HANFORD TANK WASTE ORGANIC COMPOUND STABILITY ASSESSMENT AND IN SITU SYNTHESIS EVALUATION IN SUPPORT OF THE PRIVATIZATION REGULATORY DQO

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ABSTRACT

The 54 million gallons of high-level radioactive waste stored in 177 underground storage tanks at the Hanford Site are designated under the *Resource Conservation and Recovery Act of 1976* and the Washington *Hazardous Waste Management Act of 1976* as listed, characteristic, and criteria waste. Characterization data are needed for the tank waste to ensure compliant treatment, storage, and disposal of the waste. The Department of Energy and Washington Department of Ecology through a Data Quality Objective (DQO) process have defined 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 the Hanford waste. In the analyte selection process, each of the regulated compounds was evaluated, in part, with respect to the plausibility of existing in the waste. One of the plausibility decisions addressed the compound's chemical stability in the waste environment and the potential for the generation of regulated compounds through in situ synthesis during waste storage.

The technical basis, assumptions, and results of the tank waste stability assessment are discussed. The tank waste properties considered in the stability evaluation are high alkalinity, an oxidizing environment, and high levels of radioactivity leading to the radiolysis of organics. The technical approach consists of documented reactions of organic compounds as a function of their structure and functionality. Most of the functional groups associated with the regulated compounds are known to be unstable under tank waste conditions. The general exceptions are some simple-substituted aromatic and polycyclic aromatic compounds that resist oxidation and the multiply substituted aliphatic and aromatic halides that hydrolyze or dehydrohalogenate slowly under tank waste conditions.

The final list of 125 organic compounds provides initial target analytes for characterization of the Hanford DST and SST waste and has been used in early permit preparation activities for the tank waste treatment facility.

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 objectives, and risk assessment requirements. The DOE and Ecology through the Regulatory Data Quality Objectives (DQO) process have defined and documented (1) characterization needs for the Hanford Site single-shell tank (SST) and double-shell tank (DST) waste.

Through the DQO process, a limited number of regulated compounds were selected for measurement in Hanford DST and SST waste. The analyte selection process was completed through implementing a series of technically defensible logic steps that are described by Wiemers et al. (1) and summarized in Figure 1. 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 included the Underlying Hazardous Constituents (40 CFR 268.2(i)) and Universal Treatment Standards (40 CFR 268.48), and the Washington State Toxic Air Pollutant (TAP) Class A (WAC 173-460-150) and Class B (WAC 173-460-160). In the analyte selection logic, the regulated compounds was evaluated with respect to the plausibility of existing in the Hanford Site SST and DST waste, its relative toxicity, and the availability of methods for analysis in alkaline, high-level waste. One aspect 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 chemical stability and in situ synthesis assessments are the focus of this paper.

The stability and in situ synthesis assessments were used in a two-prong approach to examine the plausibility of individual regulated compounds being present in the waste and thus, to provide a technical basis for selection for measurement. Both the stability and in situ synthesis assessments were based on fundamental organic chemistry. For regulated organic compounds that had not previously been reported in DST or SST waste, the stability assessment was applied, including an assessment identifying regulated compounds that may form through in situ synthesis during storage of the waste. A stability assessment of the detected, regulated, organic compounds was also performed. Inclusion of this step provided insights as to the validity of the technical basis, the analytical data, and potential in situ synthesis pathways. These are discussed in further detail below and a comprehensive discussion of the stability assessment and in situ synthesis is provided by Wiemers et al. (2)

