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ABSTRACT

In this report, we examine several long-term issues: the effect of pump operation on future gas release events (GREs), uncontrolled chemical reactions, chronic toxic gas releases, foaming, and erosion and corrosion. Heat load in excess of the design limit, uncontrolled chemical reactions, chronic toxic gas releases, foaming, and erosion and corrosion have been shown not to be safety concerns. The effect of pump operation on future GREs could not be quantified.

The problem with evaluating the long-term effects of pump operation on GREs is a lack of knowledge and uncertainty. In particular, the phenomena governing gas retention, particle size distribution, and settling are not well understood, nor are the interactions among these factors understood. There is a possibility that changes in these factors could increase the size of future GREs. Bounding estimates of the potential increase in size of GREs are not possible because of a lack of engineering data.

Proper management of the hazards can reduce, but not eliminate, the possibility of undesirable changes. Maintaining temperature within the historical limits can reduce the possibility of undesirable changes. A monitoring program to detect changes in the gas composition and crust thickness will help detect slowly occurring changes. Because pump operation has be shown to eliminate GREs, continued pump operation can eliminate the hazards associated with future GREs.

INTRODUCTION

The major long-term safety issue associated with mixer pump operation is the possibility that extended operation will result in irreversible or slowly reversible changes to the tank, which could make the tank behavior worse. In discussing pump-induced changes, it is important to remember that the waste tank is not static. The question is not whether mixing will change the tank. The tank will change regardless of whether the mixer pump is operated. The question is whether mixing will alter future tank behavior in an undesirable way over an extended period of time.

The safety concerns are divided into six categories:

1. worsening of gas release events (GREs),
2. heat load in excess of the design limit,
3. uncontrolled chemical reactions,
4. chronic toxic gas releases,
5. excessive foaming, and
6. accelerated erosion or corrosion.

Each concern is addressed in a separate section. Concern #1 is the most challenging in terms of defining a safety envelope. Consequently, the discussion of this topic is lengthy compared to other topics.

CONCERNS REGARDING GAS RELEASE EVENTS

The current pump is a test pump and has a limited life. Consequently, it cannot be relied on to mix the waste indefinitely. Also, pump breakdown or termination of operation because of instrument failure is possible. Once the pump is shut down, the tank will generate and accumulate gas, leading to subsequent GREs. The primary concern is whether operating the mixer pump will cause an increase in the severity or frequency of GREs after the pump is shut down. Although the discussion in this section applies to natural rollovers, many of the issues also apply to induced rollovers.

Method of Evaluation

The impact of long-term pump operation on the waste is not completely understood. The concern that GREs could be worse if the mixer pump fails arises because there is a lack of knowledge. A method for identifying hazards that arise from uncertainty and incomplete knowledge is used to identify possible adverse consequences of pump operation on GREs. This method is based on a hazards and operability study (HAZOPS).[1] A HAZOPS is a systematic method of examining the causes and consequences of deviations of process parameters from the nominal operating conditions. In this evaluation of uncertainty, the nominal model predictions are analogous to the normal operating conditions in a HAZOPS; the deviations are errors in the model. These errors can be represented by alternative assumptions. The first step in this method is to tabulate all assumptions. Next, each assumption is examined to determine possible deviations or alternative assumptions, and the consequences of the deviations are determined. This method of identifying lack-of-knowledge hazards was used in the evaluation of mitigation by dilution.[2]

Description of the Conceptual Model

The basis of the hazard evaluation method used in this section is a model. Although there is an insufficient understanding of the tank to develop a detailed quantitative model, it is possible to develop a conceptual model of the gross behavior. This section describes briefly a conceptual model. It is important to emphasize that the model is conceptual and contains many assumptions that cannot be verified directly. However, indirect evidence for this model is provided at the end of this discussion.

Before pump installation and operation, the waste in Tank 101-SY was layered. If pump operation stops, the layers observed in the past are expected to form again. The top layer, or crust, consists of floating solids. The crust is highly porous, and it creates a stagnant layer of liquid near the top of the tank. The second layer is the convective layer (C layer). The window convective core sample analysis[3] indicates that this layer consists of solids, liquid, and gas, with ~11 wt % solids. This is called the C layer because fluid mixing occurs possibly as a result of thermal convection. The third and bottom layer consists of sludge and is called the nonconvective layer (NC layer) because it appears that no mixing occurs during the period between GREs. The solids form flocks; therefore, the NC layer has a compressive yield strength, and the solids fraction in the layer depends on the thickness of the layer. At nominal conditions, the NC layer contains ~37 wt % solids and has shear strength.[4] The solids fraction, strength, and thickness of the NC layer may not be uniform.

Gas is generated in both the C and NC layers. The major products of the gas generating reactions are hydrogen, nitrous oxide, nitrogen, and ammonia.[5] Small amounts of methane also are generated.[6] The mechanism is complex and consists of several reactions. Both ordinary chemical reactions and radiolysis reactions appear to contribute. The primary source of gas appears to be liquid-phase reactions.

The decomposition of the organic chelating agents plays an important role in gas generation. Decomposition of the organics, as well as radiolysis of water, produces hydrogen. Reduction of the nitrite ions by the organics generates nitrous oxide, nitrogen, and ammonia. The gas generation rate increases with temperature. The activation energy for overall gas generation is reported to be ~1.0×10^8 J/kg-mole (~24,000 cal/mole).[7] If the waste is heated to temperatures greater than those observed in the waste tank, the methane concentration may increase and nitric oxide may form.[7] The ratio of hydrogen to other gases increases with decreasing waste temperature.[8]

Although gas is generated and retained in the C layer, it is believed to have achieved some steady-state value; therefore, gas is released from the C layer as it is generated. All or most of the gas generated in the NC layer accumulates in that layer, causing the tank level to rise during the period between GREs.

The details of gas bubble retention are not known. Some of the possible mechanisms are: (1) the solids behave as a porous media, and bubbles are trapped in the pores; (2) bubbles are bound to the solids by surface forces; and (3) the NC layer behaves as a homogeneous Bingham plastic and retains gas as a result of shear strength. More than one mechanism may exist. The second mechanism always will exist to some degree. All three mechanisms favor gas retention as small bubbles. Gas accumulation is likely to vary with position.

Solubility also is a mechanism of gas retention. Hydrogen, nitrogen, and methane essentially are insoluble in the waste; therefore, solubility is not a significant retention mechanism for these gases. Nitrous oxide is slightly soluble, but solubility is not an important mechanism of retention because ~90% of the nitrous oxide is retained in the bubbles. Ammonia is very soluble in the waste: over 90% of the ammonia retained by the tank is in solution. Material balance calculations also indicate that the ammonia inventory may not have reached a steady state.[9]

When sufficient gas accumulates in the NC layer, buoyancy forces are sufficient to overcome the strength of the slurry, and some of the gas-containing sludge will rise to the surface and mix with the C layer. The fraction of the NC layer that participates in the rollover varies from event to event because of nonuniformities in density, void fraction, and strength. The thickness of the sludge that does not participate in the rollover may not be uniform. The history of the previous releases may affect the variations. As the mass of the NC layer rises to the surface, it releases gas and settles to the bottom of the tank; the cycle begins again.

Gas is released from the waste by two mechanisms: direct release of bubbles and mass transfer. Sparsely soluble gases are released only in the bubbles. Ammonia is released in the bubbles and as a result of mass transfer from the surface of the tank. The concentration of ammonia in the bubbles is governed by equilibrium. Bubbles released during a rollover are saturated at the conditions of the NC layer because there is very little mass transfer to the bubbles as they rise to the surface. During the rollover, the liquid-phase mass-transfer resistance at the tank surface is very small. Between rollovers, the surface is stagnant; therefore, mass transfer in the liquid is approximated as diffusion in a stagnant pool with infinite depth.

Cyclic heating and cooling also accompany the rollover cycle. Heat is generated in the tank from radioactive decay and chemical reaction. Heat loss occurs through the surface and sides of the tank; possible salt cake on the tank walls will inhibit heat loss. Convection enhances heat transfer in the C layer; therefore, cooling occurs in this layer during the period between GREs. Because of a lack of mixing, heat accumulates in the NC layer. Mixing of the layers during a GRE transfers heat from the NC layer to the C layer. Because of radioactive decay, there may be a net decrease in the average temperature with time.

Cooling of the C layer causes salts to precipitate and settle, which increases the mass of solids in the NC layer. Conversely, heating of the NC layer causes solids to dissolve. Because of the lack of mixing in the NC layer, temperatures are not uniform; the maximum temperature is in the middle of the layer. Heating and cooling of the NC and C layers, as well as the nonuniform temperature profile in the NC layer, may influence the GRE cycle.

Tank data, experimental studies, and modeling studies support this conceptual model. Past temperature profile data and Window C core samples give evidence of three separate layers.[3,10] The nearly constant temperature in the C layer indicates mixing. The temperature profile near the surface of the waste indicates that conduction is the dominant heat-transfer mechanism, which implies either a crust or a stagnant layer. The "bulging" profile in the NC layer also is characteristic of conduction in solids, which implies no mixing.

The solids fraction in the NC layer is much lower than for a closely packed arrangement, which indicates that flocks may have formed. The ability to increase the solids fraction in the Window C core samples by centrifugation indicates that the settled solids are compressible, which is characteristic of flocculating solids.[11] The ability to increase the solids fraction by centrifugation also indicates that the solids fraction in the NC layer is a function of thickness.

The thickness of the NC layer has increased over time as a result of precipitation of solids that occurs from the gradual cooling of the tank. After the Window G event, there was a large increase in the thickness of the NC layer at the thermocouple tree, without a corresponding drop in the average tank temperature. This sudden increase supports the theory that the thickness of the NC layer is not uniform.

Only indirect evidence is available for the assumption that gas is generated by liquid-phase chemical reactions. In a study of the effect of temperature changes on the growth of the NC layer, only models that included liquid-phase gas generation were capable of simultaneously predicting that the interval between rollovers would increase with an increasing NC layer, with reasonable values for the background hydrogen concentration, and with a decrease in background hydrogen with increasing NC-layer thickness. The results of this study are summarized in App. A. Preliminary results from experiments with the actual waste also support the liquid-phase gas generation model. If the waste is heated to 100°C (212°F), most of the solids will dissolve, and preliminary results from the experiment indicate increase gas generation.[7] If solid-phase or heterogeneous-phase reactions were responsible for the gas generation, dissolving the solids should decrease the rate of reaction. Waste simulant studies show that gas generation by thermal reactions may be catalyzed by the solids, but radiolysis experiments with simulants show that solids have no impact on the rate of gas generation.[8] Thus, the available evidence shows that the liquid-phase reaction model is reasonable.

Experimental studies using waste simulants indicate that significant gas generation does not occur unless organics are present,[12–13] supporting the proposition that organic decomposition accounts for the gas generation. Isotopic labeling experiments demonstrate that nitrogen and nitrous oxide come from an inorganic source.[12] The main sources of inorganic nitrogen are the nitrates and nitrites.[12–13] The lack of significant nitrous oxide production without organics present supports the theory that nitrous oxide is produced by a reaction between organics and nitrates or nitrites.

Isotope labeling studies with waste simulants indicate that ~90% of the ammonia is produced from inorganic nitrogen sources and 10% from organic sources,[12] which supports the conceptual model. However, other experiments[13] indicate that no ammonia is produced without organics. Lack of ammonia production without organics may indicate that the organics act as a reducing agent for nitrous oxide rather than as an organic source of ammonia.

The background hydrogen and nitrous oxide concentrations show that gas is continually released from the tank. The background hydrogen concentration can be estimated by a simple model that assumes that (1) gas generation per unit volume of liquid is uniform in the tank, (2) all gas generated in the C layer is released, and (3) all gas generated in the NC layer is retained.[14] This model predicts reasonable values for the background hydrogen concentration, which supports the conceptual model.

The observed level rise is direct evidence that gas accumulates in the tank between GREs, but there is no clear evidence that can be used to support any of the bubble retention mechanisms listed above. Pump-operating data indicate that some of the bubbles are bound to the solids by surface forces. The neutral buoyancy model predicts that the level of the tank with all of the gas removed should be <9.91 m (<390 in.),[15] but vigorous pumping has not reduced the level below 10.16 m (400 in.). This comparison indicates that some of the gas is tightly bound to the solids by surface forces. As stated above, all three models of bubble retention favor small bubbles. The geometry of the particles limits bubble size in the porous media and surface force mechanisms. The reason for small bubbles in the Bingham plastic model is more complicated. Gas is approximately uniform throughout the NC layer; therefore, the creation of large bubbles requires transport of the gas to the bubbles either by diffusion or bubble migration. The diffusion of the gases in the liquid is too slow to account for the formation of large bubbles. The ability of the Bingham plastic to retain large bubbles is inconsistent with bubble migration. If small bubbles have enough mobility in the fluid to coalesce, the shear strength is not sufficient to retain large bubbles. Estimates of the Henry's law constant indicate that solubility is not a significant mechanism of gas retention for any gases except ammonia.[16]

The thermal mixing observed during a GRE indicates that the episodic gas releases are the result of a buoyancy-driven rollover. Tank data show an inherent variability in the duration, size, and level of the GREs. However, it is difficult to explain the observed variability without postulating the existence of nonuniformities in the tank. The thermal balance calculations summarized in App. B show that the size of the GRE depends on the volume of the NC layer that participates in the rollover. Temperature profile data demonstrate that the thickness of the remaining NC layer is nonuniform. A second thermocouple tree was installed in the tank after Event I. The thickness of the remaining NC layer as determined from the temperature profiles was found to be significantly different at the two locations.

