

RESOLVING THE SAFETY ISSUE FOR RADIOACTIVE WASTE TANKS WITH HIGH ORGANIC CONTENT

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ABSTRACT

An overview of the Waste Tank Safety Organic Program is provided. The overview discusses the history of the wastes containing high concentrations of organics, existing safety criteria associated with those tanks, and details of thermodynamic studies by Westinghouse Hanford Company bounding potential reactivity. The program to be discussed contains the elements of the collection and analysis of tank historical information; reevaluation of organic tank-listing criteria; the performance of detailed studies on simulated waste; completion of waste characterization for each affected tank; and, as part of issue closure, the preparation of short-term and long-term safety and risk assessments based on results from characterization and the waste simulant studies. This document reports on a number of simplified thermodynamic calculations that were performed to ascertain combustion limits for simple surrogates of organic materials in a nitrate-nitrite containing alkaline waste. For expected waste species, the results of these calculations indicate that the range of reactivity encompasses energies that vary only by a factor of three over the range of normal paraffin hydrocarbon (NPH) (a fuel rich solvent) to sodium oxalate (a degradation product resulting from in situ organic complexant destruction in Hanford Site wastes). Quantification of sodium oxalate in actual tank 241-SY-101 waste is in progress. Data on simulated waste studies by Georgia Institute of Technology identified sodium oxalate as a primary degradation product in the decomposition of complexants (1, 2, 3). A summary is also provided of a detailed analysis by the Pacific Northwest Laboratory (PNL), based on the available chemical literature, of mechanisms by which organic materials added to the waste tanks could have become more concentrated, therefore increasing potential fuel value and reactivity of the waste.

BACKGROUND

Radioactive waste from defense operations has been accumulating in underground waste tanks at the Hanford Site since the early 1940's. There are 177 waste tanks: 149 single-shell tanks and 28 double-shell tanks. Over the years, waste has been systematically disposed of among the various tanks. In this process, the two primary objectives were to segregate different types of waste and to reduce the need for additional tanks by concentrating the waste. In addition to the fission products created by the processing of irradiated fuel, the major constituents of the waste are sodium nitrate; sodium nitrite; metal silicates; aluminates; hydroxides, phosphates, sulfates, carbonates of iron, calcium, and other metals; a variety of organic materials; ferrocyanide; and uranium salts.

The presence of organic chemicals in the Hanford Site waste tanks became an issue needing reevaluation when information became available on the deflagration of a waste tank in Kyshtym, U.S.S.R., which occurred September 29, 1957 (4). The Soviet tank event occurred because cooling was disrupted; the aqueous salts evaporated to dryness; and the mixture of oxidizing salts and organic chemical waste self-heated to deflagration-initiating temperatures. The constituents in the tank that caused this incident were sodium nitrate and sodium nitrite mixed with sodium acetate. The chemical safety issue associated with the Hanford Site organic-containing tanks is the possibility of exothermic reactions occurring because of the presence of heated organic waste components mixed with oxidizing salts (e.g., sodium nitrate and sodium nitrite) under conditions of low moisture.

The potential for reactions of nitrate with organic constituents stored in Hanford Site waste tanks has been studied. For example, a paper published in April 1976 described some combustion screening studies with sodium nitrate (5). However, in keeping with the concerns at that time, this work was

directed toward the oxidative power of sodium nitrate rather than the reactivity of specific organic tank waste chemicals.

A screening study was conducted at the Hanford Site in 1989 (4). Twenty-six tests were performed to study the reactivity of mixtures containing various proportions of sodium acetate, sodium nitrate/sodium nitrite, and diluents. The results were used to define an upper limit for organic carbon constituents in the waste. The limit was defined as 10 percent organic calculated as sodium acetate (sodium acetate equivalent). This corresponds to 3 percent total organic carbon (TOC). The latter is the present Organic Tanks Watchlist criteria. The results of this study, along with process engineering knowledge, form the basis for placing waste tanks on the Organic Tanks Watchlist. Three percent TOC (dry weight basis) was formally established as the safety specification for single-shell tanks containing organic materials. Process engineering knowledge involves evaluating process flow sheets, the waste inventory database, and other plant records. Eight single-shell tanks were identified as possibly having an organic content in excess of the 3 percent TOC threshold concentration and were placed on the list. These tanks are identified in Table I.

