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Mixing of Incompatible Materials in Waste Tanks Technical Basis Document

K. R. Sandgren
CH2M HILL Hanford Group, Inc.
Richland, WA 99352
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This document presents onsite radiological, onsite toxicological, and offsite toxicological consequences, risk binning, and control decision results for the mixing of incompatible materials in waste tanks representative accident.

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Mixing of Incompatible Materials in Waste Tanks Technical Basis Document

Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management

CH2MHILL
Hanford Group, Inc.
Richland, Washington

Contractor for the U.S. Department of Energy
Office of River Protection under Contract DE-AC27-99RL14047

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Prepared By
K. R. Sandgren
CH2M HILL Hanford Group, Inc.

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CH2MHILL
Hanford Group, Inc.

P. O. Box 1500
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LIST OF TERMS

AC	administrative control
ARF	airborne release fraction
DCRT	double-contained receiver tank
DSA	documented safety analysis
DST	double-shell tank
HEPA	high-efficiency particulate air (filter)
PFP	Plutonium Finishing Plant
SMP	safety management program
SOF	sum of fractions
SSC	structures, systems, and components
SST	single-shell tank
TEEL	Temporary Emergency Exposure Limit
TSR	technical safety requirement
TWG	Technical Working Group
ULD	unit-liter dose

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1.0 INTRODUCTION

1.1 PURPOSE

This technical basis document was developed to support the Tank Farms Documented Safety Analysis (DSA) and describes the risk binning process, the technical basis for assigning risk bins, and the controls selected for the mixing of incompatible materials representative accident and associated represented hazardous conditions. The purpose of the risk binning process is to determine the need for safety-significant structures, systems, and components (SSCs) and/or technical safety requirement (TSR)-level controls for a given representative accident or represented hazardous conditions based on an evaluation of the frequency and consequence. Note that the risk binning process is not applied to facility workers, because all facility worker hazardous conditions are considered for safety-significant SSCs and/or TSR level controls. (See RPP-14286, *Facility Worker Technical Basis Document).* Determination of the need for safety-class SSCs was performed in accordance with DOE-STD-3009-94, *Preparation Guide for U.S. Department of Energy Nonreactor Nuclear Facility Documented Safety Analyses*, as described below.

1.2 BACKGROUND INFORMATION

1.2.1 Representative Accident

Routine tank farm operations include a number of material transfer activities such as waste transfers between tanks, incoming waste transfers from non-tank farm facilities (e.g., Plutonium Finishing Plant [PFP], 222-S Laboratory, T-Plant), and bulk chemical additions to double-shell tanks (DST) for corrosion control. When considering the related hazards within tank farms, it was postulated that the mixing of incompatible material in a waste tank could result in a chemical reaction that produces aerosols and enough internal pressure to expel headspace gases, vapors, and aerosolized waste. Incompatible materials that could potentially be transferred to tank farm facilities were studied to determine a bounding case. The scenarios that were considered were:

Scenario 1. Addition of an incompatible material due to a waste transfer from an internal or external source
- Case A. Misrouting or transfer of incompatible tank waste
- Case B. Incompatible waste addition from external source.

Scenario 2. Inadvertent addition of an incompatible chemical due to a vendor or paperwork error when making a chemical addition to a tank
- Case A. Addition of excess base to a waste tank
- Case B. Addition of acid to a waste tank waste.

As the tank wastes are similar, reactions due to a transfer from one tank to another will not result in a significant release according to Reynolds, 2001, "Potential for Tank Farm Systems to Give Off Toxic Chemicals or Pressurizing Due to Chemical Incompatibility." Reynolds (2001) was

included as an appendix to RPP-9689, *Offsite Radiological Consequence Calculation for the Bounding Mixing of Incompatible Materials Accident.* Therefore, Case A of Scenario 1 was discarded as a potential bounding case.

The majority of waste that is generated externally to tank farms would come from the PFP, the 222-S Laboratory, and T-Plant. Each of these facilities utilizes practices that ensure the final facility waste solution is not transferred to incompatible tank waste. In addition, the transfer lines are not compatible with strong acids (the most common incompatible material) and would fail before large volumes could be transferred. Therefore, Case B of Scenario 1 was discarded as the bounding case.

Inadvertent addition of chemicals was then examined. The addition of excess base to tank waste was examined for the potential to react and produce ammonia. Substantial amounts of ammonia are dissolved or trapped in some tank wastes. Ammonia is produced by the decomposition of nitrogen-containing compounds that were added to process solutions that eventually ended up as waste. Amine chelating agents such as ethylenediaminetetraacetic acid are among the chief sources. There is some potential for the ammonia in these wastes to be released into the vapor space of tanks and vented to the atmosphere.

The solubility of ammonia increases with decreasing pH due to an increasing fraction of the dissolved ammonia existing as the ammonium ion. As pH is raised, the ammonium ion is converted to the neutral, molecular ammonia solute (aqueous NH_3). The neutral aqueous ammonia desorbs to become gaseous or vapor phase ammonia. The main reactions are as follows:

$$NH_4^+ + OH^- \rightleftharpoons NH_{3(aqueous)} + H_2O$$
$$NH_{3(aqueous)} \rightleftharpoons NH_{3(vapor)}.$$

The potential exists for strong bases to be accidentally added to waste tanks in amounts that may reduce the solubility of ammonia. A series of calculations were performed to predict the solubility of ammonia in a simulated waste and the effect of adding various amounts of 100% sodium hydroxide to the worst-case tank waste. It was found that a large amount of sodium hydroxide (slightly over 4 moles/L of waste) must be added to reach the ammonia saturation point before any ammonia is released by the reaction. An estimate of the bounding ammonia release was calculated in WHC-SD-WM-CN-074, *Chemical Reaction in a DCRT Leading to a Toxic Release.* It was shown that the consequences of an ammonia release are well within conservative guidelines. Therefore, Scenario 2, Case A, was not selected as the representative case.

Since direct chemical additions can be made to the waste tanks, an accident was postulated in which bulk delivery of an unexpected chemical is made to a waste tank (e.g., instead of the caustic addition expected, the delivery truck contains an acid). Since the delivery was assumed to be from a large tanker truck, only common chemicals that are routinely shipped in bulk quantities were considered. Common industrial acids were evaluated for their potential to react with tank waste resulting in vapor generation. Sulfuric acid was found to react the most exothermically with tank waste producing large quantities of steam. The addition of concentrated sulfuric acid to the tank waste was identified as the bounding case and is presented here.

1.2.2 Bounding Offsite Accident

The mixing of incompatible materials accident is the bounding, low-energy atmospheric vapor/gas/aerosol release event, and has been quantitatively analyzed for comparison to the DOE-STD-3009-94, Appendix A, "Evaluation Guideline," of 25 rem. The bounding quantitative analysis for the mixing of incompatible materials accident is documented in RPP-9689, and shows that offsite radiological consequences are less than 1 rem. Therefore, no safety-class equipment or TSR-level controls need to be considered for offsite radiological exposures for any of the low-energy atmospheric vapor/gas/aerosol release events. It is important to note that DOE-STD-3009-94 does not provide any other evaluation guidelines (i.e., evaluation guidelines are not provided for offsite toxicological, onsite radiological, and onsite toxicological exposures). These exposures were evaluated for the representative accident and associated hazardous conditions in accordance with the risk binning process described in Section 1.3.

1.2.3 Associated Hazardous Conditions

In addition to the hazardous condition that defines the representative accident, the current hazard evaluation database lists a number of hazardous conditions that are represented by the mixing of incompatible materials accident. The hazardous conditions typically involve chemical reactions caused by mixing incompatible materials and are postulated to occur in the various tanks (DSTs, single-shell tanks [SST], and double-contained receiver tanks [DCRT]). Also grouped under the mixing of incompatible materials representative accident are various types of conditions that result in the release of ammonia vapors. The ammonia release conditions were assigned to the mixing of incompatible materials accident because they most closely resembled the ammonia releases that were due to the inadvertent addition of excess base. Some type of waste disturbing activity is generally the cause of these ammonia release events.

1.3 RISK BINNING METHODOLOGY

The risk binning process was conducted in accordance with direction provided by the U.S. Department of Energy, Office of River Protection (Klein and Schepens, 2003, "Replacement of Previous Guidance Provided by RL and ORP"). Risk binning begins with a qualitative evaluation of the frequency and consequence of the representative accident. Consequences are evaluated for the following receptors and exposures: offsite toxicological, onsite radiological, and onsite toxicological. These consequences are assigned to one of three categories: high, moderate, or low. Based on the frequency and consequence, risk bins (ranging from I to IV) are assigned. It is important to note that for offsite toxicological, onsite radiological, and onsite toxicological exposures, safety SSCs and/or TSR-level controls are required for accidents or hazardous conditions that are assigned to risk bins I or II, and are considered for accidents or hazardous conditions that are assigned to Risk Bin III. For accidents or hazardous conditions assigned to Risk Bin IV, safety SSCs and TSR-level controls are not expected. Safety management programs (SMP) are acceptable for addressing the residual risk posed by Risk Bin IV conditions. Table 1 and 2 show the criteria for assigning the frequency and consequence categories, and the risk bins, which are assigned to the various combinations of frequency and consequence. After the risk binning process is completed for the representative accident, the

process is then repeated for the represented hazardous conditions associated with the representative accident.

Table 1. Offsite (Toxicological Only) Risk Bins.

Consequence category (toxicological only[1])	Event frequency			
	$<10^{-6}$/yr Beyond extremely unlikely	**10^{-4} to 10^{-6}/yr Extremely unlikely**	**10^{-2} to 10^{-4}/yr Unlikely**	**$>10^{-2}$/yr Anticipated**
>ERPG-2 / TEEL-2 (High)	III	II	I	I
>ERPG-1 / TEEL-1 <ERPG-2 / TEEL-2 (Moderate)	IV	III	II	I
< ERPG-1 / TEEL-1 (Low)	IV	IV	III	III

safety SSCs and/or TSR-level controls required.

safety SSCs and/or TSR-level controls considered.

[1] Radiological consequences for the offsite receptor are evaluated in accordance with DOE-STD-3009-94, 2002, *Preparation Guide for U.S. Department of Energy Nonreactor Nuclear Facility Documented Safety Analyses*, Change Notice No. 2, Appendix A, U.S. Department of Energy, Washington D.C.

ERPG = emergency response planning guideline.
SSC = structures, systems, and components.
TEEL = Temporary Emergency Exposure Limit.
TSR = technical safety requirement.

Table 2. Onsite (100 m) Risk Bins.

Consequence category (radiological/ toxicological)	Event frequency			
	$<10^{-6}$/yr Beyond extremely unlikely	**10^{-4} to 10^{-6}/yr Extremely unlikely**	**10^{-2} to 10^{-4}/yr Unlikely**	**$>10^{-2}$/yr Anticipated**
>100 rem >ERPG-3 / TEEL-3 (High)	III	II	I	I
25 to 100 rem >ERPG-2 / TEEL-2 <ERPG-3 / TEEL-3 (Moderate)	IV	III	II	I
<25 rem <ERPG-2 / TEEL-2 (Low)	IV	IV	III	III

safety SSCs and/or TSR-level controls required.

safety SSCs and/or TSR-level controls considered.

ERPG = emergency response planning gideline.
SSC = structures, systems, and components.
TEEL = Temporary Emergency Exposure Limit.
TSR = technical safety requirement.

