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Complexant Stability Investigation Task 2 - Organic Complexants

E. C. Martin

June 1985

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COMPLEXANT STABILITY INVESTIGATION
TASK 2 - ORGANIC COMPLEXANTS

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Pacific Northwest Laboratory
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SUMMARY

The safety of high-level defense waste operations has always been given highest priority at the Hanford site. This document is part of the continued effort to appraise and reevaluate the safety of the waste stored in underground tanks on the Hanford Reservation. Hanford high-level defense waste consists mainly of moist, inorganic salts, NaNO_3 , $\text{NaAl}(\text{OH})_4$, Na_2CO_3 , and other sodium salts. However, in addition to these salts, quantities of organic compounds constitute a significant portion of the waste. The potential reaction of the organic compounds with inorganic salts to form explosive substances is examined and found to be nonexistent or negligible. The concept that the waste mixture might react exothermically is found to be untenable under the present storage conditions. The phenomenon of slurry growth in double-shell waste storage tanks is expected to cause no increase in exothermic reaction potential within the waste.

The results of this study indicate that the presence of organic material in the high-level defense waste does not constitute undue hazard under the present storage conditions.

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INTRODUCTION

Large quantities of various organic compounds, including organic complexants such as citric acid, ethylenediaminetetraacetic acid (EDTA), N-(hydroxyethyl)-ethylenediamine triacetic acid (HEDTA), and hydroxyacetic acid, were placed in the 200 Area single-shell waste tanks over a period of many years as a result of the normal operations of the Hanford separations plants. The wastes contained in the single-shell waste tanks are being prepared for long-term interment by removal of pumpable amounts of aqueous phase. The potential for rapid exothermic reactions between the organic compounds and oxidants (primarily nitrate and nitrite salts) also present in the wastes has been a concern. The determination of the potential for these reactions occurring in both the single-shell and double-shell waste tanks is the objective of the present study.

Prediction of conditions resulting in rapid exothermic reactions requires review of the possible chemical reactions of the various organic species, and the determination of the thermodynamics and kinetics of these reactions. A review of existing information has been made, and the results of that review are reported herein. Conclusions are given as well as recommendations for further study if alterations in the tank environment are made in the future.

CONCLUSIONS AND RECOMMENDATIONS

This report has addressed the rapid exothermic reaction potential of the organic-containing wastes found in Hanford single-shell waste tanks. Although reaction of organics with waste constituents such as NaNO_3 or NaNO_2 results in significant release of energy, no reaction is expected without an initiating event. The potential for formation of organic compounds of an explosive nature has been assessed and found to be remote.

There appears to be no discernible path by which explosive compounds will be formed from the organic waste in any of the underground single or double-shell waste storage tanks, the aqueous alkaline environment prevents direct nitration or nitroesterification of the organic compounds. The presence of a radiation field and elevated temperatures will permit safe degradation of any hazardous explosive material that may have been introduced inadvertently into the tank or formed by an unknown or undetermined route. However, failure to maintain the following conditions may lead to the formation of hazardous explosive substances in the tanks:

1. an aqueous environment
2. alkaline solution
3. controlled temperature profiles (lower than 300°C).

If tank management practices predict the loss of any of the conditions listed above, experimental studies are recommended to determine the actual explosive hazard potential for exothermic reactions in the tanks. Such experimental studies could define the minimum temperature required for initiation of a rapid exothermic reaction. In addition, the rate of decomposition, energy release, and rate and quantity of gas evolution could be determined as a function of temperature for waste compositions typical of those found in the Hanford single-shell waste tanks.

HISTORICAL PERSPECTIVE

The Hanford separations plants have operated intermittently for approximately 40 years (ERDA 77-44 1977). The waste solutions from these plant operations, after neutralization, have been stored in underground tanks. Significant quantities of ^{137}Cs and ^{90}Sr have been removed and isolated from the remainder of the wastes to reduce the thermal loading of the waste tanks. In addition, both past needs for additional tank space and concerns regarding the storage of liquid wastes in single-shell tanks led to various efforts to reduce single-shell waste tank volumes. The volume of the waste was reduced initially by self-evaporative processes, then by in-tank solidification techniques and finally by evaporator crystallization operations. The goal of these operations has been the removal of any residual aqueous phase and conversion of all single-shell tank wastes to a solid material. All 149 single-shell tanks now contain moist sludge and/or salt cake. Although efforts continue to remove as much liquid as possible, some nonpumpable liquid is present in the tanks, mainly as interstitial liquid.

To minimize the possibility of tank leakage and to attain the highest level of safety achievable, all high level waste presently generated by Hanford separations plants is stored in double shell waste tanks, i.e. a tank within a tank. In addition, the double-shell tanks have been the repository for the liquid waste transferred from the single-shell tanks as efforts continue to stabilize them and reduce their tank leakage potential. Significant reductions in the total liquid waste volume have been made using evaporative techniques in which volatile organic compounds and water have been removed as nonradioactive condensate and discarded. However, in spite of the liquid waste transfers, the single-shell tanks still retain significant quantities of organic compounds dissolved in the interstitial liquid of the salt cakes or in the moist sludge. Schulz (1900) reported the analysis of samples of both solid and liquid waste taken from a dozen single-shell underground storage tanks. The concentration of organic carbon in the salt cake was generally small, 0.053 to 0.21 M; the liquid waste, however, contained organic carbon ranging from 4 to 10.8 M. It is this organic material that remains in the single-shell tanks in intimate contact with oxidants such as nitrate and nitrite salts that is of concern.

The organic constituents in the waste resulted from four basic chemical process operations: 1) Bismuth Phosphate Process; 2) Tributyl Phosphate solvent extraction of uranium from Bismuth Phosphate Process wastes; 3) Redox Process; and 4) PUREX Process. Wastes from the B-Plant Waste Fractionation process were also added to the tanks. The resultant waste is a very complex mixture of a large number of organic complexants, solvents, and ancillary chemicals.

