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**An Assessment of the Stability and the Potential
for In-Situ Synthesis of Regulated Organic Compounds
in High Level Radioactive Waste Stored at Hanford,
Richland, Washington
(PNNL-11943)**

**Pacific Northwest
National Laboratory**

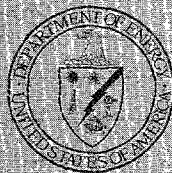
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**An Assessment of the Stability and the
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Regulated Organic Compounds
in High Level Radioactive Waste Stored
at Hanford, Richland, Washington**

K.D. Wiemers
H. Babad
R.T. Hallen

L.P. Jackson
M.E. Lerchen

December 1998



Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

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1.0 Introduction

The Hanford Site has 177 underground storage tanks that contain 54 million gallons of high-level radioactive waste. The U.S. Department of Energy (DOE), Washington State Department of Ecology (Ecology), and the U.S. Environmental Protection Agency (EPA) have entered into the Hanford Federal Facility Agreement and Consent Order (Tri-Party Agreement or TPA) under the *Resource Conservation and Recovery Act of 1976* (RCRA) and the *Washington Hazardous Waste Management Act of 1976* (HWMA). Under the RCRA and HWMA, the tank waste is designated as listed, characteristic, and criteria waste. Characterization data are needed for the tank waste to ensure compliant treatment, storage, and disposal of the waste, including requirements for meeting land disposal restrictions, delisting, and risk assessment. The DOE and Ecology through the Regulatory Data Quality Objectives (DQO) process have defined and documented (Wiemers et al. 1998) characterization needs for the Hanford Site single-shell tank (SST) and double-shell tank (DST) waste.

The DQO process included selection of regulated analytes to be measured in Hanford DST and SST waste. The analyte selection process was completed through a series of technically defensible logic steps that are described by Wiemers et al. (1998). The analyte selection logic begins with a large universe of regulated compounds compiled from a number of applicable regulatory-related compound lists. These input lists include the Underlying Hazardous Constituents and Universal Treatment Standards (40 CFR 268.48) and the Toxic Air Pollutant (TAP) Class A (WAC 173-460-150) and Class B (WAC 173-460-160). In the analyte selection logic, each of the regulated compounds were evaluated, in part, with respect to the plausibility of existing in the Hanford Site SST and DST waste. One of the plausibility decisions addressed the compound's chemical stability in the Hanford DST and SST waste environment and the potential for the generation of regulated compounds through in-situ synthesis during waste storage. The tank waste properties considered in the assessment were high alkalinity (pH above about 9.0 to 10.0), high concentration of nitrate and nitrite (oxidizing), and radioactivity. The assumptions applied to the stability and in-situ assessments are presented in Sections 2.0 and 3.0, respectively. The results of the assessment are provided in Section 4.0. Compounds not previously detected and assigned as unstable in the tank waste matrix were excluded from further consideration in the Regulatory DQO analyte selection logic.

2.0 Organic Compound Stability Assessment

The stability assessment examined 269 non-detected regulated compounds (Table 2.1). The technical basis for the tank waste stability assessment consisted of known and documented reactions of organic compounds (Bordwell 1963; Furniss et al. 1989; March 1992; Morrison and Boyd 1973; Roberts and Caserio 1964) under conditions similar to the tank waste environment. The Hazardous Substance Data Bank was also used as a primary reference for most of the compound's chemistries. Each of the selected regulated organic compounds was evaluated independently by a team of three chemists and concurrence was reached with the technical staff of Ecology. The assessment considered the susceptibility of functional groups to various reaction types under tank waste conditions. The tank waste conditions considered were high alkalinity (pH above about 9 to 10), high concentration of nitrate and nitrite (oxidizing), and radioactivity. Reactions were extrapolated based upon the presence of various

functional groups to similar compounds lacking referenced stability data. Factors decreasing reactivity were also considered such as steric hindrance of adjacent substitution to the functional group(s) in question. The functional groups and reaction chemistries considered for the tank waste stability assessment are described in Sections 2.1 and 2.2, respectively.

2.1 Functional Groups

Functional groups used for classification were

- Carbon/hydrogen functionality: aliphatic and alicyclic hydrocarbons, the monocyclic and tar-based polycyclic aromatic compounds (PAH), aliphatic carbon-carbon double bond (alkenes), and acetylene derivatives (alkynes).
- Carbon/oxygen functionality: alcohols and phenols; ethers, epoxides, and peroxides; aldehydes and ketones; carboxylic acids and the esters including the self-esters lactones and acid anhydrides.
- Carbon/nitrogen functionality: aliphatic and aromatic amines (anilines); aliphatic and aromatic nitro compounds; amides and nitriles (related to carboxylic acids); compounds that contained nitrogen-nitrogen bonds (e.g., hydrazine or N-nitroso derivatives); nitrate esters; and compounds derived from isocyanate based chemistry (e.g., carbamates, ureas, and urethanes).
- Carbon/sulfur functionality: thiols/mercaptans (analogous to alcohols but much more acidic); sulfides and disulfides (sulfur analogs of ether and peroxide); oxidized sulfur acids and esters and thiocyanate based derivatives.
- Carbon/halide functionality: mono and polyfunctional alkyl and aromatic ring substituted halides (F, Cl, Br, and I).
- Carbon/phosphorous functionality: reduced phosphorus compounds (phosphines); phosphorous and phosphoric acid and their esters.

2.2 Reaction Chemistries

Reaction types considered include

- hydrolysis;
- substitution (nucleophilic displacement by hydroxide ion);
- elimination (dehydrohalogenation);
- radical reductive dehalogenation;
- addition, condensation, and radical coupling; and
- oxidation.

The assignment of a compound as “unstable” required the destruction of one or more of the functional groups defined in Section 2.1 by one or more of the reaction types listed above.

For the stability assessment, special consideration was given to acid-base chemistries. The functional groups such as carboxylic acids (and analogous phosphorus and sulfur acids), phenols, and thiols can exist in aqueous media as either the protonated "free" (or undissociated) acid or as the basic salt (anion form). Tank waste ranges in alkalinity from a pH of approximately 9 for some SSTs (Wodrich et al. 1992) to those with pH an upper limit of 12. The carboxylic acids and phenols have a wide range of dissociation constants, pKa, values. Most are less than 10, so these compounds can be expected to be primarily in the salt form in the tank waste. However, in general such compounds are listed as the undissociated, acid form in the regulatory analyte input list. The SW-846 (EPA 1997) methods for analysis of these compounds requires acidification as part of the sample preparation, therefore, distinguishing the form in which the compound exists in the waste is not appropriate. The free acid and its salt may present different associated risks depending on the processing and/or environmental pathways. Neither of these pathways have been well defined. Given these uncertainties, the reversible acid-base reaction of an acidic compound was not considered to constitute a basis for assigning the compound to be "unstable." However, usually an acid or a phenol contained an additional reactive functional group that dominated the stability assessment.

Since new waste materials have recently been and continue to be added to the double-shell tanks as the Hanford cleanup mission progresses, and in the absence of tank-specific kinetic data, engineering judgment was used to assign a half-life based criteria for stability assessment. If a compound was believed to decompose with a half-life of less than or equal to approximately 1 year, it was considered unstable.

The following contains a generic description of the pathways leading to degradation of organic molecules in a tank waste environment and identification of the affected functional groups. Tank waste chemistry can lead to the transformation of organic chemicals into new species. Examples are hydrocarbons and polycarboxylic acid-containing complexants added to the tank waste. The general degradation schemes usually result in oxidation of the organic compounds, usually to species with fewer carbons than the starting materials, and lead to a parallel production of reduced gaseous species. The reactions considered for evaluating the stability of the functional groups in the aqueous, oxidizing, alkaline, and radioactive medium are described below. The examples provided with each generic reaction type consist of simple "flow" equations for the destruction of the functional groups and are provided to elucidate the generic products of the degradation reactions. The reactions for the most part proceed in a similar fashion with both alkyl-[R] and aryl [Ar] substituted functional groups, and both the - "R" and "Ar" type structures are illustrated. Where differences in pathways occur, explicit examples of materials with aryl substituents are provided.

