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Waste Tank Ventilation Rates Measured with a Tracer Gas Method

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Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

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Waste Tank Ventilation Rates Measured with a Tracer Gas Method

Fiscal Year 1998 Summary

J. L. Huckaby
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Pacific Northwest National Laboratory
Richland, Washington 99352

Summary

Passive ventilation with the atmosphere is used to prevent accumulation of waste gases and vapors in the headspaces of 132 of the 177 high-level radioactive waste Tanks at the Hanford Site in Southeastern Washington State. Measurements of the passive ventilation rates are needed for the resolution of two key safety issues associated with the rates of flammable gas production and accumulation and the rates at which organic salt-nitrate salt mixtures dry out.

Direct measurement of passive ventilation rates using mass flow meters is not feasible because ventilation occurs via multiple pathways to the atmosphere (i.e., via the filtered breather riser and unsealed tank risers and pits), as well as via underground connections to other tanks, junction boxes, and inactive ventilation systems. The tracer gas method discussed in this report provides a direct measurement of the rate at which gases are removed by ventilation and an indirect measurement of the ventilation rate. The tracer gas behaves as a surrogate of the waste-generated gases, but it is only diminished via ventilation, whereas the waste gases are continuously released by the waste and may be subject to depletion mechanisms other than ventilation.

The tracer gas method requires that a tracer gas be injected into the tank headspace and samples be collected periodically and analyzed to determine the tracer gas concentration as a function of time. If key assumptions about headspace mixing and tracer loss mechanisms are satisfied, the tracer gas concentration will decrease logarithmically with time, and the ventilation rate of the tank can be calculated from the headspace volume and the rate at which the tracer gas concentration decreases. Depending on the ventilation rate and the amount of tracer introduced, the tracer gas method can provide rate measurements for periods ranging from several days (if the ventilation rate is high) to several months (if the ventilation rate is low). The primary tracer gas used in this study was helium, because it is chemically and radiolytically inert and only sparingly soluble in waste liquids. Sulfur hexafluoride gas was also used as a tracer, but because there has been evidence that it may decompose in the radiation field of the tank headspaces, it was used only for qualitative assessment of intertank connections.

Tracer samples were routinely analyzed for both the helium tracer and hydrogen (a waste gas). Given concurrent ventilation rate measurements, the hydrogen measurements allow calculation of hydrogen release rates. Calculated average ventilation rates and hydrogen generation rates are listed in Table S.1 for the seven tanks studied. Tolerances given for the ventilation rates in Table S.1 define the 95% confidence limits calculated with a standard treatment of random errors. The ventilation rates listed in Table S.1 tend to reinforce the findings of previous tracer studies (e.g., Huckaby et al. 1997), which indicate passive ventilation rates for most tanks are in the 2- to 10-m^3/h range. The high ventilation rate observed for Tank C-104 is consistent with previous observations that the tank is actively ventilated via its cascade line connection to Tank C-105, a tank that is mechanically exhausted (Huckaby and Bratzel 1995).

The fiscal year 1998 tracer studies provide new evidence that significant exchange of air occurs between tanks via the underground cascade pipes. Most of the single-shell waste tanks are connected via 7.6-cm diameter cascade pipes to one or two adjacent tanks. Tracer gas studies of the Tank U-102/U-103 system indicated that the ventilation occurring via the cascade line could be a significant fraction of the total ventilation. In this two-tank cascade, air evidently flowed from Tank U-103 to Tank U-102 for a time and then was observed to flow from Tank U-102 to Tank U-103.

Table S.1 Calculated Average Ventilation and Hydrogen Release Rates for Tank TX-104

Tank	Time Period	Average Ventilation Rate		Hydrogen Release Rate
		ft^3/min	m^3/h	g/day
C-104	4/14/98 – 4/17/98	67 ± 4	114 ± 9	7.5
TX-104	1/14/98 – 2/12/98	3.5 ± 0.3	5.9 ± 0.5	0.17
U-102	1/9/98 – 3/24/98	2.1 ± 0.1	3.5 ± 0.2	3.7
U-103	11/18/97 – 1/8/98	2.3 ± 0.1	4.0 ± 0.2	5.1
U-106	1/9/98 – 3/24/98	1.3 ± 0.1	2.2 ± 0.1	2.2
U-111	1/9/98 – 3/24/98	1.9 ± 0.1	3.2 ± 0.2	2.4

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The authors gratefully acknowledge the support of numerous people who contributed to this research. Dale Wanner, Dan Green, Steve Carter, and Mike Sumsion of Lockheed Martin Hanford Company helped to plan, schedule, and accomplish the field work associated with this study. Jim Andersen of COGEMA managed field engineering of the project. Jeff Edwards and Diana Bellofatto of PNNL cleaned, shipped, and received SUMMA(a) canister samples; and Milt Goheen and his laboratory staff (also PNNL) performed the helium analyses by mass spectroscopy.

(a) SUMMA is a trademark of Molectrics Corporation.

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1.0 Introduction

Passive ventilation with the atmosphere prevents accumulation of waste gases and vapors in the headspaces of 132 of the 177 high-level radioactive waste tanks at the Hanford Site in Southeastern Washington State. Measurements of the passive ventilation rates are needed for the resolution of two key safety issues associated with the rates of flammable gas production and accumulation and the rates at which organic salt-nitrate salt mixtures dry out.

Direct measurement of passive ventilation rates using mass flow meters is not feasible because ventilation occurs via multiple pathways to the atmosphere (i.e., via the filtered breather riser and unsealed tank risers and pits), as well as through underground connections to other tanks, junction boxes, and inactive ventilation systems. Ventilation rates have been indirectly measured for a small number of flammable gas-generating tanks by monitoring the decrease in hydrogen concentration after a significant amount of trapped hydrogen was released by the waste (Wilkins et al. 1997; Sklarew and Huckaby 1998). Although this method provides credible results, it cannot be applied to tanks that do not trap and release significant amounts of hydrogen or tanks without hydrogen monitoring instrumentation. Numerical models have been developed and used to estimate passive ventilation rates;(a) however, such models depend heavily on estimates of physical parameters (e.g., an effective cross-section area of the ventilation pathways) that cannot be specified a priori. Simple models have also been suggested to bound the ventilation rate (Epstein et al. 1994; Cowley et al. 1997), but these do not agree with rates derived from hydrogen monitoring data (Huckaby and Sklarew 1997).

The tracer gas method discussed in this report provides a direct measurement of the rate at which gases are removed by ventilation and an indirect measurement of the ventilation rate. The tracer gas behaves as a surrogate of the waste-generated gases except that it is only diminished via ventilation, whereas the waste gases are continuously released by the waste and may be subject to depletion mechanisms other than ventilation.

The tracer method, as applied to the waste tanks, and the assumptions it is based on are described in Section 2.0. Section 3.0 describes tracer gas injection, sample collection, and analytical methods. The mathematical equations used to relate headspace tracer gas concentrations to ventilation rates and a simple treatment of error propagation are given in Section 4.0. Section 5.0 presents, by tank, the results of the tracer studies conducted in fiscal year 1998.

(a) Personal communications with Don Ogden, Numatec Hanford Corp., and Zen Antoniak, PNNL.

2.0 Method Description

The tracer gas method for measuring tank ventilation rates requires injecting a tracer gas into the tank headspace and collecting and analyzing samples from the headspace periodically to determine the tracer gas concentration as a function of time. If key assumptions are satisfied, the tracer gas concentration will decrease logarithmically with time, and the ventilation rate of the tank can be calculated from the headspace volume and the rate at which the tracer gas concentration decreases.

One key assumption in the method is that the only significant change in tracer gas concentration is loss through ventilation. The tracer gas must therefore be chemically and radiolytically inert and insoluble in the wastes. The validity of this assumption was investigated by Huckaby et al. (1997) for two tracer gases, helium (He) and sulfur hexafluoride (SF_6). They found that the SF_6 loss rate was higher than the He loss rate in several, but not all of the waste tanks and attributed the higher rate of SF_6 loss to radiolytic decomposition. In the current study, helium has been the primary tracer gas for quantitative vent rate measurements in each tank, and SF_6 has been employed only for qualitative assessment of inter-tank air exchange in Tanks C-104 and U-102.

A second key assumption in the method is that the tracer gas is essentially uniformly distributed within the tank headspace. If this assumption is valid, it is mathematically simple to describe the tracer gas concentration as a function of time. This condition is also required to ensure that representative samples can be collected using any available tank riser. Two aspects of this assumption are that the injected tracer gas be well mixed within the headspace before its baseline concentration is measured, and that fresh air brought into the headspace via the ventilation system be mixed within the headspace in a relatively short time period (i.e., the concentration of tracer in the air leaving the tank must be approximately the average concentration in the headspace). These aspects of mixing were considered by Huckaby et al. (1997), and found to be satisfied for the eight passively ventilated tanks they studied.