Winters (1981) has identified a number of references which describe the variety and amounts of some of these waste constituents. The listing below identifies some of the organic compounds:

- ethylenediaminetetracetic acid (EDTA)
- N-hydroxyethylethylenediaminetriacetic acid (HEDTA)
- hydroxyacetic acid
- citric acid
- sodium tartrate
- sodium oxalate
- diethylenetriaminepentaacetic acid (DTPA)
- nitrilotriacetic acid (NTA)
- sodium acetate
- sucrose
- tributylphosphate (TBP)
- dibutylphosphate (DBP)
- monobutylphosphate (MBP)
- dibutylbutylphosphonate (DBBP)
- bis-2-ethylhexylphosphoric acid (HDEHP)
- methylisobutyl ketone
- kerosene
- normal paraffin hydrocarbon (NPH)

In addition to the compounds indicated, their degradation products and other organic impurities are also present in the Hanford wastes (McFadden 1980).

Allen (1976) has estimated the amounts of some of the major complexants that have been added to the wastes from 1944 through 1975 are:

Hydroxyacetic acid - 9.0×10^6 moles

Citric acid - 3.3×10^6 moles

HEDTA - 2.7×10^6 moles

EDTA - 0.57×10^6 moles

The distribution of the organic material in some single-shell waste tanks is indicated in Table 1. It is evident from the data given in Table 1 that organic materials are present in both the water soluble and water insoluble phases of the waste. The concentration of the organic material in the tanks is appreciable, i.e. Tank 104T contains 8.5 moles of carbon per 1000 g of

TABLE 1. Total Organic Carbon Content of Some Hanford Waste (Jungfleisch 1980)

Tank No.	Type of Waste	TOC (g/g)	
		Water Soluble	Water Insoluble
107-BX	1st cycle Bismuth Phosphate Process Sludge	-----	7.3×10^{-4}
110-BX	1st cycle Bismuth Phosphate Process Sludge	1.69×10^{-4}	6.00×10^{-4}
112-BX	1st cycle Bismuth Phosphate Process Sludge	1.2×10^{-3}	8.9×10^{-3}
104-T	1st cycle Bismuth Phosphate Process Sludge	2.9×10^{-3}	1.02×10^{-1}
102-TY	Evaporator bottom	2×10^{-3}	--
103-TY	Uranium Metal Recovery Process	1.1×10^{-3}	$<1.2 \times 10^{-3}$
104-TY	Uranium Metal Recovery Process	1×10^{-3}	2.8×10^{-2}
105-TY	Uranium Metal Recovery Process	$<1 \times 10^{-2}$	$<6 \times 10^{-3}$
106-TY	Uranium Metal Recovery Process	9.18×10^{-4}	3.69×10^{-3}
106-C	PUREX	2×10^{-2}	--

solid (Jungfleisch 1980). It is estimated that there are 70 tons of organic carbon in the interstitial liquid of the waste in the single-shell tanks (RHO 1980), 220 to 550 tons of organic carbon in the double-shell slurry, and 800 to 1100 tons in the complex concentrates contained in the double-shell tanks (DOE 1980).

Although the total quantity of organics is large, inorganic materials are the major constituents of the Hanford tank wastes. The inorganic salts in the waste, and their estimated total quantities, are shown in Table 2.

Thus large quantities of organic material must be assumed to be intimately mixed with an excess of inorganic salts, including oxidants such as NaNO_3 and NaNO_2 . In addition, considerable modification of the original organic compounds may have occurred under the influence of temperature and radiation to produce partially oxidized compounds that are more readily susceptible to further oxidation. These compounds would include hydroxylated and unsaturated compounds that would be particularly susceptible to reaction with nitrate ion.

TABLE 2. Inorganic Constituents of Hanford Waste
(RHO 1980, DOE 1980)

<u>Salt</u>	<u>Estimated^(a) Total Amount</u>
NaNO_3	150,000 tons
NaNO_2	19,000
Na_2CO_3	3,900
NaAlO_2	10,000
NaOH	15,000
Na_3PO_4	16,000
Cancrinite ^(b)	2,700
Al(OH)_3	2,300
Fe(OH)_3	1,200

(a) Only those compounds are listed whose quantity exceeds 1000 tons.

(b) Known silica additions are assumed to have reacted with aluminates and hydroxides to form cancrinite (assumed to be $2\text{NaAlSiO}_4 \cdot 0.52 \text{NaNO}_3 \cdot 0.68 \text{H}_2\text{O}$).

CHEMISTRY

Sufficient organic material exists in the waste to produce a large scale exothermic reaction, but before such an event could take place an initiating reaction must occur. Stated in other words, sufficient activation energy must be added to the system before a catastrophic event could ensue. In general, it is assumed herein that a highly energetic compound must be formed as a result of chemical and/or radiolytic reactions of the organics in the waste tanks in order for an initiating reaction to occur. Much of the remainder of this report is devoted to an evaluation of the likelihood of formation of various energetic compounds and initiating reactions.

EXPLOSIVES

The present report seriously considers the possibility that extremely unstable compounds of the nature of explosives may have formed in the waste tanks. The materials considered include initiating high explosives, noninitiating high explosives, and low grade explosives. If formed, the presence of explosive compounds is assumed to be sufficient to initiate a large-scale rapid exothermic reaction within the waste tanks.

As outlined in the Kirk-Othmer Encyclopedia of Chemical Technology (1965), a wide variety of chemical compounds can undergo explosion. These compounds include nitrate esters, nitro compounds, nitroso compounds, nitramines, fulminates, azides, perchlorates, peroxides, and compounds containing carbon atoms with double and triple bonds. Of course, not all members of these classes of compounds undergo explosions. For example, ammonium nitrate and lead azide explode; sodium and potassium nitrates and azides are non-explosive.