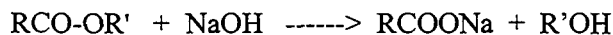
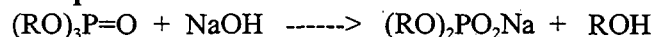
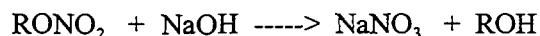
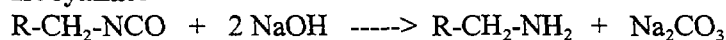
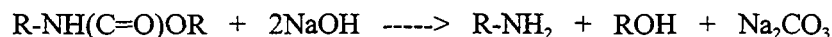
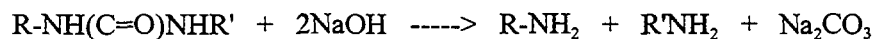
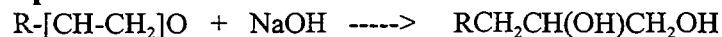
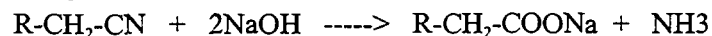
It is also important to note that if a degradation reaction produces an unstable functional group, further sequential degradation of that group can occur until a final product is produced that is stable to the waste environment (refer to Section 3.0).

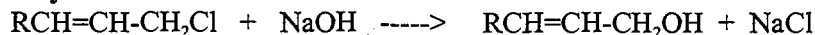
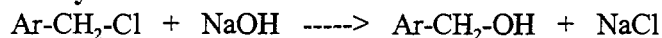
- **Hydrolysis/Alkaline Hydrolysis.** The following types of reactions take place in aqueous and aqueous alkaline conditions and are grouped together here under the general classification of hydrolysis. As stated above the stability assessment did not use the reversible acid-base reaction of organic acids (both carboxylic acids and phenols) or amine base salts as reason for the assignment of "unstable." Acid halides are very moisture sensitive and reaction produces the organic acid and the inorganic salt of the halide under basic conditions. Anhydrides react with water and in alkaline conditions to produce organic acid anions. Esters (carboxylates, phosphates, O-substituted nitrates,

etc.), lactones (cyclic esters), amides, lactams (cyclic amides), isocyanates, carbamates, ureas, and nitriles are hydrolyzed to yield organic acids and alcohols (from the esters) and ammonia or amines (from the amides). Epoxides can undergo ring opening with hydroxide yielding the corresponding diol.

Allyl halides including allylic unsaturated compounds with a halide on the carbon atom adjacent to the double bond also hydrolyze. This is sometimes called either a substitution or a nucleophilic displacement reaction. Some alkyl halides, and alpha-halogenated alkylbenzenes are reactive and undergo substitution with hydroxide to yield the corresponding alcohols.

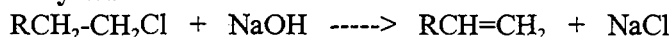
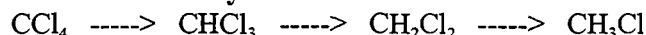
General examples of functional group degradation are provided below. In all cases, the reactions take place in a high ionic strength, aqueous, and/or radioactive media. Water is not included in the illustrative equations. Please note that unless a molecule is severely sterically hindered, preventing the approach of aqueous alkali to the functional group, the reactions described will occur with either aliphatic or aromatic substituents. [R is an Alkyl and Ar is an Aryl Group]

Acid Chloride**Acid Anhydride****Ester****Phosphate Ester****Nitrate Ester****Isocyanate****Carbamate****Urea****Epoxide****Nitrile**

Allyl Chloride**Benzyl Chloride**

- **Dehalogenation or Dehydrohalogenation of Alkyl Halides.** Alkyl halides containing one or more halogen (X = Br, Cl, F, and I) atoms distributed among two or more adjacent carbon atoms and containing at least one hydrogen on the adjacent carbons can eliminate HX to yield an olefin or an olefinic halide. These reactions can be accelerated by base when a reactive proton can be removed, especially when a benzylic hydrogen is activated by an aryl group.

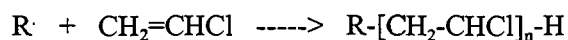
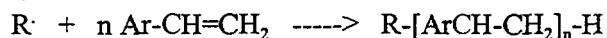
The polychlorinated alkyl halides such as carbon tetrachloride can be sequentially reduced to simpler halides such as chloromethane by radiation-induced sequential radical cleavage of carbon halide bonds followed by abstraction of hydrogen by the haloalkyl radical. Again note that in all cases, these reactions take place in a high ionic strength aqueous radioactive matrix.

Alkyl Halides**Reduction of Alkyl Halides**

- **Condensation and Coupling Reactions.** Hydrocarbon molecules with two adjacent double bonds or a double bond attached to a phenyl ring, ester, halide, or acid (e.g., vinyl derivatives) will condense with each other or with other unsaturated molecules into large molecules in reactions generally known as coupling reactions. Molecules with two adjacent double bonds can condense with themselves in a dimerization reaction known as the Diels-Alder reaction.

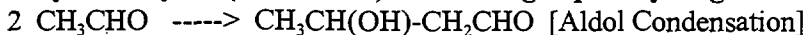
Aldehydes and ketones containing at least one hydrogen atom on the carbon adjacent to the carbonyl group will condense under alkaline conditions in the Aldol Condensation to yield aldols, a reaction that can either be reversible or lead to polymeric products depending on the reaction conditions. The Cannazaro reaction (simultaneous oxidation and reduction of the aldehyde group) is always in competition with condensation of aldehydes. It is known to occur in tank wastes and by a non-traditional pathway to be a source of hydrogen generation (Ashby et al. 1993).

Although rare in dilute solution, hydrocarbon-based radical species can couple or even polymerize to form longer chain hydrocarbon derivatives. Evidence that such reactions may take place in the separable organic phase in tanks C-103 has been reported (Campbell et al. 1996b).

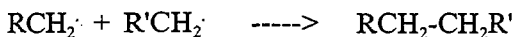
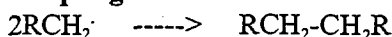
Olefins

Where n is a small number

Alkyl Aldehydes (or Ketones) Containing Alpha Hydrogens



Coupling Reactions



- **Oxidation.** Alcohols, aldehydes, and ketones are also susceptible to oxidation under the conditions of high nitrate/nitrite concentration in the tank waste. Compounds from these classes yield various organic acids. The carboxylic acids decompose slowly to carbon dioxide or sodium carbonate. For example, the aliphatic organic acids continue to be consumed one carbon at a time (as long as there is a hydrogen atom adjacent to the acid group) until they are completely converted to carbon dioxide, however, these reactions are quite slow and may have a half-life of greater than 1 year. The oxidation of the organic species is, for the organic complexant cases studied, known to be accompanied by the formation of hydrogen, ammonia, and nitrous oxide gas.

Amines and anilines (aromatic amines) as well as compounds containing a nitrogen-nitrogen bond also react in the oxidizing conditions of the tank waste to produce a wide variety of unstable and oxidation products. The stability assessment differentiated between primary, secondary, and tertiary aliphatic amines and their aromatic analogs. In all instances, for molecules not containing an additional reactive functional group, compounds containing a triply substituted nitrogen were considered stable. The tertiary compounds were considered stable because of their lower reactivities. Beta hydroxyl groups have been found to accelerate the rate of thermal oxidation of amines by nitrite, including tertiary amines.

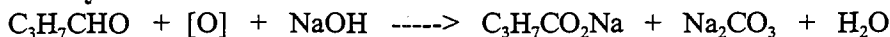
In addition most sulfides, disulfides, thiols, and other reduced sulfur containing organics are oxidized to sulfones or sulfoxides and/or their "sulfite or sulfate" analogs.

Finally, although only circumstantially considered an oxidation reaction, the nitration of carbon-hydrogen bonds either does not seem to occur under tank waste conditions or forms unstable intermediates that have not been isolated in the wastes.

