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**Pacific Northwest  
National Laboratory**

Operated by Battelle for the  
U.S. Department of Energy

**Flammable Gas Release Estimates  
for Modified Sluicing Retrieval of  
Waste from Selected Hanford  
Single-Shell Tanks**

J.L. Huckaby  
B.E. Wells

May 2003



Prepared for the U.S. Department of Energy  
under Contract DE-AC06-76RL01830

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Richland, Washington

## Executive Summary

The high-level radioactive wastes in many single-shell tanks (SSTs) at the Hanford Site are to be retrieved by a modified sluicing method. Retrieval operations will hydraulically erode and dissolve the saltcake waste, and the resulting brine will then be pumped to a double-shell tank (DST). Waste gases residing in the solid waste matrix will be released into the tank headspace when the matrix is eroded or dissolved. These retained waste gases include the flammable species hydrogen, methane, and ammonia; a concern exists that these gases could produce a flammable mixture in the tank headspaces during the retrieval operations. This report combines conservative retained gas inventory estimates and tank data with anticipated waste retrieval rates to estimate the potential headspace flammability of selected SSTs during waste retrieval operations. Considered here are 10 of the 12 tanks from 241-S tank farm (241-S-107 and 241-S-111 are not considered here) and Tank 241-U-107.

This report is intended to support the specification of process controls that ensure flammable conditions do not develop in the tank headspaces. Consequently, the physical scenarios considered, the models developed to estimate retained gas releases and the tank headspace compositions under these scenarios, and the model input data are intended to assess (and very likely exaggerate) the potential to reach headspace flammability conservatively. Flammable retained gas inventories, for example, are based on the 95th percentile developed by Barker and Hedengren (2003), giving 95 % confidence that actual inventories are smaller than those used in the calculations. Gas releases and headspace flammability were evaluated for three general scenarios: a very aggressive dissolution and erosion of saltcake waste by water jets impinging on the waste surface, the drainage of interstitial liquids from saltcake during a shutdown of the retrieval process, and the dissolution of saltcake by unsaturated liquids during a shutdown of the retrieval process.

The simple model of waste retrieval using the modified sluicing approach indicated that the flammable gas headspace concentrations can rapidly approach the action level of 25 % of the lower flammability limit (LFL) when the tank is passively ventilated. It is not necessary to use the portable exhauster to maintain the headspace hydrogen concentration below this action level, but retrieval rates may be limited by the slow removal of flammable gases by passive ventilation. Use of the portable exhauster anywhere in the assumed operating range of 270 to 475 cfm would prevent the headspaces from reaching the action level, even if the water jets are very effective at eroding the saltcake.

Under the very conservative scenarios, models, and the model inputs used, a process shutdown by drainage of liquids from the saltcake and by dissolution of saltcake by unsaturated liquids left in the tank are both indicated to have the potential to raise the headspace flammability from an operationally acceptable condition (25% of the LFL) to an unacceptable condition (100% of the LFL). Guidelines for maintaining free liquid inventories in each waste tank obtained from the models are given in Table S.1.

**Table S.1. Process Water and Central Pool Liquid Level Guidelines**

| <b>Tank</b> | <b>Maximum Allowable Tank Inventory of Process Water (kgal)</b> | <b>Minimum Level of Liquid in Central Pool (in.)</b> |
|-------------|---|--|
| S-101       | 147   | 20   |
| S-102       | 154   | 30   |
| S-103       | 181   | 0  |
| S-104       | 324   | 0  |
| S-105       | 213   | 0  |
| S-106       | 160   | 0  |
| S-108       | 211   | 0  |
| S-109       | 210   | 0  |
| S-110       | 158   | 0  |
| S-112       | 160   | 24   |
| U-107       | 139   | 0  |

## **Acknowledgments**

The authors would like to thank Steve Barker for providing key retained gas inventory and composition data, Lenna Mahoney for conducting a peer review, and Blaine Barton, Mike Grigsby, Larry Kripps, Ryan Smith, and Sheldon Stahl for helpful comments on early drafts of this report. Thanks are also due to Sheila Bennett, our technical editor.

## Acronyms and Abbreviations

|      |                                   |
|------|-----------------------------------|
| atm  | atmosphere                        |
| DST  | double-shell tank                 |
| gal  | gallon                            |
| gpm  | gallons per minute                |
| kgal | thousands of gallons              |
| LFL  | lower flammability limit (in air) |
| scfm | standard cubic feet per minute    |
| SpG  | specific gravity                  |
| SST  | single-shell tank                 |
| TCD  | Tank Characterization Database    |
| vol% | volume percent                    |
| wt%  | weight percent                    |

## List of Symbols

|              |  |
|--------------|--|
| $\alpha$     | Retained gas void fraction   |
| $\beta_{LC}$ | Volume of brine created by dissolution per volume of water added     |
| $\beta_{BW}$ | Volume of bulk waste dissolved per volume of water                   |
| $\chi_H$     | Volume fraction of the retained gas                                  |
| $\Gamma$     | Ratio of waste volumes above and below the interstitial liquid level |
| $\lambda$    | Fraction of retained gas that is flammable                           |
| $\phi$       | Porosity   |
| $\rho_{BR}$  | Saturated brine density  |
| $\rho_{IL}$  | Interstitial liquid density  |
| $\rho_S$     | Solids density   |
| $C_{CH_4}$   | Fraction of CH <sub>4</sub> in flammable portion                     |
| $C_{H_2}$    | Fraction of H <sub>2</sub> in flammable portion                      |
| $C_i$        | Volume fraction (i.e., concentration)                                |
| $C_{NH_3}$   | Fraction of NH <sub>3</sub> in flammable portion                     |
| $C_H(t_1)$   | Concentration of the gas at time $t_1$                               |
| $F$          | Specified mass fraction of undissolved solids in the product stream  |
| $h_{IL}$     | Initial height of interstitial liquid                                |
| $h_{POOL}$   | Initial height of liquid in the central pool                         |
| $LFL_{MIX}$  | Lower flammability limit in air of the mixture                       |
| $LFL_i$      | Lower flammability limit of the $i^{th}$ species in air              |
| $M_{DS}$     | Mass of dissolved solids per volume of water applied                 |

|             |  |
|-------------|--|
| $M_{IL}$    | Mass of interstitial liquid per bulk waste volume                                  |
| $M_S$       | Mass of solids per bulk waste volume   |
| $P_{HS}$    | Tank headspace pressure  |
| $P_W$       | Average hydrostatic pressure on retained gas                                       |
| $P_{W^*}$   | Average hydrostatic pressure on retained gas after drainage of interstitial liquid |
| $Q_{BOUT}$  | Volumetric flow of waste out via the retrieval pump                                |
| $Q_{FG}$    | Volumetric flammable gas release rate  |
| $Q_{H2O}$   | Volumetric water application rate  |
| $Q_{RG}$    | Volumetric retained gas release rate   |
| $Q_{VOUT}$  | Volumetric flow of air out via ventilation system                                  |
| $Q_{WIN}$   | Volumetric flow of water into the tank   |
| $R$         | Radius of the tank   |
| $r$         | Effective radius of central pit  |
| $T_{HS}$    | Temperature of the headspace   |
| $T_W$       | Temperature of the retained gas  |
| $T_{W^*}$   | Temperature of the retained gas after drainage of interstitial liquid              |
| $V_B$       | Volume of bulk waste disturbed per volume of water applied                         |
| $V_G$       | Volume of retained gas at atmospheric pressure and headspace temperature           |
| $V_{H2O}$   | Volume of water available for saltcake dissolution in tank                         |
| $V_{HS}$    | Volume of tank headspace   |
| $V_{HS^*}$  | Volume of tank headspace after drainage of interstitial liquid                     |
| $V_{HS0}$   | Volume of tank headspace at time zero  |
| $V_{IL}$    | Volume of interstitial liquid  |
| $V_S$       | Volume of dry void-free solids in the tank   |
| $V_T$       | Volume of waste  |
| $V_{TANK}$  | Volume of (empty) tank   |
| $V_{W<ILL}$ | Volume of waste below the interstitial liquid level                                |



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# 1.0 Introduction

The high-level radioactive wastes in many single-shell tanks (SSTs) at the Hanford Site are to be retrieved by a modified sluicing method. Retrieval operations will hydraulically erode and dissolve the saltcake waste, and the resulting brine will then be pumped into a double-shell tank (DST). Insoluble sludge wastes that remain in the tank after dissolution of the saltcake will be sluiced to the inlet of the retrieval pump and pumped to a DST.

Waste gases residing in the solid waste matrix will be released into the tank headspace when the matrix is eroded or dissolved. These retained waste gases include the flammable species hydrogen, methane, and ammonia, and there is a concern that these gases could produce a flammable mixture in the tank headspaces during the retrieval operations. This report combines conservative retained gas inventory estimates and tank data with anticipated waste retrieval rates to estimate the potential headspace flammability of selected SSTs during waste retrieval operations. The SSTs considered here are 10 of the 12 tanks in the 241-S tank farm (only Tanks 241-S-107 and 241-S-111 are excluded) and Tank 241-U-107 (U-107).<sup>(a)</sup>

## 1.1 Retained Gas Configuration

The wastes in the 11 tanks of interest are composed primarily of water-soluble salts with various lesser amounts of metal oxides and other water-insoluble species. The solid wastes were generally laid down in layers via settling and precipitation as batches of slurry waste were added and the supernatant liquids were subsequently removed from the tanks. Gradual salt crystal growth caused by cooling of the waste and Ostwald ripening has resulted in the formation of saltcake, a hard granular solid that has significant structural strength (Hedengren et al. 2001). Though most of the tanks of interest have had their drainable liquid wastes removed, much liquid remains as trapped droplets held by surface tension in the interstices of the drained saltcake, and much liquid remains below the level at which drainage due to gravity is effective.

Chemical and radiolytic processes in the aqueous waste generate gases (e.g., hydrogen, nitrogen) that form small bubbles within the solid matrix. These may grow within the confines of the matrix but do not generally deform the solid matrix itself.<sup>(b)</sup> When small, the bubbles are effectively separated from other bubbles and the headspace by droplets of interstitial liquid and are relatively immobile. Gradual bubble growth results in larger bubbles that migrate upward through the matrix and eventually are released into the tank headspace. In dry waste regions above the interstitial liquid level, the interstices of the solid matrix are sufficiently interconnected to allow waste gases to diffuse upward to the headspace (Peurrung et al. 1996; Huckaby et al.

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(a) Hanford tanks are designated by the prefix 241- followed by the tank farm label and tank number. In this report, as in common usage, the prefix is omitted.

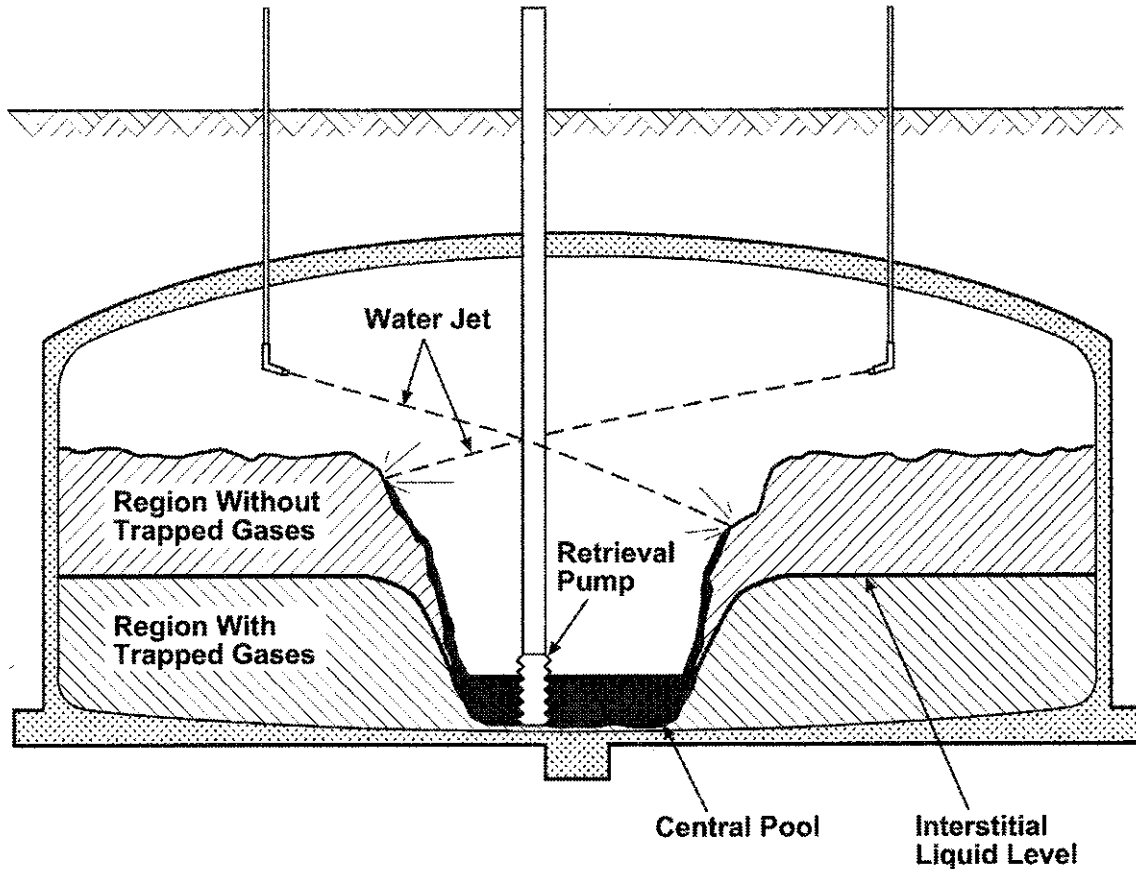
(b) Particle-displacing bubbles can be formed under certain conditions, as described by Stewart et al. (1996), but are not significant in the tanks of interest in this report.