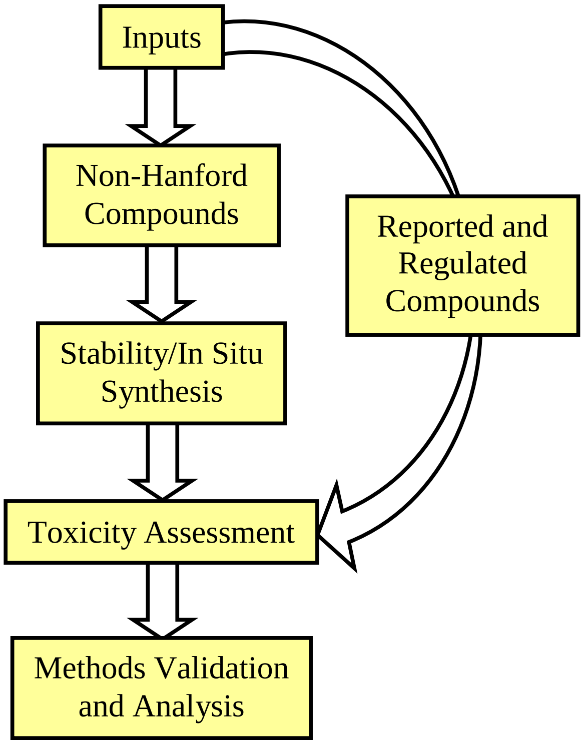

Fig. 1. Privatization Regulatory Data Quality Objectives Analyte Selection Logic.

TECHNICAL BASIS FOR ORGANIC COMPOUND STABILITY ASSESSMENT

The technical basis for the tank waste stability assessment consisted of known and documented reactions of organic compounds (3-7) under conditions similar to the tank waste environment. The Hazardous Substance Data Bank was also used as a primary reference for most of the compounds' chemistries. Each of the selected regulated organic compounds was evaluated independently by a team of 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), an oxidizing environment (high concentration of nitrate and nitrite), and radioactivity (presence of beta and gamma emitters.) 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 below.

Functional Groups

Functional groups used for classification were

- Carbon/hydrogen functionality: aliphatic and alicyclic hydrocarbons, the monocyclic and tar-based polycyclic aromatic compounds, 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.

Reaction Chemistries

The assignment of a compound as “unstable” required the destruction of one or more of the functional groups defined in the previous subsection by one or more of the following reaction pathways:

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

The reaction pathways and affected functional groups are summarized in Table I.

Table I. Summary of Reaction Pathways and Associated Unstable Functional Groups

Reaction Pathway	Functional Group Examples	Description
Alkaline Hydrolysis	Acid Chloride Acid Anhydride Epoxide Ester Phosphate Esters Nitrate Ester Allylic Halide Benzylic Halide	Hydrolysis, under aqueous alkaline conditions. Substitution (nucleophilic displacement by hydroxide ion).
Alkaline Hydrolysis	Isocyanates Carbamates Ureas	Hydrolysis, under aqueous alkaline conditions. Substitution (nucleophilic displacement by hydroxide ion). This pathway can be treated as a special case of hydrolysis.
Alkaline Hydrolysis	Amide Nitrile	Hydrolysis, under aqueous alkaline conditions. This pathway can be treated as a special case of hydrolysis.
Dehydrohalogenation	Activated Haloalkane	Elimination (dehydrohalogenation).
Coupling Condensation	Activated Olefins	Addition, condensation and radical coupling.
Aldolization	Aldehydes and some Ketones	Addition, condensation and radical coupling.
Oxidation	Alcohols	Oxidation (thermal and/or radiolytic).
Oxidation	Aldehydes Ketones	Oxidation (thermal and/or radiolytic).
Oxidation	Amines Anilines	Oxidation (thermal and/or radiolytic).
Oxidation	Mercaptans Sulfides	Oxidation (thermal and/or radiolytic).
Reduction	Polychloro Alkanes	Radical reductive dehalogenation.

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 (8) to those with up to a 4 molar concentration of alkali. 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, such compounds are generally listed as the undissociated, acid form in the regulatory analyte input list. The regulatory (9) 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, many of the acidic and phenolic compounds contained an additional reactive functional group that was not stable in the tank waste environment.

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 (10-24) suggests that the rates of radiolysis are a function of the cesium-137 and strontium-90 concentrations, and are 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. Thermal and radiolytic degradation pathways were considered during the stability assessment using best available information and professional judgment.

Since new waste materials have recently been and continue to be added to the DST 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 for this assessment.