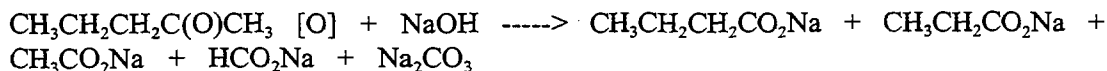
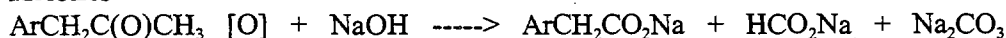
Alcohols

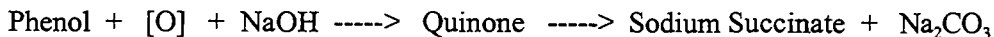
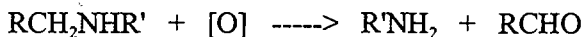
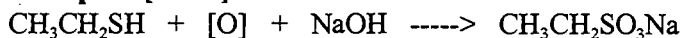


Aldehydes



Ketones



Phenols**Amines****Mecaptan [Thiol]****Sulfide**

3.0 In Situ Regulated Compound Synthesis

There are two possible routes for detectable concentrations of regulated compounds to be present in the tank waste:

1. Disposal of varying quantities of regulated chemicals to the tanks, which are relatively stable in the tank waste conditions or isolated from reactive conditions (e.g., phase separation), and
2. The regulated chemical is a reaction product resulting from the decomposition of chemical components disposed of to the tanks, and are generated fast enough under tank waste conditions so concentrations can build up to detectable levels.

The disposal of regulated chemicals into waste storage tanks and the individual chemical's relative stability have been addressed in Section 2.0. The technical basis for the stability assessment provided a foundation for examining potential pathways for in situ synthesis of regulated organic compounds as well as the likelihood that synthesized compounds would be stable in the tank waste environment. The scope of the in situ synthesis assessment is focused primarily on the modification of materials known to have been added to the tanks such as solvents and complexants. Specific tank waste conditions and pathways for modifications that may lead to the generation of regulated compounds are discussed.

The tank wastes encompass a large variety of chemical constituents that have been exposed to continuous radiation from radioactive decay and elevated temperature as a result of historical processing conditions and radionuclide decay. Experimental work (Sittig 1991; Meisel et al. 1992, 1997; Stock and Pederson 1997; Ashby et al. 1992, 1994; Pederson and Strachan 1993; Carlson 1997; Camaioni et al. 1994, 1995, 1996, 1997; Campbell 1996a, 1996b; Wilson 1974) suggests that the rate of radiolysis is a function of the cesium-137 and strontium-90 concentration, and is insensitive to temperature over normal tank waste temperatures. This is in contrast to thermally initiated reactions, which are very slow for most of the starting materials (e.g., complexants and solvents) and their respective aging products at temperatures below 50°C. Although the two paths, radiolysis and thermolysis, result in the ultimate fragmentation of complex organic compounds, the paths can produce somewhat different reaction

products. In the absence of available experimental data, best professional judgment was used in considering potential reaction pathways for in situ synthesis and associated kinetics.

Compounds synthesized in the tank waste and containing functional groups that were reactive to tank waste conditions are subject to the reaction pathways described in Section 2.0. All of the intermediate products produced from hydrocarbon oxidation products except for the simple aliphatic carboxylic acids themselves tend to be reactive to tank waste conditions. Materials resulting from degradation of the complexants (e.g., ethylenediaminetetraacetic acid [EDTA], citric acid), solvents (e.g., normal paraffin hydrocarbons [NPH]), and extractants (e.g., tributyl phosphate) degrade to lower molecular weight and structurally simpler salts of carboxylic and phosphoric acid (Camaioni et al. 1996). Occasionally, small amounts of NO_x have been detected in tank vapor space of tanks usually associated with high (near boiling) temperatures. The NO_x may be formed by way of an organic degradation route but no experimental data exist for such transformations at tank temperatures. However, mechanistic studies using radiolabeled carbon and nitrogen compounds suggest that the largest concentration of nitrogen-based species produced in the waste and found in the vapor space are due to reduction of nitrite ion (Ashby et al. 1994). This occurs while the organic carbon-containing species are oxidized by nitrite. By interaction with nitrogenous species in the tank waste, the oxidative degradation of hydrocarbons or alcohols can also lead to the nitriles, which have been observed in the vapor phase but not, to date, in the condensed phase (Camaioni et al. 1995). Hydrocarbon-based radical fragments can react with each other in one of the few instances leading to small concentrations of longer carbon chain hydrocarbon species, which also follow the typical degradation pathways described above. Campbell et al. (1996b and references contained therein) has found evidence of NPH via spectra resembling paraffin crude oil in a few waste sample extracts. However, these findings are the exception rather than the general trend.

No mechanisms were identified that could generate halogen- or nitrogen-substituted aromatics from materials known to be disposed of to the tanks. Generation of halide-substituted carbon compounds was not considered possible. The generation of nitro aliphatic compounds may be possible but detailed speciation of tank wastes and wastes simulants subjected to radiolysis and thermolysis has not detected their presence.

A difficult question in identifying "stable," in situ synthesized compounds lies in the ability to assess those compounds that would be present in exceedingly low steady state or transient concentrations. The stored wastes undergo dynamic chemical reactions with the continuous generation and reaction of new compounds. It is likely that these compounds would only be detected if they were removed/isolated from the reactive environment, such as being swept out of the tank into the dome space vapor phase (or headspace of a liquid sample) or as a less likely alternative, adhere to the tank waste solids. The detection of compounds nominally considered as unstable in the tank waste environment may provide some evidence for this hypothesis. A list of the detected, regulated, organic compounds is provided in Table 3-1. Table 3-1 also provides the number of reported hits for vapor and liquid/solid phases and stability assessment assignments based on the criteria described in Section 2.0. The authors would like to first point out that a majority of these organic compounds were reported for the vapor phase only. These reported numbers of hits should be used only as a rough indicator of the vapor/liquid partitioning, as it is not known how many times the constituents were analyzed for and not found in each phase. Second, in a majority of cases, the species identification was made by reference to a mass spectroscopy compound identification library. The library is used when standards and spikes were not used during the analysis. Compounds identified in this manner are designated as tentatively identified compounds (TICs). Their presence has not been verified by means of an actual analysis compared to standards that

are analyzed on the mass spectrometer used for sample analysis with standards, therefore a relatively high degree of uncertainty exists with respect to the compound's identification. Examination of the predicted compound stability in the tank waste environment results in a majority of the detected compounds being assigned as unstable. The following explanations may account for these observations:

- the compound is transient, present in the waste at relatively low concentrations, and detected only because it was removed from the reactive environment (i.e., swept into the vapor phase);
- stability assumptions may be not be applicable, and/or
- the compound is incorrectly identified.

A combination of all three explanations, to varying degrees, likely accounts for the apparent discrepancies between detected compounds and their stability assignments. Further characterization of these compounds will depend in part on the availability of appropriate sample collection and analytical methods for measurement of volatiles and the end-users' applications.

4.0 Conclusion

The stability assessment examined 269 non-detected regulated compounds, first seeking literature references of the stability of the compounds, then evaluating each compound based upon the presence of functional groups using professional judgment. Compounds that could potentially survive for significant periods in the tanks (>1 year) were designated as stable. Most of the functional groups associated with the regulated organic compounds were considered unstable under tank waste conditions. The general exceptions with respect to functional group stability are some simple substituted aromatic and polycyclic aromatic compounds that resist oxidation and the multiple substituted aliphatic and aromatic halides that hydrolyze or dehydrohalogenate slowly under tank waste conditions. One-hundred and eighty-one (181) regulated, organic compounds were determined as likely unstable in the tank waste environment (Table 2.2a).

5.0 References

Ashby, EC, A Annis, EK Barefield, D Boatright, F Doctorovich, CL Liotta, HM Neuman, A Konda, CF Yao, K Zhang, and NG McDuffie. 1994. *Synthetic Waste Chemical Mechanism Studies*. WHC-EP-0823. Westinghouse Hanford Company, Richland, Washington.

