren) was carried out with the HEATING7 (Childs 1991) computer code. The three-dimensional model was configured to represent a buried waste tank with boundary conditions at the ground-air interface and at the ground water level 200 ft below grade. Heat flow in all directions was accounted for. Results from these parametric runs demonstrated that the factor F in Equation D-1 varied less than $\pm 4\%$ as waste depth and heat source distribution were varied over broad ranges. These results, along with studies that show airspace temperature to be quite uniform throughout the headspace (Wood 1993) provide technical support for the validity of Equation D-1.

Head loads for all ferrocyanide tanks have been calculated from measured airspace temperature by Crowe et al. 1993. Results are listed in Table D-1. As indicated, calculated head loads fall in the range of 0.9 to 3.0 kw.

While a detailed error analysis has not been carried out, a brief review of potential errors in inputs to Equation (D-1) suggests that error bands of ± 30 percent would be appropriate for the decay heat loads in Table D-1 attributed to Crowe et al. 1993.

Heatloads Based on Inventory of Radionuclides

Head loads calculated from the inventory of ^{137}Cs and ^{90}Sr based on historical process records (Grigsby et al. 1992) provide an independent estimate. Values are reported in Table D-1 separately for inventories from TRAC records and those recalculated for the ferrocyanide sludge by Borsheim and Simpson 1992. Comparisons of inventory-based heat loads with those of Crowe et al. 1993 show reasonable agreement for most tanks. The TRAC estimate shows the greatest discrepancy as compared to other values, and is considered less accurate than the Borsheim and Simpson estimate. Recent samples taken from tanks C-112 (Simpson et al. 1993a) and C-109 (Simpson et al. 1993b) yielded nuclide concentrations that lead to calculated heat loads of 2.2 kw and 2.8 kw respectively. These inventory-based estimates agree well with those of Crowe et al. 1993 for these tanks.

Heatloads Based on Analysis of Temperature Profiles

McLaren (1991 and 1992) has calculated heat loads for selected tanks by trial-and-error fit to measured vertical temperature profiles. It is now realized that McLaren's original calculations used too low a value for the conductivity of soil above the tanks. The magnitude of the correction required has been reviewed by one of the authors (J. M. McLaren), and has been assigned a value of 1.6. This factor, 1.6, has been applied to the original values published by McLaren and the corrected values have been listed in Table D-1. McLaren's adjusted values agree reasonably with those of Crowe et al. and of Borsheim and Simpson (1991).

Comparison with Earlier Estimates

The frequently published heat loads (Hanlon 1993) are also listed in Table D-1 for comparison. While most of Hanlon's heat loads are consistent with the more accurate recent estimates listed in Table D-1, values cited by Hanlon 1993 for tanks BY-108 and BY-111 are unrealistically high. These high values are based on earlier analyses of water evaporation and are judged to be of lower accuracy than the more recent estimates.

Passive Cooling Mechanisms

The heat loads in all ferrocyanide tanks are low; the highest best-estimate heat load is 3.0 kw (Crowe et al. 1993) for tank BY-106. These low heat loads are distributed over a large tank, 75 ft in diameter, so heat fluxes are very low. Furthermore, heat removal is entirely by the passive mechanisms of conduction through the sludge and soil and natural convection and radiation through the gas space. There is no forced coolant flow or any active cooling mechanism which could fail. Nor does cooling depend on the evaporation or condensation of water. Two different calculations illustrate this. First, for the present passively ventilated tanks the evaporation rate of 50 gal/yr (Appendix C) removes only 14 watts of heat, a negligible fraction of decay heat. Second, calculations illustrate that the head load can be transferred through the tank headspace with very low temperature differences (1 to 2 °F) by radiation and dry convection (Crowe et el. 1993).

D.3.0 WASTE TEMPERATURES

The highest temperature measured at any location in each tank is also given in Table D-1. These temperatures range from 16 to 54 °C, which is much lower than that required for significant chemical reaction. These temperatures were measured in the vertical plane by one or two thermocouple trees in each tank, and higher temperatures are possible at other locations. A rough estimate of the magnitude of the possible variation of temperature with

lateral position may be obtained from the tanks containing two thermocouple trees or one tree plus measurements in a liquid observation well (LOW). The difference in peak temperatures between the two trees ranges from 1 to 8 °C, as seen in Table D-2 (Hanlon 1993). In all these tanks but C-109 and C-112, the two thermocouple trees were at different radii, and the higher temperature was closer to the tank centerline, as would be expected.