Environmental consequences are also assigned during the risk binning process. There are four categories of environmental consequences (E0, E1, E2, and E3, in order of increasing severity); these categories are defined in Table 3.

Table 3. Environmental Consequence Categories.

Category	Definition
E3	Offsite discharge or discharge to groundwater
E2	Significant discharge onsite
E1	Localized discharge of hazardous material
E0	No significant environmental consequence

2.0 RISK BINNING RESULTS

A risk binning team meeting was conducted on July 17, 2002, to obtain consensus on the assignment of frequencies, consequences, and risk bins. The attendees represented a wide range of expertise in the areas of engineering, licensing, and operations, and included representatives from the U.S. Department of Energy, Office of River Protection. Appendix A lists the attendees and the organization each attendee represents. After the meeting, the risk binning results were distributed to the Technical Working Group (TWG) for review and concurrence. The TWG concurred with the final risk bin results, which are summarized in Tables 4 and 8. See RPP-15116, *Proceedings of the Nuclear Working Group and the Technical Working Group.*

2.1 MIXING OF INCOMPATIBLE MATERIALS REPRESENTATIVE ACCIDENT WITHOUT CONTROLS

2.1.1 Accident Scenario

Large quantities of sodium hydroxide or sodium nitrite are added to DSTs, as necessary, to maintain the waste chemistry within the limits specified in the corrosion control program. These chemicals are delivered in tanker trucks and typically are added directly to the DST that requires chemical adjustment.

In the accident scenario without controls, the wrong chemical is delivered and 5,000 gal of concentrated sulfuric acid is added to a DST or DCRT. Heat is generated in the tank due to the dilution and neutralization of the acid. The acid-waste mixture heats up and begins to boil. The tank pressurizes and the high-efficiency particulate air (HEPA) filters fail. Aerosolized waste is released as a result of the tank pressurization.

2.1.2 Frequency Determination

A frequency of "unlikely" was qualitatively assigned to the mixing of incompatible materials representative accident. The initiating event (an inadvertent acid addition to a DST or DCRT) is considered "anticipated" because it is due to human error. However, an inadvertent addition to a nominal tank (with respect to waste volume and hydroxide concentration) would not result in a significant release. In order for the accident to result in significant consequences, two conditions must be met. The receiving tank must (1) have a hydroxide concentration close to the bounding value of 5 molar and (2) contain a minimal volume of waste. (Quantities greater than 60,000 gal would not result in a release, while extremely small volumes or lower hydroxide concentrations would not completely neutralize the waste lowering the energy released.) These conditions do not currently exist but may be seen during waste retrieval. However, a DST or DCRT with only a small heel of waste that is rich in hydroxide is not a likely candidate for a bulk chemical addition. Also, the addition is assumed to consist of a bounding volume of the most energetic pure common industrial acid. If the acid concentration was less than 14 molar, the consequences would be negligible. Therefore, the accident was split into two conditions: an "unlikely" event

where the combination of bounding conditions produces the bounding consequences, and an "anticipated" event where more realistic conditions produce low consequences.

2.1.3 Consequence Determination

This scenario of a bulk addition of acid to a DST or DCRT has not been previously analyzed. To provide an estimate of the radiological and toxicological consequences, calculations were performed and are documented in Appendix B. The analyzed scenario assumes that a cargo tanker filled with 5,000 gal of 100% sulfuric acid (18.7 M) is inadvertently emptied into a tank at an assumed addition rate of 175 gal/min. The receiving tank is assumed to contain a small quantity of waste (50,000 gal for the DST case) with a high sodium hydroxide concentration that is sufficient to completely neutralize the incoming acid. This assumption ensures that the heat of reaction is distributed across a minimal volume of waste. The reaction between the sulfuric acid and sodium hydroxide is conservatively assumed to occur instantaneously. The reaction produces sufficient energy to heat the acid-waste mixture to the boiling point. The remainder of the energy produces steam. This vaporization of water results in the buildup of aerosols in the tank headspace and pressurizes the tank. The HEPA filters are assumed to fail. Although the contribution from a potential dome collapse was considered, it was not included because the pressure buildup from boiling would not be instantaneous, allowing pressure relief due to lifted cover blocks, or other factors. This is a departure from the more conservative offsite radiological consequence analysis documented in RPP-9689, where a dome collapse is assumed. The DCRT case assumed a 25,000 gal waste volume with the bounding caustic concentration found in DCRTs. The calculations documented in Appendix B for the DCRT case show that insufficient heat is generated to cause bulk boiling and that there is no associated release from the steam generated. The DST case is shown to be the bounding case.

The toxicological sums of fractions (SOF) for the waste are from RPP-8369, *Chemical Source Terms for Tank Farms Safety Analysis*. The breathing rate and the radiological unit-liter dose (ULD) for the waste are from RPP-5924, *Radiological Source Terms for Tank Farms Safety Analysis*. The onsite dispersion factor is from RPP-13482, *Atmospheric Dispersion Coefficients and Radiological/Toxicological Exposure Methodology for Use in Tank Farms.*

Analysis assumptions and inputs are described below:

- A minimal waste volume of 50,000 gal in a 1,000,000-gal tank (minimizes the energy absorbed before the onset of boiling)
- Instantaneous reaction (conservative; would require instantaneous mixing)
- No heat lost to the surrounding environment (maximizes the energy available for boiling)
- 5,000 gal addition (conservative as this volume would exceed the weight that tanker trucks can transport)
- 175 gal/min rate of addition (only affects toxicological consequences)
- The acid is 18.7 M sulfuric acid

- Bounding sodium hydroxide content of waste (sodium hydroxide concentration is assumed to be sufficient to completely neutralize the sulfuric acid in the DST)
- Initial temperature of the acid-waste mixture is 40 °C
- The airborne release fraction (ARF) of 2.0×10^{-3} and the respirable fraction of 1.0 are based on those associated with boiling of aqueous solutions in flowing air from DOE-HDBK-3010-94, *Airborne Release Fractions/Rates and Respirable Fractions for Nonreactor Nuclear Facilities*
- The source term used for the aerosol in the analysis is 10% DST solids and 90% DST liquids
- Condensation of the steam on the walls of the tank was assumed to be insignificant
- The pressurization resulting from the accident fails the HEPA filters
- The inventory on the HEPA filters is equivalent to that which would produce a contact dose rate of 200 mrem/h
- The pressurization resulting from the accident is insufficient to result in dome collapse
- The concentration of sodium hydroxide was assumed to be the bounding concentration found from a survey of the *Tank Waste Information Network System* (PNNL 2002).

It is important to note that the key assumptions listed above were selected to maximize the calculated consequences of the inadvertent acid addition, and that it is the combination of conservative assumptions that truly drive the accident consequences. Each of the assumptions, the potential effect of changes in the assumption on the frequency or consequence bin (qualitatively judged), and the need to evaluate or protect the assumptions are detailed in Table 5.

2.1.3.1 Assignment of Consequence Bins for the Onsite Radiological Receptor.

Although the evaluation of consequences was intended to be qualitative, there were no previous analyses of an inadvertent large acid addition that could provide an additional frame of reference for the qualitative judgment. Therefore, the radiological consequences were estimated as shown in Appendix B. Also while determining the offsite toxicological, onsite radiological, and onsite toxicological consequence bins, the meeting participants considered an actual operational experience where a transfer of unneutralized PUREX waste occurred. While the line between the valve pit and the distributor was damaged, there was no noticeable reaction with the tank waste. This occurrence (Occurrence #85-34 [RPP-13121, *Historical Summary of Occurrences from the Tank Farms Final Safety Analysis Report*]) provides support for the conclusion that very specific conditions are required to produce significant consequences. Table 6 compares the onsite radiological consequences of the bounding representative accident to the radiological risk evaluation guidelines. Since the bounding condition resulted in low consequences to the onsite radiological receptor, the hazardous condition was assigned a consequence bin of "low" for the onsite radiological receptor.

2.1.3.2 Assignment of Consequence Bins for the Onsite and Offsite Toxicological Receptor

As noted in the previous section, there were no previous analyses of an inadvertent large acid addition to influence the qualitative assignment of consequences. Thus, the toxicological consequences were also estimated as shown in Appendix B. Consequence bins were assigned based on the analysis presented in Appendix B and the occurrence discussed above. Table 7 compares the toxicological consequences of the bounding representative accident to the risk evaluation guidelines. Reviewing the consequences shows that the offsite toxicological consequences are low, while the moderate onsite toxicological consequences are exceeded for the bounding condition. Since the bounding condition resulted in low consequences to the offsite toxicological receptor, the represented hazardous condition was assigned a consequence bin of "low" for the offsite toxicological receptor. A consequence bin of "moderate" was assigned to the onsite toxicological receptor based on the results of the analysis. A consequence bin of "moderate" was also assigned to the inadvertent chemical addition to a DCRT. This was done due to the sensitivity of the consequences to the hydroxide concentration. Under current conditions, there would be no release from the inadvertent addition of acid. Waste transfers could be postulated, however; that would result in conditions that could challenge the "moderate" guideline.

It should be noted that "moderate" consequences can only be seen from bulk additions. Smaller drum-sized additions will not result in consequences for a number of reasons. First, over 4,700 gal would need to be added before the onset of boiling in the waste heel. Also, the rate of addition will be much lower than 100 gal/min. As drums are drained and the pump is transferred to other drums,the addition rate is expected to average around 10 gal/min. Since toxicological consequences are based on the rate of release, the consequences will be significantly lower. Lastly, if boiling is initiated it is not credible to assume that the facility workers will continue to replace the empty drums with full drums in the midst of a cloud of steam. Therefore, once boiling begins only one to two drums would be added before the facility worker would self-evacuate, thus terminating the addition.

Table 4. Summary of Final Risk Binning Results for Represented Conditions.

Postulated accident/hazardous condition	Frequency	Consequences				Risk bin		
		Onsite radiological	Offsite toxicological	Onsite toxicological	Environmental	Onsite radiological	Offsite toxicological	Onsite toxicological
Inadvertent chemical addition to a DST (Bounding case w/extremely small heel & high hydroxide)	U	L	L	M	E2	III	III	II
Inadvertent chemical addition to a DCRT	U	L	L	M	E2	III	III	II

Notes:
DCRT = double-contained receiver tank.
DST = double-shell tank.
L = low.
M = moderate.
U = unlikely.

