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High Organic Containing Tanks - Assessing the Hazard Potential

Prepared for the U.S. Department of Energy
Office of Environmental Restoration and
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Westinghouse Hanford Company Richland, Washington

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HIGH ORGANIC CONTAINING TANKS - ASSESSING THE HAZARD POTENTIAL

By R. C. Philip Hill and Harry Babad
(Westinghouse Hanford)

ABSTRACT

Eight Hanford Site tanks contain organic chemicals at concentrations believed to be greater than 10 mole percent sodium acetate equivalent mixed with the oxidizing salts sodium nitrate/sodium nitrite. Also, three of the hydrogen and ferrocyanide tanks appear on the organic tank list. Concentrations of organics that may be present in some tanks could cause an exothermic reaction given a sufficient driving force, such as high temperatures. However, the difference between ignition temperatures and actual tank temperatures measured is so large that the probability of such a reaction is considered very low. The consequences of the postulated reaction are about the same as the scenarios for an explosion in a "burping" hydrogen tank. Although work on this issue is just beginning, consideration of hazards associated with heating nitrate-nitrite mixtures containing organic materials is an integral part of both the hydrogen and ferrocyanide tank efforts.

High concentrations of organic compounds have been inferred (from tank transfer, flow sheet records, and limited analytical data) in eight single-shell tanks. Many organic chemicals, if present in concentrations above 10 dry weight percent (sodium acetate equivalent), have the potential to react with nitrate-nitrites constituents at temperatures above 200 °C (392 °F) in an exothermic manner. The concentrations of organic materials in the listed single-shell tanks, and their chemical identity, is not accurately known at present. A tank sampling program has been planned to provide more information on the contents of these tanks and to serve as a basis for laboratory testing and safety evaluations.

Evaluation of records relating to material transfers to the remaining single-shell tanks and double-shell tanks continues. If additional tanks are identified that meet the organic concentration requirements, the tanks will then be added to the organic tank list.

BACKGROUND

Since the early 1940s, radioactive wastes from defense operations have been accumulating at the Hanford Site in underground waste tanks. Presently, there are 177 waste storage tanks at the Hanford Site, of which 149 are single-shell tanks and the remainder are double-shell tanks.

During the years of tank farms facilities operation, wastes have been systematically distributed among the tanks. In this process, two of the objectives were to segregate different types of wastes and to reduce the need for additional tanks. The known major constituents of the wastes are sodium nitrate, sodium nitrite, silicates, aluminates, hydroxides, phosphates,

sulfates, carbonates, organics, ferrocyanides, uranium, copper, and calcium in addition to the fission products present from the processing of irradiated fuel.

The presence of organic chemicals in Hanford Site waste storage tanks became an issue for reevaluation as a consequence of the U.S.S.R. releasing more information (Nikipelov 1957) on the explosion of a waste tank, on September 29, 1957, in Kyshtym, U.S.S.R. The U.S.S.R. tank exploded because of a mixture of oxidizing salts with organic chemical wastes was allowed to self heat to an explosion initiation temperature. The principal constituents in the tank that were the cause of this incident were sodium nitrate and sodium nitrite mixed with sodium acetate. There appears to be no similarity in waste composition between the Kyshtym tank to any of the Hanford Site tanks.

In the past, the potential for danger from reactions in organic constituents stored in the waste tanks has been studied at the Hanford Site. For example, in April 1976 a paper was published describing combustion studies with sodium nitrate (Bietel 1976). However, in keeping with the concerns at that time, this report was directed more towards the oxidative power of sodium nitrate than to the reactivity sensitivity of specific tank waste mixtures.

In 1989, renewed concern as a result of knowledge gained about the Kyshtym incident prompted a new study at the Hanford Site in 1989. This study included a series of 26 preliminary tests that examined the reactivity of waste tank acetate mixtures. The results were used to define an upper limit for an acceptable concentration of total organic carbon constituents in the wastes. The limit was defined as "10 percent organic equivalent weight to sodium acetate," which corresponds to approximately 3.0 percent "total organic carbon." Results of this study and process engineering knowledge of tank contents form the current basis for identifying tanks for the organic program. Presently, there are eight tanks listed on the organic programs, but further studies may add or subtract tanks from the list.

