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Assessment of Chemical Vulnerabilities in the Hanford High-Level Waste Tanks

J. E. Meacham et al.

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Abstract: The purpose of this report is to summarize results of relevant data (tank farm and laboratory) and analysis related to potential chemical vulnerabilities of the Hanford Site waste tanks. Potential chemical safety vulnerabilities examined include spontaneous runaway reactions, condensed phase waste combustibility, and tank headspace flammability. The major conclusions of the report are the following: Spontaneous runaway reactions are not credible; condensed phase combustion is not likely; and periodic releases of flammable gas can be mitigated by interim stabilization.

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Assessment of Chemical Vulnerabilities in the Hanford High-Level Waste Tanks

H. K. Fauske
Fauske and Associates, Inc.

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**ASSESSMENT OF CHEMICAL VULNERABILITIES
IN THE HANFORD HIGH-LEVEL WASTE TANKS**

H. K. Fauske

ABSTRACT

The purpose of this report is to summarize the analyses of relevant data (tank farm and laboratory) related to potential chemical vulnerabilities of the Hanford Site waste tanks. Potential chemical safety vulnerabilities examined include spontaneous runaway reactions, condensed phase waste combustibility, and tank headspace flammability. Operational safety and aspects related to tank intrusive activities and remediation are beyond the scope of this report.

The significant observations made in this report are the following:

- Spontaneous runaway reactions (no ignition source required).
 - The Hanford waste has remained stable for periods much longer than the waste characteristic cooling times. This demonstrates that the chemical heat is removed safely.
 - The waste characteristic cooling times are not adversely affected by waste dryout.
 - Post interim stabilization waste temperatures in passively ventilated tanks continue to decline consistent with radionuclide decay.
- Condensed phase combustion.
 - Credible internal ignition sources cannot initiate organic solvent fires or condensed phase combustion reactions. This is true even for stoichiometric fuel-oxidizer conditions.
 - Testing and analysis show that sparks, shocks, and impacts lack sufficient energy to initiate combustion. Robust and/or sustained energy sources are required.
 - The waste is aging to an overall less energetic state and interim stabilization operations have decreased fuel concentrations in the single-shell tanks.

- Headspace flammability.
 - Tank headspaces appear to be well mixed and sampling data indicate that steady-state flammable gas concentrations are much lower than the lower flammability limit (LFL).
 - Episodic gas release events (GREs) observed in tanks with large amounts of supernatant can result in high flammable gas concentrations. Interim stabilization prevents GREs; no GREs are known to have occurred in stabilized tanks.
 - Concerning the difficulty of ruling out credible internal ignition sources (such as sparks), the occurrence of significant GREs requires mitigation.

- Lightning.
 - It appears difficult to deterministically eliminate lightning as an external ignition source. However, the probability of a lightning strike initiated event is low. Taken together with the low probability of challenging the tank integrity in case of a solvent fire or the low probability of satisfying condensed-phase combustible conditions, this suggests that external ignition sources do not represent a significant threat.

Based on these observations, it is concluded that the condensed phase of the waste is substantially more stable and more difficult to ignite than originally thought. Episodic gas release events leading to potential concentrations in excess of flammability limits can be mitigated by removing supernatant from the tanks.

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1.0 INTRODUCTION

Several potential chemical safety vulnerabilities have been identified for Hanford Site high-level waste tanks. Postulated scenarios include:

- gaseous combustion of flammable hydrogen mixtures in the tank head spaces - highlighted by the tank SY-101 behavior,
- tank head space organic solvent fires - highlighted by the floating organic layer in tank C-103,
- condensed-phase spontaneous bulk runaway chemical reactions similar to the 1957 Kyshtym incident¹ in tanks known to contain ferrocyanide and/or organic complexants, and
- condensed-phase combustion of ferrocyanide and/or organic complexants.

The following sections examine phenomenology associated with these chemical safety vulnerabilities. Section 2.0 reviews tank waste characteristics with respect to fuel content, tank headspace mixing, decay heat removal, and chemical heat removal. Section 3.0 examines the role of supernatant in episodic releases of flammable gas. Section 4.0 examines the credibility of spontaneous runaway or combustion of ferrocyanide waste. Section 5.0 addresses spontaneous runaway of organic complexant waste and the ignition requirements for combustion of organic complexants and organic solvents.

A brief description and interpretation of the Kyshtym incident is provided in Appendix A.

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2.0 TANK FARM AND WASTE CHARACTERISTICS

The waste tank farm at Hanford consists of 177 tanks including 28 double shell tanks (DSTs) and 149 single shell tanks (SSTs). Of the SSTs, 133 are passively ventilated (PS), and 113 are interim stabilized (IS). Interim stabilization operations continue. Various waste forms of interest are illustrated in Figure 2-1 (Hanlon 1995).

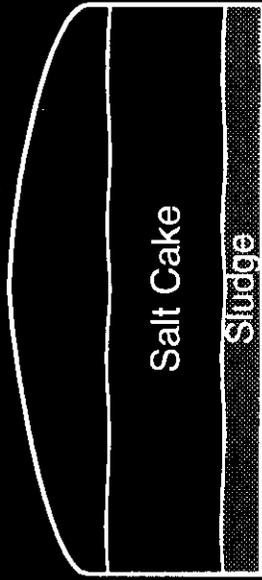
2.1 WASTE AGING, SOLUBILITY, AND COMBUSTIBILITY POTENTIAL

None of the SSTs has received waste since 1977 and they are considered to be in inactive use. No significant adverse physical or chemical events are known to have occurred in these tanks since 1977. While generally not yet quantified, the waste composition changes with time due to both radiolysis and other chemical reactions including loss of chemicals due to evaporation losses. The waste fuel energy content is therefore continuously decreasing with time since no new addition of chemicals is taking place. The ongoing aging of waste chemical species generally lead to lesser energetic forms. As an example the decomposition of ferrocyanide in the tank waste is nearly complete (as indicated by both the simulant aging studies and by the lack of ferrocyanide in the sampled waste) (Grigsby et al. 1995).

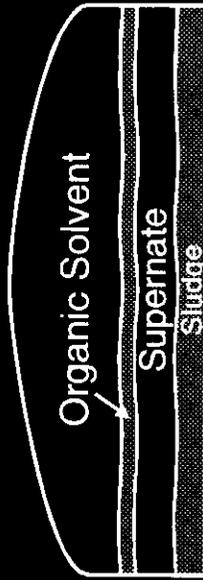
Sampling results show that HEDTA and other organic complexants added to the tanks are also present in significantly lower concentration than expected on the basis of the historical storage records (Agnew 1995) and that the wastes contain appreciable amounts of the structurally simpler and more highly oxidized degradation products (lower energy species such as sodium formate and sodium oxalate). This finding is in agreement with laboratory studies on aging (Ashby et al. 1992 and 1994, Meisel et al. 1992 and 1993, Camaioni et al. 1994, 1995). Where both liquid and solid phase sample data are available, the low energy sodium oxalate (a low solubility degradation product) dominate the solid phases when correction is made for organic compounds in the solution filled void volume of the non-convective layer. This finding is also consistent with laboratory studies dealing with the solubility of various organic complexants in salt solutions (Barney 1994 and 1995). The implication of this understanding is that measurable waste aging to lower energy species has occurred during waste storage and the energy rich components of the waste are indeed associated with the aqueous phase. This together with the relatively low concentration of total organic carbon measured in the Hanford waste supernatants as discussed below, suggest the absence of combustible solid waste conditions.

Process flowsheet compositions and recorded waste volumes sent to underground waste storage tanks suggest that the majority of the disposed organic complexants are those shown in Table 2-1 (Babad and Turner 1993).

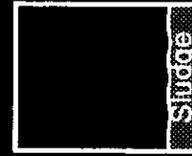
Figure 2-1. Examples of Hanford Tank Farm Waste Forms



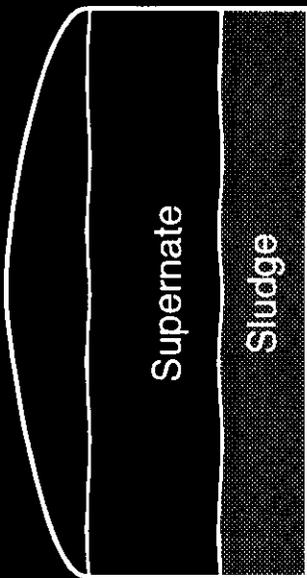
BY-106
SST_s: 750,000 gal



C-103
SST_s: 500,000 gal



C-201
SST_s: 56,000 gal



SY-101, AN-105 etc.
DST_s



A-101
SST_s: 1,000,000 gal

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Table 2-1. Organic Complexants Disposed to Storage Tanks

Organic Chemical	Formula for Sodium Salt	Quantity (metric tons)
Hydroxyacetic Acid	$\text{NaC}_2\text{H}_3\text{O}_3$	880
Citric Acid	$\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$	850
HEDTA	$\text{Na}_3\text{C}_{10}\text{H}_{15}\text{O}_7\text{N}_2$	830
EDTA	$\text{Na}_4\text{C}_{10}\text{H}_{12}\text{O}_8\text{N}_2$	220

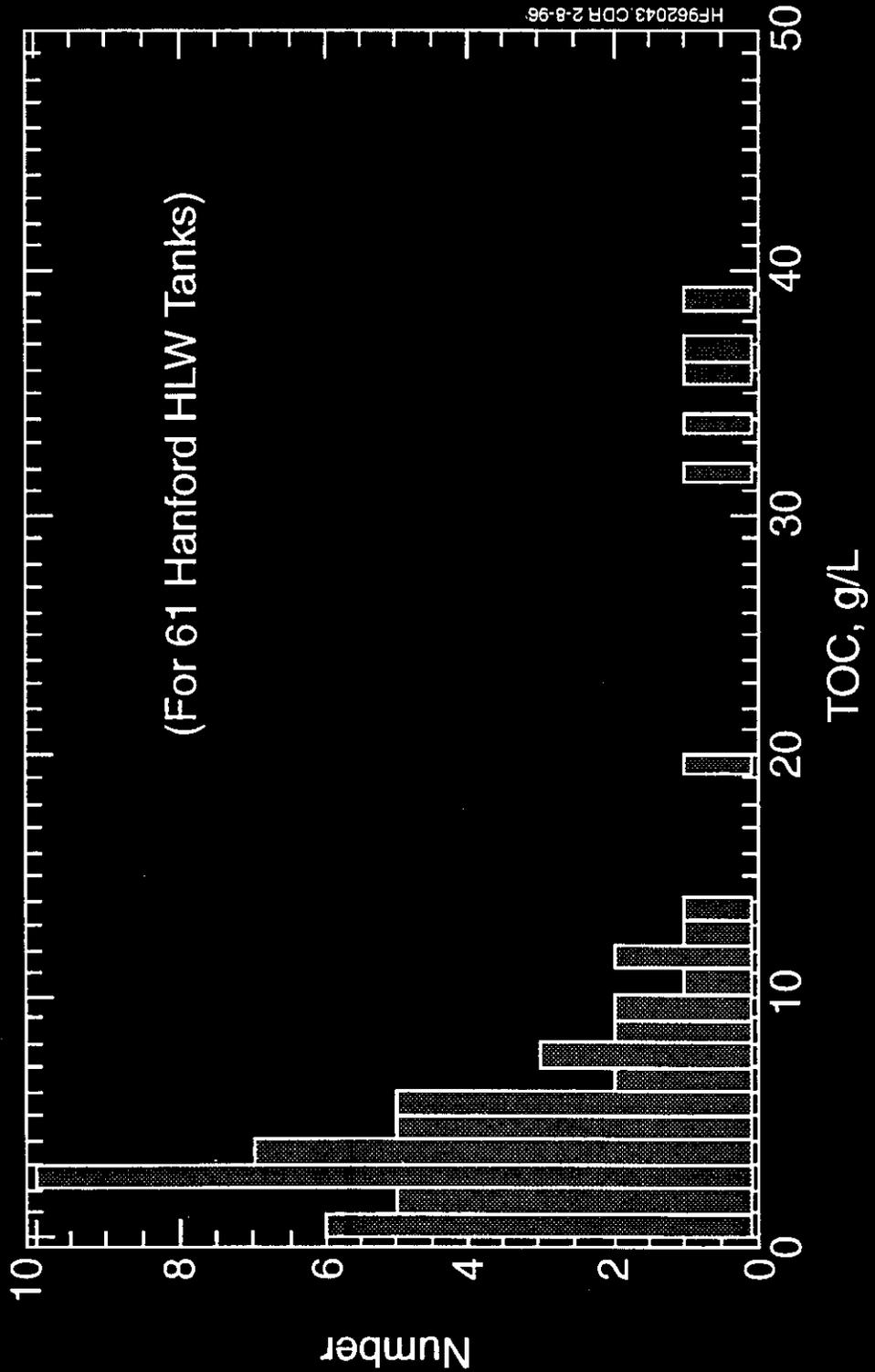
Considering sodium nitrate (NaNO_3) as the oxidizing agent and using Burger's (1995) maximum theoretical values, a mass-weighted average fuel energy of about 7,300 J/g of fuel is estimated. The corresponding ratio of total organic carbon (TOC) to organic complexant is about 0.28 or an energy value of about 26,000 J/g of carbon.

Laboratory combustion studies with the above organic complexants indicate that an energy level of about 1600 J/g mixture in the absence of moisture is required to sustain combustion using a large ignition source (Fauske et al. 1995). For the above mixture of organic complexants (Table 2-1), this is equivalent to about 6 wt% TOC.

As noted earlier, laboratory studies also demonstrate that the energy rich complexants listed in Table 2-1 have high solubility (Barney 1994 and 1995). Information from actual waste solutions suggests that the complexants are largely present in the aqueous phase. Therefore, fuel is removed by interim stabilization operations. The TOC values in grams of organic carbon per liter of solution have been collected for supernate solutions in 61 high level waste tanks at the Hanford site (Van Vleet 1993a and 1993b). The frequency distribution for these 61 values is shown in Figure 2-2. The bulk of the TOC values are less than 14 g/L of organic carbon. For SSTs, Toth et al. (1995) have calculated a mean value of 5.2 g/L organic carbon (at the 95% confidence level) for the tank supernate solutions. This mean was calculated from analyses of 143 samples from 78 different single-shell tanks (Barney 1995). It is of particular interest to note that the highest measured value of TOC of about 40 g/L is below the measured solubility limits.

Based upon the above observations a bounding assessment of the combustibility potential can be made. Consider a worst case in which the liquid phase is transported to the surface, the water evaporates, leaving a layer containing the solids. It is assumed that the TOC values represent only unaged energy rich organic complexants with an energy value of 26,000 J/g of carbon. Considering saturated salt solutions (solids content consisting of 45 wt% dissolved salts plus organic complexants) whose densities are about 1400 g/L, the upper range of measured TOC values of 40 g/L organic carbon results in about 5 wt% TOC on a dry basis which is below the suggested requirement of 6 wt% TOC for sustained combustion given an adequate ignition source. The estimated mean value by Toth et al. (1995) of 5.2 g/L organic carbon (at the 95% confidence level) result in about 0.7 wt% TOC on a dry basis. The predicted absence of combustible conditions will receive further confirmation from liquid and solid tank waste samples.

Figure 2-2. Frequency Distribution of Total Organic Carbon (TOC) Concentrations Measured in Supernate Solutions in 61 Different Hanford Site HLW Tanks (Barney 1994)



2.1 TANK HEADSPACE MIXING

In contrast to the non-convective waste forms such as sludge and saltcake, the tank headspace gases appear to be well mixed and homogeneous. Where available, vapor space temperature profiles show nearly uniform temperatures from the waste surface to the tank top (Kummerer 1994). Limited measurements and sampling in such environments therefore provides general information about temperature and chemical compositions.

A measure of headspace gas mixing is obtained by considering the potential for Rayleigh-Benard type convection². Since the average temperature of the headspace gas (T_v) exceeds the average atmospheric temperature (T_∞) the flow of heat through the tank dome is, on the average, upward and into the overlying soil. It follows that on the average, the temperature of the waste surface exceeds the dome temperature and the headspace gas undergoes turbulent Rayleigh-Benard type convection. The effectiveness of the natural convection is determined by evaluating the Rayleigh number (Rohsenow and Hartnett 1973).

$$Ra = \frac{g H^3 \Delta T}{T_v \alpha \nu} \quad (2-1)$$

where g (m/s^2) is the gravitational constant, H (m) is the height of the tank headspace, α ($2.2 \times 10^{-5} m^2 s^{-1}$) is the headspace (air) thermal diffusivity, and ν ($1.6 \times 10^{-5} m^2 s^{-1}$) is the headspace (air) kinematic viscosity and ΔT is the temperature drop across the headspace and can be estimated from (Crowe et al. 1993, Epstein 1995)

$$\Delta T = \frac{2 (T_v - T_\infty)}{1 + 8\epsilon\sigma T_v^3 H_{soil}/k_{soil}} \quad (2-2)$$

where the physical properties used in this calculation are from Crowe et al. (1993). σ is T_∞ (13.8 °C) is the average temperature of Hanford atmosphere, ϵ (0.62) is the emissivity, H_{soil} (4 m) is the average height of the tank overburden and K_{soil} ($0.93 W m^{-1} K^{-1}$) is the thermal conductivity of the overburden soil.

Evaluation of Rayleigh numbers for the Hanford Tank Farm using Equations (2-1) and (2-2) along with average head space gas temperature, T_v , results in values in excess of 10^6 . This suggests that the headspace gases are well mixed where the thermal convective temperature field is characterized by a thin boundary layer structure (a few cm) with steep gradients near each bounding surface and a well mixed isothermal core in the central region represented by the measured value T_v (see, e.g., Chu and Goldstein 1973). Examples of Ra values for the

The Rayleigh-Benard problem refers to natural convection of a gas confined between two horizontal boundaries, the lower boundary being warmer than the upper boundary.

passively ventilated 1,000,000 - Gallon SSTs are provided in Table 2-2. The small temperature differences noted in Table 2-2, are consistent with the notion that the vapor space air in these passively ventilated tanks is generally well mixed thermally.

Table 2-2. 1,000,000 Gallon SSTs; Passively Ventilated Tank Head Space Height, H, Temperature Difference ΔT , and Rayleigh Number, Ra

Tank	H, m	T_v , °C	ΔT , °C	Ra
A-101 ^{a,c}	3	37	1.3	3×10^9
A-102	11.4	32.2	1.1	1.5×10^{11}
A-103	8.4	29.8	1.0	5.4×10^{10}
A-104 ^d	11.5	89	2.5	3×10^{11}
A-105 ^{d,b}	11.6	--	--	--
A-106	10.6	40.9	1.5	1.5×10^{11}
AX-101 ^c	4.9	32	1.1	1.2×10^{10}
AX-102 ^a	11.4	24	0.7	9.8×10^{10}
AX-103 ^c	10.8	32.4	1.1	1.7×10^{11}
AX-104	11.7	34.5	1.2	1.7×10^{11}
SX-113	11.4	23.4	0.7	9.5×10^{10}
SX-115 ^b	11.6	--	--	--

^a Organic watch list.
^b Data not available
^c Flammable gas watch list.
^d High heat tank.

However, it should be noted, as a result of annual temperature changes in the atmosphere which repeat themselves, a periodic flow of heat occurs in the soil above the waste tank. During some months of the year this periodic flow may overwhelm the upward flow of decay heat from a tank with a low waste heat output and actually reverse the flow of heat through the tank dome from upward to downward. The temperature of the dome is now higher than that of the waste surface and Rayleigh-Benard convection is no longer operative (although some weaker mode of headspace gas natural convection may persist due to heat flow through the tank walls).

An assessment of the waste tank conditions that may result in the temporary suppression of the Rayleigh-Benard convection is presented in Appendix B. The analysis predicts that the headspace gas undergoes Rayleigh-Benard convection all-year long if its average temperature exceeds 19.4 °C (see Table 2-3), which corresponds to a waste heat output of only about 1000 W. Furthermore, the analysis suggests that Rayleigh-Benard type convection is always assured at the minimum 6 months out of the year for the lowest waste heat output. It is

noted that none of the tanks on the flammable gas watch list currently have average tank headspace temperatures less than 19.4 °C (see Tables 2-4 through 2-9).