The following table categorizes some of the compounds listed above as high or low, initiating or noninitiating explosives.

Each of these classes of materials will be discussed in terms of synthesis, radiation effect, spontaneous thermal degradation, and potential for formation in Hanford waste tanks.

TABLE 3. Types of Explosives (Breger, Carroll and Bolt 1963)

High Explosives

Primary (explosion initiating compounds)

fulminates

azides

styphnates (resorcinol derivatives)

diazo compounds

Secondary (noninitiating explosives)

polynitrated phenolic compounds

nitramines

nitrated heterocyclic compounds

polynitrated hydrocarbons

Low Explosives

nitrocellulose

nitroglycerine

Primary High Explosives (Explosion Initiating Compounds)

Fulminates

The standard initiator in explosive technology is mercury fulminate, $\text{Hg}(\text{CNO})_2$. The nature of this material can be judged by some of its characteristics (shown in Table 4).

TABLE 4. Mercury Fulminate

Impact Test to achieve detonation

fall of 2 kg weight 2 in. (5 cm)

fall of 1 kg weight 24 cm

Minimum temperature to cause explosion

in 0.1 sec 263°C

in 5.0 sec 210°C

Decomposition in storage at 80°C

5% decomposition in ~4 hours

at 50°C

5% decomposition in 8.25 months

at 30-35°C

5% decomposition in 20.0 months

The synthesis of mercury fulminate is very simple. Mercury is dissolved in nitric acid, and an equivalent amount of 95% ethanol is added. Upon cooling, crystalline mercuric fulminate precipitates out. Other equally simple syntheses involve the use of acetaldehyde or nitromethane.

It is unlikely that any appreciable amount of mercury fulminate would be generated in the tank farm system because concentrations of mercury are minimal and because the entire waste system is maintained at a pH of 8-10 (ERDA 1538 1975). The absence of an acidic environment and appreciable quantities of mercury virtually preclude synthesis of this substance.

The process inventory indicates that $\text{Hg}(\text{NO}_3)_2$ has been used in plant operations; a typical inventory in the processing area was 350 lbs. Used material was disposed of in the underground tank facility. Preliminary data (RHO 1980) indicates that there are 1800 lbs of Hg^+ in the total bulk sludge of the single-shell waste tanks.

The volatility of the organic components necessary for synthesis and the sensitivity of the product to temperature further mitigate against the presence of mercury fulminate in any of the tanks.

Lead Azide

The chemical formula of lead azide is

The simplest and most direct synthesis of lead azide involves the use of sodium azide. The slow addition of sodium azide to a dilute or constantly stirred solution of lead acetate or lead nitrate yields lead azide. Although lead nitrate has been used in the separation plants, sodium azide has not been reported as a process chemical. However, it is possible to generate a scenario in which sodium azide could be produced from materials (Jones 1973) used in the separation plants. Both hydrazine and lead nitrate have been used in process chemistry in the 200 Area. The Final Environmental Statement (ERDA

1538 1975) indicates an inventory of 10,000 lbs of hydrazine was maintained in the 275-EA warehouse or in the 234-5 Building for process chemical purposes. An inventory of 5000 lbs of lead* nitrate was also maintained in the 275-EA warehouse. The final disposal of the hydrazine and presumably of the lead nitrate was to the underground tanks. Although it is unlikely that hydrazoic acid could be generated in the basic waste solution of the tanks, an opportunity may have occurred for hydrazine to react with nitrous acid in the chemical processing equipment, Equation 1. If this occurred, contact with the basic waste solution would stabilize the hydrazoic acid as a sodium salt, Equation 2. Subsequent contact with lead ion would produce lead azide, Equation 3.

The presence of both hydrazine and lead nitrate gives some plausibility to the possible adventitious formation of lead azide and its presence in the tank. Other metals, particularly silver, copper, mercury, and cadmium** also form water insoluble azide salts that may explode by impact or friction. Lead ion is not essential to the formation of an explosive azide salt (Sisler 1956).

*Other lead containing compounds have been used. Among these are PbS_2O_8 which was used as a carrier for ^{90}Sr precipitation (Bray and Van Tuyl 1961).

**ERDA 1538 (1975) states that an inventory of 15,000 lbs of cadmium nitrate was maintained as a neutron poison. Ultimate disposal was to the Z9 crib or to underground tank storage.

The following table displays characteristics of lead azide (Kirk-Othmer 1965).

TABLE 5. Lead Azide (Crystalline)

Heat of explosion	367 cal/g
<u>Impact Test</u>	
fall of 2 kg weight	2 inches (5 cm)
fall of 1 kg weight	43 cm
<u>Min. temperature to cause explosion in</u>	
0.1 sec	383°C
5 sec	345°C
<u>100° Vacuum Stability Test</u>	
mLs of gas in 40 hours	0.4

The aqueous solubility of lead azide is 0.023% at 18°C, 0.09% at 70°C (Merck 1976).

The crystalline density of the two crystalline forms of lead azide are: orthorhombic, 4.71; and monoclinic, 4.93 (Kirk-Othmer 1965). Normally, the precipitated lead azide is stored under water. Thus, it is not impossible that heavy metal azides have formed a part of the sludge layer and remain in a quiescent state under a blanket of water.