Process knowledge was needed to identify tanks for the organic program because of limitations in the historical records. In the past, records were generally maintained most accurately for radioactive constituents. At that time, the future need for detailed chemical constituent information was not anticipated.

Organic materials entered the tank waste streams in many forms and from a variety of processes. Such materials included solvents [e.g., NPH (normal paraffin hydrocarbon), hexone, and carbon tetrachloride], complexing agents [EDTA (ethylenediaminetetraacetic acid) and HEDTA (N-(hydroxyethyl)-ethylenediaminetriacetic acid], reagents for solvent actinide and fission product extraction, buffering or denitrification reagents (e.g., citric acid and sugar), and general laboratory reagents.

Tanks in the organic program may be subject to a number of operating restrictions to minimize the possibility of an unsafe event occurring. The following is a listing of activities that can be restricted for an organic tank:

- Waste transfers in and out of tanks
- Waste core sampling
- In-tank photography
- Work in primary tank air space or on the associated ventilation/exhaust systems
- Work in tank annulus or on associated annulus peripheral equipment
- Work in the vicinity of the tank or exhaust systems.

The Organic Tank Safety program covers a wide range of activities that include (1) characterization of the tank wastes, (2) an evaluation of the current criteria for listing tanks in the program, and (3) testing using simulated waste mixtures as well as corrective actions to the tank contents, if required. The program objective is to resolve safety issues associated with the tanks. Program closure is achieved when contents of all of the tanks are satisfactorily mitigated, remediated, or are determined to be readily amenable to interim stabilization before remediation or disposal.

Table I provides a listing of the eight organic tanks in the program.

Table I. Organic Waste Tanks.

Tank	Tank capacity kilogallons	Waste volume percent of tank capacity	Temperature fahrenheit	Waste heat load Btu/H
241-B-103	500	20	60	<10,000
241-C-103	500	40	131	18,000
241-S-102	750	100	109	11,900
241-SX-106	1,000	85	115	<<40,000
241-TX-105	750	85	103	20,000
241-TX-118	750	50	75	4,900
241-U-106	500	60	84	6,500
241-U-107	500	100	81	13,800

The tanks are listed because of the possibility of organic chemicals being present in quantities sufficient to sustain a reaction that may result in a potential for release of high-level waste due to uncontrolled increases in the temperature or pressure of the tank contents.

PROGRAM SCOPE AND OBJECTIVES

The overall scope of work for the program is to resolve the known safety and technical issues associated with the eight organic waste tanks. Resolution of these issues will lead to safe disposition of the tank contents either by mitigation, remediation, or interim stabilization until final disposal. Activities associated with issue resolution include, but are not limited to, short and long term safety assessments, management and control of tank storage operations, collection and analysis of tank historical information as well as characterization and testing of tank waste samples.

The principal objective of the program is centered on ensuring that safety, using safety evaluation techniques, for each listed tank. These evaluations will determine whether or not the tank contents are currently being stored safely. If it is determined that tank contents are not stored safely, then necessary remediation or mitigation action will be taken to ensure safe storage. In addition to the principal objective, the organic program also will review the results of characterization of other single-shell tanks to ensure that they do not pose a risk because of their organic contents. The single-shell tanks presently are being characterized under the environmental restoration/remediation action program. The object of the review will be to provide ensurance that tanks meet the criteria for safe interim storage of organic containing nitrite-nitrate wastes.

The work activity sequences associated with the program are depicted in the Organic Tank Program Logic Chart (Figure 1). Figure 1 depicts the relationships between the major program activities. It shows that two routes exist to achieve program closure. The direct route would be to discover a means of processing the tank contents that allows for safe storage without the activities covered by the Organic Tank Safety program.