Table 2-3. Average Headspace Gas Temperature Required for Rayleigh-Benard-Type Free Convection

Headspace Temperature Greater Than	Period of Rayleigh-Benard Type Free Convection
13.8 °C (56.8 °F) ^a	6 months (mid December to mid June)
15.4 °C (59.7 °F)	7 months (end November to end June)
16.8 °C (62.2 °F)	8 months (mid November to mid July)
17.8 °C (64.8 °F)	9 months (end October to end July)
18.8 °C (65.8 °F)	10 months (mid October to mid August)
19.2 °C (66.6 °F)	11 months (end September to end August)
19.4 °C (67.0 °F)	12 months

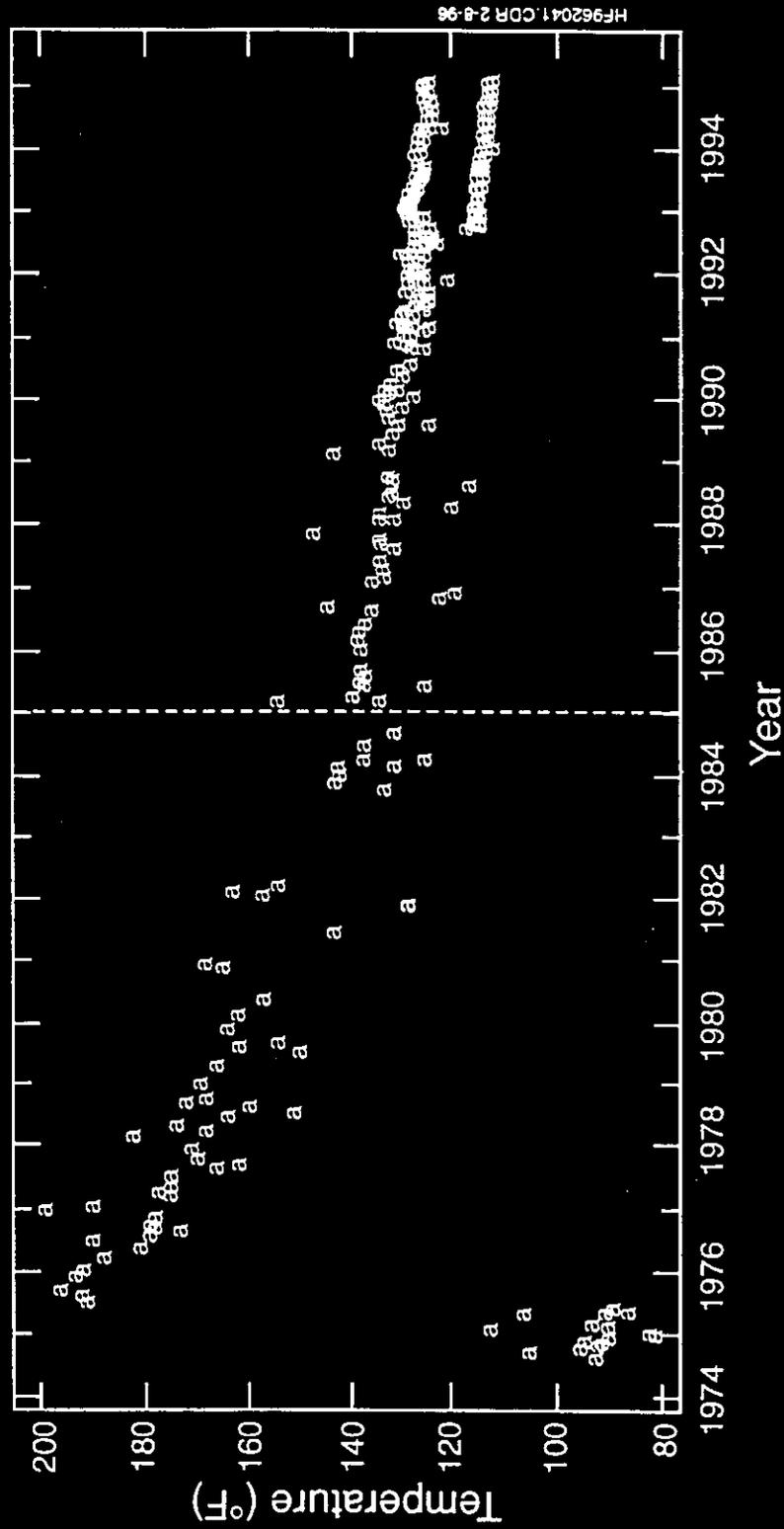
^aAverage temperature of Hanford site atmosphere-lower limit to headspace gas temperature.

2.3 DECAY HEAT REMOVAL

The bulk of the radioactivity in the SSTs is ¹³⁷Cs and ⁹⁰Sr, and are also the major heat generating sources within the tanks. The half life of both these isotopes is about 30 years. As such, over the last 18 years the decay heats have decreased about 34%.

Historic temperature data show that the waste temperatures are slowly decreasing with time in a manner consistent with the decrease in decay heat and also appear to continue to decrease following stabilization of the tanks (Lechelt 1995). An example is illustrated in Figure 2-3. The tanks (133 out of the total of 177) are passively ventilated which assures that decay heat removal is entirely by passive means. An increase of the waste temperature following stabilization can only come about from a decrease in waste thermal conductivity in connection with continued moisture removal, and as such would only change the temperature profile in the waste material itself. The temperature profiles within the tank airspace and the soil layer outside the tank would remain unaltered. A rather conservative estimate of the increase in the waste temperature can be made by considering the change in the waste thermal conductivity resulting from complete removal of free moisture, keeping all other conditions the same, such as the volumetric heating rate, Q, and the waste height H, and using the measured headspace temperature, T_v, as the point of reference. As such, an estimate of the waste temperature, T, for the postulated decay heat disruption can be obtained by assuming one-directional heat conduction and uniform heat source.

Figure 2-3. Temperature Trending for Tank BY-104 Before and After Interim Stabilization



$$T = T_v + \frac{Q H^2}{2k}$$

The numerical value of the thermal conductivity, k (w/m-K) is set equal to 0.5 to reflect that the waste is dry (see Appendix C). Equation (2-3) represents a simple heat transfer model in which the bottom of the tank is an adiabatic boundary so that all the heat generated in the waste is conducted upward toward the tank air space.

$$\approx T_v + Q H^2 \tag{2-3}$$

Relevant thermal data (Kummerer 1994) and evaluated values of T for all 133 passively ventilated tanks are provided in Tables 2-4 through 2-7. The value of Q (W/m^3) is obtained by dividing the heat load W with the waste volume. Only five tanks have T values that exceed or approach $100^\circ C$, these are summarized in Table 2-8. The majority of the tanks have T values well below $100^\circ C$.

A more realistic assessment of the actual long term waste temperature behavior is obtained by considering both variation in the solid waste thermal conductivity and the heat generation rate as the waste loses water. Since water is not required to remove decay heat, any water loss following tank stabilization can be related to tank breathing and natural convection exchange flow through multiple risers (Epstein et al. 1994). A conservative estimate of these losses are less than 1000 kg/year. Considering that the thermal conductivity going from a saturated waste to a dry porous waste decreases by a factor 2 for a porosity value of 0.4 (see Appendix C), and that the decay heat also decreases by a factor of 2 over a 30-year period (half lives for Sr and Cs), Q will decrease faster than k , and therefore the waste temperatures will continue to decrease according to Equation (2-3) when the waste height H satisfies the following equation

$$H \cdot A \cdot 0.4 \cdot \rho_{H_2O} > 30 \cdot 1000$$

$$H > 75/A \tag{2-4}$$

where A (m^2) is the waste surface area. In the case of the 1,000,000, 750,000 and 500,000 gallon tanks $A = 410 m^2$ and

$$H > 0.18 m \tag{2-5}$$

while for the 200 series tanks $A = 29 m^2$ and

$$H > 2.6 m. \tag{2-6}$$

Table 2-5. 750,000 Gallon SSTs; Passively Ventilated

Tank	H,m	T _v , °C	T _w , °C	Heat Load W	Q w/m ³	T _v + QH ² °C	t _c ≈ H ² /4α
BY-101	3.6	18.8	23.5	1084	.74	28.4	194 days
BY-102	3.4	24.4	N/A	1622	1.3	39.4	163 days
BY-103 ^b	3.9	21.3	27.2	1611	1.1	38	217 days
BY-104 ^b	3.3	25.8	52.9	2549	1.7	44.3	160 days
BY-105 ^b	4.6	25.6	45.7	2549	1.3	53.1	301 days
BY-106 ^b	6.1	27.2	53.7	2959	1.2	71.8	1.5 years
BY-107 ^b	2.6	26.3	35.0	2608	2.6	43.9	99 days
BY-108 ^b	2.3	26.8	42.4	2696	3.1	43.2	76 days
BY-109	4.1	15.5	N/A	304	.19	18.7	241 days
BY-110 ^b	3.8	23.2	47.7	2022	1.3	42.0	210 days
BY-111 ^b	4.4	21.1	31.2	1611	.93	39.1	282 days
BY-112 ^b	2.9	22.2	28.2	1787	1.6	35.6	119 days
S-101	4.1	32.8	46.1	4025	2.5	74.8	249 days
S-102 ^{a,c}	5.3	24.9	40.2	2441	1.2	58.6	1.1 years
S-103	2.5	21.8	29.2	1676	1.8	33.0	88 days
S-104	2.9	28.7	39.7	3095	2.8	52.2	121 days
S-105	4.4	18.7	22.8	1096	0.63	30.9	279 days
S-106	5.2	18.8	34.3	1135	.55	33.7	1.1 years
S-107	3.6	26.7	41.5	2733	2.0	52.6	187 days
S-108	5.8	19.5	29.9	1290	.56	38.1	1.3 years
S-109	5.4	24.4	28.3	2339	1.1	56.5	1.2 years
S-110	6.6	24.6	46.6	2274	1.6	94.3	1.7 years
S-111 ^{a,c}	5.7	22.2	31.3	1873	.83	49.2	1.3 years
S-112 ^c	6.1	19.6	22.8	1309	.54	39.7	1.4 years

^a Organic watch list tank.

^b Ferrocyanide watch list tank.

^c Flammable gas watch list tank.

Table 2-5. 750,000 Gallon SSTs; Passively Ventilated (Continued)

Tank	H,m	T _v , °C	T _w , °C	Heat Load W	Q w/m ³	T _v + QH ² °C	t _c ≈ H ² /4α
TX-101	1.0	N/A	N/A	NC	NC	--	14.6 days
TX-102	1.2	N/A	N/A	NC	NC	--	21.5 days
TX-103	1.6	14.4	14.4	188	.32	15.2	39.2 days
TX-104	0.8	15.6	15.5	403	1.6	16.6	9.1 days
TX-105 ^a	5.8	22.7	35.0	1988	.86	51.6	1.3 years
TX-106	4.4	15.0	15.0	314	.18	18.5	279 days
TX-107	0.5	15.0	18.3	292	2.1	15.5	3.9 days
TX-108	1.4	15.6	16.1	408	.80	17.2	29.7 days
TX-109	3.8	16.7	17.8	656	.45	23.2	203 days
TX-110	4.5	27.2	N/A	2882	1.6	59.6	287 days
TX-111	3.6	22.2	18.3	1803	1.3	39	187 days
TX-112	6.2	26.7	22.8	2852	1.2	72.8	1.5 years
TX-113	5.8	21.1	17.8	1637	.7	45	1.3 years
TX-114	5.1	N/A	N/A	NC	NC	--	1.0 years
TX-115	6.1	21.1	18.3	1646	.68	46.4	1.5 years
TX-116	6.0	N/A	N/A	NC	NC	--	1.4 years
TX-117	6.0	N/A	N/A	NC	NC	--	1.4 years
TX-118 ^{a,b}	3.0	20.3	23.7	1403	1.1	30.2	129 days
TY-101 ^b	1.3	18.2	17.7	920	2.1	21.7	24.6 days
TY-102	0.8	17.5	N/A	795	3.3	19.6	9.1 days
TY-103 ^b	1.7	18.8	20.3	1057	1.7	23.7	42.1 days
TY-104 ^{a,b}	.6	18.1	18.0	889	5.1	20.0	5.4 days
TY-105	2.3	18.6	24.8	1032	1.2	24.9	78 days
TY-106	0.3	15.6	15.4	410	6.4	16.2	1.6 days

^a Organic watch list tank.

^b Ferrocyanide watch list tank.

^c Flammable gas watch list tank.

Table 2-6. 500,000 Gallon SSTs; Passively Ventilated

Tank	H,m	T _v , °C	T _w , °C	Heat Load W	Q w/m ³	T _v + QH ² °C	t _c ≈ H ² /4α days
B-101	1.2	33.2	42.1	3,786	8.8	46.2	21.5
B-102	0.5	17.5	17.1	757	6.2	19.5	3.4
B-103 ^a	0.7	16.5	15.4	569	2.5	17.5	7.7
B-104	3.6	17.1	18.7	733	0.52	24.1	190
B-105	3.0	17.3	19.2	757	0.65	23.3	132
B-106	1.3	16.5	16.5	589	1.3	18.5	24
B-107	1.7	16.5	16.6	606	.97	19.5	42
B-108	1.1	16.5	16.5	575	1.6	18.5	16
B-109	1.4	16.2	16.1	515	1.1	18.2	27
B-110	2.5	19.9	20.1	1265	1.4	28.9	88
B-111	2.4	29.8	29.8	3,216	3.6	50.8	82
B-112	0.5	17.3	17.3	715	5.7	18.3	3.4
BX-101	0.6	17.7	18.1	801	5.0	19.7	5
BX-102	1.0	18.6	17.5	974	2.7	21.3	15
BX-103	0.8	25.0	N/A	1,682	6.7	29	9
BX-104	1.1	30.5	N/A	1,819	4.8	36.5	17.4
BX-105	0.7	18.9	22.6	1,031	5.3	21.9	6.5
BX-106	0.6	17.4	17.6	736	6.3	19.4	5.4
BX-107	2.4	22.4	N/A	1,352	1.0	28.4	86
BX-108	0.4	18.6	22.2	959	9.7	20.6	2.6
BX-109	2.0	23.8	24.8	2,012	2.7	34.8	57
BX-110	2.0	16.9	19.6	675	0.9	20.9	60
BX-111	2.3	18.2	18.7	928	1.2	24.2	78
BX-112	1.7	18.3	21.8	926	1.5	22.3	42
C-101	1.0	29.6	30.7	3,074	9.2	38.6	15
C-102 ^a	4.1	32	N/A	3,795	2.4	72	249
C-103 ^a	2.1	40.7	48.1	5,331	7.2	72.7	65.5
C-104	2.9	30.2	31.9	3,343	3.0	55.2	124
C-107	3.3	42.6	49.9	5,796	5.6	113.6	157
C-108	0.8	22.7	21.9	1,747	7.0	26.7	8.3
C-109	0.8	24.3	23.1	2,063	8.8	30.3	8.3
C-110	2.0	18.3	18.5	934	1.3	23.3	60.4

Table 2-6. 500,000 Gallon SSTs; Passively Ventilated (Continued)

Tank	H,m	T _v , °C	T _w , °C	Heat Load W	Q w/m ³	T _v + QH ² °C	t _c ≈ H ² /4α days
C-111 ^b	0.7	23.3	23.4	1870	8.7	27.7	7.7
C-112 ^b	1.2	25.0	22.7	2210	5.6	33.1	19.4
T-101	1.4	19.9	18.9	1227	3.2	26.2	29.7
T-102	0.5	23.9	N/A	1126	9.3	26.2	3.4
T-103	0.4	15.2	14.9	315	3.1	15.7	2.6
T-104	4.3	18.0	N/A	950	.56	28.3	267
T-105	1.1	23.2	N/A	1461	3.9	27.9	17.4
T-106	0.4	15.2	15.1	315	4.0	15.8	2.3
T-107 ^b	1.9	17.1	16.7	708	1.0	20.7	50.0
T-108	0.6	17.2	N/A	644	3.9	18.6	5.4
T-109	0.7	16.7	N/A	519	2.4	17.9	7.7
T-110 ^b	3.7	15.2	15.4	346	.24	18.5	197
T-111	4.4	14.7	15.1	241	.14	17.4	283
T-112	0.8	14.9	14.8	265	1.0	15.5	9.8
U-101	0.4	19.4	N/A	1123	11.8	21.3	2.6
U-102	3.7	21.7	27.1	1670	1.2	38.1	194
U-103 ^{a,c}	4.5	22.8	28.8	1932	1.1	45.1	295
U-104	1.3	N/A	N/A	NC	NC	--	25
U-105 ^{a,c}	4.1	22.6	30.1	1867	1.2	42.8	238
U-106 ^a	2.3	21.9	24.8	1649	1.9	31.9	75.6
U-107 ^{a,c}	3.9	21.3	23.7	1604	1.0	36.6	223.5
U-108 ^c	4.5	22.8	29.1	1932	1.1	45.1	293
U-109 ^c	4.5	21.9	27.7	1718	.98	41.7	290
U-110	1.9	20.2	22.1	1314	1.9	27.1	53.4
U-111 ^a	3.2	20.8	24.2	1476	1.2	33.1	151
U-112	0.6	16.2	16.0	506	2.7	17.2	5.9

^a Organic watch list tank.
^b Ferrocyanide watch list tank.
^c Flammable gas watch list tank.

Table 2-7. 55,000 Gallon SSTs; Passively Ventilated

Tank	Waste Height, m	Vapor Space Temp., °C	Heat Load, W	Q, W/m ³	T _v + QH ² , °C	t _c ≈ H ² /4α
B-201	3.8	14.9	54.2	.5	25.1	213 days
B-202	3.6	15.0	58.0	.6	22.8	185 days
B-203	6.7	14.6	42.8	.2	23.6	1.8 years
B-204	6.6	14.7	47.2	.3	27.8	1.7 years
C-201	0.3	16.7	114.3	15.1	18.1	1.6 days
C-202	0.2	16.2	98.2	25.9	17.2	0.6 days
C-203	0.7	15.2	62.4	3.3	16.8	7.6 days
C-204	0.5	NA	NC	NC	--	3.1 days
T-201	3.8	3.6	4.1	.04	14.2	213 days
T-202	2.8	13.8	10.3	0.1	14.6	113 days
T-203	4.6	24.2	402.9	3.0	87.7	308 days
T-204	5.0	13.9	14.7	0.1	16.4	362 days
U-201	0.7	NA	NC	NC	--	7.6 days
U-202	0.7	14.9	50.4	2.7	16.2	7.6 days
U-203 ^a	0.5	17.2	146.5	12.9	20.4	3.1 days
U-204 ^a	0.5	26.6	473.5	41.6	37.0	3.1 days

^a Organic watch list.

Table 2-8. Passively Ventilated SSTs; Summary of Highest Temperature Wastes

Tank	Size, Gal	H, m	T _v , °C	T _w , °C	Q, W/m ³	T = T _v + QH ² °C
A-101 ^{a,c}	1,000,000	8.8	37	68	1.5	153
A-104 ^d	1,000,000	0.3	89	90	144	100
AX-101 ^c	1,000,000	6.9	32	58	1.5	104
S-110	750,000	6.6	24.6	46.6	1.6	94.3
C-107	500,000	3.3	42.6	49.9	5.6	113.6

^a Organic watch list.
^c Flammable gas watch list.
^d High heat tank.

Inspection of Tables 2-4, 2-5 and 2-6 shows that all tanks with the exception of tank AX-104 satisfy Equation (2-5), indicating that the waste temperatures will continue to decrease as the wastes approach drier equilibrium states. Note that the highest temperature corresponding to our conservative estimate (Equation 2-3) is only about 35 °C for tank AX-104.

In the case of the 200 series tanks, both the B and T farm tanks satisfy Equation (2-6), again suggesting that the temperature will continue to decrease with continuing moisture loss. For the C and U farm tanks Equation (2-6) is not satisfied, but the highest value corresponding to our conservative estimate (Equation 2-3) is only 37 °C (U-204). We conclude therefore that a Kysthym-like incident in connection with decay heat removal is not a credible event for the passively ventilated SSTs. The Kysthym incident resulted from the loss of cooling from an actively cooled waste tank where the decay heat level was several orders of magnitude higher than the levels typical of Hanford Tank Farm Wastes. (A brief description of the Kyshtym incident is provided in Appendix A).

Of the actively ventilated SSTs (16), only tank C-106 would have a waste temperature T calculated from Equation (2-3), greater than 200 °C, should the waste dry out due to absence of periodic water addition (see Table 2-9). Furthermore, postulating failure of the active ventilation system as well, for this "high heat" tank the magnitude of the decay heat is such that even ignoring all natural heat losses it would take at least a year to approach this temperature level (Kummerer 1994). Of the remaining ventilated tanks (28 DSTs) the absence of ventilation and assuming adiabatic heat up, it would take at least one year to reach the boiling temperature (~100 °C) (Kummerer 1994).

2.4 CHEMICAL HEAT REMOVAL

Finally, as discussed in more detail in Section 5.0, a Kysthym like incident can also be ruled out in connection with chemical heating. The characteristic time of cooling considering the Hanford non-convective waste is dominated by heat conduction can be approximated from (Gygax 1990)

$$t_c \approx \frac{H^2}{4\alpha} \quad (2-7)$$

where H (m) is the waste height, α (2×10^{-7} m²/s) is the estimated waste thermal diffusivity (see Appendix D) and as seen in Tables 2-4 through 2-9 are all well below the waste storage exposure time of at least 18 years; the largest value being about 3 years for tank A-101. This observation rules out the possibility of spontaneous runaway chemical reactions. The heat from chemical reactions in the wastes is safely removed by passive conductive means through the wastes, i.e., the values of t_c are much smaller than the corresponding adiabatic chemical runaway times since no disruptive events are known to have occurred during the Hanford waste storage period.

Table 2-9. Actively Ventilated SSTs; Watch List and High Heat Tanks

Tank	H, m	T _v , °C	T _w , °C	Heat Load	Q, W/m ³	T _v + QH ²	t _c ≈ H ² /4α
C-106 ^d	2.32	26.8	67.5	32,200	37.1	226.8	77.8 days
SX-101 ^c	4.36	30.2	53.1	3,700	2.1	70.2	275 days
SX-102 ^c	5.15	32.9	64.5	4,400	2.1	89.9	1.05 years
SX-103 ^{a,c}	6.16	46.7	78.7	8,100	3.3	171.7	1.50 years
SX-104 ^c	5.79	29.3	73.9	3,600	1.5	79.3	1.33 years
SX-105 ^c	6.43	29.9	80.8	3,700	1.7	99.9	1.64 years
SX-106 ^{a,c}	5.09	27.9	42.5	7,900	3.9	128.9	1.03 years
SX-107 ^d	1.10	47.4	72.7	16,000	40.7	92.4	17.4 days
SX-108 ^d	1.19	55.9	88.4	16,400	37.6	108.9	20.4 days
SX-109 ^{c,d}	2.44	51.2	60.9	9,100	9.6	108.2	86 days
SX-110 ^d	0.70	48.3	75.3	11,900	50.8	73.3	7.1 days
SX-111 ^d	1.28	50.8	83.7	17,900	37.7	112.8	23.7 days
SX-112 ^d	0.96	50.2	68.2	12,200	34.9	82.2	13.8 days
SX-114	1.80	57.2	83.3	17,200	25.1	138.2	46.8 days

^a Organic watch list tank.

^c Flammable gas watch list tank.

^d High heat tank.

3.0 HEADSPACE FLAMMABILITY

The waste compositions are slowly changing with generation of hydrogen, ammonia, nitrous oxide and other decomposition products. Generation of such gases is especially relevant to tanks known to contain organic materials. If the gases are released to the tank headspaces at approximately the same rate as they are generated, measurements indicate that passive ventilation is sufficient to keep the concentration levels well below 25% of the lower flammability limit (LFL). Sampling and analysis results from 43 passively ventilated SSTs which include all the tanks (20) on the organic watch list show flammable gas concentrations at least an order of magnitude below 25% of the LFL (Huckaby et al. 1995). Tanks with measured gas concentrations greater than 0.25% of the LFL are listed in Table 3-1³.

On the other hand, if the gaseous decomposition products are not continuously released, periodic flammable gas release events (GREs) can occur. The short duration GREs may lead to headspace concentrations that can approach or even exceed 25% of the LFL (Hopkins 1994). Since the required spark ignition energies are very small (< 0.1 mJ) (Stull 1977), prevention of GREs is desirable in order to prevent a deflagration event that could challenge the tank integrity. An example is tank SY-101 where the mitigation pump converts an otherwise periodic release into a nearly continuous vented release.