Initiators Possessing Phenolic Rings in their Structure

Typical initiators having phenolic rings in their structure include:

Diazodinitrophenol (DDNP)

Lead Styphnate: 2,4,6 trinitroresorsinate

Lead Dinitroresorcinolate

Lead Dinitrosoresorcinolate

The first of these initiators is formed by diazotizing picramic acid with sodium nitrite and hydrochloric acid. The last three compounds involve the use of dihydroxylated aromatic compounds, sodium or magnesium styphnate (2,4,6-trinitroresorcinol), dinitroresorcinol, and resorcinol. The use of these compounds is not mentioned in any of the literature surveyed. In fact, very few aromatic organic compounds have been utilized in B Plant, Redox, or PUREX process operation; the metal recovery process used Shell Spray Base E-2342 as a diluent for TBP. This material was a naphthenic based kerosene fraction. (Naphthenes are saturated cyclic hydrocarbons such as alkyl derivatives of cyclopentane and cyclohexane.) Although naphthenes are capable of losing hydrogen atoms, forming benzene rings, there is little

probability that the aromatic compounds would form in sufficient concentration to produce any meaningful concentration of this type of initiator in the waste tanks. For example, resorcinol is normally obtained by fusion of m-benzene disulfonic acid with excess sodium hydroxide (Merck 1976). It is inconceivable that such a reaction could occur in the separations plants or the waste tanks.

Secondary High Explosives (Noninitiating Explosives)

Secondary explosives are those that are too insensitive to detonate spontaneously from impact, friction or momentary heating. As a consequence of this behavior, they are also termed noninitiating explosives. This category of compounds includes chiefly nitrates, nitro compounds, and nitramines.

Ammonium Nitrate

Ammonium nitrate is regarded as the only important inorganic high explosive for the systems of present interest. Its heat of formation is calculated to be 87.93 kcal/mole at constant temperature. When heated, ammonium nitrate can decompose in a number of ways based on the condition of heating. Some of the more important reactions are listed below:

At ordinary temperatures and pressures NH_4NO_3 is so insensitive to impact and friction it can be regarded as essentially nonhazardous. However, its

sensitivity increases with temperature; at 175°C its sensitivity to impact has increased by a factor of 2.6. Ammonium nitrate will explode in three seconds at a temperature of 325°C (Kirk-Othmer 1965).

Ammonium nitrate has been used as a process chemical in the 200 Area (100,000 lbs has been maintained as an inventory in the 202-A Building). Ammonia (45,000 lbs inventory) and nitric acid (200,000 lbs inventory) have also been used (ERDA 1538 1975). The ultimate disposal of these materials has been to the underground storage tanks. If significant quantities of ammonium nitrate remained in the waste tanks, a potentially serious hazard would exist. However, ammonium nitrate is expected to decompose readily, without hazard, under waste tank conditions. The alkalinity (~pH 10) of the waste tank liquids should have promoted conversion of ammonium ion, NH_4^+ , to ammonia, NH_3 , by the following reaction:

Venting of the tanks and elevated temperatures would have aided destruction of the ammonium ion by removing the ammonia as a gaseous product.

The information above indicates there is no hazard resulting from the NH_4NO_3 that has been added to the underground storage tanks. Complete destruction of NH_4^+ with subsequent loss of ammonia has taken place.

Polynitrated Aromatic Compounds

This group of compounds constitutes the most important of the noninitiating, high explosives. It includes compounds such as TNT (2,4,6-trinitrotoluene), tetryl (N-methyl-N,2,4,6-tetranitroaniline), picric acid (2,4,6-trinitrophenol), and similar compounds. Selected characteristics of these compounds are given in Table 6.

TABLE 6. Characteristics of Selected Polynitrated Aromatic Compounds (Kirk-Othmer 1965)

Compound	Crystal Density	Water Solubility g/100 g	Explosion ^(a) Temp. (5 sec) °C	Impact Test ^(a) cm
TNT	1.654	0.1475	475	100+
2,4-dinitrotoluene	1.688	0.087	550	40
1,3,5-trinitrobenzene	1.521	0.102	--	100+
m-dinitrobenzene	1.571	0.32	--	100+
picric acid	1.763	6.8	322	82
ammonium picrate	1.717	74.8	318	100
tetryl	1.73	0.181	257	26

(a) See Appendix A for explanation of tests.

It is unlikely that any significant amount of these compounds could be generated either prior to or after placement in the waste storage tanks. First, there has never been any significant use of aromatic compounds for the chemical separations processes. The hydrocarbon solvents used in the separations plants did not contain aromatic compounds. Initially, Shell Spray Base E-2342, a paraffin naphthenic based kerosene fraction, was used as a diluent for TBP. Later, Soltrol, an oligomeric propylene, and finally a mixture of normal paraffin hydrocarbons which consisted mainly of C₁₁, C₁₂, C₁₃ straight chain hydrocarbons were used as the hydrocarbon diluent.

Second, even if the assumption is made that an appreciable amount of aromatic compounds was present in the waste tanks as a result of inadvertent additions or by cyclization and dehydrogenation of a straight chain hydrocarbon, it is unlikely that nitration would occur. The process of nitration has long been determined to result from the formation of a nitronium ion species, NO₂⁺. This ion is normally formed from the interaction of "mixed-acid," nitric and sulfuric acid, as shown by Equation 9.

However, as indicated in Ingold (1953) it is possible to generate the nitronium ion from concentrated nitric acid alone.

Inherent in the generation of the nitronium ion is the necessity that water concentration be maintained at a minimum, otherwise the nitronium ion would either not form or would be reconverted to nitric acid.

Once formed, the nitronium ion attack on the aromatic ring system proceeds as follows.

Polynitration occurs under increased temperatures and increased acid strengths.

There are other nitronium generating systems, e.g., nitric acid in glacial acetic acid, fuming HNO_3 , nitric acid in acetic anhydride, benzoyl nitrate, and acetyl nitrate. It is imperative in all of the systems mentioned that water be excluded. The fact that all of the waste tanks contain significant quantities of water mitigates against in-tank nitration.