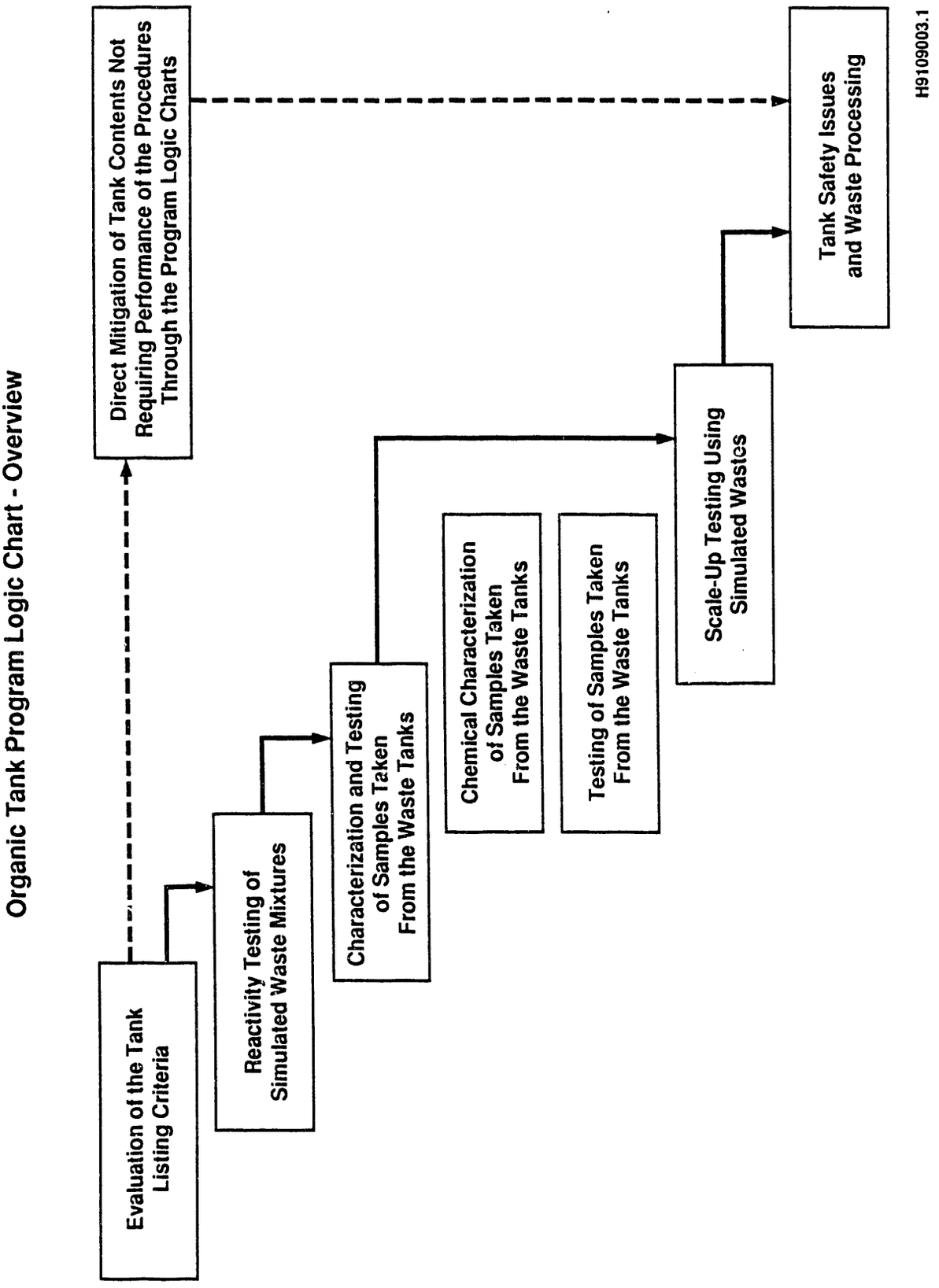
Evaluation of the Tank Listing Criteria

The first activity is to complete a comprehensive determination of the safety limits of organic waste constituents in the tanks. Completion of this task will allow for verification, through an operations safety review, of the existing criteria or its revision to a new standard. Achieving this objective also will allow for an evaluation of the maximum safe operating temperatures for the eight organic watch list tanks as well as other tanks that may be discovered to violate the operations safety review.

Reactivity Testing of Simulated Waste Mixtures

Simulated waste mixture testing will be done to define safe concentration limits for the variety of organic materials that may be in the wastes. Determinations of concentration effects on mixtures reactivities will be

Figure 1. Organic Tank Program Logic Chart.



performed using waste samples that approximate the tank contents. The samples will be gram quantities synthetic mixtures of organic chemicals that are the known major organic waste constituents with the oxidizing salts and diluents. Constituents used in test mixtures may not be limited to chemicals identified as present in large quantities in the waste tanks. Waste constituents that could act as catalysts or reaction initiators also will be tested.

