

Strategy for Resolution of the Organic Complexant and Organic Solvent Safety Issues

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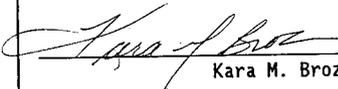
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**STRATEGY FOR RESOLUTION OF THE ORGANIC COMPLEXANT
AND ORGANIC SOLVENT SAFETY ISSUES**

EXECUTIVE SUMMARY

A basic strategy and logic for resolving the organic complexant and organic solvent safety issues are presented. Interim safe storage can be ensured in one of three ways:

(1) demonstrate through theory, modeling, sampling, and testing that the waste lacks sufficient fuel to combust; (2) show through modeling and monitoring that the waste contains sufficient moisture to prevent ignition and combustion; or (3) demonstrate that ignition sources are adequately controlled. Mitigation is required if controls are deemed inadequate.

Presently, no single alternative is believed sufficient to ensure interim safe storage for all organic tanks. Therefore, activities for all three alternatives are summarized in this strategy.

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LIST OF TERMS

EDTA	ethylenediaminetetraacetic acid
g/L	grams per liter
MJ/kg	megajoules per kilogram
TOC	Total Organic Carbon
wt%	weight percent

1.0 INTRODUCTION

1.1 OBJECTIVE AND SCOPE OF DOCUMENT

The objective of this document is to describe a general strategy for the resolution of the organic solvent and complexant safety issues. The strategy is comparable to the best practices in the chemical and petroleum industries (American Institute of Chemical Engineers 1989, 1992, 1995a, 1995c, 1995d, 1995e) and is applicable for all tanks with organic complexants and/or organic solvents. The scope of the strategy is limited to interim static storage and does not include dynamic operation such as retrieval or disposal operations.

1.2 THE ORGANIC COMPLEXANT HAZARD

During the defense mission at the Hanford Site, organic complexants including glycolic acid, citric acid, hydroxyethylethylenediaminetriacetic acid, and ethylenediaminetetraacetic acid (EDTA) were used during fuel reprocessing, metal recovery operations, and waste management separations. These materials were discharged to the tanks, where they mixed with sodium hydroxide, sodium nitrate and nitrite, and other inorganic diluents already present in the tanks. In the presence of oxidizing materials, such as nitrates or nitrites, organic complexants can be made to react exothermically by heating to high temperatures (above 220 °C) or by an initiator of sufficient energy (Fauske et al. 1995). Three hazards have been examined for organic complexants: (1) headspace flammability; (2) spontaneous chemical runaway (self heating) reactions occurring throughout the waste mass; and (3) ignition of propagating exothermic chemical reactions (combustion) typified by a moving reaction front.

1.2.1 Headspace Flammability

Although decomposition of organic complexants can generate flammable gases, organic complexant salts themselves are nonvolatile and exert no vapor pressure. Thus, organic complexant salts are not a headspace flammability hazard in Hanford Site waste tanks.

1.2.2 Spontaneous Chemical Runaway

The rate of heating must exceed the rate of cooling for a spontaneous chemical runaway reaction to occur (Gygax 1990). If the temperature is not controlled, then undesirable deflagrations can occur when the large activation energy barriers are exceeded. Preventing spontaneous chemical runaway has been thoroughly studied in the chemical and petroleum industries (American Institute of Chemical Engineers 1989, 1992, 1995a, 1995b, 1995c, 1995d, and 1995e). Hanford Site tank wastes have been assessed using similar methodology (Fauske 1996).

The potential for a spontaneous chemical runaway reaction was evaluated by comparing the characteristic time of cooling (i.e., the time required to reach a new equilibrium temperature following an instantaneous change in heating rate) with the waste storage time. Calculations indicate that the characteristic time of cooling ranges from a few hours to 3.1 years for the Hanford Site tanks (Fauske 1996). Some waste has been stored for more than 40 years, and there have been no transfers of waste into the single-shell tanks for about 15 years. Several characteristic times of cooling have passed during the last 15 years of storage; consequently, bulk runaway reactions are highly unlikely to be a hazard under current storage conditions.

In addition, no credible mechanisms to increase tank temperatures to chemical runaway reaction levels have been identified. Drying the wastes can decrease the thermal conductivity; however, this decrease would not be sufficient to lead to spontaneous chemical runaway (Fauske 1996). Waste temperatures after removal of the pumpable liquid (interim stabilization) have continued to decline consistent with the principal heat load from radioactive decay rates. One hundred fourteen of the 149 single-shell tanks have been interim stabilized.