The temperatures measured in the ferrocyanide tanks are slowly decreasing on a year-to-year basis. This is illustrated in Figures D-1 to D-4 in which the temperatures measured near the bottom of the tank are shown for the four ferrocyanide tanks with the highest temperatures. The line on these graphs marked "-1.7 °F/year" is the rate of decrease calculated for decay of ^{137}Cs and ^{90}Sr with 30-year half-lives, a sludge temperature of 54 °C and a mean atmospheric temperature of 13 °C. The general trend of decreasing temperature is seen to be that which would be expected from radioactive decay.

Table D-2. Comparison of Temperatures Measured at Two Positions.

Tank	Peak Temperature (°F)		Difference	
	Tree A	Tree B	°F	°C
BY-104	129	115	14	8
BY-105	122	114	8	4
BY-110	119	109	10	6
BY-111	86	82	4	2
BY-112	90	81	9	5
C-109	78	74	4	2
C-112	78	77	1	1

D.4.0 SUMMARY OF DECAY HEAT DISSIPATION

The following statements summarize conclusions regarding decay heat dissipation in ferrocyanide Watch List tanks.

- The decay heat loads in all the ferrocyanide tanks are relatively low, being only a few kilowatts.
- Heat removal is entirely by passive mechanisms and does not rely significantly on evaporative cooling.

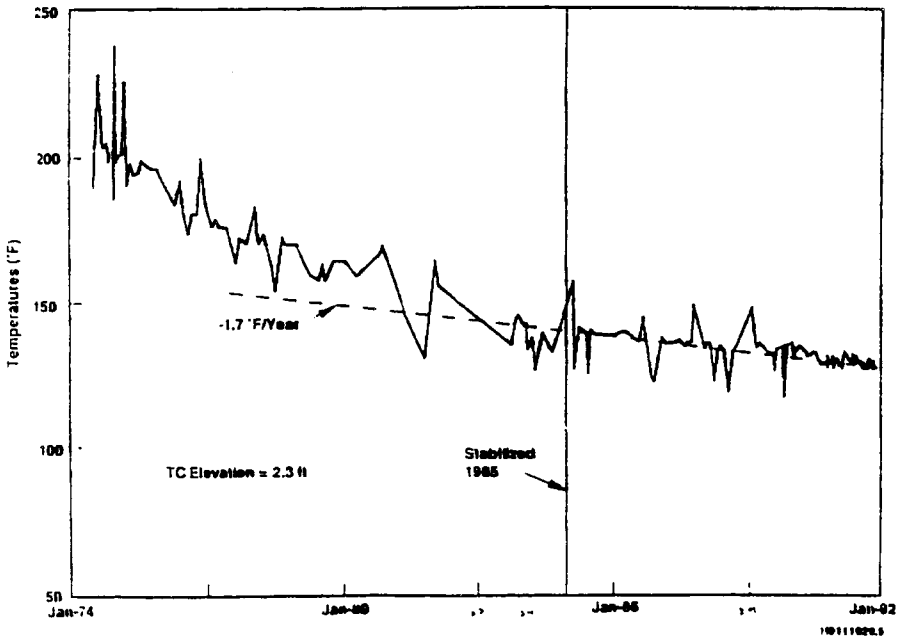

Figure D-1. Tank 241-BY-104 Temperature.