1999). Thus gases that have migrated to the top of the interstitial liquid diffuse relatively quickly through the dry waste to the headspace.

## 1.2 Retrieval Process Description

The retrieval of waste from the tanks of interest will involve dissolution, erosion, and sluicing to mobilize and transfer the waste solids to the suction of a retrieval pump. While some changes to the retrieval strategy and methods can be expected, the general approach is expected to follow four stages:

- In the first stage, water will be added to the well created during the installation of the retrieval pump and allowed to soak and dissolve the saltcake surrounding the pump. The resulting brine will be pumped out to a DST. Several fill, soak, and pump cycles will be necessary to enlarge the well to a size that supports continuous application of water. This first stage will involve relatively small quantities of water (less than 10,000 gal at any one time), and the retrieval of waste (and the release of gases) will be relatively slow.
- During the second retrieval stage, three remotely operated nozzles in the tank headspace will direct jets of water at the waste surface to erode and dissolve the saltcake. Water supply limitations result in a nominal water application rate of about 80 gpm and an estimated maximum application rate of about 100 gpm. The brine and any suspended solids produced by this method will drain to the pump and be pumped out at a nominal rate of 80 gpm. This is depicted in Figure 1.1. While distribution of some water to the relatively horizontal upper waste surface is inevitable, the retrieval strategy is to direct the water jets at the sloping wall of waste around the central pool, as depicted in Figure 1.1, to limit the accumulation of liquid in the tank. The second stage will begin as soon as the central pit is large enough to support a continuous process and last until the central pit extends roughly to the tank wall.
- The third stage of retrieval will involve removing waste from the tank wall by hydraulically eroding, dissolving, and undercutting the waste. Undercutting is intended to cause the waste to slough away from the wall while minimizing the amount of water sprayed directly at the wall. Though this may cause small sections of the waste to collapse and release retained gases, the inventory of retained gases will be reduced (and the tank headspace enlarged) to the point that it is impossible to reach a flammable condition in the headspace.
- The fourth and last stage will consist of sluicing the remaining waste, much of which will have already released its gas, toward the pump inlet. Only minor gas releases are expected during this last retrieval period. These stages and other aspects of the retrieval strategy are described in *Process Control Plan for Saltcake Dissolution Retrieval Demonstration in Tank 241-S-112* (Barton et al. 2003).



**Figure 1.1.** Illustration of the S-112 Center-Out Waste Retrieval Strategy

Figure 1.1 also illustrates that, because a center-out retrieval strategy is being applied, erosion and dissolution of waste over any extended period of time (i.e., hours) will include waste that is above the interstitial liquid level (in the tanks where such waste exists). Water applied to erode and dissolve the upper, gas-free portion of the waste will cause very little gas release. Similarly, gas releases will not be increased if chunks of the upper, gas-free portion of the waste slough or break off and tumble into the central pool.

### 1.3 Previous Studies

In past work, gas release rates during retrieval of saltcake SSTs by water dissolution were evaluated for typical interim stabilization brine-pumping rates of 5–10 gpm (Stewart 2001). The generic tank represented in that study was assumed to have waste properties and gas content similar to Tank U-107. Stewart (2001) argued that gas release rates would be limited by the waste dissolution rate, which, for operational reasons, was approximately equal to the brine-pumping rate. With a 10-gpm pumping rate, a retained gas volume fraction of 0.2, and estimated passive ventilation of 2.5 scfm, the headspace hydrogen concentration was predicted to exceed the action limit of 6,250 ppm in about three days, but the headspace was predicted to remain

below the lower flammability limit (LFL) of 4 vol% hydrogen to the end of the planned U-107 dissolution tests, about six weeks later.

Later work specific to retrieval of Tank S-112 considered brine pumping rates from 1 to 1,000 gpm with tank headspace ventilation rates from 1 to 1,000 scfm.<sup>(a)</sup> In that study the headspace hydrogen concentration was predicted to remain well below the LFL at the highest pumping rates even without active ventilation because the retained gas inventory in S-112 was estimated to be relatively low. A ventilation rate of 100 scfm was predicted to be adequate to keep the hydrogen concentration below the 6,250 ppm action limit for pumping rates up to 100 gpm. Mahoney revised gas release estimates to adjust for changes in retained gas inventory due to saltwell pumping of Tank S-112 but also used the relatively low estimate of retained gas inventory.<sup>(b)</sup> Neither Stewart and Morrissette nor Mahoney addressed hydraulic erosion of the saltcake as a potentially significant impact on the gas release rate.

This report deviates from previous studies of retrieval gas release rates by considering the higher retained gas content developed by Barker and Hedengren (2003). It also proposes and applies a bounding rate for the erosion of saltcake and estimates gas release rates accordingly.

## 1.4 Organization of the Report

Section 2 develops retained gas inventories, compositions, and flammability estimates for each tank studied in this report. Section 3 considers the mechanisms by which the retained gas could be released during retrieval by sluicing. Simple models to estimate gas release under different scenarios are developed and their results presented in Section 4. Section 5 discusses the results of the study, and Section 6 contains cited references. Derivation of the models is provided in the appendixes.

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(a) Stewart CW and DJ Morrissette. September 2001. "Preliminary Assessment of Gas Releases at High Dissolution Rates in Tank 241-S-112." PNNL Letter Report TWS01.31 Rev. 1.

(b) Mahoney LA. November 2002. "Assessment of Gas Releases at High Retrieval Rates in Tank 241-S-112." PNNL Letter Report TWS03.016.

## 2.0 Retained Gas Inventories and Properties

In this section, values for the retained gas inventory, composition, and flammability are developed for each tank considered in this report. Because the estimated inventories of retained flammable gases are to be used in subsequent analyses of safety-related scenarios, their development is intended to provide reasonably conservative values rather than most-probable or best-estimate values.

### 2.1 Retained Gas Inventories and Composition

The retained gas inventories of the waste tanks have been estimated by several techniques. Tanks that have a liquid waste surface exhibit fluctuations in the surface level as barometric pressure changes cause the retained gases to expand or compress, and the quantity of retained gas can be estimated from the magnitude of the level fluctuations (Whitney 1995). This technique is not applicable to all tanks because many have a solid waste surface that does not fluctuate with barometric pressure changes. Retained gas volumes from regions of selected waste tanks have been measured using a specially designed retained gas sampler. This also allows the composition of retained gases to be determined, but of the tanks of interest here, retained gas samples have been collected from only Tanks S-102 and S-106 (Mahoney et al. 1999). Vertical neutron probe logging of the waste, routinely conducted to measure the interstitial liquid level, has been analyzed to estimate waste void fraction and retained gas volumes. However, the results obtained depend heavily on the waste properties in the immediate vicinity of the liquid observation well and are not necessarily representative of the tank. Lastly, a gradual rise in the liquid level in a tank (either supernatant or interstitial liquid) is generally indicative of retained gas accumulation and can be used to estimate changes in the retained gas volume. Unfortunately, interstitial liquid level measurements were not available prior to about 1981, so any gases present in the waste before that time would not be included in such estimates. In summary, a variety of methods have been used to estimate retained gas inventories with varying applicability and confidence in the results.

The compositions and inventories of the retained gases in all 149 SSTs and 28 DSTs have recently been evaluated for the safety analysis by Barker and Hedengren (2003). Using available data from all saltcake tanks and estimates of the uncertainty in those data, Barker and Hedengren conducted a Monte Carlo simulation to establish probability distributions for the retained gas composition and inventory of all the Hanford high-level radioactive waste tanks. Table 2.1 lists selected results for the tanks of interest (described in more detail in Appendix A). These data were developed for, but not specifically presented in the Barker and Hedengren (2003) report. In this table the median value is that for which half the Monte Carlo simulations gave higher values and half gave lower values, and the 95<sup>th</sup> percentile value is that value for which 95% of the simulations gave lower values.

**Table 2.1. Retained Gas Monte Carlo Simulation Results<sup>(a)</sup>**

| Tank  | Hydrogen Median (vol%) | Hydrogen 95%ile (vol%) | Ammonia Median (vol%) | Ammonia 95%ile (vol%) | Methane Median (vol%) | Methane 95%ile (vol%) | Void Fraction Median | Void Fraction 95%tile |
|-------|------------------------|------------------------|-----------------------|-----------------------|-----------------------|-----------------------|----------------------|-----------------------|
| S-101 | 40.9                   | 70.0                   | 1.8                   | 10.8                  | 3.5                   | 16.6                  | 0.150                | 0.248                 |
| S-102 | 33.5                   | 42.9                   | 1.0                   | 1.7                   | 0.6                   | 0.9                   | 0.153                | 0.255                 |
| S-103 | 40.9                   | 68.8                   | 1.7                   | 10.5                  | 3.6                   | 16.9                  | 0.151                | 0.254                 |
| S-104 | 40.9                   | 69.2                   | 1.8                   | 10.5                  | 3.6                   | 17.0                  | 0.011                | 0.098                 |
| S-105 | 41.0                   | 69.5                   | 1.8                   | 10.9                  | 3.5                   | 16.0                  | 0.150                | 0.254                 |
| S-106 | 63.3                   | 77.7                   | 0.5                   | 0.9                   | 0.9                   | 1.7                   | 0.153                | 0.254                 |
| S-108 | 40.6                   | 69.2                   | 1.8                   | 10.6                  | 3.4                   | 16.7                  | 0.150                | 0.251                 |
| S-109 | 40.8                   | 69.2                   | 1.7                   | 10.5                  | 3.6                   | 17.4                  | 0.151                | 0.250                 |
| S-110 | 40.6                   | 69.3                   | 1.7                   | 10.6                  | 3.5                   | 17.4                  | 0.154                | 0.255                 |
| S-112 | 41.0                   | 69.1                   | 1.7                   | 10.7                  | 3.7                   | 17.4                  | 0.152                | 0.253                 |
| U-107 | 40.3                   | 69.4                   | 2.2                   | 12.2                  | 3.5                   | 17.0                  | 0.152                | 0.252                 |

(a) All values are from Barker (2003).

In Table 2.1 the retained gas void fractions are the volume fractions of all gases (at the pressure and temperature the gas experiences) in the waste below the interstitial liquid level. Note that nitrogen (N<sub>2</sub>) and nitrous oxide (N<sub>2</sub>O) constitute a significant portion of the retained gases (i.e., are included in the void fraction estimate) but are not included in Table 2.1 nor discussed in detail because they are non-flammable. The void fraction distributions in Table 2.1 are based on the fraction of saltcake waste and sludge waste present in each tank.

The Monte Carlo analysis and results given in Table 2.1 were based on published tank conditions as of November 15, 2001 and do not include recent changes associated with the removal of interstitial liquid by saltwell pumping. Saltwell pumping decreases the region of waste where retained gases can reside. It also lowers the hydrostatic pressure experienced by the retained gas, causing it to expand, which in turn enhances the rate of upward bubble migration through the saltcake (Huckaby et al. 1999). Headspace hydrogen concentration monitoring data clearly show that saltwell pumping causes a significant fraction of retained gases to be released into the headspace (Huckaby et al. 1999).<sup>(a)</sup>

To maintain reasonable consistency with the safety documentation of Barker and Hedengren (2003) and yet account for likely gas releases due to saltwell pumping, this study uses the 95<sup>th</sup> percentile void fraction in Table 2.1 as the bounding value to calculate the current retained gas inventory. It is assumed that all the waste below the interstitial liquid level has a uniform retained gas void fraction and is subject to an average hydrostatic pressure,  $P_w$ , in inches of H<sub>2</sub>O, which is estimated by the following expression:

(a) See also: Peurrung LM and JL Huckaby. March 2000. "Gas Release Behavior During Salt-Well Pumping." PNNL Letter report TWS00.39.



$$P_W = P_{HS} + \frac{1}{2} SpG h_{IL} \quad (2.1)$$

where  $P_{HS}$  is the tank headspace pressure in units of inches of  $H_2O$ , and  $SpG$  is the specific gravity of the interstitial liquid.