Table 5. Qualitative Evaluation of Analysis Assumptions for Representative Accident. (7 sheets)

Analysis assumptions (AA) with references/basis	Assumption type	Sensitivity (frequency/consequence)	Need to Protect AA	Protection basis
The waste tank is assumed to contain a minimal waste heel sufficient to completely neutralize the incoming acid (50,000 gal in a 1,000,000 gal tank). This volume was considered the reasonably conservative minimum volume for an active tank.	Reasonably conservative value based on operating experience with tank levels.	No anticipated effect on consequence bin. The assumed volume of 50,000 gal minimizes the energy absorbed before the onset of boiling. If the bounding pH is assumed and the minimum stoichiometric volume is postulated, the volume would be slightly smaller (41,000 gal of acid and waste). When the conservatisms of the analysis are considered, the consequence bin of this remote possibility is judged to be unchanged. If the assumed volume is greater than 50,000 gal more energy is absorbed, and as the waste heel approaches 100,000 gal, the energy absorbed before bulk boiling would exceed the total energy produced by the neutralization reaction with no associated release.	No	N/A
An instantaneous reaction rate is assumed. This assumption compresses the release into the minimum time maximizing toxicological consequences.	Bounding (physically limited) assumption. It is expected that the boiling would continue for a period longer than the time required to perform the addition.	No anticipated effect on consequence bin. More realistically, the reaction would be slowed by the diffusion of acid through a region depleted of caustic as the reaction proceeds, which would reduce the toxicological consequences.	No	N/A
No credit is taken for heat lost to the surrounding environment. The tank is considered to be perfectly insulated.	Bounding (physically limited assumption. Steam condensation would occur on the walls of the tank lowering the volume of steam released.	No anticipated effect on consequence bin. Any energy lost to the environment would not be available for bulk boiling. As energy is lost, the consequences would decrease.	No	N/A

Table 5. Qualitative Evaluation of Analysis Assumptions for Representative Accident. (7 sheets)

Analysis assumptions (AA) with references/basis	Assumption type	Sensitivity (frequency/consequence)	Need to Protect AA	Protection basis
An addition rate of 175 gal of acid per minute is assumed. The addition rate is based on RPP-14442.	Reasonably conservative assumption.	Could affect toxicological consequence bin if the addition rate were to be increased. To increase the rate of addition would require tanker pressurization higher than currently allowed or a failure in the pressure regulating system. (Realistically, the rate controlling step would be the diffusion of acid through the zone depleted of sodium hydroxide, not the rate of acid addition. As the acid addition rate is increased the aerosol being produced would attain a constant release rate controlled by diffusion.)	Yes	The addition rate is documented in the facility description of the Tank Farms DSA. A configuration change to allow a rate of addition greater than 175 gal/min would require a safety evaluation and a DSA amendment.
Acid is 18.7 M sulfuric acid.	Bounding (physically limiting) assumption.	No anticipated effect on consequence bin. Pure sulfuric acid is 18.7 M. Sulfuric acid is the most energetic common acid. This is a bounding assumption.	No	N/A
The sodium hydroxide concentration is assumed to be sufficient to completely neutralize the sulfuric acid. Excess sodium hydroxide does not increase the energy available for boiling.	Bounding (physical limiting) assumption. If less is assumed, then less energy will be available for boiling, reducing the release.	No effect on consequence bin. Excess hydroxide will not increase the consequences and hydroxide concentrations that are insufficient to completely neutralize the sulfuric acid would lower the energy produced resulting in lower consequences.	No	N/A
Initial temperature of the acid-waste mixture is assumed to be 40 °C based on a survey of temperatures found in the *Tank Waste Information Network System* (PNNL 2002) and an acid addition at ambient temperature.	Reasonably conservative assumption based on operating experience (temperature observations).	No anticipated effect on consequence bin. For the starting temperature to be significantly elevated would require the reaction to have occurred in a "high heat" tank. High heat tanks contain sufficient volume to preclude boiling. If small heels are assumed, the heat loading would be insufficient to maintain the waste at a temperature approaching the boiling point.	No	N/A
A breathing rate of 3.33×10^{-4} m^3/s from RPP-5924 is used.	Reasonably conservative assumption.	No anticipated effect on consequence bin. This is a standard analysis assumption.	No	N/A

Table 5. Qualitative Evaluation of Analysis Assumptions for Representative Accident. (7 sheets)

Analysis assumptions (AA) with references/basis	Assumption type	Sensitivity (frequency/consequence)	Need to Protect AA	Protection basis
Boiling point temperature of the acid-waste mixture is based on the boiling point of the waste tanks that contain high sodium hydroxide concentrations (RPP-14892).	Reasonably conservative assumption.	No anticipated effect on the consequence bin. Tanks with dissolved solids low enough to have a significantly lowered boiling point would have sodium hydroxide concentrations low enough to preclude boiling.	No	N/A
An atmospheric dispersion coefficient of 2.22×10^{-5} s/m^3 was used for offsite consequences and an atmospheric dispersion coefficient of 3.28×10^{-2} s/m^3 was used for onsite consequences.	Reasonably conservative assumption.	No anticipated effect on consequence bin. The atmospheric dispersion coefficients are from RPP-5924 and represents the 95th percent overall value for accidents less than one hour. No credit is taken for either plume meander or deposition.	No	N/A
An ARF of 2.0×10^{-3} and a respirable fraction of 1.0 are based on those associated with boiling of aqueous solutions in flowing air from DOE-HDBK-3010-94.	Bounding value presented in the handbook for this type of phenomenon.	No anticipated effect on consequence bin. The ARF being used is a conservative value chosen because of the uncertainty involved with the churn turbulent flow conditions generated by the boiling rates encountered during this accident. It is expected that the capture of secondary drops by the large number of primary bubbles would limit the release to an ARF less than that chosen. The ARF chosen is based on, and bounds, a vigorous boiling experiment that, conservatively, included solution splattered from the vessel onto the glassware in the calculated ARF (DOE-HDBK-3010-94).	No	N/A
The source term used for the aerosol in the analysis is 10% DST solids and 90% DST liquids.	Reasonably conservative estimate of solids in the aerosol.	No anticipated effect on consequence bin. This is a modeling assumption that cannot be verified but is considered to be conservative because boiling will occur in the vicinity of the incoming acid stream. The agitation caused by the boiling will not cause the solid waste to be thoroughly mixed with the liquid. In addition, the solids will settle out as they pass through the liquid phase toward the surface. It should also be noted that the SOFs for DST liquids and solids are similar so there is little sensitivity.	No	N/A

Table 5. Qualitative Evaluation of Analysis Assumptions for Representative Accident. (7 sheets)

Analysis assumptions (AA) with references/basis	Assumption type	Sensitivity (frequency/consequence)	Need to Protect AA	Protection basis
Condensation of steam on the walls of the tank is assumed to be insignificant.	Bounding (physically limiting) assumption.	No anticipated effect on consequence bin. Any condensation that would occur would decrease the quantity of aerosol that is released, thus lowering the consequences.	No	N/A
The pressurization resulting from the accident fails the HEPA filters.	Bounding assumption. If the HEPA filters do not fail, then they will filter out much of the release instead of contributing to the release.	No anticipated effect on consequence bin. If the HEPA filters do not fail, then the consequences would be decreased since there is no credit for waste retention.	No	N/A
The inventory on the HEPA filters is equivalent to that which would produce a contact dose rate of 200 mrem/h. This is a modeling assumption based on current tank farm practices.	Conservative value based on operating experience (filter replacement).	No anticipated effect on consequence bin. The contribution from the HEPA filters is insignificant to the overall consequences. The contribution of the HEPA filters to the toxicological dose is ~0.5% and the contribution of the HEPA filters to the radiological dose is ~0.01%. The contribution of the HEPA filters would have to increase by over an order of magnitude to be a significant contributor, which is not considered credible.	No	N/A

Table 5. Qualitative Evaluation of Analysis Assumptions for Representative Accident. (7 sheets)

Analysis assumptions (AA) with references/basis	Assumption type	Sensitivity (frequency/consequence)	Need to Protect AA	Protection basis
The pressurization resulting from the accident would not cause a dome collapse. The basis for this assumption is that the pressure buildup from boiling would not be instantaneous and would, therefore, allow the pressure to be relieved through lifted cover blocks or other leakage paths. This because the expected failure pressure for a DST is 60 lb/in^2 gauge (WHC-SD-TWR-RPT-003).	Reasonably conservative assumption. Pressures sufficient to cause structure failure are not expected.	No anticipated effect on consequence bin. Note that a dome collapse was assumed in the offsite radiological consequence calculations where a greater degree of conservatism was applied, but was not assumed in the qualitative evaluation of the other exposures where more realistic assumptions were made. Even if failure is assumed, the increase in consequence would only be around 15% (as shown in RPP-9689), thus the conclusions are not challenged.	No	N/A
The radiological ULDs used were the bounding DST liquid and saltcake values provided in RPP-5924.	The bounding values reported in RPP-5924 were used.	The ULD would have to be increased by nearly an order of magnitude for the moderate consequence bin to be challenged.	Yes	Protected by AC: Source Term Controls
Material released is saltcake solids.	Reasonably conservative assumption.	No anticipated effect on consequence bin. Saltcake is selected because it has the highest ULD of DST waste surface layers given current tank waste conditions. Sludges generally have higher ULDs, but are typically covered by saltcake such that they are not impacted by the reaction.	No	N/A
The toxicological SOFs used were the bounding DST liquid and solid values provided in RPP-8369.	The bounding values reported in RPP-8369 were used.	The SOF would have to be increased by a factor of two to challenge the onsite high consequence bin.	Yes	Protected by AC: Source Term Controls

Table 5. Qualitative Evaluation of Analysis Assumptions for Representative Accident. (7 sheets)

Analysis assumptions (AA) with references/basis	Assumption type	Sensitivity (frequency/consequence)	Need to Protect AA	Protection basis
The volume of the acid addition was assumed to be 5,000 gal. Based on the density of sulfuric acid, this exceeds the allowable gross vehicle weight for tanker trucks. (While tanker trucks contain a nominal capacity of 5,000 gal, they are limited by total weight of the filled tanker. Generally, the maximum weight that can be transported is 45,000 lb which is the equivalent weight of 3,000 gal of sulfuric acid. The analysis conservatively assumes the tanker contains the full nominal capacity of sulfuric acid.)	Reasonably conservative assumption due to weight limitation.	Could affect consequence bin if conditions change allowing tanker trucks to transport much larger quantities. If current transportation regulations were changed to make larger shipments credible, the radiological consequences would increase. The allowed quantities would have to be greater than 10,000 gal before the consequence bin would need to be reevaluated. Toxicological consequences would not require reevaluation since they are based on the peak release and not the total release.	No	N/A
Qualitative Evaluation of Analysis Assumptions for Other Represented Conditions.				
It is assumed that there will be no chemical additions to SSTs.	Reasonably conservative assumption.	Could affect consequence bin if additions to SSTs are proposed. If additions are proposed to SSTs, the hazards would have to be identified, analyzed, and appropriate controls applied before additions were permitted.	No	N/A

Table 5. Qualitative Evaluation of Analysis Assumptions for Representative Accident. (7 sheets)

Analysis assumptions (AA) with references/basis	Assumption type	Sensitivity (frequency/consequence)	Need to Protect AA	Protection basis
The concentration of hydroxide in DCRTs was assumed to be 3.6 M. This concentration was the bounding hydroxide concentration found from a survey of the *Tank Waste Information Network System* (PNNL 2002).	Reasonably conservative assumption that bounds current hydroxide content in DCRTs.	Could affect consequence bin if hydroxide concentrations are increased to 4.5 M or greater. This could occur through caustic additions or the transfer of undiluted SST waste into an empty DCRT. However, there are no current plans for addition of caustic to DCRTs, and there are few SSTs with sufficient caustic concentration. However, due to the sensitivity of the consequences to the hydroxide concentration, the onsite toxicological consequence was conservatively assigned a risk bin of moderate, thereby requiring the application of controls.	No	N/A

Notes:

DOE-HDBK-3010-94, 2000, *Airborne Release Fractions/Rates and Respirable Fractions for Nonreactor Nuclear Facilities*, Change Notice No. 1, U.S. Department of Energy, Washington, D.C.

PNNL, 2002, *Tank Waste Information Network System,* September 18, Tank Characterization Databases, available at http://twins.pnl.gov/data/data.asp.