Conditions favorable or not favorable for GREs are illustrated in Figure 3-1. Continuous gaseous bubble formation in solids eventually leads to interconnected porosity as the swell fraction approaches about 0.25, allowing the gas to escape at the same rate as it is being produced. A similar observation applies to solid waste forms where gases are being generated and released at near steady state conditions by eventually forming suitable pathways (e.g., interconnected porosity, fumaroles, etc.). Periodic GREs may therefore be experienced in the presence of a substantial supernatant layer (see left side of Figure 3-1). For such waste configurations, the possibility exists for various forms of instabilities to set in if the sludge density should become less than the overlying supernatant density prior to reaching a sufficient swell fraction to allow nearly steady-state gas release. Such instabilities (e.g., rollover) could lead to substantial GREs as typified by the SY-101 GREs prior to the installment of the mitigation pump.

Recalling the discussion in Section 2.0, it is noted that the headspace vapors in these tanks can be considered well mixed. The headspace gas is predicted to undergo Rayleigh-Benard turbulent convection all-year long since the current average headspace vapor temperatures for these tanks all exceed the critical value of about 19.4°C (see Tables 2-3 and 3-1).

Table 3-1. Sampled SSTs with Measured Levels Greater Than 0.25% of the LFL
(H₂ > 100 ppmv; NH₃ > 375 ppmv)

Tanks	Interim Stabilized	Average Tank Vapor Space Temp, °C	Measured Hydrogen, ppmv	% LFL	Measured Ammonia, ppmv	% LFL
A-101 ^{a,c}	N	37	758	1.9	754	.5
BY-104 ^b	Y	25.8	295	.7	-	-
BY-107 ^b	Y	26.3	267	.7	972	.6
BY-108 ^b	Y	26.8	399	1.0	1040	.7
BY-110 ^b	Y	23.2	180	.5	401	.3
C-101	Y	29.6	434	1.1	-	-
C-102 ^a	Y	32.0	158	0.4	-	-
C-103 ^a	N	40.7	782	2.0	-	-
C-107	Y	42.6	230	.6	-	-
C-109 ^b	Y	24.3	125	.3	-	-
C-112 ^b	Y	25.0	204	.5	-	-
S-102 ^{a,c}	N	24.9	669	1.7	412	.3
S-111 ^{a,c}	N	22.2	391	1.0	-	-
U-103 ^{a,c}	N	22.8	555	1.4	730	.5
U-106 ^a	N	21.9	210	.5	988	.7
U-107 ^{a,c}	N	21.3	500	1.3	453	.3
U-111 ^a	N	20.8	247	.6	676	.5

^aOrganic watch list tank.

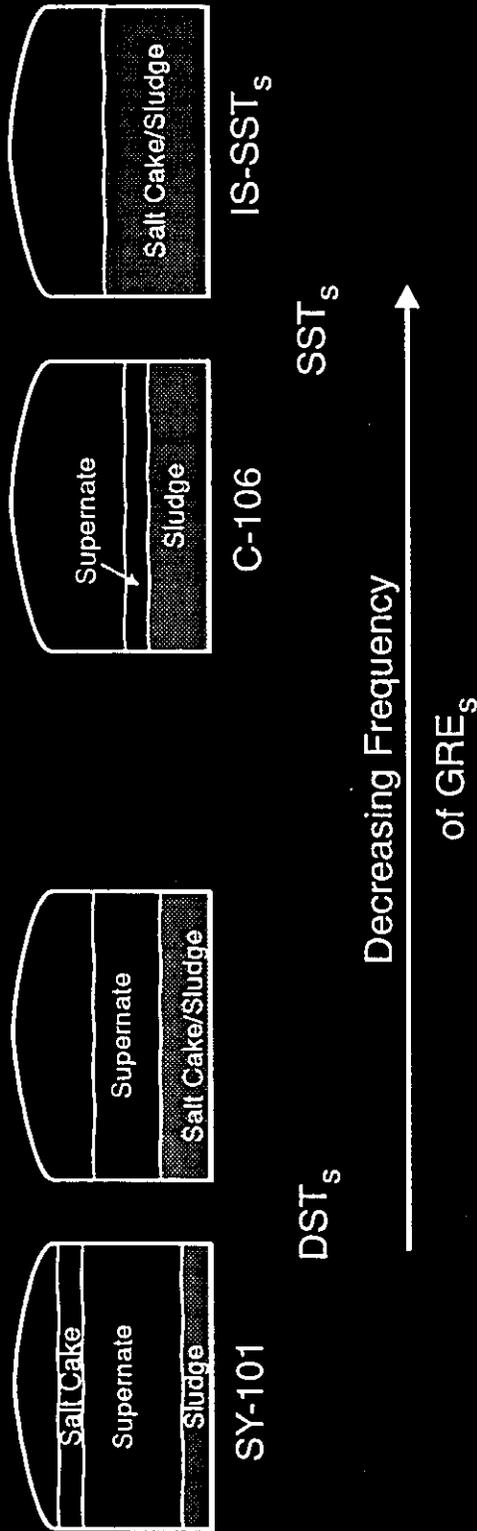
^bFerrocyanide watch list tank.

^cFlammable gas watch list tank.

The conditions prevailing in the SY-101 tank appear to be optimum for GREs. In addition to the tank being filled to capacity (i.e., minimum headspace), it has a floating saltcake layer implying that the supernatant layer above the gas containing sludge is saturated with salt giving rise to a rather high density of about 1400 kg/m³. The underlying sludge, which may have a density as high as about 1700 kg/m³ in the absence of any entrapped gas, would experience a density less than 1400 kg/m³ as the sludge swell fraction exceeds 0.2, which may be less than that required for a continuous gas release. Similar conditions may prevail for other tanks that have experienced GREs, such as tanks SY-103, AN-105, AW-101. These are all DSTs containing large amounts of supernatants. Passive mitigation of these tanks could therefore be accomplished by removing the supernatant layers.

The above observations are consistent with the absence of GREs in the SSTs, where the majority of the tanks have been interim stabilized (113 out of 149) and the remaining tanks also have relatively shallow or no supernatant layers (see right hand side of Figure 3-1).

Figure 3-1. Illustration of Conditions Favorable (Left Side) and Not Favorable (Right Side) for Periodic GREs



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For the passively ventilated 1,000,000-Gallon SSTs (see Table 2-4) all tanks except A-101 and AX-101 have been interim stabilized. However, these two tanks do not contain any excess supernate. As such, any physical instabilities that may lead to GREs for either the saltcake wastes (A-101, A-102, AX-102 and AX-103) or the sludge wastes appear to be absent. No GREs are known to have occurred in these tanks. While flammable gases stored in the wastes result in continuous gas releases, the concentrations in the tank headspaces are much too small to represent a flammability issue.

For the actively ventilated SSTs (see Table 2-9) tanks SX-107 through SX-114 have been interim stabilized, but only tank SX-106 has significant excess supernate. But even for this tank the supernatant layer is only about 10% of the solid waste layer, reducing the potential for a significant instability event (Allemann 1995). No GREs are known to have occurred.

As for the passively ventilated 750,00-Gallon SSTs (see Table 2-5), while a number of tanks have not been interim stabilized (BY-103, BY-105, BY-106, BY-109, S-101, S-102, S-103 and S-106 through S-112) none of the tanks have significant excess supernate (the largest amount is 17 K Gal for tank S-103) to suggest the likelihood of a physical instability and GRE concern. No GREs are known to have occurred.

Similarly for the passively ventilated 500,000-Gallon SSTs (see Table 2-6), while a number of tanks have not been interim stabilized (C-102, C-107, T-104, T-107, T-110, U-102, U-103, U-105 through U-109 and U-111) only tank C-103 has a significant excess supernate layer (~133 K Gal). However, the absence of saltcake waste in this tank suggests perhaps that the supernate density is too low to satisfy the condition for sludge - supernate interface instabilities. No GREs are known to have occurred.

Finally, the passively ventilated 55,000-Gallon SSTs (see Table 2-6) have all been stabilized, reducing the possibility of physical instabilities. No GREs are known to have occurred.

In summary, a prerequisite for a tank headspace flammability issue would appear to be the occurrence of GREs¹. Such GRE events apparently can only occur by satisfying certain conditions for physical instabilities in connection with trapping of gases and releasing in the solid waste forms. GREs have also been observed in tanks with substantial supernatant layers relative to the solid waste layers. Only the DSTs exhibit such conditions. No significant GREs are known to have occurred in the SSTs after interim stabilization operations.

Several other gas release mechanisms are also being considered (Allemann et al., 1995). These include fumaroles, dendritic bubble networks, caverns, etc. However, it is hard to conceive of a large gas release from a tank that has been stabilized and therefore is relatively dry.

Removal of excess supernate, if practicable, therefore would appear to represent the best solution to a potential headspace flammability issue. It is noted that the flammable gases generally present within the solid waste forms in connection with continuous gas releases would not appear to represent an issue since sustained combustion within the solid waste matrix even if ignition should be possible is unlikely due to the large mismatch in the solid to gas heat capacities. Considering that flammable gases are present in nearly all the Hanford waste tanks, the continuing efforts are justified to better understand 1) the flammability potential within the waste, 2) gas evolution mechanisms and 3) to further reduce the possibility of significant periodic gas releases.

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4.0 FERROCYANIDE

Early assessments of potential exothermic reactions between ferrocyanides and nitrates/nitrites identified two potential hazards, a spontaneous runaway reaction and a propagating combustion reaction.

For spontaneous runaway reactions, the ferrocyanide was originally assumed to be heated to its ignition temperature by radioactive decay. However, as discussed in Section 2.0, the decay heat loads are too low to heat the waste to the ignition temperature, even for the most severely postulated dryout conditions. Measured as well as estimated temperatures for all the ferrocyanide tanks of concern (see Tables 2-2 through 2-6) are well below 100 °C with the highest measured temperature of about 52 °C for tank 241-BY-104 (Cash and Meacham 1996). More importantly, chemical degradation (aging) experiments (Lilga et al. 1993, 1994, and 1995) and waste samples gathered from ten of the ferrocyanide tanks (Grigsby et al. 1996) show that the ferrocyanide fuel has degraded to levels insufficient to support runaway reactions. Spontaneous runaway reactions (no ignition sources required) can also be ruled out since the characteristic cooling times for all the Hanford waste tanks are much smaller than the waste storage times (> 18 years). (See last column in Tables 2-2 through 2-6).

Considerable experimental studies over the past six years have demonstrated that propagating-type reactions can only occur at ferrocyanide concentrations greater than 15 wt% $\text{Na}_2\text{NiFe}(\text{CN})_6$ in the absence of free moisture (Fauske 1993a, Grigsby et al. 1996). Measurements made of the rate at which sodium nickel ferrocyanide is destroyed by aging reactions as a function of radiation, temperature, and pH (Lilga et al. 1993, 1994, and 1995) show that the ferrocyanide added 38 or more years ago would have been largely destroyed by now. This observation is confirmed by tank waste samples that have been taken from a number of the ferrocyanide tanks (Grigsby et al. 1996). These samples show little or no cyanide remaining and significant amounts of nickel, the signature analyte of the nickel ferrocyanide campaigns of the 1950s. This is the only source of high nickel concentrations in the Hanford Site waste tanks. Maximum exotherms measured in the samples (see Table 4-1) are far below the estimated theoretical threshold value of 1,200 J/g required to support a propagating reaction (Fauske et al. 1995). Note that the ferrocyanide tanks sampled to date include the four tanks (241-C-108, C-109, C-111, and C-112) which received In-Farm flowsheet sludge, the most concentrated in ferrocyanide of any added to the Hanford Site waste tanks. The very low exotherms observed for these tank samples, supported by the basic chemical degradation studies, show that the ferrocyanide in all tanks has been nearly destroyed by aging to well below any concentration of concern.

Table 4-1. Exotherms of Ferrocyanide Tank Samples

Tank ^a	Flowsheet	DSC Exotherms, J/g	Reference
C-108	In-Farm	0 to 109	Cash et al. 1995
C-109	In-Farm	0 to 52	Simpson et al. 1993b
C-111	In-Farm	All zero	Meacham et al. 1995a
C-112	In-Farm	17 to 38	Simpson et al. 1993a
T-107	U-Plant	All zero	Sasaki and Valenzuela 1994
TY-104	T-Plant	All zero	Cash et al. 1995

^a Other ferrocyanide tanks have been sampled, but the analytical results are not yet available.

5.0 ORGANIC SOLVENTS AND COMPLEXANTS

The organic chemicals used at Hanford in bulk quantity include both solvents, normal paraffin hydrocarbons (NPH) and tributyl phosphate (TBP), and complexants (hydroxyacetic acid, hydroxyethylenediaminetriacetic acid (HEDTA), ethylenediaminetetraacetic acid (EDTA), and citric acid. These substances were discharged to the tanks where they were placed in alkaline solution. The neutral compounds such as NPH and TBP separated into separate liquid phases, and the acidic compounds were converted into soluble sodium carboxylates. Radiolysis and hydrolysis have slowly transformed these substances into an array of other compounds; for example, TBP hydrolyzes to provide sodium dibutyl phosphate in alkaline solution, and EDTA undergoes radiolysis to provide principally sodium diiminoacetate, sodium oxalate, and sodium formate. Further decomposition of the organic compounds provides sodium carbonate. A large body of recent work (Delegard 1980 and 1987, Meisel et al. 1992 and 1993, Ashby et al. 1994, Barefield et al. 1995, Camaioni et al. 1994 and 1995) indicates that the original complexants are slowly converted into more oxidized, less energetic materials as the reduced products, hydrogen and ammonia, evolve from the tanks (Meisel et al. 1992 and 1993, Strachan 1994, Bryan and Pederson 1994). The insoluble organic solvents also undergo radiolysis, but their reactions are slower than the reactions of the complexants (Camaioni et al. 1994 and 1995). However, they are more volatile and have distilled slowly from the tanks.

Investigations of the chemistry of the wastes (Meisel et al. 1992 and 1993, Camaioni et al. 1994 and 1995) indicate that the reactive initial products of the radiolysis undergo radical coupling reactions in which the first-formed organic species react with nitrogen-containing radicals and ions to produce new molecules with carbon-nitrogen bonds. Some of these new substances may be more energetic than the original organic molecules from which they were formed. It has also been observed that the headspace gases contain low concentrations of a homologous series of nitriles, aldehydes, and ketones (Huckaby and Story 1994) and that the alkaline solutions contain an array of new sodium carboxylates. One preliminary report from Los Alamos National Laboratory indicates that sodium nitroalkane-carboxylates have been detected (Camaioni et al. 1994). These empirical observations imply that the complex organic compounds in the tank wastes have produced a variety of new molecules in low concentrations over the past few decades. Furthermore, some of these substances (for example, the nitroalkanecarboxylic acids) are soluble in the waste and therefore are very difficult to detect. It has been pointed out in the organic chemistry literature that the more energetic substances undergo hydrolysis in warm alkaline solutions to produce the types of molecules that have been detected in the vapor phase. Consequently, the potentially hazardous molecules should not accumulate in the wastes. However, WHC has elected to address this problem by studying the chemistry of likely molecules under the conditions that exist in the waste tanks.

Potential chemical vulnerabilities include tank headspace flammability in connection with organic solvents and condensed-phase runaway reactions in connection with the organic complexants.

5.1 ORGANIC SOLVENTS

Vapor Phase Deflagration. The concern related to combustion of organic solvents is highlighted by the floating organic layer in tank C-103 (see Figure 2-1). The flashpoint of dodecane, the most volatile constituent of the original NPH, is 74 °C. However, additions to the SSTs were completed about 18 years ago, and the remaining liquid mixtures of solvents have flash points in excess of 100 °C due to the loss of the more volatile species (Meacham et al. 1995b). The solvent layer in tank C-103 has been determined to have a flash point temperature of about 120 °C. This, together with the maximum headspace temperature of about 40 °C, eliminates any concern related to gaseous deflagration, as the organic vapor concentration in the tank headspace is about 1% of its lower flammability limit. Tanks with organic solvents can be identified by headspace vapor sampling. Not all SSTs potentially containing organic solvents have yet been identified. Therefore, a headspace vapor sampling program is in progress. Tanks with organic solvents can be identified by headspace vapor samples. Not all the SSTs that may contain organic solvents have yet been identified; therefore, a headspace vapor sampling program is underway.

Organic Solvent Ignitability. The organic liquid layer in tank C-103 is a subflash liquid. That is, the current temperature of the organic layer is about 80 °C below its flashpoint of 120 °C. Theoretically speaking, local heating must be adequate to bring the local surface to a temperature above the flashpoint before ignition can occur. Glassman and Dryer (1980/1981) have shown that ignition requires that the surface temperature be raised to the "firepoint", in this case a temperature of about 150 °C.

Even if ignition should occur, flame spreading on the subflash organic liquid is difficult to achieve unless the ignited region is very large (> 15 cm diameter). Flames smaller than 15 cm diameter self extinguish (Epstein et al. 1995). Experimental data obtained with dodecane (flashpoint 74 °C) illustrate this requirement including a critical organic layer thickness for flame extinction (see Figure 5-1). This thickness can be estimated by equating the thermocapillary force due to the local heat source (F_{σ}) and the hydrostatic force (F_g) (see Figure 5-2) (Epstein et al. 1995)

$$\delta_{cr} = \left[\frac{2 \sigma' (T_{fire} - T_{\infty})}{\rho g} \right]^{1/2} \quad (5-1)$$

where g (ms^{-2}) is the gravitational constant, σ' ($9 \times 10^{-5} \text{ kg s}^{-2} \text{ K}^{-1}$) is the variation of surface tension with temperature, T_{fire} (150 °C) is the fire point temperature, T_{∞} (40 °C) is the tank ambient temperature, ρ (800 kg/m^3) is the solvent density, and results in $\delta_{cr} \approx 1.5 \text{ mm}$. This compares to the experimental value of about 2 mm (Figure 5-1).

Figure 5-1. Flame Spreading/Extinction Results (Epstein et al. 1995)

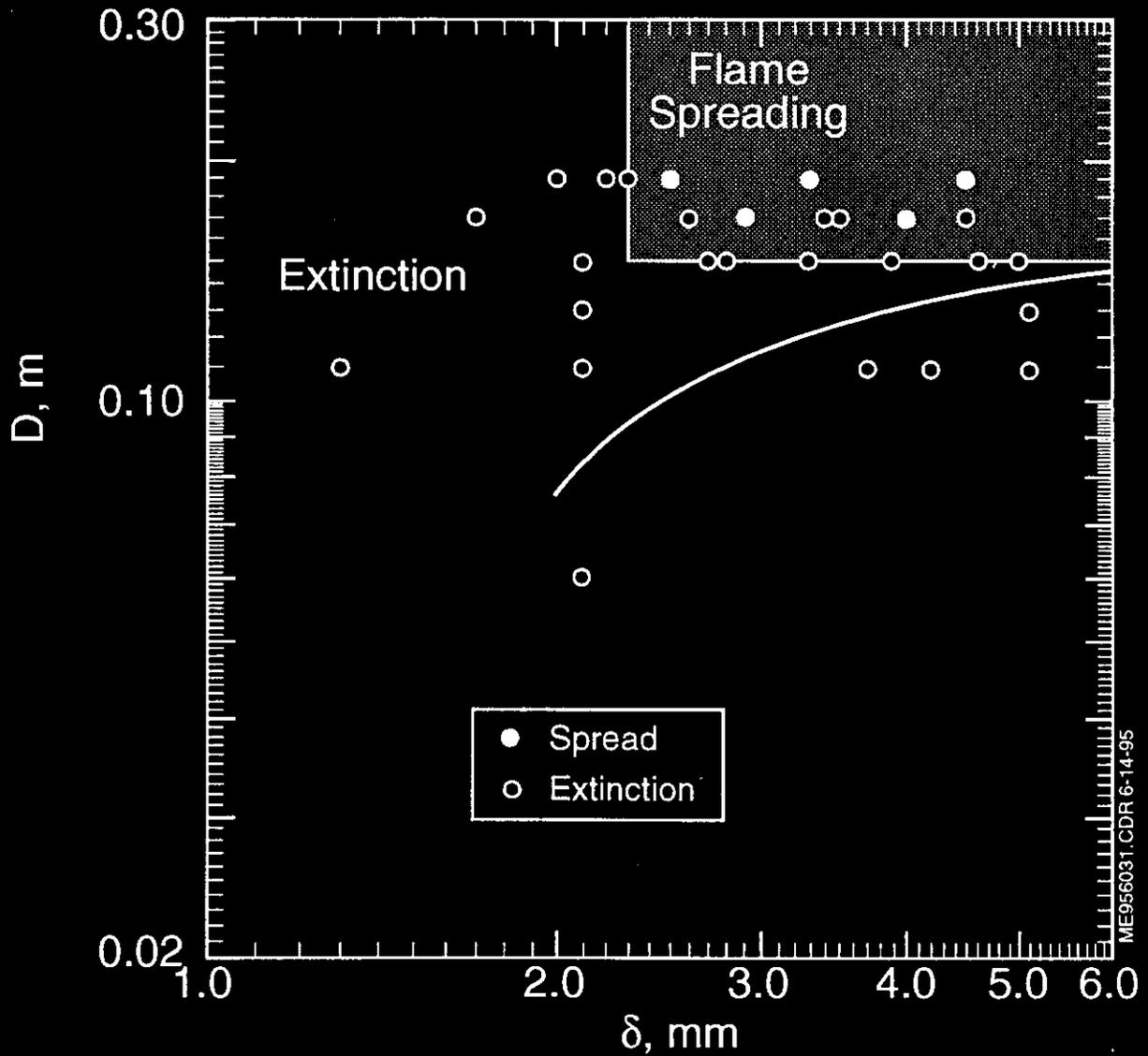
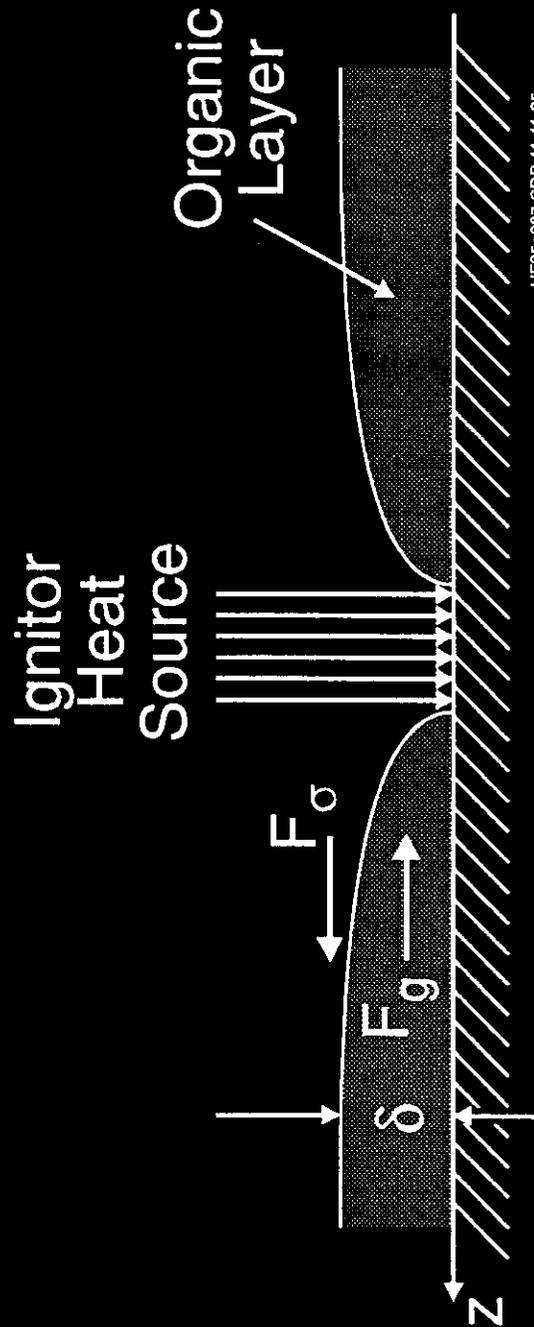


Figure 5-2. Illustration of Extinction Film Thickness Model (Epstein et al. 1995)



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A conservative estimate of the spark energy required to ignite the organic solvent can be estimated from Equation 5-2 which was derived on the basis of the point source spark radiation that was necessary to heat the conducting organic solvent (Epstein et al. 1995)

$$E = \frac{10 (T_{\text{fire}} - T_{\infty}) k R^2}{(\alpha/t_s)^{1/2}} \quad (5-2)$$

where k ($0.15 \text{ W m}^{-1} \text{ K}^{-1}$) is the organic solvent thermal conductivity, α ($8.7 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$) is the organic solvent thermal diffusivity, t_s (10^{-5} s) is the spark duration and R (0.075 m) is the required size of flammable region for flame spreading, and results in $E = 10 \text{ J}$. Internally generated spark energies of this magnitude are not credible.