The current inventory of retained gas,  $V_G$ , at atmospheric pressure and headspace temperature can be calculated directly from the volume of waste below the interstitial liquid level,  $V_{W<ILL}$ , the void fraction,  $\alpha$ , the temperatures of the retained gas,  $T_W$ , and headspace,  $T_{HS}$ , the average hydrostatic pressure on the retained gas,  $P_W$ , and the headspace pressure,  $P_{HS}$ , using the following expression:

$$V_G = \alpha V_{W<ILL} \frac{P_W}{P_{HS}} \frac{T_{HS}}{T_W} \quad (2.2)$$

These equations allow the total retained gas inventory in a tank, at headspace conditions, to be calculated directly. Table 2.2 lists the parameter values and calculated retained gas volumes for each tank of interest in this study, assuming the 95<sup>th</sup> percentile void fractions in Table 2.1.

**Table 2.2.** Input Parameter Values and Calculated Retained Gas Inventories

| Tank  | Liquid $SpG^{(a)}$ | $h_{IL}^{(b)}$<br>(inches) | $P_W^{(c)}$<br>(atm) | $T_W^{(d)}$<br>(K) | $T_{HS}^{(e)}$<br>(K) | $V_{W<ILL}^{(f)}$<br>(gal) | $V_{gas}^{(g)}$<br>(ft <sup>3</sup> ) |
|-------|--------------------|----------------------------|----------------------|--------------------|-----------------------|----------------------------|---------------------------------------|
| S-101 | 1.40               | 144.1                      | 1.247                | 314.8              | 303.8                 | 371,412                    | 14,848                                |
| S-102 | 1.38               | 168.5                      | 1.286                | 307.9              | 298.4                 | 438,609                    | 18,609                                |
| S-103 | 1.46               | 92.2                       | 1.166                | 298.7              | 295.7                 | 228,479                    | 8,940                                 |
| S-104 | 1.37               | 111.0                      | 1.187                | 309.4              | 302.2                 | 280,255                    | 4,268                                 |
| S-105 | 1.46               | 55.0                       | 1.099                | 296.9              | 293.9                 | 125,950                    | 4,650                                 |
| S-106 | 1.44               | 52.7                       | 1.093                | 295.6              | 292.2                 | 119,632                    | 4,399                                 |
| S-108 | 1.46               | 62.7                       | 1.113                | 300.9              | 294.7                 | 147,237                    | 5,379                                 |
| S-109 | 1.37               | 65.0                       | 1.109                | 300.2              | 292.9                 | 153,571                    | 5,566                                 |
| S-110 | 1.43               | 129.4                      | 1.227                | 314.1              | 298.7                 | 330,928                    | 13,142                                |
| S-112 | 1.46               | 115.3                      | 1.206                | 300.1              | 294.0                 | 292,097                    | 11,665                                |
| U-107 | 1.41               | 91.5                       | 1.158                | 297.1              | 295.9                 | 226,724                    | 8,811                                 |

(a) Tank Characterization Database (TCD) (2003) liquid sample densities and specific gravity values were averaged and the larger of the two averages selected. Tanks S-105 and S-108 had no liquid density or specific gravity data on the TCD; these tanks were assigned the specific gravity of S-112, which had the highest reported values.

(b) Interstitial liquid heights are the TCD values from April 7 or 10, 2003.

(c) A unit conversion factor of 0.0024583 atm/in.  $H_2O$  was applied to Eq. (2.1).

(d) Waste temperatures were calculated by averaging the TCD values for all thermocouples below the interstitial liquid level between April 16, 2002 and April 15, 2003.

(e) Headspace temperatures were calculated by averaging the TCD values for all thermocouples above the waste surface level between April 16, 2002 and April 15, 2003.

(f) Volumes of waste below the interstitial liquid levels were calculated using the  $h_{IL}$  and algorithms given by Barker (2003).

(g) Calculated retained gas volumes are for 1 atm pressure and  $T_{HS}$ . Calculated values include a conversion factor of 0.13368 ft<sup>3</sup>/gal.

In this report the concentrations of the three flammable species hydrogen, methane, and ammonia in the retained gas are assumed to be the median values given in Table 2.1. These median values, when combined with the median void fraction, give the best-estimate inventories for each of these gases. When combined with the 95<sup>th</sup> percentile void fraction, the median concentrations from Table 2.1 give the 95<sup>th</sup> percentile values for the gas inventories, assuming a Monte Carlo analysis that held the gas composition fixed. Because the values and distributions of the void fraction are independent of (and mutually exclusive with) the values and distributions of the retained gas constituent concentrations, combining the 95<sup>th</sup> percentile void fraction with the 95<sup>th</sup> percentile retained gas concentrations would give approximately the 99<sup>th</sup> percentile values for the hydrogen, methane, and ammonia inventories.

## 2.2 Flammability of Retained Gas Mixtures

The LFLs in air are different for each of the three flammable species in the retained gas (hydrogen, methane, and ammonia). The flammability of a mixture of these three gases may be estimated using Le Chatelier's linear mixing law:

$$LFL_{MIX} = \frac{1}{\sum_{i=1}^n \frac{C_i}{LFL_i}} \quad (2.3)$$

where  $LFL_{MIX}$  is the LFL in air of the mixture, and  $C_i$  and  $LFL_i$  are the volume fraction (i.e., concentration) and LFL of the  $i^{th}$  species. It is also required that

$$\sum_{i=1}^n C_i = 1. \quad (2.4)$$

Table 2.3 lists the published LFLs for the individual gases used in this report.

**Table 2.3.** Lower Flammability Limits in Air of Flammable Retained Gases

| Constituent  | LFL in air <sup>(a)</sup><br>(volume fraction) |
|--|--|
| Hydrogen   | 0.04   |
| Methane  | 0.05   |
| Ammonia  | 0.15   |
| (a) LFL values for individual species are from Zabetakis (1965). |  |

The LFL of the flammable gas mixture in each tank will be different because each tank has a different estimated retained gas composition. Using the median hydrogen, methane, and ammonia retained gas concentrations given in Table 2.1, the relative contributions of each gas [i.e., the  $C_i$  of Eq. (2.3) and (2.4)] and the LFL of their mixture have been calculated and are listed in Table 2.4. As expected, the mixture LFLs are similar to the LFL of hydrogen, because the dominant flammable gas in each tank is hydrogen.

**Table 2.4.** Lower Flammability Limits in Air of Retained Gas Mixtures by Tank

| Tank  | Fraction of H <sub>2</sub> in flammable portion,<br>$C_{H_2}$ | Fraction of CH <sub>4</sub> in flammable portion,<br>$C_{CH_4}$ | Fraction of NH <sub>3</sub> in flammable portion,<br>$C_{NH_3}$ | Flammability in air,<br>$LFL_{MIX}$<br>(volume fraction) |
|-------|---|---|---|--|
| S-101 | 0.885   | 0.077   | 0.039   | 0.0418   |
| S-102 | 0.955   | 0.017   | 0.027   | 0.0410   |
| S-103 | 0.885   | 0.077   | 0.038   | 0.0418   |
| S-104 | 0.884   | 0.077   | 0.038   | 0.0418   |
| S-105 | 0.886   | 0.076   | 0.039   | 0.0418   |
| S-106 | 0.978   | 0.014   | 0.007   | 0.0403   |
| S-108 | 0.886   | 0.075   | 0.039   | 0.0418   |
| S-109 | 0.885   | 0.078   | 0.038   | 0.0418   |
| S-110 | 0.886   | 0.077   | 0.037   | 0.0418   |
| S-112 | 0.884   | 0.079   | 0.037   | 0.0418   |
| U-107 | 0.877   | 0.076   | 0.047   | 0.0421   |

### 2.3 Flammability of Released Gases

In addition to the inventory, composition, and flammability of the retained gases in each tank, the potential for the tank headspace to reach a flammable condition also depends on the volume of the headspace. Table 2.5 summarizes the key tank parameters needed to calculate whether the headspace could reach a flammable condition, and gives the calculated headspace flammability as a percentage of the LFL.

As indicated in Table 2.5, Tank S-112 would have the highest headspace flammability if all the retained gas were released instantaneously. However, it is important to note that Tanks S-101, S-102, and S-110 each have higher estimated flammable gas inventories, and that the relatively small S-112 headspace is an important factor that will change as the waste is retrieved and the headspace volume increases.

**Table 2.5. Calculated Headspace Flammability by Tank**

| <b>Tank</b> | <b>Waste Volume<sup>(a)</sup><br/>(kgal)</b> | <b>Headspace Volume<sup>(b)</sup><br/>(ft<sup>3</sup>)</b> | <b>Fraction of Retained Gas that is Flammable<sup>(c)</sup></b> | <b>Flammable Retained Gas Volume<sup>(d)</sup><br/>(ft<sup>3</sup>)</b> | <b>Headspace Flammability<br/>(% of LFL)</b> |
|-------------|--|--|---|---|--|
| S-101       | 394  | 87,692   | 0.462   | 6,864   | 187  |
| S-102       | 439  | 81,676   | 0.350   | 6,521   | 195  |
| S-103       | 238  | 108,546  | 0.463   | 4,135   | 91   |
| S-104       | 288  | 101,862  | 0.462   | 1,974   | 46   |
| S-105       | 406  | 86,088   | 0.463   | 2,151   | 60   |
| S-106       | 455  | 79,537   | 0.648   | 2,848   | 89   |
| S-108       | 550  | 66,838   | 0.458   | 2,465   | 88   |
| S-109       | 533  | 69,110   | 0.461   | 2,564   | 89   |
| S-110       | 389  | 88,360   | 0.458   | 6,022   | 163  |
| S-112       | 614  | 58,282   | 0.464   | 5,410   | 222  |
| U-107       | 311  | 71,977   | 0.459   | 4,049   | 134  |

(a) All waste volumes from Hanlon (2003).  
 (b) Calculated by subtracting waste volumes from empty tank volumes. All 241-S farm tanks have an empty tank volume of 140,362 ft<sup>3</sup>, and U-107 has an empty tank volume of 113,552 ft<sup>3</sup> (Barker 2003).  
 (c) Calculated by summing individual gas median volume fractions in Table 2.1.  
 (d) Values are at average tank headspace temperature and 1 atm pressure. Calculated by multiplying values in fourth column by  $V_{gas}$  values from Table 2.2.

## 3.0 Retained Gas Release Mechanisms

Three mechanisms have been identified for the release of gases retained in the waste during modified sluicing retrieval of the waste. Retained gases will be released by drainage of the interstitial liquid from the undisturbed solid matrix, dissolution of the saltcake solid matrix, and hydraulic erosion of the solid matrix with water jets.

### 3.1 Supernatant and Interstitial Liquid Removal

The removal of liquids from a waste tank can induce the release of retained gases by decreasing the hydrostatic pressure on the retained gas and by uncovering retained gas bubbles. Independent of whether the liquid is supernatant or interstitial, the removal of liquid reduces the hydrostatic head on the retained gas. This causes the gas to expand, the bubbles of retained gas to grow larger, and the rate of their upward migration to increase (Stewart et al. 1996). Some bubbles that had been essentially immobilized in the solid matrix by liquid droplets will become large enough to start their migration upward. Once the supernatant liquids have been removed from a tank the drainage of interstitial liquid essentially uncovers the bubbles, allowing the gas to diffuse upward through the porous matrix to the headspace.

Headspace hydrogen concentration data collected during saltwell pumping have indicated that the rate of retained gas release is approximately proportional to the interstitial liquid drainage rate.<sup>(a)</sup> This is consistent with the retained gases existing in the interstices of the saltcake as small bubbles separated and trapped by the interstitial liquid. To a first approximation, the fraction of retained gas released by gravitational drainage is equal to the fraction of interstitial liquid drained. For example, if half the interstitial liquid in a region of waste is drained, about half the retained gas in that region of waste will be released.

The rate at which interstitial liquid can be drained to a central well depends on the permeability of the waste, the height of the interstitial liquid in the waste, and the depth of liquid in the central well. Consequently, the drainage rates during the retrieval operations will vary with spatial variations in the waste and changes in the size, shape, and depth of the central pool around the retrieval pump. Given that modified sluicing has not been conducted before and many key waste characteristics are not known, these factors can be predicted reliably. However, consideration of the extended time (months) required to drain interstitial liquid during saltwell pumping of saltcake tanks suggests that this process is slower than the planned retrieval rate. For example, during the September and October 2002 saltwell pumping of Tank S-112, the maximum sustained pumping rate (which is limited by and thus approximately equivalent to the drainage rate) was about 1.5 gpm.<sup>(b)</sup> By contrast, the erosion and dissolution of waste during retrieval operations is expected to allow a nominal retrieval pumping rate of 80 gpm.

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(a) Peurrung LM and JL Huckaby. March 2000. "Gas Release Behavior During Saltwell Pumping." PNNL Letter report TWS00.39.

(b) On September 22, 2002 an estimated 1,758 gal of waste liquids were pumped from Tank S-112 over a 19.8-hour period. By the following day the drainage rate had dropped, limiting the pumping rate to about 0.55 gpm.