3.0 Sample Collection and Analysis

3.1 Tracer Gas Injection and Sampling

Tracer gases were released into the tank headspaces via tubing that extended through a tank riser to a location approximately halfway between the waste surface and the bottom of the riser. Helium was supplied directly from a commercial high-pressure gas cylinder. Helium volumes of 5.4 to 6 m^3 (190 to 200 ft^3 at atmospheric pressure) were injected, resulting in estimated initial concentrations of 1,100 to 4,100 parts per million by volume (ppmv). Tanks C-104 and U-102 also received about 1.3-L of SF_6 gas to investigate their connections with other tanks. The SF_6 was supplied by the laboratory in flow-through cylinders that were purged with the He being injected. After the tracer gas was introduced, the tank headspaces were allowed to stabilize for one day before baseline (time zero) samples were collected.

Headspace samples were collected in evacuated SUMMA™ passivated stainless steel canisters from the mid-elevation of the headspace via stainless steel or PFA Teflon tubing. The tubing was purged with headspace air using a combustible gas meter at a nominal flow rate of 500 mL/min for at least five minutes before collecting samples. Samples were collected in triplicate to examine sampling precision and provide spare samples if needed. Headspace samples collected before the tracer gas was injected were used to establish background levels of tracer gas in each tank headspace.

Samples were typically collected at one day and seven days after tracer gas injection to establish an approximate ventilation rate for each tank. If this initial ventilation rate was high, the sampling schedule was accelerated to complete sampling before the tracer gas concentrations dropped below measurable levels. If the ventilation rate of a tank was expected to be very high (as for Tanks AX-101 and C-104), the sampling schedule was accelerated to obtain daily samples. Actual sampling dates and times are listed in the appendix for the six tanks studied.

3.2 Helium and Hydrogen Analysis by Gas Chromatography

Helium and hydrogen were analyzed by a micro gas chromatograph (GC) equipped with an integral thermal conductivity detector (TCD) (P200H Micro GC from MTI Analytical Instruments, Inc.) as described in PNNL Technical Procedure PNNL-TVP-11 Rev. 1. The SUMMA™ canister samples were pressurized with ultra-high-purity nitrogen to exactly double the initial filling pressure and facilitate removal from the canister during analysis. Gas samples from the SUMMA™ canister were flowed through a sampling loop attached to the GC. The GC performed an automatic injection (50-millisecond injection time) of a very small aliquot of the gas from the sampling loop onto a 4-m long, 0.32-mm-diameter 5Å molecular sieve column. High-purity argon was used as the carrier gas; column pressure was 15 psig. The oven was held isothermal at 35°C for the one-minute analysis time. Under these conditions, helium and hydrogen eluted as well-separated peaks in the 11- to 17-second time range. A small correction for an unresolved neon component found in ambient air was included in all calculations.

Commercially prepared and certified mixtures of helium and hydrogen in nitrogen were used for daily calibration of the instrument. Nominal concentrations used were 2000, 1000, 500, 200, 50, 10, and 2 ppmv for both constituents. The instrument exhibited a very high degree of linearity for both components over that range. Sensitivity requirements were demonstrated daily through repeat analyses of the low-level standard (2 ppmv). Each daily calibration was also verified using an independently prepared standard at the 100-ppmv level. The method requirement of 10% agreement for the analysis of the independent standards was easily met in all cases. All samples were analyzed in duplicate. The precision of the method was typically found to be 1–3% in most cases. Overall accuracy requirements were set at 10%; however, most available data showed significantly better performance. The instrument detection limit was estimated to be 1 ppmv, based on the sensitivity of the integration algorithm, and the estimated quantitation limit was 2 ppmv based on the use of a lower-level standard.

Extensive data packages containing all raw and interpreted data were prepared, independently reviewed by the author of the analytical procedure, and finalized as part of the permanent project records. Data in electronic form were also included in the data packages.

3.3 Helium Analysis by Mass Spectroscopy

Two samples from Tank U-103 (collected on October 22, 1997) were analyzed for helium by a high sensitivity mass spectrometer (MS) equipped with both a Faraday cup detector (operated in the current mode and linear to 1 part in 100,000) and a secondary electron multiplier (SEM) that was used for ion counting. In this method, which was based on PNNL Procedure ALO 284 Rev. 1 and applicable to all ideal gases, all gas species were scanned, their relative amounts determined, and the results normalized.

The MS system used has a replicate precision of about 2% RSD for He. The helium concentrations measured in Tank U-103 and listed in Table A.3 of the appendix are estimated to be accurate to within ±5 ppmv of their true values. The instrument detection limit is typically less than 1 ppmv.

3.4 SF_6 Analysis by Gas Chromatography

SF_6 was analyzed by a GC with an electron capture detector (ECD) according to PNNL Technical Procedure SF6-97. SUMMA^{TM} canister samples were first pressurized with ultra-high-purity nitrogen to exactly double the initial filling pressure. A 2-mL gas sample loop was filled with a gas sample taken by syringe from the SUMMA^{TM} canister and injected onto a 2.4 m molecular sieve (HP5Å 45/60 mesh) GC column. A 15-m-long, 0.53-mm-diameter ID HP-5 (cross-linked 5% phenyl silicone) column was used to generate back pressure on the split-splitless injector. The argon-5% methane carrier gas flow rate was 22 mL/min. The oven temperature was held isothermal at 40°C for the eight-minute analysis. Column back pressure was held at 3.6 psig for the first four minutes and increased to 15 psig for the last four minutes of the run time to facilitate purging of the column. The ECD was held at 250°C.

Commercially purchased calibration standards with concentrations of SF_6 certified to 5% accuracy were used to calibrate the GC-ECD. Three calibration ranges were needed to minimize the effects of the nonlinear response of the ECD to this strongly electron-capturing compound (Farwell et al. 1981). The three calibration curves ranged from 0.030 to 1.0 ppbv (linear regression based on 3 points), 1 to 20 ppbv (quadratic fit based on 4 points), and 20 to 160 ppbv (cubic fit based on 5 points).

The GC-ECD system used for SF_6 had a relative standard deviation (RSD) of less than 8% for each of the three calibration ranges. The estimated instrument detection limit was 0.006 ppbv, and the estimated quantitation limit was 0.032 ppbv.

4.0 Calculation of Ventilation Rates

4.1 Ventilation Rate Calculations

The tracer gas concentration in a tank headspace follows a first-order rate equation if several assumptions about the physical situation are satisfied. The tracer gas must be inert and insoluble in the waste, so that its only depletion mechanism is ventilation. The tracer must also be absent from, or at a relatively low constant level in, the ambient air introduced to the headspace. Also, the tracer must be uniformly distributed in the headspace so its concentration in the exhausted air is approximately its average concentration in the headspace. Under these conditions, the decrease in tracer concentration with time is proportional to its concentration:

$$\frac{dC}{dt}=\frac{v}{V}C \tag{4.1}$$

where C is the concentration of the tracer, v is the volumetric ventilation rate, V is the headspace volume, and t is time. This equation can be solved for the ventilation rate, v, between any two sample events:

$$v=\frac{V}{(t_i-t_j)}\ln\left(\frac{C_j}{C_i}\right) \tag{4.2}$$

where C_i and C_j are the concentrations of the tracer gas at any two different times, t_i and t_j, respectively.

When concentration is plotted against time on a log-linear scale, the slope of the resulting line is proportional to the estimated ventilation rate. Figure 4.1 illustrates this with data from Tank U-111. Nonlinearity of more than two points may be caused by sampling and analytical measurement errors or by real differences in the average ventilation rate.

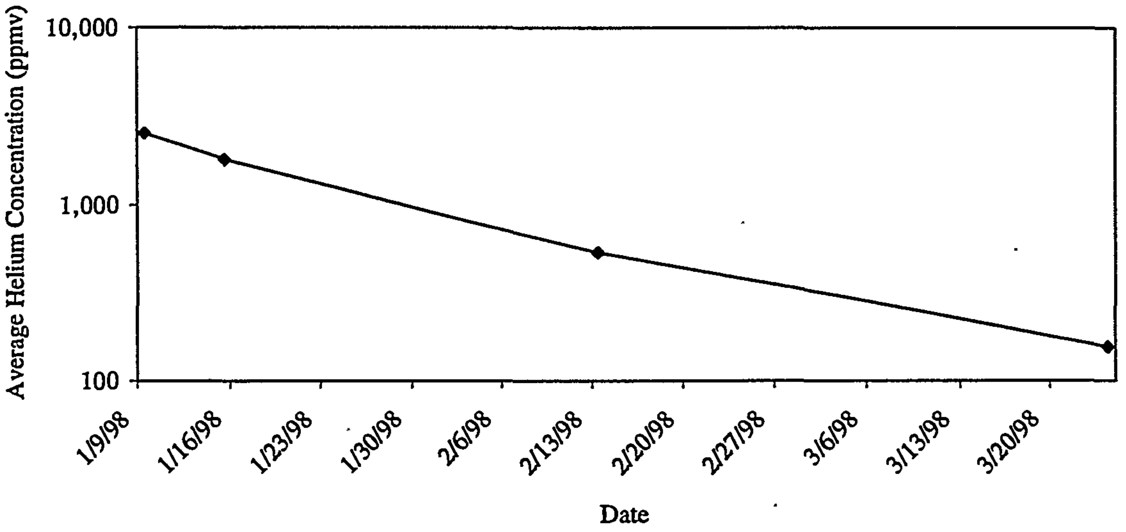

Figure 4.1. Logarithmic Plot of Helium Tracer Concentration in Tank U-111

4.2 Ventilation Rate Uncertainties

An analysis of uncertainties was performed to establish confidence limits on the calculated ventilation rates. The analysis assumes the average ventilation rate and each measured independent variable are normally distributed variables with means corresponding to their true values, and that their variances are associated with random errors. The variance of the ventilation rate, $\sigma^2(v)$, was related to the variances of headspace volume, $\sigma^2(V)$, measured tracer gas concentrations, $\sigma^2(C_i)$ and $\sigma^2(C_j)$, and sampling times, $\sigma^2(t_i)$ and $\sigma^2(t_j)$, using the following standard treatment of random error propagation:

$$\sigma^2(v)=\left(\frac{\partial v}{\partial V}\right)^2\sigma^2(V)+\left(\frac{\partial v}{\partial C_i}\right)^2\sigma^2(C_i)+\left(\frac{\partial v}{\partial C_j}\right)^2\sigma^2(C_j)+\left(\frac{\partial v}{\partial t_i}\right)^2\sigma^2(t_i)+\left(\frac{\partial v}{\partial t_j}\right)^2\sigma^2(t_j) \quad (4.3)$$