The conceptual model states that the sparsely soluble gases are released only in the form of bubbles. The model is reasonable because there are insufficient amounts of these gases dissolved in the waste for mass transfer from the liquid to be a significant contributor to the released gas. On the other hand, ammonia is very soluble. Analysis of tank data shows that mass transfer is the major mechanism of ammonia release.[17] Approximately 60% of the ammonia is released by mass transfer from the surface of the waste, and 40% is released in the form of bubbles. Because of the long period between GREs, the bubbles trapped in the waste are expected to be saturated with ammonia. Calculations show that there is very little mass transfer to the bubbles during the rollover. Comparison to data shows that the stagnant pool model is reasonable during the period between events, and the liquid-phase mass-transfer resistance is negligible during the rollover.

The existence of salt cake on the walls has not been confirmed experimentally in the tank. Such a layer has been observed in simulated waste experiments. We postulated the existence of a salt cake layer on the wall to make tank heat-transfer calculations match observed temperatures;[18] however, gamma-scan data indicate that the salt cake layer is relatively thin.

The available data support the conceptual model of the tank, but they do not prove that the model is correct. However, proof of the model is not necessary because the purpose of the model is not to predict the effect of the mixer pump operation on long-term behavior but to provide a basis for discussing long-term issues.

Hazard Analysis

In examining the effect of pump operation on long-term behavior, the tank must be considered as a system. Since cessation of air lancing in 1989, no new materials have been added to the system, with the exception of some minor amounts of water, instruments, and mechanical equipment. With the exception of core samples and instruments, gases and water vapor are the only materials removed from the system. The hazard analysis considers the impact of pump operation on the waste tank system, assuming that there are no significant amounts of material added or removed from the waste tank.

The first step in the hazard evaluation process is to prepare a list of assumptions on which the conceptual model is based. A list of assumptions for the model of GREs and the impact of pump operation on GREs is given in App. C. The table gives the assumption, its basis, and its use in the analysis. The basis of the assumption is a brief statement of the data or rationale. The use of the assumption is a brief statement of how the assumption is used in the model.

The next step in the hazard evaluation process is to predict the future behavior of the rollover cycle, assuming that the mixer pump was never installed. Examination of this reference case is important because determining whether the mixer pump has a negative impact on the rollover cycle requires a comparison to the expected behavior without pump operation.

If the mixer pump had never been installed, gas generation in the waste would have continued at about the same rate. Because of continued gas generation, the cycle of GREs would have continued. Ammonia also would have continued to accumulate in the liquid phase. When all of the organics have been consumed, hydrogen production would be expected to decrease significantly and nitrous oxide, nitrogen, and ammonia production would be expected to cease. However, the conceptual model cannot predict the time required to consume the organics. The waste would continue to cool if the mixer pump had not been installed. Cooling would cause more solids to precipitate, which would result in larger GREs. The amount of ammonia released would be expected to decrease with time. Although the ammonia concentration in the liquid would be expected to increase, the effect of temperature on the Henry's law constant would be expected to be much greater. Cooling would be not expected to cause a significant growth of any salt cake layer because the concentration gradients near the walls of the tank are too small for significant mass transfer.

Based on the assumptions given in App. C, the mixer pump will have no impact on GREs that occur if the pump operation is terminated. However, if the model is not correct, future GREs could be worse. Appendix D contains tables summarizing the sensitivity of the model to deviations from the assumptions. The tables list the assumption, possible deviations from the assumption, the deviation source indicating why the deviation was considered, the consequence of the deviation on the model predictions, and comments concerning the deviation. The primary purpose of these tables is to identify hazards that could arise from uncertainty and lack of knowledge so that appropriate action can be taken.

The long-term hazards associated with a lack of complete knowledge can be divided into three broad categories: uncertainty in the current waste behavior and properties, changes that occur naturally, and changes that occur as a result of pump operation. Hazards that arise as a result of uncertainty in modeling current waste behavior are not discussed in this report because this behavior is not a long-term issue. Naturally occurring changes are considered because they may invalidate assumptions made in the safety analysis. The hazards identified in the analysis are:

- **Increase in Cooling Rate:** An increase in cooling rate may occur as a result of pump operation increasing the heat transfer or as a result of other operational changes. An increase in the cooling rate is undesirable because lower temperatures increase the solids inventory, which increases the size of GREs; lower temperatures may increase the strength of the waste, which could increase gas retention, and lower temperatures may change gas composition in undesirable ways. Although increased cooling is undesirable, data do not indicate that pump operation has accelerated the cooling rate.[19] Although increasing the cooling rate is a hazard, it is not expected to be a problem.

- **Uncertainty in Solubility:** Uncertainty in solubility is a hazard because knowledge of solubility is required to predict the sensitivity of the waste to changes in temperature. Changes that are affected by solubility are changes in gas retention and in gas composition with temperature. Uncertainty in solubility is not affected by pump operation.

- **Uncertainty in Waste Composition:** As with uncertainty in solubility, uncertainty in waste composition is a hazard because knowledge of solubility is required to predict the sensitivity of the waste to changes in temperature. The impact of uncertainty in composition is the same as uncertainty in solubility. Uncertainty in waste composition is not affected by pump operation.

- **Uncertainty in Gas Generation Kinetics:** Uncertainty in gas generation kinetics is a hazard because knowledge of the kinetics is required to predict the sensitivity of the gas generation rate and gas composition with temperature. Changing the gas generation rate affects the frequency of GREs, and changing the gas composition may increase the flammability hazard. Uncertainty in the kinetics is not affected by pump operation, except in the unlikely case involving heterogeneous reactions between the liquid and the solids. If this mechanism is true, pump-induced changes in gas composition could change the gas generation rate and gas composition.

- **Carbon Dioxide Absorption:** Carbon dioxide absorption increases the carbonate inventory in the waste. This could result in increased crust thickness, which would increase the structural hazards associated with crust movement; it also could result in an increase in the inventory of settled solids, which would increase the size of GREs. Because the magnitude of carbon dioxide absorption is unknown, its significance is unknown. In addition, pump operation could increase carbon dioxide absorption by increasing the mass-transfer rate.

- **Significant Increase in Shear Strength:** If shear strength is increased significantly, gas retention and the size of GREs could increase. Increasing the solids fraction and decreasing the temperature are expected to increase the strength of the slurry. The effect of crystal size distribution on strength is not known. Pump operations could affect the solids fraction in the NC layer and also affect the crystal size distribution. The shear strength of the NC layer is estimated to be ~5000 Pa (~0.73 lb/in.^{2}),[3] and it appears to have an insignificant effect on the maximum gas accumulation. Large changes in the solids fraction are required before strength has a significant impact on gas retention. The effect of retained gas on the shear strength of the NC layer is not understood. It usually is presumed that retained gas decreases the shear strength of the NC layer, but there are no data to support this claim. Gas retention could increase the shear strength.

- **Decrease the Amount of Unreleasable Gas:** As discussed above, some of the gas is bound tightly to the solids; thus, it is not liberated during GREs. Pump-induced changes in crystal size distribution could change the amount of unreleasable gas per mass of solid particles. The minimum level achieved as a result of vigorous pump operation is an indirect measure of the amount of unreleasable gas in the waste. Vigorous pump operation has not reduced the waste level significantly below 10.16 m (400 in.) since the pump was installed in July 1993; this indicates that the pump has not caused significant changes in the amount of unreleasable gas.[19] Although changes in unreleasable gas still must be considered a hazard, it is not expected to be a problem.

- **Increased Ammonia Release:** There are two mechanisms by which the pump could increase the ammonia release: pump operations could enhance mass transfer at the surface of the waste, and thinning of the crust could increase mass transfer at the surface of the waste during normal pump operation and during GREs. Analysis of data indicates that pump operations increase mass transfer, but not enough to cause a problem.[17] Calculations also show that even if there is a significant increase in ammonia mass transfer during the period between events, there is no safety problem as long as the ventilation system is operating.[17] Bounding mass-transfer calculations indicate that thinning the crust could increase the ammonia release significantly during GREs, as well as during the periods between events.[17] However, there is no indication that the crust is thinning,[19] although thinning of the crust must be considered to be a safety problem because the mechanisms of crust formation and destruction are not understood.

- **Increased Settling:** Pump operation could cause the solids suspended in the C layer to settle, which would increase the amount of retained gas, as well as the size of the GREs. Because the mechanism of suspending solids in the C layer is not known, the long-term impact of pump operation on settling is not known. The maximum impact of increased settling is a 40% increase in the size of GREs.

- **Thinning of the Crust:** There are two safety problems associated with thinning of the crust. First, thinning of the crust could increase ammonia mass transfer. This problem is discussed above. Second, thinning of the crust would result in increased solids in the NC layer, which would increase the amount of retained gas, as well as increase the size of GREs. There is no indication that the crust is thinning;[19] however, thinning of the crust must be considered a safety problem because the mechanisms of crust formation and destruction are not understood.

- **Crust Growth:** The mechanism of crust formation is not understood. Absorption of carbon dioxide to form sodium carbonate may play a role. Carbon dioxide absorption has been occurring over the entire history of the tank; this process could be enhanced by pump operation. A thicker crust would increase the structural consequences of impact during GREs. There is no indication that the crust is thickening;[19] however, crust growth must be considered a safety problem because the mechanisms of crust formation and destruction are not understood.

- **Lowering Waste Level below 10.21 m (402 in.):** Waste level is a measure of gas inventory. The historic minimum level before pump operation was 10.21 m (402 in.) Lowering the gas inventory lower below its historic minimum could promote additional settling and a greater solids fraction in the NC layer. As discussed above, both factors could increase the size of GREs. Lowering the level also increases the time between GREs, and increasing the time between events could affect the size. Aging of the slurry appears to increase the strength,[26] which may increase the size of GREs, as discussed above. Temperature nonuniformities, which increase with time, also can result in larger GREs.[27]

  A study of aluminate solubility[28] at 25°C (77°F) indicates that most changes occur during the first 3 to 4 months of aging. Measuring the aluminate solubility is much more difficult than measuring the solubility of nitrates and nitrites,[29] which implies that nitrates and nitrites age more quickly than aluminates. The waste temperature is >25°C (>77°F); therefore, aging of the waste is expected to occur more quickly than is indicated by this study. Because the bulk of the aging process occurs in less time than the period between natural rollovers, increasing the interval between events should not result in increased strength because of additional aging.

  As noted above, vigorous pump operation has not reduced the waste level significantly below 10.16 m (400 in.) since the pump was installed in July 1993; this indicates that the pump has not caused significant changes in the amount of unreleasable gas.[19] Therefore, this hazard does not pose a significant risk.

Managing the Hazards

The hazards discussed in the previous section are the result of uncertainty in the waste behavior. Although it is impossible to eliminate this uncertainty or demonstrate by analysis that the uncertainty is unimportant, it is possible to manage the uncertainty by (1) placing limits on waste tank operations, (2) initiating a monitoring program, or (3) providing equipment that prevents the undesirable phenomena from occurring.

Temperature Limits

Many sources of uncertainty are hazards because they impact the sensitivity of the waste to changes in temperature. The solubility of the salts in the waste, the composition of the waste, and the gas generation kinetics directly affect the sensitivity of the waste behavior to temperature changes. Solubility and composition also are factors that affect the shear strength to temperature. Upper and lower temperature limits based on historic operating limits will help maintain the amount and composition of retained gas within the historical values and minimize the likelihood of unexpected and undesirable changes.

Waste Level Limits

During the initial testing phases of the mixer pump, a rate-of-level-rise control was motivated in part by the long-term issue of preventing undesirable, pump-induced increases in gas generation and retention. Because continued operation of the mixer pump has maintained the waste at a constant level, the rate of level rise no longer is a useful method of detecting and controlling undesirable changes in the gas generation rate. A minimum level control also was used during the initial phases of pump testing. Vigorous pump operation has not lowered the level significantly below 10.16 m (400 in.). Also, currently there is a spare mixer pump available. The inability of the pump to lower the waste below 10.16 m (400 in.) minimizes the need for this control, and the availability of a spare mixer pump minimizes the potential for undesirable consequences in the event of pump failure at a low level. Therefore, a minimum level control is not needed.

Gas Composition Limits

During the initial phases of pump testing, limits on the maximum concentration of hydrogen and ammonia were motivated by the concern that long-term pump operation could induce changes in the gas generation kinetics and enhance ammonia mass transfer. Operating data do not indicate that pump operation affects the gas generation kinetics, nor does the operation enhance ammonia mass transfer. Also, additional kinetic studies indicate that pump operation should not produce any major changes in the gas generation kinetics. Thus, maximum hydrogen and ammonia limits no longer are useful for controlling long-term effects.

Gas Composition Monitoring
Although operational limits on gas composition are not useful for controlling long-term changes in the gas generation chemistry, gas composition should be monitored to determine if there are undesirable changes in gas composition. Undesirable changes include an increase in the background hydrogen or ammonia concentration, an increase in the hydrogen to nitrous oxide ratio, an increase in the ammonia to nitrous oxide ratio, and the presence of previously undetected toxic or flammable gases.