1.2.3 Ignition of Organic Complexants

If enough fuel is present and the waste is sufficiently dry, an organic-nitrate/nitrite propagating combustion event could be initiated by a variety of sources. Potential credible ignition sources include hot metal objects, rotary core upsets, burning gasoline spills from a ruptured vehicular fuel tank, or lightning (Webb et al. 1995). An organic complexant propagating combustion event would lead to consequences above risk evaluation guidelines; therefore, ignition of organic complexants is addressed in this strategy document.

1.3 THE ORGANIC SOLVENT HAZARD

Various separation processes involving organic solvents have been used at the Hanford Site. These organic solvents were inadvertently and/or purposely sent to the underground storage tanks, and subsequent waste transfer operations might have distributed organic solvent among several of the 177 high-level waste tanks at the Hanford Site (Sederburg and Reddick 1994). The principal organic solvents are tributyl phosphate and mixtures of normal paraffinic hydrocarbons. The solvents are only partially soluble in the aqueous wastes and can therefore exist either in separate phases dispersed among other liquid and solid phases or in a separate layer atop the aqueous phase. Three potential hazards have been identified for organic solvents: (1) contribution to headspace flammability; (2) spontaneous chemical runaway; and (3) ignition of organic solvents that are entrained in the waste or pooled on the waste surface.

1.3.1 Headspace Flammability

At current tank temperatures, the organic solvent vapor contribution to headspace flammability is low (Claybrook and Wood 1994). Most of the organic solvents remaining in the tanks have low vapor pressures. Sampling data from all tanks sampled to date supports this conclusion (Huckaby et al. 1995). Organic solvent vapors in tank 241-C-103 (which contains a floating organic solvent layer) amount to less than 5% of the lower flammability limit (Huckaby and Story 1994, Postma et al. 1994). Consequently, organic solvents do not constitute a headspace flammability hazard as presently stored in the tanks.

1.3.2 Spontaneous Chemical Runaway

As discussed in Section 1.2.2, the potential for spontaneous chemical runaway has been assessed for the Hanford Site tanks (Fauske 1996). Several characteristic times of cooling have passed during waste storage, and bulk runaway reactions are not a hazard under current storage conditions. This conclusion is applicable whether the fuel source is organic complexants or organic solvents.

1.3.3 Ignition of Organic Solvents

Organic solvents can be entrained or dispersed throughout a waste, or may be present in a separate layer. If a portion of the organic solvent were heated to the flash point by a large initiator, combustion in air would ensue. An organic solvent combustion might lead to consequences above risk evaluation guidelines (Postma et al. 1994); therefore, ignition of organic solvents is addressed in this strategy document.

1.4 CONDITIONS NECESSARY FOR COMBUSTION

An organic solvent or organic complexant combustion event cannot occur unless oxygen (oxidizer), fuel, and temperature (initiators) are all present in sufficient amounts. Because all three conditions must be sufficient for a reaction to occur, waste can be stored safely if one or more of the conditions for reaction are not met. Therefore, the strategy is to demonstrate that one of the conditions of fuel, oxidizer, or temperature (initiators) is not sufficient or that at least one condition is controlled or mitigated.

If sufficient fuel and oxidizer are present, moisture can prevent combustion of organic complexants. Moisture prevents combustion by two main mechanisms: (1) moisture behaves as an inert diluent (lowering the effective fuel concentration); and (2) moisture provides a large heat sink that inhibits ignition and propagation. For a reaction to propagate, enough energy must be supplied to overcome the sensible and latent heat of the moisture present.

Small ignition sources such as sparks, impacts, and shocks lack sufficient energy to initiate an organic complexant or organic solvent combustion. Credible ignition sources have been narrowed to only robust or sustained energy sources. Administrative controls have been implemented in the tank farms to reduce the potential to introduce ignition sources (WHC 1996). Controls will remain in place on a tank until removal of the controls can be technically justified.