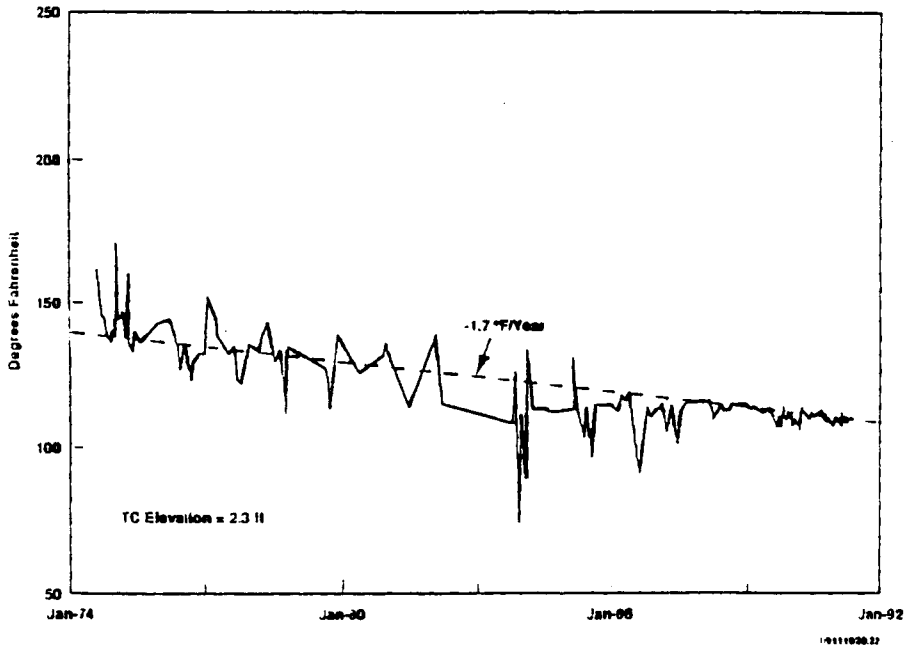

Figure D-2. Tank 241-BY-105 Temperature.

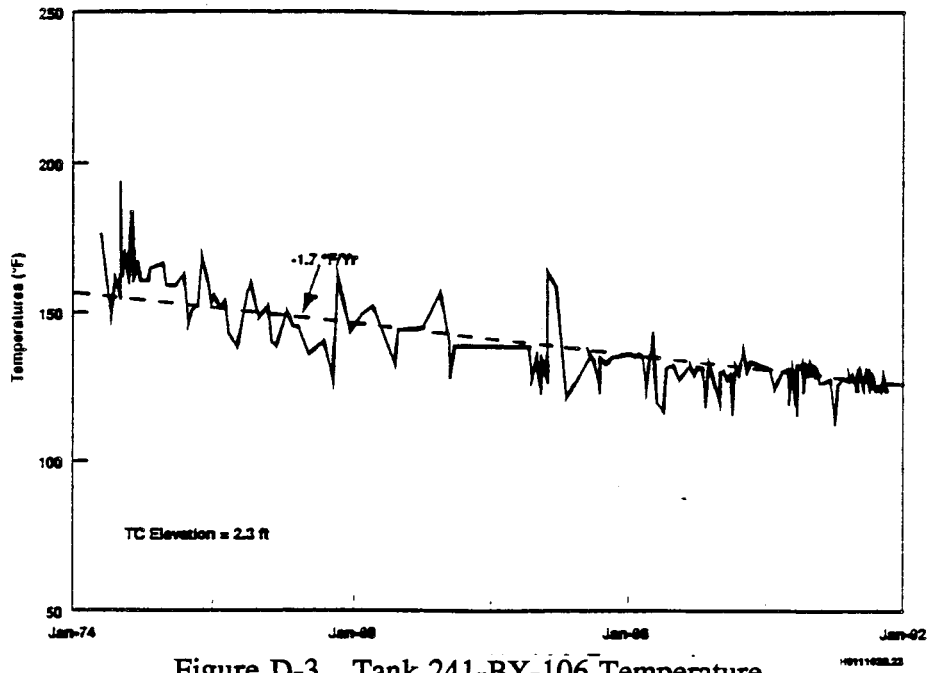

Figure D-3. Tank 241-BY-106 Temperature.