The partial differential terms in this equation are obtained by differentiating equation (4.2) and evaluating the expressions.

The variances of the independent variables were related to estimated measurement errors. Headspace volumes were assumed to be within 5% of their true values with 95% confidence. Because it was assumed to be normally distributed, it follows that

$$2\sigma(V)\approx 0.05V$$

or

$$\sigma^2(V)\approx 0.000625V^2 \quad (4.4)$$

Similarly, measured tracer concentrations were estimated to be within 5% of their true values with 95% confidence, so

$$\sigma^2(C_{i\,or\,j})\approx 0.000625\,C^2_{i\,or\,j} \quad (4.5)$$

Variance in the time measurements was assumed to be associated with the 17 minutes required to collect a set of three samples. Sample collection procedures required each evacuated SUMMA™ canister to be opened for five minutes (to allow the headspace and canister pressures to completely equalize), and about one minute was required to change canisters on the sampling manifold. It was then assumed that the average sample collection time used in calculations was correct to within 8.5 minutes with 95% confidence:

$$2\sigma(t\ )\approx 8.5\,\text{min} \quad (4.6)$$

or

$$\sigma^2(t)\approx 18.1\,\text{min}^2 \quad (4.7)$$

The independent variable variances are used in equation (4.3) to evaluate the variance of v. The upper and lower 95% confidence values for the vent rate estimate are then given by

$$v\pm 2\sigma(v) \quad (4.8)$$

Confidence limits are tabulated with results in Section 5.0.

4.3 Analysis of Multiple Tank Systems

Two of the tanks studied here, U-102 and U-103, are connected via an underground cascade line that allows air to move between the tanks. The cascade line between U-102 and U-103 is not unique to these tanks (most of the single-shell tanks are similarly connected to one or two adjacent tanks), but these are the only two so arranged that have been studied simultaneously with tracer gases. The tanks were originally the second and third tanks in a three-tank cascade, but the cascade line between Tank U-102 and the first tank (Tank U-101) has been cut and blanked.

The cascade line was observed, as will be discussed in Section 5.2, to play a significant role in the ventilation of both tanks, and in the interpretation of tracer gas data. Figure 4.2 depicts the connections and tracer-containing airflows of Tanks U-102 and U-103. The airflows indicated in Figure 4.2 are non-negative (either zero or positive), and for calculating average airflow rates, either v_3 or v_4 must be zero. Assuming the tracer is uniformly distributed (well-mixed) in each tank headspace, the concentrations of tracer in Tank U-102, C_{102}, and in Tank U-103, C_{103}, are described by the following coupled differential equations:

$$\frac{dC_{102}}{dt} = -\frac{v_1 + v_3}{V_{102}} C_{102} + \frac{v_4}{V_{102}} C_{103} \tag{4.9}$$

$$\frac{dC_{103}}{dt} = -\frac{v_2 + v_4}{V_{103}} C_{103} + \frac{v_3}{V_{103}} C_{102} \tag{4.10}$$

where the average volumetric flow rates v_i are as indicated in Figure 4.1, and V_{102} and V_{103} are the headspace volumes of Tanks U-102 and U-103, respectively. Solution of this equation system yields

$$C_{102} = C_{102}^0 \exp\left(-\frac{v_1 + v_3}{V_{102}} t\right) + C_{103}^0 \frac{\frac{v_4}{V_{102}}\left(\exp\left(-\frac{v_2 + v_4}{V_{103}} t\right) - \exp\left(-\frac{v_1 + v_3}{V_{102}} t\right)\right)}{\frac{v_1 + v_3}{V_{102}} - \frac{v_2 + v_4}{V_{103}}} \tag{4.11}$$

$$C_{103} = C_{103}^0 \exp\left(-\frac{v_1 + v_4}{V_{103}} t\right) + C_{102}^0 \frac{\frac{v_3}{V_{103}}\left(\exp\left(-\frac{v_1 + v_3}{V_{102}} t\right) - \exp\left(-\frac{v_2 + v_4}{V_{103}} t\right)\right)}{\frac{v_2 + v_4}{V_{103}} - \frac{v_1 + v_3}{V_{102}}} \tag{4.12}$$

where C_{102}^0 and C_{103}^0 are the concentrations of tracer in Tanks U-102 and U-103, respectively, at $t = 0$. Note that there are only two equations and three unknown flow rates. If there is air flow from Tank U-103 into U-102, then v_1, v_2, and v_4 are unknown (and v_3 is set to zero); and if there is air flow from Tank U-102 into U-103, then v_1, v_2, and v_3 are unknown (and v_4 is set to zero). The system is consequently indeterminate, and an additional constraint must be imposed to obtain a solution. Two constraints were considered, one that maximizes the ventilation rate of a given tank (either $v_1 + v_3 =$ maximum or $v_2 + v_4 =$ maximum), and one that minimizes the ventilation rate of a given tank (either $v_1 + v_3 =$ minimum or $v_2 + v_4 =$ minimum). The system of equations (4.11), (4.12) and a constraint were solved numerically using the Excel software package.

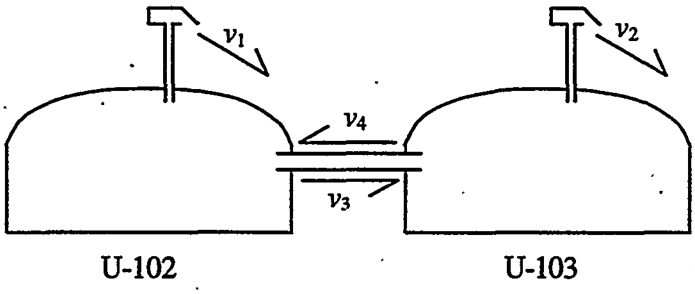

Figure 4.2. Schematic of Airflow in Tanks U-102 and U-103 Cascade

4.4 Hydrogen Release Rate

The rate at which hydrogen is released by the waste can be estimated from hydrogen concentrations measured in the tracer samples and calculated ventilation rates. This has been done using the following equation:

$$R_{ij} = v_{ij}\left(\frac{C_i + C_j}{2}\right) + \frac{V(C_j - C_i)}{\Delta t} \tag{4.13}$$

Where R_{ij} is the release rate and v_{ij} the calculated ventilation rate for the period between the ith and jth samplings, C_i and C_j are the concentrations of hydrogen associated with the ith and jth samplings, and Δt is the time between samplings. The hydrogen concentration, which is reported in ppmv, to a mass concentration, is converted using the ideal gas law and average headspace temperatures. Average headspace temperatures were calculated from readings of thermocouples in the headspaces.

5.0 Results and Discussion

5.1 Tank TX-104

Tank TX-104 is the fourth tank in a four-tank cascade. It is connected via a 7.6-cm (3-in.)-diameter, 7.6-m (25-ft)-long underground pipe to Tank TX-103. It has an estimated headspace volume of 3,735 m^3 (131,900 ft^3) that is allowed to breathe with the atmosphere via a high efficiency particulate air (HEPA) filter. No other open connections to other tanks or the atmosphere were identified.

Approximately 5.5 m^3 of helium was injected into the headspace of Tank TX-104 on January 13, 1998. Headspace samples were collected on January 14 and 22 and February 12, 1998. The tracer gas testing of this tank was halted because the HEPA filter was removed on February 11, 1998, and the associated riser sealed during waste sampling operations. Sample collection dates, times, and measured helium and hydrogen concentrations are listed in the appendix, Table A.1.

Table 5.1 lists the calculated average ventilation rate of Tank TX-104 for the two time periods studied and the overall average ventilation rate observed. Ventilation rate tolerances given in Table 5.1 represent the 95% confidence limits described in Section 4.2.