Process engineering knowledge of waste composition, rather than actual assay results, is required because of limitations in the historical records. The most accurate records generally were maintained for the radioactive constituents. In the past, the need for detailed chemical constituent information was not anticipated. Thus, it is not precisely known what chemicals actually went into the tanks, what chemicals remain in the tanks, and what chemicals have been formed from reactions between stored waste components. Without this information, process knowledge had to be used to obtain a conservative listing for the Organic Tanks Watchlist. Table II lists the organic and sodium nitrate/nitrite concentrations in

the Organic Watchlist tanks on a dry weight basis. The double-shell tanks that contain mostly aqueous waste were not included because they present no credible organic deflagration-related safety concern.

Public Law 101-510, Section 3137, "Safety Measures for Waste Tanks at Hanford Nuclear Reservation," (6) requires that Westinghouse Hanford Company develop plans to resolve issues for tanks that could lead to excessive temperature changes or pressure increases or a release of material from any high-activity waste single-shell tank or double-shell tank on the Watchlist at the Hanford Site. Fifty-three tanks have been identified and categorized by tank contents. Categories

TABLE I
Organic Watchlist Tanks

Single-shell tank	Sources of waste
C-103	PUREX and insoluble strontium-rich sluicing solids (this tank contains a separate floating layer of organic solvents)
B-103	First and second cycle waste from B Plant and in-tank solidification and waste evaporator bottoms*
S-102	REDOX process
SX-106	Salt waste and first cycle condensate from REDOX and evaporator bottoms
TX-105 and -118 U-106 and -107	Tributyl phosphate process waste and 242-T Evaporator bottoms

* The in-tank solidification and the evaporators were used to gain additional tank space by concentrating dilute radioactive wastes produced in Hanford Site processes and disposing of the resulting nonradioactive water.
PUREX = Plutonium-Uranium Extraction.
REDOX = Reduction Oxidation.

TABLE II
Organic and Sodium Nitrate/Sodium Nitrite Concentrations in Organic Watchlist Tanks

Tank	Sodium Acetate Equivalent (wt.% dry)	NaNO ₃ and NaNO ₂ (wt.% dry)	Data Source
B-103	11.4	60.5	SD-WM-TI-057 ¹
S-102	21.0	41.0	RHO-SA-51 ²
SX-106	14.6	80.9	SD-WM-TI-057 ¹
TX-105	12.8	52.7	SD-WM-TI-057 ¹
TX-118	20.2	50.4	RHO-SA-51 ²
U-106	46.6	52.4	RHO-SA-51 ²
U-107	14.7	75.4	SD-WM-TI-057 ¹

¹F. M. Jungfleisch, "Preliminary Estimates of the Waste in Hanford Tanks Through 1980," SD-WM-TI-057, Rev. 0, Rockwell Hanford Operations (1984).

²W. W. Schulz, "Removal of Radionuclides from Hanford Defense Waste Solutions," RHO-SA-51, Rockwell Hanford Operations (1984).

include those tanks that (a) contain ferrocyanide compounds, (b) have the potential for flammable gas generation, (c) contain organics, or (d) have high-heat loads. These form four distinct, but related, programs. Logic for the resolution of these safety issues, as well as candidate technologies for resolution or mitigation of the safety issues, shows a large degree of commonality among the programs (7). Discussions of the flammable gas and ferrocyanide programs were reported at Waste Management '92 (8, 9). In addition, three of the organic tanks also are included in the flammable gas or ferrocyanide tanks program, as shown in Table III.

This paper addresses the research, development, characterization, and analysis activities that have resulted in initial insight into the severity of the organic tank safety issue. Ultimately, the completion of these activities will lead to the resolution of organic safety issues.

