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AN ORDER-OF-MAGNITUDE ESTIMATION OF BENZENE CONCENTRATION IN SALTSTONE VAULT

A. S. Choi

February 2005

Immobilization Technology Section
Savannah River National Laboratory
Aiken, SC 29808

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EXECUTIVE SUMMARY

The contents of Tank 48 that include the tetraphenylborate (TPB) precipitates of potassium and cesium will be grouted and stored in the Saltstone vault. The grouting process is exothermic, which should accelerate the decomposition of TPB precipitates eventually to benzene. Because the vault is not currently outfitted with an active ventilation system, there is a concern that a mixture of flammable gases may form in the vapor space of each cell filled with the curing grout. The purpose of this study was to determine if passive breathing induced by the diurnal oscillations of atmospheric pressure would provide any mitigating measure against potential flammability.

Specifically, it was requested that a set of algorithms be developed that would predict the equilibrium concentration of benzene as a function of benzene generation rate, fill height, and the amplitude of the barometric pressure oscillations. These algorithms were to be derived based on several simplifying assumptions so that order of magnitude estimates could be made quickly for scoping purposes. This memo documents the resulting algorithms along with those key assumptions made. These algorithms were then applied to simulate several test cases, including the baseline case where the cell was filled to the maximum height of 25 ft at the bulk benzene generation rate of 3.4 g/hr.

Based on the results of this study, the following conclusions can be drawn:

- At 3.4 g/hr benzene generation rate, passive breathing induced by the diurnal oscillations of atmospheric pressure is sufficient enough to limit the maximum benzene concentration below 50% of the LFL, thus mitigating potential flammability in the Saltstone vault vapor space without installing any active ventilation system.

- At 34 g/hr benzene generation rate, it is estimated to take 23 and 5 days to reach 100% and 25% of the LFL, respectively, at 25 ft fill height. At 17 ft fill height, it is estimated to take 30 days to reach 25% of the LFL with the maximum equilibrium concentration of benzene at just below the LFL.

- At 34 g/hr benzene generation rate, the advantage of atmospheric breathing over the non-breathing case becomes only marginal at 25 ft fill height.

- At benzene generation rates higher than 340 g/hr, the atmospheric breathing no longer has any positive impact on the time to LFL at both 17 and 25 ft fill levels.

The following algorithms are further recommended for a quick estimation of the equilibrium benzene mole fraction y_{BZN} in the Saltstone Vault vapor space at given benzene generation rate $\dot{m}_{BZN}$ in *g/hr* without any active ventilation device:

- At 25 ft fill height: $$\frac{1}{y_{BZN}} = 0.37627 + \frac{586.581}{\dot{m}_{BZN}}$$

- At 17 ft fill height: $$\frac{1}{y_{BZN}} = 0.46973 + \frac{2{,}915.163}{\dot{m}_{BZN}}$$

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ACRONYMS

AB	atmospheric breathing
EXH	exhaling
INH	inhaling
LFL	lower flammability limit
NAB	no atmospheric breathing
TPB	tetraphenylborate

1.0 INTRODUCTION AND BACKGROUND

The contents of Tank 48 that currently include the tetraphenylborate (TPB) precipitates of potassium and cesium will be grouted and stored in the Saltstone vault. The grouting process is exothermic, which should accelerate the decomposition of TPB precipitates eventually to benzene. Since the vault is not currently outfitted with an active ventilation system, there is a concern that a mixture of flammable gases may form in the vapor space of each cell filled with the curing grout. The purpose of this study was to determine if the passive breathing induced by the diurnal oscillations of the barometric pressure would provide any mitigating measure against potential flammability.

Specifically, it was requested that a set of algorithms be developed that would predict the equilibrium concentration of benzene as a function of benzene generation rate, fill height, and the amplitude of the barometric pressure oscillations. These algorithms were to be derived based on several simplifying assumptions so that order of magnitude estimates could be made quickly for scoping purposes. This report documents the resulting algorithms along with those key assumptions made. These algorithms were then applied to simulate several test cases, including the baseline case where the cell was filled to the maximum height of 25 ft and the rate of benzene generation was fixed at 3.4 g/hr.

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2.0 ANALYSIS

Figure 1 shows a schematic of one of the six cells in the Saltstone Vault #4 that are to be filled with the Tank 48 grout. Each 100 ft by 100 ft cell is 26 ft high at the outer wall (H_o) and 28 ft high (H_i) at the inner wall, and the walls are 18-inch thick. When the wall thickness is taken into consideration, the internal cell dimensions become 98.5 ft by 98.5 ft for a total cell volume of 261,961 ft^3.[1] The roof is 4 to 6 inch thick and has two diagonally-opposed 12-inch diameter vents, and the total vent opening is equivalent to less than 0.02% of the surface area of the roof.