## 3.2 Dissolution of the Solid Waste Matrix

The dissolution of the gas-bearing saltcake matrix will release the gases trapped in the saltcake. Though the rate of saltcake dissolution during waste retrieval has yet to be established, it is inherently limited by the water application rate. An upper bound on the rate of gas release can be obtained by assuming that the water applied to the waste becomes instantaneously saturated and releases all the gases trapped in the saltcake it dissolves.

If dissolution is slow relative to water addition, the amount of water (or unsaturated brine) in the tank may be increased to increase the liquid residence time in the tank. In this event, the amount of water in the tank could be enough to dissolve saltcake and release enough flammable gas to raise the headspace to a flammable condition. Thus gas releases due to dissolution can be both a rate issue and a tank water inventory issue. Both issues are considered in Section 4.

## 3.3 Hydraulic Erosion of the Solid Waste Matrix

Retained gases will also be released when water jets are applied to hydraulically erode the solid waste matrix. Hydraulic erosion will occur when the force of the impacting water jet exceeds the shear strength of the saltcake matrix. Attempts to estimate the erosion rate given the waste shear strength, initial power of the water jet, power losses and inefficiencies have been unsuccessful due to a lack of relevant experimental data. In lieu of suitable erosion rate data, an upper bound on the rate of erosion can be established by realizing that the rate of erosion is effectively limited by the rate at which solids can be fluidized and carried away by the liquid. Sustained erosion of saltcake will require the removal of solids from the point where the jet impacts the saltcake or the jet will not impinge on undisturbed saltcake and erosion will be reduced. Thus erosion can occur no faster than the loosened solids are removed by the liquid.

To bound the rate at which solids can be removed by liquid, it is assumed that the impact of water on the saltcake could result in a slurry containing 30 wt% solids. This is a relatively high solids loading for slurry given that solid saltcake itself has a high liquid content. A composite of core sample 292 from Tank S-112, for example, which included sample from the well-drained waste above the interstitial liquid level, was estimated to have only about 64 wt% solids.<sup>(a)</sup>

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(a) Core composite liquid content was based on analyses of water content and the aqueous phase chloride, nitrite, and cesium-137 constituents. Personal communication, Lenna Mahoney, PNNL, March 2003.

## 4.0 Models for Gas Release Rates and Headspace Flammability

This section develops simple models to estimate gas releases under various scenarios, applies the conservative flammable gas inventories developed in Section 2 and presents the tank-specific results. The models are developed and inputs selected to ensure that results overstate, rather than understate, the probability of a flammable tank headspace.

### 4.1 Gas Release Model Description

A simple model was developed to estimate flammable gas release rates during the modified sluicing retrieval operations. The model is based on the following assumptions:

1. Water applied to the waste instantaneously dissolves its capacity of salt (i.e., the water is instantaneously saturated).
2. The maximum sustainable saltcake erosion rate is that which results in the production of a slurry with 30 wt% solids in saturated brine.
3. The waste below the interstitial liquid level has a uniform retained gas void fraction, and essentially no retained gas exists above the interstitial liquid level.
4. Water is applied to the waste above and below the interstitial liquid level in proportion to the volumes of these two waste regions.
5. Gas releases due to interstitial liquid drainage (Section 3.1) are negligible compared with the gas releases due to waste erosion and dissolution. A rigorous accounting for gas releases associated with drainage would result in a corresponding decrease in gas releases due to erosion and dissolution, and its effect on the results would not be significant compared with the uncertainty inherent in the calculations.
6. The waste porosity (liquid volume fraction + gas volume fraction) is a nominal 0.50 throughout the waste in each tank.

The derivation of an expression for the gas release rate is presented in Appendix B, and only the result is presented here. Given the assumptions listed above, the volume of retained gas released per volume of water applied can be expressed as

$$Q_{GAS} = \frac{V_G V_B}{V_T} \left( \frac{P_W}{P_{HS}} \right) \left( \frac{T_{HS}}{T_W} \right) Q_{H2O} \quad (4.1)$$

where  $V_G$  is the total retained gas volume in the waste,  $V_B$  is the volume of bulk waste disturbed per volume of water applied,  $V_T$  is the total waste volume, and  $Q_{H2O}$  is the volumetric water application rate. Note that  $Q_{GAS}$  in Eq. (4.1) has been adjusted to headspace pressure,  $P_{HS}$ , and

headspace temperature,  $T_{HS}$ . The volume of bulk waste disturbed per volume of water applied,  $V_B$ , is given by

$$V_B = \frac{M_{DS} + F}{M_S - F(M_S + M_{IL})} \quad (4.2)$$

where  $M_{DS}$  is the mass of dissolved solids per volume of water applied,  $F$  is the specified mass fraction of undissolved solids in the product stream (e.g., 0.3 for a 30 wt% solids loading),  $M_S$  is the mass of solids per bulk waste volume, and  $M_{IL}$  is the mass of interstitial liquid per bulk waste volume. The quantities  $M_{DS}$ ,  $M_S$ , and  $M_{IL}$  can be calculated from waste properties and dissolution parameters via the following expressions:

$$M_{DS} = \beta_{LC} \rho_{BR} - 1 \quad (4.3)$$

$$M_S = \frac{\rho_S V_S}{V_T} \quad (4.4)$$

$$M_{IL} = \frac{\rho_{IL} V_{IL}}{V_T} \quad (4.5)$$

where  $\beta_{LC}$  is the volume of brine created by dissolution per volume of water added;  $\rho_{BR}$ ,  $\rho_S$ , and  $\rho_{IL}$  are the saturated brine, bulk solid, and interstitial liquid densities, respectively; and  $V_S$  is the total volume of dry void-free solids in the tank.

Note that the only parameters in Eq. (4.1) through (4.5) that depend on the dissolution properties of the waste are  $\beta_{LC}$  (the volume of brine created by dissolution per volume of water added) and  $\rho_{BR}$  (the saturated brine density).

## 4.2 Gas Release Model Inputs and Results

The retained gas release rates for each tank of interest can be estimated using Eq. (4.1) through (4.5) with suitable waste properties and dissolution parameters. Total waste volume,  $V_T$ , and retained gas inventory,  $V_G$ , for each tank are given in Tables 2.5 and 2.2, respectively. Interstitial liquid densities for each tank are given in Table 2.2.<sup>(a)</sup> The volumes of (dry, void-free) solid waste,  $V_S$ , and interstitial liquid,  $V_{IL}$ , are not well established for any of the tanks, but are related to  $V_T$  and  $V_G$  using the waste porosity,  $\phi$ , by the following expressions:

$$V_S = (1 - \phi)V_T \quad (4.6)$$

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(a) Specific gravity ( $SpG$ ) values given in Table 2.2 are equal to density in units of kg/L.



$$V_{IL} = \phi V_{w<ILL} - V_G \quad (4.7)$$

As specified in Section 4.1, the porosity of saltcake waste was assumed to have a nominal value of 0.5.

To calculate gas release rates for each tank of interest, values must be established for the waste physical property  $\rho_S$  (solids density) and the two waste dissolution properties  $\beta_{LC}$  (the volume of brine created by dissolution per volume of water added) and  $\rho_{BR}$  (the saturated brine density). For establishing retrieval safety guidelines, it is assumed that these parameters are approximately the same for the tanks of interest here, and the values are those established for Tank S-112 by Barton et al. (2003). Table 4.1 lists the parameter values and their sources. This should be reasonably conservative for calculating gas release rates for the following reasons:

- Among tank composite waste samples that have been tested, those from S-112 were found to be the most highly soluble in water (Herting and Edmonson 1998; Herting 1999, 2000, 2001, 2002). This equates to a relatively high value for  $\beta_{LC}$  and a correspondingly high value for the gas release rate,  $Q_{RG}$ .
- The high solubility of S-112 waste is directly associated with its high  $\text{NaNO}_3$  and low sludge contents (Barton et al. 2003). These characteristics result in a relatively low average solids density,  $\rho_S$ , a high average brine density,  $\rho_{BR}$ , and a correspondingly high value for the gas release rate,  $Q_{RG}$ .

Retained gas release rates calculated with Eq. (4.1) through (4.7) and values from Tables 2.3, 4.1, and 4.2 for the nominal 80-gpm water application rate are listed in Table 4.2. Also given in Table 4.2 is the flammable gas release rate,  $Q_{FG}$ , calculated by multiplying the retained gas release rate by the fraction of flammable gas in the retained gas of each tank given in Table 2.5.

The model developed for gas release rates can be extended to estimate the increase in headspace flammability as a function of the flammable gas release rate, the flammability of the released gases (i.e., the LFL of the retained gas mixture), and the headspace volume. The change in headspace flammability, expressed as a percent of the LFL of the tank headspace, is given by the expression

$$\text{Rate of change in headspace flammability} = \frac{Q_{FG}}{V_{HS} LFL_{MIX}} \times 100\% \quad (4.8)$$

**Table 4.1.** Tank S-112 Waste Dissolution Parameters

| Parameter   | Symbol       | Value | Source                          |
|---|--------------|-------|---------------------------------|
| Density of dry (void-free) solids (kg/L)            | $\rho_S$     | 2.25  | Barton et al. (2003), Table B-2 |
| Volume of brine created per volume of water applied | $\beta_{LC}$ | 1.334 | Barton et al. (2003) Table B-3  |
| Density of brine created (kg/L)                     | $\rho_{BR}$  | 1.44  | Barton et al. (2003) Table B-2  |

**Table 4.2.** Gas Release Rates by Tank for 80 gpm Water Application Rate

| Tank  | Retained Gas Release Rate, $Q_{GAS}$ (ft <sup>3</sup> /min) | Flammable Gas Release Rate, $Q_{FG}$ (ft <sup>3</sup> /min) | Rate of Change in % of LFL in Headspace (% of LFL/hr) |
|-------|---|---|---|
| S-101 | 6.4   | 3.0   | 4.9   |
| S-102 | 7.5   | 2.6   | 4.7   |
| S-103 | 6.2   | 2.9   | 3.8   |
| S-104 | 2.7   | 1.2   | 1.7   |
| S-105 | 1.6   | 0.7   | 1.2   |
| S-106 | 1.3   | 0.9   | 1.6   |
| S-108 | 1.4   | 0.6   | 1.4   |
| S-109 | 1.5   | 0.7   | 1.4   |
| S-110 | 5.5   | 2.5   | 4.1   |
| S-112 | 3.0   | 1.4   | 3.4   |
| U-107 | 4.5   | 2.1   | 4.1   |

where  $V_{HS}$  is the headspace volume (see Table 2.5). The calculated rate of change in headspace flammability for each tank is given in the last column of Table 4.2. Note that these values are based on the current headspace volume estimates and should decrease as waste is removed and the headspace volume increases. Note also that the results given in Table 4.2 take no credit for ventilation of the headspace, and in this respect represent the worst-case scenario results.

### 4.3 Model Extended for Ventilation of Headspaces

The model given by Eq. (4.1) through (4.8) allows the estimation of the retained gas release rates and potential increases in headspace flammability during the modified sluicing retrieval of saltcake wastes. It is adequate and appropriate, with allowance for the specified assumptions, for calculating the increase in headspace flammability when it can be assumed that both ventilation and changes in the headspace volume are negligible. To examine the effects of ventilation on the headspace flammability, the gas release rate model has been combined with a simple model for tank headspace gas concentrations.