Sustained local heating induces both surface and subsurface convection, the surface convection being particularly strong due to changes in surface tension with temperature. The organic liquid that flows away from the heat source loses heat by convection and radiation to the atmosphere and as the hot liquid flows away, it is continually replaced by a submerged current of cooler liquid. Hence, a sustained passive energy source is required to ignite an organic layer of thickness δ over a surface area of radius R . Equation 5-3 was derived theoretically and tested to examine this point (Epstein et al. 1995, FAI 1994).

$$Q = 1.45 \pi R^2 h (T_{\text{fire}} - T_{\infty}) \left[\frac{k_e \delta (T_{\text{fire}} - T_{\infty})^2}{R^4 h} \right]^{0.43} \quad (5-3)$$

where

$$k_e = \frac{\rho C_p (\sigma')^2 \delta^4}{1680 \alpha \mu^2} \left(1 + \frac{7}{20} B_o + \frac{19}{864} B_o^2 \right)$$

$$B_o = \frac{g \rho \beta \delta^2}{\sigma'}$$

σ' ($9 \times 10^{-5} \text{ kg s}^{-2} \text{ K}^{-1}$) is the variation of surface tension with temperature, h ($15.0 \text{ W m}^{-2} \text{ K}^{-1}$) is the liquid surface heat-loss coefficient, β (10^{-3} K^{-1}) is the liquid expansion coefficient, C_p ($2300 \text{ J kg}^{-1} \text{ K}^{-1}$) is the liquid specific heat, μ ($8 \times 10^{-4} \text{ kg m}^{-1} \text{ s}^{-1}$) is the liquid viscosity, ρ (800 kg m^{-3}) is the liquid density, and R (0.075 m) is the required size of flammable region for flame spreading, and result in the following values of the power Q .

δ , mm	Q, W
5.0	3.6×10^3
4.0	2.0×10^3
3.0	1.0×10^3
2.0 ^a	4.0×10^2
^a Organic fuel layers ≤ 2.0 mm in depth will not support a propagating flame	

Q is the power transmitted to the liquid surface and usually is a small fraction of the total igniter power. The total power produced by a candle is approximately 10 W while the power transmitted downward by a fire of diameter 0.05 m (large wick or match) is about 100 W. Thus passive (radiant) energy sources are not credible ignition sources.

Experiments and analysis have also shown that "fluid mechanically active" igniters (e.g., an oxyacetylene torch) produce surface currents that prevent significant overheating of the liquid surface and also are not credible ignition sources (FAI 1994). The extreme difficulty of igniting organic solvents was shown in two ways. First 1/16, 3/32, and 3/16 inch steel particles heated to about 1300 °C were injected into 0.05-m diameter dodecane puddles or 0.05-m dodecane saturated saltcake. These energy sources, which correspond to 10, 35, and 270 J did not result in sustained ignition (Fauske 1995). Second, the injection of a 138 J match with a release time of 3 ms under the same conditions also failed to produce ignition.

Potential credible external ignition sources include gasoline fires resulting, for example, from the rupture of a gasoline tank of a vehicle that has collided with a riser as the vehicle was driven over the top of a tank, and lightning strikes. The probability of a significant gasoline fire can be limited using existing controls. The annual frequency of lightning striking tank C-103 is estimated to be about 5×10^{-4} (MacFarlane 1994). The likelihood that a secondary lightning current would be capable of igniting the poorly conductive, highly "subflash" organic liquid layer is currently being evaluated and will be included in a forthcoming report on lightning evaluations.

The consequences of organic solvent fires have been examined. Tanks with organic solvents can be mitigated by either providing lightning protection or ensuring the availability of adequate vent paths. Lightning protection can further reduce the frequency of potential ignition. The provision of an adequate vent path achieves mitigation by ensuring tank integrity in the event of a fire, thereby keeping the consequences of the fire within risk acceptance guidelines.

Meacham et al. (1995b) quantified the potential consequences of an organic pool fire in tank C-103. A postulated fire is ignited locally and then spreads to the surrounding fuel regions until the fire self-extinguishes at the oxygen extinguishment limit. The opening of leak paths (lifting of unbolted riser covers and pit cover blocks) caused by the fire-generated internal

pressurization of the tank was accounted for. It was concluded that the fire burns out before the tank overpressure exceeds the tank structural capabilities and the consequences would be within risk acceptance guidelines. It is believed that the pool fire case envelopes other scenarios such as entrained organic solvent fires as the fire spread rate for the latter is well below that for the pool fire case.

5.2 ORGANIC COMPLEXANTS

The presence of degraded solvents and organic complexants along with oxidizer materials like sodium nitrate and sodium nitrite present the potential for uncontrollable condensed-phase chemical reactions including spontaneous bulk runaway reactions of the Arrhenius type and propagating combustion reactions.

Spontaneous Runaway Reaction. Spontaneous bulk runaway reaction without ignition sources can occur when the chemical heat generation rate produced by an Arrhenius type reaction exceeds the rate of heat dissipation by conduction in some volume of the substance (Gygax 1990). The requirement for stability is therefore often expressed in terms of two characteristic time constants (Gygax 1990)

$$t_a > t_c \quad (5-4)$$

where t_a is the characteristic time of adiabatic runaway

$$t_a = \frac{T^2}{\dot{T} E_a/R} \quad (5-5)$$

and t_c is the characteristic cooling time which for an infinite slab geometry is approximately

$$t_c \approx \frac{H^2}{4\alpha} \quad (5-6)$$

Here T (K) is the temperature, \dot{T} (K/s) is the rate of temperature rise corresponding to temperature T due to chemical heating, E_a is the activation energy (J/mol), R (8.314 J/mol·K) is the gas constant, H (m) is the total waste height and α (m²/s) is the thermal diffusivity. It is pertinent to note that Equation 5-4 and definitions 5-5 and 5-6 are consistent with the classical Frank-Kamenetskii model (1955) for systems with a high Biot number, in which heat transfer occurs conductively within the reacting mass.

While values for t_c can be estimated for the waste tanks (see Tables 2-4 through 2-9), values for t_a are not known. Fortunately, it can be shown that

$$t_c < t_s \quad (5-7)$$

where t_s is the time the Hanford waste has been demonstrated to be stored safely. Since t_s is well in excess of the characteristic cooling times, t_c , which range from a few hours to about 3 years (see Tables 2-4 through 2-9) and the fact that no runaway conditions have been experienced to date, provides secure evidence that Equation 5-4 is indeed satisfied. This observation can be made without requiring a knowledge of t_a , water content, or waste uniformity, and will not be altered by interim stabilization including possible long term moisture loss (see Section 2.0). Shrinkage associated with moisture loss (decreasing H) as well as increasing gaseous porosity (increasing α) both have the effect of decreasing the characteristic cooling times. (See Appendices C and D).

Condensed-Phase Combustibility and Propagating Reactions. In addition to satisfying a certain minimum fuel concentration similar to the lower flammability limit (LFL) for gases, a substantial ignition source must be available to assure sustained combustion in the condensed phase. Measured flammability or combustion characteristics for several surrogate organic complexants are summarized in Table 5-1 (Fauske et al. 1995).

Table 5-1. Approximate LFL, Ignition Temperature, T_{ig} , and Burn Velocity, U_b

Fuel	LFL, wt% ^b	T_{ig} , °C	U_b , ms ⁻¹
NaAcetate	20.5 (6)	300	3.3×10^{-4}
NaAcetate·3H ₂ O	No reaction	No reaction	No reaction
Na ₃ Citrate·2H ₂ O	33 (8)	230	3×10^{-4}
Na ₃ HEDTA·2H ₂ O	19 (6)	220	2.5×10^{-4}
^b Measured at $T_o = 30$ °C. The effect of ambient temperature is discussed in Appendix G and the effect of water is discussed in Appendix H. Numbers in parenthesis are wt% total organic carbon (TOC).			

Several characteristics noted in Table 5-1 deserve further discussion. The LFL values for the organic complexants exceed 50% of the stoichiometric values which is similar to flammable hydrocarbon mixtures (Stull 1977). Historical records and measurements of the composition of the wastes and the current understanding of aging and solubility strongly infer that such high fuel concentrations are not present in the Hanford waste tanks (see Section 2.0).

The measured ignition temperatures, T_{ig} , are much higher than the current waste ambient temperatures (see Tables 2-4 through 2-9). Onset of combustion, therefore, also requires the presence of an adequate ignition source. It is noted that available Reactive System Screen Tool (RSST) adiabatic calorimetry data with actual waste samples (such as tank SY-101),

synthetic waste samples which simulate tank SY-101) (Bechtold 1992) and surrogate samples containing only organic complexant and sodium nitrate (Fauske et al. 1995) all indicate approximately the same onset temperature for significant exothermic activity of about 180 °C.

Measurable exothermic activity is generally noted at a lower temperature than the ignition temperature when the sample satisfies the LFL. Onset temperatures for significant exothermic activity of about 150 °C are noted with samples containing materials like tributyl phosphate such as the waste sample from tank C-204 (Bechtold 1995), simulant samples of waste resulting from processing PUREX acid sludge (Scheele et al. 1995) and simple surrogate samples consisting of tributyl phosphate and sodium nitrate (Fauske 1995). These data provide support for the applicability of the surrogate data to actual Hanford waste. Additional calorimetry tests with waste simulants and actual waste samples from selected tanks are ongoing to further confirm this conclusion.

The burn velocities presented in Table 5-1 are especially noteworthy. These extremely low burn velocities indicate the need for a very strong ignition source in order to initiate sustained combustion. These observations are consistent with the finding that materials like ferrocyanides (Cady 1992) and various organic complexants (U.S. Bureau of Mines 1993) mixed with oxidizing materials like nitrates and nitrites are in general insensitive to spark, impact, shock or friction. Again, confirmatory testing with appropriate waste simulants and actual waste samples from selected tanks are being performed to test the strong inference of the recent work that the wastes require high initiation temperatures for the onset of combustion.

Potential ignition sources including sparks, flames, hot objects and lightning are discussed in this section. It is assumed that the combustible conditions exist, i.e., the fuel concentration exceeds the LFL.

Sparks. An estimate of the minimum ignition energy (MIE) to initiate combustion can be obtained from

$$Q_{\min} = \frac{4}{3} \pi r_{\text{crit}}^3 \rho c (T_{\text{ig}} - T_o) \quad (5-8)$$

where ρ (kg/m³) is the density of the combustible mixture, c (J/kg·K) is the specific heat of the combustible mixture, T_{ig} (K) is the ignition temperature, T_o (K) is the ambient temperature, and r_{crit} (m) is the critical radius. This expression was derived from the heat balance for the system.

$$\frac{4}{3} \pi r^3 \rho c (T_f - T_o) \frac{U_b}{r} = 4\pi r^2 k \frac{dT}{dr} \approx 4\pi r k (T_f - T_o) \quad (5-9)$$

where U_b/r (t) is a characteristic time, T_f (K) is the flame temperature, and k (w/m·K) is the thermal conductivity, and results in

$$r_{crit} = \frac{3\alpha}{U_b} \tag{5-10}$$

where α (m²/s) is the thermal diffusivity.

First, this ignition theory can be used to predict the MIE of a combustible stoichiometric gas mixture. Considering the following property values for a typical hydrocarbon gas mixture such as methane-air evaluated at $T_{ig} = 810$ K; $\rho \approx 0.45$ kg/m³, $c = 1000$ K, $\alpha = 9 \times 10^{-5}$ m²/s, $U_b = 0.45$ m/s and $T_o = 300$ K, Q_{min} is estimated to be 0.21 mJ, which is in excellent agreement with the measured spark energy value of 0.29 mJ (Stull 1977). The suggested strong sensitivity to the burn velocity (Q approximately equal to U_b^{-3}) is also consistent with experimental observation (Stull 1977).

Verification of the strong burn velocity dependence is especially significant for condensed-phase combustion involving organic complexants because the burn velocities (Table 5-1) are quite small. Application of this ignition theory using the following property values evaluated at $T_{ig} = 520$ K; $\rho = 1500$ kg/m³, $c = 1500$ J/kg-K, $\alpha = 2 \times 10^{-7}$ m²/s, $U_b = 5 \times 10^{-4}$ m/s and $T_o = 320$ K, leads to a Q_{min} of 3.3 J; i.e., about four orders of magnitude larger than for flammable hydrocarbon mixtures. This energy is well in excess of the maximum spark energies expected from discharge of various types of electrically conducting objects that could be present in the Hanford waste tanks. Typical maximum theoretical spark energies associated with various objects are illustrated in Table 5-2 (Eckhoff 1991).

Table 5-2. Maximum Theoretical Spark Energies From Discharge of Various Types of electrically Conducting Objects

Object	Energy, mJ
Single Screw	0.2
Flange	2
Shovel	4
Small Container (bucket, 50 L drum)	2-20
Funnel	2-20
Drum (200 L)	20-60
Person	20-60
Major Plant Items (reaction vessels)	20-200
Road Tanker	200

The assessment of the MIE value for short-duration sparks in condensed-phase combustion is quite conservative. In contrast to a combustible gaseous mixture, the energy from the spark must be delivered to the condensed phase material. While the power density of the spark is enormous, the short duration (microsecond time scale) prevents sustained combustion prior to the dissipation of the spark energy. This feature is demonstrated by the following analysis.

Rewriting Equation (5-9) for a plane geometry, the critical ignition thickness is

$$\delta_{\text{crit}} \approx \frac{\alpha}{U_b} \quad (5-11)$$

The corresponding ignition time, t_{ig} , can be obtained by equating the thermal boundary layer thickness

$$\delta \approx \sqrt{\alpha t} \quad (5-12)$$

with the critical ignition front thickness resulting in

$$t_{ig} = \frac{\alpha}{U_b^2} \quad (5-13)$$

Setting $\alpha = 2 \times 10^{-7} \text{ m}^2/\text{s}$ and $U_b = 5 \times 10^{-4} \text{ m/s}$, the critical ignition time is of the order of 1 s. The significance of this value is that potential ignition sources such as sparks which have extremely high power densities but also are extremely short-lived (microsecond range) are not capable of initiating sustained combustion in condensed-phase materials of interest. The thermal boundary layer resulting from such ignition sources are much too small to satisfy the requirement for sustained combustion.

Flames. Flames readily ignite combustible gas mixtures; hence, it is of interest to evaluate the potential for a flame to initiate a condensed-phase combustion event. Elementary heat balance considerations indicate that the maximum condensed-phase material temperature, T_{max} , following a postulated burn can be estimated from (Epstein 1990)

$$T_{\text{max}} - T_o \approx 0.35 \left[\frac{\sigma \epsilon \rho_{g,o} C_{v,g} T_{g,o}^5 \alpha_s V}{k_s^2 A} \right]^{1/2} \quad (5-14)$$

where σ is the Boltzman constant, ϵ is the emissivity, $\rho_{g,o}$ (kg/m³) is the initial gas density, $C_{v,g}$ (J/kg·K) is the gas specific heat, $T_{g,o}$ (K) is the initial flame temperature, α_s (m²/s) is the thermal diffusivity of the solid phase, V (m³) is the volume of the burn, A (m²) is the corresponding surface area of the burn or the surrounding condensed-phase material and k_c (w/m-K) is the conductivity of the condensed-phase material. Tabulated values of $(T_{max} - T_o)$ and $T_{g,o}$ are provided in Table 5-3 based on $\epsilon = 1$, $C_{v,g} = 1000$ J/kg-K, $V/A = 1$, $\alpha_s = 2 \times 10^{-7}$ m²/s, $k = 0.5$ w/m-K and $\rho_{g,o} = 1.1$ kg/m³. These values are comparable to the results that were obtained by Fox (1991) on the basis of detailed numerical analysis.

Table 5-3. Initial Flame Temperatures and Maximum Condensed-Phase Temperatures

$T_{g,o}$, K	$T_{max} - T_o$, K
1500	219
1400	184
1300	153
1200	125
1100	101
1000	79

Considering that transient burning (if at all credible) would be limited to temperatures of about 1000 °K, this type of ignition source would not appear to be a threat to initiating condensed-phase combustion.

Hot Objects. The necessary minimum temperature of a hot object to initiate sustained combustion if brought in direct contact with condensed-phase combustible material can be estimated from the Contact Temperature Ignition (CTI) criterion (Fauske et al. 1995)

$$T_H = \frac{1}{\sigma} (T_{ig} - T_o) + T_{ig} \tag{5-15}$$

where T_H (K) is the temperature of the hot object and σ is given by

$$\sigma = \sqrt{\frac{(k\rho c)_H}{(k\rho c)_o}} \tag{5-16}$$

where subscript o refers to the combustible condensed-phase material. Equations 5-15 and 5-16 are exact for a planar interface and conservative for a curved interface.

In the case of a hot steel object, the value of σ is about 8, requiring T_H to be only about 10% higher than T_{ig} , i.e., about 250 °C for condensed-phase combustion of the substances in Table 5-1. Furthermore, the dimensions of the steel object can also be assessed by recalling the critical ignition time is about 1 second, the minimum steel thickness (considering plane geometry) is given by Equation 5-17

$$x_{\min} \approx \sqrt{\alpha t} \quad (5-17)$$

Setting $\alpha = 5 \times 10^{-6} \text{ m}^2/\text{s}$, x_{\min} is approximately 2 mm. It is therefore not surprising that a small hot steel ball (diameter of about 1.6 mm, and $T_H \approx 1300 \text{ °C}$ and energy content of 10 J) is capable of producing sustained combustion when brought into contact with combustible mixtures such as summarized in Table 5-1 (Fauske 1995). Such ignition sources, however, can be removed from consideration by controlling and/or limiting intrusive activities.

For completeness, it is relevant to mention that the waste must be essentially dry for such ignition sources to be effective. Small quantities of water will prevent the contact temperature from reaching the ignition temperature, even for stoichiometric mixtures. This aspect of the problem is discussed further in Appendix H.

External Ignition Sources. Two credible external ignition sources, gasoline fires and lightning strikes, were discussed previously. The probability of a significant gasoline fire can be limited using existing controls and/or limiting intrusive activities. The annual frequency of lightning striking a Hanford waste tank is estimated to be about 5×10^{-4} (MacFarlane 1994). The likelihood that lightning currents inside the tank would be capable of igniting the waste is currently being evaluated and will be included in a forthcoming report on lightning evaluations. A preliminary evaluation including some simple scoping experiments (see Appendix I) suggest that the likelihood is low. The above observations together with the predicted absence of solid waste combustible conditions in the Hanford tank farms, suggest that external ignition sources do not represent significant risk threats.

5.3 SUMMARY

This discussion of chemical vulnerabilities including tank headspace flammability in connection with organic solvents and condensed-phase reactions in connection with the organic complexants leads to the following conclusions:

- In contrast to flammable gases, sustained combustion of organic solvents require very large ignition sources. In as much as no internal ignition sources are available, only external ignition sources such as ignitable gasoline spills and lightning strikes represent potential ignition sources. Gasoline spills can be limiting by controlling and/or limiting intrusive activities and lightning strikes are estimated to have low frequencies (5×10^{-4} per year per tank). Furthermore, given the unlikely scenario

that an organic solvent fire would occur, the consequences are predicted to be within risk acceptance guidelines.

- Condensed-phase spontaneous (no ignition source required) bulk runaway reactions are not possible, and
- Similar to the organic solvents, initiation of condensed-phase combustion in dry wastes also require very large ignition sources. This reduces the likelihood of potential ignition sources to gasoline spills and lightning strikes and together with the predicted absence of combustible conditions in the Hanford tank farms, suggest condensed-phase combustion scenarios do not represent significant risk threats.