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.

NON-DETECTED REGULATED ORGANIC COMPOUNDS STABILITY ASSESSMENT RESULTS

Using the technical basis discussed in the previous section the stability of 269 regulated compounds not previously reported in SST or DST waste was examined. Most of the functional groups associated with this set of regulated organic compounds were concluded to be unstable under tank waste conditions. One hundred seventy-nine (179) regulated compounds were determined as likely unstable in the tank waste environment. Some examples of compounds considered unstable are provided in Table II along with the justification for considering the compound unstable. A complete list of compounds addressed in this assessment is provided by Wiemers et al. (2). Compound groups considered stable and retained for further consideration in the analyte selection logic included chlorinated biphenyls, polyaromatic hydrocarbons, and polynitrated aromatics. Overall, this part of the assessment resulted in 90 regulated organic compounds to examine further under the analyte selection logic

IN SITU REGULATED COMPOUND SYNTHESIS

Two possible routes for detectable concentrations of regulated compounds to be present in the tank waste follow:

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).

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.

Table II. Examples of Regulated Non-Detected Compounds Containing Functional Groups Unstable to Tank Conditions (Complete list is provided in [2])

CAS	Compound Name	Justification for Degradation
101-68-8	Methylene bis(phenyl isocyanate)	Alkaline Hydrolysis
101-90-6	Diglycidyl resorcinol ether	Alkaline Hydrolysis
106-44-5	4-Methylphenol	Oxidation
107-07-3	Ethylene chlorohydrin	Alkaline Hydrolysis
107-15-3	Ethylene diamine	Oxidation
108-24-7	Acetic anhydride	Alkaline Hydrolysis
109-79-5	n-Butyl mercaptan	Oxidation
110-75-8	2-Chloroethyl vinyl ether	Aldolization, Alkaline Hydrolysis
115-86-6	Triphenyl phosphate	Alkaline Hydrolysis
122-66-7	1,2-Diphenylhydrazine	Oxidation
123-31-9	Hydroquinone	Oxidation
131-11-3	Dimethyl phthalate	Alkaline Hydrolysis
137-05-3	Methyl-2-cyanoacrylate	Aldolization, Alkaline Hydrolysis
138-22-7	n-Butyl lactate	Alkaline Hydrolysis
141-43-5	Ethanolamine	Oxidation
3068-88-0	B-Butyrolactone	Alkaline Hydrolysis
330-54-1	Diuron	Alkaline Hydrolysis
4016-14-2	Isopropyl glycidyl ether (IGE)	Alkaline Hydrolysis
541-85-5	Ethyl amyl ketone	Oxidation
542-75-6	1,3-Dichloropropene	Alkaline Hydrolysis, Dehydrohalogenation
57-57-8	B-Propiolactone	Alkaline Hydrolysis
57-74-9	Chlordane	Dehydrohalogenation
5952-26-1	Diethylene glycol, dicarbamate	Alkaline Hydrolysis
628-96-6	Ethylene glycol dinitrate	Alkaline Hydrolysis
64-67-5	Diethyl sulfate	Alkaline Hydrolysis
68-11-1	Thioglycolic acid	Oxidation
68-12-2	Dimethylformamide	Alkaline Hydrolysis
76-01-7	Pentachloroethane	Reductive Dehalogenation
79-04-9	Chloroacetyl chloride	Alkaline Hydrolysis
89-72-5	o-sec-Butylphenol	Oxidation
91-59-8	2-Napthylamine	Oxidation
96-09-3	Styrene oxide	Alkaline Hydrolysis
98-01-1	Furfural	Oxidation
999-61-1	2-Hydroxypropyl acrylate	Alkaline Hydrolysis, Aldolization, Oxidation

The stability of regulated chemicals that may have been disposed of directly into waste storage tanks was addressed in the previous section. The technical basis used in this 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 have been studied.

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 the previous section. 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., ethylenediaminetetraacetric acid, 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 acids (20).

