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2	1	Cog. Mgr. K.M. Hodgson	<i>K.M. Hodgson</i>	6/19/97	R2-11	1	1	J.G. Kristofzski	<i>J.G. Kristofzski</i>	6/24/97	R2-12
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Calculation Note: Hydrogen Generation Rates at Steady-State Flammable Gas Concentrations for Single Shell Tanks

L. A. Stauffer

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Abstract: This calculation note analyzes headspace concentrations of hydrogen in single shell tanks dependent upon assumed ventilation flow rates provided by the waste tank ventilation system operation or calculated from Standard Hydrogen Monitoring System data. The analyses are based on measured or estimated steady-state hydrogen release rates. Specific analyses include: 1) The hydrogen generation rate at steady-state hydrogen concentrations and 2) The headspace hydrogen concentration as a function of time, as well as the time required to reach 25% and 100% of the Lower Flammability Limit with barometric breathing in the tank.

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Title:

Calculation Note: Hydrogen Generation Rates at Steady-State Flammable Gas Concentrations for Single-Shell Tanks

Purpose:

This calculation note analyzes headspace concentrations of hydrogen in single-shell tanks (SST) dependent upon assumed ventilation flow rates provided by the waste tank ventilation system operation or calculated from Standard Hydrogen Monitoring System (SHMS) data. The analyses are based on measured or estimated steady state hydrogen release rates. Specific analyses include:

- 1) The hydrogen generation rate at steady state hydrogen concentrations.
- 2) The headspace hydrogen concentration as a function of time, as well as the time required to reach 25% and 100% of the Lower Flammability Limit (LFL) barometric breathing in the tank.

Methodology:

The calculations utilize referenced values of steady-state hydrogen concentrations and ventilation rates in SSTs. The calculations are performed and documented using Microsoft Excel version 5.0c.

Once the hydrogen concentration (%H₂) and the ventilation flow rate (Vr) is known for each of the tanks, the expression $Vr / ((1/[\%H_2]/100) - 1)$ equals the hydrogen generation rate (Gr) in cubic feet per minute can be used to calculate the generation rate. The generation rate is then used with the barometric breathing rate to calculate the domespace hydrogen concentration with time (see input data and calculations section).

Assumptions:

- The minimum flow rate in The SSTs is assumed to be the barometric breathing rate. Changes in barometric pressure cause passively ventilated storage tanks to exchange an average of 0.45 percent of the volume of gas in their headspaces with atmospheric air per day (Crippen 1993). Zero ventilation rate is not assumed as the minimum flow rate because the tanks are not pressure vessels and could not be made leak tight. The tanks are interconnected by pipes and vent systems. The domes are unsealed concrete and micro cracking allows air paths. Barometric breathing is the next most conservative case.
- The times to reach 25% of the LFL and 100% of the LFL are based on the barometric breathing rates. The assumption is that the passive or active ventilation is lost, but because the tanks can't be made leak tight barometric breathing rate will exist in the tanks.
- The hydrogen concentrations for the following tanks are based on grab sampling data: 241-A-101, 241-AX-101, 241-AX-103, 241-S-102, 241-S-111, 241-S-112, 241-SX-101, 241-SX-102, 241-SX-103, 241-SX-104, 241-SX-105, 241-SX-106, 241-SX-109, 241-T-111, 241-U-103, 241-U-1-5, 241-U-107, 241-U-108, and 241-U-109 (Wilkins 1997).
- The assumed composition of gases generated in the tanks cause the LFL to occur at 3.7 volume percent hydrogen, and 25% LFL to occur at 0.93 volume percent hydrogen. (See Appendix A)

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Passively Ventilated Single-Shell Tanks:

-An average hydrogen concentration was assumed for tanks that did not have hydrogen concentrations available. The average of the available hydrogen concentrations for passively ventilated SSTs (excluding flammable gas watch list and 200 series tanks) is 0.0135%. The data used to calculate the average hydrogen concentration was retrieved from the Tank Characterization Database (TCD) (Schaffer 1997). The hydrogen concentration for the 200 series tanks was assumed to be 0.0025%. This assumption was based on the highest measured detection limit for the 200 series tanks. The hydrogen concentrations for passively ventilated SSTs are shown in Table 1.

-The calculated ventilation flow rates were available for tanks 241-S-102, 241-S-111, 241-S-112, 241-U-103, 241-U-105, 241-U-107, 241-U-108, and 241-U-109. These ventilation rates are based on SHMS data (Wilkins 1997). The waste temperatures of tanks without ventilation rate readings were compared to the waste temperatures of those tanks listed above. The tanks were grouped into two temperatures ranges: $< 110^{\circ}\text{F}$ and $> 110^{\circ}\text{F}$. Based on the calculated ventilation rates, tanks with temperatures $< 110^{\circ}\text{F}$ were assumed to have a maximum ventilation rate of 7 cfm and tanks with temperatures $> 110^{\circ}\text{F}$ were assumed to have a maximum ventilation rate of 10 cfm.

Actively Ventilated Single Shell Tanks:

-The hydrogen concentrations for tanks 241-SX-107, 241-SX-108, 241-SX-110, 241-SX-111, 241-SX-112, and 241-SX-114 were not available. The assumed hydrogen concentrations for these tanks are based on the average hydrogen concentration for passively ventilated SSTs. This is a conservative assumption since the passively ventilated SSTs have a much lower ventilation rate than the actively ventilated SSTs.

-The hydrogen concentrations for tanks 241-C-105 and 241-C-106 were retrieved from the TCD (Schaffer 1997).

-Ventilation flow rates for tanks 241-SX-103, 241-SX-104, 241-SX-105, 241-SX-106, and 241-SX-109 are based on SHMS data (Wilkins 1997). The ventilation rates for tanks 241-C-105, 241-C-106, 241-SX-101, 241-SX-102, 241-SX-107, 241-SX-108, 241-SX-110, 241-SX-111, 241-SX-112, and 241-SX-114 are taken from psychrometric data that was obtained from Tank Farm Operations.