These conclusions do not depend on a detailed knowledge of the fuel and water contents of the wastes or their heterogeneity. The conclusions will be valid after the completion of interim stabilization and possible long-term dryout of the wastes. Confirmatory testing with appropriate waste simulants and actual waste samples from selected tanks are being performed to further verify the above observations.

The principal elements of this analysis are under critical test in studies of carefully designed waste simulants and actual wastes from selected tanks.

6.0 CONCLUDING REMARKS

The significant observations made in this report are the following:

- Spontaneous runaway reactions (no ignition source required).
 - The Hanford waste has remained stable for periods much longer than the waste characteristic cooling times. This demonstrates that the chemical heat is removed safely.
 - The waste characteristic cooling times are not adversely affected by waste dryout.
 - Post interim stabilization waste temperatures in passively ventilated tanks continue to decline consistent with radionuclide decay.
- Condensed phase combustion.
 - Credible internal ignition sources cannot initiate organic solvent fires or condensed phase combustion reactions. This is true even for stoichiometric fuel-oxidizer conditions.
 - Testing and analysis show that sparks, shocks, and impacts lack sufficient energy to initiate combustion. Robust and/or sustained energy sources are required.
 - The waste is aging to an overall less energetic state and interim stabilization operations have decreased fuel concentrations in the single-shell tanks.
- Headspace flammability.
 - Tank headspaces appear to be well mixed and sampling data indicate that steady-state flammable gas concentrations are much lower than the lower flammability limit (LFL).
 - Episodic gas release events (GREs) observed in tanks with large amounts of supernatant can result in high flammable gas concentrations. Interim stabilization prevents GREs, none are known to have occurred in such tanks.
 - Concerning the difficulty of ruling out credible internal ignition sources (such as sparks), the occurrence of significant GREs requires mitigation.

- Lightning.

- It appears difficult to deterministically eliminate lightning as an external ignition source. However, the probability of a lightning strike initiated event is low. Taken together with the low probability of challenging the tank integrity in case of a solvent fire or the low probability of satisfying condensed-phase combustible conditions, this suggests that external ignition sources do not represent a significant threat.

Based on these observations, it is concluded that the condensed phase of the waste is substantially more stable and more difficult to ignite than originally thought. Episodic gas release events leading to potential concentrations in excess of flammability limits can be mitigated by removing supernatant from the tanks.

7.0 REFERENCES

- Agnew, S. F., 1995, *Hanford Defined Wastes: Chemical and Radionuclide Compositions*, LA-UR-94-2657, Rev. 2, Los Alamos National Laboratory, Los Alamos, New Mexico.
- Allemann, R. T., 1995, *A Discussion of Some Mechanisms for Sudden Gas Release from Single-Shell Waste Tanks* PNL-WTS-101095, Pacific Northwest Laboratory, Richland, Washington.
- Ashby, E. T., C. Jonah, D. Meisel, L. R. Pederson, and D. M. Strachan, 1992, *Gas Generation and Retention in Tank 241-SY-101: A Summary of Laboratory Studies, Tank Data, and Information Needs*, PNL-8124, Pacific Northwest Laboratory, Richland, Washington.
- Ashby, E. C., A. Annis, E. K. Barefield, D. Boatright, F. Doctorovich, C. L. Liotta, H. M. Neumann, A. Konda, C. F. Yao, K. Zhang, and N. G. McDuffie, 1994, *Synthetic Waste Chemical Mechanism Studies*, WHC-EP-0823, Westinghouse Hanford Company, Richland, Washington.
- Babad, H., and D. A. Turner, 1993, *Interim Criteria for Organic Watch List Tanks at the Hanford Site*, WHC-EP-0681, Westinghouse Hanford Company, Richland, Washington.
- Barefield, E. K., C. L. Liotta, D. Boatright, H. M. Neumann, A. Deshpande, S. Seymore, and F. Doctorovich, 1995, *Flammable Gas Safety Program: Mechanisms of Gas Generation from Simulated SY Tank Farm Wastes - FY 1994 Progress Report*, PNL-10822, Pacific Northwest Laboratory, Richland, Washington.
- Barney, G. S., 1994, *The Solubilities of Significant Organic Compound in HLW Tank Supernate Solutions*, WHC-SA-2565-FP, Westinghouse Hanford Company, Richland, Washington.
- Barney, G. S., 1995, *The Solubilities of Significant Organic Compounds in HLW Tank Supernate Solutions - FY1995 Progress Report*, WHC-EP-0988, December, Westinghouse Hanford Company, Richland, Washington.
- Bechtold, D. B., 1992, *Adiabatic Calorimetry Interim Progress Report for April 1992*, (internal memorandum to distribution, May 5), Westinghouse Hanford Company, Richland, Washington.
- Bechtold, D. B., 1995, *Results of Adiabatic Calorimetry of Tank C-204 Auger Material*, Westinghouse Hanford Company, Richland, Washington.

- Bryan, S. A., and L. R. Pederson, 1994, *Composition, Preparation, and Gas Generation from Simulated Wastes of Tank 241-SY-101*, PNL-10075, Pacific Northwest Laboratory, Richland, Washington.
- Burger, L. L., 1995, *Calculations of Reaction Energies and Adiabatic Temperatures for Waste Tank Reactions*, PNL-8557, Rev. 1, Pacific Northwest Laboratory, Richland, Washington.
- Cady, H. H., 1992, *Evaluation of Ferrocyanide/Nitrate Explosive Hazard*, LA-12589-MS, Los Alamos National Laboratory, Los Alamos, New Mexico.
- Camaioni, D. M., W. D. Samuels, B. D. Lenihan, S. A. Clauss, K. L. Wahl, and J. A. Campbell, 1994, *Organic Tanks Safety Program: Waste Aging Studies*, PNL-10161, Pacific Northwest Laboratory, Richland, Washington.
- Camaioni, D. M., K. L. Wahl, W. D. Samuels, J. A. Campbell, S. A. Clauss, W. J. Shaw, B. D. Lenihan, 1995, *Organic Tanks Safety Program: FY95 Waste Aging Studies*, PNL-10794, Pacific Northwest Laboratory, Richland, Washington.
- Cash, R. J., J. E. Meacham, and G. T. Dukelow, 1995, *Quarterly Report on the Ferrocyanide Safety Program for the Period Ending March 31, 1995*, WHC-EP-0474-16, Westinghouse Hanford Company, Richland, Washington.
- Cash, R. J., and J. E. Meacham, 1996, *Quarterly Report on the Ferrocyanide Safety Program for the Period Ending December 31, 1995*, WHC-EP-0474-19, Westinghouse Hanford Company, Richland, Washington.
- Chu, T. V., and R. J. Goldstein, 1973, "Turbulent Convection in a Horizontal Layer of Water," *J. Fluid Mechanics* vol. 60, pp. 141-159.
- Crowe, R. D., M. Kummerer, and A. K. Postma, 1993, *Estimation of Heat Load in Waste Tanks Using Average Space Temperatures*, WHC-EP-0709, Westinghouse Hanford Company, Richland, Washington.
- Delegard, C. H., 1980, *Laboratory Studies of Complexed Waste Slurry Volumes: Volume Growth in Tank 241-SY-101*, RHO-LD-124, Rockwell Hanford Operations, Richland, Washington.
- Delegard, C. H., 1987, *Identities of HEDTA and Glycolate Degradation Products in Simulated Hanford High-Level Waste*, RHO-RE-ST-55P, Rockwell Hanford Operations, Richland, Washington.
- Eckhoff, R. K., 1991, *Dust Explosions In the Process Industries*, Butterworth-Heinemann, Oxford, England.

- Epstein, M., 1990, *Maximum Crust Temperature Following a Burn in the Waste Tank*, (memorandum to D. D. Stepnewski, Westinghouse Hanford Company, July 2), Fauske and Associates, Inc., Burr Ridge, Illinois.
- Epstein, M., H. K. Fauske, and J. Burelbach, 1995, *Ignitability of Organic Solvent In Hanford Tank 103-C Following Interim Stabilization*, FAI/95-17, Fauske and Associates, Inc., Burr Ridge, Illinois.
- Epstein, M., H. K. Fauske, M. D. Crippen, D. R. Dickinson, J. D. McCormack, R. J. Cash, J. E. Meacham, and C. S. Simmons, 1994, *Ferrocyanide Safety Program: An Assessment of the Possibility of Ferrocyanide Sludge Dryout*, WHC-EP-0816, Westinghouse Hanford Company, Richland, Washington.
- Epstein, M., 1995, *Turbulent Free - Convection Mixing In a Tank Headspace*, FAI/95-63, Fauske and Associates, Inc., Burr Ridge, Illinois.
- FAI, 1994, *Hazard Assessment Techniques for Hanford Waste Tanks Presently or Previously Containing Liquid Organic Layers*, FAI/94-91, Fauske and Associates, Inc., Burr Ridge, Illinois.
- Fauske, H. K., 1995, *Summary of Laboratory Scoping Tests Related to Organic Solvents Combustion by Nitrate Oxidation and Organic Solvent Ignitability*, Fauske and Associates, Inc., Burr Ridge, Illinois.
- Fauske, H. K., M. Epstein, D. R. Dickinson, R. J. Cash, D. A. Turner, and J. E. Meacham, 1995, *The Contact-Temperature Ignition (CTI) Criteria for Propagating Chemical Reactions Including the Effect of Moisture and Application to Hanford Waste*, WHC-SD-WM-ER-496, Rev. 0, Westinghouse Hanford Company, Richland, Washington.
- Frank-Kamenetskii, D. A., 1955, *Diffusion and Heat Exchange in Chemical Kinetics*, Princeton University Press, Princeton, New Jersey.
- Glassman, I., and F. L. Dryer, 1980/1981, *Flame Spreading Across Liquid Fuels*, *Fire Safety Journal*, vol. 3, pp. 123-138, Elsevier, Netherlands.
- Grigsby, J. M., A. K. Postma, R. J. Cash, J. E. Meacham, D. R. Dickinson, M. A. Lilga, H. K. Fauske, and M. Epstein, 1996, *Assessment of the Potential for Ferrocyanide Propagating Reaction Accidents*, WHC-SD-WM-SARR-038, Rev. 0, Westinghouse Hanford Company, Richland, Washington.
- Gygax, R. W., 1990, *Scale up Principles for Assessing Thermal Runaway Risks*, *Chemical Engineering Progress*, p. 53, February.

- Hanlon, B. M., 1995, *Waste Tank Summary Report for Month Ending July 31, 1995*, WHC-EP-0182-88, Westinghouse Hanford Company, Richland, Washington.
- Hopkins, J. D., 1994, *Criteria for Flammable Gas Watch List Tanks*, WHC-EP-0702, Westinghouse Hanford Company, Richland, Washington.
- Huckaby, J. L., and M. S. Story, 1994, *Vapor Characterization of Tank 241-C-103*, WHC-EP-0780, Westinghouse Hanford Company, Richland, Washington.
- Huckaby, J. L., H. Babad, and D. R. Bratzel, 1995, *Headspace Gas and Vapor Characterization Summary for the 43 Vapor Program Suspect Tanks*, WHC-WM-SD-ER-514, Rev. 0, Westinghouse Hanford Company, Richland, Washington.
- Kummerer, M., 1994, *Topical Report on Heat Removal Characteristics of Waste Storage Tanks*, WHC-SD-WR-SARR-010, Rev. 0, Westinghouse Hanford Company, Richland, Washington.
- Lechelt, J. A., 1995, *Temperatures of Interim Stabilized Saltcake Tanks*, (internal memorandum to M. A. Payne, April 28), Westinghouse Hanford Company, Richland, Washington.
- 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.
- Lilga, M. A., E. V. Alderson, D. J. Kowalski, M. R. Lumetta, and G. F. Schiefelbein, 1994, *Ferrocyanide Safety Project, Task 3: Ferrocyanide Aging Studies - FY 1994 Annual Report*, PNL-10126, Pacific Northwest Laboratory, Richland, Washington.
- Lilga, M. A., E. V. Alderson, R. T. Hallen, M. O. Hogan, T. L. Hubler, G. L. Jones, D. J. Kowalski, M. R. Lumetta, G. F. Schiefelbein, and M. R. Telander, 1995, *Ferrocyanide Safety Project: Ferrocyanide Aging Studies - FY 1995 Annual Report*, PNL-10713, Pacific Northwest Laboratory, Richland, Washington.
- MacFarlane, D. R., 1994, *Probabilistic Safety Assessment for Hanford High-Level Waste Tank 241-SY-101*, LA-UR-93-2730, TSA-6-93-R111, Los Alamos National Laboratory, Los Alamos, New Mexico.
- Meacham, J. E., R. J. Cash, and G. T. Dukelow, 1995a, *Quarterly Report on the Ferrocyanide Safety Program for the Period Ending June 30, 1995*, WHC-EP-0474-17, Westinghouse Hanford Company, Richland, Washington.

- Meacham, J. E., D. A. Turner, J. C. Van Keuren, M. G. Plyś, M. Epstein, H. K. Fauske, J. P. Burelbach, J. M. Grigsby, and A. K. Postma, 1995b, *Risk from Organic Solvent fires in C-103 Following Interim Stabilization*, WHC-SD-WM-SARR-001, Supplement 1, Westinghouse Hanford Company, Richland, Washington.
- Meisel, D., C. D. Jonah, M. S. Matheson, M. C. Sauer, Jr., F. Barnabas, E. Cerney, Y. Cheng, and T. Wojta, 1992, *Radiation Chemistry of High-Level Wastes ANL/CHM Task Force on Gas Generation in Waste Tanks*, ANL-92/40, Argonne National Laboratory, Argonne, Illinois.
- Meisel, D., C. D. Jonah, S. Kapoor, M. S. Matheson, and M. C. Sauer, Jr., 1993, *Radiolytic and Radiolytically Induced Generation of Gases from Synthetic Wastes*, ANL-93/43, Argonne National Laboratory, Argonne, Illinois.
- Rohsenow, W. M., and J. P. Hartnett, 1973, *Handbook of Heat Transfer*, McGraw-Hill Book Company, New York, New York.
- Sasaki, L. M., and B. D. Valenzuela, 1994, *Ferrocyanide Safety Program: Data Interpretation Report for Tank 241-T-107 Core Samples*, WHC-EP-0796, Westinghouse Hanford Company, Richland, Washington.
- Scheele, R. D., R. L. Sell, J. L. Sobolik, and L. L. Burger, 1995, *Organic Tank Safety Project: Preliminary Results of Energetics and Thermal Behavior Studies of Model Organic Nitrate and/or Nitrite Mixtures and a Simulated Organic Waste*, PNL-10213, 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.
- Strachan, D. M., 1994, *Status and Integration of the Gas Generation Studies Performed for the Hydrogen Safety Program - FY 1993*, PNL-9459,
- Stull, D. R., 1977, "Fundamentals of Fire and Explosion", *AIChE Monograph Series*, 10, Volume 73, American Institute of Chemical Engineers, New York, New York.
- Toth, J. J., P. G. Heasler, M. E. Lerchen, J. G. Hill, and P. D. Whitney, 1995, *Analysis of Organic Carbon and Moisture in Hanford Single-Shell Tank Waste*, PNL-10360 Pacific Northwest Laboratory, Richland, Washington.

U.S. Bureau of Mines, 1993, *Testing of Organic Waste Surrogate Materials In Support of the Hanford Organic Tank Program*, U.S. Bureau of Mines, Pittsburgh Research Center, Pittsburgh, Pennsylvania.

Van Vleet, R. J., 1993a, *Radionuclide and Chemical Inventories for the Single Shell Tanks*, WHC-SD-WM-TI-565, Rev. 1, Westinghouse Hanford Company, Richland, Washington.

Van Vleet, R. J., 1993b, *Radionuclide and Chemical Inventories for the Double Shell Tanks*, WHC-SD-WM-TI-543, Rev. 1, Westinghouse Hanford Company, Richland, Washington.

APPENDIX A

THE 1957 KYSHTYM INCIDENT

The Kyshtym incident resulted from disruption of decay heat removal leading to severe overheating followed by combustion of a sodium acetate - sodium nitrate mixture (Fisher 1990). A layout of a typical Kyshtym tank (1 of 60) is shown in Figure A-1. During normal operation (see Figure A-2), the actively cooled tank contained about 175 m³ of waste solution with about 100 g/L of sodium nitrate and about 60 g/L of sodium acetate. The estimated decay heat of about 200 kW² was removed at temperatures well below 100 °C. Disruption of the active cooling system, however, led to complete loss of all water leaving behind a solid residue (containing ~10,000 kg of NaAcetate) which continued to overheat and resulted in a severe over-pressurization event when the temperature reached about 300 °C (Figures A-3 and A-4).

Consistent with the above observation, Reactive System Screening Tool (RSST) calorimeter tests with various sodium acetate-sodium nitrate mixtures have demonstrated the onset of combustion at a temperature of about 300 °C when the sodium acetate concentration exceeded about 20 wt% (Babad and Turner 1993). A simulation of the Kyshtym incident is illustrated in Figure A-5. Extrapolation of the noted RSST pressure to the Kyshtym tank suggests a pressure buildup of about 400 psi in the case the tank does not vent. However, the required overpressure to lift the 160,000 kg tank head plate is only about 4 psi. This plate was found some distance from the incident tank.

REFERENCES

- Babad, H., and D. A. Turner, 1993, *Interim Criteria for Organic Watch List Tanks at the Hanford Site*, WHC-EP-0681, Westinghouse Hanford Company, Richland, Washington.
- Fisher, F. D., 1990, *The Kyshtym Explosion and Explosion Hazards with Nitrate-Nitrite Bearing Wastes with Acetates and Other Organic Salts*, WHC-SD-CP-LB-033, Westinghouse Hanford Company, Richland, Washington.

The decay heat loads for the Hanford tank farms are much smaller (see Tables 2-4 through 2-9).

