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COMPLEXANT STABILITY INVESTIGATION
TASK 1 - FERROCYANIDE SOLIDS

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MASTER

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INTRODUCTION

Large quantities of ferrocyanide (hexacyanoferrate (II)) precipitates were placed in the 200 Area single shell waste tanks over a period of several years. The question of the long term safety of these residues has been raised. Since irreversible decisions regarding the management of these tanks may soon be made it is desirable to review the safety aspect. In order to predict conditions that might lead to rapid exothermic reactions between these solids and nitrate salts, it is necessary to review the chemistry of the cyanide complexes and the thermodynamics and kinetics of the possible reactions. It is also necessary to determine the amounts of cyanide solids in a given tank along with the concentration, i.e., dilution with inert materials, that may exist.

The purpose of this report is to review the existing information on these precipitates, on the potential reactions that may occur, and to make recommendations for a study which would better establish the chemistry involved, determine the precise location of the cyanide precipitates and thus permit the development of a long range storage plan.

CONCLUSIONS AND RECOMMENDATIONS

Up to 900 kmols of ferrocyanide precipitates (~140 t of CN^-) are known to have been placed in Hanford waste tanks about 25 to 30 years ago. Although the records show that large amounts were placed in at least 14 tanks, at present, we are unable to conclusively state the quantities that reside in individual tanks. The composition of the other constituents in the waste tanks containing ferrocyanides is also unknown. Similarly, no information exists on the possible layering of ferrocyanide precipitates in the waste tanks or the potential for their intimate contact with nitrate salts.

The energy released by the reaction of cyanide ion and nitrate ion is significant. The "worst case" scenario described in this report predicts this energy release from a single waste tank could be equivalent to that of 36 tons of TNT. The conditions necessary for reaction (or for "rapid" reaction) are not known, nor are any kinetic parameters known.

At present, there is insufficient information to state that the hazard of a potentially violent cyanide reaction does not exist. A better information base is required to permit a safe program for long term tank management.

The following actions are required to obtain the information necessary for a definitive hazard evaluation and are listed in order of decreasing priority:

1. Obtain and analyze the available information on tank histories for those tanks known to have held $Fe(CN)_6^-$ in large quantities at one time.

2. Conduct radiolysis tests under simulated tank conditions to determine the rate of disappearance of CN^- and to identify the radiolysis products. The radiolysis tests should be conducted both with an aqueous phase present and on settled sludges alone.

3. Determine the kinetic parameters of the CN^- and NO_3 reaction by both experiment and calculation. The effect of inert materials is especially important and must be included in these studies. The information obtained from these studies would allow realistic conclusions to be made regarding the potential for rapid exothermic

reactions in waste tanks containing ferrocyanide solids. In addition, the conditions for potentially hazardous reactions would be known and could be precluded by tank management practices.

4. Obtain tank samples and conduct chemical analyses for soluble and insoluble cyanides, cyanate, nitrate, fission products, and water content.

5. Obtain the temperature profile of the tank to give information on temperature maxima and on possible layering of solids.

6. Obtain the γ profile to provide much the same information as (5) above.

It is our recommendation that continued studies be directed to obtaining the information indicated in the above list.

HISTORICAL PERSPECTIVE

In the early 50's it became apparent that the impending shortage of underground storage could be alleviated by concentrating the active wastes and cribbing the supernate. Ferrocyanide scavenging was a practical solution to the problem (Burns 1953) and began with active operation in the uranium recovery plant in September 1954 (Smith and Coppinger 1954; Schulz 1955). The flowsheet was described by Sloat (1954). T-Plant was still operating, and scavenging of T-Plant wastes probably began there in December 1954. Both U-Plant and T-Plant scavenging processes were carried out in-plant, and the wastes sent to available underground tanks. In general, the tanks were chosen to be easily accessible to usable crib sites.[a]

In-farm scavenging started in East Area with the C-farm in November 1955 and began in West Area the following year (Sloat 1955a).