Calibration Probe Monitoring
Crust thickness is determined most easily from the temperature profile. Because thermocouple spacing on the instrument trees is at 0.91-m (24-in.) intervals, precise monitoring of the crust thickness is not possible. Periodic calibration probe data could be used to determine if a change in crust thickness is occurring.

Pump Operation Requirements
Several of the hazards discussed above are influenced by unmeasurable quantities such as crystal size distribution; thus, it is impossible to develop controls or monitoring programs to manage these hazards. The hazards that cannot be controlled or monitored effectively are an increase in shear strength, a decrease in unreleasable gas, an increase in settling, a thinner crust, a thicker crust, and a lowering the waste level below 10.16 m (400 in.). These hazards can be realized only if the tank reverts to periodic GREs. These hazards are not a problem if the waste is mixed. Test results demonstrate that pump mixing eliminates GREs. Therefore, long-term hazards are controlled best by continued pump operation. Having a spare mixer pump available should provide an additional degree of protection.

CONCERNS REGARDING EXCESSIVE HEAT LOAD

Operation of the mixer pump will add thermal energy to the waste. Concerns have arisen that the total thermal power in the tank during testing will exceed the design specifications for the tank. The bases for the temperature and heat generation limits for Tank 101-SY are discussed in this section, and their application to the mixer pump operation is evaluated. We concluded that temperate controls are sufficient to permit all currently planned pump operations.

Limitations on tank maximum temperature and heat generation rate are given in the "Tank Farm Plant Operating Procedure," or OSD.[20] These operating specifications were designed to prevent damage to the primary liner and reinforced concrete. The maximum operating specifications are:

Maximum waste temperature: 121°C (250°F)
Maximum heat generation: 11.7 kW (40,000 Btu/h)

The OSD references the functional design criteria (FDC)[21] as the basis for these specifications. The temperature limit applies for protection of both the primary liner and the concrete shell of the tank. According to the OSD,[20] the heat generation limit exists to avoid thermal degradation of the concrete. This latter limit does not agree with that given in the FDC. According to the FDC, the reinforced concrete tank shall be designed for ". . . thermal loads caused by a temperature gradient induced by material in the primary tank at temperatures up to 121°C (250°F) *and* with a heat generation rate up to 50,000 Btu/h (14.05 kW) . . ." (emphasis added). The reason for the 20% reduction factor[1] is not documented. The Safety Analysis Report (SAR) for the SY Tank Farm uses the 14.6 kW (50,000-Btu/h) value.[22] Reference 20 also gives a secondary limitation of 20.5 kW (70,000 Btu/h) to avoid local boiling. This limit exists because the ventilation systems for the double-shell tanks were not designed for boiling wastes. Review of the original reference for this limit[23] shows that this limitation assumes a particular tank ventilation configuration (with less heat removal capability than is available in Tank 101-SY) and a waste temperature of 121°C (250°F) at 101 kPa (1 atm.)

At present, the maximum temperature in Tank 101-SY is <57.2°C (<135°F), and the best estimate for the radiolytic heat load based on tank sampling is 12.3 kW (41,900 Btu/h).[24] This heat generation rate is above the limit given in Ref. 20. Any additional heat generation resulting from pump operation apparently would result in a further breach of the specification.[1]

The specification for heat generation[20] is much more restrictive than that given in any of the supporting documentation listed above and is extremely conservative. If the maximum waste temperature is restricted to 57.2°C (135°F), we will show that this requirement satisfies both design concerns without reference to the tank heat load and that therefore, the planned pump operations are acceptable.

As noted in the FDC, the thermal load that the concrete shell experiences depends on the temperature gradient to which it is subjected. At a maximum waste temperature of 57.2°C (135°F), this gradient will be only ~40% of the limit implied in the FDC assuming a sink temperature of 15.6°C (60°F). Thus, thermal damage to the reinforced concrete under quasi-steady conditions can be precluded.

If the temperature of the tank contents were to increase rapidly, transient thermal stresses in the concrete could be produced. When the temperature increase is slow, this is not a concern. The rate of temperature increase resulting from pump operation can be estimated conservatively by assuming that the tank heats up adiabatically. The adiabatic temperature increase as a result of pump operation is

$$\frac{dT}{dt} = \frac{\eta P}{V_T \rho c_p} ,$$

where

T = tank-average temperature,
V_T = tank volume,
ρ = tank-average density of waste,
c_p = tank-average capacity heat of waste,
P = pump power at maximum speed, and
η = duty factor.

For the values given in Table I, this results in a temperature increase of ~0.61η°C/d (~1.1η°F/d). Thus, for a pump operation time of 4 h at 920 rpm, the maximum rate of tank heating would be ~0.1°C/d (~0.2°F/d). The actual temperature rise will be much less than this. Thus, transient thermal shocks can be neglected, as well.

Local boiling of the waste is not possible if an upper limit is placed on the waste temperature that is sufficiently less than the boiling point of the waste. Therefore, the heat generation rate is unimportant, provided that there is a maximum temperature control. No additional controls are needed to preclude damage to the reinforced concrete or to avoid local boiling.

CONCERNS REGARDING UNCONTROLLED REACTIONS

The waste is a chemical system that is not fully understood. Uncontrolled reactions induced by pump operation have not been observed in the 16-month operating history. However, because of the uncertainty involved, there is still concern that pump operation could trigger an unanticipated, uncontrolled reaction in the tank, which could result in uncontrolled heatup, increased gas generation, or generation of a more flammable mixture.

The waste tank effectively is a nonadiabatic, batch chemical reactor. Barring the presence of high explosives in the tank, any possible uncontrolled reaction will be the result of a thermal runaway. A thermal runaway occurs in an exothermic reacting system when the heat generated by reaction is more sensitive to temperature changes than to the rate of heat loss. This situation exists when the rate of reaction

TABLE I
PARAMETERS FOR ESTIMATING TANK TEMPERATURE INCREASE

Parameter	Value
Tank Volume	3800 m^3
Tank Density	1.55 g/cm^3
Tank Specific Heat	2090 J/kg°C
Pump Power	82 kW at 920 rpm (Ref. 6)

is governed by Arrhenius temperature dependence and heat loss is governed by thermal convection.

The primary mechanism of heat generation in the waste tank is nuclear decay. Chemical reactions account for only a small portion of the total heat generation. If the activation energy of the reaction is large and the heat generated by chemical reaction is small compared to other sources, the first-order criteria for a thermal runaway in a batch reactor is

$$0.3 < \frac{R\,(-\Delta H)\,V\,r_o}{E_a\,U\,A},$$

where

R = gas constant,
ΔH = enthalpy of reaction,
V = volume,
r_o = initial reaction rate,
E_a = activation energy,
U = heat-transfer coefficient, and
A = heat-transfer area.

The quantity $(-\Delta H)Vr_o$ is the total heat generated by chemical reaction. If 10% of the total heat is assumed to be the result of chemical reactions, the quantity $(-\Delta H)Vr_o$ is ~1.17 kW (~4000 Btu/h). The activation energy for gas generation is reported to be ~1.0×10^8 J/kg-mole (~24,000 cal/mole).[7] Based on an overall heat balance on the tank, the quantity UA is ~0.37 kW/°C (~700 Btu/h°F). The value for the right-hand side of the inequality is estimated to be 3×10^{-4}, which is much less than the critical value of 0.3. Even if there are large errors in the parameters, the reaction is very stable. Because the nuclear heat source is much greater than the chemical energy, a very large perturbation to the chemical reaction is required to create a thermal imbalance.

The pump must cause an increase in the reaction rate of at least a factor of 1000 to create a danger of a thermal runaway. As discussed in the section on GREs, the contents of the tank are not changing significantly; therefore, the only possible way to increase the rate of reaction is to increase the temperature. On the basis of the effective activation energy for gas generation, the temperature must increase by ~75°C (~135°F) to increase the reaction rate by a factor of 1000. An increase of 75°C (135°F) would increase the waste temperature above its boiling point, which is unlikely to occur. The possibility of an uncontrolled chemical reaction is not a significant safety concern, particularly if the waste temperature is maintained below its historic maximum.

CONCERNS REGARDING TOXIC GASES

Ammonia is a toxic gas with a threshold limit value (TLV) of 25 ppm.[30] Experiments in which waste samples were heated to 100°C (212°F) show that nitrogen oxides (NO_x) are formed.[7] The TLV for nitric oxide is 25 ppm, and the value for nitrogen dioxide is 5 ppm.[30] Toxic gas releases during GREs were considered in the evaluation of worsening GREs. This section evaluates chronic hazards associated with the gradual release of toxic gases from the waste.

Before pump operation, we postulated that mixing in the tank would enhance the liquid mass-transfer coefficient at the waste surface and release large amounts of ammonia. The measured ammonia concentrations in the vapor space of the tank during Phase B testing do not indicate that large amounts of ammonia are released as a result of pump operation. Analysis of data indicates that operating the pump at the maximum speed increases the liquid-phase mass-transfer coefficient only by a factor of ~2.[17] The data indicate that operating the current pump will not result in hazardous ammonia releases during normal operations.

Dispersion calculations show that nitric oxide or nitrogen dioxide concentrations must exceed 9000 ppm for the maximum ground concentration to exceed 5 ppm over an 8-h period.[31] FTIR data indicate that neither nitric oxide nor nitrogen dioxide is released at current tank conditions.[32] Based on the experimental data at elevated temperature,[7] ground concentrations will be approximately an order of magnitude less than the TLV for nitrogen dioxide, even if the waste is heated to 100°C (212°F). A maximum waste temperature control is implemented; therefore, the results at 100°C (212°F) are very conservative. Thus, there is no NO_x release hazard.

The analysis summarized in this section shows that no chronic toxic gas hazard is posed by ammonia, nitric oxide, or nitrogen dioxide.

CONCERNS REGARDING UNCONTROLLED FOAMING

Foaming was observed in simulated waste studies. As a result, previous assessments of long-term effects considered the possibility of foaming both as a result of induced rollovers and continuous pump operation.

No foaming has been observed during natural rollovers. Phase B testing induced several rollovers with no observed foaming. No foaming has been observed for the 16-month operating history of the pump, which included extended pump operation at the maximum allowable speed.

Based on test results, pump operation does not cause foaming. The foaming observed in simulated waste studies probably occurred because the chemical composition of the simulant was not identical to composition of the actual waste. Thus, foaming observed in simulant studies is not relevant to actual pump operation.

CONCERNS REGARDING ACCELERATED EROSION AND CORROSION

Both the mechanical and thermal energies added to the tank by the pump may accelerate the erosion or corrosion rates of the tank wall. Factors affecting erosion and corrosion are composition of the mixture in the tank, temperature, any protective layer formed by the corrosion layer or salt cake deposited on the walls, and fluid motion or shearing near the surface.

Because no significant amounts of material are being added or removed from the tank, the overall composition of the waste tank is approximately constant; therefore, possible changes in composition are not a concern. As long as temperatures are maintained within their historical limits, changes in temperature are not likely to remove any salt cake deposited on the wall, nor are they likely to accelerate the corrosion rate. Therefore, the primary factors affecting erosion and corrosion are the effects of shearing and erosion on any protective layer, shearing on the corrosion rate, and erosion on the metal surface.

If the salt cake layer remains on the wall of the tank during pump operation, changes in the corrosion and erosion rates are unlikely. Resistance of the salt cake to mass transfer is likely to be much greater than the resistance of the boundary layer on the surface of the salt cake. The salt cake also provides physical protection against erosion. Pump operation is unlikely to affect the salt cake.

In the unlikely event that the jet impinges on the wall, corrosion would be accelerated moderately,[33] but consequences would be acceptable because of the limited duration of impingement. In conclusion, accelerated erosion or corrosion of the tank wall is not expected to be a problem.

SUMMARY AND CONCLUSIONS

We examined several long-term issues: the effect of pump operation on future GREs, uncontrolled chemical reactions, chronic toxic gas releases, foaming, and erosion and corrosion. Uncontrolled chemical reactions, chronic toxic gas releases, foaming, and erosion and corrosion have been shown not to be safety concerns. The effect of pump operation on future GREs could not be quantified.

The problem with evaluating the long-term effects of pump operation on GREs is uncertainty and a lack of knowledge. In particular, the phenomena governing gas retention, particle size distribution, and settling are not well understood, nor are the interactions among these factors understood. Changes in these factors could increase the size of future GREs. Bounding estimates of the potential increase in size of GREs are not possible because of a lack of engineering data.

Proper management of the hazards can reduce, but not eliminate, the possibility of undesirable changes. Maintaining temperature within the historical limits can reduce the possibility of these changes. A monitoring program to detect changes in the gas composition and crust thickness will help detect slowly occurring changes. Because pump operation has been shown to eliminate GREs, continued pump operation can eliminate the hazards associated with future GREs.

In conclusion, the possibility of undesirable changes to the waste during pump operation can be eliminated completely because all important variables cannot be measured and controlled. The element of risk associated with pump operation cannot be completely removed because all important considerations and facts are not known.

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APPENDIX A
IMPACT OF GROWTH OF THE NONCONVECTIVE LAYER

INTRODUCTION

Before the September 2, 1993, rollover (Window G), the temperature profile data indicated an NC-layer thickness of ~5.08 m (~200 in.). Temperature profile data after this event indicate that the NC-layer thickness had grown to ~6.35 m (~250 in.).