Table 5.1. Calculated Average Ventilation and Hydrogen Release Rates for Tank TX-104

Time Period	Average Ventilation Rate		Hydrogen Release Rate
	ft^3/min	m^3/h	g/day
1/14/98 – 1/22/98	3.5 ± 0.8	6.0 ± 1.4	0.19
1/22/98 – 2/12/98	3.5 ± 0.4	5.9 ± 0.6	0.17
1/14/98 – 2/12/98	3.5 ± 0.3	5.9 ± 0.5	0.17

Hydrogen concentrations measured in samples collected on January 13, 14, and 22 and February 12, 1998, averaged 17.0 ppmv. The standard deviation of all hydrogen analyses (24 analyses total of the 12 samples) was 1.2 ppmv. The consistency of headspace hydrogen concentrations measured on different dates supports the observed consistency in the ventilation rates for the two time periods studied. Table 5.1 lists the average hydrogen release rates calculated with equation (4.13) and an average headspace temperature of 18.1 °C.

5.2 Tanks U-102 and U-103

Tanks U-102 and U-103 are discussed together because each was found to affect the other's ventilation. The tanks are connected to each other via a 7.6-cm-diameter, 7.6-m-long underground cascade line, and each tank is vented to the atmosphere via a HEPA filter. As mentioned in Section 4.3, the tanks were originally the second and third tanks in a three-tank cascade, but the cascade line between Tank U-102 and the first tank (U-101) has been cut and blanked. No other open connections to other tanks or to the atmosphere were identified. Visual inspection of the pit covers and the above-ground portions of risers in January 1998 indicated no significant pathways for air leakage on either tank.

Tank U-103 received injections of tracer gases on February 26, July 14, and November 17, 1997. On February 26, 1997 both helium and SF_6 were injected to compare their performance as tracers. In Tank U-103 the two tracers indicated very similar ventilation rates, but because SF_6 was found to be problematic in certain other tanks, it was discontinued for rate measurements (Huckaby et al. 1997), and helium was the only tracer injected into Tank U-103 on July 14 and November 17, 1997. Tank U-102 received an injection of helium and approximately 1.3-L of SF_6 on January 8, 1998. SF_6 was added with the helium tracer in Tank U-102 to help determine whether or not air was moving from Tank U-102 to Tank U-103 via their cascade line.

Table 5.2 summarizes the average ventilation rates for Tank U-103 between February 27, 1997, and January 8, 1998. Ventilation rates for Tank U-103 between February 27 and July 15, 1997, are based on SF_6 measurements because a relatively small amount of helium was injected, and helium measurements were made for only about six weeks. The sampling dates and analytical results through September 1997 are given by Huckaby et al. (1997), and sampling dates and analytical results after October 1997 are listed in Table A.2. No ventilation rate was obtained for the October 22 through November 17 period because samples collected on November 17 were contaminated in the laboratory. Ventilation rate tolerances given for the last two periods represent the 95% confidence limits described in Section 4.2.

Table 5.2. Calculated Average Ventilation Rates for Tank U-103

Time Period	Tracer	Average Ventilation Rate		Hydrogen Release Rate
		ft^3/min	m^3/h	g/day
2/26/97 – 3/6/97	SF_6	2.9	4.9	--
3/697 – 3/31/97		2.4	4.0	--
3/31/97 – 4/9/97		3.1	5.2	--
4/997 – 5/28/97		1.5	2.6	--
5/28/97 – 7/15/97		1.3	2.2	--
7/15/97 – 7/22/97	He	2.1	3.5	--
7/2297 – 8/13/97		1.4	2.4	--
8/13/97 – 10/1/97		1.3	2.2	--
10/1/97 – 10/22/97		2.0	3.4	--
11/18/97 – 12/15/97		2.5 ± 0.2	4.3 ± 0.3	5.0
12/15/97 – 1/8/98		2.1 ± 0.1	3.6 ± 0.3	5.3

Results in Table 5.2 were obtained using equation (4.2), which assumes incoming ventilation air has a constant, known concentration of tracer. That assumption is valid if the incoming air comes directly from the atmosphere, but it may not be valid if the ventilation of the tank involves a second tank with a tracer gas concentration different from that in ambient air.

Evidence that Tanks U-102 and U-103 exchange air via their cascade line was obtained with the start of the tracer study of Tank U-102. Table 5.3 lists the average helium concentrations in samples from these two tanks for the January 8 through March 24, 1998, period. Note that the January 8, 1998, helium concentration in Tank U-102 was significantly higher than the 5-ppmv background level, despite the fact that helium had not previously been injected directly into this tank. This observation clearly indicates that air from Tank U-103 had flowed into Tank U-102 and that the cascade line between the two tanks is not plugged. Airflow in the other direction (from Tank U-102 to Tank U-103) was also indicated by the

Table 5.3. Helium Concentrations Measured in Tanks U-102 and U-103

Date	Average Helium Concentration (ppmv)	
	Tank U-102	Tank U-103
11/17/97 tracer injection	No tracer injected	5.8-m^3 of helium injected
1/8/98	195	119
1/8/98 tracer injection	5.7-m^3 of helium injected	No tracer injected
1/9/98	2,085	140
1/15/98	1,637	215
1/13/98	265	135
1/24/98	71	38

temporary rise in helium concentrations in Tank U-103after the January 8 injection of helium into U-102. Given that helium results clearly indicate airflows between the tanks, analysis of samples for SF_6 was deemed unnecessary.

Though the airflow between Tanks U-102 and U-103 can evidently change direction and may do so frequently, the tracer method, as applied to these tanks, provides only enough data for an examination of average flow rates and limiting cases. Equations (4.11) and (4.12) were used to estimate maximum and minimum ventilation rates for the Tank U-102/U-103 system, and results of the analysis are listed in Table 5.4. Values in this table for Tank U-102 prior to January 9, 1998 are based on the assumption that the helium concentration in the tank on November 18, 1997 was equal to that in the ambient air. The nominal flow rates listed at the bottom of Table 5.4 were calculated by taking the mean of the corresponding maximum and minimum flow rates. Though consistent with the data and useful as bounding estimates, the maximum and minimum ventilation rates listed in Table 5.4 generally require improbable conditions. For example, the maximum ventilation rate of Tank U-103 during the January 15–February 13, 1998, period would occur only if all the exhaust air from Tank U-102 went through the cascade line into Tank U-103.

Average ventilation rates and associated 95% confidence limit tolerances are listed for Tank U-102 in Table 5.5. Also given in this table are the estimated hydrogen release rates based on measured hydrogen concentrations and a headspace temperature of 21.8°C. The hydrogen concentration measured in Tank U-102 samples collected on January 8, 9, and 15, February 13, and March 24, 1998, averaged 511 ppmv and had a standard deviation (based on a total of 30 analyses of the 15 samples) of 65 ppmv. Analytical results for helium and hydrogen are listed by sample in Table A.3.

Table 5.4. Range of Average Ventilation Rates of Tanks U-102 and U-103

	U-102			U-103		
Dates	v_3 (out via cascade) m^3/h	v_1 (out via HEPA) m^3/h	$v_3 + v_1$ (total out) m^3/h	v_4 (out via cascade) m^3/h	v_2 (out via HEPA) m^3/h	$v_4 + v_2$ (total out) m^3/h
Total U-103 Flow Maximized						
11/18/97–12/15/97	0.0	0.4	0.4	3.9	0.4	4.3
12/15/97–1/8/98	0.0	0.4	0.4	3.2	0.4	3.6
1/9/98–1/15/98	3.0	0.0	3.0	24.7	0.0	24.7
1/15/98–2/13/98	4.8	0.0	4.8	13.4	0.0	13.4
2/13/98–3/24/98	2.7	0.0	2.7	7.5	0.0	7.5
Ave. 1/9/98–3/24/98			3.5			11.2
Total U-102 Flow Maximized						
11/18/97–12/15/97	0.0	6.0	6.0	0.7	3.6	4.3
12/15/97–1/8/98	0.0	6.0	6.0	0.0	3.6	3.6
1/9/98–1/15/98	0.5	2.5	3.0	0.5	0.0	0.5
1/15/98–2/13/98	0.2	4.6	4.8	1.8	0.0	1.8
2/13/98–3/24/98	0.0	2.7	2.7	2.1	0.0	2.1
Ave. 1/9/98–3/24/98			3.5			1.9
Total U-103 Flow Minimized						
11/18/97–12/15/97	0.0	0.4	0.4	3.9	0.4	4.3
12/15/97–1/8/98	0.0	0.4	0.4	3.2	0.4	3.6
1/9/98–1/15/98	0.5	2.6	3.0	0.5	0.0	0.5
1/15/98–2/13/98	0.0	5.0	5.0	1.0	0.0	1.0
2/13/98–3/24/98	0.0	2.7	2.7	2.1	0.0	2.1
Ave. 1/9/98–3/24/98			3.5			1.6
Total U-102 Flow Minimized						
11/18/97–12/15/97	0.0	0.4	0.4	3.9	0.4	4.3
12/15/97–1/8/98	0.0	0.4	0.4	3.2	0.4	3.6
1/9/98–1/15/98	0.5	2.6	3.0	0.5	0.0	0.5
1/15/98–2/13/98	4.8	0.0	4.8	13.4	0.0	13.4
2/13/98–3/24/98	0.5	2.2	2.7	3.1	0.0	3.1
Ave. 1/9/98–3/24/98			3.5			6.9
Nominal Flow						
11/18/97–12/15/97	0.0	3.2	3.2	2.3	2.0	4.3
12/15/97–1/8/98	0.0	3.2	3.2	1.6	2.0	3.6
1/9/98–1/15/98	1.7	1.3	3.0	12.6	0.0	12.6
1/15/98–2/13/98	2.4	2.5	4.9	7.6	0.0	7.6
2/13/98–3/24/98	1.3	1.3	2.7	4.8	0.0	4.8
Ave. 1/9/98–3/24/98			3.5			6.5