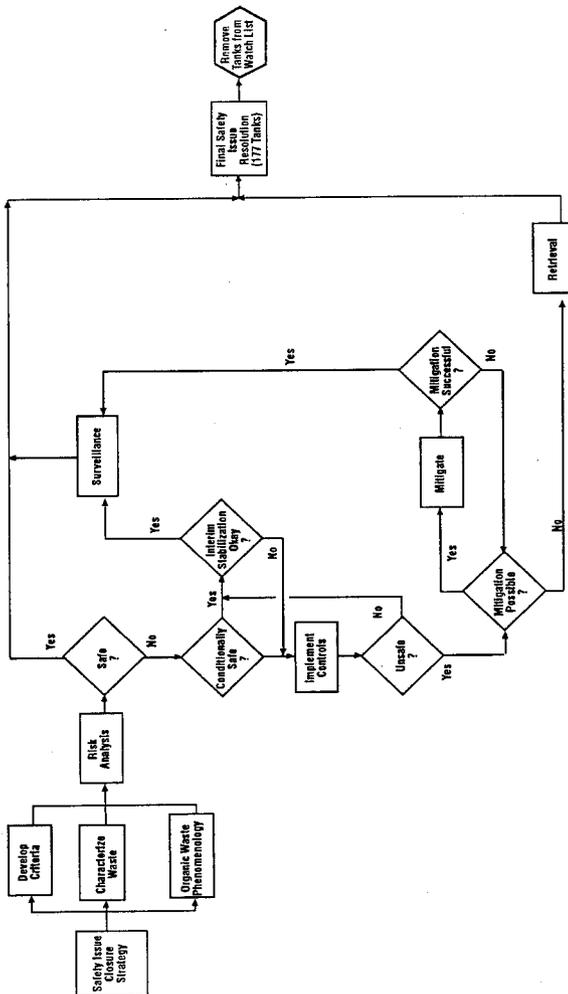
2.0 STRATEGIC LOGIC FOR RESOLUTION OF THE SAFETY ISSUES

The strategic logic (see Figure 2-1) for resolution of the safety issues is comprised of four elements.

- Element 1. Identification of the applicable organic safety issue. This element of the strategy was discussed in Section 1.0.
- Element 2. Identification of criteria and conditions under which the wastes can be safely stored. Safe storage criteria are discussed in Section 3.0.
- Element 3. Theory, modeling, sampling, and testing are used to develop an understanding of waste phenomenology. The technical information is critically evaluated in a risk-based assessment to determine the safety status of the waste, and the tanks are categorized as *safe*, *conditionally safe*, or *unsafe*. Specific tasks that examine waste phenomenology are listed in Section 4.0.
- Element 4. The safety issues are resolved by demonstrating one of the following: (1) the waste lacks sufficient fuel concentration for a propagating combustion; (2) the waste retains sufficient moisture to prevent a propagating combustion; or (3) credible ignition sources are precluded through controls or the conditions are mitigated. Monitoring and mitigation are discussed in Section 5.0.

Presently, it is not possible to rule out that any given tank will be placed in one of the three categories. Therefore, activities for all three eventualities are presented in this strategy.

Figure 1. Strategy for Resolution of the Organic Safety Issues.



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3.0 CRITERIA FOR SAFE STORAGE

3.1 ORGANIC COMPLEXANT CRITERIA

Specific conditions of fuel, moisture, and temperature (initiators) are all required in order for a propagating combustion event to occur. Based on an initial evaluation (Babad and Turner 1993), the current fuel and moisture criteria are 3 wt% total organic carbon (TOC) and 17 wt%, respectively. However, recent theoretical analyses and experiments with waste simulants indicate the minimum fuel concentration is considerably higher (Fauske et al. 1995).

The minimum required fuel concentration has been determined using a contact-temperature ignition model (Fauske et al. 1995). Experiments with waste simulants indicate that a necessary (but not sufficient) condition for a condensed-phase propagating chemical reaction is that the fuel concentration be greater than 4.5 wt% TOC (1.2 MJ/kg on an energy equivalent basis). For fuel concentrations between 4.5 and 7.9 wt% TOC (dry basis), the waste moisture concentration required to prevent a propagating combustion varies linearly from 0 to 20 wt%. Above 20 wt%, the fuel-moisture linear relationship no longer holds because the mixture becomes liquid continuous. A stoichiometric fuel-oxidizer mixture will not propagate when the moisture concentration exceeds 20 wt% (Fauske et al. 1995). These new criteria are being confirmed on actual waste samples (Bechtold 1996).

In summary, safe storage can be assured if the following inequalities are met (Equations 1 and 2):

$$\text{wt\% TOC} \leq 4.5 + 17 x_w \quad (1)$$

or in terms of energy (ΔH)

$$\Delta H (\text{MJ/kg}) \leq 1.2 + 4.5 x_w \quad (2)$$

where x_w is the mass fraction of water for values less than 0.2 (20 wt%).