During this period, other decisions regarding Hanford production impacted waste storage. For example, because of special production runs a decision was made in June 1955 to continue T-Plant through June 1958 and run B-Plant from July 1955 to June 1957 (Peterson 1954). Direct evaporation was also employed to develop new storage space. Evaporations were started on dilute wastes in January 1955 (Abrams 1956), although some evaporation was apparently practiced as early as 1949.

During a portion of the time, calcium or strontium salts were added to increase the strontum decontamination by carrying it on the phosphate precipitate (Sloat 1955b). The first calcium additions were made in March 1955 (Abrams 1956). Occasionally, phosphate was added to the tanks.

During the scavenging campaigns more than 100 tons of cyanide were added to the tanks (Backman et al. 1964). The final disposition of these wastes is largely unknown, because of the method of routing and rerouting of wastes. However, some tanks can be designated as probably having considerable quantities of cyanide precipitates.

(a) R. J. Sloat - personal communication, January 1984.

The scavenging flowsheet varied somewhat depending on the application, but basically it consisted of the following steps (Sloat 1954, Schmidt and Stedwell 1954):

1. add $K_4Fe(CN)_6$ to obtain a concentration of 0.005 M
2. adjust the pH to 8-10, preferably about 9
3. add $NiSO_4$ to obtain a concentration of 0.005 M
4. agitate 10 minutes
5. discharge by jetting to underground storage.

A settling time of about 7 days was generally adequate to permit the supernate to be pumped to the cribs. Specifications were set on the activity permitted to be transferred to the cribs.

CHEMISTRY

The transition metal cyano complexes are very strong. In the case of Fe(II), the hexacyano complex is strong enough that the salts are often considered nontoxic.

Metals such as Ni and Co also form strong anionic complexes. Most of the heavy metal salts of these complex acids are insoluble in water. Thus, nickel, zinc, and copper ferrocyanides are easily precipitated. In early laboratory studies a variety of ferro- and ferricyanide precipitates were tested and found to be excellent Cs carriers. These included Fe(II), Fe(III), Cu(II), Ni(II), Co(II), Zn(II), and Mn(II) ferrocyanide and Fe(II) Ni(II), and Co(II) ferricyanide. All but the Co and Ni ferrocyanides were rejected because of inferior behavior in the pH range required. Cobalt was ruled out because of cost (Stedwell 1956).[a]

Sillén (1964) gives the solubility product of $Ni_2Fe(CN)_6$ as log K = -13.1 to -14.9. This gives a $Fe(CN)_6^{4-}$ concentration in water at 25° of $(0.7\text{-}3)\times10^{-5}$ mol/L. The simple cyanide salts of the heavy metals are also quite insoluble, but most form anionic complexes with excess CN^-. The solubility of $Cs_2NiFe(CN)_6$ has not been reported.

Reactions of interest include hydrolysis to form the CN^- ion, oxidation of the ferro complex to the ferri complex, replacement of one or more CN^- ligands by H_2O, NO, NO_2 , etc., and oxidation of CN^- to CNO^-.

No data were found for the free energies or enthalpies of the cyanide solids of interest. However, it is useful to examine the aqueous species. (Data are from Wagman et al. 1982). The reaction

$$Fe(CN)_6^{4-} \rightarrow Fe(CN)_6^{3-} + e^- \qquad (1)$$

(a) Later studies concerned with Cs recovery from Purex wastes (Van Tuyl 1957a, 1957b) involved zinc ferrocyanide. Cobalticyanides were also briefly considered.

represents a free energy change of + 8.2 kcal. For the hydrolysis reactions:

$$Fe(CN)_6^{4-} + 2\ OH^- \rightarrow 6\ CN^- + Fe(OH)_2 \qquad (2)$$

and

$$Fe(CN)_6^{3-} + 3\ OH^- \rightarrow 6\ CN^- + Fe(OH)_3 \qquad (3)$$

the free energies at 298K are +40 kcal and + 19 kcal, respectively. Using the entropy values, the free energies at 350K were estimated as 33 kcal and 14 kcal. Using these data, the equilibrium constants of Table 1 were calculated.