Table 5.5. Calculated Ventilation and Hydrogen Release Rates for Tank U-102

Time Period	Average Ventilation Rate		Hydrogen Release Rate
	ft^3/min	m^3/h	g/day
1/9/98–1/15/98	1.8 ± 0.5	3.0 ± 0.9	5.3
1/15/98–2/13/98	2.8 ± 0.2	4.8 ± 0.3	5.0
2/13/98–3/24/98	1.6 ± 0.1	2.7 ± 0.2	2.4
1/9/98–3/24/98	2.1 ± 0.1	3.5 ± 0.2	3.7

5.3 Tank U-106

Tank U-106 is the third tank of a three-tank cascade. It is connected via a 7.6-cm-diameter, 7.6-m-long underground pipe to Tank U-105, which is, in turn, connected via a similar pipe to Tank U-104. Each tank in the cascade is ventilated to the atmosphere through a HEPA filter. No other open connections to other tanks or the atmosphere were identified. Visual inspection of the pit covers and the above-ground portions of risers in January 1998 indicated no significant pathways for air leakage.

Approximately 5.4-m^3 (191-ft^3 at atmospheric pressure) of helium was injected into the headspace of Tank U-106 on January 8, 1998. Tracer samples were collected on January 9, and 15, February 13, and March 24, 1998. Sample collection dates, times, and measured helium and hydrogen concentrations are listed in Table A.4.

Table 5.6 lists the calculated average ventilation rate of Tank U-106 for the three time periods studied and the overall average ventilation rate observed. Ventilation rate tolerances given in Table 5.6 represent the 95% confidence limits described in Section 4.2.

Hydrogen concentrations measured in background samples collected on January 8, 1998 (prior to injection of helium into the tank) are inconsistent and much lower than found in subsequent headspace samples. These results are considered suspect, and were not used in calculating ventilation rates or hydrogen release rates. The hydrogen concentration measured in samples from January 9 and 15, February 13, and March 24, 1998, are very similar, averaging 444 ppmv and having a standard deviation (based on a total of 24 analyses of the 12 samples) of 31 ppmv. Estimated hydrogen release rates between sample collection times have been calculated, assuming a headspace temperature of 21.6°C, and are listed in Table 5.6. The average hydrogen release rate for the entire study is a weighted average of the individual periods.

Table 5.6. Calculated Average Ventilation and Hydrogen Release Rates for Tank U-106

Time Period	Average Ventilation Rate		Hydrogen Release Rate
	ft^3/min	m^3/h	g/day
1/9/98–1/15/98	1.5 ± 0.7	2.5 ± 1.2	2.6
1/15/98–2/13/98	1.3 ± 0.2	2.2 ± 0.3	2.0
2/13/98–3/24/98	1.2 ± 0.1	2.1 ± 0.2	2.2
1/9/98–3/24/98	1.3 ± 0.1	2.2 ± 0.1	2.2

5.4 Tank U-111

Tank U-111 is the second tank in a three-tank cascade. It is connected via 7.6-cm-diameter, 7.6-m-long underground pipes to Tanks U-110 and U-112 and is ventilated to the atmosphere through a HEPA filter. No other open connections to other tanks or the atmosphere were identified. Visual inspection of the pit covers and the above-ground portions of risers in January 1998 indicated no significant pathways for air leakage.

Approximately 5.7 m^3 (202 ft^3 at atmospheric pressure) of helium was injected into the headspace of Tank U-111 on January 8, 1998. Tracer samples were collected on January 9, and 15, February 13, and March 24, 1998. Sample collection dates, times, and measured helium and hydrogen concentrations are listed in Table A.5.

Table 5.7 lists the calculated average ventilation rate of Tank U-111 for the three time periods studied. The overall average ventilation rate listed for January 9 to March 24 was calculated from helium concentrations measured on those two dates. At the relatively small ventilation rates observed, the tracer gas method is thought to be valid.

The hydrogen concentration measured in samples collected on January 8, 9, and 15, February 13, and March 24, 1998 averaged 389 ppmv, and had a standard deviation (based on a total of 30 analyses of the 15 samples) of 39 ppmv. Estimated hydrogen release rates between sample collection times have been calculated, assuming a headspace temperature of 20.7°C, and are listed in Table 5.7. The average hydrogen release rate for the entire study is a weighted average of the individual periods.

Table 5.7. Calculated Average Ventilation and Hydrogen Release Rates for Tank U-111

Time Period	Average Ventilation Rate		Hydrogen Release Rate
	ft^3/min	m^3/h	g/day
1/9/98–1/15/98	2.8 ± 0.6	4.8 ± 1.0	2.6
1/15/98–2/13/98	2.0 ± 0.2	3.5 ± 0.3	2.5
2/13/98–3/24/98	1.6 ± 0.1	2.7 ± 0.2	2.4
1/9/98–3/24/98	1.9 ± 0.1	3.2 ± 0.2	2.4

5.5 Tank C-104

Tank C-104 is the first tank in a three-tank cascade. It is connected via a 7.6-cm-diameter, 7.6-m-long underground pipe to the actively ventilated Tank C-105. A similar cascade line connects Tank C-105 to Tank C-106, which is also actively ventilated. Vapor samples obtained in 1994 from the headspace of Tank C-104 and the exhaust riser of Tank C-105 indicated that Tank C-104 was being actively ventilated via the cascade line (Huckaby and Bratzel 1995), and tracer tests appear to confirm this.

Approximately 5.7 m^3 (200 ft^3 at atmospheric pressure) of helium and 1.3 L of SF_6 were injected into the headspace of Tank C-104 on April 13, 1998. Samples were collected from the tank headspace on April 14, 16, and 17, 1998. Sample collection dates, times, and measured helium and hydrogen concentrations are listed in Table A.6. Average ventilation rates, calculated from measured helium

Table 5.8. Calculated Average Ventilation and Hydrogen Release Rates for Tank C-104

Time Period	Average Ventilation Rate		Hydrogen Release Rate
	ft^3/min	m^3/h	g/day
4/14/98–4/16/98	66 ± 4	113 ± 7	8.3
4/16/98–4/17/98	68 ± 5	115 ± 9	6.0
4/14/98–4/17/98	67 ± 4	114 ± 9	7.5

concentrations and equation (4.2), are listed in Table 5.8. The ventilation rates for the two periods considered are essentially identical and clearly indicate that the ventilation rate of Tank C-104 at that time was much higher than those of other passively ventilated tanks.

Samples were also collected from the ventilation risers of Tanks C-105 and C-106 on April 14, 1998, and the ventilation rates of both tanks were measured by LMHC Vent and Balance on the same day. Samples from the Tank C-105 ventilation riser had an average helium concentration of 112 ppmv, well above background helium levels and qualitatively consistent with the measured airflows of Tanks C-104 and C-105 and the premise that Tank C-104 is venting via the cascade line. Samples from the ventilation riser of Tank C-106 did not have elevated helium concentrations but did have detectable levels[(a)] of SF_6, indicating that the cascade line between Tanks C-105 and C-106 is not plugged.

Figure 5.1 depicts the Tank C-104, C-105, and C-106 cascade and labels the airflows of the system. The ventilation rates of Tanks C-105 and C-106 were reported to be v_4 = 15-m^3/min (521 ft^3/min) and v_7 = 83-m^3/min (2,919 ft^3/min), respectively, on April 14. To estimate the ventilation rate of Tank C-104 when the ventilation rate of Tank C-105 is different, it may be assumed that the ratio of the tanks' ventilation rates is constant:

$$\frac{v_2}{v_4} = \frac{1.9\ \mathrm{m^3/h}}{15\ \mathrm{m^3/h}} = 0.13 \tag{5.1}$$

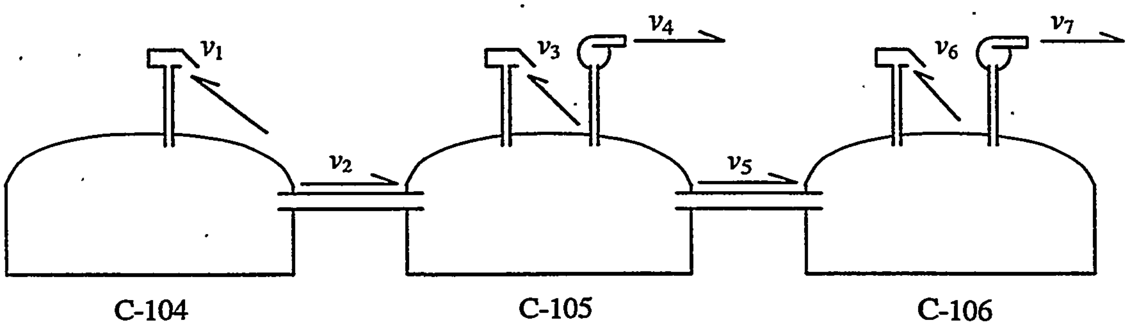

Figure 5.1. Schematic of Air Flow in Tank C-104, C-105, and C-106 Cascade

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(a) Samples from Tank C-106 were estimated to contain about 0.006 ppbv of SF_6. This value was below the analytical quantitation limit, but above the detection limit of the method. Tank C-104 and C-105 samples were not analyzed for SF_6 because helium levels were sufficient to verify the airflow dynamics.