Input Data and Calculations:

Variables:

Gr = hydrogen generation rate (cfm)
 Vr = ventilation rate (cfm)
 Vr_{bb} = barometric breathing rate (cfm)
 %H₂ = volume percent hydrogen
 %H_{2(LFL)} = volume percent hydrogen at LFL
 Vol = tank headspace volume
 t = time

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Hydrogen concentration as a function of time can be expressed as follows (Estey 1997a):

$$[\%H_2](t) = \{ Gr - [Gr - (Gr + Vr) \times [\%H_2]_0 / 100] \times \text{EXP}[-(Gr+Vr) / \text{Vol} \times t] \} / (Gr + Vr) \times 100$$

When the system reaches steady state (with $t = \text{infinity}$), the hydrogen concentration can be expressed as follows:

$$[\%H_2] / 100 = Gr / (Gr + Vr)$$

The hydrogen generation rate at steady state can be calculated with the known volume percent hydrogen and the ventilation rate.

$$Gr = Vr / ((1/([\%H_2]/100)) - 1)$$

Considering the ventilation system is operating at the barometric breathing rate, the ventilation rate is

$$Vr_{bb} = 0.0045 \times \text{Vol} / \text{day} \quad (\text{Crippen 1993})$$

Solving for time (t) as a function of the current concentration of hydrogen contained in the tank headspace is

$$t = -[\text{Vol}/(Gr + Vr_{bb})] \times \{ \ln[Gr - (Gr + Vr_{bb})/\text{Vol} \times \%H_{2(LFL)} \times \text{Vol}/100] - \ln[Gr - (Gr + Vr_{bb})/\text{Vol} \times \%H_2 \times \text{Vol}/100] \}$$

Tables 2 and 3 contain the input data for the passively ventilated SSTs and actively ventilated SSTs, respectively. The input data include ventilation rate, hydrogen concentration, and headspace volume.

Results:

Table 2 contains the calculated values for hydrogen generation rate, barometric breathing rate, time to reach 25% of the LFL and 100% of the LFL, and the maximum hydrogen concentration for passively ventilated tanks using the formulas given in the calculation section.

Table 3 contains the same information as Table 1 for the actively ventilated SSTs.

Figure 1 depicts the hydrogen concentration versus time for three representative tanks. Tank 241-A-103 represents tanks in which the hydrogen concentrations will exceed 25% of the LFL, but will not exceed 100% of the LFL. Tank 241-B-101 represents tanks in which the hydrogen concentration will not exceed 25% of the LFL. Tank 241-SX-108 represents tanks in which the hydrogen concentration will exceed 100% of the LFL.

The results for tank 241-C-106 calculated in Estey 1997b are different due to different initial assumptions.

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**Table 1. Hydrogen Concentrations for Passively Ventilated
Single Shell Tanks**

Tank	H2 Concentration (ppmv)	Tank	H2 Concentration (ppmv)
241-A-101	758	241-C-111	12
241-A-102	297	241-C-112	204
241-A-103	474	241-C-201	< 17
241-AX-101	103	241-C-202	< 17
241-AX-102	< 98	241-C-204	< 17
241-AX-103	< 98	241-S-101	442
241-B-102	< 17	241-S-102	750
241-B-103	< 17	241-S-103	79
241-B-103	< 98.6	241-S-105	21
241-B-105	< 17	241-S-106	< 17
241-B-107	< 17	241-S-107	362
241-B-202	< 17	241-S-108	22
241-BX-102	< 17	241-S-109	< 17
241-BX-103	154	241-S-110	135
241-BX-104	94	241-S-111	391
241-BX-105	49	241-S-112	< 25
241-BX-106	< 17	241-T-104	12
241-BX-107	11	241-T-107	< 94
241-BX-110	< 17	241-T-110	< 25
241-BX-111	< 17	241-T-111	< 94
241-BY-101	29	241-TX-105	< 98.6
241-BY-102	34	241-TX-111	109
241-BY-103	21	241-TX-118	97
241-BY-104	250	241-TX-118	< 94
241-BY-105	85	241-TY-101	< 93
241-BY-106	55	241-TY-102	< 3.1
241-BY-107	692	241-TY-103	< 93
241-BY-108	425	241-TY-104	< 49
241-BY-110	< 160	241-U-103	555
241-BY-111	67	241-U-104	< 17
241-BY-112	< 94	241-U-105	< 49
241-C-101	436	241-U-106	210
241-C-102	158	241-U-107	500
241-C-103	776	241-U-108	522
241-C-104	70	241-U-109	748
241-C-107	270	241-U-111	247
241-C-108	15	241-U-112	232
241-C-109	125	241-U-203	< 25
241-C-110	< 94	241-U-204	< 25

Data is from Tank Characterization Database (Schaffer 1997)

Table 2. Passively Ventilated Single Shell Tanks (sheet 1 of 5)

Tank	Input Data			Calculated Data				
	Passive Ventilation Rate Vr (cfm)	H ₂ Concentration % H ₂	Headspace Volume Vol (ft ³)	H ₂ Generation Rate Gr (cfm)	Barometric breathing rate Vr _{bb} (cfm)	Time to reach 25% LFL (0.93 % H ₂) w/barometric breathing (days)	Time to reach 100% LFL (3.7 % H ₂) w/barometric breathing (days)	Maximum H ₂ Concentration % H ₂
*241-A-101	10	0.104	41551	1.04E-02	0.13	24.6	138.5	7.44
241-A-102	7	0.030	163468	2.08E-03	0.51	not possible	not possible	0.41
241-A-103	10	0.047	119353	4.74E-03	0.37	287.8	not possible	1.26
241-A-104	10	0.014	165206	1.35E-03	0.52	not possible	not possible	0.26
241-A-105	10	0.014	166409	1.35E-03	0.52	not possible	not possible	0.26
241-A-106	10	0.014	152239	1.35E-03	0.48	not possible	not possible	0.28
*241-AX-101	10	0.006	68956	6.40E-04	0.22	not possible	not possible	0.30
241-AX-102	7	0.014	163735	9.45E-04	0.51	not possible	not possible	0.18
*241-AX-103	10	0.003	153977	2.60E-04	0.48	not possible	not possible	0.05
241-AX-104	7	0.014	168013	9.45E-04	0.53	not possible	not possible	0.18
241-B-101	10	0.014	99294	1.35E-03	0.31	not possible	not possible	0.43
241-B-102	7	0.002	110122	1.19E-04	0.34	not possible	not possible	0.03
241-B-103	7	0.002	106513	1.19E-04	0.33	not possible	not possible	0.04
241-B-104	7	0.014	64804	9.45E-04	0.20	not possible	not possible	0.46
241-B-105	7	0.002	73494	1.19E-04	0.23	not possible	not possible	0.05
241-B-106	7	0.014	98759	9.45E-04	0.31	not possible	not possible	0.31
241-B-107	7	0.002	92343	1.19E-04	0.29	not possible	not possible	0.04
241-B-108	7	0.014	101834	9.45E-04	0.32	not possible	not possible	0.30
241-B-109	7	0.014	97423	9.45E-04	0.30	not possible	not possible	0.31
241-B-110	7	0.014	81514	9.45E-04	0.25	not possible	not possible	0.37
241-B-111	7	0.014	82718	9.45E-04	0.26	not possible	not possible	0.36
241-B-112	7	0.014	109989	9.45E-04	0.34	not possible	not possible	0.27
241-B-201	7	0.003	4291	1.75E-04	0.01	280.3	not possible	1.29
241-B-202	7	0.003	4559	1.75E-04	0.01	318.7	not possible	1.21
241-B-203	7	0.003	1350	1.75E-04	0.00	56.6	564.6	3.98
241-B-204	7	0.003	1484	1.75E-04	0.00	63.1	not possible	3.64
241-BX-101	7	0.014	108652	9.45E-04	0.34	not possible	not possible	0.28
241-BX-102	7	0.002	101567	1.19E-04	0.32	not possible	not possible	0.04
241-BX-103	7	0.015	105310	1.08E-03	0.33	not possible	not possible	0.33