TABLE 1. Hydrolysis Constants for Hexacyanoferrates

$$K = \frac{(CN)^{-6}}{(Fe(CN)_6^{-x})} \frac{1}{(OH)^{-(6-x)}}$$

Hydrolysis Constant as a Function of Temperature

Species	298 K	350 K
$Fe(CN)_6^{3-}$	1.2×10^{-14}	1.8×10^{-9}
$Fe(CN)_6^{4-}$	3.8×10^{-30}	2.5×10^{-21}

At a pH of 10 and assuming that the $Fe(CN)_6^{4-}$ concentration is equivalent to that given by the solubility product of $Ni_2Fe(CN)_6$, about 2×10^{-5} M, the concentration of CN^- at 350 K is of the same order of magnitude, i.e., 10^{-6} to 10^{-5} M. Both solubility and hydrolysis increase with temperature.

It is possible that much of the ferrocyanide has been oxidized to ferricyanide by the results of radiolytic decomposition of the water-nitrate mixture, thus increasing the tendency for decomposition in the highly alkaline environment. However, the maximum CN^- concentration will be

controlled by the complexes resulting from the presence of Ni^{2+} and Fe^{2+} in the tanks.

Another process that contributes to the decomposition is the formation of complexes such as $Fe(CN)_5H_2O^{3-}$(I), $Fe(CN)_5NO^{3-}$(II), $Fe(CN)_5NO_2^{4-}$ (III), etc. Formation of I is promoted by radiation. II is reported to convert to III in hydroxide solutions (Sharpe 1976).

Removal of CN^- and hence of the cyanide complexes depends on subsequent CN^- reactions. This can occur through oxidation or as a result of radiolysis. Oxidation produces the cyanate ion and can occur by

$$CN^- + 2\ OH^- \rightarrow CNO^- + H_2O + 2e^- \tag{4}$$

for which $\Delta G = -46$ kcal. Thus, at a pH of 10

$$\frac{(CNO^-)}{(CN^-)} = 5.4 \times 10^{25}. \tag{5}$$

However, the reaction is apparently slow under ordinary conditions. An important driving force tending to solubilize and permit the destruction of cyanide ion is the stability and insolubility of ferric hydroxide.

RADIOLYSIS

One of the reasons for considering the solubility is the potential for radiolysis which is probably a maximum in the aqueous phase. Several studies have been carried out on radiolysis of dilute CN^- solutions over a wide pH range. (Touhill et al. 1969; Ogura et al. 1972; Behar 1974; Bielski and Allen 1977; Liaw and Woodbridge 1977; Draganic, Draganic, and Niketic 1977; and Shen-chu, Shao-hua, and Ji-lan 1981). Radiolytic destruction is quite effective and G values for destruction in the vicinity of 6 are consistently reported.[a]

The compounds formed include CNO^-, NH_3, $CHONH_2$, NH_2CH_2COOH, and smaller amounts of $COOH^-$, CO_2, urea, and probably N_2. The initial mechanism is apparently the attachment of the OH radical (from the radiolysis of water) to the CN^- ion. It is perhaps surprising that the free radical complex rearranges to form a high yield of organic compounds rather than mostly CNO^- since the OH radical is an excellent oxidant.

The cyanate ion is quite stable while the organic compounds will be gradually decomposed.

Using a G value of 6, a radiation dose of 10^6 rad would destroy 6 mmol/L. A rough calculation will illustrate the effectiveness of radiolysis:

> Assume 10^6 g CN^- in 1/10 tank volume, i.e. 2×10^5 L of water-saturated sludge. Then the bulk cyanide concentration is 0.02 mol/L. If the aqueous phase is 10% of the waste volume, 3.3×10^7 rad would be required to destroy the cyanide.