The nitration of alkanes follows a route different from that of the nitration of aromatic compounds. Direct nitration with nitric acid is possible, but it involves high temperature, vapor phase nitration. This process is assumed to be a free radical mechanism. Thermal conditions for this process are in the range of 420-470°C (Roberts and Caserio 1965). An additional requirement for a successful reaction is the necessity for the gases to pass

through a narrow reaction tube which ensures intimate contact between the gases.

An extensive review of the past thermal records of the waste tanks has been reported (Dahlke and DeFigh-Price 1983). The highest temperature of the waste reported was 594°F (315°C). Tank #241-A-106 reached this temperature for an extended period in 1963-64. It is significantly lower than that specified for alkane nitration.

The inadequate temperature, the unconfined reaction area (head space) and the alkaline nature of the tank waste point out the impossibility of direct nitration of alkanes.

An alternate avenue exists for the preparation of nitrated alkanes, however. This involves the displacement of a group by nitrite ion.

This reaction normally involves the reaction of an alkyl halide or a similarly substituted alkane (Roberts and Caserio 1965) with sodium or silver nitrite. The normal solvents for such reactions are dimethyl formamide, dimethyl sulfide, or diethyl ether. Solubility factors and solvent reactivity exclude water as a suitable solvent for this reaction.

There are no compounds listed in Table II.1-F-1 of the Final Environmental Statement, Waste Management Operations (ERDA 1538 1975) that would serve as the alkyl halide. Thus, because of the nonavailability of suitable alkyl compounds, lack of appropriate solvent, and potential interference from the basic aqueous solution, this route to a nitro alkane likewise is inoperative. All available evidence indicates there is no justifiable reason to assume the synthesis of nitro compounds in the waste in the underground tanks.

Nitrate Esters

The nitrate esters comprise another group of explosives that might be presumed to form in the waste solution. This group includes nitroglycerine

(glycerylnitrate), cellulose nitrate, starch nitrate, glycol dinitrate, pentaerythritol tetranitrate (PETN), and similar compounds. Table 7 illustrates the sensitivity characteristics of some of these explosives.

The presence of any of these compounds in the tanks would be a serious concern because of their high sensitivity for detonation. Some of these compounds in the dry state can be ignited by an electric spark (Kirk-Othmer 1965).

The possible presence of these types of explosives in the waste is a significant concern because numerous hydroxylated compounds have been employed in the chemical separation plants. These hydroxylated compounds include sugar, tartaric acid, citric acid, hydroxyacetic acid, HEDTA, and sodium gluconate. These hydroxylated compounds would seem to be prime candidates for

TABLE 7. Sensitivity Characteristics of Explosives
(Kirk-Othmer 1965)

<u>Explosive</u>	<u>Impact Test^(a) (inch)</u>	<u>Pendulum Friction Test^(a)</u>	<u>Explosion Temp. °C^(a)</u>
glycerylnitrate	1	100	222
cellulose nitrite (13.3% N)	3	--	230
nitrostarch	5	--	217
glycol dinitrate	2	70	257
PETN	6	50	225

(a) See appendices for explanation of tests.

the generation of nitrate esters. However, the mechanism for forming nitrate esters involves the use of mixed acids, concentrated H_2SO_4 and HNO_3 .

Increased levels of nitration can be achieved only with the use of stronger mixed acids, (i.e., with increased H_2SO_4 acid and decreased water content). A representative reaction is,

The equation above indicates the reaction results in an equilibrium mixture of reactants and products. To achieve a high yield of nitrate ester it is necessary to lower the water component in the reaction mixture. This is the function the H_2SO_4 performs. The absence of the H_2SO_4 dehydrating agent would greatly limit the formation of the ester. The presence of water in the waste tank virtually assures that the nitrate ester will not form.

A number of polynitrated esters, such as cellulose nitrate and starch nitrate decompose in the presence of aqueous alkali (or dilute H_2SO_4 (Kirk-Othmer 1965)). For the reasons stated above, the nitrate esters are not expected to form in the aqueous tank environment. If they formed in the separation process cycle they would not survive the alkalinity of the tank waste.

Thermal degradation also reduces nitrate ester concentrations. For example, nitroglycerine is relatively stable at temperatures in the range of 50°C but decomposes more readily as the temperature is raised. At 145°C (293°F) decomposition sets in at such a rate the liquid appears to boil. The explosive temperature for nitroglycerine is 222°C (431.6°F) (Kirk-Othmer 1965).

Based on the information given above, there is little likelihood that nitrate esters could form, and, if formed, the possibility for their survival and concentration in the waste is negligible.

Black Powder Explosives

This category of explosives must be carefully considered because analogies exist between the constituents of black powder and the constituents of Hanford tank wastes. The bulk of the salt cake in the tanks is NaNO_3 , the major constituent of type B, black powder. The percent NaNO_3 in the solid waste of the 12 tank farms varies from 75-85%.*

*Solid waste in the SX Tank Farm contains 50% NaNO_3 (ERDA 1538 1975).

TABLE 8. Composition of Black Gunpowder (Kirk-Othmer 1965)

	Black Gunpowder	
	Type A(%)	Type B(%)
KNO_3	74.0	--
NaNO_3	--	71
Charcoal	15.0	16.5
Sulfur	10.4	12.5

The carbon content of the interstitial liquid in the single-shell tanks is 1.0% after water evaporation (RHO 1980), considerably lower than the values shown in the table above. However, the mixture of materials in the waste tank is undoubtedly nonhomogeneous. It is conceivable that certain portions of the waste contain NaNO_3 and carbonaceous material in concentrations equivalent to those found in Type B gunpowder.

Both black powder formulations imply sulfur is a necessary ingredient to achieve the desired explosive characteristics. This is not the case. Formulations termed "sulfurless black powder" have been devised and employed in naval ordinance by both Germany and Great Britain (Urbanski 1967).