3.2 ORGANIC SOLVENT CRITERIA

Experiments and analyses have improved understanding of the phenomena associated with potential organic solvent combustion in Hanford Site tanks (Fauske 1996). Results of the experiments indicate that the organic solvents currently in Hanford Site tanks are difficult to ignite. Credible ignition sources have been narrowed to robust and/or sustained energy sources.

Even if organic solvent could be ignited, radiological consequences from such a combustion event would be within risk evaluation guidelines if an adequate vent path were available. The vent requirements are determined by comparing calculated headspace pressure increases to tank design pressure. An organic solvent combustion event would heat tank headspace gases and pressurize the tank. The combustion event would continue until the oxygen was depleted. The pressurization from a postulated combustion event would increase with the flame spread rate. If an adequate vent path were available, the tank dome would not fail and the radiological consequences would be within risk evaluation guidelines. Therefore, it is desired to identify which tanks might contain the equivalent of a one-square-meter or larger pool of organic solvent.

A direct relationship exists between liquid organic solvent in a tank and the organic solvent vapors found in the headspace. The mass transfer of a semivolatle species in an organic liquid (e.g., dodecane, tridecane, or tributyl phosphate) to the headspace vapor is determined by several parameters, including temperature, the mass transfer coefficient, gas-liquid contact area, ventilation flow rate, and headspace volume. If organic solvent is present, organic solvent vapors should be detectable in a tank headspace, even if the tank is actively ventilated. Most single-shell tanks are only passively ventilated (i.e., the ventilation flow rate is quite small); thus, the organic solvent vapors should be present at about equilibrium concentrations. Indeed, this was the case for tank 241-C-103, which contains a floating organic solvent pool (Huckaby and Story 1994).

Organic vapor screening criteria are being drafted. The concentration of total nonmethane hydrocarbons will be measured and compared to the concentration anticipated from a one-square-meter pool at tank temperature. If the total nonmethane hydrocarbon concentration criterion is exceeded, then the required vent path area will be calculated. The vent path area will be checked against this calculation, and if the actual vent path area is inadequate, then controls against potential ignition sources will be required. Mitigation, such as increasing the vent path area, will be required if controls are deemed inadequate.

4.0 WASTE PHENOMENOLOGY

Waste phenomenology will be assessed using many sources of information. In addition to the information generated within the organic safety program, new research programs on the chemical and physical behavior of tank wastes have been initiated by the Basic Energy Sciences and Environmental Management divisions of the Department of Energy. This information will supplement the information derived from the activities described in this section.

4.1 IDENTIFICATION OF ORGANIC WASTE TANKS

One of the most challenging tasks in the resolution of the safety issues is the accurate identification of the organic tanks. No single approach appears sufficient to identify organic tanks, but a combination of information sources can be used to achieve this goal. Organic tanks are being identified using historic data, waste transfer records, waste processing data, and recent sampling data (headspace vapors and condensed phase). Information will be examined on a tank-by-tank basis or on a farm-by-farm basis to determine whether a tank or a group of tanks contains sufficient organic material to be deemed a potential hazard.

4.1.1 Historical Records

Historical sampling data, waste transfer records, and waste processing data are being systematically evaluated to develop organic content models (Toth et al. 1995, Webb et al. 1995, Agnew 1996). Some of the work provides scoping information regarding the quantity and type of material that was purchased and used at Hanford. Other information provides averages of the types of wastes that were dispersed to different tank farms. In some instances, detailed information concerning the substances that were discharged into a particular tank are available from process data (Agnew 1996).

Modeling activities will continue to examine tank grouping schemes and organic concentration estimates. Generalized conclusions on waste conditions may be appropriate within a waste type, within a tank, or across a family of similar tanks, depending on the model and the confidence in the model. Models will be benchmarked through sampling and characterization.

4.1.2 Characterization

The total organic carbon content of many of the Hanford Site wastes has been measured in the past, and additional measurements will be made during the current characterization program (Turner et al. 1995). The exothermic energy concentration and moisture concentration of the waste will also be measured. These measurements do not discriminate among the different organic species found in the wastes, but these two parameters are central to the ignition and combustion characteristics of the waste.