The assumption is made that the radiolysis at cyanide concentrations of 10^{-6} - 10^{-5} M has the same efficiency as at 10^{-4} - 10^{-3} M where most of the measurements have been made. The data of Liaw and Woodbridge (1977) and of Ogura et al. (1972) suggest that the G value may drop as the concentration does. On the other hand, no credit is taken for decomposition of the solid

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(a) The G value is the number of molecules destroyed (or formed) by the absorption of 100 eV of energy, in the present case, energy absorbed by the solution. A "normal" value for a pure substance is about 1.

phase. Unknowns include the radiolytic yields from complexed CN^- and the effect of NO_3 radiolysis on the overall reaction.

It is seen that a radiation dose of 10^7 to 10^9 rad, depending on the localized concentration, could convert most of the cyanide to CNO^-, and other low energy compounds. 10^8 rad over a period of 25 years would require an in-tank dose rate of about 450 r. This is approximately what 1 Ci of ^{137}Cs/L would produce.

As mentioned above, no credit is given to radiolytic decomposition of the solid. A brief mention was made of experiments with $Cs_2ZnFe(CN)_6$ by Hepworth, McClanahan, and Moore (1957). Surprisingly little decomposition was indicated. The conditions used were not typical of the waste tank environment.

Thus, while the radiation received over the 25-30 year period could have destroyed the cyanide under ideal conditions, it is not known what the effectiveness has been. Besides the unknown effects of NO_3 and of complexing of the CN^- mentioned above, other uncertainties are the amount of aqueous phase and the actual cyanide solubility. Laboratory experiments are required to answer these questions.

ENERGETICS

It is apparent from the enthalpies and free energies of formation shown in Table 2, that most cyanide compounds are thermodynamically unstable. Little work has been reported on kinetics, but it is quite likely that the activation energies are quite high. However, for the present it must be assumed that the temperature is adequate or that some other mechanism will permit the reaction. We are then only concerned with the heat of reaction, ΔH.

Experience with explosive reactions of the ferrocyanide precipitates was briefly reviewed in RL-SEP-65 (Backman et al. 1964). The work was reported by Wirta and Koski (1957) and by Hepworth, McClanahan, and Moore et al. (1957). A second comment appears in a Chemical Research and Development Section Monthly Report (Cooper 1957) to the effect that for an aqueous phase of greater than 0.09 M NO_3, in contact with solid $Cs_2ZnFe(CN)_6$, the threshhold temperature was 375°C. If solid nitrates were added to the dry Cs compound, localized explosions and flames accompanied by dense white fumes were observed.

As further evidence that the reactions are potentially violent, patents exist for explosives, e.g. (Eiter, Vogl, and Michl 1954):

- Mixtures of $NaNO_2$ and $K_4Fe(CN)_6$ (47%) or with $Hg(CN)_2$ (73%)
- $Ba(NO_2)_2$ + NaCN (28%)

The patent abstract does not give further information. The explosive reaction of molten $NaNO_3$ and NaCN is mentioned by the National Board of Fire Underwriters, Research Report No. 2 (1950) and by Sax (1957). Thus, there is no question that the reaction of cyanide compounds with either solid nitrates or nitrites may be explosive provided the concentrations and temperatures are adequate.

The products of potential explosive reactions are uncertain, but plausible ones can be assumed and ΔH values calculated. Two examples are given below.