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Author: *Shirley* Date: *1/19/97*Checked by: *Shirley*Date: *6/19/97*

Table 2. Passively Ventilated Single Shell Tanks (sheet 2 of 5)

Tank	Input Data			Calculated Data				
	Passive Ventilation Rate Vr (cfm)	H ₂ Concentration % H ₂	Headspace Volume Vol (ft ³)	H ₂ Generation Rate Gr (cfm)	Barometric breathing rate Vr _{bb} (cfm)	Time to reach 25% LFL (0.93 % H ₂) w/barometric breathing (days)	Time to reach 100% LFL (3.7 % H ₂) w/barometric breathing (days)	Maximum H ₂ Concentration % H ₂
241-BX-104	7	0.009	101166	6.58E-04	0.32	not possible	not possible	0.21
241-BX-105	7	0.005	107582	3.43E-04	0.34	not possible	not possible	0.10
241-BX-106	7	0.002	109320	1.19E-04	0.34	not possible	not possible	0.03
241-BX-107	7	0.001	68280	7.70E-05	0.21	not possible	not possible	0.04
241-BX-108	7	0.014	110924	9.45E-04	0.35	not possible	not possible	0.27
241-BX-109	7	0.014	88600	9.45E-04	0.28	not possible	not possible	0.34
241-BX-110	7	0.002	86728	1.19E-04	0.27	not possible	not possible	0.04
241-BX-111	7	0.002	92744	1.19E-04	0.29	not possible	not possible	0.04
241-BX-112	7	0.014	92343	9.45E-04	0.29	not possible	not possible	0.33
241-BY-101	7	0.003	88865	2.03E-04	0.28	not possible	not possible	0.07
241-BY-102	7	0.003	103570	2.38E-04	0.32	not possible	not possible	0.07
241-BY-103	7	0.002	87128	1.47E-04	0.27	not possible	not possible	0.05
241-BY-104	10	0.025	86326	2.50E-03	0.27	not possible	not possible	0.92
241-BY-105	10	0.009	73359	8.50E-04	0.23	not possible	not possible	0.37
241-BY-106	10	0.006	54777	5.50E-04	0.17	not possible	not possible	0.32
241-BY-107	7	0.069	105041	4.85E-03	0.33	212.5	not possible	1.46
241-BY-108	7	0.041	110121	2.84E-03	0.34	not possible	not possible	0.82
241-BY-109	7	0.014	84053	9.45E-04	0.26	not possible	not possible	0.36
241-BY-110	7	0.014	87395	9.45E-04	0.27	not possible	not possible	0.34
241-BY-111	7	0.007	79240	4.69E-04	0.25	not possible	not possible	0.19
241-BY-112	7	0.014	101699	9.45E-04	0.32	not possible	not possible	0.30
241-C-101	7	0.044	102636	3.05E-03	0.32	932.7	not possible	0.94
241-C-102	7	0.015	72157	1.02E-03	0.23	not possible	not possible	0.45
241-C-103	10	0.079	88332	7.87E-03	0.28	82.1	not possible	2.77
241-C-104	7	0.007	74964	4.83E-04	0.23	not possible	not possible	0.21
241-C-107	10	0.026	82718	2.63E-03	0.26	558.6	not possible	1.01
241-C-108	7	0.002	105577	1.05E-04	0.33	not possible	not possible	0.03
241-C-109	7	0.013	105577	8.75E-04	0.33	not possible	not possible	0.26
241-C-110	7	0.001	90605	8.40E-05	0.28	not possible	not possible	0.03

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Author SA Stappeler Date 6/19/97Checked by J.L. UtterDate 6/19/97

Author *SA Stacker* Date *1/19/97*Checked by *J. H. Stacker*Date *6/19/97*

Table 2. Passively Ventilated Single Shell Tanks (sheet 3 of 5)