The headspace concentration of a gas is relatively easily modeled if it can be assumed that the gas is well mixed within the headspace. This is generally a good assumption in passively ventilated tank headspaces, because thermally induced convection currents mix the headspace.<sup>(a)</sup> Stronger mixing is expected in actively ventilated tanks because thermal convection currents are augmented by convection due to the flow of air into and out of the headspace. It is therefore assumed that retained gases released into the headspace are instantaneously mixed within the

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(a) The waste surface is generally warmer than the tank walls and dome because radioactive decay within the waste produces heat that must be carried away. Headspace air warmed by contact with the waste surface becomes buoyant and rises, then, cooled by contact with the tank dome and walls, cools and sinks. Huckaby et al. (1997) examined mixing in a passively ventilated SST and found an injected gas essentially completely mixed within about an hour.

headspace. The equations describing the headspace concentration of a gas under this assumption are developed in Appendix C. The general equation for the gas concentration,  $C_H$ , at time  $t_2$  is

$$C_H(t_2) = \frac{Q_{GAS} \chi_H}{Q_A} + \left( C_H(t_1) - \frac{Q_{GAS} \chi_H}{Q_A} \right) \left( \frac{V_{HS0} - Q_B t_2}{V_{HS0} - Q_B t_1} \right)^{\frac{Q_A}{Q_B}} \quad (4.9)$$

where  $\chi_H$  is the volume fraction of the gas in the retained gas,  $V_{HS0}$  is the headspace volume at time zero, and  $C_H(t_1)$  is the concentration of the gas at time  $t_1$ . The quantities  $Q_A$  and  $Q_B$  are defined to be

$$Q_A = Q_{VOUT} - Q_{WIN} + Q_{BOUT} + Q_{GAS} \frac{P_{HS}}{P_W} \quad (4.10)$$

$$Q_B = Q_{WIN} - Q_{BOUT} - Q_{GAS} \frac{P_{HS}}{P_W} \quad (4.11)$$

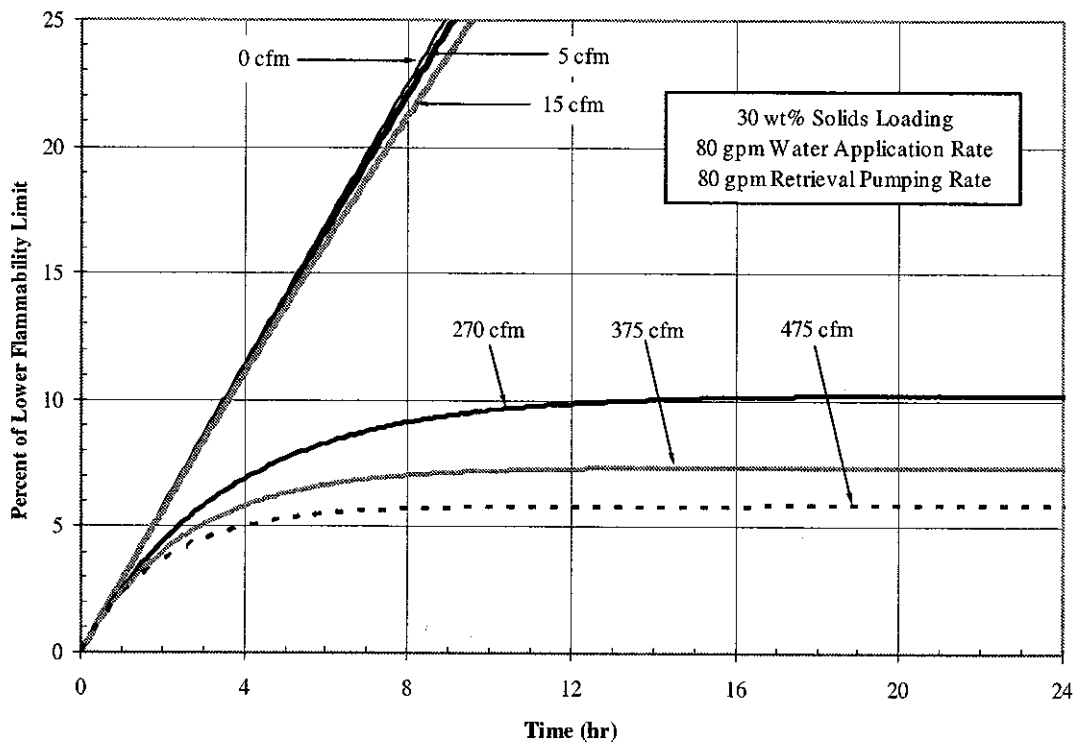
where  $Q_{VOUT}$  is the volumetric flow of air out via the ventilation system (i.e., the exhaust rate),  $Q_{BOUT}$  is the volumetric flow of waste out via the retrieval pump, and  $Q_{WIN}$  is the volumetric flow of water into the tank (i.e., the dissolution/erosion water).

#### 4.4 Model Results for Ventilated Headspaces

The model consisting of Eq. (4.1) through (4.11) was applied to examine headspace concentrations of the flammable gas portion of the retained gas as a function of time. Figure 4.1 illustrates the results for Tank S-112 for various ventilation rates. In this figure the nominal water application and retrieval pump rates are both 80 gpm, and the saturated brine leaving the point of water jet impact is assumed to have a 30 wt% solids loading. Low ventilation rates, such as occur when the headspace is passively ventilated, are shown in Figure 4.1 to have only a small effect on the rise of headspace flammability. The lower three ventilation rates correspond to nil, expected, and high passive ventilation rates,<sup>(a)</sup> and the three higher ventilation rates correspond to the low, expected, and high rates of a typical portable exhauster to be installed on

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(a) Passive ventilation rates vary with time and can vary significantly among tanks. Higher rates are typically associated with better/larger connections with adjacent tanks and the atmosphere (Huckaby et al. 1998). To maximize passive ventilation during S-112 retrieval, the process control plan specifies that two filtered ventilation pathways be open between the headspace and atmosphere when the portable exhauster is not running (Barton et al. 2003). The nominal value of 5 cfm is consistent with other safety analyses (Hu and Barker 2002) and agrees well with the 4.5 cfm value calculated from headspace hydrogen monitoring data by Mahoney (see footnote b on p.1.4). The average passive ventilation rate during retrieval will probably be significantly higher due to the second filtered pathway.

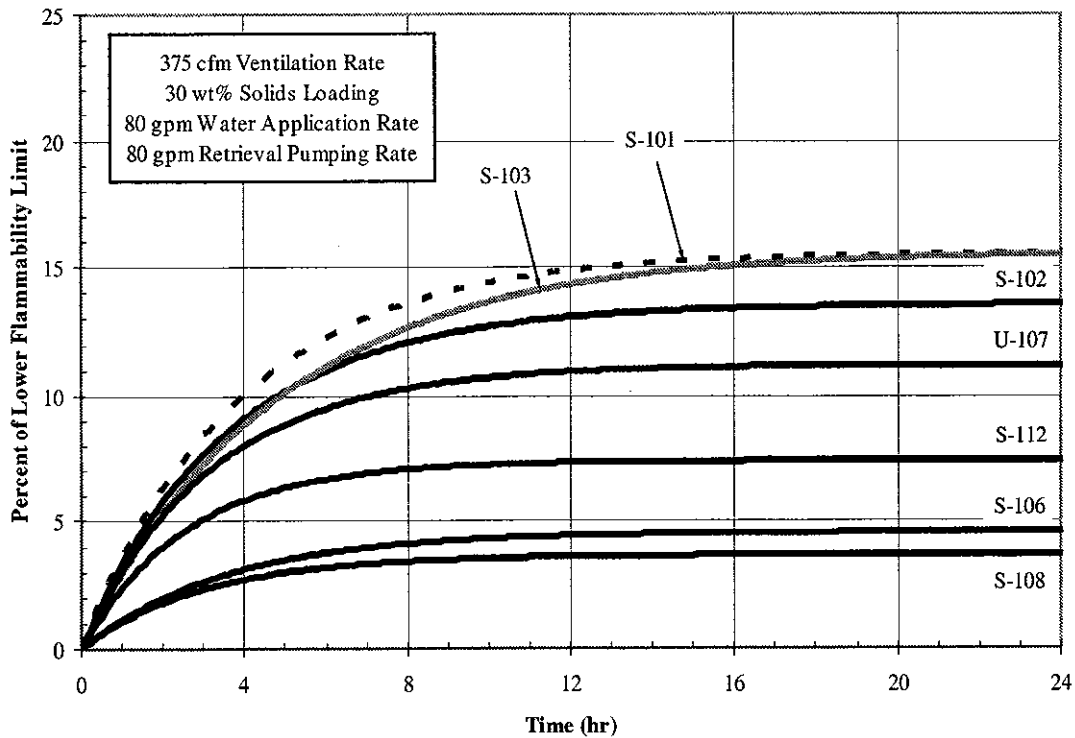


**Figure 4.1.** Tank S-112 Headspace Flammability as Function of Time for Various Ventilation Rates

the tanks.<sup>(a)</sup> The initial slope of each curve is the same (3.4% of LFL/hr) (see Table 4.2), but then the curves deviate from this, with higher ventilation rates causing the most dramatic deviations. The headspace flammability values at the three highest ventilation rates have essentially reached a pseudo-steady state after 14 hours. At its nominal rate of 375 cfm, the headspace hydrogen concentration reaches a pseudo-steady state value of approximately 7.4% of the LFL.

Plots of headspace flammability as a function of time for the other tanks are very similar in appearance to that for Tank S-112 in Figure 4.1. Figure 4.2 presents results for six tanks in addition to S-112, assuming the nominal ventilation rate of 375 cfm. The tanks selected include the one with the highest pseudo-steady state headspace flammability, Tank S-103, and the one with the lowest steady-state headspace flammability, Tank S-108. Note that the tanks with smaller headspaces (e.g., S-112) approach their pseudo-steady state conditions more quickly than tanks with larger headspaces (e.g., S-103).

(a) Terry Kaiser, March 2003, personal communication.



**Figure 4.2.** Headspace Flammability as a Function of Time for Several Tanks Given a Ventilation Rate of 375 cfm

## 4.5 Gas Releases during Process Shutdowns

The model described in the preceding sections was developed to obtain reasonably conservative estimates of the flammable retained gas release rates in the tanks of interest. It supposes very aggressive waste retrieval rates (e.g., instantaneous saturation of applied water plus erosion leading to 30 wt% solids loading) and assumes all retained gases in the affected waste are released. Gas release rates are consequently tied to the application of water, and it is tacitly assumed that if the application of water were stopped, gas releases would also stop. However, some continued release of retained gases is inevitable and must be considered as a potential safety hazard.

It is assumed that the worst-case condition is one in which both the retrieval pump and the ventilation system are unavoidably shut down. It is also assumed that, upon loss of the retrieval pump, all water application can be stopped manually within a relatively short time and that gas releases during that short time are negligible. Once water application has been stopped, two phenomena can cause the continued release of retained gases. First, if the liquid level in the central pool is lower than the interstitial liquid level, drainage of interstitial liquid will release gases from the surrounding saltcake. Second, if a large quantity of water has been added to the

tank just before the process shutdown, this water would eventually dissolve saltcake and release any retained gases it contained. These two scenarios are considered separately below.

#### 4.5.1 Liquid Drainage after Process Shutdown

Consider the scenario of a partially-retrieved waste tank having an open central pit as depicted in Figure 1.1. With the water application and retrieval pumps shut down, the drainage of interstitial liquid from the surrounding ring of saltcake will release retained gases in the drained waste and gradually fill the central pit with liquid. Clearly, the greatest drainage and associated gas releases will occur if the central pit is initially empty. Drainage (and gas releases) stop when the interstitial liquid level has dropped to the same level as the surface of the central pool. The height of the interstitial liquid at that point is given by

$$h_{IL*} = \frac{h_{POOL0} + h_{IL}(\phi - \alpha)\left(\frac{R^2}{r^2} - 1\right)}{1 + (\phi - \alpha)\left(\frac{R^2}{r^2} - 1\right)} \quad (4.12)$$

where  $h_{POOL0}$  is the initial height of liquid in the central pool,  $h_{IL}$  is the initial height of interstitial liquid,  $R$  is the radius of the tank,  $r$  is the effective radius of the central pit (assumed to be approximately a cylinder), and  $\phi$  and  $\alpha$  are the waste porosity and retained gas void fraction, respectively. Lowering the interstitial liquid level to  $h_{IL*}$  will, as discussed in Section 3.1, release some of the gases trapped in the region between  $h_{IL}$  and  $h_{IL*}$  and reduce the hydrostatic pressure on the retained gases that remain below  $h_{IL*}$ . Conservatively assuming that all the interstitial liquid is drained (and all the retained gas is released) from the waste between  $h_{IL}$  and  $h_{IL*}$  and that the expansion of gases below  $h_{IL*}$  has resulted in a new retained gas inventory based on the original void fraction at the decreased hydrostatic pressure  $P_{W*}$ , the total volume of gas released by the drainage is given by

$$\Delta V_{GAS} = \alpha \left(1 - \frac{r^2}{R^2}\right) \left(\frac{T_{HS}}{P_{HS}}\right) \left\{ V_{W<ILL} \left(\frac{P_W}{T_W}\right) - \left[ V_{W<ILL} - \pi R^2 (h_{IL} - h_{IL*}) \right] \left(\frac{P_{W*}}{T_{W*}}\right) \right\} \quad (4.13)$$

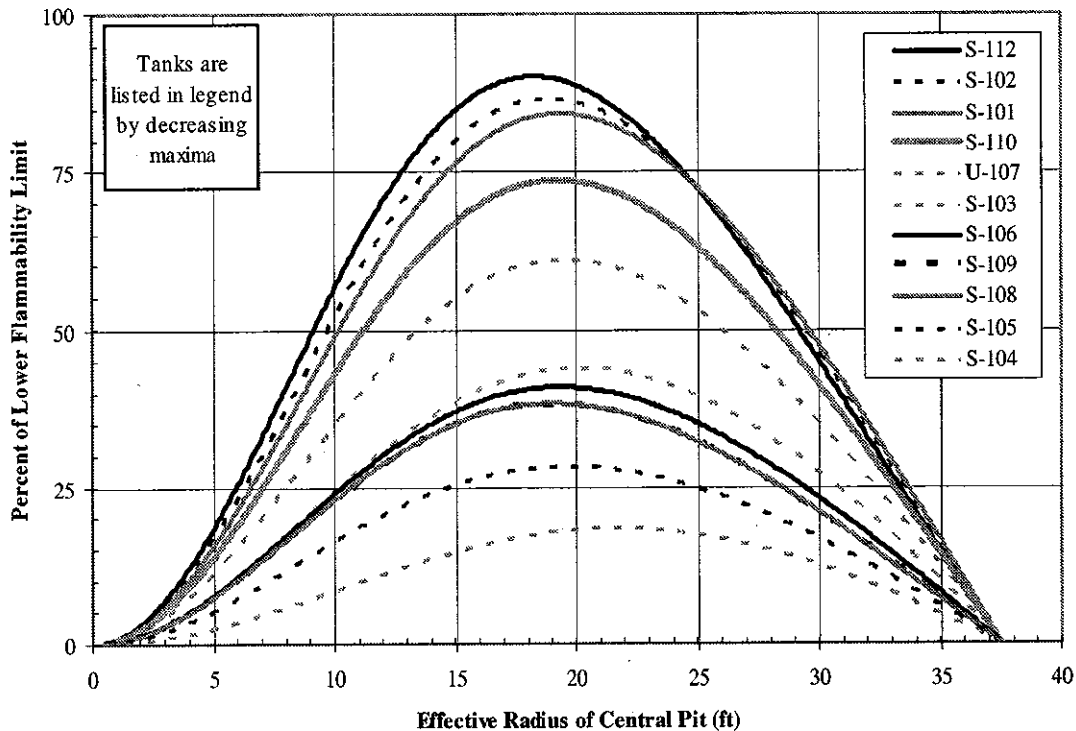
where  $T_{W*}$  is the average temperature of the retained gas after drainage. Appendix B provides the derivation of Eq. (4.12) and (4.13).