TABLE 2. Thermodynamic Properties of Compounds (Wagman et al. 1982)

Compound[a]	ΔH_f kJ mol^{-1}	ΔG_f kJ mol^{-1}	S° J mol^{-1} K^{-1}
$Fe(CN)_3$	561.9	729.4	270.3
$Fe(CN)_4$	455.6	695.08	95.0
$K_4Fe(CN)_6$	-594.1	-453.0	418.8
$K_3Fe(CN)_6$	-249.8	-129.6	426.1
$Fe_4(Fe(CN)_6)_3$	1184.	--	--
$Zn_2Fe(CN)_6 \cdot 2H_2O$	--	-163.0	--
$Cu_2Fe(CN)_6$	--	736.5	--
NaCN	-87.49	-76.43	115.6
CN^-	150.6	172.4	94.1
OCN^-	-146.0	-97.4	106.7
OH^-	-229.99	-157.24	-10.75
$H_2O(P)$	-285.83	-237.13	69.91
$H_2O(g)$	-241.82	-228.57	188.82
$NaNO_2$	-358.65	-284.55	103.8
$NaNO_3$	-467.85	-367.0	116.52
NaOH	-425.61	-379.49	64.45
Na_2O	-414.22	-375.46	75.06
$Fe(OH)_3$	-823.0	-696.5	106.7
$Fe(OH)_2$	-569.0	-486.5	88
FeO	-272		
Fe_2O_3	-824.2	-742.2	87.4
NO(g)	90.25	86.55	210.76
$NO_2(g)$	33.18	51.31	240.06
CO(g)	-110.52	-117.76	132.6
$CO_2(g)$	-393.51	-394.36	213.74

(a) The states not indicated are crystalline solids except for the ions where the reference state is the 1 m solution.

$K_4 Fe(CN)_6$ is not the best choice as the reactant since it is not present as a solid, and because it represents a reasonably stable compound. However, it is one for which there are reliable data. The other extreme may be $Fe_4(Fe(CN)_6)_3$ which is a possible reactant and probably represents the stability of other potential ferro or ferricyanides.

$$K_4Fe(CN)_6 + 6\ NaNO_3 + 5\ H_2O = 6\ NaOH + 4\ KOH + 6\ CO_2 + 6\ N_2 + FeO \quad (6)$$

$$\Delta H = -2056\ kJ$$
$$= -82\ kcal\ per\ mol\ CN^-$$

$$Fe_4(Fe(CN)_6)_3 + 18\ NaNO_3 + 9\ H_2O = 3\ FeO + 2\ Fe_2O_3 + 18\ CO_2 + 18\ N_2 + 18\ NaOH \quad (7)$$

$$\Delta H = -7398\ kJ$$
$$= -98\ kcal\ per\ mol\ CN^-$$

$$NaCN + NaNO_3 + H_2O = CO_2 + 2NaOH + N_2 \quad (8)$$

$$\Delta H = -447.6\ kJ$$
$$= -107.0\ kcal\ per\ mol\ CN^-$$

Substitution of ferricyanides results in an increase of energy release of 10-15 kcal per mol of CN^-. Substitution of sodium nitrite for nitrate increases the energy by about 5-10 kcal per mol of CN^-. Nitrite is present in the tanks as a result of the long-term radiolysis of nitrate. If NO is produced in place of N_2, the energy is greatly reduced - a factor of about 3. If Na_2O is produced in place of NaOH, the energy is reduced by 10-20 kcal per mol CN^-. The latter must result if the mixture is dried. Thus, a maximum energy of about 95 15 kcal (400 kJ) per mol of CN^- may be expected. For comparison, conversion of 1 mol of carbon to CO_2 by the $NaNO_3$ reaction will release about 85 kcal (355 kJ).

The heat capacities of the sludge components are small. Typical values, (Table 3) J/mol-K, are: $NaNO_3$, 93; NaOH, 59; $AlPO_4$, 93; $Al_2(SO_4)_3 \cdot 6\ H_2O$, 493; $H_2O_{(L)}$, 75; $H_2O_{(g)}$, 34. An estimated C_p for hydrated sludge is 1.2-2 J/g-K.