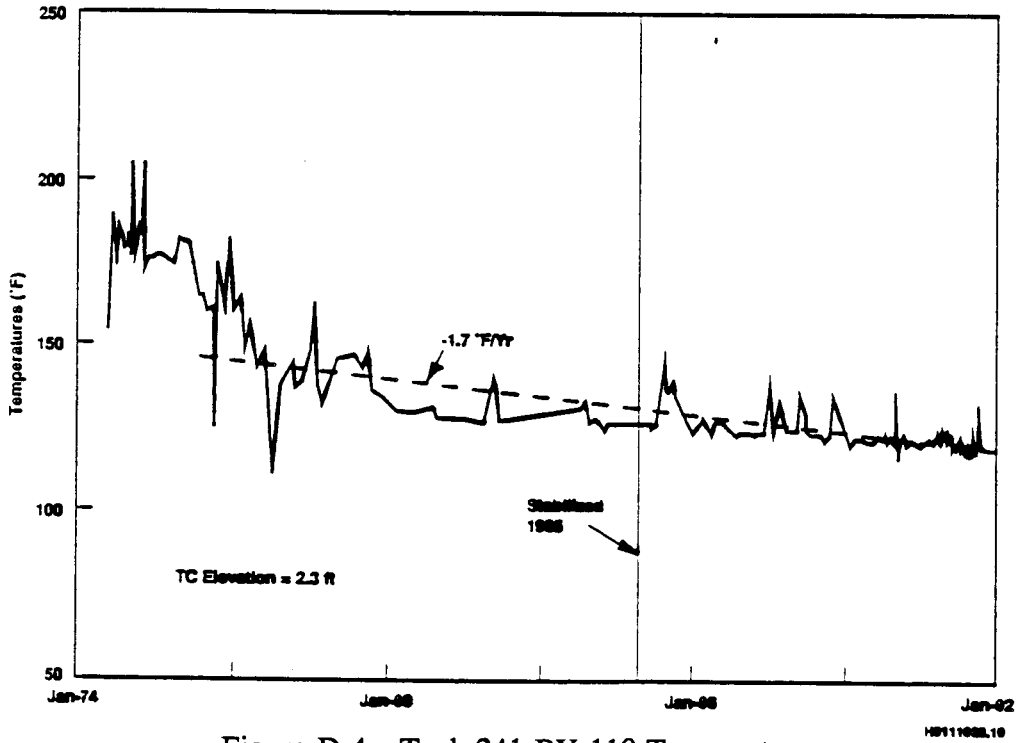

Figure D-4. Tank 241-BY-110 Temperature.

- The resulting measured sludge temperatures are low, being all no greater than 54 °C, and are decreasing. Data from seven tanks with two thermocouple trees do not suggest large lateral temperature variations.

D.5.0 REFERENCES

Borsheim, G. L. and B. C. Simpson, 1991, *Assessment of the Inventories of the Ferrocyanide Watch List Tanks*, WHC-SD-WM-ER-133, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Childs, K. W., 1991, "Heating 7.1 User's Manual," K/CSD/TM-96, ORNL Martin Marietta, Oak Ridge, Tennessee.

Crowe, R. D., M. Kummerer, and A. K. Postma, 1993, *Estimate of Heat Load in Waste Tanks Using Average Vapor Space Temperature*, WHC-EP-0709, Westinghouse Hanford Company, Richland, Washington.

Dickinson, D. R., J. M. McLaren, G. L. Borsheim, and M. D. Crippen, 1993, *Credibility of Dryout in Ferrocyanide Sludge Due to Local Hot Spots*, WHC-EP-0648, Westinghouse Hanford Company, Richland, Washington.

Grigsby, J. M., D. B. Bechtold, G. L. Borsheim, M. D. Crippen, D. R. Dickinson, G. L. Fox, D. W. Jeppson, M. Kummerer, J. M. McLaren, J. D. McCormack, A. Padilla, B. C. Simpson, and D. D. Stepnewski, 1992, *Ferrocyanide Waste Tank Hazard Assessment - Interim Report*, WHC-SD-WM-RPT-032, Rev. 1, Westinghouse Hanford Company, Richland, Washington.

Hanlon, B. M., 1993, *Tank Farm Surveillance and Waste Tank Summary Report for June 1993*, WHC-EP-0182-63, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

McLaren, J. M., *Heat Load and Thermal Characteristics Determination for Selected Tanks*, WHC-SD-WM-ER-139, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

McLaren, J. L., 1991, *Single-Shell Tank 104-BY Thermal Hydraulic Analysis*, WHC-EP-0521, Westinghouse Hanford Company, Richland, Washington.

Simpson, B. C., G. L. Borsheim, and L. Jensen, 1993a, *Tank Characterization Data Report: Tank 241-C-112*, WHC-EP-0640, Rev. 1, Westinghouse Hanford Company, Richland, Washington.

Simpson, B. C., G. L. Borsheim, and L. Jensen, 1993b, *Tank Characterization Report: Tank 241-C-109*, WHC-EP-0668, Westinghouse Hanford Company, Richland, Washington.