The first issue to be resolved is whether the growth is real. The old thermocouple was replaced during Window G, so there is some question as to whether the change is the result of real growth or an instrument change. If the growth is real, there are many safety issues that must be addressed. An increased NC layer could result in more retained gas and larger gas releases.

This appendix summarizes the analysis used to determine the cause of the observed increase in the NC layer and to determine the impact on safety. The neutral buoyancy model was modified to investigate the various mechanisms of NC-layer growth. Three mechanisms are considered: (1) precipitation of solids caused by a temperature decrease, (2) increased settling of solids suspended in the C layer, and (3) decreased packing of solids in the NC layer.

The various mechanisms were evaluated by comparing predictions of rate of level rise, background hydrogen concentration, maximum level before a rollover, maximum level drop, and time between rollovers. Based on these comparisons, the likely mechanism is identified. The impact of level growth caused by this mechanism is then evaluated.

SUMMARY OF THE MODEL

The model used in this study was a modification of the simple neutral buoyancy model. The modified model includes (1) simple material balances so that it can be used to predict the thicknesses of the C and NC layers, (2) solubility as a function of temperature, and (3) a new gas generation rate model.

The basic neutral buoyancy model is similar to those used by others. Three layers are considered in the model: (1) the crust layer, (2) the C layer, and (3) a single NC layer. A rollover is assumed to occur when the average bulk density of the NC layer equals the bulk density of the C layer. The gas release model also is based on neutral buoyancy. It is assumed that the NC layer rises to the surface. The NC layer releases enough gas at the surface to make the slurry neutrally buoyant at that location. At this point, the NC layer begins to settle.

The material balances used in the model consist of three components: water, inorganic salts, and organics. The correlation for solubility given in App. B is used to determine the solubility of the inorganic salts. The solubility of organics is based on the assumption that the organics do not exist as a separate phase. A simple partition coefficient model is used to describe the distribution of organics. The partition coefficient is assumed to be independent of temperature and was estimated from window convective core sample data.[1]

The gas generation model assumes that the gas generation rate is proportional to the amount of organics in the liquid phase, and the gas generation rate is assumed to be independent of temperature. The rate constant was estimated from the average rate of level rise, which is 0.20 cm/d (0.078 in./d). The model predicts reasonable values for the background hydrogen concentration. Two other models were considered: the gas generation rate that is assumed proportional to the organics in the solid phase and the gas generation rate that is assumed proportional to the total organics in the tank. The most realistic values are found by assuming that gas generation is proportional to the organics in the liquid phase.

RESULTS OF THE EVALUATION

The first step in the evaluation was to determine the change in the hypothesized parameter required to produce a 1.27-m (50-in.) increase in the NC-layer thickness. The results of the three mechanisms are summarized below.

1. A temperature decrease of 3.1°C (5.6°F) is required to produce a growth of 1.27 m (50 in.) in the NC layer. This increase corresponds to a 14% increase in crystal mass. In addition, analysis of past temperature data indicates that the NC layer has grown gradually.[2] The observed growth as a function of temperature is comparable to the predicted values.

2. For the increased settling mechanism, we predict that all solids suspended in the C layer must settle to produce a 1.27-m (50-in.) increase in the NC layer.

3. For the decreased packing fraction mechanism, we predict that the crystal fraction in the NC layer must decrease from a nominal value of 0.275 to 0.21 to produce an increase of 1.27 m (50 in.) in the NC layer. This change corresponds to a decrease in the bulk density from 1.67 to 1.62 g/cm^3.

All models predict that the rate of level rise should increase. The predicted rates of level rise corresponding to a 1.27-m (50-in.) NC layer growth are:

nominal rate	0.20 cm/d (0.078 in./d)
decreased temperature	0.24 cm/d (0.095 in./d)
increased settling of solids in C layer	0.28 cm/d (0.11 in./d)
decreased NC-layer density	0.33 cm/d (0.13 in./d)

There is no evidence to confirm that the rate of level rise has increased. For the period from July 1990 to February 1993, the measured rate of level rise between events varied between 0.08 to 0.28 cm/d (0.03 and 0.11 in./d). It is probable that the actual rate of level increase is nearly constant. The rate of level rise is least sensitive to temperature change. Reasonable changes to the organic solubility model could decrease the sensitivity of the rate to changes in temperature. In spite of this observation, the comparison of rate of level increase is inconclusive.

All mechanisms predict that the background hydrogen concentration should decrease with growth of the NC layer. The background hydrogen concentrations for the various explanations are:

calculated for reference state	35 ppm
decreased temperature	22 ppm
increased settling of solids in C layer	27 ppm
decreased NC layer density	24 ppm

The reference state corresponds to a 5.08-m (200-in.) NC layer. Tank data show that the background hydrogen concentration has decreased. Because of inaccuracies in the model, background hydrogen concentration cannot be used to distinguish between models, but it is an indicator of NC-layer growth.

If the observed NC-layer growth is caused by a temperature change, the model predicts that the tank level before a rollover will increase. An NC-layer growth of 1.27 m (50 in.) corresponds to a 9.4-cm (3.7-in.) increase in the maximum tank level. If the NC-layer growth is caused by increased settling of the C layer or decreased solids packing in the NC layer, there will be no change in the maximum level before a rollover. The rollover data from July 1990 to February 1993 were divided into two segments: rollovers that occurred at average tank temperatures <50°C (<122°F) and rollovers that occurred at temperatures >50°C (>122°F). For rollovers at temperatures >50°C (>122°F), the average maximum level was 10.472 m (412.3 in.); for temperatures <50°C (<122°F), the average maximum level was 10.544 m (415.1 in.). This increase is statistically significant, and it is consistent with the theory that the observed NC-layer growth is caused by a temperature decrease.

All proposed mechanisms predict that the level drop during a rollover should increase with increased NC-layer thickness. The increases predicted by the model are:

decreased temperature	24%
increased settling of solids in C layer	25%
decreased NC-layer density	8%

The data indicate that the size of the rollovers may be increasing, which is consistent with the growth of the NC layer. However, changes in the size of the level drop cannot be used to distinguish between the postulated mechanisms.

The time between rollovers is estimated by the following equation:

$$\text{time between events} = \frac{\text{level drop}}{\text{rate of level rise}} .$$

If the increase in the NC layer is caused by a decrease in temperature, the model predicts that the interval between rollovers will increase. If the increase in NC-layer thickness is caused by increased settling of solids forming the C layer or decreased solids packing in the NC layer, the model predicts that the interval between rollovers will decrease. Tank data indicate that the time between rollovers is increasing. The data support the postulation that the increase in the NC layer is caused by a decrease in temperature.

The results of this evaluation indicate that the increase in NC-layer thickness is real. The most direct evidence is the detailed analysis of past temperature profile data.[2] The observed increase in size of the level drops and observed decrease in the background hydrogen concentration support this conclusion.

All three factors play a role in the observed changes in the tank, but the observed temperature decrease in the tank is the best explanation of the observed growth of the NC layer. The supporting evidence for this conclusion follows.

1. The observed temperature decrease is sufficient to explain the NC-layer growth;

2. Only a decrease in temperature can explain the observed increase in time between events; and

3. A temperature decrease predicts an increase in the maximum level before a rollover, which is consistent with observations.

SAFETY IMPLICATIONS

If current trends continue, the thickness of the NC layer will continue to grow, and the size of the GREs will increase. The nominal rate of temperature decrease is ~1.7°C (~3°F/yr). At this rate of temperature decrease, the NC layer will grow at a rate of ~0.69 m/yr (~27 in./yr). The data indicate that the actual rate of growth is ~0.86 m/yr (~34 in./yr).[2] The average size of the level drops is expected to increase by ~3.8 cm/yr (~1.5 in./yr).

It is unlikely that a steady decrease in tank temperature will result in an abrupt change in the tank. Thermodynamic considerations indicate that the solubility of a given salt should be nearly a linear function of temperature. The only way for a drastic change in the overall solubility as a function of temperature to occur is for an additional salt to precipitate. The precipitation of an additional salt is unlikely to cause significant changes in the overall solubility in the waste tank. The major salt components in the waste are sodium nitrate, sodium nitrite, and sodium aluminate. The species already exists as solid salts. Any additional salts that precipitate will be minor components and will not contribute significantly to the overall mass of solids.

Sensitivity studies show that the maximum gas release from a specified level is relatively insensitive to the average waste temperature. The magnitude of the predicted change is small compared to the uncertainty in estimating the gas release volume. The sensitivity study shows that the volume of gas released as a result of an induced rollover depends primarily on waste level and not average waste temperature.

Although the maximum possible level drop from a *specified* level is not sensitive to an increase in the NC layer, the level drop from the neutral buoyancy point will increase with the NC-layer thickness. If the tank temperature drops below the range of the data, NC-layer growth could increase the maximum possible size of a natural GRE.

CONCLUSIONS

The results of the analysis summarized in this appendix indicate that the thickness of the NC layer has grown and that the growth primarily is caused by a decrease in tank temperature. This growth is likely to continue and may result in continued growth in the size of the rollovers, which could impact the size of the GREs. However, the primary safety concern is whether the change will impact the level controls. The analysis indicates that there will be no impact on induced rollovers from a specified level, but the release from natural events should increase.

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APPENDIX B
THERMAL BALANCE CALCULATIONS

INTRODUCTION

An undisturbed NC layer remained at the bottom of the tank after the February 2, 1993, rollover. The thickness of this layer was estimated to be ~2.54 m (~100 in.). The mixer pump was not installed after this event because pump installation could induce a rollover of the undisturbed portions of the NC layer. This experience indicated that the extent of the rollover must be taken into account when determining if pump installation is safe.

The shape of the axial temperature profile measurements provides a means of determining whether an undisturbed portion of the NC layer remains after a rollover. It also provides a means of estimating the thickness of the undisturbed layer. However, the tank is very large, and the axial temperature profile is measured with sufficient spatial resolution only at one location. Detection of a disturbed layer at the thermocouple locations does not provide sufficient data to guarantee a significantly undisturbed portion of the NC layer.

This appendix presents another method of estimating the fraction of the NC layer that participates in a rollover based on a thermal balance. This appendix also demonstrates that the level drop is proportional to the volume of the NC layer that participates in the rollover.

ASSUMPTIONS

The following assumptions were used in the thermal balance analysis:

1. The axial temperature profile does not depend on the radial or azimuthal position.

2. The C layer and the portion of the NC layer that participates in the rollover are well mixed after a rollover.

3. The volume fraction of crystals in the C and NC layers on a gas-free basis is constant.

4. Any solution or dissolution of solids that occurs during mixing is neglected.

5. Heat loss during the rollover is assumed to be insignificant.

6. The average crust thickness is constant.

BASIC DATA

The thermal balance calculations require densities, heat capacities, and volume fraction of crystals in the various layers of the tank.

The density of the crystals and liquid is estimated to be 2.22 and 1.46 g/cm^3, respectively. The liquid density is based on data from the Window C core sample analysis.[1] Densities are assumed to be independent of temperature.

The heat capacity of the crystals is estimated to be 0.25 cal/g°C (0.25 Btu/lb°F). The liquid is a saturated electrolyte solution. The heat capacity of an electrolyte solution is approximately equal to the heat capacity of the solvent times the fraction of solvent in the mixture. Based on data reported by Herting and Cleavenger,[2] the solubility of waste is approximately

$$S\,(g/100\,g\,H_2O) = 3.4\,T\,(°C) - 31\ .$$

This solubility equation and the approximation give a liquid heat capacity of

$$c_{p,L}\,(cal/g\,°C) = \frac{1}{0.69 + 0.034\,T\,(°C)}\ .$$

The volume fraction of crystals in the C and NC layers is based on the density data obtained from the window convective core samples.[1] The densities on a gas-free basis for the C and NC layers are 1.46 and 1.67 g/cm^3, respectively. These densities correspond to 7.4 vol % solids in the C layer and 27.5 vol % solids in the NC layer.

THERMAL BALANCE EQUATIONS

The thermal balance for a rollover is given by

$$V_{cl}\,\rho_{cl}\,c_{p,cl}\,(T_{mix} - T_{cl}) = V_{ncl}\,\rho_{ncl}\,c_{p,ncl}\,(T_{ncl} - T_{mix})\ ,$$

where

V_{cl} = total volume of C layer,
V_{ncl} = volume of NC layer that participates in the rollover,
ρ_{cl} = density of the C layer,
ρ_{ncl} = density of the NC layer,
$c_{p,cl}$ = heat capacity of the C layer,
$c_{p,ncl}$ = heat capacity of the NC layer,
T_{cl} = average temperature of the C layer,
T_{ncl} = average temperature of the NC layer, and
T_{mix} = average temperature of the mixture after the rollover.

The above equation can be solved for the volume of the NC layer that participates in the rollover.

$$V_{ncl} = V_{cl} \frac{\rho_{cl}\, c_{p,cl}\, (T_{mix} - T_{cl})}{\rho_{ncl}\, c_{p,ncl}\, (T_{ncl} - T_{mix})} \;.$$

The volume of the C layer can be determined from level data, as follows:

$$V_{cl} = A\,(Z - \Delta Z_{cr} - Z_{ncl}) \;,$$

where

A = tank area,
Z = tank level,
ΔZ_{cr} = average crust thickness, and
Z_{ncl} = level of the NC layer.