PROGRAM SCOPE

Activities associated with organic tanks safety issue resolution include the following:

- Collection and analysis of tank historical information
- Reevaluation of tank-listing criteria for tanks on the Organic Tanks Watchlist
- Simulated waste studies
 - Test surrogate waste mixtures for chemical reactivity and shock sensitivity. Surrogates are simple benchmark compounds that represent organic reactivity and fuel richness spectrum.
 - Test simulated waste mixtures, approximating tank compositions for chemical reactivity and shock sensitivity (thermodynamic and kinetics studies).
 - Identify and evaluate waste aging (e.g., in situ organic oxidation) and concentration (e.g., enrichment) mechanisms.
- Waste characterization
 - Develop organic chemical constituent and functional group analytical methods for high-activity waste matrices.
 - Complete chemical characterization of waste samples obtained from taking cores from the Watchlist tanks.
 - Identify volatile products (possibly noxious) resulting from in-tank processes.
- Monitoring, mitigation, remediation
 - Upgrade existing monitoring systems in the Watchlist tanks.
 - Evaluate and install new monitoring systems to measure tank waste parameters.
 - Identify and implement waste treatment processes if they are required to mitigate or remediate tank conditions.
- Issue Closure
 - Prepare short-term and long-term safety and risk assessments. (For details on the Waste Tank Safety Program's issue resolution strategy, see "A Strategy for Resolving High-Priority Hanford Site Radioactive Waste Storage Tank Safety Issues" (7), in these proceedings.)

The sources of the organics in the single-shell tanks are listed in Table I. Table II and III provide data on general organic tank contents and temperatures. High concentrations of organic compounds have been inferred (from tank transfer and flow sheet records and limited analytical data) in these eight single-shell tanks. The exact concentrations of organic materials are not yet accurately known.

Table IV contains a list of the primary organic chemicals used in waste management and chemical processing operations that are of particular concern, and identifies potential degradation products under alkaline oxidation and/or radiolysis conditions.

Many organic chemicals are flammable and when mixed with nitrate and nitrite salts may deflagrate if dried and heated above 180°C. The Organic Watchlist tanks are so designated because of their "potential for release of high-level waste due to uncontrolled increases in the temperature or pressure." High concentrations of organic chemicals could support an exothermic reaction at elevated temperatures (10). In certain scenarios involving overheating of the tank, a mixture of organic chemicals and sodium nitrate and/or nitrite could react rapidly, possibly damaging the tank and allowing a release of radioactive material to the environment. However, the moisture contents of the tanks are relatively high, and the margin between ignition temperatures and measured tank temperatures is large enough that the probability of a reaction is considered very low.

Tank waste temperatures and constituents have been reviewed to assess the potential for exothermic reactions. Baseline temperatures for these tanks range from 17 to 52°C (62 to 126°F), and no individual tank temperature has exceeded its baseline by more than about 6°C (10°F) during the past 2 years. Laboratory results indicate that none of the tanks could sustain exothermic reactions below 200°C (392°F). These data indicate that imminent exothermic reactions in these eight tanks are not a concern. These tanks are within the safety envelope defined by the safety analysis reports for the single-shell tank farms.

UPPER LIMIT THEORETICAL ESTIMATE OF REACTION ENERGETICS

This section reports on a number of calculations that were performed to ascertain combustion limits (fuel or energy potential) for organic wastes in a nitrate-nitrite containing alkaline waste. It will show, based on simplified thermodynamic calculations, that the (many as yet unidentified) organic constituents that are in the waste tanks can be well approximated by the measure of TOC of any given tank. Furthermore, the calculations strongly suggest that relatively low concentrations of organics can lead to potentially exothermic reactions with sodium nitrate under adiabatic conditions. It concludes that the guaranteed safe concentration of organics, based only on conservative thermodynamic considerations, is below present limits used at the Hanford Site as criteria for the identification of waste tanks placed on the Organic Tanks Watchlist.