Wood, S. A., 1993, *Cover Gas Space Analysis for Tank 241-C-109*, WHC-SD-WM-ER-183, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

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APPENDIX E

POSSIBILITY OF LOCAL DRYOUT OF FERROCYANIDE SLUDGE BY HOT SPOTS

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APPENDIX E

POSSIBILITY OF LOCAL DRYOUT OF FERROCYANIDE SLUDGE BY HOT SPOTS

E.1.0 AREA OF CONCERN

The ferrocyanide sludge is wet, as discussed in Appendix C, and therefore not capable of sustaining a chemical reaction. However, it has been suggested that a local dry spot might be produced by a concentration of decay heat. If such a situation were credible, a local region of dry fuel could exist in a nominally wet tank, and a chemical reaction might be possible. A hot spot severe enough to dry out some region of the sludge might also heat it sufficiently to initiate a reaction.

E.2.0 TANK HEAT LOADS

The total decay heat loads, (^{90}Sr and ^{137}Cs) in each tank are given in Appendix D. These heat loads are low, being only a few kilowatts in a 75-foot diameter tank. This is easily removed by conduction unless highly concentrated.

E.3.0 MECHANISMS OF DRYOUT BY HOT SPOT

A local concentration of heat might produce a dry region in either of two ways, which are discussed separately.

1. Boiling of water with convection flow of water vapor under a pressure gradient. Temperatures above the boiling point are required.

2. Low-temperature evaporation with transport of water vapor by diffusion through the sludge and saltcake.

E.4.0 DRYOUT BY BOILING

E.4.1 HEAT CONCENTRATION REQUIRED TO REACH BOILING POINT

The heat generation rate within a hot spot of given size, shape, and location within a given waste tank that is required to produce a peak temperature equal to the boiling point of the sludge liquid (120 °C) has been calculated using two- and three-dimensional heat-transfer codes for a range of hot spots (Dickinson et al. 1993). The worst case (easiest to reach 120 °C) was found to be a hot spot near the bottom of tank BY-104 having an equidimensional shape. The concentration of decay heat required for the peak temperature of such a hot spot to reach 120 °C is shown in Figure E-1 as a function of hot spot diameter. The required concentration is expressed both as a concentration factor, the ratio of heat generation per unit volume in the hot spot to that in the tank as a whole, and as the fraction of the total tank heat load which must be concentrated into the hot spot. A hot spot smaller than 1.25 m would require concentrating the radionuclides by a factor of over 100, while a larger hot spot would require more than 10 percent of the total tank heat load.