TABLE 3. Heat Capacities of Typical Compounds[a]

	J mol^{-1} K^{-1}	J g^{-1} K^{-1}
NaOH	59.5	1.5
$NaNO_3$	92.5	1.1
$NaNO_3$(P)	154.8	1.8
$Fe(OH)_3$	101.6	1.0
Fe_2O_3	103.8	0.6
$Al(NO_3)_3 6\ H_2O$	433.0	1.4
$Al_2O_3 3H_2O$	183.5	1.2
$AlPO_4$	93.2	0.8
$Al_2Si_4O_{10}(OH)_2$	294	0.8
H_2O(P)	75.3	4.2
H_2O(g)	33.6	1.9
N_2	29	1.0
NaOH(P)	87.8	2.2
$Fe(OH)_2$	97.0	1.1
NaCN	68.5	1.3

(a) Typical temperature effects would increase C_p by 10-30% at 1000 K. 20% was used as an average in the ΔT estimate.

Other heat sinks are: volatilization of water, 40 kJ/mol; fusion of $NaNO_3$, 15 kJ/mol; and fusion of NaOH, 7 kJ/mol.

Three adiabatic reaction cases were calculated, I-pure reactants, II-pure reactants plus 1 mol H_2O per mol of CN^-, and III-2 mols of H_2O per mol of CN^- plus 2 extra mols of $NaNO_3$. Maximum calculated temperature rises are roughly 1800°C, 1200°C, and 500°C, respectively. The effect of increasing C_p with T was only estimated. The melting and vaporization of various components would reduce the temperature rise especially for the upper values. It may be significant that the materials having the greatest heat capacity (including phase transitions) are those that may be present in appreciable

amounts, such as H_2O and $NaNO_3$. NaOH and the product gases contribute to the heat capacity of the reaction products. It is seen that even with appreciable dilution, the potential temperature rise is great. The real impact of the diluents is not so much the reduction of temperature rise - since even a ΔT of 500°C would seem serious - but rather on the rate of reaction. The latter determines to a large extent the ultimate consequences of the exothermic reaction. Unfortunately, nothing is known of the reaction mechanism.

Another question is the initiation of the reaction. Any source of heat that could produce a temperature of 350 to 400°C is the most likely. This has not been identified although a sludge temperature as high as 315°C has been measured (Dahlke and DeFigh-Price 1983). Shock waves and contact friction are two additional methods that could give temperatures in this range, maybe only in a very small region.

Kinetic data and the effects of dilution can be obtained from laboratory tests. The question as to whether a sufficient quantity of ferrocyanide is concentrated in one place to be a hazard can perhaps be answered by tank sampling and by laboratory radiolysis tests.

TANK SURVEY

A brief review of early HW documents and discussions with present and former Hanford personnel indicates that the cyanide scavenged waste was spread over many tanks in many tank farms in both E and W Areas. The available information gave no obvious pattern for the disposal of cyanide sludges. The decision to use a particular tank, or to empty a given tank, was influenced by special tests, location of the scavenging operation, available crib sites, etc. A number of tanks have been identified that at least at one time contained sizable amounts of nickel ferrocyanide sludge. These include 101C, 108C, 109C, 112C, 105BY, 106BY, 107BY, 108BY, 110BY, 112BY, 101T, 101TY, 103TY, 104TY, 105TY, and 106TY.

An effort was made by F. M. Jungfleisch of Rockwell Hanford Operations to determine the state of some of these tanks through the records used for the TRAC program. The initial results were encouraging, and suggested the actual records are better than the information contained in the early Hanford documents. As this report was being completed, results of this tank survey were made available (Pickett 1984). Some 59 in-plant tributyl phosphate (TBP) waste campaigns, one in-plant test, and 29 in-tank campaigns were reviewed. Table 4 lists the effective scavenging volumes and the amounts of hexacyano ferrate (II) that could be present. Twelve tanks received the solutions just after treatment and it is assumed that all of the ion precipitated in these tanks. Two tanks, BY-104 and BY-105 received cyanide by transfer from BY-106, BY-107, BY-108, and BY-110. The total amount of hexacyanoferrate that is presumed to have been added is 9×10^5 moles or 5.4×10^6 moles of CN (140 t).