The energy content of the principal waste constituents has been evaluated theoretically and empirically (Burger 1993, Scheele et al. 1995, Fauske 1996). There are large differences in the energy liberated and the propagating combustion behavior of the different organic molecules. For example, EDTA is a relatively energetic species; however, radiolysis destroys this material under waste storage conditions. By contrast, sodium oxalate

(a relatively long-lived product of radiolysis) has a low energy content and cannot support a propagating combustion even under stoichiometric conditions (Fauske et al. 1995). Therefore, future work will include combustion testing and organic chemical speciation of actual waste. These data will be used to corroborate organic aging and solubility models.

4.2 FUEL CONCENTRATION

4.2.1 Propagating Combustion Testing

Consistent with procedures developed by the American Institute of Chemical Engineers, the energy concentration of actual waste will be screened by differential scanning calorimetry and determined by adiabatic calorimetry. If screening definitely indicates that exothermic decomposition of the waste has occurred, then additional measurements will be conducted using adiabatic calorimetry.

The reasons for adiabatic calorimetry testing are twofold. First, relatively large samples (five grams or more) are tested; results from larger samples provide greater assurance that the sample tested is representative of the bulk of the sampled material. Second, the observed self-heating behavior yields evidence about kinetics and energetics of the reactions in dried waste, and is a direct test for a propagating combustion. Those materials that propagate show a dramatic step increase (a sharp peak) in the self heating rate, while the materials that do not propagate show a more gradual increase (typical Arrhenius behavior).

Waste samples from six tanks (241-AN-107, -BY-104, -BY-108, -C-201, -C-204, and -SY-101) have been tested by adiabatic calorimetry (using the Reactive System Screening Tool).¹ None of the wastes tested supported a propagating combustion event. Adiabatic calorimetric measurements will be obtained on waste samples from many more tanks in fiscal years 1997 and 1998.

4.2.2 Organic Decomposition (Aging)

Studies indicate that organic complexants and solvents undergo hydrolytic and radiolytic decomposition (aging) under tank waste conditions (Camaioni et al. 1994, 1995). However, the influence of temperature and radiation dose on the rate of these reactions is not sufficiently defined to quantify aging. Kinetic data for these decomposition reactions are being investigated using waste simulants. The composition of actual waste will be examined to corroborate aging in the tanks.

¹Trademark of Fauske and Associates, Inc. of Burr Ridge, Illinois.

The amounts of organic chemicals that were transferred into the tanks are so large that the substances formed as byproducts may become important constituents of the waste. Most of these byproducts are unstable and quickly convert to other less reactive materials by radiolysis or hydrolysis. However, it is not assumed that this situation prevails universally. Chemical speciation and propagating combustion testing will also help address these issues.

All available surveillance records are being examined to assess the temperature and radiation dose histories of the organic complexant wastes. Once confirmed by organic speciation, the aging model could be used in conjunction with the historical data, characterization data, and other information to estimate current and future organic concentrations.

4.2.3 Organic Solubility

The solubility properties of organic complexants (organic solvents are essentially insoluble) are being investigated (Barney 1994, 1996). Tests with waste simulants indicate that with the important exception of sodium oxalate, all the other sodium carboxylate salts and their principal decomposition products are very soluble in the alkaline supernatant solutions in the tanks. If the energetic complexants are present in the non-combustible aqueous phases, then most of the fuel could be removed by interim stabilization (pumping of the liquid from the tanks).

Supernatant solutions from 61 tanks have been analyzed for total organic carbon concentration. Only five of these tank supernatants had total organic carbon concentrations greater than 14 g/L (Van Vleet 1993a, 1993b). The highest measured value for total organic carbon was about 40 g/L. This value is substantially below the measured solubility limit for the energetic complexants (EDTA, nitrilotriacetate, glycolate, succinate, dibutylphosphate, and citrate), which is about 100 g/L. Therefore, it is anticipated that most all of the energetic complexants are contained in the liquid phase.

Additional work on organic solubility is needed to investigate: (1) the influence of high valent ions; (2) the effect of solution densities; (3) the impact of having many organic species; and (4) the effect of organophosphate compounds in the liquid waste. Results with waste simulants will be confirmed through analysis (organic speciation) of actual waste samples.

4.3 MOISTURE CONCENTRATION

If sufficient fuel and oxidizer are available, moisture can play a key role in preventing an organic complexant propagating combustion event. Waste that contains greater than 20 wt% water cannot support a propagating combustion event, even under stoichiometric fuel-oxidizer conditions (Fauske 1996). Also, experiments on simulants indicate that many of the postulated ignition scenarios can be excluded from consideration if the surface layer of the waste has more than about 5 wt% water (Fauske 1996).