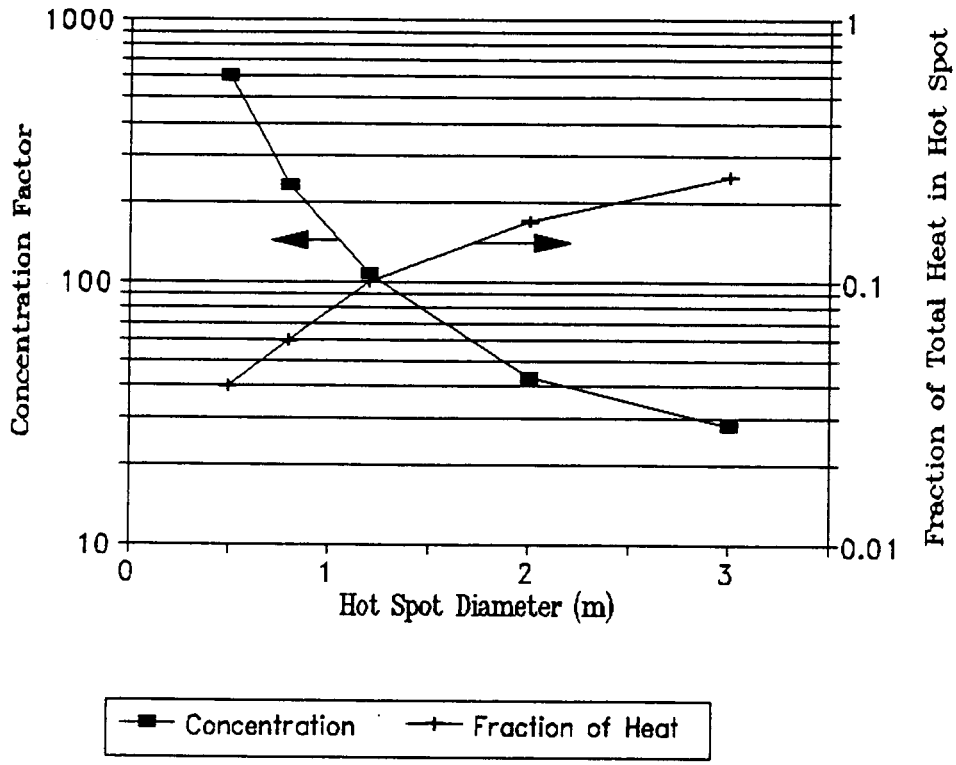
E.4.2 FURTHER BARRIERS AGAINST DRYOUT

Simply reaching the boiling point is not sufficient to cause dryout of a significant volume of sludge. Water flow driven by gravity and capillary forces will tend to rewet and cool any incipient dry spot. No credit is being taken for this effect at present, because it has not been adequately analyzed.

The ferrocyanide sludge contains fine particles, and will respond to internal steam generation by homogeneous flow of the sludge rather than by displacement of water from the pores in a bed of solids. This has been shown both theoretically and experimentally by Epstein and Fauske (1993). The abstract of their report states:

The conditions under which ferrocyanide waste sludge flows as a homogeneous non-Newtonian two-phase (solid precipitate-liquid) mixture rather than as a liquid through a porous medium (of stationary precipitate) are examined theoretically, based on the notion that the preferred rheological behavior of the sludge is the one which imposes the least resistance to the sludge flow. The homogeneous two-phase mixture is modeled as a power-law fluid and as a Bingham-like fluid and simple criteria are derived that show that the homogeneous rheology (power-law or Bingham-like sludge-flow) is a much more likely flow situation than the porous medium model of sludge flow. Experiments have been carried out involving gas and vapor void growth in Kaolin particle-water mixtures and in synthetic ferrocyanide In Farm 1 flow sheet material. In all cases the hydrodynamic response of these simulant-sludge materials was clearly homogeneous, in agreement with the conclusion derived from the theoretical study.

Figure E-1. Requirements for Dryout (120 °C).



The implication of this finding is that vaporization of water will produce a steam bubble without producing dry sludge. Expansion of the bubble will expand the surrounding high-heat-generating sludge into a geometry with a larger surface, which is more easily cooled. Therefore, such an event would tend to be self limiting with no significant dryout.

E.5.0 LOW-TEMPERATURE EVAPORATION

If the region between the hot spot and the tank surface is dry enough to contain connected gas porosity, a hot spot can promote evaporation of water at temperatures below the boiling point. In such a case, however, the water vapor must be transferred to the head space by diffusion through the pores in the solid bed. Because diffusion is slow, the evaporation rate will be low and there will be time for in flow of water under gravitational and capillary forces to replace the water that is lost. Because the water evaporated from the warm regions will condense in cool regions, no net water loss would occur beyond that discussed in Appendix C for uniform evaporation.

A quantitative analysis is needed to bound possible water loss or dryout by this mechanism. Such work is planned.

E.6.0 POSSIBLE MECHANISMS FOR CONCENTRATIONS OF HEAT GENERATION

Several mechanisms were identified which might tend to concentrate the heat-generating radionuclides. These were analyzed to determine whether any could produce the high degree of concentration identified in Section 4.1 as required for dryout. The work of Dickinson et al. (1993) is summarized below.

E.6.1 GRAVITATIONAL SETTLING

Preferential settling of particles containing radionuclides, especially ^{90}Sr, is possible. However, sludge was added to the tanks in several batches which settled before the next addition. Hence, settling would produce concentration in several layers distributed over the sludge depth. More important, even concentration into a single-horizontal layer would not produce temperatures approaching boiling.

The ferrocyanide slurries added to the waste tanks were sufficiently mobile that they spread rapidly over the tank area before settling occurred.

E.6.2 CONVECTION CURRENTS

In general, convection currents would act to promote mixing and reduce high-level concentrations. Stringent conditions would have to be satisfied for convection currents to produce concentrations.

1. Cesium or strontium must be rendered soluble.

2. A mechanism must be in place to precipitate and retain radionuclides in some local region.

3. These conditions for precipitation must be absent over the flow paths leading to the region of concentration.

Because solubility generally increases with temperature, the expectation is for convection currents to dissolve radionuclides from warm regions and precipitate them in cooler regions, thereby alleviating any hot spots.

The magnitude of convection currents which can develop is limited by the low permeability of the sludge [on the order of $10^{-14}m^2$, (Jeppson and Wong 1993)] and by the small driving force available from temperatures or concentration gradients.