Tank	Input Data			Calculated Data				
	Passive Ventilation Rate Vr (cfm)	H ₂ Concentration % H ₂	Headspace Volume Vol (ft ³)	H ₂ Generation Rate Gr (cfm)	Barometric breathing rate Vr _{bb} (cfm)	Time to reach 25% LFL (0.93 % H ₂) w/barometric breathing (days)	Time to reach 100% LFL (3.7 % H ₂) w/barometric breathing (days)	Maximum H ₂ Concentration % H ₂
241-C-111	7	0.001	106780	8.40E-05	0.33	not possible	not possible	0.03
241-C-112	7	0.020	100497	1.43E-03	0.31	not possible	not possible	0.45
241-C-201	7	0.002	7901	1.19E-04	0.02	not possible	not possible	0.48
241-C-202	7	0.002	8034	1.19E-04	0.03	not possible	not possible	0.47
241-C-203	7	0.003	7500	1.75E-04	0.02	not possible	not possible	0.74
241-C-204	7	0.002	7767	1.19E-04	0.02	not possible	not possible	0.49
241-S-101	10	0.044	83518	4.42E-03	0.26	172.6	not possible	1.67
*241-S-102	3	0.062	67209	1.85E-03	0.21	not possible	not possible	0.87
241-S-103	7	0.008	107447	5.53E-04	0.34	not possible	not possible	0.16
241-S-104	7	0.014	101298	9.45E-04	0.32	not possible	not possible	0.30
241-S-105	7	0.002	79642	1.47E-04	0.25	not possible	not possible	0.06
241-S-106	7	0.002	76567	1.19E-04	0.24	not possible	not possible	0.05
241-S-107	7	0.036	90336	2.53E-03	0.28	not possible	not possible	0.89
241-S-108	7	0.002	80444	1.54E-04	0.25	not possible	not possible	0.06
241-S-109	7	0.002	64669	1.19E-04	0.20	not possible	not possible	0.06
241-S-110	10	0.014	88464	1.35E-03	0.28	not possible	not possible	0.49
*241-S-111	4	0.007	60926	2.88E-04	0.19	not possible	not possible	0.15
*241-S-112	4	0.003	70685	1.08E-04	0.22	not possible	not possible	0.05
241-SX-113	7	0.014	167144	9.45E-04	0.52	not possible	not possible	0.18
241-SX-115	7	0.014	169016	9.45E-04	0.53	not possible	not possible	0.18
241-T-101	7	0.014	100765	9.45E-04	0.31	not possible	not possible	0.30
241-T-102	7	0.014	110122	9.45E-04	0.34	not possible	not possible	0.27
241-T-103	7	0.014	110791	9.45E-04	0.35	not possible	not possible	0.27
241-T-104	7	0.001	65205	8.40E-05	0.20	not possible	not possible	0.04
241-T-105	7	0.014	101299	9.45E-04	0.32	not possible	not possible	0.30
241-T-106	7	0.014	111593	9.45E-04	0.35	not possible	not possible	0.27
241-T-107	7	0.014	91273	9.45E-04	0.29	not possible	not possible	0.33
241-T-108	7	0.014	108518	9.45E-04	0.34	not possible	not possible	0.28
241-T-109	7	0.014	106647	9.45E-04	0.33	not possible	not possible	0.28

Author SA Stuebler Date 6/19/97 Checked by A. G. G. G. Date 6/19/97

Table 2. Passively Ventilated Single Shell Tanks (sheet 4 of 5)

Tank	Input Data			Calculated Data				
	Passive Ventilation Rate Vr (cfm)	H ₂ Concentration % H ₂	Headspace Volume Vol (ft ³)	H ₂ Generation Rate Gr (cfm)	Barometric breathing rate Vr _{bb} (cfm)	Time to reach 25% LFL (0.93 % H ₂) w/barometric breathing (days)	Time to reach 100% LFL (3.7 % H ₂) w/barometric breathing (days)	Maximum H ₂ Concentration % H ₂
*241-T-110	7	0.001	63735	4.90E-05	0.20	not possible	not possible	0.02
241-T-111	7	0.014	54778	9.45E-04	0.17	not possible	not possible	0.55
241-T-112	7	0.014	105443	9.45E-04	0.33	not possible	not possible	0.29
241-T-201	7	0.003	4291	1.75E-04	0.01	280.3	not possible	1.29
241-T-202	7	0.003	5361	1.75E-04	0.02	504.8	not possible	1.03
241-T-203	7	0.003	3489	1.75E-04	0.01	194.0	not possible	1.58
241-T-204	7	0.003	3088	1.75E-04	0.01	160.9	not possible	1.78
241-TX-101	7	0.014	128970	9.45E-04	0.40	not possible	not possible	0.23
241-TX-102	7	0.014	111591	9.45E-04	0.35	not possible	not possible	0.27
241-TX-103	7	0.014	119612	9.45E-04	0.37	not possible	not possible	0.25
241-TX-104	7	0.014	131911	9.45E-04	0.41	not possible	not possible	0.23
241-TX-105	7	0.014	59188	9.45E-04	0.18	not possible	not possible	0.51
241-TX-106	7	0.014	80043	9.45E-04	0.25	not possible	not possible	0.38
241-TX-107	7	0.014	135787	9.45E-04	0.42	not possible	not possible	0.22
241-TX-108	7	0.014	122687	9.45E-04	0.38	not possible	not possible	0.25
241-TX-109	7	0.014	89267	9.45E-04	0.28	not possible	not possible	0.34
241-TX-110	7	0.014	78839	9.45E-04	0.25	not possible	not possible	0.38
241-TX-111	7	0.011	91138	7.63E-04	0.28	not possible	not possible	0.27
241-TX-112	7	0.014	53841	9.45E-04	0.17	not possible	not possible	0.56
241-TX-113	7	0.014	59456	9.45E-04	0.19	not possible	not possible	0.51
241-TX-114	7	0.014	69081	9.45E-04	0.22	not possible	not possible	0.44
241-TX-115	7	0.014	55044	9.45E-04	0.17	not possible	not possible	0.55
241-TX-116	7	0.014	56247	9.45E-04	0.18	not possible	not possible	0.53
241-TX-117	7	0.014	56916	9.45E-04	0.18	not possible	not possible	0.53
241-TX-118	7	0.010	94213	6.79E-04	0.29	not possible	not possible	0.23
241-TY-101	7	0.014	154846	9.45E-04	0.48	not possible	not possible	0.19
241-TY-102	7	0.000	162064	2.17E-05	0.51	not possible	not possible	0.00
241-TY-103	7	0.014	148964	9.45E-04	0.47	not possible	not possible	0.20
241-TY-104	7	0.014	164471	9.45E-04	0.51	not possible	not possible	0.18

Author SA Stouffer Date 6/19/97 Checked by A. B. Gentry Date 6/19/97

Table 2. Passively Ventilated Single Shell Tanks (sheet 5 of 5)