The work modeled the following six organic reagents or solvents, used extensively in reprocessing plant and waste management operations, which are of principle interest:

- Ethylenediaminetetraacetic acid (EDTA), $C_{10}H_{16}O_8N_2$
- N hydroxy-ethylenediaminetriacetic acid (HEDTA), $C_{10}H_{18}O_7N_2$

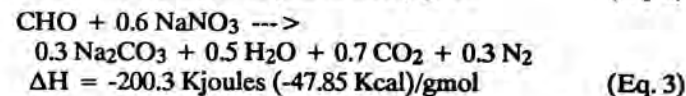
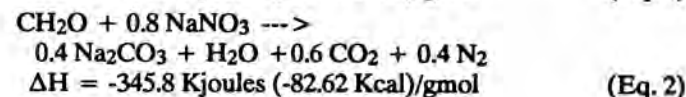
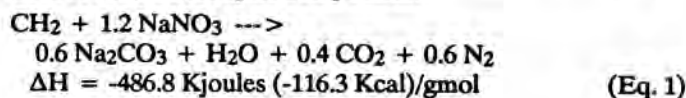
- Citric acid, $C_6H_8O_7$
- Acetic acid, $C_2H_4O_2$
- Oxalic acid, $C_2H_2O_4$
- NPH (normal paraffin hydrocarbons or kerosene), $C_{14}H_{30}$ (on average).

Because these are acid-starting materials, the corresponding compounds that actually should exist in the strongly basic tanks would be sodium salts of: EDTA, $Na_4C_{10}H_{12}O_8N_2$; HEDTA, $Na_3C_{10}H_{15}O_7N_2$; citrate, $Na_3C_6H_5O_7$; acetate, $NaC_2H_3O_2$; oxalate, $Na_2C_2O_4$; as well as NPH, $C_{14}H_{30}$. Tributyl phosphate, sugar, and hexone (methyl isobutyl ketone) were also used extensively, but because their "fuel value" falls within the bounds described by the species listed, they were not implicitly treated in these calculations. It is also known that in tank 241-SY-101 (1, 11) the salts of EDTA, HEDTA, and citrate have degraded to form sodium oxalate and sodium formate.

For the purposes of this study, the following approximations were made.

- Hydrocarbons or essentially hydrocarbon-like chemicals can be summarized as $(CH_2)_n$ or more simply, CH_2 . Hexone would fall into this category.
- Carbohydrates, sugars, EDTA, and HEDTA can be estimated as CH_2O .
- Citrate, oxalate, and formate can be estimated as CHO .

These approximations will also accommodate the myriad degradation products that can be imagined to also exist in the tanks, as well as other organic chemicals added to the tanks in smaller amounts. The following are the combustion equations for these surrogate compounds:



These reactions modeled are the most energetic possible because they produce the maximum amount of sodium carbonate, carbon dioxide, and nitrogen. We did not model oxidation reactions that produce less energy by making products such as carbon monoxide or oxides of nitrogen. Therefore, they present the conservative bound for our estimate. It is instructive to note several things about this series. The energy of each reaction decreases from equations 1 to 3, as does the amount of hydrogen. Conversely, the fraction of oxygen increases from Eqs. 1 to 3. Of course, the amount of sodium nitrate oxidizer required to complete the reaction also decreases. In effect, these compounds represented by Eqs. 2 and 3 are already partially oxidized.

As a check, one can compare the actual combustion energy for sodium acetate represented by:

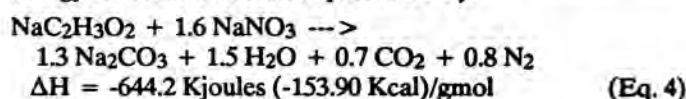


TABLE III
Tank Waste Volume and Temperature

ORGANIC TANK WASTE					
Tank	Total waste kgal	Liquid kgal	Sludge kgal	Salt cake kgal	Baseline Temperature °C (°F)
C-103 ¹	195	133	62	0	52 (126)
B-103	59	0	59	0	17 (62)
S-102 ²	549	230	4	315	43 (109)
SX-106 ^{2,3}	538	255	12	271	43 (109)
TX-105	609	20	0	589	39 (102)
TX-118 ⁴	347	27	0	320	23 (74)
U-106	226	83	26	117	29 (84)
U-107	406	178	15	213	27 (81)

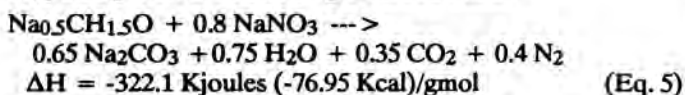
¹Contains a floating organic layer containing mostly normal paraffin hydrocarbon and tributyl phosphate.
²Tanks with the potential to accumulate combustible gases.
³Also ventilated with exhaust fan through SX-109. Tanks without this note are only ventilated passively through high-efficiency particulate air filters.
⁴A ferrocyanide-containing tank.