This assumes that both v_2 and v_4 are turbulent flows, so they behave similarly to changes in system pressure differentials. Given that SF_6 was detected in the Tank C-106 exhaust, air was apparently flowing from Tank C-105 to Tank C-106 (i.e., $v_5 > 0$), but since the magnitude of this airflow was not determined, it is assumed here to not appreciably affect the relationship of equation (5.1).

Current plans to reconfigure the ventilation of Tanks C-105 and C-106 may result in eliminating the active ventilation of Tank C-105 (i.e., $v_4 = 0$) and reducing the make-air flow rate of Tank C-106 to a much lower value (e.g., $v_7 \approx 10$ m^3/min). To estimate the ventilation rate of Tank C-104 under these conditions, it is supposed that flow resistances in the Tank C-105/C-106 system are comparable to that recently observed in the Tank C-104/C-105 system. Specifically, it is supposed that, when the active ventilation of Tank C-105 is stopped,

$$\frac{v_5}{v_7} \approx \frac{v_2}{v_5} \approx 0.13 \qquad (5.2)$$

In lieu of a more definitive set of measurements, the application of equations (5.2) for a future scenario in which $v_7 = 10$ m^3/min yields the estimated values of $v_5 \approx 1.3$ m^3/min and $v_2 \approx 0.17$ m^3/min.

The hydrogen concentration measured in samples collected on April 13, 14, 16, and 17 averaged 36 ppmv and had a standard deviation (based on a total of 23 analyses of the 12 samples) of 5 ppmv. Estimated hydrogen release rates between sample collection times have been calculated assuming a headspace temperature of 27.7°C and are listed in Table 5.7. The average hydrogen release rate for the period of April 14 to April 17 is a weighted average of the individual periods.

5.6 Tank AX-101

Tank AX-101 is one of four tanks in AX-farm. The AX-farm tanks were the last single-shell tanks constructed, and they are not connected via cascade lines like their predecessors; they are, however, connected via an underground ventilation system, which was originally part of the A- and AX-farm exhaust system. The ventilation system in AX-farm has been isolated from that exhauster, but the 51-cm (20-in.) and 61-cm (24-in.)-diameter air ducts that connect the headspaces of the four tanks remain open. An earlier tracer study indicated that the ventilation rate of Tank AX-102 was relatively high (Huckaby et al. 1997), and it has been reasoned that the high rate observed was associated with the system of large air ducts that connect the four AX-farm tanks.

Approximately 5.4-m^3 of helium was injected into the Tank AX-101 headspace on March 5, 1998, to provide a calculated initial tracer concentration of about 1,100 ppmv. Samples were collected one and four days after tracer injection, with unexpected results, and the study was aborted.

Table 5.9 lists sample collection dates and times, and replicate analytical results for helium and hydrogen measured in the Tank AX-101 samples. As shown in Table 5.9, the three samples collected on March 6 contained significantly different concentrations of helium, even though they were collected only minutes apart. No sampling problems had been noted, and the consistency of hydrogen concentrations measured in the same samples suggests no accidental dilution or partial filling of the samples occurred.[a]

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[a] Hydrogen is typically present at about 0.5 ppmv in ambient air, and if some of the samples had been diluted with ambient air, the hydrogen level in those samples should be different.

Replicate analyses of individual samples, given in Table 5.9, gave very consistent results, and there were no indications of an analytical problem. A possible explanation for the inconsistent helium results is that, because the samples were collected from a headspace location near the opening of the underground ventilation system, they may have been affected by a transient inflow of air from the other AX-farm tanks.

Samples collected four days after sample injection, on March 9, were found to have essentially ambient air levels of helium. These samples may also have been affected by an inflow of air from the AX-farm ventilation system, but it is also possible that the helium level in the headspace had actually been reduced to this low level via a moderate ventilation rate combined with poor mixing of the tracer. If, for example, the ventilation air introduced into Tank AX-101 was cooler than the bulk headspace, it would tend to displace the tracer-containing air in the headspace without proper mixing. Ventilation air leaving the headspace would be correspondingly concentrated in the tracer and cause the ventilation rate calculated from equation (4.2) to appear higher than it is. The tracer method was deemed to have failed on Tank AX-101, due possibly to an inappropriate sampling location and/or that the tracer was not uniformly distributed throughout the headspace.

Table 5.9. Measured Helium and Hydrogen Concentrations in Tank AX-101

Sample Date & Time	Sample Identification Number	Helium (ppmv)	Hydrogen (ppmv)
3/5/98 9:53 AM	V0011-A01.125	6.8 6.6	6.4 6.4
3/5/98 9:59 AM	V0011-A02.290	6.6 6.4	6.2 6.4
3/5/98 10:05 AM	V0011-A03.295	6.8 6.6	6.4 6.4
3/5/98 10:16 AM	Helium Injection Started	--	--
3/5/98 10:46 AM	Helium Injection Stopped	--	--
3/6/98 9:48 AM	V0011-B01.298	218.0 217.8 218.8 220.4	6.8 7.2 7.0 7.4
3/6/98 9:54 AM	V0011-B02.317	112.8 113.0	7.0 7.2
3/6/98 10:00 AM	V0011-B03.323	82.8 83.6 83.4 83.2	7.4 7.2 7.2 7.6
3/9/98 10:08 AM	V0011-C01.351	7.8 7.6	5.4 5.8
3/9/98 10:15 AM	V0011-C02.403	6.6 5.4	5.8 7.6
3/9/98 10:21 AM	V0011-C03.404	6.6 7.8	6.2 6.8

6.0 References

Cowley WL, JM Grigsby, and AK Postma. 1997. *Organic Solvent Topical.* WHC-SD-WM-SARR-036 Rev. 1A, Duke Engineering Systems Hanford, Richland, Washington.

Epstein M, HK Fauske, DR Dickinson, MD Crippen, JD McCormack, RJ Cash, JE Meacham, and CS Simmons. 1994. *Ferrocyanide Safety Program: An Assessment of the Possibility of Ferrocyanide Sludge Dryout.* WHC-EP-0816, Westinghouse Hanford Company, Richland, Washington.

Farwell SO, DR Gage, and RA Kagel. 1981. Current status of prominent selective gas chromatographic detectors: a critical assessment. *J. Chromatogr. Sci.* 19, pp. 358-376.

Huckaby JL and DR Bratzel. 1995. *Tank 241-C-105 Headspace Gas and Vapor Characterization Results for Samples Collected in February 1994.* WHC-SD-WM-ER-443 Rev. 1A, Westinghouse Hanford Company, Richland, Washington.

Huckaby JL and DS Sklarew. 1997. *Screening for Organic Solvents in the Hanford Waste Tanks Using Organic Vapor Concentrations.* PNNL-11490, Pacific Northwest National Laboratory, Richland, Washington.

Huckaby JL, JC Evans, KB Olsen, KM Remund, and DS Sklarew. 1997. *Measurements of Waste Tank Passive Ventilation Rates Using Tracer Gases.* PNNL-11683, Pacific Northwest National Laboratory, Richland, Washington.

Olschewski A, U Fischer, M Hofer, and R Schulin. 1995. *Sulfur hexafluoride as a gas tracer in soil venting operations. Environ. Sci. Technol.* 29, pp. 264-266.

Sklarew DS and JL Huckaby. 1998. *Ventilation Rates Calculated from Hydrogen Release Data in Tanks Equipped with Standard Hydrogen Monitoring Systems (SHMS).* PNNL-11926, Pacific Northwest National Laboratory, Richland, Washington.