Because of the importance of moisture in ensuring safe storage, studies are underway to determine the factors that govern moisture retention and dryout of the organic wastes. Important parameters include the tank breathing rate, relative humidity, and the physical/chemical properties of the waste. Tank breathing rates will be measured using gas tracer studies. Experiments on waste simulants and actual waste samples are investigating the effect of relative humidity on the rate of dryout. These experiments will also determine the final (minimum) equilibrium moisture concentration in the waste. Results will be coupled with theoretical work to develop a predictive model for moisture concentration.

4.4 IGNITION REQUIREMENTS

Tube propagation tests with waste surrogates and theoretical analyses have shown that ignition sources greater than three joules are required to initiate an organic complexant propagating combustion event (Fauske et al. 1995, Fauske 1996). Organic solvents are even more difficult to ignite. Hot steel spheres (up to 270 joules) and an electronic match (about 138 joules) failed to ignite organic solvent simulant (dodecane) during ignition experiments (Fauske 1996). Sparks, impacts, and shocks lack sufficient energy to ignite organic complexants or organic solvents.

It may be possible to show that no credible initiators exist for an organic solvent or organic complexant combustion event, or that the presence of water greatly diminishes the risk of initiation of such reactions. Therefore, laboratory tests using waste simulants are being conducted to define the energy requirements for ignition of the dry wastes, and to determine the minimum waste moisture concentrations required to preclude initiation of organic complexant propagating combustions. Work will also continue on examining ignition source requirements for organic solvent pools and entrained organic solvent.

4.5 RISK ANALYSIS

Information from historical records, characterization, propagating combustion testing, organic aging experiments, and organic solubility testing will be critically evaluated in a risk based assessment. This risk analysis will be used to determine the safety status of the waste and to direct any necessary monitoring or mitigation activities.

5.0 MONITORING AND MITIGATION

For waste tanks that lack sufficient fuel to sustain a propagating combustion event, safe interim storage can be achieved through prudent waste management operations or minimal interim operational safety requirement controls. Monitoring is not required for these tanks.

5.1 MONITORING

If it is not possible to demonstrate that a waste cannot combust, monitoring might be required to confirm interim safe storage of organic waste. Monitoring is also required on the 20 organic tanks identified in response to the Wyden Amendment (Public Law 101-510, Section 3137 [1990]). The Wyden Amendment states that "the Secretary shall determine whether continuous monitoring is being carried out to detect a release or excessive temperature or pressure at each tank so identified." Temperature and pressure monitoring are discussed below. Because of the importance of moisture, moisture monitoring is also discussed below.

5.1.1 Temperature and Pressure Monitoring

In the unlikely circumstance of an organic complexant or organic solvent combustion event, temperature/pressure monitoring would detect the occurrence in real time. Temperature/pressure monitoring would not facilitate interdiction of an event because pressures capable of compromising dome integrity are reached in less than one hour (effectively precluding the possibility of timely interdiction).

Temperature/pressure monitoring might, however, facilitate timely implementation of emergency response measures. Therefore, such monitoring has a significant benefit. For each tank at risk from an event, the strategy is to have either continuous temperature monitoring or continuous pressure monitoring.

5.1.2 Moisture Monitoring

Moisture can prevent combustion of waste that contains sufficient fuel and oxidizer to otherwise combust. Routine, in situ measurements of the moisture concentration of the wastes provide a secure basis for evaluating their safety. Development work will continue on moisture monitoring until the monitoring equipment and procedures can be integrated into normal tank farm operations.

5.2 MITIGATION

If controls alone are not adequate to prevent credible ignition sources from contacting dry reactive waste, then mitigation will be required. The simplest mitigation scheme is to add water to the tanks. However, many of the single-shell tanks are assumed leakers. Therefore, a carefully controlled system for adding the minimum water required for safety is under development. If mitigation is not possible, then retrieval and remediation are necessary.

6.0 CONCLUSIONS

Three alternative paths for resolving the organic safety issues are being pursued simultaneously: (1) demonstrate through theory, modeling, sampling, and testing that the waste lacks sufficient fuel to combust; (2) show through modeling and monitoring that the waste contains sufficient moisture to prevent ignition and combustion; or (3) demonstrate that ignition sources are adequately controlled. Mitigation is required if controls are deemed inadequate. Presently, no single alternative is believed sufficient to ensure interim safe storage for all organic tanks. Therefore, activities for all three approaches are planned. The organic safety program work will continue until the necessary equipment and procedures are integrated into normal tank farm operations.

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