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 (15). This most likely occurs while the organic carbon-containing species are oxidized by nitrite reference. 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 liquid or solid waste phases (19).

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. ([23] 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 rule.

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 waste 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 otherwise unstable compounds would only be detected if they were removed/isolated from the reactive environment, such as being swept out of the tank waste into the dome space vapor phase (or headspace of a liquid sample) or alternatively, adhering 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.

IN SITU SYNTHESIS RESULTS

With the possible exception of nitriles, no direct pathways were identified for synthesis of stable, regulated organic compounds in tank waste. One hundred and forty-six (146) detected, regulated, organic compounds were evaluated for stability based on the technical basis provided in a previous section. A majority of the “detected” organic compounds were reported for the vapor phase only. For many of the compounds, it could not be discerned from the information reviewed, whether the compound had been analyzed from the liquid or solid waste phase samples. Additionally, the species identification was most often made by reference to a mass spectroscopy compound identification library. Compounds identified in this manner are referred to as tentatively identified compounds. A relatively high degree of uncertainty exists with respect to these compound’s identification. Some examples of the 42 detected regulated compounds concluded to be unstable are provided in Table III along with the justification for considering the compound unstable.

Table III. Examples of Regulated Detected Compounds Containing Functional Groups Unstable to Tank Conditions (Complete list provided in [2])

CAS #	Compound Name	Justification for Degradation
100-42-5	Styrene	Depolymerization of Ion Exchange Resins
10061-02-6	Trans-1,3-Dichloropropene	Radical Dehalogenation of Residual Degreasing Compounds
106-35-4	3-Heptanone	Hydrocarbon Oxidation
106-93-4	Ethylene dibromide	Unknown
108-10-1	4-Methyl-2-pentanone	Residual Redox Solvent or Hydrocarbon Oxidation
108-94-1	Cyclohexanone	Hydrocarbon Oxidation Early Purex Solvent
110-43-0	2-Heptanone	Hydrocarbon Oxidation
110-62-3	n-Valeraldehyde	Hydrocarbon Oxidation
123-86-4	Acetic acid n-butyl ester	Hydrocarbon Oxidation Followed By Limited Esterification
563-80-4	3-Methyl-2-butanone	Hydrocarbon Oxidation or MIBK Rearrangement
591-78-6	2-Hexanone	Hydrocarbon Oxidation
64-17-5	Ethyl alcohol	Hydrocarbon Oxidation
71-23-8	n-Propyl alcohol	Hydrocarbon Oxidation
71-36-3	n-Butyl alcohol	Hydrolysis of Adsorbed TBP or Hydrocarbon Oxidation
74-87-3	Chloromethane	Radical Dehalogenation of Carbon Tetrachloride
75-00-3	Chloroethane	Radical Dehalogenation of Residual Degreasing Compounds
75-05-8	Acetonitrile	Hydrocarbon Oxidation and Interaction With Nitrogenous Species
75-07-0	Acetaldehyde	Hydrocarbon Oxidation
75-65-0	2-Methyl-2-propanol	Hydrocarbon Oxidation
78-93-3	2-Butanone	Hydrocarbon Oxidation
79-00-5	1,1,2-Trichloroethane	Radical Dehalogenation of Residual Degreasing Compounds

The following explanations may account for a detected compound being considered unstable in the tank waste matrix:

- 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
- 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.

All of the detected compounds were included for further examination under the analyte selection logic. Future tank waste sampling and analysis of analytes selected for measurement under the DQO should provide additional basis for validating this study's results.

CONCLUSION

The stability assessment examined 269 non-detected regulated compounds (see Table I for examples), 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. Examples of the 181 regulated, organic compounds were determined as likely unstable in the tank waste environment. The complete list is available in Wiemers et al. (2).

The results of the tank waste stability and in situ formation assessments have provided a technical basis for the focused sampling based assessments of tank waste in support of regulatory requirements. This technique was found technically defensible and may be applied to stability assessments in other Hanford high-activity waste storage tanks as well as other DOE complex wastes that contain regulated organic constituents.

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