Substituting for V_{cl} gives the volume of the NC layer that participates in the rollover in terms of known quantities, given by

$$V_{ncl} = A\,(Z - \Delta Z_{cr} - Z_{ncl}) \frac{\rho_{cl}\, c_{p,cl}\, (T_{mix} - T_{cl})}{\rho_{ncl}\, c_{p,ncl}\, (T_{ncl} - T_{mix})} \;.$$

The product of heat capacity and density can be determined from the physical properties of the crystals and the saturated liquid, given by

$$\rho\, c_p = v_{cr}\, \rho_{cr}\, c_{p,cr} + (1 - v_{cr})\, \rho_l\, c_{p,l} \;,$$

where

v_{cr} = volume fraction of crystals in the mixture,
ρ_{cr} = density of the crystals,
ρ_l = density of the liquid,
$c_{p,cr}$ = heat capacity of the crystals, and
$c_{p,l}$ = heat capacity of the liquid.

The ratio of the product of density and heat capacity is obtained by substitution.

$$F = \frac{\rho_{cl}\, c_{p,cl}}{\rho_{ncl}\, c_{p,ncl}} = \frac{v_{cr,cl}\, \rho_{cr}\, c_{p,cr} + (1 - v_{cr,cl})\, \rho_l\, c_{p,l}}{v_{cr,ncl}\, \rho_{cr}\, c_{p,cr} + (1 - v_{cr,ncl})\, \rho_l\, c_{p,l}} \;.$$

From July 1990 to September 1992, the average tank temperature measured between 55 and 45°C (131 and 113°F). Over this temperature range, F varies between 1.008 and 1.030. Thus, unity is a reasonable approximation for F and results in the following approximation for the volume of the NC layer that participates in the rollover:

$$V_{ncl} = A\,(Z - \Delta Z_{cr} - Z_{ncl})\,\frac{(T_{mix} - T_{cl})}{(T_{ncl} - T_{mix})}\ .$$

UNCERTAINTY ANALYSIS

The thermal balance calculations are subject to uncertainty that arises from the errors introduced by the modeling assumptions and uncertainty in the model parameters. A linear propagation of errors was performed to estimate the impact of parameter uncertainty on the results.

The error in temperatures is assumed to have a standard deviation of 0.25°C (0.45°F), which is typical of thermocouple errors. The error in the volume fraction of solids is assumed to have a standard deviation of 0.05, which corresponds to a standard deviation of 0.04 g/cm^3 in bulk density. Based on an analysis of the level history data, the standard deviation for measuring the average tank level is 4.1 cm (1.6 in.). The uncertainty in the crust thickness is assumed to have a standard deviation of 0.15 m (6 in.). The standard deviation for the error in the level of the NC layer also is assumed to be 0.15 m (6 in.). Because thermocouples are located at 0.61-cm (24-in.) intervals, it is assumed that the interface between the C and NC layers can be located within this 0.61-cm (24-in.) interval. A standard deviation of 0.15 m (6 in.) approximates a 0.61-cm (24-in.) interval.

The propagation-of-error calculations were performed using the standard, well-known, linear propagation-of-error formula.

THERMAL BALANCE CALCULATIONS AND RESULTS

Thermal balance calculations were performed for the eight rollover events that occurred between August 1990 and September 1992. In most cases, the average temperatures used in the thermal balance were evaluated as follows:

1. The average temperature of the C layer before the rollover was evaluated from the temperature profile data on the day before the rollover.

2. The average temperature of the NC layer before the rollover was evaluated from the temperature profile data on the day before the rollover. Only the thermocouples that changed significantly during the rollover were included in the average.

3. The average temperature of the mixture was evaluated 5 d after the rollover. The average was based on the same thermocouples used to evaluate the average temperature of the C layer.

There are two exceptions to these rules. Several days before the GRE of February 16, 1991, there was a rollover in the NC layer that did not release gas. In this case, the average temperature of the NC layer was based on all thermocouples in the NC layer; the average temperature of the mixture was evaluated the day after the rollover. The second exception was the rollover of September 3, 1992, in which the thermocouple tree was bent. The thermocouples used for evaluating the average temperature after the September 1992 rollover take into account the bend in the thermocouple tree.

The data for the thermal balance calculations are given in Table B-1. The results of the calculations are summarized in Table B-2. Although the uncertainty in these calculations is large, the results indicate that there is significant variation in the amount of material that participates in a rollover.

In Fig. B-1, the measured level drop is plotted as a function volume of the NC layer that participates in the rollover. The error bars in this plot correspond to 1.0 std dev. The plot indicates that the level drop is proportional to the volume of the NC layer that participates in the rollover. A linear regression analysis gives the following correlation for level drop:

$$\Delta Z = 0.000186\, V_{ncl} \;,$$

where ΔZ is in inches and V_{ncl} is in cubic feet. The correlation coefficient for this equation is 0.97.

TABLE B-1
DATA FOR THERMAL BALANCE CALCULATIONS

Date	Level before Rollover (in.)	Level of NC Layer (in.)	Level Drop (in.)	Average Temperature (°C)		
				C Layer	NC Layer	Mixture
08/04/90	415.9	196	5.1	49.92	55.56	51.53
10/23/90	413.3	196	11.3	49.40	55.96	52.62
02/16/91	409.3	196	4.6	49.06	51.15	50.43
05/16/91	411.9	184	7.0	47.74	54.60	50.10
08/27/91	411.1	184	5.6	47.38	54.08	49.31
12/03/91	416.1	196	10.4	45.58	52.80	48.73
04/19/92	414.6	184	9.6	43.32	48.72	45.59
09/03/92	416.5	208	14.5	43.78	48.60	46.59

TABLE B-2
RESULTS OF THE THERMAL BALANCE CALCULATION

Date	Volume of NC Layer Participating in Roll-over (ft^3)		Fraction of NC Layer Participating in Roll-over (%)		Level Drop (in.)
	Mean	Std Dev	Mean	Std Dev	
08/04/90	28,100	7800	0.389	0.110	5.1
10/23/90	66,400	12,800	0.920	0.184	11.3
02/16/91	22,000	10,900	0.306	0.153	4.6
05/16/91	38,400	7900	0.567	0.120	7.0
08/27/91	29,400	6900	0.435	0.104	5.6
12/03/91	54,200	9700	0.751	0.140	10.4
04/19/92	53,600	12,700	0.792	0.193	9.6
09/03/92	72,900	17,700	0.952	0.237	14.5

CONCLUSIONS

The analysis presented in this appendix shows how a simple thermal balance can be used to estimate the volume of the NC layer that participates in a rollover. The calculations show that there is considerable variability in the fraction of the NC layer that participates in a rollover. The numerical values range from ~30 to 95% of the NC layer. The thermal balance calculations are subject to considerable uncertainty; these calculations are not without ambiguity. Considerable judgment and subjective interpretation of the temperature profiles are needed to obtain the average temperatures required in analysis.

This analysis shows that there may be a strong correlation between the level drop and the volume of the NC layer that participates in the rollover. This observation is useful in explaining the observed variability in the size of the rollover. The observed variability appears to be caused by variability in the fraction of the NC layer that participates in the rollover.

In determining whether a particular activity can be performed in the tank, it is useful to know how much of the NC layer remains undisturbed after a rollover. A thermal balance calculation provides a means of estimating the volume of the undisturbed material. However, it is difficult to establish criteria based on a thermal balance because of the ambiguities involved in these calculations. Level

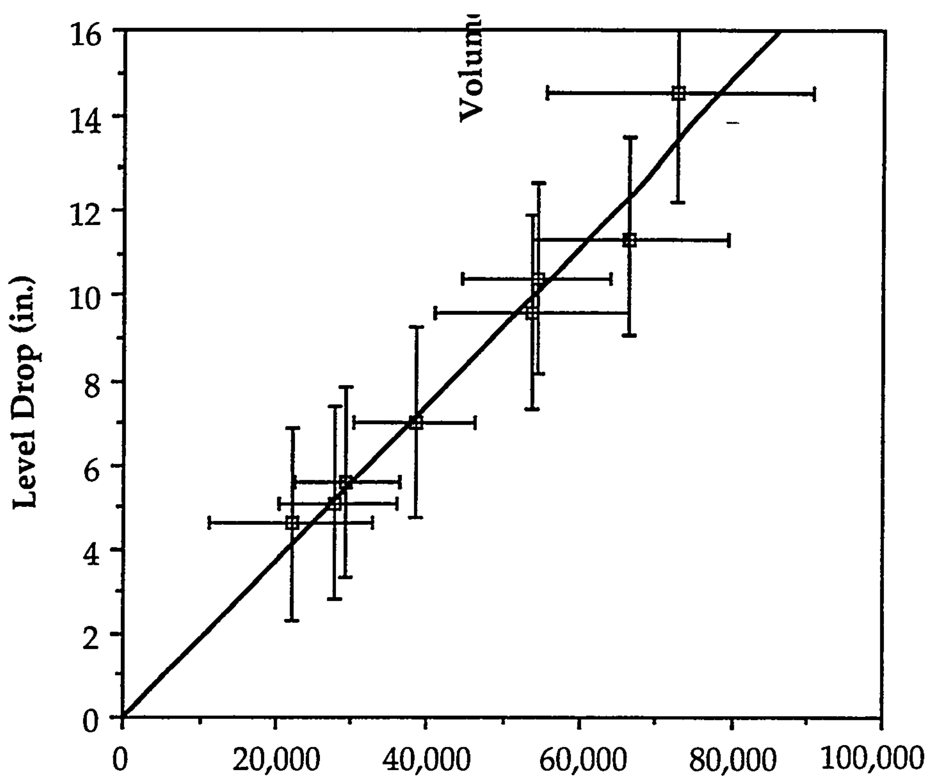

Fig. B-1. Measured level drop as a function of the volume of NC layer that participates in the rollover.

drop measurement is much less ambiguous than temperature profile. Therefore, it is better to use the level drop and the correlation developed in this appendix to estimate the volume of the NC layer that participates in the rollover than to use a thermal balance when establishing criteria.

REFERENCES

1. D. L. Herting, D. B. Bechtold, B. A. Crawford, T. L. Welsh, and L. Jensen, "Laboratory Characterization of Samples Taken in May 1991 from Hanford Waste Tank 241-SY-101," Westinghouse Hanford Company report WHC-SD-WM-DTR-024 (1991).

2. D. L. Herting and R. M. Cleavenger, "Solubility Phase Diagram—Final Report," Rockwell Hanford Operations report SD-WM-TI-078 (May 1983).

APPENDIX C
LIST OF ASSUMPTIONS FOR GAS RELEASE EVENT MODEL

MITIGATION OF TANK 241-SY-101 BY PUMP MIXING LONG-TERM EFFECTS OF PUMP OPERATION ON ROLLOVERS		Hazard Evaluation Assumption Sheet Date: 11/8/94 — Page 1 of 6
Assumption	**Basis**	**Use**
101-SY consists of three uniform layers before mixer pump operation: the crust, the C layer, and the NC layer.	• Temperature profile data • Window C core samples • Window E core samples	Estimating tank inventory
The neutral buoyancy point was 416.5 in. before mixer pump operation.	Waste level before September 1992 event	• Estimating tank inventory • Estimating mass of settled solids
The NC-layer thickness before the September 1992 event was 220 in.	Temperature profile data before September 1992 event	• Estimating tank inventory • Estimating mass of settled solids
The thickness of the crust is 30 in.	Assumed value based on temperature profile data	Estimating tank inventory
There is <6 in. of salt cake on the walls of the tank.	Analysis of gamma scan data	• Estimating tank inventory • Estimating heat losses
The bulk density of the NC layer on a gas-free basis is 1.67 g/cm^3.	Window C core samples	• Estimating tank inventory • Estimating gas release volume
The bulk density of the C layer on a gas-free basis is 1.54 g/cm^3.	Window C core samples	Estimating tank inventory
The bulk density of the crust including gas is 1.35 g/m^3.	Window E core samples	Estimating tank inventory
The liquid density is 1.46 g/cm^3.	Window C core samples	• Estimating tank inventory • Calibrating liquid density model • Estimating gas release volume
The average tank temperature was 46°C (115°F) during the September 1992 event.	Temperature profile data before September 1992 event	• Calibrating solubility correlations • Estimating tank inventory
Before pump operation, the waste was cooling at an average rate of 1.7°C/yr (3°F/yr).	Analysis of temperature profile data	Predicting future behavior of the waste
The average temperature of the NC layer increases during the period between GREs.	Analysis of temperature profile data	• Predicting future behavior of the waste • Estimating gas release volume