Ashby, EC, R Doctorovich, CL Liotta, HM Neuman, EK Barefield, A Konda, K Zhang, J Hurley, and DD Siemer. 1993. "Concerning the Formation of Hydrogen in Nuclear Waste: Quantitative Generation of Hydrogen via a Cannizzaro Intermediate." *Journal of the American Chemical Society*. Vol. 115, pp.1171.

Ashby, EC, C Jonah, D Meisel, LR Pederson, and DM Strachan. 1992. *Gas Generation and Retention in Tank 241-SY-101: A Summary of Laboratory Studies, Tank Data, and Information Needs*. PNL-8124. Pacific Northwest Laboratory, Richland, Washington.

Bordwell, FG. 1963. "Organic Chemistry" The Macmillan Co., New York.

Camaioni, DM, WD Samuels, BD Lenihan, SA Clauss, KL Wahl, and JA Campbell. 1994. *Organic Tank Safety Program Waste Aging Studies*. PNL-10161. Pacific Northwest Laboratory, Richland Washington.

Camaioni, DM, WD Samuels, SA Clauss, BD Lenihan, AK Sharma, KL Wahl, and JA Campbell. 1996. *Organic Tanks Safety Program FY-96 Waste Aging Studies*. PNL-11312. Pacific Northwest Laboratory, Richland Washington.

Camaioni, DM, WD Samuels, SA Clauss, BD Lenihan, KL Wahl, JA Campbell, and WJ Shaw. 1995. *Organic Tanks Safety Program FY-95 Waste Aging Studies*. PNL-10794. Pacific Northwest Laboratory, Richland Washington.

Camaioni, DM, WD Samuels, BD Lenihan, AK Sharma, MO Hogan, ML Lilga, SA Clauss, KL Wahl, and JA Campbell. 1997. *Organic Tanks Safety Program FY-97 Waste Aging Studies*. PNNL-11670. Pacific Northwest National Laboratory, Richland Washington.

Campbell, JA, SA Clauss, KE Grant, V Hoopes, GM Mong, J Rau, R Steele, and KL Wahl. 1996a. *Flammable Gas Safety Program: Actual Waste Analysis FY 1996 Progress Report*. PNNL-11307, Pacific Northwest National Laboratory. Richland, Washington.

Campbell, JA et al. 1996b. *Organic Tanks Safety Program: Advanced Organic Analysis FY 1996 Progress Report*. PNNL-11309. Pacific Northwest National Laboratory, Richland, Washington.

Carlson, CD. 1997. *Speciation of Organic Carbon in Hanford Waste Storage Tanks: Part 1*. PNNL-11480. Pacific Northwest National Laboratory, Richland, Washington.

EPA. 1997. *Test Methods for Evaluation Solid Waste Physical/Chemical Methods*. SW-846, 3rd Edition, as amended by Updates I (July, 1992), IIA (August, 1993), IIB (January, 1995), and III (Dec 1997). U.S. Environmental Protection Agency, Washington, D.C.

Furniss, BS, AJ Hannaford, PWG Smith, and AR Tatchell. 1989 *Vogel's Textbook of Practical Organic Chemistry* 5th Edition, Longman Scientific and Technical, New York.

Hazardous Waste Management Act of 1976. Ch. 70.105 RCW.

March, J. 1992. *Advanced Organic Chemistry* 4th Edition, John Wiley and Sons, New York.

Meisel D, H Diamond, EP Horowitz, CD Jonah, MS Matheson, MC Sauer, Jr., and JC Sullivan. 1991. *Radiation Chemistry of Synthetic Waste*. ANL-91/40. Argonne National Laboratory, Argonne, Illinois.

Meisel, D, CD Jonah, MS Matheson, MC Sauer Jr, F Barnabas, E Cerney, Y Cheng, and T Wojta. 1992. *Radiation Chemistry of High-Level Wastes ANL/CHM Task Force on Gas Generation in Waste Tanks*, ANL-92/40. Argonne National Laboratory, Argonne, Illinois.

Meisel, D, CD Jonah, S Kapoor, MS Matheson and MC Sauer, Jr. 1993. *Radiolytic and Radiolytically Induced Generation of Gases from Synthetic Wastes*, ANL-93/43. Argonne National Laboratory, Argonne, Illinois.

Meisel, D, DM Camaioni, N. Dimitirievic, A Cook, and N Zevos. 1997. *The NOx System in Nuclear Waste*. Annual Report to the DOE-HQ EMSP. September 30, 1997. Argonne National Laboratory, Argonne, Illinois.

Morrison, RT and RN Boyd. 1973. *Organic Chemistry*. Third Edition. Allyn and Bacon, Inc, Boston.

Pederson, LR. and DM Strachan. 1993. *Status and Integration of the Gas Generation Studies Performed for the Hydrogen Safety Program, FY 1992 Annual Report*. PNL-8523. Pacific Northwest Laboratory, Richland, Washington.

Roberts, JD and MC Caserio. 1964. "Basic Principles of Organic Chemistry." WA Benjamin, Inc., New York.

Sittig, MP. 1991. "Handbook of Toxic, Hazardous and Carcinogenic Chemicals." 3rd Edition Noyes Publications.

Stock, LM and LR Pederson. 1997. *Chemical Pathways for the Formation of Ammonia in Hanford Wastes*. PNNL-11702, Rev. 1. Pacific Northwest National Laboratory, Richland, Washington.

Wiemers, KD, M Lerchen, M Miller, and K Meier. 1998. *Regulatory Data Quality Objectives Supporting Tank Waste Remediation System Privatization Project*. PNNL-12040, Rev. 0. Pacific Northwest National Laboratory, Richland, Washington.

Wilson, JE. 1974. *Radiation Chemistry of Monomers, Polymers, and Plastics*. Marcel Dekker, Inc, New York.

Wodrich, DD, GS Barney, GL Borsheim, DL Becker, WC Carlos, MJ Klem, RE Van der Cook, and JL Ryan. 1992. *Summary of Single-Shell Waste Tank Stability*. WHC-EP-0347. Supplement. Westinghouse Hanford Company, Richland, Washington.

Table 2-1. Regulated Non-Detected Compounds Reviewed for Stability in Tank Waste Environment (269 Compounds). (1 of 7 Pages)

CAS #	Constituent
100-02-7	4-Nitrophenol
100-21-0	Phthalic acid
100-25-4	1,4-Dinitrobenzene
100-37-8	Diethylaminoethanol
100-61-8	N-Methylbenzenamine
100-63-0	Phenyldrazine
100-74-3	N-Ethylmorpholine
101-55-3	4-Bromophenylphenyl ether
101-68-8	Methylene bis(phenyl isocyanate)
101-90-6	Diglycidyl resorcinol ether
102-81-8	2-N-Dibutylaminoethanol
1024-57-3	Heptachlor Epoxide
1031-07-8	Endosulfan Sulfate
105-46-4	sec-Butyl acetate
105-67-9	2,4-Dimethylphenol
106-44-5	4-Methylphenol
106-50-3	p-Phenylenediamine
106-87-6	Vinyl cyclohexene dioxide
106-92-3	Allyl glycidyl ether
107-07-3	Ethylene chlorohydrin
107-15-3	Ethylene diamine
107-21-1	Ethylene glycol
107-66-4	Dibutylphosphate
107-98-2	Propylene glycol monomethyl ether
108-11-2	Methyl isobutyl carbinol
108-18-9	Diisopropylamine
108-21-4	Isopropyl acetate
108-24-7	Acetic anhydride
108-43-0	Chlorophenols
108-60-1	Bis(2-Chloroisopropyl) ether
108-83-8	Diisobutyl ketone
108-84-9	sec-Hexyl acetate
108-91-8	Cyclohexylamine
109-59-1	Isopropoxyethanol
109-60-4	n-Propyl acetate
109-73-9	n-Butylamine
109-79-5	n-Butyl mercaptan
109-86-4	2-Methoxyethanol
109-89-7	Diethylamine
109-94-4	Ethyl formate