Figure A-1. Kyshtym Tank Layout

KYSHTYM Tank Layout

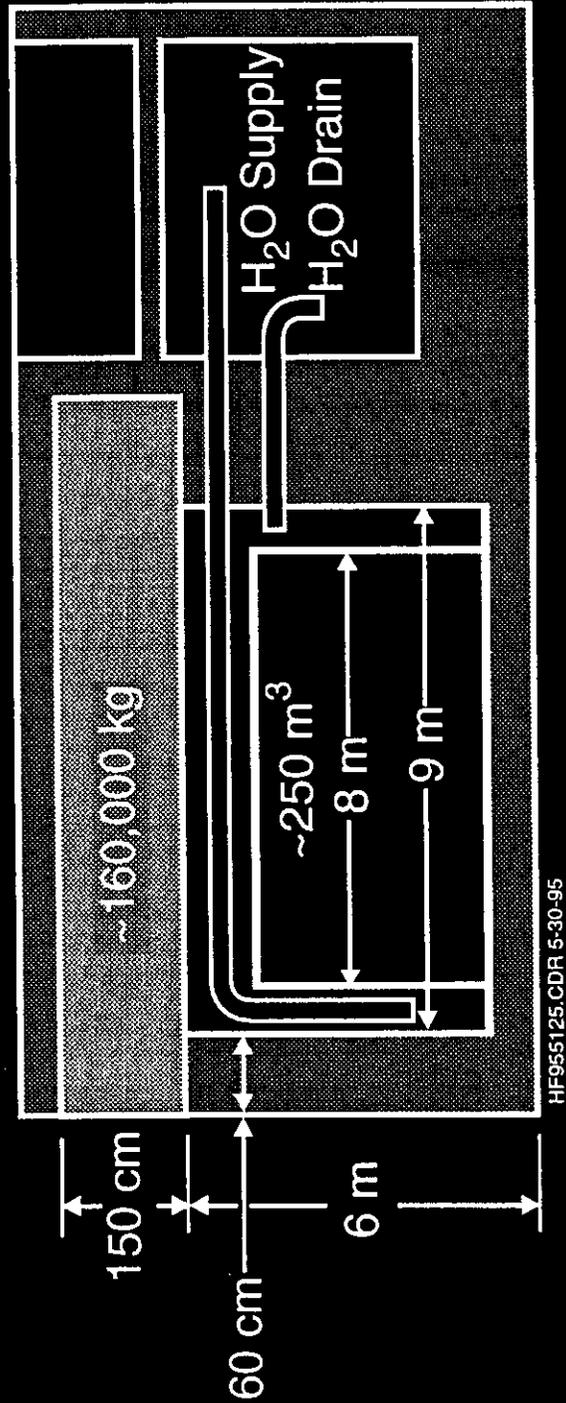


Figure A-2. Kyshtym Normal Operation

KYSHTYM - Normal Operation

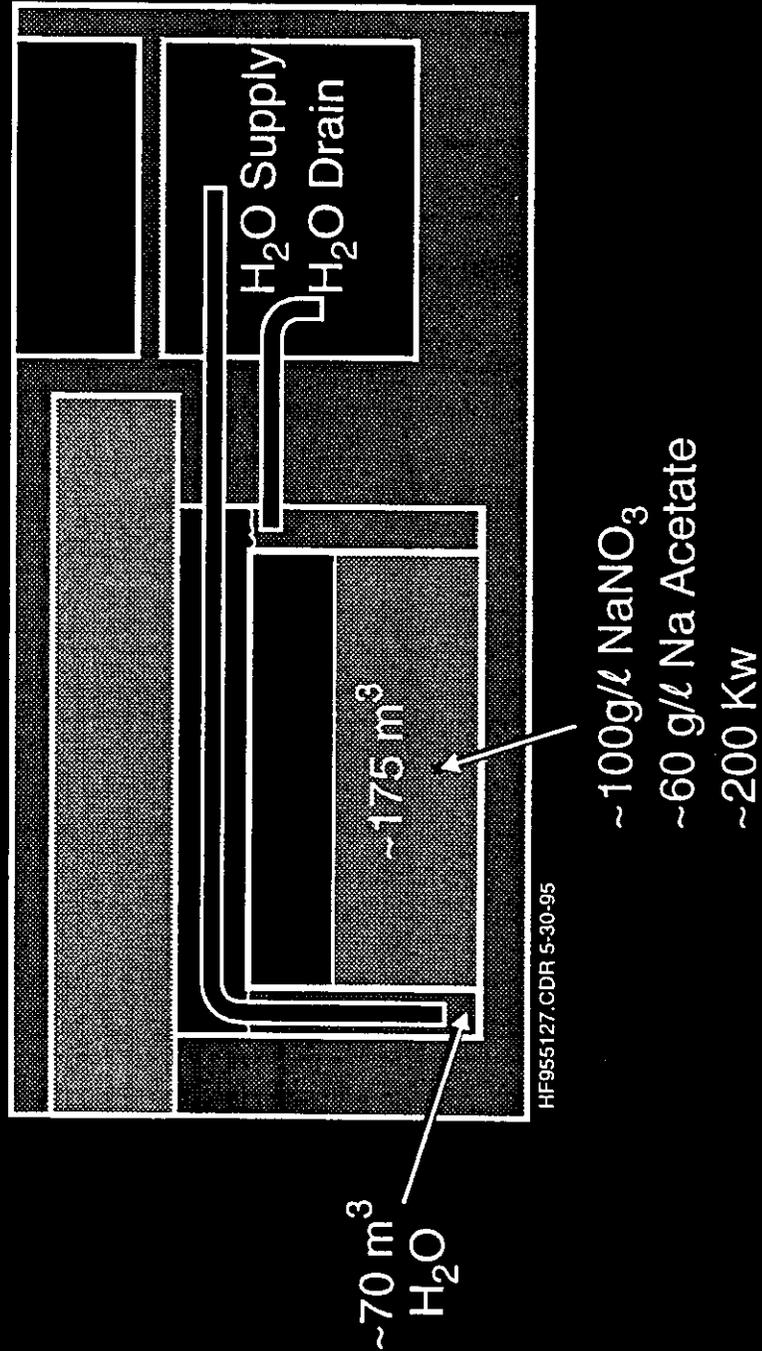
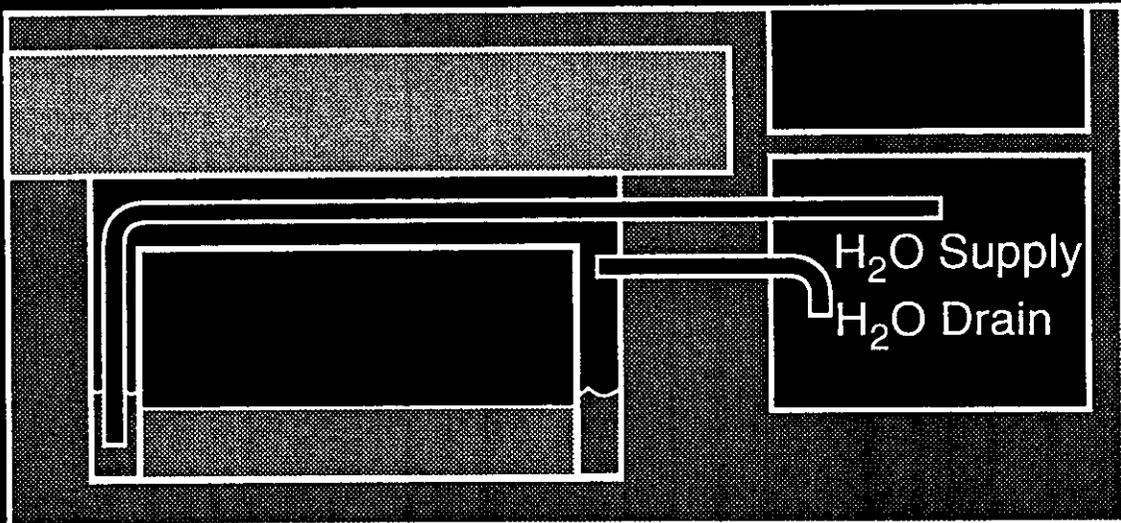


Figure A-3. Kyshtym Incident - Loss of Coolant

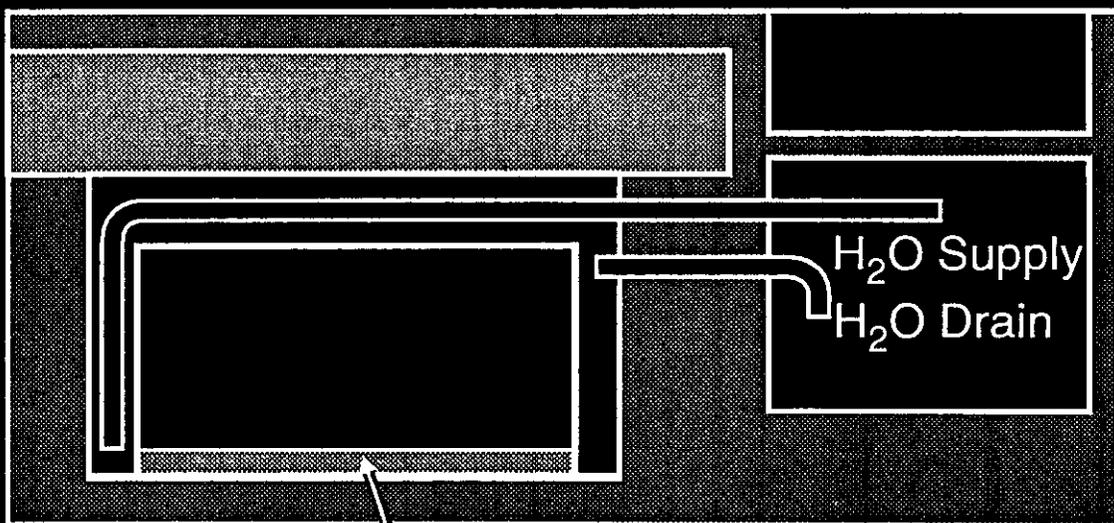
KYSHTYM INCIDENT - Loss of Coolant



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Figure A-4. Kyshtym Incident - Final Stage

KYSHTYM INCIDENT - Final Stage

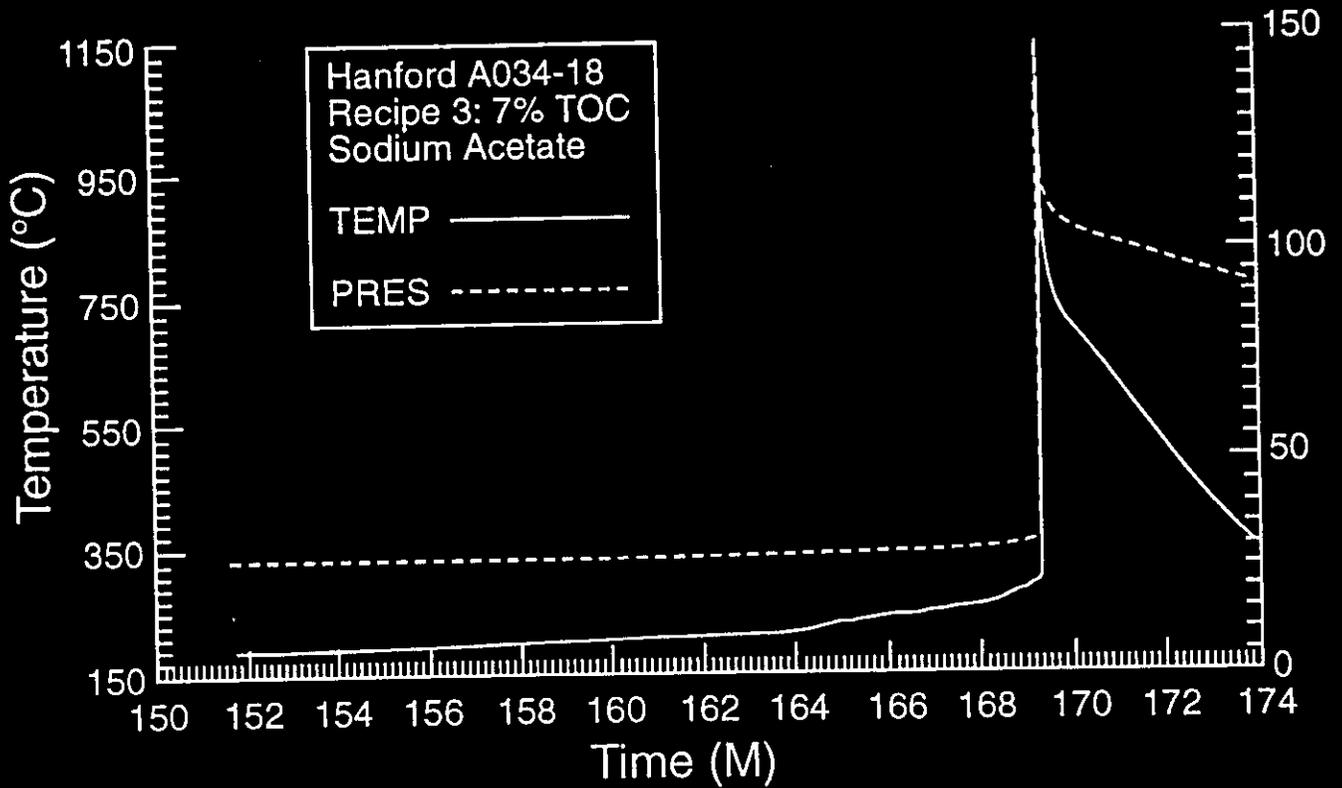


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Solid Residue (~10,000 kg Na Acetate)
300-350 °C

Estimated Damage, 5-10 tonnes Eqv. TNT

Figure A-5. RSST Simulation of Kyshtym Incident - Following Loss of Water



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APPENDIX B

TANK HEADSPACE MIXING CONSIDERATIONS

Gravitational instability of the Rayleigh-Benard type² occurs for a headspace gas when the temperature of the waste surface exceeds the temperature of the waste tank dome. This waste-tank Rayleigh-Benard problem was examined theoretically for the case where a high-molecular weight liquid-organic floats on top of the waste and it was demonstrated that the headspace gas undergoes high Rayleigh number turbulent convection (Epstein 1995). The analysis was based on the yearly average temperatures of the headspace gas and the Hanford atmosphere above the soil that covers the tank. Since the average temperature of the headspace gas always exceeds the average atmospheric temperature the flow of heat through the tank dome is, on the average, upward and into the overlying soil. It follows that, on the average, the temperature of the waste surface exceeds the dome temperature and the headspace gas undergoes turbulent Rayleigh-Benard type convection. However, as a result of annual temperature changes in the atmosphere which repeat themselves, a periodic flow of heat occurs in the soil above the waste tank. During some months of the year this periodic flow may overwhelm the upward flow of decay heat from a tank with a low waste heat output and actually reverse the flow of heat through the tank dome from upward to downward. The temperature of the dome is now higher than that of the waste surface and Rayleigh-Benard convection is no longer operative (although some weaker mode of headspace gas natural convection may persist due to heat flow through the tank walls). Here we desire to determine the waste tank conditions that result in the temporary suppression of Rayleigh-Benard convection.

From heat conduction theory the temperature T of the soil as a function of distance z measured from the surface of the soil is approximately (Carslaw and Jaeger 1959, Crowe et al. 1993)

$$T = T_{avg} + \frac{q_o z}{k} + (T_{max} - T_{avg}) e^{-\beta z} \cos(\omega t - \beta z) \quad (B-1)$$

where

k = thermal conductivity of soil,

q_o = average heat flux through the top of the tank over a one-year cycle,

t = time relative to July 15 when the maximum atmospheric temperature T_{max} occurs,

*Prepared by M. Epstein, January, 1996.

**The Rayleigh-Benard problem refers to natural convection of a gas confined between two horizontal boundaries, the lower boundary being warmer than the upper boundary.

T_{avg} = average temperature of the atmosphere over a one-year cycle,
 T_{max} = maximum temperature of atmosphere during one-year cycle,
 β = temperature wave number (inverse of wave length),
 ω = frequency of atmospheric temperature oscillations.

Note that $T_{max} - T_{avg}$ in Equation (B-1) is half the complete atmospheric temperature range. The wave number β is related to the thermal diffusivity of the soil α by the expression

$$\beta = \left(\frac{\omega}{2\alpha} \right)^{1/2} \quad (B-2)$$

The heat flux through the soil q at any depth z can be determined by differentiating Equation (B-1) with respect to z . The result is

$$q = q_o - k\beta(T_{max} - T_{avg}) e^{-\beta z} [\cos(\omega t - \beta z) - \sin(\omega t - \beta z)] \quad (B-3)$$

The heat flux q is taken to be positive in the upward direction. We note that the local heat flux is comprised of two terms: the average upward heat flux q_o generated by the waste and a periodic component due to the periodic temperature variation of the atmosphere above the soil. Clearly the local heat flux may be directed upward (positive) or downward (negative) depending on the magnitude of the periodic term relative to q_o . With increasing depth z the amplitude of the periodic term diminishes. We are interested in the sign of q at the top of the tank, that is at $z = z_{eff}$, where z_{eff} is the effective depth of the soil covering the tank. In particular we are interested in the conditions that cause the right-hand side of Equation (B-3) to be positive at $z = z_{eff}$; that is

$$q_o \geq k\beta(T_{max} - T_{avg}) e^{-\beta z_{eff}} [\cos(\omega t - \beta z_{eff}) - \sin(\omega t - \beta z_{eff})] \quad (B-4)$$

Whenever q_o obeys the above equation the flow of heat through the tank dome is upward and the headspace gas is experiencing Rayleigh-Benard convection.

Equation (B-4) can be converted to a more convenient form by noting that the average upward heat flux can be expressed in terms of the average headspace gas temperature T_{hs} over a one-year cycle; namely,

$$q_o = \frac{k(T_{hs} - T_{avg})}{z_{eff}} \quad (B-5)$$

Thus the criterion (B-4) for Rayleigh-Benard convection of the headspace gas becomes

$$T_{hs} \geq T_{avg} + \beta z_{eff}(T_{max} - T_{avg}) e^{-\beta z_{eff}} [\cos(\omega t - \beta z_{eff}) - \sin(\omega t - \beta z_{eff})] \quad (B-6)$$

For a given average headspace gas temperature T_{hs} we can numerically evaluate the magnitude of the right-hand side of Equation (B-6) to determine, say, the number of months during a one-year cycle in which the headspace gas is in turbulent free convection. Calculations were carried out using the following physical property and parameter estimates taken from Crowe et al. (1993): soil thermal diffusivity $\alpha = 5.2 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$, $\omega = 1 \text{ cycle (year)}^{-1} = 2 \times 10^{-7} \text{ radian s}^{-1}$, $\beta = 0.44 \text{ m}^{-1}$ (see Equation B-2), $z_{eff} = 4.0 \text{ m}$, $T_{avg} = 13.8 \text{ }^\circ\text{C}$, and $T_{max} = 27 \text{ }^\circ\text{C}$. Recall that the time t in Equation (B-6) is measured from July 15 when $T = T_{max}$ at $z = 0$ in Equation (B-1). The results are presented in Table B-1. We note that the headspace gas undergoes Rayleigh-Benard convection all-year long if its average temperature exceeds $19.4 \text{ }^\circ\text{C}$ ($67 \text{ }^\circ\text{F}$).

Table B-1. Average Headspace Gas Temperature Required for Rayleigh-Benard-Type Free Convection

Headspace Temperature Greater Than	Period of Rayleigh-Benard-Type Free Convection
13.8 °C (56.8 °F) ^a	6 months (mid December to mid June)
15.4 °C (59.7 °F)	7 months (end November to end June)
16.8 °C (62.2 °F)	8 months (mid November to mid July)
17.8 °C (64.8 °F)	9 months (end October to end July)
18.8 °C (65.8 °F)	10 months (mid October to mid August)
19.2 °C (66.6 °F)	11 months (end September to end August)
19.4 °C (67.0 °F)	12 months
^a Average temperature of Hanford site atmosphere-lower limit to headspace gas temperature.	

REFERENCES

- Carslaw, H. S. and Jaeger, 1959, *Conduction of Heat in Solids*, 2nd ed., Oxford University Press, London.
- Crowe, R. D., Kummerer, M., and Postma, A. K., 1993, *Estimation of Heat Load in Waste Tanks Using Average Vapor Space Temperatures*, WHC-EP-0709, Westinghouse Hanford Company, Richland, Washington.
- Epstein, M., 1995, *Turbulent Free-Convection Mixing in a Tank Headspace*, FAI/95-63, Fauske and Associates, Inc., Burr Ridge, Illinois.

APPENDIX C

THERMAL CONDUCTIVITY OF DRY WASTE MATERIAL

Based upon laboratory observations with both sludge and saltcake like materials, dry (no free moisture) waste material can be considered a porous media where the solids represent the continuous phase. As such, the thermal conductivity of dry waste material is best estimated with Russel's equation.

$$\frac{k_{\text{comp}}}{k_{\text{cont}}} = \frac{\nu p^{2/3} + 1 - p^{2/3}}{\nu(p^{2/3} - p) + 1 - p^{2/3} + p} \quad (\text{C-1})$$

where k_{comp} is the thermal conductivity for the composite mixture and k_{cont} is the thermal conductivity for the continuous phase, p is the porosity and ν is the ratio of the thermal conductivity of the porosity material to that of the continuous phase.

In the case of a saturated saltcake waste, where the porosities are filled with saturated salt solution, the value of ν is of the order 1, i.e., the thermal conductivity of the wet waste k_{comp} is approximately equal to the thermal conductivity of the solid waste k_{cont} . On the other hand, if the saltcake waste is assumed to be dry, i.e., the porosities are filled with gas rather than liquid, $\nu \ll 1$, and Equation (C-1) reduces to

$$\frac{k_{\text{comp}}}{k_{\text{cont}}} \approx \frac{1 - p^{2/3}}{1 - p^{2/3} + p} \quad (\text{C-2})$$

Considering the upper range of typical porosity values of 0.4, Equation (C-2) suggests that the thermal conductivity of the dry saltcake is at most reduced by a factor of 2 relative to the wet saturated saltcake configuration. A similar discussion applies to wet saturated sludge waste material which is subsequently assumed to dry out. Considering that the wet waste thermal conductivity is usually taken to be 1 w/m-K, the thermal conductivity for dry waste is estimated to be 0.5 w/m-K.

The above observation of a factor of 2 reduction in the thermal conductivity for dry versus wet waste material appears to be in reasonable agreement with thermal conductivity measurements made with actual waste tank samples (Bouse 1975). Measurements included data for dry samples at elevated temperatures, and should therefore provide valid data for the worst possible tank conditions, that is if the tank should become completely dry and heat up. The ratios of as received sample measured thermal conductivity to dry heated sample thermal conductivity are summarized in Table C-1.

Table C-1. Measured Thermal Conductivities (Bouse 1975)

Tank Number	$K_{as\ received}/k_{dry}$
SX-104	~ 2.06
S-108	~ 2
S-107	~ 5.13
S-105	~ 1.22
S-110	~ 1.71
SX-105	~ 2.39
SX-101	~ 0.68
S-109	~ 1.55
S-106	~ 2.30
SX-102	~ 1.92
S-112	~ 1.66
Y-107	~ 1.48

With the exception of tank S-107 measurements, the ratios provided in Table 1 are consistent with the above observation. Excluding for the moment the 107-S measurements, the average value of the ratios is about 1.7.

It is of interest to note that Bouse (1975) refers specifically to the 107-S dry sample as soft powder, which would not be characteristic of dried-out solid waste materials. For this sample the solids are perhaps better characterized as the discontinuous phase, i.e., the gas is the continuous phase and Equation (C-1) simplifies to ($\nu \gg 1$)

$$\frac{k_{comp}}{k_{cont}} = \frac{1}{1 - p^{1/3}} \quad (C-3)$$

With a porosity value of about 0.6 (reflecting the powder) and $k_{cont} \approx 0.025 \text{ W m}^{-1} \text{ K}^{-1}$ (reflecting the gas), we estimate $k_{comp} \approx 0.16 \text{ W m}^{-1} \text{ K}^{-1}$ which compares to the Bouse's dry measured value of about $0.15 \text{ W m}^{-1} \text{ K}^{-1}$.

REFERENCES

Bouse, D. G., 1975, *Thermal Conductivity of Hanford Waste Tank Solids and SX Tank Farm Soil Samples*, ARH-CD-378, Atlantic Richfield Hanford Company, Richland, Washington

APPENDIX D**THERMAL DIFFUSIVITY**

For transient analysis of heating or cooling of the tank contents with respect to potential thermal runaway, the thermal diffusivity of the materials is the crucial parameter. Thermal diffusivity is a measure of the speed at which heat propagates through a material and is related to other material properties by the relation

$$\alpha = \frac{k}{\rho c} \quad (\text{D-1})$$

where

α (m^2/s) = thermal diffusivity,

k ($\text{w}/\text{K}\cdot\text{m}$) = thermal conductivity,

ρ (kg/m^3) = density,

c ($\text{J}/\text{kg}\cdot\text{K}$) = specific heat.

As determined in Appendix C, the variation in k going from saturated sludge or saltcake with a porosity value of 0.4 is about a factor of 2. For the wet waste, a value of $k = 1 \text{ w}/\text{m}\cdot\text{K}$ appears reasonable with a corresponding value of $k = 0.5 \text{ w}/\text{m}\cdot\text{K}$ for dry wastes.

The values of ρ for saturated saltcake is about $1900 \text{ kg}/\text{m}^3$ and for dry saltcake about $1360 \text{ kg}/\text{m}^3$. Similar the values of c are about $2300 \text{ J}/\text{kg}\cdot\text{K}$ for a saturated saltcake and about $1200 \text{ J}/\text{kg}\cdot\text{K}$ for a dry saltcake.

It follows that the values of α are about $2.3 \times 10^{-7} \text{ m}^2/\text{s}$ and $3.0 \times 10^{-7} \text{ m}^2/\text{s}$, for the wet and dry cases, respectively. A conservative value of $2 \times 10^{-7} \text{ m}^2/\text{s}$ is used in evaluating characteristic cooling times for the waste tanks.

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APPENDIX E

HOT SPOT

The difficulty of forming a hot spot can be appreciated by considering the heat-generating material-concentration enhancements required to raise the temperatures at the center of the hot spot to the critical temperature (~ 200 °C). As such, a spherical hot spot with radius R_{HS} must attract a concentration of heat-generating material from the surrounding sludge that exceeds the average tank concentration of heat-generating material by the ratio (Epstein et al. 1994)

$$\frac{Q}{Q_{avg}} = \frac{2 k (T_c - T_\infty)}{R_{HS}^2 Q_{avg}} \quad (E-1)$$

where Q_{avg} (W/m^3) is the average waste power density, k ($W/m-K$) is the waste thermal conductivity, T_c (K) is the critical temperature and T_∞ (K) is the ambient waste temperature.