Wilkins NE, RE Bauer, and DM Ogden. 1996. *Results of Vapor Space Monitoring of Flammable Gas Watch List Tanks.* HNF-SD-WM-TI-797 Rev. 0, Lockheed Martin Hanford Corporation, Richland, Washington

Appendix

Measured Helium and Hydrogen Concentrations

Table A.1. Measured Helium and Hydrogen Concentrations in Tank TX-104

Sample Date & Time	Analysis Date	Sample Name	Helium (ppmv)	Date-Averaged Helium (ppmv)	Hydrogen (ppmv)	Date-Averaged Hydrogen (ppmv)
1/13/98 2:11 PM	1/16/98	V0008-A01.444	6.6		18.8	
1/13/98 2:11 PM	1/16/98	V0008-A01.444	6.2		18.6	
1/13/98 2:17 PM	1/16/98	V0008-A02.445	6.2		18.0	
1/13/98 2:17 PM	1/16/98	V0008-A02.445	6.4		18.4	
1/13/98 2:23 PM	1/16/98	V0008-A03.446	6.4		18.0	
1/13/98 2:23 PM	1/16/98	V0008-A03.446	6.4	6.4	18.2	18.3
1/13/98 2:29 PM	Helium Injection Started					
1/13/98 3:07 PM	Helium Injection Complete					
1/14/98 9:46 AM	1/16/98	V0008-B01.447	1313		16.6	
1/14/98 9:46 AM	1/16/98	V0008-B01.447	1331		17.6	
1/14/98 9:52 AM	1/16/98	V0008-B02.448	1311		17.4	
1/14/98 9:52 AM	1/16/98	V0008-B02.448	1342		17.6	
1/14/98 9:58 AM	1/16/98	V0008-B03.449	1342		18.0	
1/14/98 9:58 AM	1/16/98	V0008-B03.449	1342	1330	17.4	17.4
1/22/98 9:05 AM	1/27/98	V0008-C01.308	986		17.0	
1/22/98 9:05 AM	1/27/98	V0008-C01.308	990		17.4	
1/22/98 9:11 AM	1/27/98	V0008-C02.309	970		16.4	
1/22/98 9:11 AM	1/27/98	V0008-C02.309	979		16.8	
1/22/98 9:17 AM	1/27/98	V0008-C03.318	973		17.0	
1/22/98 9:17 AM	1/27/98	V0008-C03.318	976	979	17.0	16.9
2/12/98 10:42 AM	2/17/98	V0008-D01.042	443		15.2	
2/12/98 10:42 AM	2/17/98	V0008-D01.042	443		15.2	
2/12/98 10:48 AM	2/17/98	V0008-D02.227	440		15.2	
2/12/98 10:48 AM	2/17/98	V0008-D02.227	448		15.4	
2/12/98 10:55 AM	2/17/98	V0008-D03.248	439		15.2	
2/12/98 10:55 AM	2/17/98	V0008-D03.248	441	443	15.0	15.2

Table A.2. Measured Helium and Hydrogen Concentrations in Tank U-103

Sample Date & Time	Analysis Date	Sample Name	Helium (ppmv)	Date-Averaged Helium (ppmv)	Hydrogen (ppmv)	Date-Averaged Hydrogen (ppmv)
7/14/97 9:59 AM	7/23/97	V0002-A01.227	4.5			
7/14/97 9:59 AM	7/23/97	V0002-A01.227	4.0			
7/14/97 10:06 AM	7/23/97	V0002-A02.241	4.2			
7/14/97 10:06 AM	7/23/97	V0002-A02.241	3.9	4.0		
7/14/97 10:15 AM	Helium Injection Started					
7/14/97 10:45 AM	Helium Injection Complete					
7/15/97 9:29 AM	7/23/97	V0002-B01.269	3465			
7/15/97 9:29 AM	7/23/97	V0002-B01.269	3488			
7/15/97 9:35 AM	7/23/97	V0002-B02.315	3476			
7/15/97 9:35 AM	7/23/97	V0002-B02.315	3482	3478		
7/22/97 8:37 AM	7/23/97	V0002-C01.085	2308			
7/22/97 8:37 AM	7/23/97	V0002-C01.085	2313			
7/22/97 8:42 AM	7/23/97	V0002-C02.118	2320			
7/22/97 8:42 AM	7/23/97	V0002-C02.118	2348	2322		
8/13/97 8:57 AM	8/15/97	V0002-D02.019	957			
8/13/97 8:57 AM	8/15/97	V0002-D02.019	976	962		
10/1/97 10:58 AM	10/3/97	V0002-E01-244	162			
10/1/97 10:58 AM	10/3/97	V0002-E01-244	163			
10/1/97 11:04 AM	10/3/97	V0002-E02-273	164			
10/1/97 11:04 AM	10/3/97	V0002-E02-273	166	164		
10/22/97 2:03 PM	*10/24/97*	*U-103-10-22-97-1403 (1)*	*50*		*590*	
10/22/97 2:03 PM	*10/24/97*	*U-103-10-22-97-1403 (2)*	*58*	*54*	*730*	*660*
11/17/97 10:07 AM	12/2/97	V0004-A01.409	[221]*		597	
11/17/97 10:07 AM	12/2/97	V0004-A01.409	[223]		604	
11/17/97 10:13 AM	12/2/97	V0004-A01.410	[198]		609	
11/17/97 10:13 AM	12/2/97	V0004-A01.410	[198]		607	
11/17/97 10:19 AM	12/2/97	V0004-A01.411	[114]		608	
11/17/97 10:19 AM	12/2/97	V0004-A01.411	[115]	[178]	610	606
11/17/97 10:25 AM	Helium Injection Started					
11/17/97 10:56 AM	Helium Injection Complete					
11/18/97 9:46 AM	12/2/97	V0004-A01.412	[3365]		558	
11/18/97 9:46 AM	12/2/97	V0004-A01.412	[3435]		569	
11/18/97 9:52 AM	12/2/97	V0004-A01.413	>UQL		577	
11/18/97 9:52 AM	12/2/97	V0004-A01.413	>UQL		573	
11/18/97 9:58 AM	12/2/97	V0004-A01.414	3281		544	
11/18/97 9:58 AM	12/2/97	V0004-A01.414	3331	3306	552	548
12/15/97 9:49 AM	12/16/97	V0004-C01.415	489		586	
12/15/97 9:49 AM	12/16/97	V0004-C01.415	497		594	

Table A.2. Measured Helium and Hydrogen Concentrations in Tank U-103

12/15/97 9:49 AM	12/23/97	V0004-C01.415	482		583		
12/15/97 9:49 AM	12/23/97	V0004-C01.415	482		584		
12/15/97 9:54 AM	12/16/97	V0004-C02.416	488		586		
12/15/97 9:54 AM	12/16/97	V0004-C02.416	498		597		
12/15/97 9:54 AM	12/23/97	V0004-C02.416	484		587		
12/15/97 9:54 AM	12/23/97	V0004-C02.416	482		584		
12/15/97 10:01 AM	12/16/97	V0004-C03.417	489		587		
12/15/97 10:01 AM	12/16/97	V0004-C03.417	496		595		
12/15/97 10:01 AM	12/23/97	V0004-C03.417	481		583		
12/15/97 10:01 AM	12/23/97	V0004-C03.417	482	488	585	588	
1/8/98 11:24 AM	1/15/98	V0009-A01.014	118		703		
1/8/98 11:24 AM	1/15/98	V0009-A01.014	123		725		
1/8/98 11:30 AM	1/15/98	V0009-A02.019	118		705		
1/8/98 11:30 AM	1/15/98	V0009-A02.019	119		713		
1/8/98 11:35 AM	1/15/98	V0009-A03.023	116		693		
1/8/98 11:35 AM	1/15/98	V0009-A03.023	119	119	707	708	
1/9/98 11:10 AM	1/15/98	V0009-B01.030	140		694		
1/9/98 11:10 AM	1/15/98	V0009-B01.030	139		685		
1/9/98 11:15 AM	1/15/98	V0009-B02.085	143		696		
1/9/98 11:15 AM	1/15/98	V0009-B02.085	142		692		
1/9/98 11:21 AM	1/15/98	V0009-B03.118	138		682		
1/9/98 11:21 AM	1/15/98	V0009-B03.118	140	140	690	690	
1/15/98 9:53 AM	1/16/98	V0009-C01.322	215		657		
1/15/98 9:53 AM	1/16/98	V0009-C01.322	216		662		
1/15/98 9:59 AM	1/16/98	V0009-C02.346	216		659		
1/15/98 9:59 AM	1/16/98	V0009-C02.346	221		677		
1/15/98 10:05 AM	1/16/98	V0009-C03.347	211		688		
1/15/98 10:05 AM	1/16/98	V0009-C03.347	213	215	684	671	
2/13/98 9:57 AM	2/17/98	V0007-D01.349	136		617		
2/13/98 9:57 AM	2/17/98	V0007-D01.349	136		618		
2/13/98 10:03 AM	2/17/98	V0007-D02.350	131		596		
2/13/98 10:03 AM	2/17/98	V0007-D02.350	135		612		
2/13/98 10:09 AM	2/17/98	V0007-D03.352	136		617		
2/13/98 10:09 AM	2/17/98	V0007-D03.352	134	135	610	612	
3/24/98 10:35 AM	4/3/98	V0009-H01.447	35		671		
3/24/98 10:35 AM	4/3/98	V0009-H01.447	36		683		
3/24/98 10:41 AM	4/3/98	V0009-H02.448	39		749		
3/24/98 10:41 AM	4/3/98	V0009-H02.448	39		744		
3/24/98 10:47 AM	4/3/98	V0009-H03.449	39		751		
3/24/98 10:47 AM	4/3/98	V0009-H03.449	40	38	765	727	

* Bracketed values are suspect due to helium contamination of a high-pressure regulator and are not used in calculations.