Choices of the reference organics will be made based on available analytical data, process engineering knowledge, and chemical technical opinion. The initial test mixtures will be simple ones, of few components, followed by more complex mixtures to be tested for catalytic effects. The testing program will proceed by evaluating dilute to more concentrated organic-containing mixtures. The organic chemical components will be progressively increased in concentration, until preestablished safety values of the test parameters are reached. At this point, the safety limit for concentrations of the organic mixtures will be determined.

Compositions of the simulated waste mixtures will be corrected, as needed, when more information becomes available from tank waste characterizations. Such new information will be used to replace process engineering knowledge that served in the initial criteria for identifying watch list tanks.

Characterization and Testing of Samples Obtained From the Waste Tanks

Waste samples obtained from the tanks will be chemically characterized and tested for reactivity and shock sensitivity. Table II tabulates the information to be obtained. Such information will act as an aid for identifying mixture compositions that will be candidates for "scale-up" testing.

Test results of actual waste can be used to evaluate the degree of risk that can be associated with continued storage of organic containing waste in the tanks. This will be done after the waste samples had been sufficiently analyzed for constituent concentrations. The waste characterization results also will act as reference information in the design of mitigation, remediation or interim stabilization processes. Determination of chemical and physical properties to asses waste behavior will be a key factor in performing issue closure.

"Scale-Up" Testing using Simulated Wastes

Performing "scale-up" testing using larger (kilogram) quantities of materials is essential to determine the affects of increased mass on the hazard potential of waste mixtures. Testing will be performed with simulated wastes, where possible, to avoid the difficulties of handling radioactive materials under test conditions. Scale-up testing will determine more accurately if a dangerous mixture in a specific tank could heat up and, if not controlled, reach an exothermic reaction initiation temperature that leads to a runaway condition. It will be necessary to take into consideration the tank environment of the waste mixture in performing the testing. This will require knowledge of the heat capacities and thermal conductivities of the waste and associated tank materials.

Table II. Waste Characterization.

Chemical analysis to determine concentrations of: - organic constituents - oxidizing salts - diluents - potential catalysts - and reaction initiators.
A determination of the spatial distributions in the tanks of the organic waste constituents and other constituents that may interact with them.
Determinations of physical chemical parameters: - reaction initiation temperatures - reaction enthalpies - reaction propagation rates.
Estimates of sensitivities to reaction triggering phenomena: - electrostatic discharges - physical shock waves (impacts) - friction - radiation, nuclear and elctromagnetic - crystal energy relaxations.
Effect of temperature on triggering mechanisms

Tank Safety Issues and Waste Processing

Tank safety issues and waste processing includes actions found necessary for interim stabilization of the organic containing tanks. Such actions may require mitigation or remediation of the safety issue associated with a given tank contents before final waste disposal. Completion of this final objective for any of the listed tanks achieves program closure for that tank. Mitigation or remediation will not be required for tanks that are determined to be in a safe condition during the course of performing the program activities.

Literature Reviews

During the course of the program, reviews of existing literature and other information will be made on the following subjects:

- Reviews of tank history
- Reviews of the literature to determine how the waste composition can change as a function of time

- Reviews of the literature for leads on runaway reactions involving nitrate or nitrite systems
- Evaluation of the literature to assess the potential for processes that would concentrate the organics in the tanks
- Reviews of the literature to facilitate the development of chemical assay methods specific to different organic species
- Reviews of existing waste chemistry information for mitigation and remediation processes.

SUMMARY

The Organic Tank Program is one in which safety issues are being evaluated that are associated with storage of organic wastes in Hanford Site tanks. Currently, a listing of eight tanks are on the program tank listing. These tanks have extra safety precautions imposed on operational activities performed in and around the tank. The imminent danger from the tanks is considered to be very low because of the low maintenance temperatures of the tanks. However, an explosion of a waste tank in the U.S.S.R. has prompted a reevaluation of the tank safety for all tanks containing organic wastes.

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