Taking the waste thermal conductivity $k = 0.5$ $W/m-K$ corresponding to the dry waste value and $Q_{avg} \approx 10$ W/m^3 , it is found from Equation (1) that a 5.0 cm radius hot spot surrounded by waste at $T_\infty = 300$ °K requires a concentration ratio $Q/Q_{avg} \approx 7000$ before the center of the hot spot will achieve a temperature of 473 K. Of course, a larger hot spot would require less heat-generating material to be brought to the critical temperature, but even a hot spot as large as 0.5 m requires a concentration ratio of about 70 before the critical temperature is reached. Such concentration ratios of the decay heat are not believed to be credible. For further discussion of the incredible nature of forming significant hot spots see references listed below.

REFERENCES

- Dickinson, D. R., J. M. McLaren, G. L. Borsheim, and M. D. Crippen, 1993, *Ferrocyanide Safety Program: Credibility of Drying Out Ferrocyanide Tank Waste by Hot Spots*, WHC-EP-0648, Rev. 0, Westinghouse Hanford Company, Richland, Washington.
- Epstein, M., H. K. Fauske, M. D. Crippen, D. R. Dickinson, J. D. McCormack, R. J. Cash, J. E. Meacham, and C. S. Simmons, 1994, *Ferrocyanide Safety Program: An Assessment of the Possibility of Ferrocyanide Sludge Dryout*, WHC-EP-0816, Westinghouse Hanford Company, Richland, Washington.
- McGrail, B. P., 1994, *Ferrocyanide Tank Safety Project: Computational Analysis of Coupled Fluid, Heat, and Mass Transport in Ferrocyanide Single-Shell Tanks - FY 1994 Interim Report*, PNL-10163, Pacific Northwest Laboratory, Richland, Washington.

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APPENDIX F

ESTIMATING ADIABATIC RUNAWAY TIMES FROM ACTUAL WASTE SAMPLES

Consider recent RSST calorimetry data obtained with a waste sample from tank C-201 (Bechtold 1995). Relevant data are shown in Figure F-1, where reasonable estimates of the activation energy, E_a , and the pre-exponential factor for the Arrhenius law are possible in the temperature range > 170 °C

$$\dot{T} = 9 \cdot 10^{13} e^{-16,538/T} \quad (F-1)$$

Extrapolated values down to the current C-201 waste temperature of about 20 °C (see Table 2-7) using Equation (F-1) are listed in Table F-1. The values of H_{\min} tabulated in Table F-1 are obtained by equating Equations (5-5) and (5-6) resulting in

$$H_{\min} \approx \left[\frac{4 \alpha T^2}{\dot{T} E_a/R} \right]^{1/2} \quad (F-2)$$

and the values of the half life, $t_{1/2}$, tabulated in Table F-1 is estimated from

$$t_{1/2} = 0.7 \frac{\Delta H_R X_f}{\dot{T} c} \quad (F-3)$$

where ΔH_R (J/kg) is the heat of reaction and set equal to 10^7 J/kg, X_f is the fuel fraction (set equal to 0.3) and c (J/kg-K) is the specific heat set equal to 2000 J/kg-K. While the resulting stability diagram in Figure F-2 clearly suggests that the C-201 waste is stable and far removed from the stability line, we have no way of verifying the validity of this result due to the enormous extrapolation involved (over 15 decades), nor do we know if the limited sample is representative of the majority of the C-201 waste. It is possible that different reactions and rates may occur at the ambient waste temperature in comparison to that projected from the above extrapolation from high temperature data, i.e., the relevant Arrhenius parameters may differ significantly at the lower temperatures corresponding to waste conditions. (It is of interest to note that if local hot spots in the waste indeed were possible (see Appendix E), the estimated half lives at elevated temperatures (see Table F-1) suggest that the fuel in such hot spots would have been exhausted a long time ago.

Figure F-1. Results of RSST Test of Tank C-201 Sample

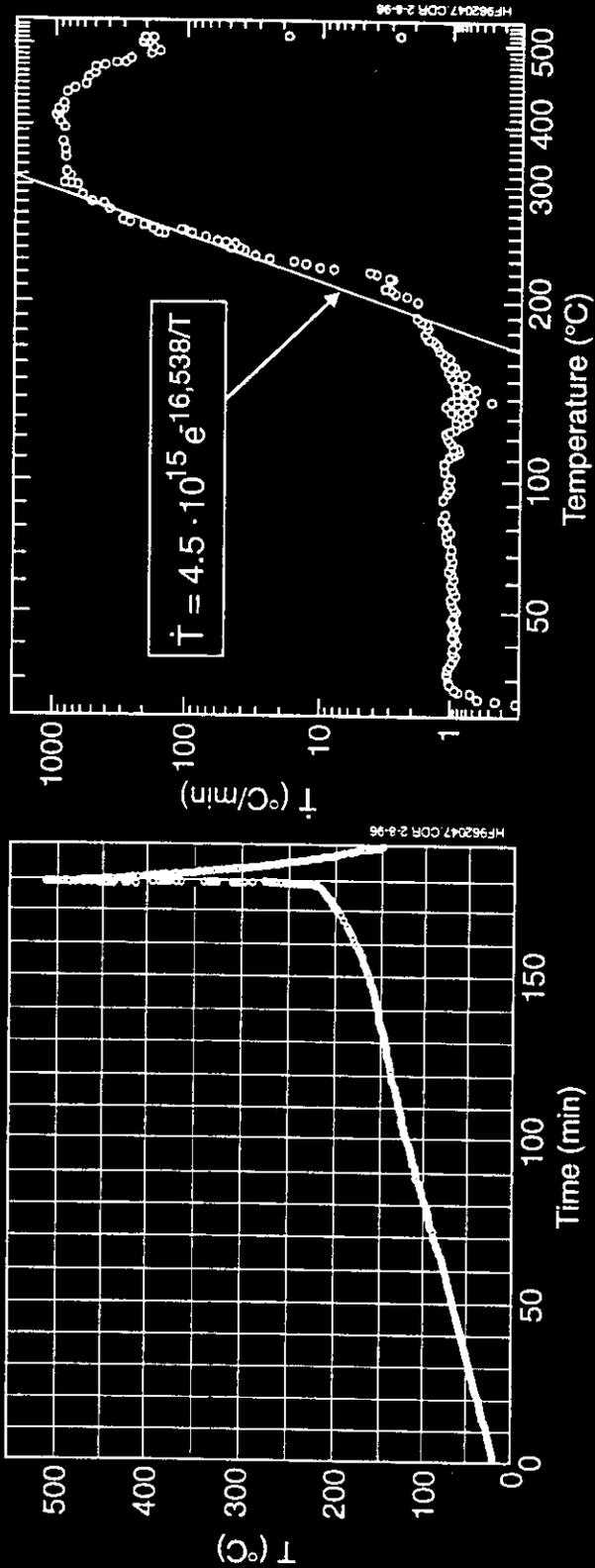


Figure F-2. Projected Stability Diagram for Tank C-201

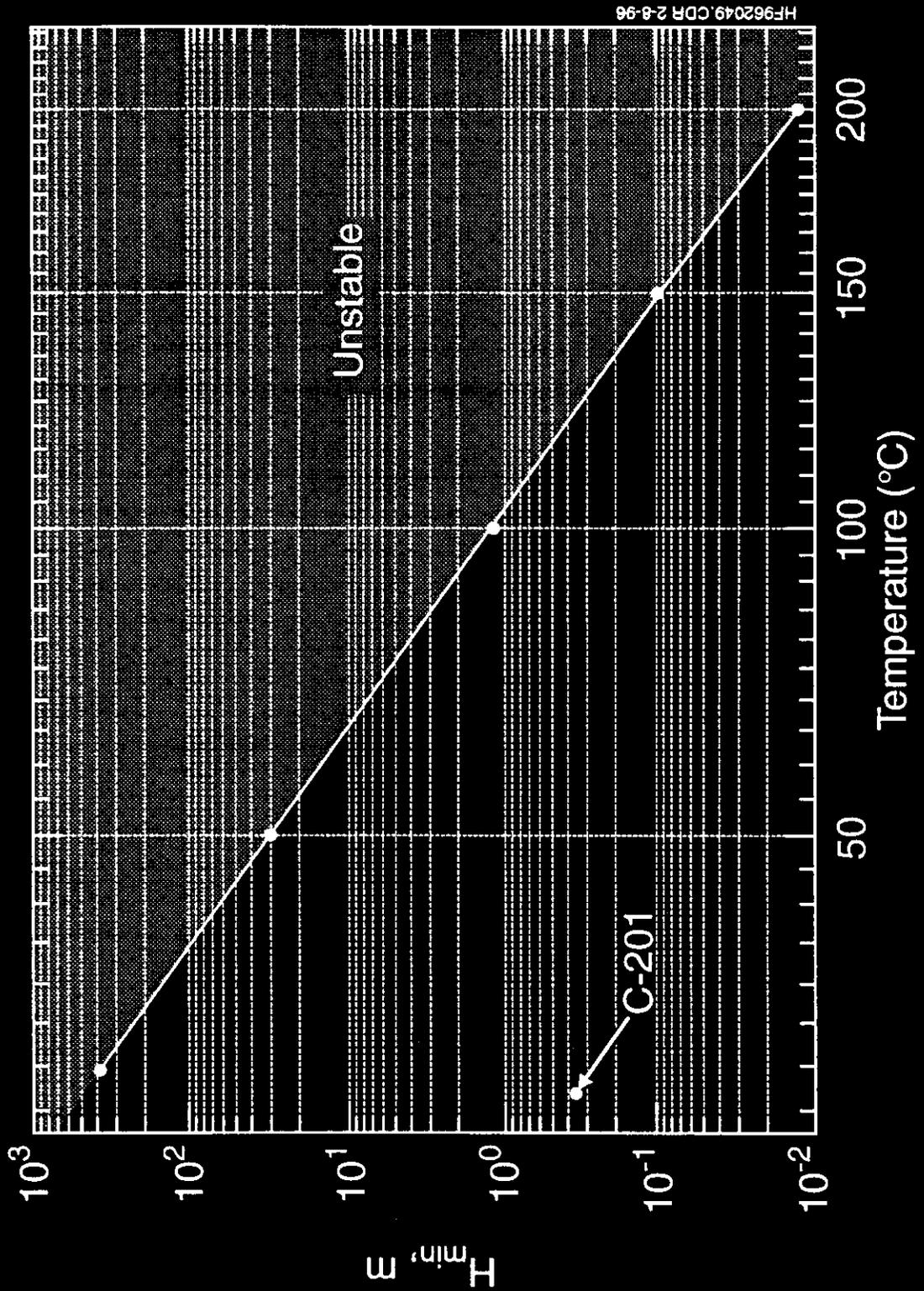


Table F-1. Extrapolated Values of Relevant Kinetic Parameters

T, °C	°C/s	H _{min} , m	t _a	t _{1/2}
20	$2.76 \cdot 10^{-11}$	383	5,962 years	10 ⁶ years
50	$5.2 \cdot 10^{-9}$	31	38.3 years	5670 years
100	$5 \cdot 10^{-6}$	1.2	19.5 days	5.9 years
150	$9.4 \cdot 10^{-4}$	0.1	3.2 hours	12.9 days
200	$5.9 \cdot 10^{-2}$	0.013	3.83 mins	4.9 hours
250	1.66	0.0029	9.9 s	10.5 mins

REFERENCES

Bechtold, D. B., 1995, *Results of Adiabatic Calorimetry of Tank C-204 Auger Material*, Westinghouse Hanford Company, Richland, Washington.

APPENDIX G

CONDENSED-PHASE COMBUSTION LIMITS AND AMBIENT TEMPERATURES

Similar to flammable gas mixtures, the lower flammability limit (LFL) for condensed-phase combustion is a relatively weak function of the ambient temperature. To a first order the decrease in the fuel concentration or energy requirement for sustained combustion can be related to the increase in sensible heat as the ambient temperature increases.

$$x_{LFL}(T) \approx x_{LFL}(T_o) - \frac{\bar{c} [T - T_o]}{\Delta H_R} \quad (G-1)$$

or

$$\Delta H_{LFL}(T) \approx \Delta H_{LFL}(T_o) - \bar{c} [T - T_o] \quad (G-2)$$

where x_{LFL} and ΔH_{LFL} are the fuel concentration and energy threshold values corresponding to the lower flammability limit, \bar{c} is the average specific heat and ΔH_R is the heat of reaction.

In our tube propagation experiments we have typically measured x_{LFL} at an ambient temperature of about 30 °C (Fauske 1995, Fauske et al. 1995). As such, the value of x_{LFL} for $Na_2NiFe(CN)_6$ is measured to be about 0.155 at $T_o = 30$ °C. For this system increasing the ambient temperature to $T = 130$ °C, a partial burn was observed with $x_{LFL} \approx 0.14$ (Fauske 1995).

The above observations are consistent with Equation 1. Setting $c \approx 1300$ J/kg-K and $\Delta H_R = 9.6 \times 10^6$ J/kg, we calculate $x_{LFL}(T = 130 \text{ °C}) \approx 0.141$. Similar, if we set the ambient temperature equal to the ignition temperature, we calculate $x_{LFL}(T = T_{ig} = 250 \text{ °C}) \approx 0.12$ based upon $\bar{c} = 1500$ J/kg-K. The relatively small difference in the x_{LFL} values are also consistent with RSST propagation tests (Fauske 1995).

The above noted sensitivity is significantly overestimated using the Contact Temperature Ignition (CTI) condition (Fauske 1995, Fauske et al. 1995). As such, it is important to recall that this condition appears necessary but not sufficient to achieve sustained combustion. Recalling the CTI condition for zero moisture condition (Fauske 1995, Fauske et al. 1995)

$$x_{LFL} > \frac{2 [T_{ig} - T_o] \bar{c}}{\Delta H_R} \quad (G-3)$$

we observe that setting $T_o = T_{ig}$, requires that

$$x_{LFL} > 0$$

This result is not very useful when compared to the actual value of about 0.12 for the $Na_2NiFe(CN)_6$ case discussed above, i.e., for increasing ambient temperature the CTI criterion in its general form becomes increasingly conservative. Therefore, in an attempt to derive at a reasonably conservative safety criterion, T_o was set equal to zero in Equation G-3,

$$x_{LFL} > \frac{2 T_{ig} \bar{c}}{\Delta H_R} \tag{G-4}$$

For the $Na_2NiFe(CN)_6$ system with $T_{ig} = 250$ °C (measured in the RSST), $\bar{c} \approx 1900$ J/kg-K, and $\Delta H_R = 9.6 \cdot 10^6$ J/kg we calculate $x_{LFL} > 0.10$. This provides a reasonable safe envelope for all ambient temperatures of interest.

The above observations also apply to the organic complexant-nitrate reactions. In terms of the energy threshold value the adopted CTI condition is (no moisture)

$$\Delta H_{LFL} > 2 T_{ig} \bar{c} \tag{G-5}$$

Using NaAcetate as the reference surrogate material with $T_{ig} \approx 300$ °C and $\bar{c} \approx 2000$ J/kg-K, we obtain the theoretical energy threshold value of 1200 J/g mixture (Fauske et al. 1995). The actual value for an ambient temperature of $T_o = 30$ °C is about 1600 J/g mixture (Fauske et al. 1995). For the highest temperature prevailing in the Tank Farm of about 100 °C, this limit according to Equation G-2 reduces to

$$\begin{aligned} \Delta H_{LFL} (T = 100^\circ C) &= 1600 - 1.3 \times 70 \\ &\approx 1510 \text{ J/g mixture.} \end{aligned}$$

We conclude that the value of about 1200 J/g mixture provides a reasonable safe value for all ambient temperatures of interest.

REFERENCES

- Fauske, H. K., 1995, *Ferrocyanide Safety Program: Adiabatic Calorimetry and Tube Propagation Tests With Synthetic Ferrocyanide Materials*, FAI/95-69, Fauske and Associates, Inc., Burr Ridge Illinois.
- Fauske, H. K., D. R. Dickinson, R. J. Cash, and J. E. Meacham, 1995, *The Contact Ignition (CTI) Criteria for Propagating Chemical Reactions Including the Effect of Moisture and Application to Hanford Waste*, WHC-SD-WM-ER-496, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

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APPENDIX H

CONDENSED-PHASE COMBUSTIBILITY AND INITIAL MOISTURE CONTENTS INCLUDING BOUND AND FREE WATER

The combustibility of a number of organic surrogate materials has been determined including the effects of both initially bound and free water present in the fuel oxidizer samples. The experimental procedures are described in Fauske (1995) and Fauske et al. (1995).

The lower flammability limit data in the absence of free water are summarized in Table H-1 along with their corresponding stoichiometric conditions. These experiments used a constant ignition energy source of about 20 watts and the igniter was left on until sustained propagation was observed (~15 - 20 seconds). In case of no combustion, the igniter was usually left on for at least 1 minute.

Table H-1. Measured Lower Flammability Limits (Fuel + NaNO₃) at Ambient Temperature of 30 °C and Corresponding Stoichiometric Conditions

Surrogate Fuel	MW	ΔH_R , J/g	Lower Flammability Limit			Stoichiometric Condition		
			TOC, wt%	ΔH , J/g	H ₂ O, wt%	TOC, wt%	ΔH , J/g	H ₂ O, wt%
NaAcetate	82	7900	~21 (~6)	~1620	0	~37.6 (~11)	2970	0
NaAcetate·3H ₂ O	136	7900	--	--	--	~50 (~8.8)	~2380	~19.8
Na ₃ Citrate·2H ₂ O	294	5700	~33 (~8)	~1650	~4	~49 (~12)	~2450	~6
Na ₃ HEDTA·2H ₂ O	380	10800	~19 (~6)	~1830	~1.9	~34 (~10.6)	~3300	~3.2
NaOxalate	134	1190	--	--	--	~80 (~14)	~960	0

The results summarized in Table H-1 illustrate that NaAcetate represents a lower bound estimate for the energy threshold, ΔH , of about 1600 J/g for sustained combustibility and that NaAcetate·3H₂O does not exhibit combustibility even for stoichiometric conditions. The latter observation is not surprising since the bound water represents about 20 wt% of the fuel-oxidizer sample. Furthermore, sodium oxalate in absence of any water, does not exhibit combustibility even for stoichiometric conditions, which is consistent with its stoichiometric energy of 960 J/g which is well below the threshold value of ~ 1600 J/g.

Data representing the effect of free water along with the proposed safety criteria are shown in Figure F-1. (Note that data with NaAcetate and free water are not shown in Figure H-1, as was done in Figure 4.2 of Reference 1, as such mixtures below 20 wt% water actually should be treated as bound water rather than free water.) The same data expressed in terms of theoretical energy releases are shown in Figure H-2. The margin of safety provided by the proposed safety criteria is substantial.

Table H-2 summarizes the data for stoichiometric conditions along with the water contents (bound + free water) that prevented sustained combustion. It is interesting to note that the combined moisture level of bound and free water did not exceed the 20 wt% level.

Table H-2. Water Contents (Bound + Free Water) That Prevents Stoichiometric Conditions^a From Combustion

Surrogate Fuel	wt% Fuel	(TOC)	ΔH	Bound Water	Free Water	Total Water
NaAcetate·3H ₂ O	50	8.8	2380	19.8	0	19.8
Na ₃ Citrate·2H ₂ O	42	10.3	2110	5	14	19.0
Na ₃ HEDTA·2H ₂ O	29	9.2	2825	2.7	15	17.7
NaOxalate	80	14.3	~960	0	0	0

^aStoichiometric conditions are based on NaAcetate·3H₂O + 1.6 NaNO₃, Na₃Citrate·2H₂O + 3.6 NaNO₃, Na₂Oxalate + 0.4 NaNO₃ and Na₃HEDTA·2H₂O + 8.8 NaNO₃.

Again we note that the above data were obtained using the 20 watts ignition source which was left on until sustained propagation was observed. This type of ignition source results in a relatively slow removal of water locally in the sample by evaporation and subsequent heat up of the dried-out region to the ignition temperature. This approach to ignition allows determination of how the initial moisture level effects the potential for sustained combustion.