The function of the sulfur in normal black powder is fourfold (Urbanski 1967, p. 338):

1. It facilitates an increase in the quantity of gases involved in the explosion. K_2SO_4 , K_2S and CO_2 are formed when sulfur is used. Without sulfur, K_2CO_3 is a prominent reaction product.
2. Sulfur reduces the initial decomposition temperature. The following table illustrates this point:

Mixture	Decomposition	Explodes
$2\text{KNO}_3 + 3\text{C}$	320°C	357°C
$2\text{KNO}_3 + \text{S}$	310°C	450°C
$2\text{KNO}_3 + \text{S} + 3\text{C}$	290°C	311°C

3. Sulfur intensifies the sensitivity of the mixture to impact.

<u>Mixture</u>	<u>Impact</u>	<u>Response</u>
$\text{KNO}_3 + \text{C}$	2 kg weight dropping 45-50 cm	no explosion
$\text{KNO}_3 + \text{S}$	2 kg weight dropping 45-50 cm	decomposes
$\text{KNO}_3 + \text{S} + \text{C}$	2 kg weight dropping 70-85 cm	explodes

4. Sulfur influences the type of reaction (explosion) products formed.

	<u>Products</u>
With sulfur	$\text{K}_2\text{S} + \text{CO}_2$
Without sulfur	$\text{CO} + \text{KCN}$

A portion of the CO formed at the elevated temperatures of the black powder explosion reacts with water to liberate H_2 as shown by Equation 15.

At least 10% S is normally included in the formulation of blasting powder to avoid accumulations of CO in confined areas (i.e., mines, etc.). Kirk and Othmer (1965, p. 650) discuss the importance of sulfur in terms of ignition and explosive temperatures. They (Kirk-Othmer 1965) state that black powder dropped on heated metal at 510°C ignites in 0.1 sec. In the explosive test (see Appendix B) it ignites in 5 sec. at 427°C . The powder is essentially nonreactive at temperatures as high as 120°C (248°F). In the absence of sulfur, all temperatures indicated above can be significantly increased. It was pointed out earlier the highest temperatures attained in a given tank were in the range of 199 – 313°C , well below the limits of self-ignition but probably at levels for nonexplosive decomposition of the mixture.

The explosive potential of black powder is known to be sensitive to moisture content. Moisture in excess of 0.2% causes a decrease in the rate of burning (Kirk-Othmer 1965). The following quotation illustrates the sensitivity of gunpowder to water. (Urbanski 1967 p. 324).

"In Great Britain and throughout the Commonwealth black powder was used to prove alcohol. In this test the alcoholic solution was poured upon a small heap of black gunpowder or 'proof powder' and a flame was applied to burn the heap. If the mixture burned with explosion it was overproof. If it didn't burn or burned with difficulty the alcohol was underproof. If the mixture burned with a 'slight' explosion it was proof spirit, i.e., containing 49% alcohol by weight."

A burning solution of alcohol containing 52% or more of water will not ignite gunpowder. The total bulk Hanford sludge contains 1.53 times as much water as NaNO_3 by weight; in the interstitial liquid the water content is 1.92 times that of NaNO_3 (RHO 1980).

Gunpowder manufacturers have expressed concern about the hygroscopicity of the charcoal because of its large surface area and its absorptive capacity for gases. Efforts to circumvent this problem have led to the use of soot and sugar carbon. However, these materials are not porous and cannot incorporate sulfur and nitrate directly into the particles of carbon as is the case with charcoal. The poorer product obtained with soot and sugar carbon resulted in reduction in the uniformity of burning rate and in a product that burned slower than that produced from charcoal. Tank waste likewise lacks the intimate mixing and grinding that produces the homogeneity of gun powder. As a result, the waste mixture would not function, or would function very poorly, as an explosive source.

Although the mixture of organic carbon and NaNO_3 may appear potentially hazardous a number of factors indicate that a safe storage situation exists under the present conditions. The factors that lead to this safety condition are:

1. high water content
2. absence of sulfur resulting in higher ignition temperatures
3. waste temperatures well below ignition temperatures

4. lack of intimate contact of organic material with nitrate

Beitel performed a number of experiments in which he attempted to detonate mixtures of either sodium nitrate or synthetic salt cake with carbonaceous materials similar to the compounds which comprise the organic portion of the waste from the separation plants (Beitel 1976a, 1976b, 1977). Beitel postulated four assumptions relative to the expected state of the tank waste after the conclusion of the solidification program. The assumptions were:

- (1) The salt cake consists of 95 percent NaNO_3 , and the bulk of the remainder is composed of NaNO_2 , NaAlO_2 , NaOH , and Na_2CO_3 .
- (2) Organic materials that may be in the salt cake are ion exchange resins, complexant,* hydrocarbon liquids, and traces of rubber, plastic, and cotton.
- (3) No nitrated organics are present.
- (4) The salt cake is dry.

From these assumptions and this experimental work he drew the following conclusions that were incorporated into a later document (Baca et al. 1978) and are repeated here:

- (1) Neither sodium nitrate nor simulated salt cake with various amounts of organic material added can be made to detonate. (Beitel 1977).
- (2) Sodium nitrate based salt cakes containing organic materials are stable against deflagration for temperatures below 250°C .
- (3) Sodium nitrate based salt cakes will ignite and react with most organic materials which are still liquid or solid at temperatures above 400°C . Ignition will occur between 380°C and 450°C . The relative degree of

* Complexant may be citric acid, ethylenediaminetetraacetic acid (EDTA), N-hydroxyethylethylenediaminetriacetic acid (HEDTA), sodium hydroxyacetate, or mixtures of all four.

reaction and the relation of sodium nitrate and organic material (charcoal) is shown in Figure 1. The relative reactivity of a simulated salt cake mixture and an organic material (charcoal) is shown in Figure 2.