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RPP-14892, 2003, *Boiling Point Calculations for Selected Double-Shell Tanks*, Rev. 0, CH2M HILL Hanford Group, Inc., Richland, Washington.

WHC-SD-TWR-RPT-003, 1996, *DELPHI Expert Panel Evaluation of Hanford High Level Waste Tank Failure Modes and Release Quantities*, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

AA = analysis assumptions.
AC = administrative control.
ARF = airborne release fraction.
DCRT = double-contained receiver tank.
DSA = documented safety analysis.
DST = double-shell tank.
HEPA = high-efficiency particulate air (filter).
N/A = not applicable.
SOF = sum of fractions.
SST = single-shell tank.
ULD = unit-liter dose.

Table 6. Summary of Onsite Radiological Consequences for the Mixing of Incompatible Materials Without Controls.

Accident	Onsite Radiological Consequences		
	Calculated Dose (rem)	**Moderate Consequence Guideline (rem)**	**High Consequence Guideline (rem)**
Mixing of incompatible materials	3.2 E+00	2.5 E+1	1.0 E+2

Table 7. Summary of Toxicological Consequences for the Mixing of Incompatible Materials Without Controls.

Case	Toxicological Consequences							
	Onsite				Offsite			
	Moderate consequence		High consequence		Moderate consequence		High consequence	
	SOF	Guideline	SOF	Guideline	SOF	Guideline	SOF	Guideline
Mixing of incompatible materials	2.0×10^{1}	1 (ERPG-1)	9.6×10^{-1}	1 (ERPG-2)	9.2×10^{-2}	1 (ERPG-2)	1.4×10^{-2}	1 (ERPG-3)

Notes:
ERPG = emergency response planning guideline.
SOF = sum of fractions.

2.1.3.3 Assignment of Environmental Consequences.

Based on operational experience and the conservative calculations in Appendix B, where the estimated release was nearly 3 L of waste, it was concluded that there is potential for material release to either the atmosphere or ground. Therefore, an environmental consequence of E2 was assigned to the mixing of incompatible materials representative accident.

2.1.3.4 Assignment of Risk Bins.

Table 4 summarizes the frequency and risk bin assignments for the mixing of incompatible mterials accident scenario without controls. The assignment of risk bins is derived from the consequences and estimated frequency of the accident. The risk bin for the onsite radiological receptor and the offsite toxicological receptor is III because the consequence is "low" and the frequency is "unlikely." The risk bin for the onsite toxicological receptor is II since the consequence is "moderate" and the frequency is "unlikely."

2.2 MIXING OF INCOMPATIBLE MATERIALS ASSOCIATED HAZARDOUS CONDITIONS

There are 44 hazardous conditions represented by the mixing of incompatible materials representative accident. (Note that the specific number of hazardous conditions reported in the hazard evaluation database may increase or decrease in the future based on changes in field configurations or operations.) The results of the risk binning process for these hazardous conditions are shown in the hazard evaluation database under the representative accidents 03 and 23. Included in the hazard evaluation database entries is a basis for each consequence and frequency.

Meeting participants considered process knowledge, operational history, and the conservatisms in the analysis when assigning consequence and frequency bins to the other represented hazardous conditions. The results are summarized in Table 8, and are discussed below.

1. Inadvertent chemical addition to a DST. The addition into a nominal or "realistic" tank was considered an "anticipated" event with "low" consequences. The frequency was considered "anticipated" because the initiating event is human error. The addition into a nominal tank with an average caustic concentration or an average waste volume would not result in a release of waste.

2. Small inadvertent addition. Inadvertent additions from small containers, such as 55-gal drums, was assigned a frequency of "unlikely" because it would have to be added to a tank with minimal volume and high caustic concentrations for any chance of a reaction. The consequences were judged to be low since scoping calculations showed that roughly 4,800 gal would have to be added before a release into the headspace would occur. In addition, the estimated additional rate would be on the order of 10 gal/min, which would lower the toxicological consequences and order of magnitude from the bounding case.

3. Tank waste mixing with tank waste conditions that result in energetic reactions. Tank waste mixing with tank waste conditions were judged to be "extremely unlikely" because process history and knowledge have shown that mixing different tank wastes does not result in an energetic reaction (Reynolds 2001). Even if a reaction were assumed to occur, it was judged that it would be significantly less than the bounding case of 5,000 gal of concentrated sulfuric acid.

4. Incompatible waste transfer from external sources (B-Plant, T-Plant, 222-S Laboratory, and PFP). Waste transfers from B-Plant were judged to be "beyond extremely unlikely" since it is physically disconnected from tank farms. Transfers from PFP, T-Plant, and 222-S Laboratory were judged to be "unlikely" due to the physical configuration and inventories of acids contained in the facilities. Even if a transfer was assumed to occur, it was judged to be significantly lower than the consequences of the bounding case of 5,000 gal of concentrated sulfuric acid.

5. Toxic gas (ammonia) release during intrusive activity. Toxic gas releases due to intrusive activities were assigned a frequency of anticipated based on the history of tank farms. The consequences were shown to be low in WHC-SD-WM-CN-074.

Table 8. Summary of Final Risk Binning Results for Associated Conditions.

Postulated accident/hazardous conditions	Frequency	Consequences				Risk bin		
		Onsite radiological	Offsite toxicological	Onsite toxicological	Environmental	Onsite radiological	Offsite toxicological	Onsite toxicological
Inadvertent chemical addition to a DST (Realistic case)	A	L	L	L	E1	III	III	III
Small inadvertent addition (55-gal drum)	U	L	L	L	E1	III	III	III
Tank waste mixing with tank waste conditions that result in energetic reactions	EU	L	L	L	E1	IV	IV	IV
Incompatible waste transfer from B-Plant	BEU	L	L	M	E1	IV	IV	IV
Incompatible waste transfers from 222-S Laboratory, T-Plant, or the PFP	U	L	L	L	E1	III	III	III
Toxic gas release during intrusive activity	A	L	L	L	E0	III	III	III

Note:

A = anticipated.
BEU = beyond extremely unlikely.
DST = double-shell tank.
EU = extremely unlikely.
L = low.
M = moderate.
PFP = Plutonium Finishing Plant.
U = unlikely.

3.0 CONTROL SELECTION

After the allocation of risk bins, a group was empanelled to select controls for the represented hazardous conditions. A multidisciplinary group representing organizations both internal and external to the tank farm contractor performed the selection of controls. The list of control decision makers is listed in Appendix C. Controls were considered and selected to prevent or mitigate consequences of the hazards that were identified as requiring controls.

3.1 PROPOSED CONTROLS FOR THE MIXING OF INCOMPATIBLE MATERIALS REPRESENTATIVE ACCIDENT

A summary of the representative accident, as well as a synopsis of the risk binning results, was presented to the control selection team. The group then proposed and discussed numerous potential mitigative and preventative controls for the representative accident. The possible mitigative controls proposed were:

- Waste temperature monitoring
- Headspace gas/vent gas monitoring
- Self-evacuation training
- Limit the chemical addition rate
- HEPA filter efficiency controls activated carbon filtration of ventilation exhaust
- Scrubbing of ventilation gases with water/caustic solution
- Personal protective equipment
- Limited area access.

Possible preventative controls were also considered:

- Perform a pH analysis to ensure compatibility
- Verify procurement/delivery paperwork prior to additions
- Use an evaluated suppliers list including periodic reviews/audits of chemical vendor quality control and assurance programs
- Control volume of additions
- Eliminate the need for liquid chemical additions
- Monitor the tank temperature during additions
- Evaluate waste volume of tank prior to allowing addition.

3.2 SELECTED CONTROL FOR THE MIXING OF INCOMPATIBLE MATERIALS REPRESENTATIVE ACCIDENT

3.2.1 Control Selection

The proposed controls were discussed and evaluated by the group. Control decision criteria are established in:

- Title 10, *Code of Federal Regulations,* Part 830, Subpart B, "Nuclear Safety Management"
- DOE-STD-3009-94, *Preparation Guide for U.S. Department of Energy Nonreactor Facility Documented Safety Analyses*
- DOE G 421.1-2, *Implementation Guide for Use in Developing Documented Safety Analyses to Meet Subpart B of 10 CFR 830*
- DOE G 423.1-1, *Implementation Guide for Use in Developing Safety Requirements*
- U.S. Department of Energy, Office of River Protection Letter, Klein and Schepens, 2003, "Replacement of Guidance Provided by RL and ORP."

The control decision preference can be summarized as follows:

1. Preventive controls over mitigative
2. Passive controls over active control
3. Engineering controls over administrative controls
4. Controls with the highest reliability
5. Controls closest to the hazard
6. Controls with the lowest implementation and maintenance costs.

A consensus was reached based on the judgment of the participants to perform a pH analysis to ensure compatibility. This analysis is a reliable and effective preventive control. It is close to the hazard and can be implemented with minimal operational or budgetary impact. The other controls were eliminated because:

- Monitoring the waste temperature or controlling the volume of the addition were considered unreliable or ineffective as a selected control.
- Monitoring the headspace gas/vent gas or limiting the chemical addition rate are mitigative controls that are considered unreliable.
- Self-evacuation training, limited area access, and personal protective equipment are effective controls for facility workers but were considered less effective for the onsite (100 m) worker.

- HEPA filter efficiency controls are mitigative controls that are only effective for non-bounding conditions as the HEPA filter fails in the analyzed accident.
- Activated carbon filtration of ventilation exhaust or the scrubbing of ventilation gases with water/caustic solution are mitigative controls that would require major plant modifications including additional safety analyses.
- Verification of procurement/delivery paperwork prior to additions and the use of an evaluated suppliers list, including periodic reviews/audits of chemical vendor quality control and assurance programs, were not considered as effective as the selected control.
- Eliminating the need for liquid chemical additions would degrade the safe storage of waste by eliminating the current corrosion control program, and hinder the tank closure effort by eliminating many potential decontamination and decommissioning proposals.
- Evaluating the waste volume of the tank prior to allowing addition would become less effective during the waste retrieval mission when the number of tanks with a small heel of waste is expected to increase.

3.2.2 Format of the Selected Control

Once the control was selected, options for how the control would be depicted were evaluated. The possibilities were:

1. The control could be documented as a new stand-alone TSR administrative control (AC).
2. The control could be a key element under a TSR AC (i.e., transfer controls).
3. The control could be included in the SMPs:
    - Reflected as a bullet point in the SMP AC, specifying the key elements
    - Reflected as a bullet point in the SMP AC, with the details listed in the DSA
    - Listed in the DSA description of the SMP.

After discussion, it was agreed to represent the control as a stand-alone AC in the TSRs. A stand-alone AC most strongly links the basis and applicability of the control with the final disposition of the control.

The precise wording of the control was then considered. The key areas of discussion were on the use of "field testing," whether a specific pH should be defined, and whether SSTs, DCRTs, and catch tanks should be included in the applicability. The consensus resulted in Table 9.

Table 9. Summary of Technical Safety Requirement Controls for Mixing of Incompatible Material.

Control	Safety function	Comments
Bulk Chemical Additions • Perform field testing to verify that bulk chemicals shipped in tanker trucks have a pH ≥ 7 before addition to DSTs, DCRTs, and catch tanks.	Prevents inadvertent additions of acids.	—
Safety Management Programs • Measuring and test equipment program	Ensures program is maintained to control tank farm measuring and test equipment used to verify parameters to comply with TSRs.	—

Notes:
DST = double-shell tank.
DCRT = double-contained receiver tank.
TSR = technical safety requirement.