Tank	Input Data			Calculated Data				
	Passive Ventilation Rate Vr (cfm)	H ₂ Concentration % H ₂	Headspace Volume Vol (ft ³)	H ₂ Generation Rate Gr (cfm)	Barometric breathing rate Vr _{bb} (cfm)	Time to reach 25% LFL (0.93 % H ₂) w/barometric breathing (days)	Time to reach 100% LFL (3.7 % H ₂) w/barometric breathing (days)	Maximum H ₂ Concentration % H ₂
241-TY-105	7	0.014	139740	9.45E-04	0.44	not possible	not possible	0.22
241-TY-106	7	0.014	168347	9.45E-04	0.53	not possible	not possible	0.18
241-U-101	7	0.014	111058	9.45E-04	0.35	not possible	not possible	0.27
241-U-102	7	0.014	64403	9.45E-04	0.20	not possible	not possible	0.47
*241-U-103	7	0.061	51837	4.30E-03	0.16	91.3	not possible	2.59
241-U-104	7	0.002	98091	1.19E-04	0.31	not possible	not possible	0.04
*241-U-105	9	0.059	58521	5.29E-03	0.18	82.3	not possible	2.81
241-U-106	7	0.021	84188	1.47E-03	0.26	not possible	not possible	0.56
*241-U-107	5	0.035	60126	1.58E-03	0.19	not possible	not possible	0.84
*241-U-108	4	0.043	51837	1.72E-03	0.16	470.0	not possible	1.05
*241-U-109	5	0.032	52506	1.62E-03	0.16	656.0	not possible	0.98
241-U-110	7	0.014	89535	9.45E-04	0.28	not possible	not possible	0.34
241-U-111	7	0.025	70419	1.73E-03	0.22	not possible	not possible	0.78
241-U-112	7	0.023	107850	1.62E-03	0.34	not possible	not possible	0.48
241-U-201	7	0.003	7500	1.75E-04	0.02	not possible	not possible	0.74
241-U-202	7	0.003	7500	1.75E-04	0.02	not possible	not possible	0.74
241-U-203	7	0.003	7767	1.75E-04	0.02	not possible	not possible	0.72
241-U-204	7	0.003	7767	1.75E-04	0.02	not possible	not possible	0.72

* Flammable gas watch list tanks.

not possible = %H₂ will not reach 25% or 100% of the LFL.

Calculations:

$$Gr = Vr / ((1 / [\%H_2 / 100]) - 1))$$

$$Vr_{bb} = 0.0045 / \text{day} * Vol / (1440 \text{ min/day})$$

$$t_{25\%} = (-[Vol / Gr + Vr_{bb}]) * \{ \ln[Gr - (Gr + Vr_{bb}) / Vol * 0.93 / 100 * Vol] - \ln[Gr - (Gr + Vr_{bb}) / Vol * [\%H_2] / 100 * Vol] \} / (1440 \text{ min/day})$$

$$t_{100\%} = (-[Vol / Gr + Vr_{bb}]) * \{ \ln[Gr - (Gr + Vr_{bb}) / Vol * 3.7 / 100 * Vol] - \ln[Gr - (Gr + Vr_{bb}) / Vol * [\%H_2] / 100 * Vol] \} / (1440 \text{ min/day})$$

$$[\%H_2]_{\max} = \{ Gr - [Gr - (Gr + Vr) * [\%H_2] / 100] * \text{EXP}[-(Gr + Vr) / Vol * 1E+20 \text{ min}] \} / (Gr + Vr) * 100$$

Table 3. Actively Ventilated Single Shell Tanks

Tank	Input Data			Calculated Data				
	Active Ventilation Rate Vr (cfm)	H ₂ Concentration % H ₂	Headspace Volume Vol (ft ³)	H ₂ Generation Rate Gr (cfm)	Barometric breathing rate Vr _{bb} (cfm)	Time to reach 25% LFL (0.93 % H ₂) w/barometric breathing (days)	Time to reach 100% LFL (3.7 % H ₂) w/barometric breathing (days)	Maximum H ₂ Concentration % H ₂
241-C-105	872	0.002	96487	1.92E-02	0.30	35.2	201.3	5.98
241-C-106	2262	0.001	96487	2.26E-02	0.30	29.5	156.1	6.98
*241-SX-101	40	0.001	109662	3.20E-04	0.34	not possible	not possible	0.09
*241-SX-102	40	0.002	98031	7.20E-04	0.31	not possible	not possible	0.23
*241-SX-103	50	0.003	83460	1.50E-03	0.26	not possible	not possible	0.57
*241-SX-104	30	0.001	88540	3.00E-04	0.28	not possible	not possible	0.11
*241-SX-105	100	0.001	79316	1.30E-03	0.25	not possible	not possible	0.52
*241-SX-106	50	0.004	98700	1.75E-03	0.31	not possible	not possible	0.56
241-SX-107	387	0.014	156717	5.23E-02	0.49	20.1	96.9	9.64
241-SX-108	455	0.014	158990	6.14E-02	0.50	17.2	80.8	11.00
*241-SX-109	30	0.001	138002	2.70E-04	0.43	not possible	not possible	0.06
241-SX-110	293	0.014	162332	3.96E-02	0.51	28.0	147.3	7.23
241-SX-111	264	0.014	153910	3.56E-02	0.48	29.5	158.6	6.90
241-SX-112	225	0.014	158321	3.04E-02	0.49	36.2	213.2	5.79
241-SX-114	325	0.014	146424	4.39E-02	0.46	22.5	111.1	8.75

* Flammable gas watch list tanks.

not possible = %H₂ will not reach 25% or 100% of the LFL.