TABLE 4. Hexacyanoferrate(II) Additions

Tank	Volume of Solution (Liters)	$Fe(CN)_6^{4-}$ (Moles)[a]	Campaign Type
BY-104[b]	4E+7	2E+5	TBP Process
BY-105[b]	3E+7	1E+5	TBP Process
BY-106	7E+6	3E+4	TBP Process
BY-107	2E+7	8E+4	TBP Process
BY-108	1E+7	7E+4	TBP Process
BY-110	2E+7	9E+4	TBP Process
BY-112	7E+5	3E+3	TBP Process
C-108	4E+6	2E+4	In-Tank
C-109[c]	9E+6	5E+4	In-Tank
C-111[c]	6E+6	3E+4	In-Tank
C-112[c]	1E+7	7E+4	In-Tank
T-101	2E+6	1E+4	T-Plant Test
TY-101	6E+6	3E+4	1C Process
TY-103	5E+6	3E+4	1C Process
TOTAL	2E+8	9E+5	All

(a) Assumes that solutions are brought to 0.005M in $Fe(CN)_6^{4-}$ during scavenging and that all $Fe(CN)_6^{4-}$ settles in the first tank that received it.
(b) Received as solids transfers from BY-106, BY-107, BY-108 and BY-110.
(c) Corrected for supernates of BY-Farm that were not treated with $Fe(CN)_6^{4-}$.

"WORST CASE" SCENARIO

Greater than 10^5 kg (100 metric tons) of ferrocyanide was placed in underground waste storage during a few years starting in 1954. It is known that it is spread over many tanks, but it is not known whether a large quantity remains in any one tank. It can be deduced from the flowsheet that greater than 10^5 moles of CN^- could have been placed in one tank per scavenging sequence. The total nitrate available is not known because the supernate was pumped off. However, a second or more batches of scavenged waste could have ended up in a given tank.

The most hazardous sequence (worst case scenario) would seem to be:

1. The $Ni_2Fe(CN)_6$ sludge representing the Cs from, for example, 3 tanks containing large amounts of $Cs_2NiFe(CN)_6$ was transferred to another tank. The total amount of ferrocyanide precipitate could amount to $(6\text{-}8)\times10^4$ moles of $Fe(CN)_6$.
2. The sludge settled in a a pocket of ~100 m^2 area, 10-20 cm deep.
3. The other major constituent in the sludge was a nitrate salt which deposited with the ferrocyanide precipitate.
4. Without further mixing, the material compacted and dried before appreciable decomposition could take place.
5. Heat from the Cs and other activities increased the temperature as the water was removed.
6. The ignition point was reached, and the 1.5×10^8 kJ (from 85 kcal/mol CN^-) is released in less than a second, (equivalent to 36 tons TNT).[a]

The complete sequence is highly improbable. Any of steps 1 through 5 might have occurred.[b]

(a) Whether the energy is released as a "detonation" or a "deflagration" is a matter of rate of propagation of the reaction. The question is not addressed at this time. Likewise, the efficiency of the reaction is not considered. 100%, which is very unlikely, was assumed in the estimates.

(b) It should be noted that the tank survey (Pickett 1984) indicated that a process similar to step one, did in fact, occur and resulted in more CN in one tank than the assumption made here. Five tanks possibly contain as much CN as the example.

An equally reasonable sequence is that the sludge settled in 2-7 days with the ferrocyanide precipitate diluted by a factor of 5-10 with other solids. A reasonably uniform deposit may have resulted. Early laboratory tests indicated that a fine precipitate was formed which settled slowly (Coppinger and Smith 1954). If the deposit were 50% ferrocyanide it might be of the order of 5-10 cm thick over the entire area of the tank. Calculations have not been done to assess the geometry effect for the system.

If other conditions are favorable for a reaction, then the drying step may be critical. Although it is reassuring that nothing has happened in 25-30 years, it must be emphasized that there are no data to indicate the actual in-tank condition as it relates to cyanide deposition or chemical environment.

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