TABLE IV
Primary Organic Chemicals Used in Waste Management and Chemical Processing Operations

Compound Name	Use	Potential Degradation Products
Normal paraffin hydrocarbons	Carrier solvent	Probably carboxylic acid fragments from carbon chain cleavage
Methyl isobutyl ketone (hexone)	Extraction solvent	Carboxylic acid fragments
EDTA and HEDTA	Complexants	Sodium formate and oxalate and other "intermediate" degradation fragments
Tributyl phosphate	Extraction solvent	Butyl alcohol and possibly carboxylic acid fragments
Citric acid	Complexant	Sodium formate and oxalate and other "intermediate" degradation fragments
Sugar	Denitrating agent (PUREX Plant)	Reaction in acid leads to carbon dioxide and nitrous gases
Di-2-ethylhexyl phosphoric acid	Complexant	2-ethylhexyl alcohol and possibly carboxylic acid fragments
Assorted organic-based surfactants	Decontamination operations	Probably carboxylic acid and ethoxylated fragments from carbon chain cleavage

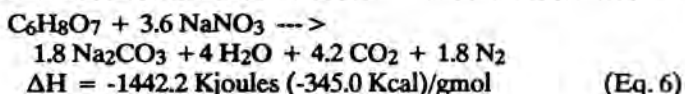
EDTA = Ethylenediaminetetraacetic acid.
HEDTA = N hydroxy-ethylenediaminetriacetic acid.
PUREX = Plutonium-Uranium Extraction.

or, putting it on the same single carbon basis:

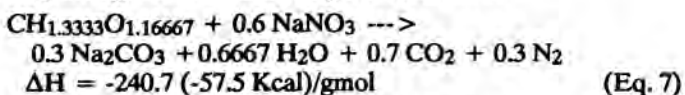


This corresponds quite closely to the results from Eq. 2.

The same check is made for the combustion of citric acid:



or, putting it on the same single carbon basis:



This corresponds reasonably closely to Eq. 3.

Together, these serve to confirm that Eqs. 1, 2, and 3 are reasonable approximations of the reactivity of the series of organic chemicals under consideration.

The next step was to determine how much dilution by excess reactants would just compensate for the reaction heat generated by oxidation processes. That is, given one mole of "CH₂," how much more sodium nitrate and/or water would it take so that the heat of reaction generated by equation 1 is just absorbed by the heat capacity of sodium nitrate and/or water? For this, it is necessary to assume some temperature difference, which was conservatively taken to be the difference between the highest tank temperature observed, approximately 65°C, and the lowest start-of-reaction temperature observed in preliminary laboratory studies, 200°C. Over this range the heat capacity of sodium nitrate is only 0.11 Kjoules (0.0262 Kcal)/gmol °C or 14.82 Kjoules (3.54 Kcal)/gmol over the range. The heat capacity for water is 50.4 Kjoules (12.04 Kcal)/gmol, which includes the heat capacity from 65 to 100°C, the heat of vaporization to steam, and the heat capacity of steam from 100 to 200°C. The outcome of this theoretical event would be that, if it could be initiated at a specific place in a million gallon tank, the wastes at that point would be heated to less than 200°C. The fuel in that location would be exhausted, the reaction could not propagate to the remaining contents of the tank, and the heated portion of the tank would start to cool.

Given the existing tank compositions, with excess nitrate present (a lean mixture) and the fact that the tanks are wet (> 20% water present), the points of most interest are the domains in which presence of an appropriate amount of water and/or nitrate lead to reaction quenching. These are shown in Table V. The TOC is also computed for each type of fuel.

At this point one could conclude that TOC is a fair and sufficient measure of the fuel value of the organics. The combustion energy computed from TOC varies by somewhat more than a factor of two over the range of expected compounds. It requires only a minimum of assumptions and shows that the great variety of possible organic compounds can be summarized into a few classes. It is easy to measure in samples and is historically available.

