Attachment III

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)
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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 (analogs 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**

\[ R-\text{COCl} + \text{NaOH} \rightarrow R-\text{COONa} + \text{NaCl} \]  
(In solutions)

**Acid Anhydride**

\[ (R-C=O)_2 \text{O} + 2\text{NaOH} \rightarrow 2R-\text{COONa} \]

**Ester**

\[ \text{RCO-OR'} + \text{NaOH} \rightarrow \text{RCOONa} + \text{R'O}H \]

**Phosphate Ester**

\[ (\text{RO})_3\text{P=O} + \text{NaOH} \rightarrow (\text{RO})_2\text{PO}_2\text{Na} + \text{ROH} \]

**Nitrate Ester**

\[ \text{RONO}_2 + \text{NaOH} \rightarrow \text{NaNO}_3 + \text{ROH} \]

**Isocyanate**

\[ R-\text{CH}_2\text{-NCO} + 2\text{NaOH} \rightarrow R-\text{CH}_2\text{-NH}_2 + \text{Na}_2\text{CO}_3 \]

**Carbamate**

\[ R-\text{NH(C=O)OR} + 2\text{NaOH} \rightarrow R-\text{NH}_2 + \text{ROH} + \text{Na}_2\text{CO}_3 \]

**Urea**

\[ R-\text{NH(C=O)NHR'} + 2\text{NaOH} \rightarrow R-\text{NH}_2 + \text{R'NH}_2 + \text{Na}_2\text{CO}_3 \]

**Epoxide**

\[ R-[\text{CH-CH}_2\text{]}\text{O} + \text{NaOH} \rightarrow \text{RCH}_2\text{CH(OH)CH}_2\text{OH} \]

**Nitrile**

\[ R-\text{CH}_2\text{-CN} + 2\text{NaOH} \rightarrow R-\text{CH}_2\text{-COONa} + \text{NH}_3 \]
Allyl Chloride
RCH=CH-CH \_Cl + NaOH \rightarrow RCH=CH-CH \_OH + NaCl

Benzyl Chloride
Ar-CH=CH \_Cl + NaOH \rightarrow Ar-CH=CH \_OH + NaCl

- **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
RCH=CH-CH \_Cl + NaOH \rightarrow RCH=CH-CH \_OH + NaCl

Reduction of Alkyl Halides
CCl\_4 \rightarrow CHCl\_3 \rightarrow CH\_2Cl \rightarrow CH\_Cl

- **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
R \_ + n Ar-CH=CH \_ \rightarrow R-[ArCH=CH \_]_n-H
R \_ + CH=CH \_Cl \rightarrow R-[CH=CH \_Cl]_n-H
Where n is a small number

**Alkyl Aldehydes (or Ketones) Containing Alpha Hydrogens**

2 CH₃CHO ———> CH₃CH(OH)-CH₂CHO [Aldol Condensation]

**Coupling Reactions**

2RCH₂ ———> RCH₂-CH₂R

RCH₂ + R'CH₂ ———> RCH₂-CH₂R'

- **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**

R-CH₂OH + [O] + NaOH ———> RCO₂Na + H₂O

**Aldehydes**

C₃H₇CHO + [O] + NaOH ———> C₃H₇CO₂Na + Na₂CO₃ + H₂O

**Ketones**

ArCH₂C(O)CH₃ [O] + NaOH ———> ArCH₂CO₂Na + HCO₂Na + Na₂CO₃

CH₃CH₂CH₂C(O)CH₃ [O] + NaOH ———> CH₃CH₂CH₂CO₂Na + CH₃CH₂CO₂Na + CH₃CO₂Na + HCO₂Na + Na₂CO₃
Phenols
Phenol + [O] + NaOH \rightarrow Quinone \rightarrow Sodium Succinate + Na_2CO_3

Amines
RCH_2NHR' + [O] \rightarrow R'NH_2 + RCHO

Mecaptan [Thiol]
CH_3CH_2SH + [O] + NaOH \rightarrow CH_3CH_2SO_3Na

Sulfide
CH_3SCH_3 + [O] + NaOH \rightarrow CH_3SOCH_3 \rightarrow CH_3SO_2CH_3 \rightarrow CH_3SO_3Na

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 parafin hydrocarbons [NPH]), and extractants (e.g., tributyl phosphate) degrade to lower molecular weight and structurally simpler salts of carboxylic and phosphoric acid (Camaiorii 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 (Camaiorii 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


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<tr>
<th>CAS #</th>
<th>Constituent</th>
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<tr>
<td>100-02-7</td>
<td>4-Nitrophenol</td>
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<td>100-21-0</td>
<td>Phthalic acid</td>
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<td>100-63-0</td>
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<td>100-74-3</td>
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<td>101-55-3</td>
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<td>101-68-8</td>
<td>Methylene bis(phenyl isocyanate)</td>
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<td>101-90-6</td>
<td>Diglycidyl resorcinol ether</td>
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<td>102-81-8</td>
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Table 2-1. Regulated Non-Detected Compounds Reviewed for Stability in Tank Waste Environment (269 Compounds).