It was noted during the evaluation that:

1. The AC bases should address the following:

   - The control does not apply to waste transfers; chemical delivery from drums (e.g., 55-gal drums) that connect to tank farm tanks or to waste transfer systems during chemical additions; or to additions of water or inhibited water. Inhibited water includes dilute concentrations of sodium hydroxide and sodium nitrite.

   - DSTs, DCRTs, and catch tanks are the only tank farm facilities where the addition of bulk chemicals from tank trucks is authorized (i.e., within the scope of the DSA). The addition of bulk chemicals to SSTs to support proposed retrieval methods would require additional safety analysis.

   - Clarification of the intent of "field testing." "Field testing" is intended to mean a test by the tank farm contractor after receipt of the shipment but before addition of the chemical.

   - Explanation of acid volumes and flow rates that would require additional controls to aid the evaluation of any proposed delivery systems as noted in Table 5 and Section 2.1.3.2.

2. The specific method(s) of testing for pH (e.g., litmus paper) will be identified and controlled by a TSR AC program for instrumentation and measuring and test equipment. Any special requirements for the identified testing method(s) will be developed and documented for program implementation.

3.3 CONTROL ALLOCATION

Of the conditions grouped under the mixing of incompatible materials accident scenario, a few conditions were identified as requiring controls due to onsite toxicological consequences of the inadvertent addition of acid. For these cases, the stand-alone AC was allocated. This new AC requires that the pH of bulk chemical additions be verified before transferring, thereby preventing the accident. Also allocated for these cases was a measuring and test equipment program that stipulates that any required instrumentation is properly calibrated or functionally tested. Defense-in-depth features were also identified for some of the represented conditions and are described in RPP-14821, *Technical Basis Document for Defense-In-Depth Features.*

4.0 REFERENCES

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RPP-9689, 2003, *Offsite Radiological Consequence Calculation for the Bounding Mixing of Incompatible Materials Accident*, Rev. 0, CH2M HILL Hanford Group, Inc., Richland, Washington.

RPP-13121, 2003, *Historical Summary of Occurrences from the Tank Farms Final Safety Analysis Report*, Rev. 0, CH2M HILL Hanford Group, Inc., Richland, Washington.

RPP-13482, 2003, *Atmospheric Dispersion Coefficients and Radiological/Toxicological Exposure Methodology for Use in Tank Farms*, Rev. 0, CH2M HILL Hanford Group, Inc., Richland, Washington.

RPP-14286, 2003, *Facility Worker Technical Basis Document*, Rev. 0, CH2M HILL Hanford Group, Inc., Richland, Washington.

RPP-14442, 2003, *Calculation of Acid Flow Rate into DSTs*, Rev. 0, CH2M HILL Hanford Group, Inc., Richland, Washington.

RPP-14821, 2003, *Technical Basis Document for Defense-In-Depth Features*, Rev. 0, CH2M HILL Hanford Group, Inc., Richland, Washington.

RPP-14892, 2003, *Boiling Point Calculations for Selected Double-Shell Tanks*, Rev. 0, CH2M HILL Hanford Group, Inc., Richland, Washington.

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WHC-SD-TWR-RPT-003, 1996, *DELPHI Expert Panel Evaluation of Hanford High Level Waste Tank Failure Modes and Release Quantities*, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

WHC-SD-WM-CN-074, 1997, *Chemical Reaction in a DCRT Leading to a Toxic Release*, Rev. 0-A, Westinghouse Hanford Company, Richland, Washington.

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APPENDIX A

RISK BINNING MEETING ATTENDEES

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APPENDIX A

RISK BINNING MEETING ATTENDEES

DSA Accident Risk Binning Attendance Sheet

Meeting Subject: Criticality (Rep Acc. 01) Incompatible material (Rep Acc. 2 & 23) Date 7/17/02

Name	Organization	Phone	Mail Stop
MILTON V. SHULTZ	CHG-NS&L	372-3740	R1-44
* David M. Carson	FFS SA+VE	372-1717	E1-64
Joseph J. Bevelacqua	ORP	376-8443	H6-60
* Steve Faulk	CHG EP	376-0688	S7-86
Richard Williams	CHG Rad Con	373-4909	S7-75
Robert D Carrell	ORP support	521-6421	H6-60
Kevin Sandgren	CHG - NS&L	372-0374	R1-49
Mark Hasty	CHG-OPS	373-9378	S7-83
Steve Fitzpatrick	ORP Support (HPMC)	528-5007	E1-60
Clifford Templeton	CHG ORS	372-0569	R2-50
Ed Ford	CHG-NS&L	373-1296	R1-44
Robert Shepard	ORP Support (LMA)	521-2680	—
* Kenny Fowler	CHG-Proc Engr	373-5930	R2-11

* only Criticality

DSA Accident Risk Binning Attendance Sheet

Meeting Subject: Mixing of Incompat Material Date 7/18/02

DAY 2

Name	Organization	Phone	Mail Stop
MILTON V. SHULTZ	CHG-NS&L	372-3240	R1-44
Ed Ford	CHG-NS&L	373-1296	R1-44
CLIFF HAMPTON	CHG OPS	372-0566	R2-50
Phil Miller	CHG ENV	373-1920	R1-57
Joseph Benevelova	ORP	376-4443	H6-60
MARK HASTY	CHG-OPS	373-9378	S7-83
Kevin Schwinkendorf	Fluor Federal Services	376-0960	
Robert Shepard	ORP-Support (LNA)	521-2680	
Steve Eischeid	ORP-Support (HPMC)	528-5007	
RYK WILLIAMS	CHG	373-4989	S7-75
BRAD SMITH	CHG-NS&L	376-1907	R1-44
Kevin Sandgren	CHG-NS&L	372-0371	R1-49

APPENDIX B

CONSEQUENCE CALCULATIONS FOR THE MIXING OF INCOMPATIBLE MATERIALS

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APPENDIX B

CONSEQUENCE CALCULATIONS FOR THE MIXING OF INCOMPATIBLE MATERIALS

B1.0 ONSITE RADIOLOGICAL CONSEQUENCES

The mixing of incompatible materials accident scenario, without controls, assumes that a cargo tanker filled with 5,000 gal of 100% sulfuric acid (18.7 M) is emptied into a waste tank instead of the chemical expected (e.g., caustic or nitrite). The receiving tank is assumed to contain a small quantity of waste that is sufficient to completely neutralize the incoming acid. This ensures that the heat of reaction is distributed across a minimal volume of waste. Heating of the waste causes vaporization of water that results in the buildup of aerosols in the tank headspace and pressurizes the tank. It is assumed that the high-efficiency particulate air (HEPA) filters fail, contributing further to the consequences. The energy released by the reaction heats the acid-waste mixture to the boiling point. The remainder of the energy produces steam; condensation of the steam on the walls of the tank was assumed to be insignificant. The reaction was conservatively considered to be instantaneous. The contributors to the radiological consequences are the HEPA filter release and the aerosolized waste. Although the contribution from a potential dome collapse was considered, it was not included because the pressure buildup from boiling would not be instantaneous allowing pressure relief due to lifted cover blocks, etc. Even if failure is assumed, the increase in consequence would only be around 15% (as shown in RPP-9689, *Offsite Radiological Consequence Calculation for the Bounding Mixing of Incompatible Materials Accident*).

B1.1 DOUBLE-SHELL TANK ONSITE CONSEQUENCES

1.1.1 Contribution from Aerosolized Waste

Sulfuric acid is a common industrial chemical. It is also typically transported at 100% concentration (18.7 M) to reduce costs and lower its corrosion potential. The reaction of sulfuric acid with sodium hydroxide is shown below:

$$H_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2H_2O.$$

The energy released by the reaction can be found using the heats of formation of the components:

$$\text{Heat of Reaction} = [(-331.46) + (2)(-68.32)] - [(-193.91) + (2)(-112.24)] = -49.71$$

where:

-331.46 kcal/g mole = heat of formation of sodium sulfate (*CRC Handbook of Chemistry and Physics* [Weast 1981])
-68.32 kcal/g mole = heat of formation of water (Weast 1981)
-193.91 kcal/g mole = heat of formation of sulfuric acid (Weast 1981)
-112.24 kcal/g mole = heat of formation of sodium hydroxide (Weast 1981).

Converting to kJ/g mole

(-49.71 kcal/g mole)(4.184 kJ/kcal) = -208 kJ/g mole

where:

4.184 J/cal is the conversion factor (Weast 1981).

The energy released is 208 kJ/mole H_2SO_4. Total energy released from reaction is calculated as follows:

(208 kJ/mole) (18.7 mole/L) (3.785 L/gal) (5,000 gal) = 7.36×10^7 kJ.

It is conservatively assumed that there will be a small heel remaining in the tank. This is extremely conservative since it is unlikely that a nearly empty tank will receive any chemical additions. The tank is assumed to contain only 50,000 gal of waste, despite its 1,000,000 gal capacity, with sufficient caustic to completely neutralize the acid (>3.7 mole/L).

Assuming that the starting temperature of the waste acid mixture is 40 °C, the energy required to heat the mixture to boiling point is calculated as follows:

(120 °C – 40 °C) (4.2 kJ/kg·°C) (50,000 gal) (3.785 L/gal) (1.1 kg/L) = 6.99×10^7 kJ

where:

4.2kJ/kg·°C	= specific heat of water (Weast 1981)
1.1 kg/L	= assumed density of the supernatant
120 °C	= assumed boiling point of the supernatant.

Some energy will be lost through the walls of the tank. It is assumed that the annulus acts as an insulator (i.e., no annulus ventilation). The energy lost to the surroundings will be small and is conservatively assumed to be zero for this accident.

Energy available for steam production = (energy from reaction) – (energy heating the solution to boiling point)

(7.36×10^7 kJ) – (6.99×10^7 kJ) = 3.70×10^6 kJ.

The mass of water vaporized is calculated as follows:

(3.70×10^6 kJ) / (2.26×10^3 kJ/kg) = 1.64×10^3 kg

where:

2.26×10^3 kJ/kg = latent heat of vaporization for water (*Basic Principles and Calculations in Chemical Engineering* [Himmelblau 1974]).

It was proposed that the boiling of the waste could result in sufficient bubble swell and insufficient bubble release (despite the low surface tension) to result in waste being carried out of the tank. Even if this were to occur, the release would be limited to the immediate vicinity. The consequences to the onsite worker (located 100 m away) will not be significantly affected.

The source term used for the aerosol in this analysis is 10% double-shell tank (DST) solids and 90% DST liquids. Boiling will occur in the vicinity of the incoming acid stream. The agitation caused by the boiling will not cause the solid waste to be thoroughly mixed with the liquid. In addition, the solids will settle out as they pass through the liquid phase toward the surface. The inclusion of 10% solids in the aerosol is a conservative assumption. An airborne release fraction (ARF) of 2.0×10^{-3} and a respirable fraction of 1.0 are based on those associated with boiling of aqueous solutions in flowing air from DOE-HDBK-3010-94, *Airborne Release Fractions/Rates and Respirable Fractions for Nonreactor Nuclear Facilities*. The ARF being used is a conservative value chosen because of the uncertainty involved with the churn turbulent flow conditions generated by the boiling rates encountered during this accident. It is expected that the capture of secondary drops by the large number of primary bubbles would limit the release to an ARF less than that chosen. The ARF chosen is based on, and bounds, a vigorous boiling experiment that, very conservatively, included solution splattered from the vessel onto the glassware in the calculated ARF (DOE-HDBK-3010-94). The radiological unit-liter dose (ULD) for the waste is from RPP-5924, *Radiological Source Terms for Tank Farms Safety Analysis*.