- (4) If a volatile hydrocarbon is added to a sodium nitrate based salt cake and subsequently heated slowly and uniformly, the hydrocarbon will evaporate unreacted before ignition temperatures (400°C) are reached.
- (5) If a volatile hydrocarbon is added to a sodium nitrate based salt cake and subsequently ignited, the hydrocarbon will flame above the salt cake, reacting with environmental gaseous oxygen. The salt cake will act as a wick, transporting the hydrocarbon to the surface by capillary action and evaporation will cool the salt cake to below ignition temperature.
- (6) The presence of water in the stored salt cake increases the difficulty of initiating a reaction. Figure 3 shows the effect of water content on a stoichiometric mixture. Stored salt cake will contain about 2 to 20 percent water.
- (7) Sodium hydroxide and sodium aluminate will also be present in quantities in excess of 5 to 10 wt%. Their presence reduces the reactivity of the salt cake.
- (8) Sodium nitrite will be present and is more reactive than sodium nitrate. However, it is less energetic and reduces the worst possible hazard.

FIGURE 1. Combustion Results for Sodium Nitrate and Charcoal (Beitel 1976a)

FIGURE 2. Combustion Results for Simulated Salt Cake and Charcoal (Beitel 1976a)

FIGURE 3. Combustion Results for 80% NaNO₃ - 20% Charcoal (Beitel 1976a)

RADIOLYTIC EFFECTS

Effect of Radiation on Explosives

Although all evidence indicates it is unlikely that an explosive compound can form in alkaline waste solution by normal chemical processes, the possibility exists that an unstable compound might form by an unexpected process. The concern then would involve the stability of this hypothetical material. It is assumed that the compound would undergo the usual deterioration as a result of alkaline hydrolysis and elevated temperature, since even under ideal temperature and humidity conditions explosives and propellants lose power with prolonged storage. In addition, the effect of radiation on this hypothetical compound and explosive compounds in general should be addressed.

A study of radiation effects on explosives was carried out in the early 1950's by Sismar and Warren at Oak Ridge National Laboratories. Their reports were summarized by Rosenwasser (1955).

The following characteristics for the irradiation process were noted:

1. Gas evolution was observed for all the explosives irradiated.
2. None of the compounds exploded (except nitrogen iodide).
3. The time for thermal degradation was reduced following irradiation.
4. The lowest dose for which degradation effects were noted was 10^6 rad.
5. The brisance, sensitivity to impact and gas evolution varied for each compound. (Brisance is defined as the shattering power developed per unit volume of an explosive.)

The pertinent results of these irradiation tests are given in Table 9. It may be concluded from the information given in Table 9 that irradiation

TABLE 9. Irradiation Effects on Selected Explosives (Rosenwasser 1955)

<u>Compound</u>	<u>Dose (Megarad)</u>	<u>Response to Irradiation</u>
Lead azide	47	No observable difference to impact sensitivity from that of unirradiated material. Slight decrease in brisance.
Mercury fulminate	26	Concentration of mercury fulminate reduced from 97.5 to 65.5 wt%. Sensitivity to impact ~ equal to original material, but a black powder fuse failed to ignite irradiated sample. Brisance was reduced by at least 50%. The initiating ability was nullified by gamma irradiation.
Lead styphnate	76	Low gas yield. Sensitivity to impact and the brisance were essentially unaltered by irradiation.
DDNP (diazodinitrophenol)	40	Impact sensitivity not impaired. Brisance reduced. Irradiated sample unreliable for use as initiator.
TNT (trinitrotoluene)	54	Low gas yield. Impact sensitivity and brisance same before and after irradiation.
Tetryl (trinitrophenyl- methylnitramine)	76	Impact sensitivity and brisance unimpaired as a result of irradiation. Sufficient impurities formed to reduce mp of compound 2°F.
RDX (cyclotrimethylene- trinitramine)	40	Sensitivity to impact slightly increased but brisance unchanged.
PETN (pentaerythritol tetranitrate)	40	Moderate gas evolution. 7°F depression of melting point as a result of irradiation.
Nitroglycerine	50	Very large gas evolution. Excessive decomposition terminated further testing.
Nitrocellulose	10	Nitrogen content of irradiated sample reduced by only 1%. Evidence of bond breakage.

produces deterioration of explosives as the dominant characteristic. Evidence exists that an increase in impact sensitivity is observed for a few compounds, e.g., RDX, primers containing a mixture of KClO_3 , $(\text{NH}_4)_2\text{S}$, lead styphnate, and lead azide. However, explosive reliability decreased indicating definite deterioration.

Formation of Peroxides and Ozonides

The presence of oxygen in a gamma radiation field leads to the generation of ozone as shown in the following equation.

The reaction of ozone is regarded as specific to the double bond structure. Under suitable conditions of low temperature and inert (i.e., non-oxidizable) solvents, the interaction of ozone and the alkene lead to an unstable, often dangerous, ozonide. Ozonides are readily hydrolyzed by water to yield mixtures of hydrogen peroxide, ketones, and aldehydes, together with carboxylic acids derived from the subsequent oxidation of aldehydes (Gilman 1954).

Although the formation of an ozonide would constitute a hazard, the problem is not germane to wastes in the underground tanks. The reduced temperature, ($\sim 0^\circ\text{C}$), and inert solvent necessary for its formation are both lacking; consequently, ozonides either will not form or will be decomposed as they are formed.

Possible hazardous reactions resulting from the generation of organo-hydroperoxides in the wastes were also considered. These compounds arise from the interaction of air or molecular oxygen with alkanes (Royals 1954). Free radicals from the organic constituents may be generated in a radiation field. The reaction between the free radical and an oxygen molecule can give rise to a chain reaction as follows:

Equations (19) and (20) are the chain propagation steps.