Calculations:

$$Gr = Vr / ((1 / [\%H_2] / 100) - 1))$$

$$Vr_{bb} = 0.0045 / \text{day} * Vol / (1440 \text{ min/day})$$

$$t_{25\%} = (-[Vol / Gr + Vr_{bb}]) * \{ \ln[Gr - (Gr + Vr_{bb}) / Vol * 0.93 / 100 * Vol] - \ln[Gr - (Gr + Vr_{bb}) / Vol * [\%H_2] / 100 * Vol] \} / (1440 \text{ min/day})$$

$$t_{100\%} = (-[Vol / Gr + Vr_{bb}]) * \{ \ln[Gr - (Gr + Vr_{bb}) / Vol * 3.7 / 100 * Vol] - \ln[Gr - (Gr + Vr_{bb}) / Vol * [\%H_2] / 100 * Vol] \} / (1440 \text{ min/day})$$

$$[\%H_2]_{\max} = \{ Gr - [Gr - (Gr + Vr) * [\%H_2] / 100] * \text{EXP}[-(Gr + Vr) / Vol * 1 \text{E} + 20 \text{ min}] \} / (Gr + Vr) * 100$$

Author SA Stouffer Date 6/19/97 Checked by A. A. Stryker Date 6/19/97

**Figure 1. Single-Shell Tank Hydrogen Concentrations vs Days
(Steady State with Barometric Breathing Rate)**

Author: LA Stauffer Date: 6/19/97 Checked by: L.D. Estey Date: 6/19/97

Conclusions:

The results show that at the barometric breathing rate 19 of the passively ventilated tanks and eight of the actively ventilated tanks will exceed 25% of the LFL. This includes tanks 241-A-101, 241-A-103, 241-B-201, 241-B-202, 241-B-203, 241-B-204, 241-BY-107, 241-C-101, 241-C-103, 241-C-107, 241-S-101, 241-T-201, 241-T-202, 241-T-203, 241-T-204, 241-U-103, 241-U-105, 241-U-108, 241-U-109, 241-C-105, 241-C-106, 241-SX-107, 241-SX-108, 241-SX-110, 241-SX-111, 241-SX-114. Of these tanks, tank 241-SX-108 will take the shortest time, 17 days, to reach 25% of the LFL.

References:

- Crippen, M. D., 1993, *Barometric Pressure Variations*, WHC-EP-0651, Westinghouse Hanford Company, Richland, Washington.
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- Wilkins, N. E., 1997, *Results of Vapor Space Monitoring of Flammable Gas Watch List Tanks*, HNF-SD-WM-TI-797, Rev. 1, Lockheed Martin Hanford Corporation, Richland, Washington.

Author LA Stauffer Date 6/19/97 Checked by S. D. Eddy Date 6/19/97

Appendix A Steady State Gas Composition

Prepared by: W. B. Barton

In order to assess the flammable gas hazard of a tank, the composition of the flammable gas in the headspace must be established. The gases of concern have been identified as hydrogen (H_2), ammonia (NH_3), and hydrocarbons as fuels and oxygen in air, and nitrous oxide (N_2O). It has been reported in the literature that N_2O disproportionates with high releases of energy, even in the absence of fuels. However, this reaction requires either high temperatures or a very energetic (>5000 joules) ignition source. Recent work by Shepherd has shown that in dilute air mixtures approaching the Lower Flammability Limit (LFL), N_2O does not significantly participate in the reaction and can be viewed as a diluent (Pfahl and Shepherd 1997). For the purposes of this discussion, N_2O will not be considered because we are investigating conditions approaching the LFL.

Hydrogen Hydrogen generation can be modeled using kinetic equations and assuming that all the gas generated is release to the dome space.

Ammonia Previous studies have attempted to model ammonia release/concentrations as a percentage of the hydrogen release. For the steady state condition, this approach is flawed since the two gases have fundamentally different retention and release mechanisms. The unique characteristic of ammonia is that in tank waste conditions it is a soluble gas. This results in greater than 99 percent of the ammonia present in a tank being stored in solutions as either an ion or a dissolved gas depending on the pH of the solution. In addition, because it is stored in solution, the total inventory of ammonia in the waste can be orders of magnitude higher than for insoluble gases such as hydrogen. Unlike hydrogen, ammonia's predominant release mechanism under steady state conditions is governed by equilibrium between the vapor and liquid phases and the rate of liquid phase mass transfer from the ammonia rich lower levels of the tank to the interface. This rate of mass transfer is slow with respect to the establishment of vapor/liquid equilibrium at the interface.

Since the waste can hold a very large inventory of ammonia, and release concentrations are governed by equilibrium, it is not appropriate to try to model domespace concentrations based on the rate of generation of ammonia and an assumption of no retention such as is used for hydrogen. Fortunately a large body of measurements of tank dome space ammonia concentrations is available. Table A-1 shows a listing of the measured domespace ammonia values for 114 single-shell tanks. This data was retrieved for the Tank Characterization Database (Schaffer 1997). In cases where more than one measurement was reported, the values are averages. The largest value reported is 988 parts per million volume (ppmv) in tank 241-U-106. The distribution of the measured concentrations is shown in Figure A-1. Based on these results it seems reasonable to conclude that the highest expected steady state ammonia concentration in the unsampled tank should not exceed two times the highest reported value. Therefore, for tanks where no ammonia data is available a default headspace concentration of 2,000 ppmv will be used. This is less than 1.3% of the ammonia LFL.

Author LA Stanger Date 6/19/97 Checked by S. D. Eddy Date 6/19/97

Table A-1. Single-Shell Tank Ammonia Concentrations

Tank	NH ₃ (ppmv)	Tank	NH ₃ (ppmv)	Tank	NH ₃ (ppmv)
241-A-101	753.8	241-BY-110	401.3	241-T-107	124.5
241-A-102	256.5	241-BY-111	59.2	241-T-108	20.0
241-A-103	264.0	241-BY-112	63.3	241-T-109	5.0
241-A-105	30.0	241-C-101	98.5	241-T-110	108.2
241-A-106	150.0	241-C-102	188.8	241-T-111	225.5
241-AX-101	41.7	241-C-103	327.4	241-T-112	40.0
241-AX-103	41.5	241-C-104	44.0	241-T-202	8.0
241-AX-102	34.0	241-C-105	2.5	241-TX-101	20.0
241-B-101	20.0	241-C-106	2.5	241-TX-102	100.0
241-B-102	4.8	241-C-107	68.4	241-TX-103	100.0
241-B-103	7.4	241-C-108	2.7	241-TX-105	19.8
241-B-105	5.6	241-C-109	10.1	241-TX-106	200.0
241-B-107	21.3	241-C-110	124.0	241-TX-109	400.0
241-B-108	30.0	241-C-111	5.6	241-TX-110	700.0
241-B-109	35.0	241-C-112	22.7	241-TX-111	611.7
241-B-110	50.0	241-S-101	772.8	241-TX-112	100.0
241-B-111	25.0	241-S-102	582.4	241-TX-113	20.0
241-B-202	2.7	241-S-103	300.0	241-TX-114	150.0
241-BX-101	50.0	241-S-104	25.0	241-TX-115	100.0
241-BX-102	2.6	241-S-105	36.5	241-TX-117	25.0
241-BX-103	90.8	241-S-106	36.5	241-TX-118	32.8
241-BX-104	246.0	241-S-107	183.0	241-TY-101	15.7
241-BX-105	146.8	241-S-108	25.7	241-TY-102	4.1
241-BX-106	46.8	241-S-109	44.9	241-TY-103	49.2
241-BX-106	50.0	241-S-110	147.5	241-TY-104	61.0
241-BX-107	82.8	241-S-111	121.5	241-TY-105	2.5
241-BX-109	20.0	241-S-112	88.7	241-U-101	100.0
241-BX-110	63.1	241-SX-101	3.8	241-U-102	400.0
241-BX-111	62.8	241-SX-102	15.5	241-U-103	730.2
241-BY-101	60.3	241-SX-103	76.8	241-U-105	325.3
241-BY-102	175.0	241-SX-104	24.7	241-U-106	988.3
241-BY-103	26.3	241-SX-105	27.5	241-U-107	452.7
241-BY-104	247.8	241-SX-106	178.8	241-U-108	691.5
241-BY-105	43.2	241-SX-109	16.8	241-U-109	577.3
241-BY-106	74.4	241-T-101	50.0	241-U-111	675.8
241-BY-107	972.0	241-T-104	105.3	241-U-112	307.8
241-BY-108	866.3	241-T-105	150.0	241-U-203	0.9
241-BY-109	40.0	241-T-106	100.0	241-U-204	0.1