Table 2-1. Regulated Non-Detected Compounds Reviewed for Stability in Tank Waste Environment (269 Compounds). (2 of 7 Pages)

CAS #	Constituent
110-19-0	Isobutyl acetate
110-49-6	2-Methoxyethyl acetate
110-75-8	2-Chloroethyl vinyl ether
110-91-8	Morpholine
111-15-9	2-Ethoxyethyl acetate
111-40-0	Diethylene triamine
111-42-2	Diethanolamine
111-44-4	Bis(2-chloroethyl) ether
111-91-1	Bis(2-Chloroethoxy)methane
1129-41-5	Metolcarb (3-methylcholanthrene)
1134-23-2	Cycloate
115-86-6	Triphenyl phosphate
118-52-5	1,3-Dichloro-5,5-Dimethyl hydantoin
118-74-1	Hexachlorobenzene
119-38-0	Isolan
120-12-7	Anthracene
120-83-2	2,4-Dichlorophenol
121-44-8	Triethylamine
121-45-9	Trimethyl phosphite
121-69-7	Dimethylaniline
122-60-1	Phenyl glycidyl ether
122-66-7	1,2-Diphenylhydrazine
123-31-9	Hydroquinone
123-42-2	Diacetone alcohol
123-92-2	Isoamyl acetate
124-40-3	Dimethylamine
124-48-1	Dibromochloromethane
129-15-7	2-Methyl-1-nitroanthraquinone
131-11-3	Dimethyl phthalate
132-64-9	Dibenzofuran
1321-64-8	Pentachloronaphthalene
1321-65-9	Trichloronaphthalene
1321-74-0	Divinyl benzene
133-06-2	Captan
133-90-4	Chloramben
1335-87-1	Hexachloronaphthalene
1335-88-2	Tetrachloronaphthalene
1336-36-3	Polychlorinated biphenyls (PCBs)
1338-23-4	Methyl ethyl ketone peroxide
134-32-7	alpha-Naphthylamine

Table 2-1. Regulated Non-Detected Compounds Reviewed for Stability in Tank Waste Environment (269 Compounds). (3 of 7 Pages)

CAS #	Constituent
135-20-6	Cupferron
135-88-6	N-Phenyl-2-naphthylamine
137-05-3	Methyl-2-cyanoacrylate
138-22-7	n-Butyl lactate
139-65-1	4,4'-Thiodianiline
140-88-5	Ethylacrylate
141-32-2	Butylacrylate
141-43-5	Ethanolamine
142-64-3	Piperazine dihydrochloride
148-01-6	Dinitolamide
150-76-5	4-Methoxyphenol
156-60-5	1,2-trans-Dichloroethene
1582-09-8	Trifluralin
16219-75-3	Ethylidene norbornene
1634-04-4	Methyl tert-butyl ether
17702-57-7	Formparanate
1836-75-5	Nitrofen
189-55-9	Dibenzo[a,i]pyrene
189-64-0	Dibenzo[a,h]pyrene
191-24-2	Benzo(ghi)perylene
191-30-0	Dibenzo(a,l)pyrene
1918-02-1	Picloram
192-65-4	Dibenzo[a,e]pyrene
193-39-5	Indeno(1,2,3-cd)pyrene
2039-87-4	o-Chlorostyrene
205-82-3	Benzo[j]fluoranthene
205-99-2	Benzo(b)fluoranthene
207-08-9	Benzo(k)fluoranthene
208-96-8	Acenaphthylene
218-01-9	Chrysene
2234-13-1	Octachloronaphthalene
2238-07-5	Diglycidyl ether
224-42-0	Dibenz[a,j]acridine
226-36-8	Dibenz[a,h]acridine
22781-23-3	Bendiocarb
22961-82-6	Bendiocarb phenol
23422-53-9	Formetanate hydrochloride
2385-85-5	Mirex
2425-06-1	Captafol
2426-08-6	n-Butyl glycidyl ether

Table 2-1. Regulated Non-Detected Compounds Reviewed for Stability in Tank Waste Environment (269 Compounds). (4 of 7 Pages)

CAS #	Constituent
2425-06-1	Captafol
2426-08-6	n-Butyl glycidyl ether
25013-15-4	Vinyl toluene
2551-13-7	Trimethyl benzene
25639-42-3	Methylcyclohexanol
26140-60-3	Terphenyls
26419-73-8	Tirpate
26952-21-6	Iso-octyl alcohol
2698-41-1	o-Chlorobenzylidene malonitrile
27154-33-2	Trichlorofluoroethane
2921-88-2	Chlorpyrifos
302-01-2	Hydrazine
3068-88-0	B-Butyrolactone
309-00-2	Aldrin
314-40-9	Bromacil
319-84-6	alpha-BHC
319-85-7	beta-BHC
319-86-8	delta-BHC
330-54-1	Diuron
33213-65-9	Endosulfan II
3333-52-6	Tetramethyl succinonitrile
334-88-3	Diazomethane
34590-94-8	Dipropylene glycol methyl ether
3697-24-3	5-Methylchrysene
3825-26-1	Ammonium perfluorooctanoate
4016-14-2	Isopropyl glycidyl ether (IGE)
4098-71-9	Isophorone diisocyanate
420-04-2	Cyanamide
463-51-4	Ketene
465-73-6	Isodrin
50-29-3	4,4'-DDT
50-32-8	Benzo(a)pyrene
504-29-0	2-Aminopyridine
51-28-5	2,4-Dinitrophenol
510-15-6	Chlorobenzilate
5124-30-1	Methylene-bis-(4-cyclo-hexylisocyanate)
52888-80-9	Prosulfocarb
53-70-3	Dibenz[a,h]anthracene
531-82-8	N-(4-(5-Nitro-2-furyl)-2-thiazolyl)acetamide
540-59-0	1,2-Dichloroethylene

Table 2-1. Regulated Non-Detected Compounds Reviewed for Stability in Tank Waste Environment (269 Compounds). (5 of 7 Pages)

CAS #	Constituent
541-85-5	Ethyl amyl ketone
542-75-6	1,3-Dichloropropene
542-92-7	Cyclopentadiene
552-30-7	Trimellitic anhydride
55285-14-8	Carbosulfan
55406-53-6	3-Iodo-2-propynyl n-butylcarbamate
556-52-5	Glycidol
55738-54-0	trans-2((Dimethylamino)methylimino)-5-(2-(5-nitro-2-furyl) vinyl-1,3,4-oxadiazole
56-49-5	3-Methylcholanthrene
56-55-3	Benzo(a)anthracene
57-57-8	B-Propiolactone
57-74-9	Chlordane
58-89-9	gamma-BHC (Lindane)
58-90-2	2,3,4,6-Tetrachlorophenol
583-60-8	o-Methylcyclohexanone
584-84-9	2,4-Toluene diisocyanate
592-62-1	Methyl azoxymethyl acetate
593-60-2	Vinyl bromide
594-42-3	Perchloromethyl mercaptan
594-72-9	1,1-Dichloro-1-nitroethane
5952-26-1	Diethylene glycol, dicarbamate
60-29-7	Ethyl ether
60-57-1	Dieldrin
600-25-9	1-Chloro-1-nitropropane
602-87-9	5-Nitroacenaphthene
603-34-9	Triphenyl amine
613-35-4	N,N-Diacetylbenzidine
62-53-3	Aniline
626-17-5	m-Phthalodinitrile
626-38-0	sec-Amyl acetate
628-63-7	n-Amyl acetate
628-96-6	Ethylene glycol dinitrate
63-92-3	Phenoxybenzamine hydrochloride
630-20-6	1,1,1,2-Tetrachloroethane
638-21-1	Phenylphosphine
64-00-6	m-Cumenyl methylcarbamate
64-67-5	Diethyl sulfate
64091-91-4	4-(Methylnitrosamino)-1-(3-pyridyl)-1-butanone
644-64-4	Dimetilan

Table 2-1. Regulated Non-Detected Compounds Reviewed for Stability in Tank Waste Environment (269 Compounds). (6 of 7 Pages)