MITIGATION OF TANK 241-SY-101 BY PUMP MIXING LONG-TERM EFFECTS OF PUMP OPERATION ON ROLLOVERS		Hazard Evaluation Assumption Sheet Date: 11/8/94 — Page 2 of 6
Assumption	**Basis**	**Use**
The average temperature of the C layer decreases during the period between GREs.	Analysis of temperature profile data	• Predicting future behavior of the waste • Estimating gas release volume
The minimum level after a GRE is 402 in.	Analysis of level data before pump operation	Predicting the maximum period between GREs
The composition of solids in the crust is the same as the solids in the NC layer.	Assumption	Estimating tank inventory
The crust is 28 wt % H_2O.	Window C core sample analysis	Estimating tank inventory
The aluminum solids are in the form of $Na_2Al_2O_4 \cdot 1.5H_2O$.	• Literature phase diagram for aluminum oxides, sodium hydroxide, and water • Solubility data of Barney	• Calibrating solubility correlations • Estimating average density of solids
Solid $Na_2Al_2O_4 \cdot 1.5H_2O$ has a density of 2.20 g/cm^3.	Assumption	Estimating average density of solids
Dissolved aluminum is in the form of $Al(OH)_4^+$.	Aluminum solubility literature	• Calibrating solubility correlations • Estimating tank inventory
Inorganic carbon is in the form of sodium carbonate.	Assumption	• Calibrating solubility correlations • Estimating average density of solids • Estimating tank inventory
Solid carbonate is in the form of $Na_2CO_3 \cdot H_2O$.	Literature data and solubility calculations	• Calibrating solubility correlations • Estimating average density of solids • Estimating tank inventory
Solid sodium sulfate is in form of Na_2SO_4.	Literature data and solubility calculations	• Calibrating solubility correlations • Estimating average density of solids • Estimating tank inventory
Organic carbon is in the form of organic acid salts.	Assumption based on the mechanism of complexant decomposition	• Calibrating solubility correlations • Estimating average density of solids • Estimating tank inventory

MITIGATION OF TANK 241-SY-101 BY PUMP MIXING LONG-TERM EFFECTS OF PUMP OPERATION ON ROLLOVERS		Hazard Evaluation Assumption Sheet Date: 11/8/94 — Page 3 of 6
Assumption	**Basis**	**Use**
Solid organic carbon salts have a density of 1.8 g/cm^3.	Assumption based on the average density of sodium salts of organic acids	Estimating average density of solids
25% of the organic carbon is in the form of completely soluble salts.	Assumption based on window E core samples	• Calibrating solubility correlations • Estimating tank inventory
50% of the organic carbon is in the form of partially soluble salts.	Assumption based on window E core samples	• Calibrating solubility correlations • Estimating tank inventory
Solubility of partially soluble organic acid salts.	Window E core sample data	• Estimating tank inventory • Estimating impact of changes on gas retention
Solubility of sodium nitrate.	Window E core sample data	• Estimating tank inventory • Estimating impact of changes on gas retention
Solubility of sodium nitrite.	Window E core sample data	• Estimating tank inventory • Estimating impact of changes on gas retention
Solubility of sodium aluminate.	Window E core sample data	• Estimating tank inventory • Estimating impact of changes on gas retention
Solubility of sodium carbonate.	• Window E core sample data • Solubility calculations	• Estimating tank inventory • Estimating impact of changes on gas retention
Solubility of sodium sulfate.	• Window E core sample data • Solubility calculations	• Estimating tank inventory • Estimating impact of changes on gas retention
Salts of heavy metals (Fe, Cr, etc.) are insoluble.	Assumption	• Estimating tank inventory • Estimating impact of changes on gas retention

MITIGATION OF TANK 241-SY-101 BY PUMP MIXING LONG-TERM EFFECTS OF PUMP OPERATION ON ROLLOVERS		Hazard Evaluation Assumption Sheet Date: 11/8/94 Page 4 of 6
Assumption	**Basis**	**Use**
Nitrous oxide, nitrogen, and ammonia are generated primarily from nitrite ion with organic acid salts acting as reducing agents.	Kinetic study of waste simulants	Estimating the future gas generation behavior
Hydrogen is generated from the decomposition of organics and the radiolysis of water.	Kinetic study of waste simulants	Estimating the future gas generation behavior
The overall activation energy for gas generation is ~24 kcal/mole.	• Kinetic study of waste simulants • Kinetic studies of waste samples	Estimating the effect of temperature on gas generation
Decrease waste temperature increases the ratio of hydrogen to other gases.	• Kinetic study of waste simulants • Kinetic studies of waste samples	Estimating the effect of temperature on gas generation
The primary source of gas generation is liquid-phase reactions.	• Waste simulant studies performed by Argonne National Laboratory • If surface reaction were important, gas generation would increase with temperature	• Estimating the effect of temperature on gas generation • Estimating the effect of changes in crystal size on gas generation
The ultimate decomposition products of the organics are sodium carbonate and sodium oxalate.	Proposed mechanism for gas generation	Estimating the accumulation of solids with time
Carbon dioxide absorption does not have a significant impact on the solids inventory.	Assumption	Estimating the accumulation of solids with time
Most of the ammonia generated in the waste is dissolved in the liquid.	• Core sample analysis • Henry's law constant	Estimating the retention and release of ammonia
Ammonia in the gas bubbles is in equilibrium with the liquid.	Assumption based on mass transfer calculations	Estimating the ammonia release
No significant amount of ammonia is retained by adsorption on the solids.	Assumption	Estimating the ammonia inventory

MITIGATION OF TANK 241-SY-101 BY PUMP MIXING LONG-TERM EFFECTS OF PUMP OPERATION ON ROLLOVERS		Hazard Evaluation Assumption Sheet Date: 11/8/94 Page 5 of 6
Assumption	**Basis**	**Use**
All gas generated in the NC layer is retained in the NC layer.	Assumption based on shear strength of the NC layer	• Estimating the rate of gas accumulation • Estimating the size of GREs
All the gas generated in the NC layer is release as it is generated.	Assumption based on lack of shear strength in the C layer	Estimating the background gas composition
The retained gas is 33% H_2.	• Assumption based on current data • Person's preliminary data indicate that hydrogen concentration is relatively insensitive to the expected temperature changes	Estimating the maximum hydrogen concentration in the dome
Shear strength does not play a significant role in gas retention.	Neutral buoyancy model predicts reasonable values for gas release volumes without considering shear strength	Estimating the maximum gas retention volume
No alumina gels form.	High hydroxide concentration	Estimating the maximum gas retention volume
The amount of gas released is proportional to the volume of the NC layer that participates in the rollover.	Results of thermal balance calculations	Estimating the size of a GRE
Rollovers can occur that involve all the material in the NC layer, although partial rollovers are possible.	September 1992 GRE	Estimating the maximum volume of gas released
The volume of unrealizable gas is 0.3 ft^3 per ft^3 of solids.	Analysis of current tank conditions assuming no shear strength	Estimating the maximum volume of gas released

MITIGATION OF TANK 241-SY-101 BY PUMP MIXING LONG-TERM EFFECTS OF PUMP OPERATION ON ROLLOVERS		Hazard Evaluation Assumption Sheet Date: 11/8/94 Page 6 of 6
Assumption	**Basis**	**Use**
During the period between GREs, ammonia release as a result of interfacial mass transfer at the waste surface is governed by diffusion in a stagnant liquid layer stabilized by the crust.	Ammonia release model	Estimating the background ammonia release
Ammonia is released as a result of mass transfer from the waste surface during GREs; the amount is equal to 6% of the gas bubbles released.	• Ammonia release model • Gas composition data	Estimating the ammonia release during a rollover
Pump operation does not have a significant impact on settling.	Assumption	Estimating the impact of pump operation on mass of settled solids
Pump operation does not have a significant impact on crystal size distribution.	Assumption	• Estimating the impact of pump operation on mass of settled solids • Estimating the impact of pump operation on shear strength
Pump operation does not change the crust thickness or density.	Assumption based on available data	• Estimating the impact of pump operation on mass of settled solids • Estimating the impact of pump operation on ammonia release • Estimating the impact of pump operation on structural consequences
Pump operation does not remove salt cake from the walls of the tank.	Assumption	Estimating the impact of pump operation on mass of settled solids
Pump operation cannot reduce the waste level significantly below 400 in.	Assumption based on available pump operating data	Estimating period between GREs
Pump operation does not result in localized pileup of solids.	Assumption	Estimating maximum volume of retained gas

APPENDIX D
LACK-OF-KNOWLEDGE HAZARDS FROM GAS RELEASE EVENTS

MITIGATION OF TANK 241-SY-101 BY DILUTION			Hazard Evaluation Sheet	
Phase: Long-Term Pump Operation	Node: SY-101		Date: 11/15/94	Page 1 of 24
Assumption	**Deviation**	**Deviation Source**	**Consequence**	**Comments**
101-SY consists of three uniform layers before mixer pump operation: the crust, C layer, and NC layer.	No crust	-	-	Visual observation confirm existence of crust
	Stratified C layer	Partial settling	None	• Model based on average layer properties • Not a safety concern
	Stratified NC layer	• Compressibility of settled solids • Stratification of heavy metal salts	None	• Model based on average layer properties • Inventory of heavy metal salts is insignificant • Not a safety concern
The neutral buoyancy point was 416.5 in. before mixer pump operation.	Greater	• Uncertainty in level measurement • Uncertainty in neutral buoyancy point	Negligible increase in maximum gas release volume	• Based on sensitivity calculations • Not a safety concern
	Less	• Uncertainty in level measurement • Uncertainty in neutral buoyancy point	Negligible increase in maximum gas release volume	• Based on sensitivity calculations • Not a safety concern
The NC-layer thickness before the September 1992 event was 220 in.	Greater	Uncertainty in determining layer thickness	• Increase solids inventory • Increase maximum gas release volume	• Part of the overall safety analysis uncertainty • Not a long-term safety issue
	Less	Uncertainty in determining layer thickness	• Decrease solids inventory • Decrease maximum gas release volume	• Part of the overall safety analysis uncertainty • Not a long-term safety issue

MITIGATION OF TANK 241-SY-101 BY DILUTION			Hazard Evaluation Sheet	
Phase: Long-Term Pump Operation	Node: SY-101		Date: 11/15/94	Page 2 of 24
Assumption	**Deviation**	**Deviation Source**	**Consequence**	**Comments**
The thickness of the crust is 30 in.	Greater	Uncertainty in determining layer thickness	• Increase total solids inventory • Increase impact of crust loss • Increase structural consequences of crust motion	• Part of the overall safety analysis uncertainty • Not a long-term safety issue
	Less	Uncertainty in determining layer thickness	• Decrease total solids inventory • Decrease impact of crust loss • Decrease structural consequences of crust motion • Increase background ammonia concentration	• Part of the overall safety analysis uncertainty • Not a significant safety issue
There is <6 in. of salt cake on the walls of the tank.	Greater	Uncertainty in determining salt cake thickness	Increase impact of salt cake loss on waste temperature	• Changes in thermal resistance of salt cake could be compensated for by changing annulus ventilation flow • Minimum average waste temperature control would eliminate excessive cooling
	Less	Uncertainty in determining salt cake thickness	Decrease impact of salt cake loss on waste temperature	Not a safety concern

MITIGATION OF TANK 241-SY-101 BY DILUTION			Hazard Evaluation Sheet	
Phase: Long -Term Pump Operation	Node: SY-101		Date: 11/15/94	Page 3 of 24
Assumption	**Deviation**	**Deviation Source**	**Consequence**	**Comments**
The bulk density of the NC layer on a gas-free basis is 1.67 g/cm^3.	Greater	Data uncertainty	• Increase estimate of solids inventory • Increase estimate of maximum gas release	• Part of the overall safety analysis uncertainty • Not a long-term safety issue
	Less	Data uncertainty	• Decrease estimate of solids inventory • Decrease estimate of maximum gas release	• Part of the overall safety analysis uncertainty • Not a long-term safety issue
The bulk density of the C layer on a gas-free basis is 1.54 g/cm^3.	Greater	Data uncertainty	• Increase estimate of solids inventory • Increase the impact of pump induced settling of solids in C layer	-
	Less	Data uncertainty	• Decrease estimate of solids inventory • Decrease the impact of pump induced settling of solids in C layer	Not a safety concern
The bulk density of the crust including gas is 1.35 g/cm^3.	Greater	Data uncertainty	• Slight increase in settled solids if the crust is eliminated • Slight increase in gas release volume is crust is eliminated	• Based on sensitivity calculations • Not a significant safety concern

MITIGATION OF TANK 241-SY-101 BY DILUTION			Hazard Evaluation Sheet	
Phase: Long-Term Pump Operation	Node: SY-101		Date: 11/15/94	Page 4 of 24
Assumption	**Deviation**	**Deviation Source**	**Consequence**	**Comments**
The bulk density of the crust including gas is 1.35 g/cm^3.	Less	Data uncertainty	• Slight decrease in settled solids if the crust is eliminated • Slight decrease in gas release volume is crust is eliminated	• Based on sensitivity calculations • Not a safety concern
The liquid density is 1.46 g/cm^3.	Greater	Data uncertainty	• Decrease estimate of solids inventory • Significantly decrease estimate of gas release volume	• Based on sensitivity calculations • Not a safety concern
	Less	Data uncertainty	• Increase estimate of solids inventory • Significantly Increase estimate of gas release volume	• Based on sensitivity calculations • Part of the overall safety analysis uncertainty • Not a long-term safety issue
The average tank temperature was 46°C (115°F) during the September 1992 event.	Greater	Uncertainty in temperature measurements	No safety consequences	Tank temperature before September 1992 event is used for model calibration
	Less	Uncertainty in temperature measurements	No safety consequences	Tank temperature before September 1992 event is used for model calibration
Before pump operation, the waste was cooling at an average rate of 1.7°C/yr (3°F/yr).	Greater cooling	• Variability in cooling rate • Changes in vent flow • Pump operation	Increase rate of increase in size of GREs	Minimum average waste temperature control would eliminate excessive cooling