In terms of headspace flammability, the release of  $\Delta V_{GAS}$  retained gas will raise the headspace flammability by

$$\text{Change in headspace flammability} = \frac{\lambda \Delta V_{GAS}}{V_{HS*} LFL_{MIX}} \times 100\% \quad (4.14)$$

where  $\lambda$  is the fraction of retained gas that is flammable and  $V_{HS^*}$  is the new headspace volume. As indicated by these equations, the eventual height of the interstitial liquid,  $h_{IL^*}$ , the volume of retained gas released by drainage, and the change in headspace flammability are each functions of the central pit radius,  $r$ .

Eq. (4.14) was applied to estimate the potential change in headspace flammability due to drainage for each tank of interest. Tank headspace volumes,  $V_{HS^*}$ , were calculated for each tank by adjusting the initial headspace volume for the cylinder of air between the surface of the central pool and the initial waste surface, and  $T_{W^*}$  was assumed to be equal to  $T_W$ . Figure 4.3 plots the change in headspace flammability due to liquid drainage as a function of  $r$  for all 11 tanks. The tanks are listed in the legend of Figure 4.3 in order of decreasing curve maxima. For example, the solid curve with the greatest maximum is for Tank S-112, the dashed curve just below it is for Tank S-102, and the lowest curve is for Tank S-104. Results for Tanks S-108 and S-109 are almost identical and essentially trace a single curve in Figure 4.3.

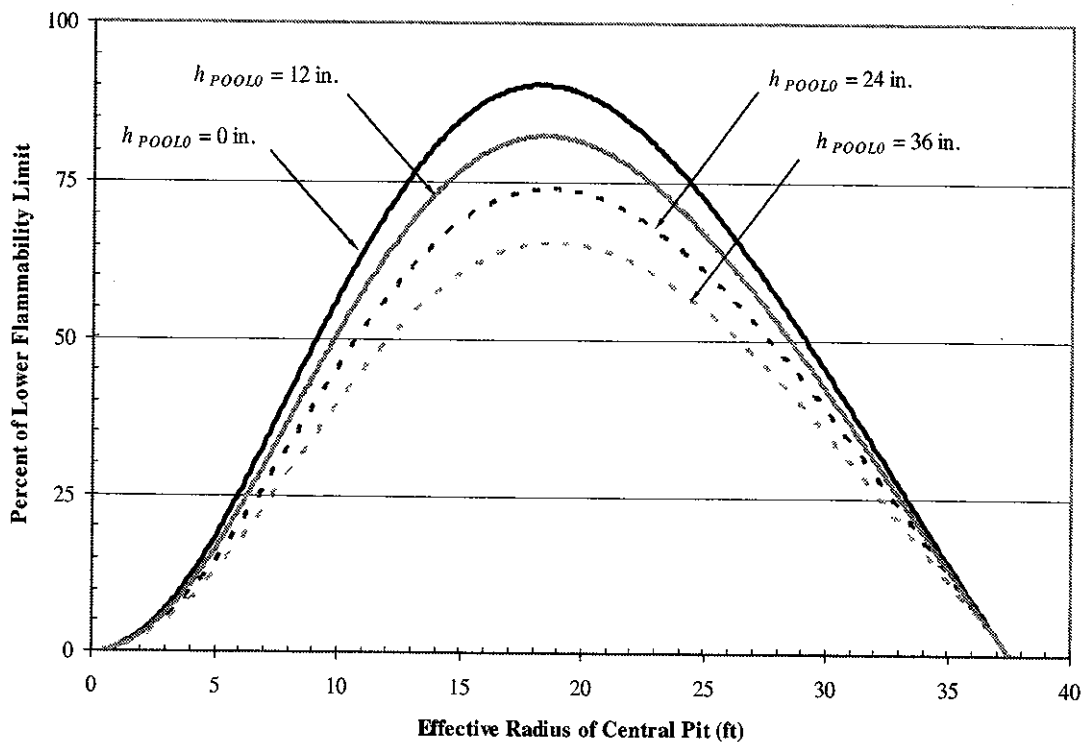


**Figure 4.3.** Change in Tank Headspace Flammability Due to Drainage of Interstitial Liquid as a Function of Effective Central Pool Radius. The initial central pool liquid height is zero in all cases.

The results depicted in Figure 4.3 suggest that if the retrieval process is being controlled to maintain the tank headspace at or below 25% of the LFL and the central pool was effectively drained when all headspace ventilation is lost, subsequent drainage of liquids in three of the

tanks (S-112, S-102, and S-101) could potentially release enough gas to raise the headspaces of these tanks above 100% of the LFL. However, note that the potential for a 75% of the LFL rise exists for only a limited range of the effective central pool radius. Drainage of interstitial liquid when the effective central pool radius is less than about 12.5 ft or more than about 25 ft could not cause a flammable headspace in any of the tanks considered.

One method to ensure the interstitial liquid drainage does not result in the headspace reaching a flammable condition would be to maintain a minimum liquid level in the central pool. This is illustrated in Figure 4.4, where the change in S-112 headspace flammability has been plotted for various values of the initial central pool surface height,  $h_{POOL0}$ . As indicated in the figure, maintaining the central pool depth at 24 in. would preclude a 75% of LFL rise (the rise from the operating limit of 25% of LFL to 100% of LFL). Similar calculations indicate Tanks S-102 and S-101 would require maintenance of liquid in the central pool at or above 30 and 20 in., respectively, to preclude a 75% of LFL rise.



**Figure 4.4.** Change in Tank S-112 Headspace Flammability Due to Drainage of Interstitial Liquid as a Function of Central Pool Effective Radius for Initial Central Pool Liquid Heights



## 4.5.2 Dissolution after Process Shutdown

To evaluate whether unsaturated liquids in the tank could dissolve enough waste to raise the headspace to a flammable condition, consider the hypothetical scenario in which a large volume of pure water is placed in the tank and then allowed to dissolve the gas-bearing waste. Assuming negligible ventilation and that dissolution continues until the water is saturated, the change in headspace flammability is given as

$$\text{Change in headspace flammability} = \frac{\beta_{BW} V_{H2O} \alpha}{LFL_{MIX} V_{HS}} \left( \frac{P_W}{P_{HS}} \right) \left( \frac{T_{HS}}{T_W} \right) \lambda \left( \frac{1}{1+\Gamma} \right) \times 100\% \quad (4.15)$$

where  $\beta_{BW}$  is the volume of bulk waste dissolved per volume of water,  $V_{H2O}$  is the volume of water present,  $\alpha$  is the retained gas void fraction,  $\lambda$  is the fraction of retained gas that is flammable, and  $\Gamma$  is the ratio of waste volume above the interstitial liquid level to waste volume below the interstitial liquid level. The derivation of Eq. (4.15) is given in Appendix B.

Note that the volume of bulk waste dissolved per volume of water,  $\beta_{BW}$ , is just equal to  $V_B$  [given by Eq. (4.2)] with  $F = 0$ . Using this relationship, the combination of Eq. (4.2), (4.2), and (4.4) gives

$$\beta_{BW} = \frac{V_T (\beta_{LC} \rho_{BR} - 1)}{\rho_S V_S} \quad (4.16)$$

The tank headspace volume for this scenario is calculated using the expression

$$V_{HS} = V_{TANK} - V_{W<ILL} (1 + \Gamma) - V_{H2O} \quad (4.17)$$

where  $V_{TANK}$  is the total volume of the (empty) tank. Because the headspace volume decreases as water is added in this scenario, even tanks that originally did not have enough retained flammable gas to reach the LFL in their headspaces (see Table 2.5) could present a hazard.

Eq. (4.15), (4.16), and (4.17) were used to calculate the volumes of water necessary to release, by dissolution of saltcake, flammable retained gases sufficient to raise the headspace of each tank by 75% of the LFL. As above, the dissolution parameters for Tank S-112 given in Table 4.1 were used for all tanks. In the first set of calculations it was assumed that each tank contained all of its original waste, both above and below the interstitial liquid. The inclusion of waste above the interstitial liquid level reduces the headspace volume but also reduces the amount of gas released per volume water added.<sup>(a)</sup> The calculated headspace and required water volumes for this case are listed in the second and third columns, respectively, of Table 4.3.

(a) See assumption 4 in Section 4.1.

**Table 4.3.** Water Volumes Potentially Resulting in a 75% of LFL Increase in Tank Headspace

| Tank  | Original Volume of Waste above Interstitial Liquid Level |                        | All Waste above Interstitial Liquid Level Removed |                        |
|-------|--|------------------------|---|------------------------|
|       | Calculated Headspace Volume (ft <sup>3</sup> )           | Volume of Water (kgal) | Calculated Headspace Volume (ft <sup>3</sup> )    | Volume of Water (kgal) |
| S-101 | 67,767   | 149                    | 71,026  | 147                    |
| S-102 | 61,056   | 154                    | 61,109  | 154                    |
| S-103 | 83,839   | 185                    | 85,602  | 181                    |
| S-104 | 58,295   | 326                    | 59,573  | 324                    |
| S-105 | 43,779   | 316                    | 95,034  | 213                    |
| S-106 | 44,454   | 262                    | 102,997   | 160                    |
| S-108 | 31,193   | 267                    | 92,410  | 211                    |
| S-109 | 33,481   | 267                    | 91,712  | 210                    |
| S-110 | 66,413   | 164                    | 75,030  | 158                    |
| S-112 | 36,863   | 160                    | 79,374  | 164                    |
| U-107 | 51,560   | 153                    | 64,596  | 139                    |

In the second set of calculations it was assumed that all the waste above the interstitial liquid level has been removed by some means, so that  $R = 0$ . This has the effect of increasing the amount of gas released per volume of water added, but also increases the headspace volumes. The calculated headspace and required water volumes for this case are listed in the fourth and fifth columns, respectively, of Table 4.3.

Currently, there are no plans to add large quantities of water to the waste tanks at the start of retrieval operations,<sup>(a)</sup> nor are there any identified mechanisms by which such large quantities of water could rapidly dissolve saltcake in the current waste configuration.<sup>(b)</sup> In the more realistic cases, where the liquid present in the tank is partially saturated or significant amounts of waste have been retrieved prior to the process shutdown, the volumes of liquid necessary to cause a dangerous rise in headspace flammability would be increased correspondingly.

(a) Smaller volumes of water, e.g., less than 20,000 gal, may be added initially to enlarge the central pit around the retrieval pump.

(b) Rapid addition of the water volumes given in Table 4.3 to their respective tanks would result in a liquid layer at the waste surface in each tank. The liquids would be expected to form a stable nonconvective layer with high-density, nearly saturated brine near the submerged solids and low-density, nearly pure water at the liquid surface. Under these conditions, dissolution would proceed only at the relatively slow rate of the diffusion of dissolved salts upward through the liquid.

## 5.0 Discussion

The results of the gas release analyses for the selected tanks show that under conservative assumptions the flammable gas headspace concentrations can rapidly approach the action level of 25% of the LFL when the tank is passively ventilated. Use of the portable exhauster is not necessary to maintain the headspace hydrogen concentration below this action level, but retrieval rates may be limited by the slow removal of flammable gases by passive ventilation. Use of the portable exhauster anywhere in the assumed operating range of 270 to 475 cfm would prevent the headspace from reaching the action level even if the water jets are very effective at eroding the saltcake (i.e., result in saturated brine with a 30 wt% solids loading).

Estimated gas release rates given in Table 4.2 and headspace flammability estimates depicted in Figures 4.1 and 4.2 are based on conservative assumptions and very likely exaggerate the potential to reach flammable conditions in the headspace. Specifically, gas void fractions used to estimate retained gas inventories are the 95<sup>th</sup> percentile values developed by Barker and Hedengren (2003), providing a 95% confidence that actual void fractions and corresponding flammable gas inventories are smaller than those used in calculations; and gas releases associated with water jets impinging on the waste (i.e., during active waste retrieval) are based on the assumptions that the water is instantaneously saturated and that erosion by the water jets results in a 30 wt% solids loading of the saturated brine produced.