Tests are presently underway on a series of actual organic compounds that were added to the waste tanks to determine the effects of composition and structure on reaction energetics, reactivity, and other parameters related to evaluating the potential for exothermic reactions of organic materials with excess of nitrate and nitrite salts. When the results become

available later this year, the present criterion for placing a tank on the Organic Tanks Watchlist will be reevaluated.

It should be emphasized that the calculated TOC values are very conservative. They provide a limit below which safety can be guaranteed. Organic concentrations somewhat higher than those identified in Table V may also be safe because of constraints on energy generation resulting from reaction kinetics and extent (e.g., completeness), actual waste and tank heat transfer characteristics, and other effects in real systems.

THEORETICAL ORGANIC CONCENTRATION MECHANISMS

An assessment of concentration mechanisms for organic compounds in the tanks was conducted by PNL in 1992 (12). The possible concentration mechanisms were evaluated for the liquid, solid, and gas phases found in the tanks. The evaluation primarily considered the NPH, complexing agents, and organic-based surfactants mentioned in Table IV. The conclusions reached in the PNL study regarding the significance of the various mechanisms are very subjective in nature and only provide a guide to those mechanisms that warrant further investigation.

An important element of the assessment involved evaluating the likely degradation mechanisms for the major chemicals that produced by-products with distinctly different chemical and physical properties than the starting materials, and assessing the effect of these new properties on the subsequent waste partitioning (e.g., concentration) to adjacent phases. One of the results of this degradation of the organics in the aqueous phase is the slow fragmentation of the water soluble organics into smaller molecules on a time scale associated with storage of the waste (e.g., tens of years). These smaller molecules ultimately convert to more stable carboxylic acids through a number of intermediate compounds consisting of aldehydes, ketones, and alcohols.

Slow degradation is also observed in a separated organic phase (e.g., the floating NPH/tributyl phosphate [TBP] layer, such as is found in tank 241-C-103). Another possibility might be the conversion of a portion of the organics to higher molecular weight molecules under the action of radiation, which tend to be water insoluble. Furthermore, radiolytic and chemical degradation of ion-exchange resins that were added to some of the tanks were also considered in the study. They are expected to produce water-soluble polyelectrolyte fragments as intermediate products that ultimately degrade to lower molecular weight carboxylic acids.

In the evaluation of the liquid phase(s) in the tanks, it was generally assumed that the primary inventory of organics would be in the aqueous phase. This assumption takes into account the fact that many of the chemicals added to the tanks and the principle degradation products are at least sparingly soluble in water. However, large quantities of hydrocarbons solvents were added to some of the tanks and could be present in sufficient quantities to produce a separate organic liquid phase. These solvents invariably contained substantial quantities of the phosphate ester extractants, which would also be in the nonaqueous organic phase. The probability of the formation of an organic liquid phase is enhanced by the presence of high concentrations of electrolytes in the aqueous phase, which can reduce the water solubility of organics by at least 1 order of magnitude. For such, usually lower density liquid phases, subsequent evaporation of the more volatile solvents and degradation products (e.g., butyl alcohol from TBP)

TABLE V
Boundaries for Reaction Quenching

Point	Fuel (wt.%)	NaNO ₃ (wt.%)	H ₂ O (wt.%)	TOC*
Calculated TOC for "CH ₂ " - kerosene, hexone				
lean damp wet	0.503	99.50	0	0.43
	2.02	77.97	20.0	1.73
	4.97	36.20	58.83	4.26
Calculated TOC for "CH ₂ O" - sugar, EDTA, HEDTA				
lean damp wet	1.51	98.50	0	0.60
	6.07	73.93	20.0	2.43
	13.9	31.5	54.5	5.56
Calculated TOC for "CHO" - citrate, acetate				
lean damp wet	2.53	97.47	0	1.05
	10.1	69.9	20.0	4.20
	19.8	34.8	45.4	8.19
*TOC is always reported on a dry weight basis. EDTA = Ethylenediaminetetraacetic acid. HEDTA = N-(hydroxyethyl)-ethylenediaminetriacetic acid. TOC = Total organic carbon.				

would deplete the organic inventory in liquid phases, but enrich them in less volatile components. Indeed, analysis of the floating layer in tank 241-C-103 showed that the NPH-TBP ratio was approximately 1:3, although the solvent used in plutonium-uranium extraction had a 3:1 composition, probably resulting from the preferential volatilization of the NPH by the ventilation system.