The waste aerosolized is calculated as follows:

$$(1.64 \times 10^3 \text{ kg})\ (2 \times 10^{-3}) = 3.28 \times 10^0 \text{ kg} = 3.28 \times 10^3 \text{ g}.$$

Converting to liters aerosolized yields

$$(3.28 \times 10^3 \text{ g}) / (1{,}200 \text{ g/L}) = 2.73 \times 10^0 \text{ L}$$

where:

1,200 g/L = assumed density of the aerosol (90% liquid and 10% solid).

Given

ULD for DST liquids $= 1.0 \times 10^3$ Sv/L (RPP-5924)
ULD for DST solids $= 1.8 \times 10^3$ Sv/L (RPP-5924)

ULD for aerosol $= [(1.0 \times 10^3 \text{ Sv/L})\ (0.9)] + [(1.8 \times 10^3 \text{ Sv/L})\ (0.1)]$
$= 1.08 \times 10^3$ Sv/L .

Onsite aerosol dose = (aerosol released) (onsite χ/Q) (onsite ULD) (breathing rate)

Onsite $D_{aerosol}$ $= (2.73 \times 10^0 \text{ L})\ (0.0328 \text{ s/m}^3)\ (1.08 \times 10^3 \text{ Sv/L})\ (3.33 \times 10^{-4} \text{ m}^3\text{/s})$
$= 3.2 \times 10^{-2}$ Sv

where:

0.0328 s/m^3 = onsite χ/Q (RPP-13482, *Atmospheric Dispersion Coefficients and Radiological/Toxicological Exposure Methodology for Use in Tank Farms*)
3.33×10^{-4} m^3/s= breathing rate (RPP-5924).

B1.1.2 Contribution from High-Efficiency Particulate Air Filter

Since the steam volume produced greatly exceeds the headspace volume, it is assumed that the tank pressurizes sufficiently to fail the HEPA filters.

Given

DST HEPA filter release due to overpressure = 5.4×10^{-5} L at 5% solids (RPP-13437, *Technical Basis Document for Ventilation System Filtration Failures Leading to an Unfiltered Release).*

Given

ULD for DST solids = 1.8×10^{3} Sv/L (RPP-5924)
ULD for DST liquids = 1.0×10^{3} Sv/L (RPP-5924)

ULD from dome collapse = $[(1.0 \times 10^{3}\ \text{Sv/L})\ (0.95)] + [(1.8 \times 10^{3}\ \text{Sv/L})\ (0.05)]$
= 1.04×10^{3} Sv/L.

Onsite HEPA dose = (material released from HEPA) (onsite χ/Q) (ULD) (breathing rate)

$$\text{Onsite } D_{HEPA} = (5.4 \times 10^{-5}\ \text{L})\ (0.0328\ \text{s/m}^3)\ (1.04 \times 10^{3}\ \text{Sv/L})\ (3.33 \times 10^{-4}\ \text{m}^3/\text{s}) = 6.1 \times 10^{-7}\ \text{Sv}$$

where:

$0.0328\ \text{s/m}^3$ = onsite χ/Q (RPP-13482)
$3.33 \times 10^{-4}\ \text{m}^3/\text{s}$ = breathing rate (RPP-5924).

B1.1.3 Overall Radiological Consequences

Total onsite radiological consequences = (aerosol contribution) + (HEPA contribution)

$$\text{Onsite } D_{Total} = (3.2 \times 10^{-2}\ \text{Sv}) + (6.1 \times 10^{-7}\ \text{Sv}) = 3.2 \times 10^{-2}\ \text{Sv} = 3.2 \times 10^{0}\ \text{rem.}$$

B1.2 DOUBLE-CONTAINED RECEIVER TANK ONSITE CONSEQUENCES

The mixing of incompatible materials accident scenario for a double-contained receiver tank (DCRT) is significantly different than for a DST. The maximum capacity of a DCRT is 31,000 gal. Since the addition postulates a 5,000 gal addition, a reasonably bounding volume of tank waste would be 25,000 gal. The concentration of hydroxide in the waste is assumed to be 3.6 M (*Tank Waste Information Network System* [PNNL 2002]). This bounds the concentration in the DCRTs, as well as the saltwell waste received for interim stabilization. Due to the limited hydroxide content, the sulfuric acid will not be completely neutralized. In other words, the energy produced in the reaction of sulfuric acid with hydroxide will be limited by the hydroxide content.

Sulfuric acid is a common industrial chemical. It is also typically transported at 100% concentration (18.7 M) to reduce costs and lower its corrosion potential. The reaction of sulfuric acid with sodium hydroxide is shown below:

$$H_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2H_2O.$$

The energy released is 208 kJ/mole H_2SO_4. The amount of acid that reacts is limited by the total hydroxide content:

$$(25{,}000 \text{ gal})\ (3.785 \text{ L/gal})\ (3.6 \text{ moles hydroxide/L}) = 3.41 \times 10^5 \text{ moles hydroxide.}$$

Since two moles of hydroxide are required for each mole of sulfuric acid:

$$(3.41 \times 10^5 \text{ moles hydroxide}) / (2 \text{ moles hydroxide/mole sulfuric acid}) = 1.70 \times 10^5 \text{ moles } H_2SO_4$$

Total energy released from reaction is calculated as follows:

$$(208 \text{ kJ/mole } H_2SO_4)\ (1.70 \times 10^5 \text{ moles } H_2SO_4) = 3.54 \times 10^7 \text{ kJ}.$$

Assuming that the starting temperature of the waste acid mixture is 40 °C, the energy required to heat the mixture to boiling point is calculated as follows:

$$(120\ °C - 40\ °C)\ (4.2 \text{ kJ/kg}\cdot °C)\ (30{,}000 \text{ gal})\ (3.785 \text{ L/gal})\ (1.1 \text{ kg/L}) = 4.20 \times 10^7 \text{ kJ}$$

where

4.2kJ/kg·°C	=	specific heat of water (Weast 1981)
1.1 kg/L	=	assumed density of the supernatant
120 °C	=	assumed boiling point of the supernatant.

Some energy will be lost through the walls of the tank. The energy lost to the surroundings will be small and is conservatively assumed to be zero for this accident.

Energy available for steam production = (energy from reaction) – (energy heating the solution to boiling point)

$$(3.54 \times 10^7 \text{ kJ}) - (4.20 \times 10^7 \text{ kJ}) = 0 \text{ kJ}.$$

Since there is no energy available for bulk boiling, the only aerosol produced would be from the increased vapor pressure of the heated waste solution. The pressurization and release from the increased vapor pressure will be insignificant compared to the DST case. Therefore, the onsite and offsite consequence of the mixing of incompatible materials in DCRTs was not analyzed further.

B2.0 TOXICOLOGICAL CONSEQUENCES

The mixing of incompatible materials accident scenario, without controls, assumes that a cargo tanker filled with 5,000 gal of 100% sulfuric acid (18.7 M) is emptied into a waste tank, instead of the chemical expected (e.g., caustic or nitrite). The rate of addition is assumed to be 175 gal/min, which is considered to be a reasonably conservative flow rate. The receiving tank is assumed to contain a small quantity of waste sufficient to completely neutralize the incoming acid (50,000 gal). This ensures that the heat of reaction is distributed across a minimal volume of waste. Heating of the waste causes vaporization of water that results in the buildup of aerosols in the tank headspace and pressurizes the tank. It is assumed that the HEPA filters fail, contributing further to the consequences. The energy released by the reaction heats the acid-waste mixture to the boiling point. The remainder of the energy produces steam; condensation of the steam on the walls of the tank was assumed to be insignificant. The reaction was conservatively considered to be instantaneous. Reactions were considered in DSTs and DCRTs. The contributors to the toxicological consequences are the HEPA filter release, the aerosolized waste, and sulfuric acid fumes. Although the contribution from a potential dome collapse was considered, it was not included since the pressure buildup from boiling would not be instantaneous allowing pressure relief due to lifted cover blocks, etc.

B2.1 DOUBLE-SHELL TANK CONSEQUENCES

B2.1.1 Contribution from Aerosolized Waste

Sulfuric acid is a common industrial chemical. It is also typically transported at 100% concentration (18.7 M) to reduce costs and lower its corrosion potential. The reaction of sulfuric acid with sodium hydroxide is shown below:

$$H_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2H_2O.$$

The energy released is 208 kJ/mole H_2SO_4. Total energy released from reaction is calculated as follows:

$$(208 \text{ kJ/mole})\ (18.7 \text{ mole/L})\ (3.785 \text{ L/gal})\ (5{,}000 \text{ gal}) = 7.36 \times 10^7 \text{ kJ}.$$

It is conservatively assumed that there will be a small heel remaining in the tank. This is extremely conservative as it is unlikely that a nearly empty tank will receive any chemical additions. The tank is assumed to contain only 50,000 gal of waste, despite its 1,000,000-gal capacity, with sufficient caustic to completely neutralize the acid (>3.7 mole/L).

Assuming that the starting temperature of the waste acid mixture is 40 °C, the energy required to heat the mixture to boiling point is calculated as follows:

$$(120\ °C - 40\ °C)\ (4.2 \text{ kJ/kg}\cdot °C)\ (50{,}000 \text{ gal})\ (3.785 \text{ L/gal})\ (1.1 \text{ kg/L}) = 6.99 \times 10^7 \text{ kJ}$$

where:

4.2kJ/kg °C	= specific heat of water (Weast 1981)
1.1 kg/L	= assumed density of the supernatant
120 °C	= assumed boiling point of the supernatant.

Some energy will be lost through the walls of the tank. It is assumed that the annulus acts as an insulator (i.e., no annulus ventilation). The energy lost to the surroundings will be small and is conservatively assumed to be zero for this accident.

Energy available for steam production = (energy from reaction) – (energy heating the solution to boiling point)

$$(7.36 \times 10^7 \text{ kJ}) - (6.99 \times 10^7 \text{ kJ}) = 3.70 \times 10^6 \text{ kJ}.$$

The mass of water vaporized is calculated as follows:

$$(3.70 \times 10^6 \text{ kJ}) / (2.26 \times 10^3 \text{ kJ/kg}) = 1.64 \times 10^3 \text{ kg}$$

where:

2.26×10^3 kJ/kg = latent heat of vaporization for water (Himmelblau 1974).

It was proposed that the boiling of the waste could result in sufficient bubble swell and insufficient bubble release (despite the low surface tension) to result in waste being carried out of the tank. Even if this were to occur, the release would be limited to the immediate vicinity. The consequences to the onsite worker (located 100 m away) will not be significantly affected.