MITIGATION OF TANK 241-SY-101 BY DILUTION			Hazard Evaluation Sheet	
Phase: Long-Term Pump Operation	Node: SY-101		Date: 11/15/94	Page 5 of 24
Assumption	**Deviation**	**Deviation Source**	**Consequence**	**Comments**
Before pump operation, the waste was cooling at an average rate of 1.7°C/yr (3°F/yr).	Less cooling	• Variability in cooling rate • Changes in vent flow • Pump operation	Decrease rate of increase in size of GREs	Not a long-term safety issue
	Heating	Excessive pump operation	Decrease size of GREs	Maximum average waste temperature control would eliminate excessive heating
The average temperature of the NC layer increases during the period between GREs.	No change	Mixing of the NC layer	No safety consequences	Mixing implies no gas retention, so there is no safety problem
	Decrease in temperature	Mixing of the NC layer plus cooling of tank	No safety consequences	Mixing implies no gas retention, so there is no safety problem
The average temperature of the C layer decreases during the period between GREs.	No change	Mixing of the C and NC layer	No safety consequences	Mixing implies no gas retention, so there is no safety problem
	Increase in temperature	Mixing of the NC layer plus heating of tank	No safety consequences	Mixing implies no gas retention, so there is no safety problem
The minimum level after a GRE is 402 in.	Greater	Uncertainty in level measurement	Decrease in estimate of maximum gas release	• Part of the overall safety analysis uncertainty • Not a safety concern

MITIGATION OF TANK 241-SY-101 BY DILUTION			Hazard Evaluation Sheet	
Phase: Long-Term Pump Operation	Node: SY-101		Date: 11/15/94	Page 6 of 24
Assumption	**Deviation**	**Deviation Source**	**Consequence**	**Comments**
The minimum level after a GRE is 402 in.	Less	• Uncertainty in level measurement • Uncertainty rollover data	Increase in estimate of maximum gas release	• Part of the overall safety analysis uncertainty • Not a long-term safety issue
The composition of solids in the crust is the same as the solids in the NC layer.	Higher nitrate or nitrite	Uncertainty in crust composition	No impact unless crust is destroyed	Not a safety concern
	Higher aluminate	Uncertainty in crust composition	No impact unless crust is destroyed	Not a safety concern
	Higher carbonate	Uncertainty in crust composition	No impact unless crust is destroyed	Not a safety concern
	Higher organics	Uncertainty in crust composition	No impact unless crust is destroyed	Not a safety concern
The crust is 28 wt % H_2O.	Greater	Uncertainty in crust composition	No impact unless crust is destroyed	Not a safety concern
	Less	Uncertainty in crust composition	No impact unless crust is destroyed	Not a safety concern
The aluminum solids are in the form of $Na_2Al_2O_4 \cdot 1.5H_2O$.	In form of $Al(OH)_3$	Uncertainty in phase diagram	• Increase average density of the solids • Slight increase in estimate of maximum gas release	• Part of the overall safety analysis uncertainty • Not a long-term safety issue
	In form of $NaAlO_2$	Uncertainty in phase diagram	• Increase average density of the solids • Slight increase in estimate of maximum gas release	• Part of the overall safety analysis uncertainty • Not a long-term safety issue

MITIGATION OF TANK 241-SY-101 BY DILUTION			Hazard Evaluation Sheet	
Phase: Long-Term Pump Operation	Node: SY-101		Date: 11/15/94	Page 7 of 24
Assumption	**Deviation**	**Deviation Source**	**Consequence**	**Comments**
Solid $Na_2Al_2O_4 \cdot 1.5H_2O$ has a density of 2.20 g/cm^3.	Greater	Uncertainty in assumption	• Increase average density of the solids • Slight increase in estimate of maximum gas release	• Part of the overall safety analysis uncertainty • Not a long-term safety issue
	Less	Uncertainty in assumption	• Decrease average density of the solids • Slight decrease in estimate of maximum gas release	Not a safety concern
Dissolved aluminum is in the form of $Al(OH)_4{}^+$.	Al^{3+}, $Al(OH)^{2+}$, or $Al(OH)2^+$	Other possible ions in solution	None	Concentration of these ions is negligible in alkaline solutions ($[OH^-]$>0.01 M)
Inorganic carbon is in the form of sodium carbonate.	More soluble salt	Core sample analyses do not specify form of inorganic carbon	Decrease estimate of initial inventory of solid inorganic carbon	• Only impacts initial conditions • Not a safety concern
	Less soluble salt	Core sample analyses do not specify form of inorganic carbon	Increase estimate of initial inventory of solid inorganic carbon	• Only impacts initial conditions • Not a safety concern
	Salt with solubility more sensitive to temperature	Core sample analyses do not specify form of inorganic carbon	• Increase sensitivity of solids inventory on temperature • Increase sensitivity of gas release size to temperature	Minimum average waste temperature control would eliminate impact of uncertainty in solubility

MITIGATION OF TANK 241-SY-101 BY DILUTION			Hazard Evaluation Sheet	
Phase: Long-Term Pump Operation	Node: SY-101		Date: 11/15/94	Page 8 of 24
Assumption	**Deviation**	**Deviation Source**	**Consequence**	**Comments**
Inorganic carbon is in the form of sodium carbonate.	Salt with solubility less sensitive to temperature	Core sample analyses do not specify form of inorganic carbon	• Decrease sensitivity of solids inventory on temperature • Decrease sensitivity of gas release size to temperature	Not a safety concern
Solid carbonate is in the form of $Na_2CO_3{\cdot}H_2O$.	Solid carbonate is in the form of Na_2CO_3	Core sample analyses do not specify form of inorganic carbon	• Changes initial estimate of solids inventory • Decreases sensitivity of overall solubility to temperature	• Impacts initial conditions • Solubility of Na_2CO_3 decreases with increasing temperature, which is the opposite of the other salts • Not a safety concern
	Solid carbonate is in the form of $Na_2CO_3{\cdot}10H_2O$	Core sample analyses do not specify form of inorganic carbon	$Na_2CO_3{\cdot}10H_2O$ does not contribute to gas retention	$Na_2CO_3{\cdot}10H_2O$ has the same density as the liquid
Solid sodium sulfate is in form of Na_2SO_4.	Solid sodium sulfate is $Na_2SO_4{\cdot}10H_2O$	Core sample analyses do not specify form of sulfate solids	$Na_2SO_4{\cdot}10H_2O$ does not contribute to gas retention	$Na_2SO_4{\cdot}10H_2O$ has the same density as the liquid
Organic carbon is in the form of organic acid salts.	Relatively soluble organics	Uncertainty in characterizing organics	Changes initial estimate of solids inventory	• Impacts initial conditions • Not a safety concern
	Relatively insoluble organics	Uncertainty in characterizing organics	Changes initial estimate of solids inventory	• Impacts initial conditions • Not a safety concern

MITIGATION OF TANK 241-SY-101 BY DILUTION			Hazard Evaluation Sheet	
Phase: Long-Term Pump Operation	Node: SY-101		Date: 11/15/94	Page 9 of 24

Assumption	Deviation	Deviation Source	Consequence	Comments
Solid organic carbon salts have a density of 1.8 g/cm^3.	Greater	Uncertainty in characterizing organics	Changes initial estimate of solids inventory	• Impacts initial conditions • Not a safety concern
	Less	Uncertainty in characterizing organics	Changes initial estimate of solids inventory	• Impacts initial conditions • Not a safety concern
25% of the organic carbon is in the form of completely soluble salts.	More partially soluble organics	Uncertainty in characterizing organics	• Changes initial estimate of solids inventory • Solids mass more sensitive to temperature • Size of GREs more sensitive to temperature	• Impacts initial conditions • Minimum average waste temperature control would eliminate impact of uncertainty in solubility
	More insoluble organics	Uncertainty in characterizing organics	Changes initial estimate of solids inventory	• Impacts initial conditions • Not a safety concern
	Less partially soluble organics	Uncertainty in characterizing organics	• Changes initial estimate of solids inventory • Solids mass less sensitive to temperature • Size of GREs less sensitive to temperature	• Impacts initial conditions • Not a safety concern
	Less insoluble organics	Uncertainty in characterizing organics	Changes initial estimate of solids inventory	• Impacts initial conditions • Not a safety concern

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Assumption	**Deviation**	**Deviation Source**	**Consequence**	**Comments**
50 % of the organic carbon is in the form of partially soluble salts.	More partially soluble organics	Uncertainty in characterizing organics	• Changes initial estimate of solids inventory • Solids mass more sensitive to temperature • Size of gas release size more sensitive to temperature	• Impacts initial conditions • Minimum average waste temperature control would eliminate impact of uncertainty in solubility
	More insoluble organics	Uncertainty in characterizing organics	Changes initial estimate of solids inventory	• Impacts initial conditions • Not a safety concern
	Less partially soluble organics	Uncertainty in characterizing organics	• Changes initial estimate of solids inventory • Solids mass less sensitive to temperature • Size of gas release size less sensitive to temperature	• Impacts initial conditions • Not a safety concern
	Less insoluble organics	Uncertainty in characterizing organics	Changes initial estimate of solids inventory	• Impacts initial conditions • Not a safety concern
Solubility of partially soluble organic acid salts.	More soluble	Uncertainty in characterizing organics	Changes initial estimate of solids inventory	• Impacts initial conditions • Not a safety concern
	Less soluble	Uncertainty in characterizing organics	Changes initial estimate of solids inventory	• Impacts initial conditions • Not a safety concern

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Assumption	**Deviation**	**Deviation Source**	**Consequence**	**Comments**
Solubility of partially soluble organic acid salts.	More sensitive to temperature	Uncertainty in characterizing organics	• Solids mass more sensitive to temperature • Size of gas release more sensitive to temperature	Minimum average waste temperature control would eliminate impact of uncertainty in solubility
	Less sensitive to temperature	Uncertainty in characterizing organics	• Solids mass less sensitive to temperature • Size of gas release more sensitive to temperature	Not a safety concern
Solubility of sodium nitrate.	More soluble	Uncertainty in solubility model	Changes initial estimate of solids inventory	• Impacts initial conditions • Not a safety concern
	Less soluble	Uncertainty in solubility model	Changes initial estimate of solids inventory	• Impacts initial conditions • Not a safety concern
	More sensitive to temperature	Uncertainty in solubility model	• Solids mass more sensitive to temperature • Size of gas release more sensitive to temperature	Minimum average waste temperature control would eliminate impact of uncertainty in solubility
	Less sensitive to temperature	Uncertainty in solubility model	• Solids mass less sensitive to temperature • Size of gas release more sensitive to temperature	Not a safety concern
Solubility of sodium nitrite.	More soluble	Uncertainty in solubility model	Changes initial estimate of solids inventory	• Impacts initial conditions • Not a safety concern

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Assumption	Deviation	Deviation Source	Consequence	Comments
Solubility of sodium nitrite.	Less soluble	Uncertainty in solubility model	Changes initial estimate of solids inventory	• Impacts initial conditions • Not a safety concern
	More sensitive to temperature	Uncertainty in solubility model	• Solids mass more sensitive to temperature • Size of gas release more sensitive to temperature	Minimum average waste temperature control would eliminate impact of uncertainty in solubility
	Less sensitive to temperature	Uncertainty in solubility model	• Solids mass less sensitive to temperature • Size of gas release more sensitive to temperature	Not a safety concern
Solubility of sodium aluminate.	More soluble	Uncertainty in solubility in mixture	Changes initial estimate of solids inventory	• Impacts initial conditions • Not a safety concern
	Less soluble	Uncertainty in solubility in mixture	Changes initial estimate of solids inventory	• Impacts initial conditions • Not a safety concern
Solubility of sodium aluminate.	More sensitive to temperature	Uncertainty in solubility model	• Solids mass more sensitive to temperature • Size of gas release more sensitive to temperature	Minimum average waste temperature control would eliminate impact of uncertainty in solubility
	Less sensitive to temperature	Uncertainty in solubility model	• Solids mass less sensitive to temperature • Size of gas release more sensitive to temperature	Not a safety concern

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Assumption	**Deviation**	**Deviation Source**	**Consequence**	**Comments**
Solubility of sodium carbonate.	More soluble	Uncertainty in solubility model	Changes initial estimate of solids inventory	• Impacts initial conditions • Not a safety concern
	Less soluble	Uncertainty in solubility model	Changes initial estimate of solids inventory	• Impacts initial conditions • Not a safety concern
	More sensitive to temperature	Uncertainty in solubility model	• Solids mass more sensitive to temperature • Size of gas release more sensitive to temperature	Minimum average waste temperature control would eliminate impact of uncertainty in solubility
	Less sensitive to temperature	Uncertainty in solubility model	• Solids mass less sensitive to temperature • Size of gas release more sensitive to temperature	Not a safety concern
Solubility of sodium sulfate.	More soluble	Uncertainty in solubility model	Changes initial estimate of solids inventory	• Impacts initial conditions • Not a safety concern
	Less soluble	Uncertainty in solubility model	Changes initial estimate of solids inventory	• Impacts initial conditions • Not a safety concern
	More sensitive to temperature	Uncertainty in solubility model	• Solids mass slightly more sensitive to temperature • Size of gas release more sensitive to temperature	• Minor component of solids • Not a significant safety concern