Figure A-1. Single-Shell Tank Ammonia Concentrations

Author LA Stauffer Date 6/19/97 Checked by L N. Eddy Date 6/19/97

Methane and other Hydrocarbons The gaseous hydrocarbons which have been measured are generally insoluble gases. For purposes of this discussion we will use methane to represent all gaseous hydrocarbons since it is the largest single species. To be properly represented they would best be modeled by using generation equations and an assumption of no retention. However, this information is not available. Therefore, another approach to modeling the steady state methane concentration is needed. As with the other constituents, methane has been measured in a number of tanks. Two basic methods of measuring were used. The first was using SUMMA¹ canisters to extract a sample from the tank that was sent to a laboratory and analyzed. This method gives very specific results by species but in many cases had minimum detection limits that were too high to provide meaningful data. The second method used an occupational safety organic vapor monitor which reports total organic vapor as methane equivalents. Since the highest results reported is less than 72 ppmv with most of the results less than 20 ppmv, the conservative default value of 150 ppmv will be used for tanks with no sample data available.

Using LeChatlier's Rule and the above mentioned concentrations for ammonia and methane, hydrogen to 25% of the LFL can be calculated using the following equations.

$$LFL_{\text{Mixture}} = 1 / (f_{H_2} / LFL_{H_2} + f_{NH_3} / LFL_{NH_3} + f_{CH_4} / LFL_{CH_4} + \dots)$$

$$\%LFL_{\text{Mixture}} = \%LFL_{H_2} + \%LFL_{NH_3} + \%LFL_{CH_4} + \dots$$

The LFLs for hydrogen, ammonia, and methane in air are 4.0%, 15.5%, and 5.0%, respectively. Applying these values into the equation gives a hydrogen concentration at 25% of the LFL of approximately 9,300 ppmv and an LFL of hydrogen of 37,000 ppmv.

References:

- Pfahl, U. and J. Shepherd, 1997, *Flammability and Flame Propagation in H₂-N₂O-CH₄-NH₃-O₂-N₂ Mixtures*, Explosion Dynamics Laboratory Report FM97-4, Graduate Aeronautical Laboratories, California Institute of Technology, Pasadena, California.
- Schaffer, J. B., 1997, *Tank Characterization Database*, HISI Registration Number 11578, Lockheed Martin Hanford Corporation, Richland, Washington.

¹SUMMA is a trademark of Molectrics, Inc.

CHECKLIST FOR PEER REVIEW

Document Reviewed: *HNF-SD-WM-CN-116 Rev. 0*

Scope of Review:

Yes	No	NA	
☐	☐	☒	* Previous reviews complete and cover analysis, up to scope of this review, with no gaps.
☒	☐	☐	Problem completely defined.
☐	☐	☒	Accident scenarios developed in a clear and logical manner.
☒	☐	☐	Necessary assumptions explicitly stated and supported.
☒	☐	☐	Computer codes and data files documented.
☒	☐	☐	Data used in calculations explicitly stated in document.
☐	☒	☐	Data checked for consistency with original source information as applicable.
☒	☐	☐	Mathematical derivations checked including dimensional consistency of results.
☒	☐	☐	Models appropriate and used within range of validity or use outside range of established validity justified.
☒	☐	☐	Hand calculations checked for errors. Spreadsheet results should be treated exactly the same as hand calculations.
☒	☐	☐	Software input correct and consistent with document reviewed.
☒	☐	☐	Software output consistent with input and with results reported in document reviewed.
☒	☐	☐	Limits/criteria/guidelines applied to analysis results are appropriate and referenced. Limits/criteria/guidelines checked against references.
☐	☐	☒	Safety margins consistent with good engineering practices.
☒	☐	☐	Conclusions consistent with analytical results and applicable limits.
☒	☐	☐	Results and conclusions address all points required in the problem statement.
☐	☐	☒	Format consistent with appropriate NRC Regulatory Guide or other standards
☒	☐	☐	* Review calculations, comments, and/or notes are attached.
☒	☐	☐	Document approved.

Scott D. Estey *Scott D. Estey*
 Reviewer (Printed Name and Signature)

6/19/97
 Date

* Any calculations, comments, or notes generated as part of this review should be signed, dated and attached to this checklist. Such material should be labeled and recorded in such a manner as to be intelligible to a technically qualified third party.