Figure H-1. Comparison Between Measured TOC Values and the Proposed Safety Criteria

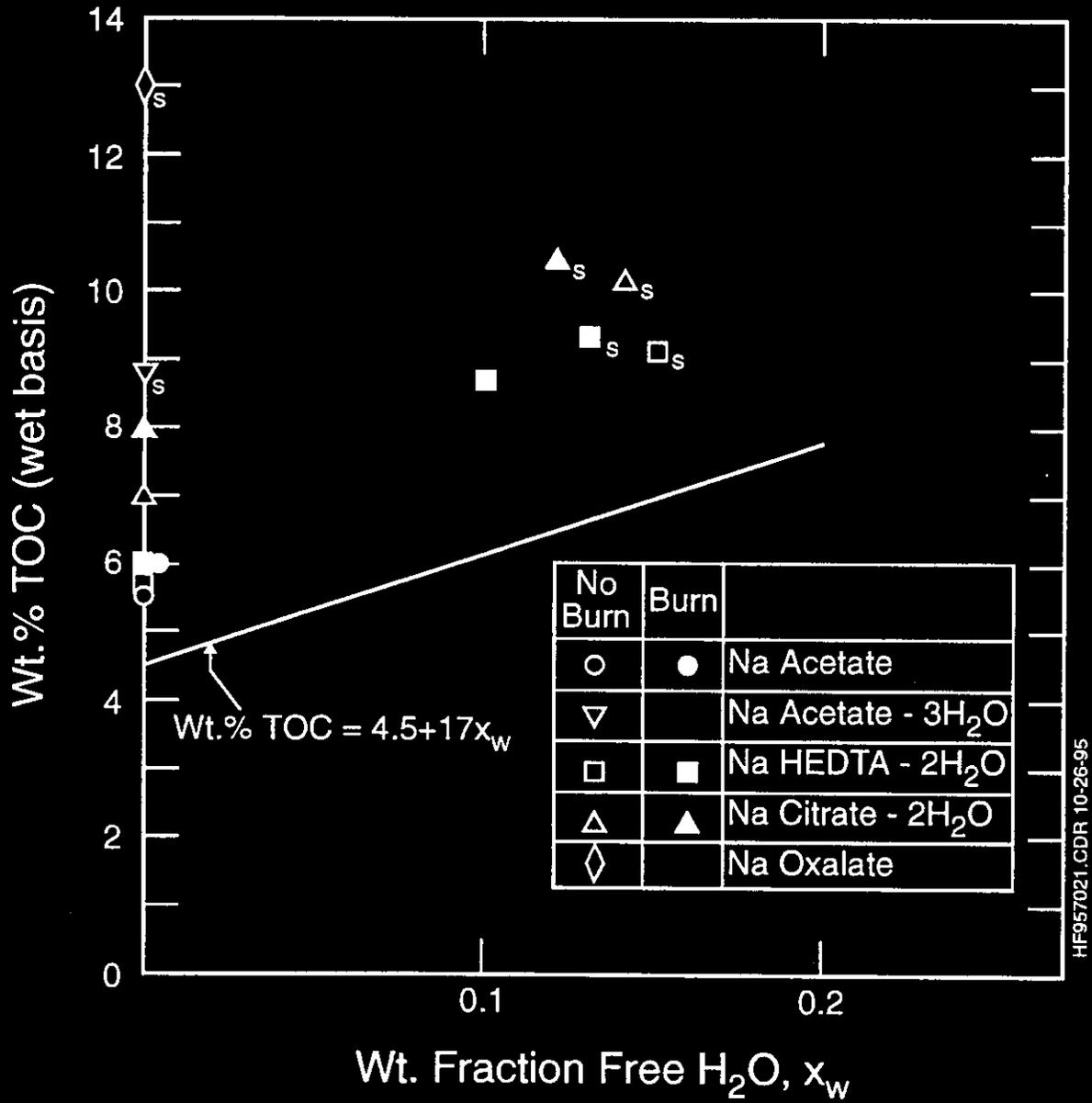
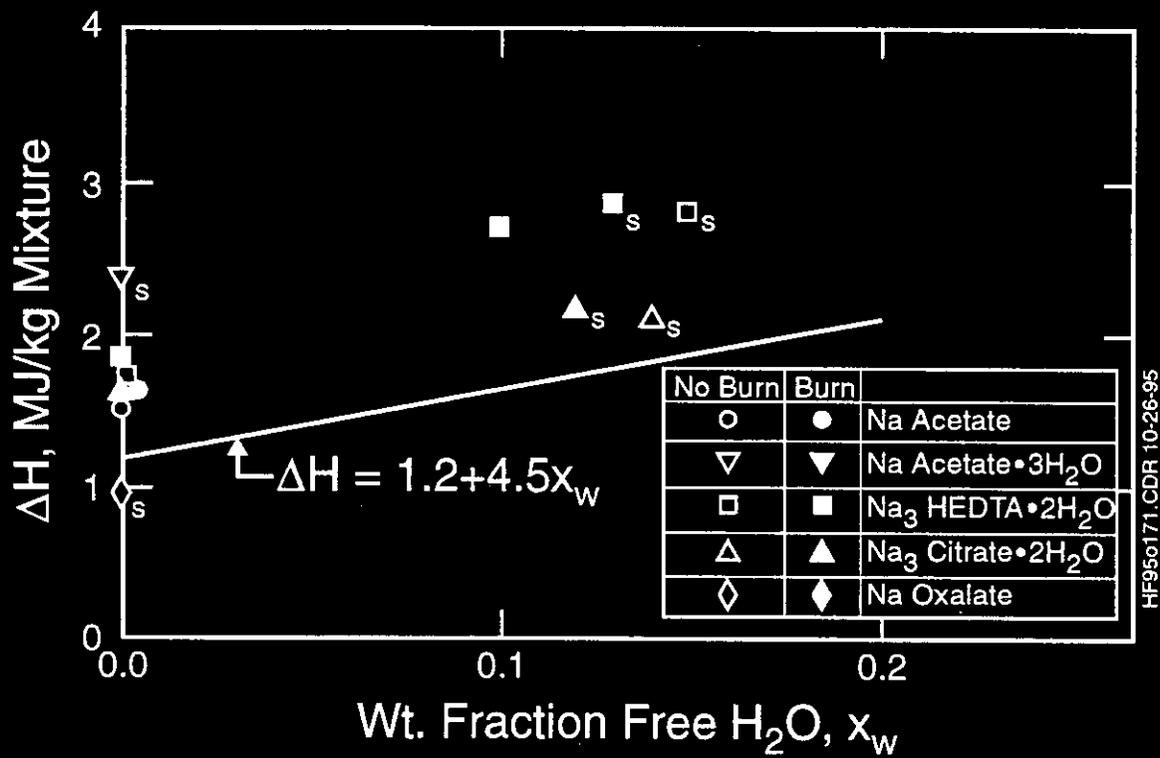


Figure H-2. Comparison Between Surrogate Data (Measured Fuel Concentration Times Theoretical Heat of Reaction) Including The Effect of Moisture and Proposed Safety Criteria



Experiments have also been completed with emphasis on clarifying minimum ignition sources required to ignite otherwise combustible mixtures including the presence of initial moisture. Ignition sources utilized to date include a pyrotechnic "electrical match" which supplied with 110 VAC releases about 140 J over a 3-5 msec period, and various size steel particles (1/16, 3/32 and 3/16 inch) heated to about 1300 °C (corresponding energy contents of 10, 35 and 270 J). These tests indicate that the presence of small amounts of free moisture (see Figure H-3) prevent ignition even for stoichiometric conditions.

The observation of no ignition with a stoichiometric mixture of NaAcetate·3H₂O and NaNO₃ which is equivalent to 19.86 wt% bound water is consistent with data presented in Figures H-1 and H-2. However, the quantity of bound water required to eliminate ignition for the sources evaluated³ would appear to approach the maximum amount of 3H₂O (see Figure H-4). The samples were made up adding water to mixtures containing NaAcetate (no bound water) and NaNO₃.

The data for stoichiometric conditions that resulted in no ignition are summarized in Table H-3.

Table H-3, Water Contents (Bound + Free Water) That Prevented Stoichiometric Conditions From Combustion With the 140 J Electrical Match

Surrogate Fuel	wt% Fuel	wt% (TOC)	ΔH, J/g	Bound Water wt%	Free Water wt%	Total Water wt%
NaAcetate·3H ₂ O	50	8.8	2380	19.8	0	19.8
Na ₃ Citrate·2H ₂ O	47	11.4	2330	5.7	5	10.7
Na ₃ HEDTA·2H ₂ O	32	10.2	3160	3	5	8
Hybrid	43*	10.2	2640	9	4	13
*16% NaAcetate·3H ₂ O + 16% Na ₃ Citrate·2H ₂ O + 11% Na ₃ HEDTA·2H ₂ O.						

³The sources evaluated should not be considered to be similar to sparks. The latter contains no hot solid particles in contrast to the sources tested to date. Any credible sparks would not initiate solid phase combustion even in the absence of any moisture (bound and free). The time duration of credible sparks is too short to satisfy sustained combustion requirements.

Figure H-3. Ignition Potential and the Effect of Free Moisture and Comparison to the Safety Criteria

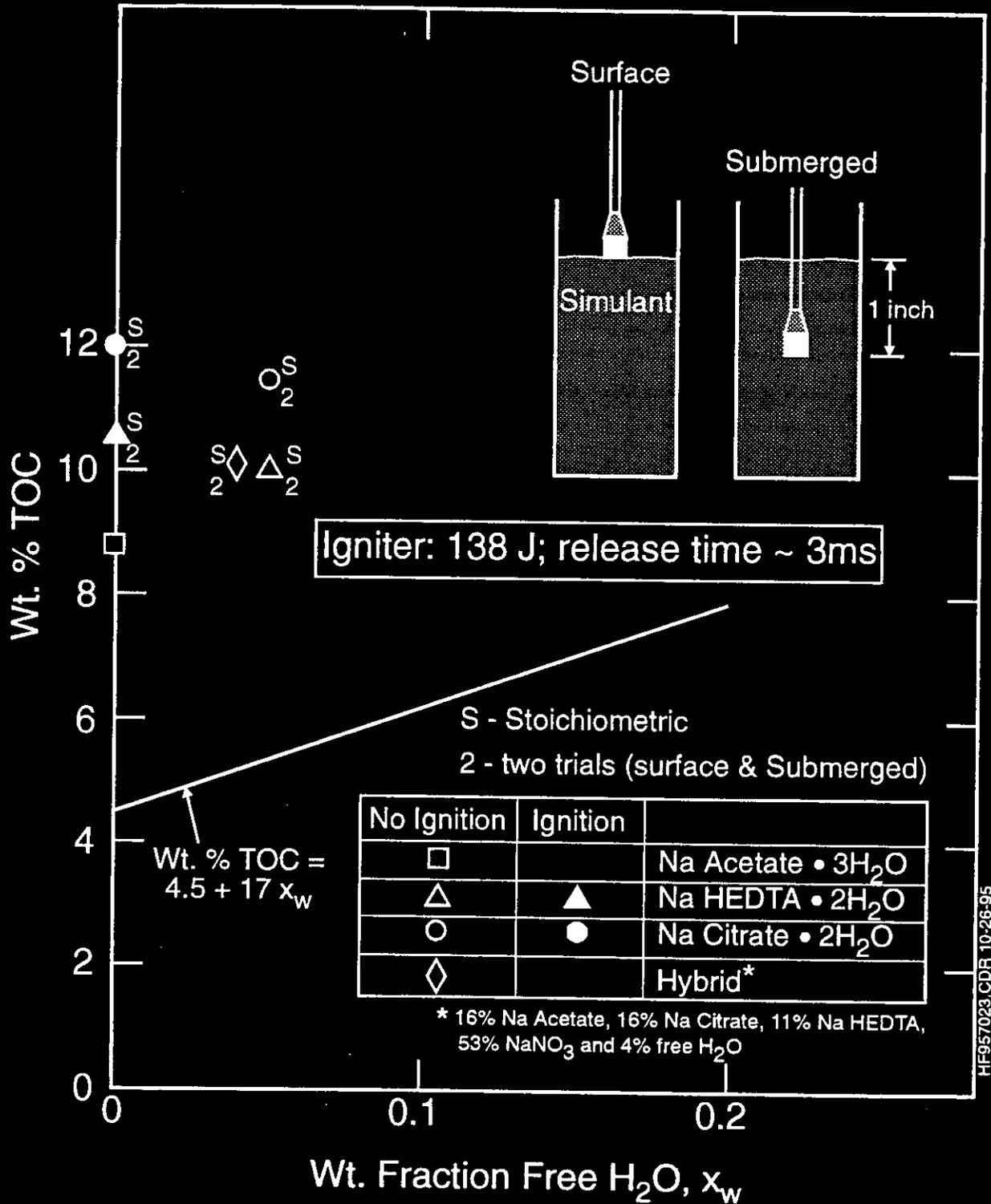
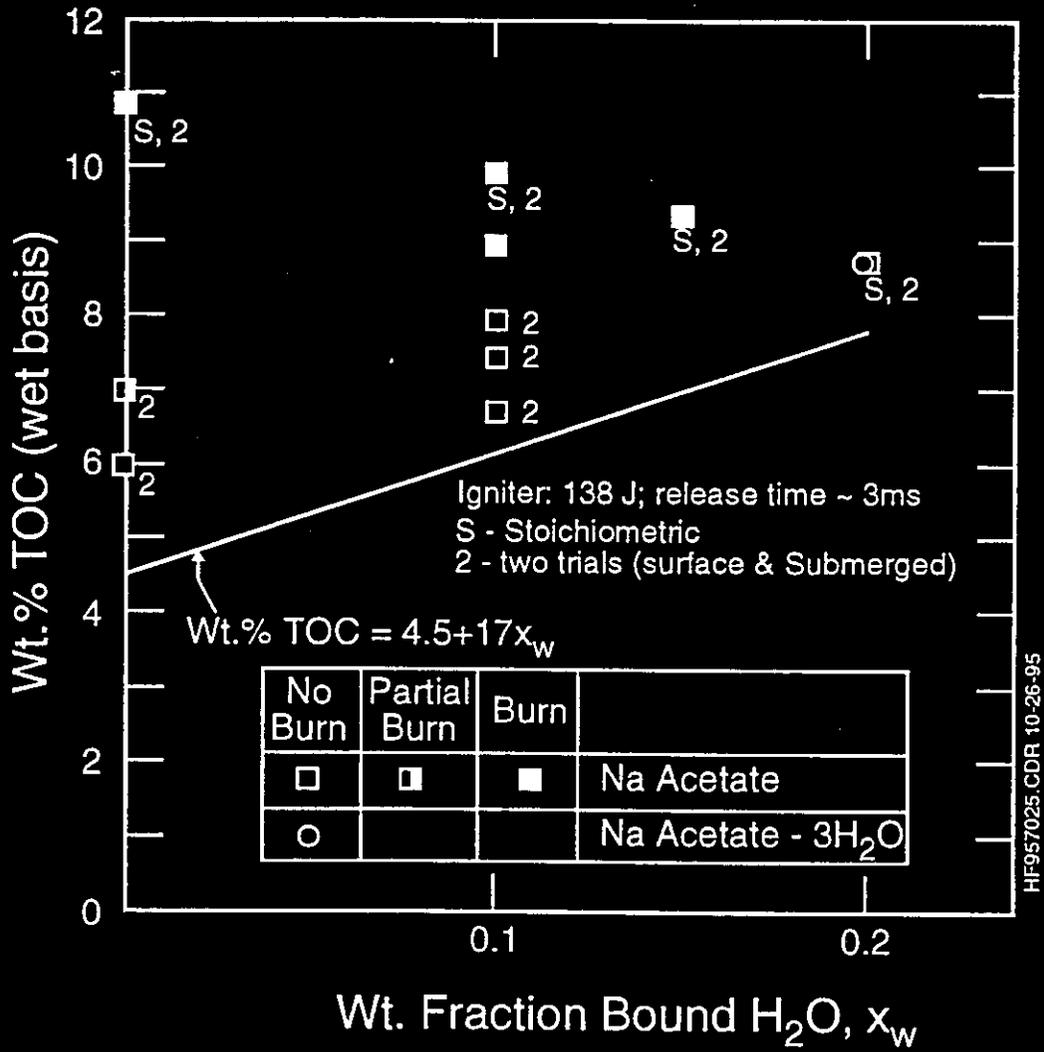


Figure H-4. Ignition Potential and the Effect of Bound Water



In summary, for the ignition sources tested to date, it would appear that very little free water would prevent ignition. It would also appear that for the ignition sources tested, free water would appear more effective in preventing ignition than bound water.

REFERENCES

Fauske, H. K., D. R. Dickinson, R. J. Cash, and J. E. Meacham, 1995, *The Contact Ignition (CTI) Criteria for Propagating Chemical Reactions Including the Effect of Moisture and Application to Hanford Waste*, WHC-SD-WM-ER-496, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Hans K. Fauske, 1995, *Summary of Laboratory Scoping Tests Related to Organic Solvents Combustion by Nitrate Oxidation and Organic Solvent Igniteability*, (memorandum to D. A. Turner, June 15), Fauske and Associates, Inc., Burr Ridge Illinois.

APPENDIX I

PRELIMINARY ASSESSMENT OF LIGHTNING AS A POTENTIAL CREDIBLE IGNITION SOURCE

The frequency of lightning striking a Hanford SST is estimated to be about 5×10^{-4} per year (MacFarlane et al. 1994). However, as discussed below, ignition of condensed-phase waste materials including organic solvents from such a scenario may not occur.

It is important to recognize that the Hanford tanks are buried and the extensive amount of rebar in the SST concrete domes provide significant overall shielding properties, so that there will be a high tendency for lightning produced current fields to be excluded from the interior of the tanks. However, there are electrically noncontinuous paths through the tanks that could result in arcing. These paths include arcing between equipment extending through risers and the risers, arcing at bolted flanges, arcing between the riser or equipment and the rebar in the concrete dome. Lightning will, if the rebar is not well connected and connected to the tank walls in the SSTs⁴ (which it is apparently not) arc to rebar and from rebar to the tank walls. As such, it would be difficult to rule out generation of sparks that would be capable of igniting the presence of a flammable gas mixture in the tank head space.

The above arcing phenomena may be more likely than arcing to the waste surface inside the tanks, as the various tank structures are likely to be preferential targets (path of least resistance) for the lightning current(s). If there is a gap in the conductors carrying a lightning current, the current may arc across the gap. Quoting Uman (1994) "the arc energy appears as heated gas, in the tens of thousands of °C range, and as heated and melted electrode material, much as in the case of purposeful arc welding. A typical lightning transfers 25 coulombs of charge and thus an arc due to lightning between metal electrodes could liberate 250 joules of energy at the arc spot, in a volume certainly less than a cubic centimeter, perhaps as small a cubic millimeter." However, further quoting Uman (1994), "it is not likely that the total lightning current would flow across one interior gap in a SST or DST because of the many parallel paths available to the lightning current. On the other hand, sparks in the millijoule range are generally thought to be capable of igniting flammable gas." It follows that significant steel melting in connection with such arcing phenomena that subsequently could fall down onto the waste surface would appear unlikely, considering that about 250 joules alone would be required to produce a molten steel droplet of about 4 mm diameter, which is less than the capillary size of about 6 mm, i.e., the melted material would quickly refreeze in place.

⁴This is not the case for DSTs, where the inner complete steel shell provides essentially a perfect Faraday Cage.

Furthermore, some simple scoping experiments were performed to determine the likelihood of arcing directly to the waste using the suggested similarity between the arcing caused by a lightning current and purposeful arc welding (Uman, 1994).

To test the effect or relationship between waste material electrical conductivity and arcing potential, small samples of simulated wastes were placed in a highly electrical conductive environment, i.e., in a small steel crucible (a pipe end cap of about 1.5 inch diameter and 1.5 inch height) clamped to a well-grounded welding table (see Figure I-1). The tungsten electrode was positioned above the waste surface, in direct contact with, as well as below the waste surface. Various types of wastes including organic solvent consisting of dodecane (1a), a stoichiometric mixture of NaCitrate·2H₂O-NaNO₃ soaked with dodecane (1b), dry stoichiometric mixture of NaCitrate·2H₂O-NaNO₃ (1c), and stoichiometric NaCitrate·2H₂O-NaNO₃ mixtures with increasing free water inventories of 5 and 10 wt% H₂O (1d and 1e) were placed in the steel crucibles and subjected to arc welding currents of about 200 amperes for about one second intervals.

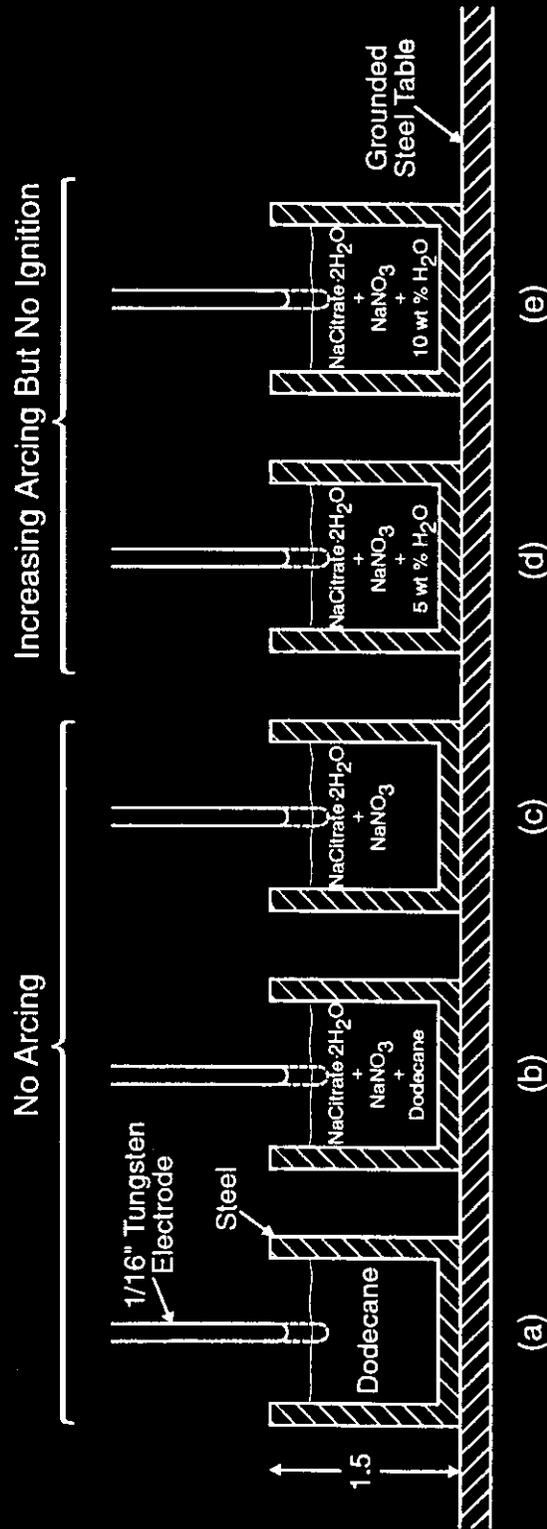
No sign of arcing were observed with waste mixtures a, b and c including variations in the electrode position relative to the waste material surface. With increasing water inventory, limiting arcing and "crackling" were observed, but in no cases were sustained ignition noticed. While the increasing presence of moisture or water clearly increases the electrical conductivity allowing current to flow, its presence also prevents ignition to occur by dissipating the arc energy by latent heat of vaporization, keeping the waste temperature well below the ignition temperature.

While the above test results are encouraging, additional tests with considerably higher electrical currents and voltages to simulate a much wider range of possible lightning currents would appear necessary in order to reach a definitive conclusion concerning a lightning strike not being a credible ignition source.

REFERENCES

- MacFarlane, D. R., 1994, *Probabilistic Safety Assessment for Hanford High-Level Waste Tank 241-SY-101*, LA-UR-93-2730 TSA-6-93-R111, Los Alamos National Laboratory, University of California.
- Uman, M. A., 1994, *Analysis of Lightning Strike Scenarios to Determine Risks to the Westinghouse Hanford Company Radioactive-Waste Storage Facilities*, Appendix A of Report WHC-SD-WM-SARR-027, Rev. 0, *Evaluation of Hazards for Lightning Strikes to Tank Farm Facilities*, by W. L. Cowley and D. D. Stepnewski, 1994, Westinghouse Hanford Company, Richland, Washington.

Figure I-1. Demonstration of Arcing and Ignition Potentials Using the Arc Welding Technique



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