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Assumption	Deviation	Deviation Source	Consequence	Comments
Solubility of sodium sulfate.	Less sensitive to temperature	Uncertainty in solubility model	• Solids mass slightly less sensitive to temperature • Size of gas release more sensitive to temperature	Not a safety concern
Salts of heavy metals (Fe, Cr, etc.) are insoluble.	Partially soluble	Uncertainty in solubility model	Slight change initial estimate of solids inventory	• Heavy solids comprise <1% of total solids • Not a safety concern
	Completely soluble	Uncertainty in solubility model	Slight change initial estimate of solids inventory	• Heavy solids comprise <1% of total solids • Not a safety concern
Nitrous oxide, nitrogen, and ammonia are generated primarily from nitrite ion with organic acid salts acting as reducing agents.	Generated from nitrate ions	Uncertainty in gas generation mechanism	No significant change in gas generation	• Nitrate ions are essentially unlimited like nitrite ions • Not a safety concern
	Generated from organic nitrogen	Uncertainty in gas generation mechanism	• Significant decrease in generation of nitrogen gases when organic nitrogen consumed • Decrease in frequency of GREs • Significant increase in hydrogen content of gas when organic nitrogen consumed	• Significant safety concern if true • Not a likely deviation based on available data

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Assumption	**Deviation**	**Deviation Source**	**Consequence**	**Comments**
Hydrogen is generated from the decomposition of organics and the radiolysis of water.	Hydrogen is generated only from decomposition of organics	Uncertainty in gas generation mechanism	No significant effect on gas generation	• This assumption is not important because gas generation rate is calibrated to observed rate of level rise • Not a safety concern
	Hydrogen is generated only from radiolysis of water	Uncertainty in gas generation mechanism	No significant effect on gas generation	• This assumption is not important because gas generation rate is calibrated to observed rate of level rise • Not a safety concern
The overall activation energy for gas generation is ~24 kcal/mole.	Greater	Uncertainty in gas generation mechanism	Increasing temperature could significantly increase frequency of rollovers	Maximum average waste temperature control and maximum waste temperature would limit impact of uncertainty in activation energy
	Less	Uncertainty in gas generation mechanism	Temperature changes have less impact on rollover frequency	Not a safety concern
Decrease waste temperature increases the ratio of hydrogen to other gases.	Increase is greater than expected	Uncertainty in gas generation mechanism	Cooling could increase flammability of gas significantly	Minimum average waste temperature control would limit impact of cooling on gas composition
	Increase is less than expected	Uncertainty in gas generation mechanism	Impact of temperature changes less than expected	Not a safety concern

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Assumption	**Deviation**	**Deviation Source**	**Consequence**	**Comments**
Decrease waste temperature increases the ratio of hydrogen to other gases.	No change in hydrogen content	Uncertainty in gas generation mechanism	None	Not a safety concern
	Decrease in hydrogen content	Uncertainty in gas generation mechanism	Heating could increase flammability of gas significantly	• Maximum average waste temperature control and maximum waste temperature would limit impact of heating on gas composition • Not a likely deviation based on the available data
The primary source of gas generation is liquid-phase reactions.	Solid-liquid reactions are important	Uncertainty in gas generation mechanism	• Changes in solid surface area as a result of pump operation could increase rate of gas generation • Increase rollover frequency	Pump operating data do not indicate that any increase in gas generation has occurred as a result of pump operation
	Solid-phase reactions are important	Uncertainty in gas generation mechanism	None	Homogeneous reactions would not be affected by pump operation
The ultimate decomposition products of the organics are sodium carbonate and sodium oxalate.	More soluble decomposition products	Uncertainty in gas generation mechanism	Increased accumulation of solids with time	• Part of the overall safety analysis uncertainty • Not a long-term safety issue
	Less soluble decomposition products	Uncertainty in gas generation mechanism	Slow accumulation of solids with time	Not a safety concern

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Assumption	**Deviation**	**Deviation Source**	**Consequence**	**Comments**
Carbon dioxide absorption does not have a significant impact on the solids inventory.	Carbon dioxide absorption significant without pump operation	Uncertainty in carbon dioxide absorption rate	• Increasing of carbonate solids in the tank • Crust growth	• Part of the overall safety analysis uncertainty • Not a long-term safety issue
	Carbon dioxide absorption significant with pump operation	• Uncertainty in carbon dioxide absorption rate • Uncertainty in impact of pump operation on mass transfer	• Increasing of carbonate solids in the tank • Crust growth	Monitoring crust thickness may indicate whether pump-induced carbon dioxide absorption is a problem
Most of the ammonia generated in the waste is dissolved in the liquid.	Most ammonia is released as it is generated	Uncertainty in ammonia inventory	Ammonia concentration in the liquid has reached a steady-state value	• Not a likely deviation • Not a safety concern
Ammonia in the gas bubbles is in equilibrium with the liquid.	Bubbles not saturated with ammonia	Uncertainty in ammonia mass-transfer rates	Increase relative importance of interfacial mass transfer on ammonia release	• Part of the overall safety analysis uncertainty • Not a long-term safety issue
	Significant mass transfer as bubbles released	Uncertainty in ammonia mass-transfer rates	None	• Not possible to distinguish between mass transfer at the waste surface and mass transfer to bubbles • Not a safety concern

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Assumption	**Deviation**	**Deviation Source**	**Consequence**	**Comments**
No significant amount of ammonia is retained by adsorption on the solids.	Significant amounts of ammonia adsorbed on solids	Importance of adsorption not known	• Increase ammonia inventory • No impact on ammonia release	• Adsorption does not change the vapor-liquid equilibrium that governs ammonia release • Not a safety concern
All gas generated in the NC layer is retained in the NC layer.	Partial retention	Uncertainty in retention mechanism	• May decrease maximum size of GRE • Slight increase in background gas release rate	Not a safety concern
	No retention	Uncertainty in retention mechanism	No rollover possible	• Not a realistic deviation • Not a safety concern
All gas generated in the NC layer is released as it is generated.	Gas trapped under impermeable crust layer	Uncertainty in crust permeability after an extended period with no rollovers	Accumulation of flammable gas below the crust	Hypothetical deviation, which should not be considered a hazard
The retained gas is 33% H_2.	More hydrogen	Uncertainty in gas generation mechanism	Increase in flammable gas hazard	• Cooling may be a mechanism for increasing hydrogen concentration • Minimum average waste temperature control would limit impact of cooling on gas composition

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Assumption	**Deviation**	**Deviation Source**	**Consequence**	**Comments**
The retained gas is 33% H_2.	Less hydrogen	Uncertainty in gas generation mechanism	Decrease in flammable gas hazard	Not a safety concern
	Contains other flammable gases	Uncertainty in gas generation mechanism	• Other likely flammable gases decrease overall LFL • Increased dome pressure in event of a burn	• Heating may increase release of other flammable gases • Maximum average waste temperature control would limit impact of heating on gas composition
Shear strength does not play a significant role in gas retention.	Shear strength important before pump installation	Uncertainty in rollovers	Increase gas retention	• Part of the overall safety analysis uncertainty • Not a long-term safety issue
	Pump operation increases shear strength enough to make it a factor	Uncertainty in impact of pump operation on shear strength	Increased gas retention	Pump operation may increase shear strength by increasing settling, particle size distribution, or solids fraction
No alumina gels form.	Alumina gels form	• Uncertainty in phase diagram • Uncertainty in kinetics	• Increase the importance of shear strength on gas retention • Increased gas retention	• Part of the overall safety analysis uncertainty • Not a long-term safety issue

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Assumption	Deviation	Deviation Source	Consequence	Comments
The amount of gas released is proportional to the volume of the NC layer that participates in the rollover.	Gas release not proportional to volume of NC layer that participates	Uncertainty in thermal balance calculations	Does not affect size of maximum gas release	Not a safety concern
Rollovers can occur that involve all the material in the NC layer, although partial rollovers are possible.	Rollovers involve less than the entire NC layer	Uncertainty in thermal balance calculations	Maximum possible gas release size may be greater than observed	• Could be a safety problem if pump operation creates conditions leading to a total rollover • Based on thermal balance calculations, this deviation is not likely
The volume of unreleasable gas is 0.3 ft^3 per ft^3 of solids.	Volume of unreleasable gas greater	Uncertainty in gas release data	Maximum possible gas release less than expected	Not a safety concern
	Volume of unreleasable gas less	Uncertainty in gas release data	Maximum possible gas release greater than expected	• Part of the overall safety analysis uncertainty • Not a long-term safety issue
	Pump operation increases unreleasable gas	Uncertainty in gas release data	Pump operation reduces size of maximum possible gas release	Not a safety concern

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Assumption	**Deviation**	**Deviation Source**	**Consequence**	**Comments**
The volume of unreleasable gas is 0.3 ft^3 per ft^3 of solids.	Pump operation decreases unreleasable gas	Uncertainty in gas release data	Pump operation increases size of maximum possible gas release	Pump operation may reduce gas retention by changing settling, particle size distribution, or solids fraction
During the period between GREs, ammonia release as a result of interfacial mass transfer at the waste surface is governed by diffusion in a stagnant liquid layer stabilized by the crust.	Mass transfer governed by liquid convection	Uncertainty in mass transfer	Background ammonia concentration more sensitive to convection in liquid	Not a safety concern if the ventilation system is operating
	Gas-phase resistance is important	Uncertainty in mass transfer	• Background ammonia release more sensitive to temperature • Background ammonia release more sensitive to ventilation flow	Not a safety concern if the ventilation system is operating
Ammonia is released as a result of mass transfer from the waste surface during GREs, and the amount is equal to 6% of the gas bubbles released.	More ammonia is released by mass transfer	Uncertainty in mass transfer	Increase in gas release volume	• Part of the overall safety analysis uncertainty • Not long-term safety issue
	Less ammonia is released by mass transfer	Uncertainty in mass transfer	Decrease in gas release volume	Not a safety concern
	Ammonia release increases as a result of pump operation	Uncertainty in mass transfer	• Increase in gas release volume • Increase in ammonia release	Pump operation could change ammonia release by changing the thickness, permeability, or density of the crust

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Assumption	**Deviation**	**Deviation Source**	**Consequence**	**Comments**
Ammonia is released as a result of mass transfer from the waste surface during GREs, and the amount is equal to 6% of the gas bubbles released.	Ammonia release decreases as a result of pump operation	Uncertainty in mass transfer	• Decrease in gas release volume • Decrease in ammonia release	• Pump operation could change ammonia release by changing the thickness, permeability, or density of the crust • Not a safety concern
Pump operation does not have a significant impact on settling.	Increases mass of crystals that settle	• Uncertainty in impact of pump on crystal size distribution • Uncertainty in gas retention mechanism	Increases gas release volume by as much as 15%	Not a safety problem as long as mixer pump is operating
	Increases mass of crystals that settle	• Uncertainty in impact of pump on crystal size distribution • Uncertainty in gas retention mechanism	Reduce gas release volume	Not a safety concern
	Change in settling increases solids fraction	Uncertainty in impact of pump on crystal size distribution	No significant impact on gas release volume	• Total mass of settled solids is the important parameter • Not a safety concern
	Change in settling increases solids fraction	Uncertainty in impact of pump on crystal size distribution	No significant impact on gas release volume	• Total mass of settled solids is the important parameter • Not a safety concern

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Assumption	**Deviation**	**Deviation Source**	**Consequence**	**Comments**
Pump operation does not have a significant impact on crystal size distribution.	Change in crystal size distribution affects settling	Uncertainty in impact of pump on crystal size distribution	See assumption on impact of pump operation on settling	-
Pump operation does not have a significant impact on crystal size distribution.	Pump operation changes surface area of crystals	Uncertainty in impact of pump on crystal size distribution	Changes gas generation rate if gas generation depends on surface reactions	Gas-generating reactions appear to be liquid-phase reactions, so change in surface area not important
Pump operation does not change the crust thickness or density.	Reduction in thickness or density	Uncertainty in the impact of pump operation on crust	• Increase amount of settled solids, which would increase gas release volume • Increase ammonia mass transfer	• Data do not indicate that pump operation has reduce crust thickness • Continued monitoring of crust thickness would help detect changes
	Increase in thickness or density	Uncertainty in the impact of pump operation on crust	• Decrease amount of settled solids ,which would reduce gas release volume • Reduce ammonia mass transfer • Increase structural consequences of crust motion	• Data do not indicate that pump operation has increased crust thickness • Continued monitoring of crust thickness would help detect changes

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Assumption	**Deviation**	**Deviation Source**	**Consequence**	**Comments**
Pump operation does not remove salt cake from the walls of the tank.	Pump operation removes salt cake from walls	• Uncertainty as to strength of pump jet at the tank walls • Uncertainty in the strength of salt cake	• Insignificant increase in mass of settled solids • Small impact on temperature	• Volume of salt cake is small compared to volume of settles solids • Salt crystals have a relatively high thermal conductivity
Pump operation cannot reduce the waste level significantly below 400 in.	Pump operation reduces level below 400 in	Uncertainty in amount of unreleasable gas	• Increase time to first rollover after pump failure • Increase density difference between layers as a result of increased temperature difference • Increase size of first GRE after pump failure	• Aging not a factor because the time scale for aging is thought to be less than the period between events • Vigorous pump operation has not reduced level significantly below 400 in. • Reducing level below 400 in. is not a problem if a spare pump is available
Pump operation does not result in localized pileup of solids.	Pump operation causes localized pileup	Uncertainty as to the impact of pump operation on solids distribution	• Increased solids temperature • No significant impact on gas release volume	Not a safety concern