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

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

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

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

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

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

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<td>105-67-9</td>
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<td>106-44-5</td>
<td>4-Methylphenol</td>
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Table 2-2a. Regulated Non-Detected Compounds with Justification to be Considered Unstable in Tank Waste Environment (181 Compounds).

(2 of 5 Pages)

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

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

(4 of 5 Pages)

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<td>644-64-4</td>
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<td>68-12-2</td>
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<td>681-84-5</td>
<td>Methyl silicate</td>
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<td>74-89-5</td>
<td>Methylamine</td>
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<td>74-96-4</td>
<td>Ethyl bromide</td>
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<tr>
<td>7421-93-4</td>
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</tr>
<tr>
<td>75-04-7</td>
<td>Ethylamine</td>
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</tr>
<tr>
<td>75-08-1</td>
<td>Ethyl mercaptan</td>
<td>OXID</td>
</tr>
<tr>
<td>75-25-2</td>
<td>Tribromomethane</td>
<td>DEHYDHAL, REDUCTDEHAL</td>
</tr>
<tr>
<td>75-31-0</td>
<td>Isopropylamine</td>
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</tr>
<tr>
<td>75-56-9</td>
<td>Propylene oxide</td>
<td>ALKHYD</td>
</tr>
<tr>
<td>7572-29-4</td>
<td>Dichloroacetylene</td>
<td>OXID</td>
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Table 2-2a. Regulated Non-Detected Compounds with Justification to be Considered Unstable in Tank Waste Environment (181 Compounds).

<table>
<thead>
<tr>
<th>CAS</th>
<th>Constituent</th>
<th>Justification</th>
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<tr>
<td>76-01-7</td>
<td>Pentachloroethane</td>
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<td>768-52-5</td>
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<td>77-47-4</td>
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<tr>
<td>77-73-6</td>
<td>Dicyclopentadiene</td>
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</tr>
<tr>
<td>78-10-4</td>
<td>Ethyl silicate</td>
<td>ALKHYD</td>
</tr>
<tr>
<td>78-59-1</td>
<td>Isophorone</td>
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<tr>
<td>79-04-9</td>
<td>Chloracetyl chloride</td>
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<td>79-11-8</td>
<td>Chloroacetic acid</td>
<td>ALKHYD</td>
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<td>79-24-3</td>
<td>Nitroethane</td>
<td>ALKHYD</td>
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<td>Acetylene tetrabromide</td>
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<td>79-41-4</td>
<td>Methacrylic acid</td>
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<td>Panfuran S (dihydroxymethylfuratrizine)</td>
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<td>8003-34-7</td>
<td>Pyrethrum</td>
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<td>822-06-0</td>
<td>Hexamethylene diisocyanate</td>
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<td>N-Nitrosodiphenylamine</td>
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<td>88-74-4</td>
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<td>959-98-8</td>
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<td>96-53-3</td>
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<td>o-Aminoazotoluene</td>
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<td>999-61-1</td>
<td>2-Hydroxypropyl acrylate</td>
<td>ALKHYD, COUPCOND, OXID</td>
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</table>

*DOE to discuss stability with other team members.

*See 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)

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Degradation Process</th>
<th>Functional Group Examples</th>
<th>Description</th>
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<tr>
<td>ALKHYD</td>
<td>Alkaline Hydrolysis</td>
<td>Acid Chloride</td>
<td>Hydrolysis, under aqueous alkaline conditions. Substitution (nucleophilic displacement by hydroxide ion). This pathway can be treated as a special case of hydrolysis.</td>
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<td>Ester</td>
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<td>Phosphate Esters</td>
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<td>Nitrate Ester</td>
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<td>Abbreviation</td>
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<td>Functional Group</td>
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<td>2-Hexanone</td>
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<td>64-17-5</td>
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<td>71-36-3</td>
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Table 3-1. Regulated Detected Organic Compounds Containing Functional Groups Unstable to Tank Conditions (42 Compounds). (2 of 2 Pages)

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<th>CAS #</th>
<th>Compound Name</th>
<th>Number of TWINS solid/liquid detects$^1$</th>
<th>Number of TWINS vapor detects</th>
<th>Potential In Situ Synthesis Route</th>
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<td>75-00-3</td>
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<td>75-01-4</td>
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<td>Depolymerization of Ion Exchange Resins</td>
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<td>75-05-8</td>
<td>Acetonitrile</td>
<td>NR</td>
<td>713</td>
<td>Hydrocarbon Oxidation and Interaction With Nitrogenous Species</td>
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<tr>
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<tr>
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<td>43</td>
<td>Oxidation of Ethyl Benzene</td>
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(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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<th>City, State, Zip</th>
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<tr>
<td>Harry Babad, Ph. D.</td>
<td>2540 Cordoba Court</td>
<td>Richland, WA 99352-1609</td>
</tr>
<tr>
<td>Mitzi Miller (3)</td>
<td>Environmental Quality Management</td>
<td>2000 Logston Blvd.</td>
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### ONSITE

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<tr>
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<td>C.E. Clark</td>
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<td>J.A. Poppiti</td>
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### 7 Lockheed Martin Hanford

<table>
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### 25 Pacific Northwest National Laboratory

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### 2 Waste Management Federal Services of Hanford, Inc.

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<td>C.M. Seidel</td>
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