In the evaluation of the solid phase found in most of the tanks, precipitation and sorption mechanisms were considered. It was concluded that precipitation was unlikely for most organic acids except sodium oxalate. The latter was considered possible because it is expected to be a principal degradation product of many of the chemicals, as previously discussed, and was itself added in quantity to the tanks. The precipitate, if present, is expected to be distributed throughout the solids in the tanks.

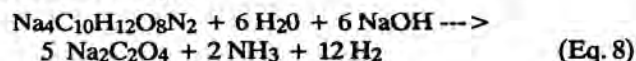
Adsorption of organics on the surfaces of the solids was found to be a potentially significant concentration mechanism. Surfactants and long-chain carboxylic acids (C₈ or more) are known to adsorb onto surfaces of minerals. Under optimum conditions these compounds can concentrate to as high as $7.5 (10)^{-6}$ mol/m² of surface. This, in turn, can produce carbon concentrations on the solids as high as several percent if the solids have high surface areas. There were too many competing factors and insufficient data to determine the likelihood of achieving these high concentrations, but plans to evaluate concentration mechanisms are part of the organic program.

Absorption of the organics into the interstitial spaces of the solids was also found to be a potentially important concentration mechanism, if a tank containing a separate organic phase was drained of free liquids. Previous experience with unsaturated soils contaminated by spills of pure organic liquids have shown that the uppermost soils could achieve organic concentrations on the order of several percent. The

relevance of the soil "sorption" model to the salt cake and sludges in the waste tanks will need to be tested if waste degradation through aging mechanism does not dominate the system.

INITIAL AGING STUDIES

Extensive work, as part of for the studies of tank 241-SY-101 (flammable gas program), suggests that complexing agents such as sodium EDTA, sodium HEDTA, and sodium citrate have undergone significant degradation during their storage in the Hanford Site waste tanks (8). Although the mechanistic studies are not complete, data from studies at PNL, the Georgia Institute of Technology, and Argonne National Laboratories suggest a complex step-wise degradation of these complexants to simpler, more highly oxidized chemicals, with the concurrent generation of hydrogen, nitrous oxide, and ammonia. There is no evidence to believe that such an aging mechanism would not be generally applicable to all complexant-containing high-activity waste tanks at the Hanford Site. An example of a simplified summary equation is provided below. Detailed summaries of this work are reported by Ashby et al. and Meisel et al. (found in Schultz and Strachan (1) and Strachan (2, 3)) and are partially discussed in Strachan et al. (11).



CONCLUSIONS

Closure of the organic issue follows the strategy defined for closure of all priority waste tank safety issues, discussed in a previous paper at this symposium (7). Issue closure will become possible by either demonstrating the absence of a dangerous inventory of organic materials in the tank (intrinsic safety); demonstrating a lack of a dangerous concentration of reactive organic in the tank (passive safety), or demonstrating

that tank conditions prevent the possibility of an uncontrolled exothermic reaction between nitrate and nitrite salts and the organics (controlled safety).

In the interim period, while collecting the data to support closure of the safety issue, administrative and technical controls remain in place to restrict activities that could cause undesirable exothermic reactions. While the probability of an exothermic reaction in the organic tank waste is probably very low, the consequences of such an event are unacceptable. Characterization efforts are being initiated under conditions that define the envelope of risk associated with organic tanks. Risk to the operating staff, the Hanford Site environment, and the general public appears to be low, but it is being reevaluated. Work to quantify the risk and provide for mitigation, if necessary to assure the short-term safe storage, is continuing at the Hanford Site on a priority basis. Results from these activities will also be factored into the longer term final disposal of waste in Hanford Site double-shell and single-shell tanks.

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