CAS #	Constituent
64-67-5	Diethyl sulfate
64091-91-4	4-(Methylnitrosamino)-1-(3-pyridyl)-1-butanone
644-64-4	Dimetilan
68-11-1	Thioglycolic acid
68-12-2	Dimethylformamide
681-84-5	Methyl silicate
684-16-2	Hexafluoroacetone
72-20-8	Endrin
72-43-5	Methoxychlor
72-54-8	4,4'-DDD
72-55-9	4,4'-DDE
74-89-5	Methylamine
74-96-4	Ethyl bromide
74-97-5	Bromochloromethane
7421-93-4	Endrin aldehyde
75-04-7	Ethylamine
75-08-1	Ethyl mercaptan
75-25-2	Tribromomethane
75-27-4	Bromodichloromethane
75-31-0	Isopropylamine
75-56-9	Propylene oxide
75-61-6	Difluorodibromomethane
75-63-8	Trifluorobromomethane
75-99-0	2,2-Dichloropropionic acid
7572-29-4	Dichloroacetylene
76-01-7	Pentachloroethane
76-03-9	Trichloroacetic acid
76-11-9	1,1,1,2-Tetrachloro-2,2-difluoroethane
76-12-0	1,1,2,2-Tetrachloro-1,2-difluoroethane
76-15-3	Chloropentafluoroethane
76-44-8	Heptachlor
768-52-5	N-Isopropylaniline
77-47-4	Hexachlorocyclopentadiene
77-73-6	Dicyclopentadiene
78-10-4	Ethyl silicate
78-59-1	Isophorone
79-04-9	Chloroacetyl chloride
79-11-8	Chloroacetic acid
79-24-3	Nitroethane
79-27-6	Acetylene tetrabromide

Table 2-1. Regulated Non-Detected Compounds Reviewed for Stability in Tank Waste Environment (269 Compounds). (7 of 7 Pages)

CAS #	Constituent
8003-34-7	Pyrethrum
82-68-8	Pentachloronitrobenzene (PCNB)
822-06-0	Hexamethylene diisocyanate
85-01-8	Phenanthrene
86-30-6	N-Nitrosodiphenylamine
87-86-5	Pentachlorophenol
88-72-2	Nitrotoluene
88-74-4	2-Nitroaniline
88-85-7	2-sec-Butyl-4,6-dinitrophenol; syn Dinoseb
88-89-1	Picric acid
89-72-5	o-sec-Butylphenol
91-22-5	Quinoline
91-58-7	2-Chloronaphthalene
91-59-8	2-Naphthylamine
92-93-3	4-Nitrobiphenyl
93-72-1	Silvex (2,4,5-TP)
93-76-5	2,4,5-T
94-36-0	Benzoyl Peroxide
94-75-7	2,4-D
95-13-6	Indene
95-49-8	o-Chlorotoluene
959-98-8	Endosulfan I
96-09-3	Styrene oxide
96-12-8	1,2-Dibromo-3-chloropropane
96-33-3	Methyl acrylate
97-56-3	o-Aminoazotoluene
98-01-1	Furfural
98-51-1	p-tert-Butyltoluene
98-82-2	Cumene
999-61-1	2-Hydroxypropyl acrylate

Table 2-2a. Regulated Non-Detected Compounds with Justification to be Considered Unstable in Tank Waste Environment (181 Compounds).
(1 of 5 Pages)

CAS	Constituent	Justification ²
100-02-7	4-Nitrophenol	OXID
100-37-8	Diethylaminoethanol	OXID
100-61-8	N-Methylbenzenamine	OXID
100-63-0	Phenylhydrazine	OXID
100-74-3	N-Ethylmorpholine	OXID
101-68-8	Methylene bis(phenyl isocyanate)	ALKHYD
101-90-6	Diglycidyl resorcinol ether	ALKHYD
102-81-8	2-N-Dibutylaminoethanol	OXID
1024-57-3	Heptachlor Epoxide	ALKHYD
1031-07-8	Endosulfan Sulfate	ALKHYD
105-46-4	sec-Butyl acetate	ALKHYD
105-67-9	2,4-Dimethylphenol	OXID
106-44-5	4-Methylphenol	OXID
106-50-3	p-Phenylenediamine	OXID
106-87-6	Vinyl cyclohexene dioxide	ALKHYD
106-92-3	Allyl glycidyl ether	ALKHYD
107-07-3	Ethylene chlorohydrin	ALKHYD
107-15-3	Ethylene diamine	OXID
107-21-1	Ethylene glycol	OXID
107-98-2	Propylene glycol monomethyl ether	OXID
108-11-2	Methyl isobutyl carbinol	OXID
108-18-9	Diisopropylamine	OXID
108-21-4	Isopropyl acetate	ALKHYD
108-24-7	Acetic anhydride	ALKHYD
108-43-0	Chlorophenols	OXID
108-60-1	Bis(2-Chloroisopropyl) ether	ALKHYD
108-83-8	Diisobutyl ketone	OXID
108-84-9	sec-Hexyl acetate	ALKHYD
108-91-8	Cyclohexylamine	OXID
109-59-1	Isopropoxyethanol	OXID
109-60-4	n-Propyl acetate	ALKHYD
109-73-9	n-Butylamine	OXID
109-79-5	n-Butyl mercaptan	OXID
109-86-4	2-Methoxyethanol	OXID
109-89-7	Diethylamine	OXID
109-94-4	Ethyl formate	ALKHYD
110-19-0	Isobutyl acetate	ALKHYD
110-49-6	2-Methoxyethyl acetate	ALKHYD
110-75-8	2-Chloroethyl vinyl ether	COUPCOND, ALKHYD

Table 2-2a. Regulated Non-Detected Compounds with Justification to be Considered Unstable in Tank Waste Environment (181 Compounds).
(2 of 5 Pages)

CAS	Constituent	Justification ²
110-91-8	Morpholine	OXID
111-15-9	2-Ethoxyethyl acetate	ALKHYD
111-40-0	Diethylene triamine	OXID
111-42-2	Diethanolamine	OXID
111-44-4	Bis(2-chloroethyl) ether	ALKHYD
111-91-1	Bis(2-Chloroethoxy)methane	ALKHYD
1129-41-5	Metolcarb (3-methylcholanthrene)	ALKHYD
1134-23-2	Cycloate	ALKHYD
115-86-6	Triphenyl phosphate	ALKHYD
118-52-5	1,3-Dichloro-5,5-Dimethyl hydantoin	ALKHYD, OXID
119-38-0	Isolan	ALKHYD
121-45-9	Trimethyl phosphite	ALKHYD
122-60-1	Phenyl glycidyl ether	ALKHYD
122-66-7	1,2-Diphenylhydrazine	OXID
123-31-9	Hydroquinone	OXID
123-42-2	Diacetone alcohol	OXID
123-92-2	Isoamyl acetate	ALKHYD
124-40-3	Dimethylamine	OXID
124-48-1	Dibromochloromethane	ALKHYD, REDUCTDEHAL
129-15-7	2-Methyl-1-nitroanthraquinone	OXID
131-11-3	Dimethyl phthalate	ALKHYD
1321-74-0	Divinyl benzene	COUPCOND
133-06-2	Captan	OXID, ALKHYD
133-90-4	Chloramben	OXID
1338-23-4	Methyl ethyl ketone peroxide	OXID
134-32-7	alpha-Naphthylamine	OXID
135-20-6	Cupferron	OXID
135-88-6	N-Phenyl-2-naphthylamine	OXID
137-05-3	Methyl-2-cyanoacrylate	COUPCOND, ALKHYD
138-22-7	n-Butyl lactate	ALKHYD
139-65-1	4,4'-Thiodianiline	OXID
140-88-5	Ethylacrylate	COUPCOND, ALKHYD
141-32-2	Butylacrylate	COUPCOND, ALKHYD
141-43-5	Ethanolamine	OXID
142-64-3	Piperazine dihydrochloride	OXID
148-01-6	Dinitolamide	ALKHYD
150-76-5	4-Methoxyphenol	OXID
16219-75-3	Ethylidene norbornene	OXID
17702-57-7	Formparanate	ALKHYD