Expressing hydrogen generation rate (Gr) as a function of ventilation rate (Vr) and hydrogen concentration (%H₂):

$$\begin{aligned}\frac{Gr}{Gr + Vr} &= \frac{\%H_2}{100} & Gr &= \frac{\%H_2}{100} \cdot (Gr + Vr) & Gr &= \frac{\%H_2}{100} \cdot Gr = \frac{\%H_2}{100} \cdot Vr & Gr \cdot \left(1 - \frac{\%H_2}{100}\right) &= \frac{\%H_2}{100} \cdot Vr \\ Gr &= \frac{\frac{\%H_2}{100} \cdot Vr}{\left(1 - \frac{\%H_2}{100}\right)} & Gr &= \left(\frac{\frac{\%H_2}{100} \cdot Vr}{\left(1 - \frac{\%H_2}{100}\right)}\right) \cdot \left(\frac{1}{\frac{\%H_2}{100}}\right) & Gr &= \left(\frac{\frac{\%H_2}{100} \cdot Vr}{\left(1 - \frac{\%H_2}{100}\right)}\right) \cdot \left(\frac{100}{\%H_2}\right) & Gr &= \frac{Vr}{\left(\frac{100}{\%H_2} - 1\right)}\end{aligned}$$

Expressing time (t) as a function of generation rate (Gr), ventilation rate (Vr), hydrogen concentration (%H₂), and tank headspace volume (vol):

$$\begin{aligned}\frac{\%H_2}{100} &= \frac{Gr - \left[Gr - (Gr + Vr) \cdot \frac{\%H_{2,0}}{100}\right] \cdot \exp\left[-\left(\frac{Gr + Vr}{vol}\right) \cdot t\right]}{Gr + Vr} \\ \%H_2 &= \frac{100}{Gr + Vr} \cdot \left[Gr - \left[Gr - (Gr + Vr) \cdot \frac{\%H_{2,0}}{100}\right] \cdot \exp\left[-\left(\frac{Gr + Vr}{vol}\right) \cdot t\right]\right] \\ \exp\left[-\left(\frac{Gr + Vr}{vol}\right) \cdot t\right] &= \frac{\frac{\%H_2}{100} \cdot (Gr + Vr) - Gr}{\left[Gr - (Gr + Vr) \cdot \frac{\%H_{2,0}}{100}\right]} & \exp\left[-\left(\frac{Gr + Vr}{vol}\right) \cdot t\right] &= \frac{\frac{\%H_2}{100} \cdot (Gr + Vr) - Gr}{(Gr + Vr) \cdot \frac{\%H_{2,0}}{100} - Gr} \\ -\left(\frac{Gr + Vr}{vol}\right) \cdot t &= \ln\left[\frac{\frac{\%H_2}{100} \cdot (Gr + Vr) - Gr}{(Gr + Vr) \cdot \frac{\%H_{2,0}}{100} - Gr}\right] & t &= \left(\frac{vol}{Gr + Vr}\right) \cdot \ln\left[\frac{\frac{\%H_2}{100} \cdot (Gr + Vr) - Gr}{(Gr + Vr) \cdot \frac{\%H_{2,0}}{100} - Gr}\right] \\ t &= \left(\frac{vol}{Gr + Vr}\right) \cdot \ln\left[\frac{(Gr + Vr) \cdot \frac{\%H_2}{100} - Gr}{(Gr + Vr) \cdot \frac{\%H_{2,0}}{100} - Gr}\right]\end{aligned}$$

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Sample calculation for tank 241-A-101:

$$V_r := 10 \frac{\text{ft}^3}{\text{min}} \quad \%H_2 := 0.1043 \quad Vol := 41551 \cdot \text{ft}^3 \quad V_{r_{bb}} := 0.13 \frac{\text{ft}^3}{\text{min}}$$

Calculated hydrogen generation rate (Gr):

$$Gr := \frac{V_r}{\left[\frac{1}{\left(\frac{\%H_2}{100} \right)} - 1 \right]} \quad \left(\frac{\text{ft}^3}{\text{min}} \right) = 0.0104$$

Time to reach 25% of LFL ($\%H_2 = 0.93$):

$$t_{25} := - \left(\frac{Vol}{Gr + V_{r_{bb}}} \right) \cdot \ln \left[\frac{(Gr + V_{r_{bb}}) \cdot \frac{0.93}{100} - Gr}{(Gr + V_{r_{bb}}) \cdot \frac{0.1043}{100} - Gr} \right] \quad \frac{t_{25}}{(\text{day})} = 24.555$$

Time to reach 100% of LFL ($\%H_2 = 3.7$):

$$t_{100} := - \left(\frac{Vol}{Gr + V_{r_{bb}}} \right) \cdot \ln \left[\frac{(Gr + V_{r_{bb}}) \cdot \frac{3.7}{100} - Gr}{(Gr + V_{r_{bb}}) \cdot \frac{0.1043}{100} - Gr} \right] \quad \frac{t_{100}}{(\text{day})} = 138.563$$

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Sample calculation for tank 241-SX-101:

$$V_r := 40 \cdot \frac{\text{ft}^3}{\text{min}} \quad \%H_2 := 0.0008 \quad Vol := 109662 \cdot \text{ft}^3 \quad V_{r_{bb}} := 0.34 \cdot \frac{\text{ft}^3}{\text{min}}$$

Calculated hydrogen generation rate (Gr):

$$Gr := \frac{V_r}{\left[\frac{1}{\left(\frac{\%H_2}{100} \right)} - 1 \right]} \quad \left(\frac{\text{ft}^3}{\text{min}} \right) = 3.2 \cdot 10^{-4}$$

Time to reach 25% of LFL ($\%H_2 = 0.93$):

$$t_{25} := - \left(\frac{Vol}{Gr + V_{r_{bb}}} \right) \cdot \ln \left[\frac{(Gr + V_{r_{bb}}) \cdot \frac{0.93}{100} - Gr}{(Gr + V_{r_{bb}}) \cdot \frac{0.1043}{100} - Gr} \right] \quad \frac{t_{25}}{(\text{day})} = -984.454$$

The negative result indicates that tank 241-SX-101 can't reach a hydrogen concentration of 0.93%.

Time to reach 100% of LFL ($\%H_2 = 3.7$):

$$t_{100} := - \left(\frac{Vol}{Gr + V_{r_{bb}}} \right) \cdot \ln \left[\frac{(Gr + V_{r_{bb}}) \cdot \frac{3.7}{100} - Gr}{(Gr + V_{r_{bb}}) \cdot \frac{0.1043}{100} - Gr} \right] \quad \frac{t_{100}}{(\text{day})} = -1.312 \cdot 10^3$$

The negative result indicates that tank 241-SX-101 can't reach a hydrogen concentration of 3.7%.

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