The source term used for the aerosol in this analysis is 10% DST solids and 90% DST liquids. Boiling will occur in the vicinity of the incoming acid stream. The agitation caused by the boiling will not cause the solid waste to be thoroughly mixed with the liquid. In addition, the solids will settle out as they pass through the liquid phase toward the surface. The inclusion of 10% solids in the aerosol is a conservative assumption. An ARF of 2.0×10^{-3} and a respirable fraction of 1.0 are based on those associated with boiling of aqueous solutions in flowing air from DOE-HDBK-3010-94. The ARF being used is a conservative value chosen because of the uncertainty involved with the churn turbulent flow conditions generated by the boiling rates encountered during this accident. It is expected that the capture of secondary drops by the large number of primary bubbles would limit the release to an ARF less than that chosen. The ARF chosen is based on, and bounds, a vigorous boiling experiment that, conservatively, included solution splattered from the vessel onto the glassware in the calculated ARF (DOE-HDBK-3010-94). The toxicological source terms for the waste are from RPP-8369, *Chemical Source Terms for Tank Farms Safety Analyses.*

The waste aerosolized is calculated as follows:

$$(1.64 \times 10^3 \text{ kg})\,(2 \times 10^{-3}) = 3.28 \text{ kg} = 3.28 \times 10^3 \text{ g}.$$

Converting to liters aerosolized yields

$(3.28 \times 10^3 \text{ g}) / (1{,}200 \text{ g/L}) = 2.73 \text{ L}$

where

1,200 g/L is the assumed density of the aerosol (90% liquid and 10% solid).

Since the release occurs over 28.6 min (based on the addition rate of 175 gal/m)

$(2.73 \text{ L}) / [(28.6 \text{ min}) (60 \text{ s/min})] = 1.59 \times 10^{-3} \text{ L/s} = 1.59 \times 10^{-6} \text{ m}^3/\text{s}$.

B2.1.1.1 Onsite Contribution of Aerosolized Waste

Given

Onsite, high consequence sum of fractions (SOF) multiplier for DST liquids $= 1.16 \times 10^7$ (RPP-8369)
Onsite, high consequence SOF multiplier for DST solids $= 8.06 \times 10^7$ (RPP-8369)

Onsite aerosol, high consequence SOF multiplier $= [(1.16 \times 10^7) (0.9)] + [(8.06 \times 10^7) (0.1)]$
$= 1.85 \times 10^7$.

And

Onsite, moderate consequence SOF multiplier for DST liquids $= 3.45 \times 10^8$ (RPP-8369)
Onsite, moderate consequence SOF multiplier for DST solids $= 7.26 \times 10^8$ (RPP-8369)

Onsite aerosol, moderate consequence SOF multiplier $= [(3.45 \times 10^8) (0.9)] + [(7.26 \times 10^8) (0.1)]$
$= 3.83 \times 10^8$.

Onsite aerosol SOF = (aerosol release rate) (onsite SOF multiplier) (onsite χ/Q)

Onsite, high consequence $SOF_{aerosol}$ $= (1.59 \times 10^{-6} \text{ m}^3/\text{s}) (1.85 \times 10^7) (0.0328 \text{ s/m}^3)$
$= 9.6 \times 10^{-1}$

Onsite, moderate consequence $SOF_{aerosol}$ $= (1.59 \times 10^{-6} \text{ m}^3/\text{s}) (3.83 \times 10^8) (0.0328 \text{ s/m}^3)$
$= 2.0 \times 10^1$

where:

0.0328 s/m^3 = onsite χ/Q (RPP-13482).

B2.1.1.2 Offsite Contribution of Aerosolized Waste

Given

Offsite, high consequence SOF multiplier for DST liquids $= 3.45 \times 10^8$ (RPP-8369)
Offsite, high consequence SOF multiplier for DST solids $= 7.26 \times 10^8$ (RPP-8369)

Offsite aerosol, high consequence SOF multiplier = $[(3.45 \times 10^8)(0.9)] + [(7.26 \times 10^8)(0.1)]$
$= 3.83 \times 10^8$.

And

Offsite, moderate consequence SOF multiplier for DST liquids = 2.74×10^9 (RPP-8369)
Offsite, moderate consequence SOF multiplier for DST solids = 1.38×10^9 (RPP-8369)

Offsite aerosol, moderate consequence SOF multiplier
$= [(2.74 \times 10^9)(0.9)] + [(1.38 \times 10^9)(0.1)]$
$= 2.6 \times 10^9$.

Offsite aerosol SOF = (aerosol release rate) (offsite SOF multiplier) (offsite χ/Q)

Offsite, high consequence $SOF_{aerosol}$ $= (1.59 \times 10^{-6}\ m^3/s)(3.83 \times 10^8)(2.22 \times 10^{-5}\ s/m^3)$
$= 1.4 \times 10^{-2}$

Offsite, moderate consequence $SOF_{aerosol}$ $= (1.59 \times 10^{-6}\ m^3/s)(2.6 \times 10^9)(2.22 \times 10^{-5}\ s/m^3)$
$= 9.2 \times 10^{-2}$

where:

$2.22 \times 10^{-5}\ s/m^3$ = offsite χ/Q (RPP-13482).

B2.1.2 Contribution from the High-Efficiency Particulate Air Filter

Since the steam volume exceeds the headspace volume, it is assumed that the tank pressurizes sufficiently to fail the HEPA filters.

Given

DST HEPA release due to overpressure = 5.4×10^{-5} L at 5% solids (RPP-13437)
Release time = 60 s (RPP-13482)

Release rate = $(5.4 \times 10^{-5}\ L) / (60\ s) = 9.0 \times 10^{-7}\ L/s = 9.0 \times 10^{-10}\ m^3/s$.

B2.1.2.1 Onsite Contribution of High-Efficiency Particulate Air Filter Release

Onsite HEPA, high consequence SOF multiplier (95% DST liquids)= 1.51×10^7

Onsite HEPA, moderate consequence SOF multiplier (95% DST liquids) = 3.64×10^8

Onsite HEPA SOF = (HEPA release rate) (onsite SOF multiplier) (onsite χ/Q)

Onsite, high consequence SOF_{HEPA} = $(9.0 \times 10^{-10}\ m^3/s)(1.51 \times 10^7)(0.0328\ s/m^3)$
$= 4.5 \times 10^{-4}$

Onsite, moderate consequence $SOF_{HEPA} = (9.0 \times 10^{-10}\ m^3/s)\ (3.64 \times 10^8)\ (0.0328\ s/m^3)$
$= 1.1 \times 10^{-2}$

where:

$0.0328\ s/m^3$ = onsite χ/Q (RPP-13482).

B2.1.2.2 Offsite Contribution of High Efficiency Particulate Air Filter Release

Offsite HEPA, high consequence SOF multiplier (95% DST liquids)= 3.64×10^8

Offsite HEPA, moderate consequence SOF multiplier (95% DST liquids) = 2.67×10^9

Offsite HEPA SOF = (HEPA release rate) (offsite SOF multiplier) (offsite χ/Q)

Offsite, high consequence $SOF_{HEPA} = (9.0 \times 10^{-10}\ m^3/s)\ (3.64 \times 10^8)\ (2.22 \times 10^{-5}\ s/m^3)$
$= 7.3 \times 10^{-6}$

Offsite, moderate consequence $SOF_{HEPA} = (9.0 \times 10^{-10}\ m^3/s)\ (2.67 \times 10^9)\ (2.22 \times 10^{-5}\ s/m^3)$
$= 5.3 \times 10^{-5}$

where:

$2.22 \times 10^{-5}\ s/m^3$ = offsite χ/Q (RPP-13482).

B2.1.3 Contribution from the Sulfuric Acid Fumes

The addition of sulfuric acid to the tank would also result in some quantity of sulfuric acid being present in the vapor as it exits from the tank. The quantity can be estimated from the partial pressure of sulfuric acid at the conditions encountered.

Mass sulfuric acid = (5000 gal) (3.785 L/gal) (1.86 kg/L) = 3.52×10^4 kg

Mass tank waste = (50,000 gal) (3.785 L/gal) (1.1 kg/L) = 2.08×10^5 kg

Weight percent sulfuric acid = $[(3.52 \times 10^4\ kg) / (3.52 \times 10^4\ kg + 2.08 \times 10^5\ kg)] \times 100 = 14.5$

where:

1.1 kg/L = assumed density of the waste
1.86 kg/L = density of sulfuric acid (Weast 1981).

The vapor pressures of sulfuric acid and aqueous waste (water) at 20% sulfuric acid and 120 °C can be found.

Partial pressure of sulfuric acid = 4.32×10^{-11} bar (*Perry's Chemical Engineer's Handbook* [Perry 1984])

Partial pressure of waste = 1.74×10^0 bar (Perry 1984)

The total amount of sulfuric acid leaving the tank can then be found as a proportion of the water being turned to steam. Partial pressures of steam and sulfuric acid vapors are proportionate to the number of moles of each.

$[(2.70 \times 10^3 \text{ kg})/(18 \text{ kg/kg mole water})]\ [(4.32 \times 10^{-11} \text{ bar})/(1.74 \times 10^0 \text{ bar} + 4.32 \times 10^{-11} \text{ bar})]$
$= 3.7 \times 10^{-9}$ kg moles sulfuric acid vapors

The venting occurs for 50 min.

$(3.7 \times 10^{-9} \text{ kg moles})\ (98 \text{ kg/kg mole}) / [(50 \text{ min})\ (60 \text{ s/min})] = 1.2 \times 10^{-10} \text{ kg/s} = 1.2 \times 10^{-7} \text{ g/s}$

B2.1.3.1 Onsite Contribution of Sulfuric Acid

Onsite sulfuric SOF = (sulfuric acid release rate) (onsite χ/Q) / (sulfuric acid temporary emergency exposure limit [TEEL])

Onsite, high consequence $SOF_{sulfuric}$ $= (1.2 \times 10^{-7} \text{ g/s})\ (0.0328 \text{ s/m}^3) / (3.0 \times 10^{-2} \text{ g/m}^3)$
$= 1.3 \times 10^{-7}$

Onsite, moderate consequence $SOF_{sulfuric}$ $= (1.2 \times 10^{-7} \text{ g/s})\ (0.0328 \text{ s/m}^3) / (1.0 \times 10^{-2} \text{ g/m}^3)$
$= 3.9 \times 10^{-7}$

where:

0.0328 s/m^3	= onsite χ/Q (RPP-13482)
$3.0 \times 10^{-2} \text{ g/m}^3$	= sulfuric acid TEEL-3 (WSMS-SAE-02-001, *ERPGs and TEELs for Chemicals of Concern*)
$1.0 \times 10^{-2} \text{ g/m}^3$	= sulfuric acid TEEL-2 (WSMS-SAE-02-001).

B2.1.3.2 Offsite Contribution of Sulfuric Acid

Offsite sulfuric SOF = (sulfuric acid release rate) (offsite χ/Q) / (sulfuric acid TEEL)

Offsite, high consequence $SOF_{sulfuric}$ $= (1.2 \times 10^{-7} \text{ g/s})\ (2.22 \times 10^{-5} \text{ s/m}^3) / (1.0 \times 10^{-2} \text{ g/m}^3)$
$= 2.7 \times 10^{-10}$

Offsite, moderate consequence $SOF_{sulfuric}$ $= (1.2 \times 10^{-7} \text{ g/s})\ (2.22 \times 10^{-5} \text{ s/m}^3) / (2.0 \times 10^{-3} \text{ g/m}^3)$
$= 1.3 \times 10^{-9}$

where:

$2.22 \times 10^{-5} \text{ s/m}^3$	= offsite χ/Q (RPP-13482)
$1.0 \times 10^{-2} \text{ g/m}^3$	= sulfuric acid TEEL-2 (WSMS-SAE-02-001)
$2.0 \times 10^{-3} \text{ g/m}^3$	= sulfuric acid TEEL-1 (WSMS-SAE-02-001).