Table 2-2a. Regulated Non-Detected Compounds with Justification to be Considered Unstable in Tank Waste Environment (181 Compounds).
(3 of 5 Pages)

CAS	Constituent	Justification ²
1918-02-1	Picloram	OXID
2039-87-4	o-Chlorostyrene	COUPCOND
2238-07-5	Diglycidyl ether	ALKHYD
22781-23-3	Bendiocarb	ALKHYD
22961-82-6	Bendiocarb phenol	ALKHYD
23422-53-9	Formetanate hydrochloride	ALKHYD
2425-06-1	Captafol	OXID, ALKHYD
2426-08-6	n-Butyl glycidyl ether	ALKHYD
25013-15-4	Vinyl toluene	COUPCOND, OXID
25639-42-3	Methylcyclohexanol	OXID
26419-73-8	Tirpate	ALKHYD
26952-21-6	Iso-octyl alcohol	OXID
2698-41-1	o-Chlorobenzylidene malonitrile	ALKHYD
2921-88-2	Chlorpyrifos	ALKHYD
302-01-2	Hydrazine	OXID
3068-88-0	B-Butyrolactone	ALKHYD
314-40-9	Bromacil	ALKHYD
330-54-1	Diuron	ALKHYD
33213-65-9	Endosulfan II	ALKHYD
3333-52-6	Tetramethyl succinonitrile	ALKHYD
334-88-3	Diazomethane	OXID
34590-94-8	Dipropylene glycol methyl ether	ALKHYD, COUPCOND
4016-14-2	Isopropyl glycidyl ether (IGE)	ALKHYD
4098-71-9	Isophorone diisocyanate	ALKHYD
420-04-2	Cyanamide	ALKHYD
463-51-4	Ketene	ALKHYD
504-29-0	2-Aminopyridine	OXID
51-28-5	2,4-Dinitrophenol	OXID
510-15-6	Chlorobenzilate	ALKHYD
5124-30-1	Methylene-bis-(4-cyclo-hexylisocyanate)	ALKHYD
52888-80-9	Prosulfocarb	ALKHYD
531-82-8	N-(4-(5-Nitro-2-furyl)-2-thiazolyl)acetamide	ALKHYD, OXID
540-88-5	tert-Butyl acetate	ALKHYD
541-85-5	Ethyl amyl ketone	OXID
542-75-6	1,3-Dichloropropene	ALKHYD, DEHYDHAL
542-92-7	Cyclopentadiene	COUPCOND, OXID
552-30-7	Trimellitic anhydride	ALKHYD
55285-14-8	Carbosulfan	ALKHYD

Table 2-2a. Regulated Non-Detected Compounds with Justification to be Considered Unstable in Tank Waste Environment (181 Compounds).
(4 of 5 Pages)

CAS	Constituent	Justification ²
55406-53-6	3-Iodo-2-propynyl n-butylcarbamate	ALKHYD
556-52-5	Glycidol	ALKHYD, OXID
55738-54-0	trans-2((Dimethylamino)methylimino)-5-(2-(5-nitro-2-furyl) vinyl)-1,3,4-oxadiazole	OXID, ALKHYD
57-57-8	B-Propiolactone	ALKHYD
57-74-9	Chlordane	DEHYDHAL
583-60-8	o-Methylcyclohexanone	OXID
584-84-9	2,4-Toluene diisocyanate	ALKHYD
592-62-1	Methyl azoxymethyl acetate	ALKHYD, OXID
593-60-2	Vinyl bromide	COUPCOND, ALKHYD
594-42-3	Perchloromethyl mercaptan	OXID
594-72-9	1,1-Dichloro-1-nitroethane	DEHYDHAL
5952-26-1	Diethylene glycol, dicarbamate	ALKHYD
600-25-9	1-Chloro-1-nitropropane	ALKHYD
613-35-4	N,N-Diacetylbenzidine	ALKHYD
62-53-3	Aniline	OXID
626-17-5	m-Phthalodinitrile	ALKHYD
626-38-0	sec-Amyl acetate	ALKHYD
628-63-7	n-Amyl acetate	ALKHYD
628-96-6	Ethylene glycol dinitrate	ALKHYD
63-92-3	Phenoxybenzamine hydrochloride	OXID
638-21-1	Phenylphosphine	OXID
64-00-6	m-Cumenyl methylcarbamate	ALKHYD
64-67-5	Diethyl sulfate	ALKHYD
64091-91-4	4-(Methylnitrosamino)-1-(3-pyridyl)-1-butanone	OXID
644-64-4	Dimetilan	ALKHYD
68-11-1	Thioglycolic acid	OXID
68-12-2	Dimethylformamide	ALKHYD
681-84-5	Methyl silicate	ALKHYD
74-89-5	Methylamine	OXID
74-96-4	Ethyl bromide	ALKHYD
7421-93-4	Endrin aldehyde	OXID
75-04-7	Ethylamine	OXID
75-08-1	Ethyl mercaptan	OXID
75-25-2	Tribromomethane	DEHYDHAL, REDUCTDEHAL
75-31-0	Isopropylamine	OXID
75-56-9	Propylene oxide	ALKHYD
7572-29-4	Dichloroacetylene	OXID

Table 2-2a. Regulated Non-Detected Compounds with Justification to be Considered Unstable in Tank Waste Environment (181 Compounds).
(5 of 5 Pages)

CAS	Constituent	Justification ²
76-01-7	Pentachloroethane	REDUCTDEHAL
768-52-5	N-Isopropylaniline	OXID
77-47-4	Hexachlorocyclopentadiene	COUPCOND
77-73-6	Dicyclopentadiene	OXID
78-10-4	Ethyl silicate	ALKHYD
78-59-1	Isophorone	OXID
79-04-9	Chloroacetyl chloride	ALKHYD
79-11-8	Chloroacetic acid	ALKHYD
79-24-3	Nitroethane	ALKHYD
79-27-6	Acetylene tetrabromide	ALKHYD
79-41-4	Methacrylic acid	COUPCOND
794-93-4	Panfuran S (dihydroxymethylfuratrizine)	OXID
8003-34-7	Pyrethrum	OXID
822-06-0	Hexamethylene diisocyanate	ALKHYD
86-30-6	N-Nitrosodiphenylamine	ALKHYD, OXID
88-72-2	Nitrotoluene	STABLE ¹
88-74-4	2-Nitroaniline	OXID
89-72-5	o-sec-Butylphenol	OXID
91-59-8	2-Napthylamine	OXID
94-36-0	Benzoyl Peroxide	ALKHYD
95-49-8	o-Chlorotoluene	STABLE ¹
959-98-8	Endosulfan I	ALKHYD
96-09-3	Styrene oxide	ALKHYD
96-12-8	1,2-Dibromo-3-chloropropane	DEHYDHAL, ALKHYD
96-33-3	Methyl acrylate	COUPCOND, ALKHYD
97-56-3	o-Aminoazotoluene	OXID
98-01-1	Furfural	OXID
999-61-1	2-Hydroxypropyl acrylate	ALKHYD, COUPCOND, OXID

¹DOE to discuss stability with other team members.

²See Table 2-2b for details of justification. When more than one degradation pathway is listed, the first item is the dominant pathway.