A detailed analysis of the possible effects of convection currents in a ferrocyanide tank was performed by McGrail et al. (1993). Computer simulations of fluid, heat, and mass transport predict that fluid convection will occur in this waste because of density-gradients induced from chemical composition differences and/or thermal gradients. The predicted velocities were approximately 3 m/yr for a sludge with 50 percent porosity, using a viscosity of 0.002 Pa • s, permeability of $3.55 \times 10^{-14}m^2$, and assuming a 50 percent density difference between a fluid overlying the waste and the interstitial fluid. Convective velocities were much smaller for the case of thermal buoyancy-driven flow, approximately 10^{-5} to 10^{-2} m/yr depending on the assumed heat generation rate and hydraulic conductivity of the waste. A model was developed to determine the extent of redistribution of ^{137}Cs as a result of diffusion and convection in the waste over a 30 yr period. Assuming arbitrarily an increasing solubility for $Cs_2NiFe(CN)_6$ as a function of increasing temperature, the results show that ^{137}Cs partially redistributes in a thin layer at the colder top of the tank. The effect of the mass redistribution is to lower the predicted centerline tank temperature by about 10 °C over the case where the ^{137}Cs is assumed to be uniformly distributed. Assuming a retrograde temperature dependence for the solubility of $Cs_2NiFe(CN)_6$ results in complex precipitation patterns in the tank. Simulations of fingering and thermal buoyancy-driven convective flows with retrograde solubility were characterized by the formation of sharp precipitation fronts. Because of the larger flow velocity for fingering convection, these simulations showed the largest increase in ^{137}Cs concentrations near the front which was about a factor of 10 over the tank average.

However, the mass redistribution had a minimal effect on the tank temperature profile with peak temperatures increasing by only about 5 °C. Consequently, redistribution of the ^{137}Cs as a result of aqueous diffusion and natural convection is of no concern in generating a localized area or hot spot that could lead to a propagating exothermic reaction.

E.6.3 DEGRADED THERMAL CONDUCTIVITY

Increased local temperatures without a concentration of the heat source could be produced by a local reduction of thermal conductivity due to bubbles of radiolytic gas. However, void fractions of sufficient magnitude over a sufficient volume to give temperatures of concern would produce an unstable buoyant region, which would rise to the surface when it would be more easily cooled.

E.7.0 RADIONUCLIDES MEASURED IN TANK SAMPLES

Core samples have been obtained from ferrocyanide tanks 241-C-109 and C-112. These provide direct measurements of the distribution of ^{90}Sr and ^{137}Cs. Cores were sampled through these risers in each tank and broken into subsegments to measure vertical variation. These data are summarized in Tables E-1 and E-2. The high concentrations of ^{90}Sr near the top of these two tanks is believed to result from later additions of strontium-rich waste from the Strontium Semiworks plant. These additions were made only to the C-Farm ferrocyanide tanks. Aside from this effect, the variations of ^{90}Sr and ^{137}Cs concentrations are modest.

Water digestion analyses for ^{137}Cs were generally less than 1 percent of the corresponding fusion analyses, indicating that cesium is present in insoluble form.

The vertical profiles of local ^{137}Cs concentrations have been measured in several ferrocyanide tanks by spectral gamma scans (Grigsby et al. 1992). These show ratios of peak to average concentrations of 1.2 to 3.1.

Table E-1. Analyses of C-112 Core Samples, μCi/g (Simpson et al. 1993a).

Sample	Core 34		Core 35		Core 36	
	^{137}Cs	^{90}Sr	^{137}Cs	^{90}Sr	^{137}Cs	^{90}Sr
1 C (top)	-	-	-	-	560	1,900
1 D	240	1,300	700	3,200	1,200	15
2 A	-	-	-	-	880	20
2 B	610	4,900	-	-	530	70
2 C	800	1,100	-	-	100	140
2 D (bottom)	510	2,500	-	-	40	200

Table E-2. Analyses of Tank 241-C-109 Core Samples, μCi/g (Simpson et al. 1993b).