Table A.3. Measured Helium and Hydrogen Concentrations in Tank U-102

Sample Date & Time	Analysis Date	Sample Name	Helium (ppmv)	Date-Averaged Helium (ppmv)	Hydrogen (ppmv)	Date-Averaged Hydrogen (ppmv)
1/8/98 10:42 AM	1/15/98	V0006-A01.135	195		608	
1/8/98 10:42 AM	1/15/98	V0006-A01.135	194		609	
1/8/98 10:47 AM	1/15/98	V0006-A02.143	192		602	
1/8/98 10:47 AM	1/15/98	V0006-A02.143	193		604	
1/8/98 10:53 AM	1/15/98	V0006-A03.223	197		610	
1/8/98 10:53 AM	1/15/98	V0006-A03.223	198	195	612	607
1/8/98 2:12 PM	Helium Injection Started					
1/8/98 2:52 PM	Helium Injection Complete					
1/9/98 10:05 AM	1/15/98	V0006-B01.293	2096		434	
1/9/98 10:05 AM	1/15/98	V0006-B01.293	2171		448	
1/9/98 10:11 AM	1/15/98	V0006-B02.297	2050		427	
1/9/98 10:11 AM	1/15/98	V0006-B02.297	2062		430	
1/9/98 10:16 AM	1/15/98	V0006-B03.313	2048		427	
1/9/98 10:16 AM	1/15/98	V0006-B03.313	2081	2085	434	433
1/15/98 10:14 AM	1/16/98	V0006-C01.226	1606		535	
1/15/98 10:14 AM	1/16/98	V0006-C01.226	1637		545	
1/15/98 10:20 AM	1/16/98	V0006-C02.235	1629		443	
1/15/98 10:20 AM	1/16/98	V0006-C02.235	1658		552	
1/15/98 10:26 AM	1/16/98	V0006-C03.277	1651		550	
1/15/98 10:26 AM	1/16/98	V0006-C03.277	1669	1642	556	530
2/13/98 9:30 AM	2/17/98	V0006-D01.307	255		495	
2/13/98 9:30 AM	2/17/98	V0006-D01.307	259		546	
2/13/98 9:37 AM	2/17/98	V0006-D02.310	275		534	
2/13/98 9:37 AM	2/17/98	V0006-D02.310	275		533	
2/13/98 9:43 AM	2/17/98	V0006-D03.319	260		504	
2/13/98 9:43 AM	2/17/98	V0006-D03.319	265	265	515	521
3/24/98 10:13 AM	4/3/98	V0006-E01.035	71.0		463	
3/24/98 10:13 AM	4/3/98	V0006-E01.035	72.0		472	
3/24/98 10:19 AM	4/3/98	V0006-E02.045	70.0		456	
3/24/98 10:19 AM	4/3/98	V0006-E02.045	69.6		453	
3/24/98 10:25 AM	4/3/98	V0006-E03.093	70.4		456	
3/24/98 10:25 AM	4/3/98	V0006-E03.093	70.6	70.6	462	460

Table A.4. Measured Helium and Hydrogen Concentrations in Tank U-106

Sample Date & Time	Analysis Date	Sample Name	Helium (ppmv)	Date-Averaged Helium (ppmv)	Hydrogen (ppmv)	Date-Averaged Hydrogen (ppmv)
1/8/98 11:04 AM	1/15/98	V0005-A01.400	6.4		2.2	
1/8/98 11:04 AM	1/15/98	V0005-A01.400	6.4		2.2	
1/8/98 11:10 AM	1/15/98	V0005-A02.401	6.4		87.8	
1/8/98 11:10 AM	1/15/98	V0005-A02.401	6.6		89.2	
1/8/98 11:16 AM	1/15/98	V0005-A03.402	8.4		208.8	
1/8/98 11:16 AM	1/15/98	V0005-A03.402	8.2	7.1	211.8	100
1/8/98 1:26 PM	Helium Injection Started					
1/8/98 2:08 PM	Helium Injection Complete					
1/9/98 10:48 AM	1/15/98	V0005-B01.403	1923		406.4	
1/9/98 10:48 AM	1/15/98	V0005-B01.403	1962		414.8	
1/9/98 10:54 AM	1/15/98	V0005-B02.404	1942		409.8	
1/9/98 10:54 AM	1/15/98	V0005-B02.404	1946		410.2	
1/9/98 11:00 AM	1/15/98	V0005-B03.405	1923		405.6	
1/9/98 11:00 AM	1/15/98	V0005-B03.405	1949	1941	411.2	410
1/15/98 9:29 AM	1/16/98	V0005-C01.406	1668		425.0	
1/15/98 9:29 AM	1/16/98	V0005-C01.406	1682		428.2	
1/15/98 9:35 AM	1/16/98	V0005-C02.407	1675		426.6	
1/15/98 9:35 AM	1/16/98	V0005-C02.407	1683		429.6	
1/15/98 9:41 AM	1/16/98	V0005-C03.408	1659		423.0	
1/15/98 9:41 AM	1/16/98	V0005-C03.408	1671	1673	426.6	427
2/13/98 11:12 AM	2/17/98	V0005-D01.345	894.2		447.0	
2/13/98 11:12 AM	2/17/98	V0005-D01.345	904.2		451.6	
2/13/98 11:21 AM	2/17/98	V0005-D02.348	887.0		443.4	
2/13/98 11:21 AM	2/17/98	V0005-D02.348	894.2		451.8	
2/13/98 11:27 AM	2/17/98	V0005-D03.353	889.2		444.4	
2/13/98 11:27 AM	2/17/98	V0005-D03.353	896.6	894	448.2	448
3/24/98 11:20 AM	4/3/98	V0005-E01.099	390.6		486.2	
3/24/98 11:20 AM	4/3/98	V0005-E01.099	394.2		491.0	
3/24/98 11:26 AM	4/3/98	V0005-E02.128	395.8		489.2	
3/24/98 11:26 AM	4/3/98	V0005-E02.128	392.4		489.2	
3/24/98 11:32 AM	4/3/98	V0005-E03.208	395.8		492.4	
3/24/98 11:32 AM	4/3/98	V0005-E03.208	400.2	395	497.4	491

Table A.5. Measured Helium and Hydrogen Concentrations in Tank U-111

Sample Date & Time	Analysis Date	Sample Name	Helium (ppmv)	Date-Averaged Helium (ppmv)	Hydrogen (ppmv)	Date-Averaged Hydrogen (ppmv)
1/8/98 10:14 AM	1/15/98	V0007-A01.317	6.6		335	
1/8/98 10:14 AM	1/15/98	V0007-A01.317	6.6		335	
1/8/98 10:20 AM	1/15/98	V0007-A02.439	6.6		323	
1/8/98 10:20 AM	1/15/98	V0007-A02.439	6.4		325	
1/8/98 10:26 AM	1/15/98	V0007-A03.437	6.4		330	
1/8/98 10:26 AM	1/15/98	V0007-A03.437	6.4	6.5	331	330
1/8/98 3:01 PM	Helium Injection Started					
1/8/98 3:32 PM	Helium Injection Complete					
1/9/98 10:28 AM	1/15/98	V0007-B01.438	2594		430	
1/9/98 10:28 AM	1/15/98	V0007-B01.438	2653		439	
1/9/98 10:33 AM	1/15/98	V0007-B02.442	2516		440	
1/9/98 10:33 AM	1/15/98	V0007-B02.442	2521		441	
1/9/98 10:39 AM	1/15/98	V0007-B03.443	2466		431	
1/9/98 10:39 AM	1/15/98	V0007-B03.443	2499	2541	437	436
1/15/98 10:33 AM	1/16/98	V0007-C01.279	1791		387	
1/15/98 10:33 AM	1/16/98	V0007-C01.279	1830		395	
1/15/98 10:39 AM	1/16/98	V0007-C02.302	1782		385	
1/15/98 10:39 AM	1/16/98	V0007-C02.302	1778		384	
1/15/98 10:45 AM	1/16/98	V0007-C03.303	1786		386	
1/15/98 10:45 AM	1/16/98	V0007-C03.303	1802	1795	389	388
2/13/98 10:46 AM	2/17/98	V0009-D01.342	540		368	
2/13/98 10:46 AM	2/17/98	V0009-D01.342	546		373	
2/13/98 10:54 AM	2/17/98	V0009-D02.343	535		365	
2/13/98 10:54 AM	2/17/98	V0009-D02.343	535		366	
2/13/98 11:00 AM	2/17/98	V0009-D03.344	537		367	
2/13/98 11:00 AM	2/17/98	V0009-D03.344	544	539	371	368
3/24/98 10:58 AM	4/3/98	V0007-E01.304	152		415	
3/24/98 10:58 AM	4/3/98	V0007-E01.304	154		423	
3/24/98 11:05 AM	4/3/98	V0007-E02.444	156		427	
3/24/98 11:05 AM	4/3/98	V0007-E02.444	156		428	
3/24/98 11:11 AM	4/3/98	V0007-E03.446	153		420	
3/24/98 11:11 AM	4/3/98	V0007-E03.446	155	154	426	423