Estimated gas release volumes and conditions leading to headspace flammability after a retrieval process shutdown are also based on conservative assumptions to ensure hazards are not underestimated. Estimated changes in the headspace flammability due to interstitial liquid drainage, depicted in Figures 4.3 and 4.4, are based on no ventilation of the headspace and complete drainage of the waste and release of all the retained gases from the region above the final interstitial liquid level (credit was not even taken for the capillary fringe). The potential for unsaturated brine in the tank to release gases was evaluated by assuming the liquid was completely unsaturated (i.e., pure water) and that no headspace ventilation occurred during the time required for the liquids to become 100% saturated. Given these assumptions, using the values in the third or last columns of Table 4.3 as maximum allowable volumes of free liquid is very conservative.

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## **Appendix A**

### **Monte Carlo Simulation Results**





## Appendix A

### Monte Carlo Simulation Results

Table A.1 presents the median and 95% confidence limit (CL) for hydrogen, ammonia, and methane gas concentrations and void fraction for the S-Farm tanks and for SST-241-U-107. These gas concentrations were taken from the computer result files for the appropriate tanks used in preparing the report *Methodology and Calculations for the Assignment of Waste Groups for the Large Underground Waste Storage Tanks at the Hanford Site* (Barker and Hedengren 2003). The results files were not included in the actual report due the size of the output (115 pages per tank for the 53 variables monitored)—and the analysis was performed for all 177 Hanford waste tanks. The electronic version of the files are available on CD from the authors of that report and are maintained by Nuclear Safety and Licensing under SafeSource.

**Table A.1. Retained Gas Monte Carlo Simulation Results**

| Tank  | Hydrogen<br>Median<br>(vol%) | Hydrogen<br>95%tile<br>(vol%) | Ammonia<br>Median<br>(vol%) | Ammonia<br>95%tile<br>(vol%) | Methane<br>Median<br>(vol%) | Methane<br>95%tile<br>(vol%) | Void<br>Fraction<br>Median | Void<br>Fraction<br>95%tile |
|-------|------------------------------|-------------------------------|-----------------------------|------------------------------|-----------------------------|------------------------------|----------------------------|-----------------------------|
| S-101 | 40.9                         | 70.0                          | 1.8                         | 10.8                         | 3.5                         | 16.6                         | 0.150                      | 0.248                       |
| S-102 | 33.5                         | 42.9                          | 1.0                         | 1.7                          | 0.6                         | 0.9                          | 0.153                      | 0.255                       |
| S-103 | 40.9                         | 68.8                          | 1.7                         | 10.5                         | 3.6                         | 16.9                         | 0.151                      | 0.254                       |
| S-104 | 40.9                         | 69.2                          | 1.8                         | 10.5                         | 3.6                         | 17.0                         | 0.011                      | 0.098                       |
| S-105 | 41.0                         | 69.5                          | 1.8                         | 10.9                         | 3.5                         | 16.0                         | 0.150                      | 0.254                       |
| S-106 | 63.3                         | 77.7                          | 0.5                         | 0.9                          | 0.9                         | 1.7                          | 0.153                      | 0.254                       |
| S-108 | 40.6                         | 69.2                          | 1.8                         | 10.6                         | 3.4                         | 16.7                         | 0.150                      | 0.251                       |
| S-109 | 40.8                         | 69.2                          | 1.7                         | 10.5                         | 3.6                         | 17.4                         | 0.151                      | 0.250                       |
| S-110 | 40.6                         | 69.3                          | 1.7                         | 10.6                         | 3.5                         | 17.4                         | 0.154                      | 0.255                       |
| S-112 | 41.0                         | 69.1                          | 1.7                         | 10.7                         | 3.7                         | 17.4                         | 0.152                      | 0.253                       |
| U-107 | 40.3                         | 69.4                          | 2.2                         | 12.2                         | 3.5                         | 17.0                         | 0.152                      | 0.252                       |

(a) All values are from Barker (2003).

### Reference

Barker SA and DC Hedengren. 2003. *Methodology and Calculations for the Assignment of Waste Groups for the Large Underground Waste Storage Tanks at the Hanford Site*. RPP-10006 Rev. 0, CH2M HILL Hanford Group, Inc., Richland, WA.



## **Appendix B**

### **Gas Release Rate Model Equations**



## Appendix B

### Gas Release Rate Model Equations

Sluicing is capable of mobilizing sediment by creating forces that exceed the strength of the material. The disruption of the sediment releases retained gas into the tank headspace. Gas release during sluicing is therefore a function of the amount of the sediment that is mobilized. The amount of waste material mobilized by a sluicing nozzle or jet is a function of the operational parameters of the jet and the waste characteristics. To bound the problem without modeling the exact physical phenomena, the waste mobilization must be limited by the ability of the product stream (sluicing liquid, solids dissolved into the sluicing liquid, interstitial liquid, and undissolved solids) to “carry” undissolved solids. This appendix presents the computation of the expected gas release as a function of the water added by sluicing based on the undissolved solids loading in the product stream.

Waste parameters that address specific waste dissolution characteristics for Tank S-112 are presented in Barton et al. (2003). These parameters include:

- $\beta_{LC}$ : Volume of brine created by dissolution per volume of water added
- $\beta_{BW}$ : Volume of bulk waste dissolved per volume of water added
- $\rho_{BR}$ : Density of brine created by dissolution
- $\rho_{IL}$ : Density of initial interstitial liquid
- $\rho_S$ : Density of dry solids (assumed the same for both soluble and insoluble)
- $w_{SS}$ : Mass fraction of soluble solids in bulk solids
- $V_T$ : Total waste volume

Parameters that further characterize the waste are:

- $\alpha$ : Volume fraction of gas in the bulk waste (Barker and Hedengren 2003)
- $h_{IL}$ : Interstitial liquid level (TWINS)<sup>(a)</sup>
- $\phi$ : Porosity of the waste (non-solid volume per total waste volume)

#### B.1 Gas Release Due to Dissolution and Erosion by Water Jet

The volume of (void-free) solids in the waste is given by

$$V_s = (1 - \phi)V_T \quad (\text{B.1})$$

The volume of interstitial liquid in the pore space is

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(a) TWINS: Tank Waste Information System database. <http://twins.pnl.gov/twins3/twins.htm>.

$$V_{IL} = V_T - V_G - V_A - V_S \quad (\text{B.2})$$

where  $V_A$  is the pore-space volume above the interstitial liquid level and  $V_G$  is the volume of gas retained in the saturated waste below the interstitial liquid level. The gas volume  $V_G$  is then

$$V_G = \alpha V_{W<ILL} \quad (\text{B.3})$$

where  $V_{W<ILL}$  is the volume of waste below the interstitial liquid level (computed from  $h_{IL}$ ). Assuming that there is no interstitial liquid above  $h_{IL}$ , the pore-space volume above the interstitial liquid level is

$$V_A = \phi(V_T - V_{W<ILL}). \quad (\text{B.4})$$

The mass of solids per bulk waste volume is

$$M_S = \frac{\rho_S V_S}{V_T} \quad (\text{B.5})$$

and the mass of interstitial liquid per bulk waste volume is

$$M_{IL} = \frac{\rho_{IL} V_{IL}}{V_T}. \quad (\text{B.6})$$

The mass of brine created by dissolution per volume of water added is

$$M_{BR} = \beta_{LC} \rho_{BR} \quad (\text{B.7})$$

and the mass of solids dissolved per volume of water added is therefore

$$M_{DS} = M_{BR} - 1. \quad (\text{B.8})$$

We use a factor  $F$  to assign the undissolved solids loading in the product stream or the mass of undissolved solids per total product stream mass. To determine the volume of bulk waste mobilized per volume of water added ( $V_B$ ) by sluicing to achieve  $F$ , consider that  $F$  is defined as

$$F = \frac{M_U}{M_U + M_{BR} + M_{IL} V_B} \quad (\text{B.9})$$

where  $M_U$ , the mass of undissolved solids in the product stream per volume of water added, is computed as

$$M_U = V_B M_S - M_{DS} \quad (\text{B.10})$$

Substituting Eq. (B.10) into Eq. (B.9) and solving for the volume of bulk waste mobilized per volume of water added yields

$$V_B = \frac{M_{DS} + F}{M_S - F(M_S + M_{IL})}. \quad (\text{B.11})$$

To account for disturbance of the nongaseous waste above the interstitial liquid level, it is assumed that the water is applied above and below the interstitial liquid level in proportion to the volumes of these two regions. The average gas volume per volume of waste is then simply the total gas volume,  $V_G$  (Eq. B.3), divided by the total waste volume,  $V_T$ . The volume of gas released adjusted to headspace temperature,  $T_{HS}$ , and pressure,  $P_{HS}$ , per volume of water added is computed from

$$V_{RG} = \frac{V_G V_B}{V_T} \left( \frac{P_W}{P_{HS}} \right) \left( \frac{T_{HS}}{T_W} \right). \quad (\text{B.12})$$

The average waste temperature is denoted by  $T_W$ , and the average pressure in units of inches of  $\text{H}_2\text{O}$  at which the retained gas is stored is given by

$$P_W = P_{HS} + \frac{1}{2} SpG h_{IL} \quad (\text{B.13})$$

where  $SpG$  is the specific gravity of the interstitial liquid. By multiplying Eq. (B.12) by the volumetric flow rate of water into the tank ( $Q_{H2O}$ ), we can compute the volumetric gas release rate as

$$Q_{GAS} = V_{RG} Q_{H2O}. \quad (\text{B.14})$$

## B.2 Gas Release Due to Interstitial Liquid Drainage During a Process Shutdown

During a shutdown of the retrieval process, drainage of interstitial liquid from the saltcake into the central pool will release retained gases. Consider the situation in which the central pit around the retrieval pump is approximately a cylinder of radius  $r$  and the height of liquid in the central pool is  $h_{POOL}$ . Liquid will drain out of the saltcake into the central pool until the new interstitial liquid level and the pool height are equal. The volume of liquid accumulated in the central pool must be equal to the amount of liquid drained from the saltcake:

$$\pi r^2 (h_{IL*} - h_{POOL0}) = \pi \theta (R^2 - r^2) (h_{IL} - h_{IL*}) \quad (B.15)$$

where  $h_{IL*}$  is the final height of the interstitial liquid,  $R$  is the radius of the tank, and  $\theta$  is the volume fraction of interstitial liquid given by

$$\theta = \phi - \alpha \quad (B.16)$$

Substituting (B.16) into (B.15) and rearranging gives

$$h_{IL*} = \frac{h_{POOL0} + (\phi - \alpha) \left( \frac{R^2}{r^2} - 1 \right)}{1 + (\phi - \alpha) \left( \frac{R^2}{r^2} - 1 \right)} \quad (B.17)$$

Gas releases associated with this change in interstitial liquid level are calculated by subtracting final retained gas inventory from the initial retained gas inventory. This addresses the reduction in pressure felt by the retained gas and the upward percolation of gas due to bubbles that have expanded as the hydrostatic head was decreased. The initial retained gas inventory (adjusted to the headspace temperature and pressure) is given by the expression

$$V_{GAS0} = \alpha V_{W<ILL} \left( 1 - \frac{r^2}{R^2} \right) \left( \frac{P_W}{P_{HS}} \right) \left( \frac{T_{HS}}{T_W} \right) \quad (B.18)$$

and the final retained gas inventory is given by

$$V_{GAS*} = \alpha V_{W<ILL*} \left( 1 - \frac{r^2}{R^2} \right) \left( \frac{P_{W*}}{P_{HS}} \right) \left( \frac{T_{HS}}{T_{W*}} \right) \quad (B.19)$$

where an asterisk (\*) has been used to denote the variable is evaluated at the final condition. In these expressions both  $V_{W<ILL}$  and  $V_{W<ILL*}$  refer to the total volume of the tank below the interstitial liquid level, initial and final, respectively. To avoid having to include the tank bottom geometry in the calculation of  $V_{W<ILL*}$ , we note that to a good approximation in the values of  $h_{IL*}$  of interest,

$$V_{W<ILL*} = V_{W<ILL} - \pi R^2 (h_{IL} - h_{IL*}) \quad (B.20)$$

The decrease in retained gas inventory must equal the gas released into the headspace, which is just the difference between Eq. (B.18) and (B.19):



$$\Delta V_{GAS} = \alpha \left( 1 - \frac{r^2}{R^2} \right) \left( \frac{T_{HS}}{P_{HS}} \right) \left\{ V_{W<ILL} \left( \frac{P_W}{T_W} \right) - \left[ V_{W<ILL} - \pi R^2 (h_{IL} - h_{IL}^*) \right] \left( \frac{P_{W^*}}{T_{W^*}} \right) \right\} \quad (B.21)$$

### B.3 Gas Release Due to Continued Dissolution of Saltcake During a Process Shutdown

The addition of water to a tank will cause retained gas releases to the extent that it dissolves gas-retaining waste. It is assumed here that water introduced or present in the tank when the retrieval process is shut down dissolves the wastes above and below the interstitial liquid level in proportion to the volumes of these waste regions. For example, if one third of the waste is above the interstitial liquid level and two thirds are below it, one third of the water will be used to dissolve the waste above the interstitial liquid level (a region that is assumed to contain no retained gas) and two thirds will be used to dissolve the waste below it. The fraction of water that is used to dissolve gas-retaining waste is

$$\frac{V_{W<ILL}}{V_T} = \frac{1}{1 + \Gamma} \quad (B.22)$$

where  $\Gamma$  is the ratio of waste volumes above and below the interstitial liquid level.