Fortunately, the alkyl hydroperoxides are unstable and will decompose as they are formed. Primary hydroperoxides such as methyl and ethyl hydroperoxides readily decompose (even violently) on heating or when subjected to a shock (Noller 1957). The tertiary alkyl hydroperoxides and peroxides are more stable; for example, t-butyl hydroperoxide is stable up to 75°C but decomposes smoothly at 95-100°C to give chiefly t-butyl alcohol and oxygen.

Thus it seems conclusive that the alkyl hydroperoxides and dialkyl peroxides will not accumulate in the waste to the extent that they could produce a large scale violent explosion. The presence of water and a relatively high temperature will prevent hazard from peroxide formation. It must be assumed that there will never be any detectable concentration of these compounds.

SLURRY GROWTH IN DOUBLE-SHELL TANKS

A phenomenon that has caused concern for waste tank management is the volume increase of slurry stored in double-shell tanks. An example of this growth is shown by the behavior of the slurry that was added to a new Hanford waste tank, 241-SY-101, in early 1977. The slurry generated from single-shell tank waste liquor by concentration in the 242-S evaporator-crystallizer was added to the tank in two separate batches. A steady volume increase of 0.92% per month was noted for the first batch which was added in April 1977. The second batch was added in November 1977. The slurry growth continued at 0.8% per month. Slurry growth has been observed periodically since that time in double-shell tanks.

It was assumed that gas evolution from decomposition of organic materials in the waste was partially trapped in the slurry and was responsible for the slurry growth. Early studies (RHO 1978) simulated slurry growth by using synthetic waste containing the complexants HEDTA and EDTA. The gases responsible for the volume increase were determined to be principally H_2 and N_2O .

Delegard (1980), using simulated slurry mixtures, determined that the slurry growth was due to the oxidative decomposition of HEDTA. He found that decomposition proceeded with first order kinetics in both $NaAlO_2$ and HEDTA concentration and required nitrate and/or nitrite to proceed. The main reaction products were ethylenediaminetriacetic acid and several gas species, namely N_2O , H_2 , and N_2 . The total gas analysis, in mole percent, was reported to be: N_2O , 56.5; N_2 , 19.2; CO , 11.4; H_2 , 4.8; CO_2 , 3.3; CH_4 , 2.3; NH_3 , 2.0; and NO_x , 0.4.

The compound formed was undoubtedly the product of oxidation at the hydroxyl site of HEDTA which eventually yielded a product identical to that identified by workers (Kirby, Rickard, and Toste 1984) investigating waste trench leachates from the Maxey Flats (KY) low level waste burial site. These investigators also found ethylenediaminetriacetic acid to be the principal complexant degradation product.

Any hazard resulting from the decomposition of HEDTA must be regarded as negligible. The final complexant, ethylenediaminetriacetic acid, is

chemically similar to HEDTA and no increase in hazard is expected because of its presence in the waste.

The presence of gases, such as, H_2 , CO , NH_3 , and CH_4 , generated during slurry growth is a problem that must be addressed but is not germane to this study which is concerned with the exothermic potential of the liquid and solid waste constituents. Since the organic chemicals present in the double-shell slurry are similar to the compounds in the single-shell tanks, it follows that this material, too, has negligible potential for a spontaneous exothermic reaction. The presence of significant quantities of water in the double-shell tanks further reduce even this low potential.

* Assume all gas generated is trapped in the slurry.

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APPENDIX A

IMPACT TESTS

Sensitivity to impact is determined by subjecting a small quantity of confined explosive to the transmitted shock of a falling weight--usually 2 kg--and determining the minimum height of fall that will produce at least one explosion in ten tests. Another approach is to determine the height of fall that will cause explosions in 50% of the tests. With the Bureau of Mines apparatus (Test B), 0.02 g of the material is spread evenly over an area 1 cm in diameter and confined by means of a 2-kg plunger with a tip 1 cm in diameter. The falling weight strikes the upper end of the plunger. If the explosive is liquid, the sample is held in position by being absorbed in a disk of dried filter paper 1 cm in diameter. With the Picatinny Arsenal apparatus (Test A), the cavity in a steel cup is filled with the solid or liquid explosive; the cup is then covered with a cylindrical brass cover which has a slip fit and a small steel plug is placed on the center of the brass cover. In this test, the falling weight strikes the steel plug.

APPENDIX B

EXPLOSION TEMPERATURE TESTS

Sensitivity to explosion when heat is applied is determined as the temperature required to produce explosion in either 5 sec, or in less than 0.1 sec. In the first case, a sample of 0.02 g is placed in a gilding-metal, blasting-cap shell, and the lower end of this shell is plunged into a bath of molten Wood's metal at a measured temperature. The time required to cause explosion, flashing, or very rapid decomposition is measured with a stop watch. The temperature for producing an explosion in 5 sec can be obtained by making a number of tests at various temperatures and plotting a temperature-time curve. The temperature required for instantaneous (less than 0.1 sec.) explosion is determined by dropping small particles of the explosive on the surface of molten metal held at a measured temperature. The time required for explosion is determined, and the temperature is varied to determine the minimum temperature required for instantaneous explosion, flashing, or decomposition. Not all explosives undergo detonation in explosion temperature tests; in some cases, decomposition is accompanied by an puff of gas or smoke, whereas in other cases, no violent evolution of gas or smoke takes place.

APPENDIX C

PENDULUM FRICTION TEST

This test determines sensitivity to friction. A 7-g sample of the explosive is spread evenly over a scored steel-base plate, and a 20-kg steel shoe suspended from a height of 1.5 m is allowed to sweep back and forth pendulum-wise across the base plate. The rod which carries the shoe must have been adjusted so that the shoe will slide across the plate 18 ± 1 times when no explosive is present. Tests of ten samples are then made and the number of snaps, cracklings, ignitions, and/or explosions is noted. If positive results are obtained, further tests employ a fiber rather than a steel shoe, the frictional effect being less with the fiber shoe.

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