B2.1.4 Overall Toxicological Consequences

B2.1.4.1 Total Onsite Toxicological Consequences

Total onsite toxicological consequences = (aerosol contribution) + (HEPA contribution) + (sulfuric acid contribution)

Onsite, high consequence SOF_{Total} $= (9.6 \times 10^{-1}) + (4.5 \times 10^{-4}) + (1.3 \times 10^{-7})$
$= 9.6 \times 10^{-1}$

Onsite, moderate consequence SOF_{Total} $= (2.0 \times 10^{1}) + (1.1 \times 10^{-2}) + (3.9 \times 10^{-7})$
$= 2.0 \times 10^{1}$

B2.1.4.2 Total Offsite Toxicological Consequences

Total offsite toxicological consequences = (aerosol contribution) + (HEPA contribution) + (sulfuric acid contribution)

Offsite, high consequence SOF_{Total} $= (1.4 \times 10^{-2}) + (7.3 \times 10^{-6}) + (2.7 \times 10^{-10})$
$= 1.4 \times 10^{-2}$

Offsite, moderate consequence SOF_{Total} $= (9.2 \times 10^{-2}) + (5.3 \times 10^{-5}) + (1.3 \times 10^{-9})$
$= 9.2 \times 10^{-2}$.

B2.2 DOUBLE-CONTAINED RECEIVER TANK CONSEQUENCES

The mixing of incompatible materials accident scenario for a DCRT is significantly different than for a DST. The maximum capacity of a DCRT is 31,000 gal. Since the addition postulates a 5,000 gal addition, a reasonably bounding volume of tank waste would be 25,000 gal. The concentration of hydroxide in the waste is assumed to be 3.6 M (PNNL 2002). This bounds the concentration in the DCRTs, as well as the saltwell waste received for interim stabilization. Due to the limited hydroxide content, the sulfuric acid will not be completely neutralized. In other words, the energy produced in the reaction of sulfuric acid with hydroxide will be limited by the hydroxide content.

Sulfuric acid is a common industrial chemical. It is also typically transported at 100% concentration (18.7 M) to reduce costs and lower its corrosion potential. The reaction of sulfuric acid with sodium hydroxide is shown below:

$$H_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2H_2O.$$

The energy released is 208 kJ/mole H_2SO_4. The amount of acid that reacts is limited by the total hydroxide content:

$$(25{,}000 \text{ gal})\ (3.785 \text{ L/gal})\ (3.6 \text{ moles hydroxide/L}) = 3.41 \times 10^{5} \text{ moles hydroxide.}$$

Since two moles of hydroxide are required for each mole of sulfuric acid:

(3.41 x 10^5 moles hydroxide) / (2 moles hydroxide/mole sulfuric acid) = 1.70 x 10^5 moles H_2SO_4

Total energy released from reaction is calculated as follows:

(208 kJ/mole H_2SO_4) (1.70 x 10^5 moles H_2SO_4) = 3.54 x 10^7 kJ.

Assuming that the starting temperature of the waste acid mixture is 40 °C, the energy required to heat the mixture to boiling point is calculated as follows:

(120 °C – 40 °C) (4.2 kJ/kg· °C) (30,000 gal) (3.785 L/gal) (1.1 kg/L) = 4.20 x 10^7 kJ

where

4.2kJ/kg· °C	= specific heat of water (Weast 1981)
1.1 kg/L	= assumed density of the supernatant
120 °C	= assumed boiling point of the supernatant.

Some energy will be lost through the walls of the tank. The energy lost to the surroundings will be small and is conservatively assumed to be zero for this accident.

Energy available for steam production = (energy from reaction) – (energy heating the solution to boiling point)

(3.54 x 10^7 kJ) – (4.20 x 10^7 kJ) = 0 kJ.

Since there is no energy available for bulk boiling, the only aerosol produced would be from the increased vapor pressure of the heated waste solutions. The pressurization and release from the increased vapor pressure will be insignificant compared to the DST case. Therefore, the offsite and onsite consequences of the mixing of incompatible materials in DCRTs were not analyzed further.

B3.0 RESULTS

Tables B3-1 and B3-2 compare the accident consequences with the risk evaluation guidelines. Reviewing the consequences shows that the mixing of incompatible materials accident is below the onsite radiological guidelines for moderate consequences. Offsite toxicological consequences are also below the guidelines. However, the toxicological release exceeds the onsite toxicological guidelines for moderate consequences.

Table B3-1. Summary of Onsite Radiological Consequences Without Controls for the Mixing of Incompatible Materials.

Case	Onsite Radiological Consequences		
	Calculated dose (rem)	**Moderate consequence guideline (rem)**	**High consequence guideline (rem)**
Mixing of incompatible materials in DSTs	$3.2 \times 10^{+0}$	$2.5 \times 10^{+1}$	$1.0 \times 10^{+2}$

Note:
DST = double-shell tank.

Table B3-2. Summary of Toxicological Consequences Without Controls for the Mixing of Incompatible Materials.

Case	Toxicological Consequences							
	Onsite				Offsite			
	Moderate consequence		High consequence		Moderate consequence		High consequence	
	SOF	**Guideline**	**SOF**	**Guideline**	**SOF**	**Guideline**	**SOF**	**Guideline**
Mixing of incompatible materials in DSTs	2.0×10^{1}	1	9.6×10^{-1}	1	9.2×10^{-2}	1	1.4×10^{-2}	1

Notes:
DST = double-shell tank.
SOF = sum of fractions.

B4.0 REFERENCES

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B5.0 PEER REVIEW CHECKLIST

Document Reviewed: RPP-12646, *Mixing of Incompatible Materials in Waste Tanks Technical Basis Document*, Rev. 0 (Appendix B only)

Scope of Review (e.g., document section or portion of calculation):

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[X]	[ ]	[ ]	1. Previous reviews are complete and cover the analysis, up to the scope of this review, with no gaps.
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[X]	[ ]	[ ]	19. Safety margins are consistent with good engineering practices.

[X]	[ ]	[ ]	20. Conclusions are consistent with analytical results and applicable limits.
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J.C. Williams J.C. Williams 2/13/03
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APPENDIX C

MIXING OF INCOMPATIBLE MATERIALS CONTROL DECISION MEETING ATTENDEES

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APPENDIX C

MIXING OF INCOMPATIBLE MATERIALS CONTROL DECISION MEETING ATTENDEES

MIXING OF INCOMPATIBLE MATERIALS
CONTROL DECISION MEETING ATTENDANCE
SEPTEMBER 16, 2002

Name	Knowledge Area(s) Represented (see below)	Organization	Telephone Number
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Kevin Sandgren	1,2,3,6,7,9,10	NS&L - CHG	373-0377
JOSEPH BEVERLAQUA	1-23	ORG	376-8743
JON C GEISBOSH		CHG/ADI	373-0486
CLIFF HAMPTON		CHG OAS	372-0586
Nancy Walker	1,2,3,4,10	NS&L DSA	373-9045
Jennifer Stewart	1,7,9		
Ed Ford	1,2,3,6,7,9,10	NS&L - CHG	373-1296
MILTON V. Shultz	1,2,3,6,7,9,10	NS&L - CHG	372-3740
Tim Infuzzarne	1,2,3,4,5,9,10		
Mark Sandman		DNFSB	373-0101
Curt Reichmuth	5	SST	6-4796
Brad Smith		CHG NS&L	376-1907

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2 *Safety Analysis*
3 Hazard Analysis
4 Engineering
5 Operations
6 Accident Analysis
7 Nuclear Safety
8 *Design Authority*
9 Technical Safety Requirements
10 *Safety Structures, Systems, and Components*
11 Emergency Preparedness
12 Radiological Control
13 Regulatory Compliance
14 Environmental Protection
15 Quality Assurance
16 *Other - specify*
17 Industrial Safety
18 *Project Management*
19 Industrial Hygiene
20 Maintenance Engineering
21 Reliability Engineering
22 Process Engineering
23 Equipment Engineering

MIXING OF INCOMPATIBLE MATERIALS
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Robin Fogg	19	EH&S	3-0630
BC Wyatt	5	CHG	3-3355
MA White	5	CHG	3-3355
K.D. Fowler	16-Crit Safety, 22	CHG	3-5936
R.D Carrell	2 3 6 7 9 10	ORP support	947-6421
Tom Black	4	SYS Eng	373-3880

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2 Safety Analysis
3 Hazard Analysis
4 Engineering
5 Operations
6 Accident Analysis
7 Nuclear Safety
8 Design Authority
9 Technical Safety Requirements
10 Safety Structures, Systems, and Components
11 Emergency Preparedness
12 Radiological Control
13 Regulatory Compliance
14 Environmental Protection
15 Quality Assurance
16 Other - specify
17 Industrial Safety
18 Project Management
19 Industrial Hygiene
20 Maintenance Engineering
21 Reliability Engineering
22 Process Engineering
23 Equipment Engineering

MIXING OF INCOMPATIBLE MATERIALS
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Kevin Sandgren	1,2,3,6,9	NS&L	372-0374
Bobby McDaniel	2,3,5,9	OPS	373-1450
CHUNN MALCOM	5	OPS	373-2525
Johnston, Julie	5	CPO	3-3578
HAMPTON, CLIFFORD	2,3,5,9,13	OPS	2-0586
Bob Carrell	2 6 7 9 10	ORP-support	521-6421
Brad Evans	1-3,6,7,9,10		
MILTON SHULTZ	2,3,6,7,9,10	CHG - NS&L	372-3740
Ed Ford	2,3,6,7,9,10	CHG - NS&L	373-1296
Mark Sautmen		DNFSB	373-0101
KENNY FOWLER	4,27,16-Crit Safety	CHG Proc Engr	373-5930
Greg Jones	1,2,3,5,7,9,10	OPS	373-5717

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5 Operations
6 Accident Analysis
7 Nuclear Safety
8 Design Authority
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10 Safety Structures, Systems, and Components
11 Emergency Preparedness
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MIXING OF INCOMPATIBLE MATERIALS
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TODD Bleak	4	DST SYS Eng	3-3880
W.J. Powell	4	Design Eng	373-1072
M.A. Fish	4	Design Eng.	372-3657
J.L. Stewart	1,7,9	NS&L	376-5633
JON SPARKS		QA	372-1749
Craig Carro	1,2,3,4,7 (PARTIAL)		
Eustolio Salinas	5	EAST TANK FARM	373-3475
Wujiele Walker	1 2 3 4 7 9 10	NS&L	373-1342
Tim Trapuzzano	1,2,3,4,5,7,9,10	NS&L	373-1342
Curt Reichmuth	5	337 OPS	6496

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2 Safety Analysis
3 Hazard Analysis
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6 Accident Analysis
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APPENDIX D

PEER REVIEW CHECKLIST

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APPENDIX D

PEER REVIEW CHECKLIST

Note: There is a separate peer review checklist for Appendix B, found in Appendix B, Section B5.0.

Document Reviewed: RPP-12646, *Mixing of Incompatible Materials in Waste Tanks Technical Basis Document*, Rev. 0

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[X]	[ ]	[ ]	39. The document was prepared in accordance with HNF-2353, Section 4.3, Attachment B, "Calculation Note Format and Preparation Instructions".
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[ ]	[ ]	[X]	20. Conclusions are consistent with analytical results and applicable limits.

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Laurie L. Kraemer Laurie L. Kraemer 3/20/03

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