As defined above,  $\beta_{BW}$  is the volume of bulk waste dissolved per volume of water, so the volume of retained gas released by dissolution of gas-bearing waste (adjusted for headspace temperature and pressure) is given by

$$V_{RG} = \alpha \beta_{BW} V_{H2O} \left( \frac{1}{1 + \Gamma} \right) \left( \frac{P_W}{P_{HS}} \right) \left( \frac{T_{HS}}{T_W} \right) \quad (B.23)$$

where  $V_{H2O}$  is the volume of water available for dissolution. The change in headspace flammability, measured as a change in the percent of the lower flammability limit (LFL) of the mixture,  $LFL_{MIX}$ , is given by the expression

$$\frac{\beta_{BW} V_{H2O} \alpha}{LFL_{MIX} V_{HS}} \left( \frac{P_W}{P_{HS}} \right) \left( \frac{T_{HS}}{T_W} \right) \lambda \left( \frac{1}{1 + \Gamma} \right) \times 100\% \quad (B.24)$$

where  $\lambda$  is the fraction of flammable gases in the retained gas mixture.

## **B.4 References**

Barker SA and DC Hedengren. 2003. *Methodology and Calculations for the Assignment of Waste Groups for the Large Underground Waste Storage Tanks at the Hanford Site*. RPP-10006 Rev. 0, CH2M HILL Hanford Group, Inc., Richland, WA.

Barton WB, SA Hartley, JL Huckaby, LA Mahoney, CW Stewart, and BE Wells. 2003. *Process Control Plan for Saltcake Dissolution Retrieval Demonstration in Tank 241-S-112*. RPP-15085 Rev. 0. CH2M HILL Hanford Group, Inc., Richland, WA

## **Appendix C**

### **Headspace Gas Concentration Model**

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## Appendix C

### Headspace Gas Concentration Model

Consider a tank containing variable volumes of waste and headspace with inflows and outflows as indicated in Figure C.1. The ventilation inflow,  $Q_{VIN}$ , and outflow,  $Q_{VOUT}$ , carry air into and the headspace atmosphere out of the tank headspace volume,  $V_{HS}$ , respectively. During dissolution, water is added to the waste volume,  $V_W$ , at a volumetric flow rate of  $Q_{WIN}$  and brine is pumped out at the rate  $Q_{BOUT}$ . Gas is released from the waste to the headspace at the volumetric rate  $Q_{GAS}$ , which is understood to be at temperature and pressure of the headspace. The headspace atmosphere and the liquid/gas/solid mixture in the waste volume are both assumed to be incompressible.

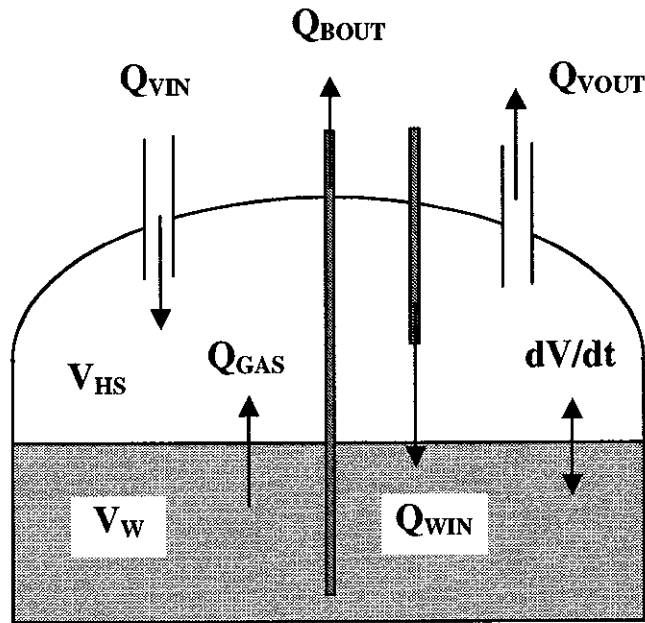


Figure C.1. Schematic of Tank Flow Paths

Let the volume of the tank be fixed but allow the headspace volume and waste volume to vary. The incompressible fluid assumption requires that

$$\frac{dV_{HS}}{dt} = -\frac{dV_W}{dt} \quad (C.1)$$

Continuity on the headspace volume can be expressed as

$$\frac{dV_{HS}}{dt} = Q_{VIN} - Q_{VOUT} + Q_{GAS} \quad (C.2)$$

Assuming the released gas leaves the waste with the pressure at which it was retained,  $P_{GAS}$ , that the volume change during dissolution is negligible, and that gas expansion in the waste due to decrease in hydrostatic pressure is minimal, continuity on the waste volume is written as

$$\frac{dV_W}{dt} = Q_{WIN} - Q_{BOUT} - \frac{P_0}{P_{GAS}} Q_{GAS} \quad (C.3)$$

Substituting Eq. (C.2) and (C.3) into Eq. (C.1) provides an expression for the ventilation outflow,  $Q_{OUT}$ , as a function of the other known inflows and outflows:

$$Q_{VOUT} = Q_{VIN} + Q_{GAS} \left( 1 - \frac{P_{HS}}{P_{GAS}} \right) + Q_{WIN} - Q_{BOUT} \quad (C.4)$$

The continuity equation for hydrogen in the headspace, assuming that the hydrogen concentration remains small, can be written as

$$\frac{d}{dt}(C_H V_{HS}) = Q_{GAS} \chi_H - Q_{VOUT} C_H \quad (C.5)$$

where  $C_H$  is the headspace hydrogen concentration (vol%) and  $\chi_H$  is the volume fraction of hydrogen in the waste gas. Expanding the derivative and substituting Eqs. (C.3) and (C.4) via Eq. (C.1) yields

$$V_{HS} \frac{dC_H}{dt} = Q_{GAS} \chi_H - C_H (Q_{VIN} + Q_{GAS}) \quad (C.6)$$

Note that, even though it appears outside the time derivative, the headspace volume is a function of time. Assuming that the water inflow, brine-pumping rate, the gas release rate and pressure are constant, Eq. (C.3) and (C.1) can be solved for the headspace volume as a function of time as follows:

$$V_{HS}(t) = V_{HS0} - \left( Q_{WIN} - Q_{BOUT} - Q_{GAS} \frac{P_{HS}}{P_{GAS}} \right) t \quad (C.7)$$

where  $V_{HS0}$  is the headspace volume at  $t = 0$ . To simplify further steps, define the following terms:

$$\begin{aligned}
Q_A &= Q_{VIN} + Q_{GAS} \\
Q_B &= Q_{WIN} - Q_{BOUT} - Q_{GAS} \frac{P_{HS}}{P_{GAS}}
\end{aligned}
\tag{C.8}$$

Now, substituting these definitions and Eq. (C.7) into Eq. (C.6) and rearranging yields the following ordinary differential equation:

$$\frac{1}{C_H - \frac{Q_{GAS}\chi_H}{Q_A}} \frac{dC_H}{dt} = - \frac{Q_A}{V_{HS0} - Q_B t}
\tag{C.9}$$

Eq. (C.9) can be integrated between  $t_1$  and  $t_2$  to give

$$C_H(t_2) = \frac{Q_{GAS}\chi_H}{Q_A} + \left( C_H(t_1) - \frac{Q_{GAS}\chi_H}{Q_A} \right) \left( \frac{V_{HS0} - Q_B t_2}{V_{HS0} - Q_B t_1} \right)^{\frac{Q_A}{Q_B}}
\tag{C.10}$$

and under the initial conditions that  $C_H = C_0$  at  $t = 0$  to yield

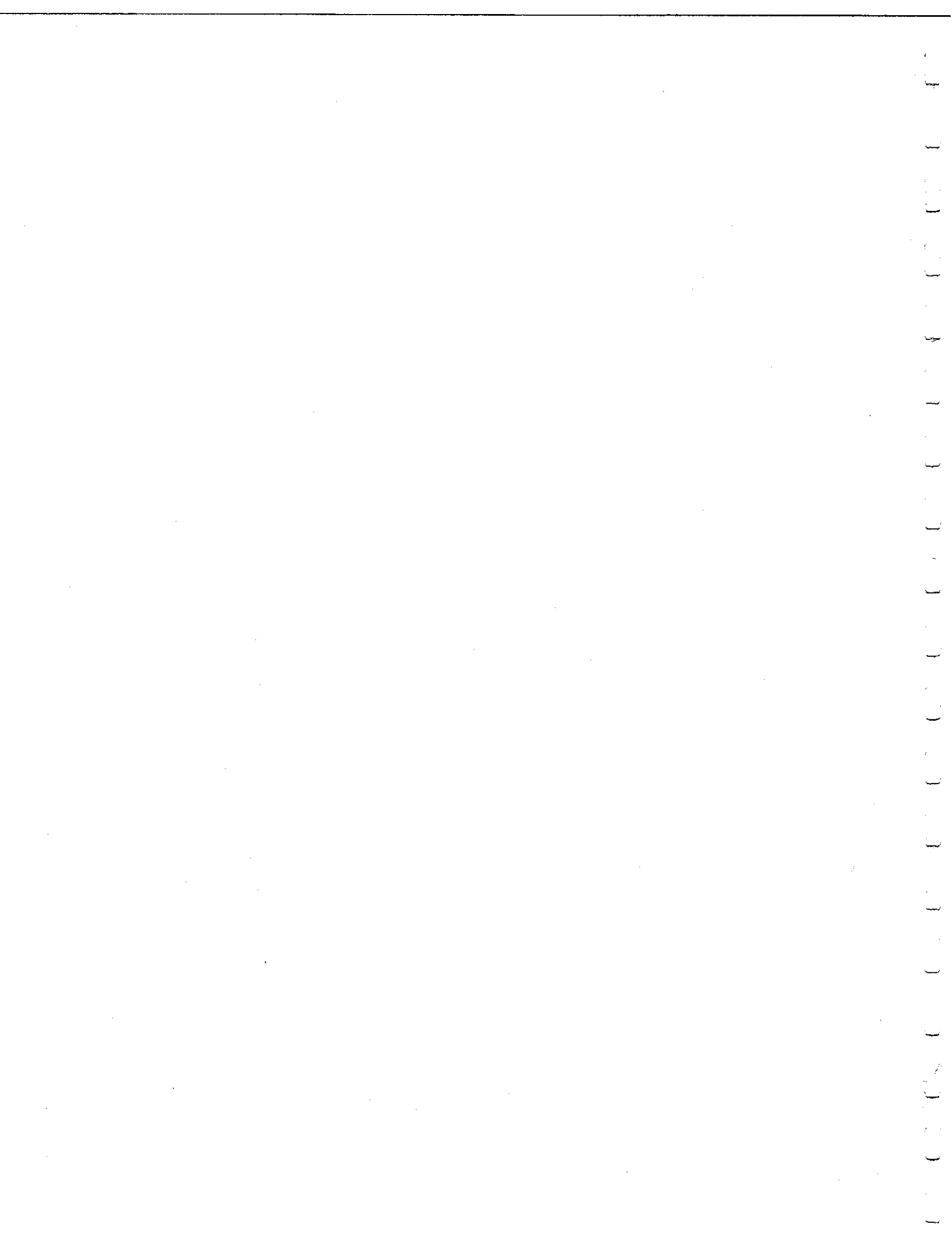
$$C_H(t) = \frac{Q_{GAS}\chi_H}{Q_A} + \left( C_0 - \frac{Q_{GAS}\chi_H}{Q_A} \right) \left( 1 - \frac{Q_B}{V_{HS0}} t \right)^{\frac{Q_A}{Q_B}}
\tag{C.11}$$

The time at which the hydrogen concentration reaches a specified value,  $C_H$ , is given by

$$t = \frac{V_{HS0}}{Q_B} \left[ 1 - \left( \frac{C_H - \frac{Q_{GAS}\chi_H}{Q_A}}{C_0 - \frac{Q_{GAS}\chi_H}{Q_A}} \right)^{\frac{Q_B}{Q_A}} \right]
\tag{C.12}$$

If the headspace volume is assumed constant, the solution to Eq. (C.9) for the hydrogen concentration as a function of time under the same initial conditions becomes

$$C_H(t) = C_0 e^{-\frac{Q_{VIN} t}{V_{HS}}} + \frac{Q_{GAS}\chi_H}{Q_A} \left( 1 - e^{-\frac{Q_{VIN} t}{V_{HS}}} \right)
\tag{C.13}$$





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