Sample	Core 47		Core 48		Core 49	
	^{137}Cs	^{90}Sr	^{137}Cs	^{90}Sr	^{137}Cs	^{90}Sr
1 B (top)	340	4,600	1,200	150	120	2,400
1 C	770	470	1,170	120	350	200
1 D	950	200	1,030	190	700	190

E.8.0 PRE-EXISTENT VERSUS DEVELOPING HOT SPOTS

A distinction should be made between hot spots resulting from radionuclide distributions or other conditions that have existed for many years and those because of presently changing conditions. Fauske (Appendix C of Grigsby et al. 1992) has shown that a pre-existing hot spot severe enough to lead to thermal runaway does not exist in the ferrocyanide waste tanks. Fauske shows that the characteristic response time for passive cooling of the tank waste is short compared to the time since the last change in tank conditions (pumping). Because no runaway has occurred, the characteristic time for adiabatic runaway must be greater than the time since the last tank change. Thus the time for adiabatic runaway is long compared to the characteristic cooling time. This satisfies the usual criteria used in the chemical process industry to ensure passive safety.

The dominant radionuclides that contribute to heating (^{137}Cs and ^{90}Sr) have half-lives of about 30 years. The ferrocyanide additions were completed 35 years ago, and other additions about 17 years ago. Therefore, any hot spots created by these operations would now have only about 45 to 68 percent of their original heat generation, and would be unlikely to cause a problem now if they did not do so in the past.

For runaway to occur at present or future time, it would be necessary to have a concentration mechanism either take place at the present time or become initiated by future changes in tank conditions.

E.9.0 CONCLUSIONS

Some inhomogeneity of the tank heat load is to be expected. However, this variation will be limited in both the magnitude of the concentration pools and the volume over which they exist. The consideration of possible concentration mechanisms fails to disclose any which could produce, or even approach, a concentration of the severity and volume found to be necessary to reach the boiling point. Similarly, heat transfer calculations show that the ^{90}Sr and ^{137}Cs concentration profiles measured in tanks 241-C-109 and C-112 are not capable of producing local temperatures reaching the boiling point. It may therefore be concluded that dryout by boiling is not credible.

Formation of a dry spot near the surface of wet sludge by local heating to temperatures below boiling has not yet been sufficiently analyzed to rule out this possibility. This event would require migration of water vapor to the surface by diffusion through the pores in the dried sludge and saltcake. Because such diffusion is slow, it appears likely that the evaporation rate would be low enough that the water evaporated would be replaced by capillary inflow. An effort is currently underway at WHC to quantify diffusional water loss.

E.10.0 REFERENCES

Dickinson, D. R., J. M. McLaren, G. L. Borsheim, and M. D. Crippen, 1993, *Credibility of Dryout in Ferrocyanide Sludge Due to Local Hot Spots*, WHC-EP-0648, Westinghouse Hanford Company, Richland, Washington.

Epstein, J. M. and H. K. Fauske, 1993, *A Theoretical and Experimental Study of Waste Tank Sludge Rheology Within a Hot Spot or During Draining*, FAI/93-83, Fauske and Associates, Inc., Burr Ridge, Illinois.

Grigsby, J. M., D. B. Bechtold, G. L. Borsheim, M. D. Crippen, D. R. Dickinson, G. L. Fox, D. W. Jeppson, M. Kummerer, J. M. McLaren, J. D. McCormack, A. Padilla, B. C. Simpson, and D. D. Stepnewski, 1992, *Ferrocyanide Waste Tank Hazard Assessment - Interim Report*, WHC-SD-WM-RPT-032, Rev. 1, Westinghouse Hanford Company, Richland, Washington.

Jeppson, D. W. and J. J. Wong, 1993, *Ferrocyanide Waste Simulant Characterization*, WHC-EP-0631, Westinghouse Hanford Company, Richland, Washington.

McGrail, B. P., D. S. Trent, G. Terrones, J. D. Hudson, and E. T. Michener, 1993, *Ferrocyanide Safety Program: Computational Analysis of Fluid Flow and Zonal Deposition in Ferrocyanide Single-Shell Tanks*, PNL-8876, Pacific Northwest Laboratory, Richland, Washington.

Simpson, B. C., G. L. Borsheim, and L. Jensen, 1993a, *Tank Characterization Data Report: Tank 241-C-112*, WHC-EP-0640, Rev. 1, Westinghouse Hanford Company, Richland, Washington.

Simpson, B. C., G. L. Borsheim, and L. Jensen, 1993b, *Tank Characterization Report: Tank 241-C-109*, WHC-EP-0668, Westinghouse Hanford Company, Richland, Washington.

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