Table 2-2b. Justification Description for Table 2-2a. (1 of 2 Pages)

Abbreviation	Degradation Process	Functional Group Examples	Description
ALKHYD	Alkaline Hydrolysis	Acid Chloride	Hydrolysis, under aqueous alkaline conditions. Substitution (nucleophilic displacement by hydroxide ion). This pathway can be treated as a special case of hydrolysis.
ALKHYD	Alkaline Hydrolysis	Acid Anhydride	Hydrolysis, under aqueous alkaline conditions. Substitution (nucleophilic displacement by hydroxide ion). This pathway can be treated as a special case of hydrolysis.
ALKHYD	Alkaline Hydrolysis	Ester	Hydrolysis, under aqueous alkaline conditions. Substitution (nucleophilic displacement by hydroxide ion). This pathway can be treated as a special case of hydrolysis.
ALKHYD	Alkaline Hydrolysis	Phosphate Esters	Hydrolysis, under aqueous alkaline conditions. Substitution (nucleophilic displacement by hydroxide ion). This pathway can be treated as a special case of hydrolysis.
ALKHYD	Alkaline Hydrolysis	Nitrate Ester	Hydrolysis, under aqueous alkaline conditions. Substitution (nucleophilic displacement by hydroxide ion). This pathway can be treated as a special case of hydrolysis.
ALKHYD	Alkaline Hydrolysis	Isocyanates	Hydrolysis, under aqueous alkaline conditions. Substitution (nucleophilic displacement by hydroxide ion). This pathway can be treated as a special case of hydrolysis.
ALKHYD	Alkaline Hydrolysis	Carbamates	Hydrolysis, under aqueous alkaline conditions. Substitution (nucleophilic displacement by hydroxide ion). This pathway can be treated as a special case of hydrolysis.
ALKHYD	Alkaline Hydrolysis	Epoxide	Hydrolysis, under aqueous alkaline conditions. Substitution (nucleophilic displacement by hydroxide ion). This pathway can be treated as a special case of hydrolysis.

Table 2-2b. Justification Description for Table 2-2a. (2 of 2 Pages)

Abbreviation	Degradation Process	Functional Group Examples	Description
ALKHYD	Alkaline Hydrolysis	Nitrile	Hydrolysis, under aqueous alkaline conditions. Substitution (nucleophilic displacement by hydroxide ion). This pathway can be treated as a special case of hydrolysis.
ALKHYD	Alkaline Hydrolysis	Allylic Halide	Hydrolysis, under aqueous alkaline conditions. Substitution (nucleophilic displacement by hydroxide ion). This pathway can be treated as a special case of hydrolysis.
ALKHYD	Alkaline Hydrolysis	Benzyl Halide	Hydrolysis, under aqueous alkaline conditions. Substitution (nucleophilic displacement by hydroxide ion). This pathway can be treated as a special case of hydrolysis.
DEHYDHAL	Dehydrohalogenation	Activated Haloalkane	Elimination (dehydrohalogenation).
COUPCOND	Coupling Condensation	Activated Olefins	Addition, condensation and radical coupling.
COUPCOND	Aldolization	Aldehydes and Ketones	Addition, condensation and radical coupling.
OXID	Oxidation	Alcohols	Oxidation (thermal and/or radiolytic).
OXID	Oxidation	Aldehydes	Oxidation (thermal and/or radiolytic).
OXID	Oxidation	Ketones	Oxidation (thermal and/or radiolytic).
OXID	Oxidation	Amines	Oxidation (thermal and/or radiolytic).
OXID	Oxidation	Mercaptans	Oxidation (thermal and/or radiolytic).
OXID	Oxidation	Mercaptans	Oxidation (thermal and/or radiolytic).
OXID	Oxidation	Sulfides	Oxidation (thermal and/or radiolytic).
REDUCTDEHAL	Reduction	Polychloro Alkanes	Radical reductive dehalogenation.

Table 3-1. Regulated Detected Organic Compounds Containing Functional Groups Unstable to Tank Conditions (42 Compounds). (1 of 2 Pages)

CAS #	Compound Name	Number of TWINS solid/liquid detects ⁽¹⁾	Number of TWINS vapor detects	Potential In Situ Synthesis Route
100-42-5	Styrene	3	195	Depolymerization of Ion Exchange Resins
10061-01-5	cis-1,3-Dichloropropene	NR	27	Unknown
10061-02-6	trans-1,3-Dichloropropene	1	28	Radical Dehalogenation of Residual Degreasing Compounds
106-35-4	3-Heptanone	7	158	Hydrocarbon Oxidation
106-93-4	Ethylene dibromide	NR	45	Unknown
107-06-2	1,2-Dichloroethane	1	15	Radical Dehalogenation of Residual Degreasing Compounds
107-87-9	2-Pentanone	NR	211	Hydrocarbon Oxidation
108-10-1	4-Methyl-2-pentanone	1	374	Residual Redox Solvent or Hydrocarbon Oxidation
108-94-1	Cyclohexanone	NR	192	Hydrocarbon Oxidation Early Purex Solvent
108-95-2	Phenol	NR	19	Depolymerization of Ion Exchange Resins followed by oxidation
110-12-3	5-Methyl-2-hexanone	NR	12	Hydrocarbon Oxidation
110-43-0	2-Heptanone	NR	209	Hydrocarbon Oxidation
110-62-3	n-Valeraldehyde	NR	54	Hydrocarbon Oxidation
110-83-8	Cyclohexene	19	2	Early Purex solvent residual
117-81-7	Bis(2-ethylhexyl) phthalate	33	1	Impurity from Plastic Labware
123-19-3	4-Heptanone	NR	44	Hydrocarbon Oxidation
123-38-6	n-Propionaldehyde	NR	56	Hydrocarbon Oxidation
123-86-4	Acetic acid n-butyl ester	NR	25	Hydrocarbon Oxidation Followed By Limited Esterification
141-78-6	Acetic acid ethyl ester	NR	10	Hydrocarbon Oxidation Followed By Limited Esterification
4170-30-3	2-Butenaldehyde	NR	37	Hydrocarbon Oxidation; acetaldehyde dimer
563-80-4	3-Methyl-2-butanone	NR	34	Hydrocarbon Oxidation or MIBK Rearrangement
591-78-6	2-Hexanone	11	248	Hydrocarbon Oxidation
627-13-4	Nitric acid, propyl ester	NR	72	Hydrocarbon Oxidation and Oxime Reaction
64-17-5	Ethyl alcohol	NR	552	Hydrocarbon Oxidation
67-56-1	Methyl alcohol	NR	594	Hydrocarbon Oxidation or Hydrolysis of Methyl Chloride
67-63-0	2-Propyl alcohol	NR	191	Hydrocarbon Oxidation
71-23-8	n-Propyl alcohol	NR	606	Hydrocarbon Oxidation
71-36-3	n-Butyl alcohol	23	775	Hydrolysis of Adsorbed TBP or Hydrocarbon Oxidation

Table 3-1. Regulated Detected Organic Compounds Containing Functional Groups Unstable to Tank Conditions (42 Compounds). (2 of 2 Pages)

CAS #	Compound Name	Number of TWINS solid/liquid detects ⁽¹⁾	Number of TWINS vapor detects	Potential In Situ Synthesis Route
74-87-3	Chloromethane	4	194	Radical Dehalogenation of Carbon Tetrachloride
75-00-3	Chloroethane	NR	82	Radical Dehalogenation of Residual Degreasing Compounds
75-01-4	1-Chloroethene	NR	26	Depolymerization of Ion Exchange Resins
75-05-8	Acetonitrile	NR	713	Hydrocarbon Oxidation and Interaction With Nitrogenous Species
75-07-0	Acetaldehyde	NR	103	Hydrocarbon Oxidation
75-34-3	1,1-Dichloroethane	NR	29	Radical Dehalogenation of Residual Degreasing Compounds
75-65-0	2-Methyl-2-propanol	NR	144	Hydrocarbon Oxidation
78-87-5	1,2-Dichloropropane	NR	13	Radical Dehalogenation of Residual Degreasing Compounds
78-92-2	1-Methylpropyl alcohol	NR	66	Hydrocarbon Oxidation
78-93-3	2-Butanone	27	642	Hydrocarbon Oxidation
79-00-5	1,1,2-Trichloroethane	NR	111	Radical Dehalogenation of Residual Degreasing Compounds
84-66-2	Diethyl phthalate	NR	24	Transesterified Impurity from Plastic Labware
96-22-0	3-Pentanone	NR	10	Hydrocarbon Oxidation
98-86-2	Acetophenone	NR	43	Oxidation of Ethyl Benzene

(1) Number of defects based on TWINS Tank Characterization Database. It is not known from the tank characterization database whether organic analysis were attempted on a condensed phase fraction of the samples in which a vapor detect was obtained.

NR = not reported

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