Also shown is the assumed sinusoidal variation of the barometric pressure due to diurnal temperature variations. The amplitude of the sinusoidal pressure oscillations is set at 2.5 mbar about the mean pressure of 1,103 mbar.[1] When the atmospheric pressure begins to fall in the evening, the system will exhale, i.e., the vapor in the cell will discharge, while the system will inhale when the atmospheric pressure begins to rise in the morning. The amplitude of atmospheric pressure oscillations is generally higher with the passage of weather fronts. However, they were not considered in this study, since they occur over a longer time-scale so that the average rate of pressure oscillations may become comparable to or even smaller than the diurnal rate.

The main focus of this work is to develop an algorithm for the equilibrium concentration of benzene in the remaining vapor space of each cell after it is filled with grout to a height *h*. The benzene that could potentially accumulate in the void spaces within the grout matrix is not the area of concern for this work.

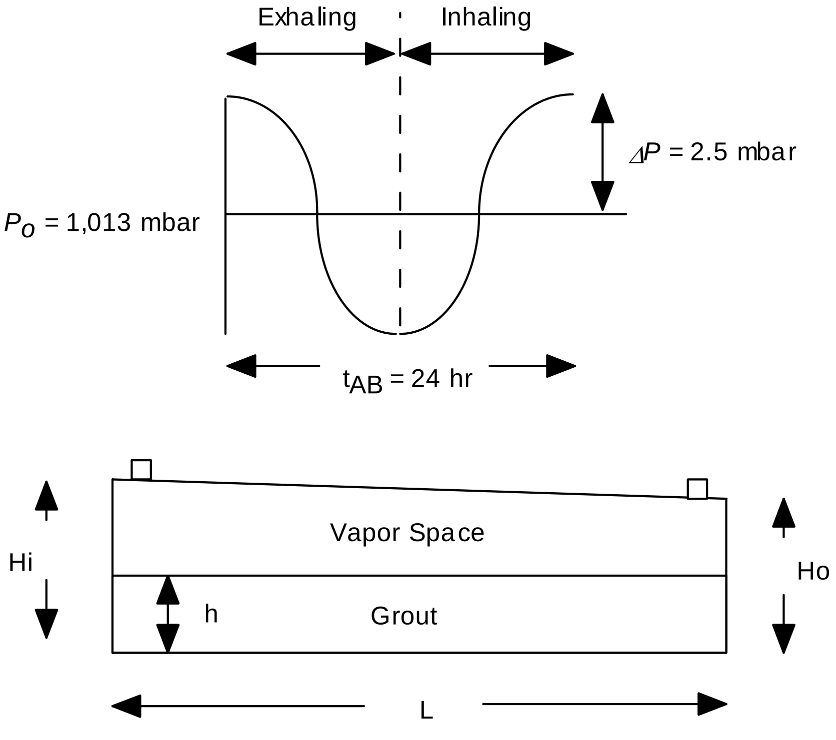

Figure 1. Schematic of Saltstone Vault Cell and Barometric Pressure Oscillation.

2.1 Assumptions

1. The rate of benzene generation is constant, i.e., time-invariant, at all fill levels.
2. Benzene is the only gas evolving from the grout matrix.
3. The initial concentration of benzene in the vapor space is zero.
4. The grout matrix covers the entire cross-sectional area of the cell and forms an impermeable boundary with no cracks. This allows the vapor space volume to be calculated as the total cell volume minus the volume of grout matrix.
5. The vapor space is perfectly mixed so the pressure, temperature and concentration are uniform throughout.
6. The diurnal atmospheric pressure oscillations are sinusoidal with the amplitude of 2.5 mbar.
7. Atmospheric breathing occurs uniformly in time during each of the exhaling and inhaling periods.

2.2 Atmospheric Breathing through Porous Media

Atmospheric breathing is induced by the pressure gradient imposed between the Saltstone vault and the surrounding atmosphere and its rate can be estimated from the results of the analysis by Auer et al.[2] They studied the transport of subsurface contaminants induced by the atmospheric pressure perturbation that varies harmonically as $P_{z=0} - P_o = \Delta P e^{i\omega t}$,[3] as shown in Figure 2, and derived the following approximation for the pore-scale air velocity at depth z:

$$v \cong -\frac{\Delta P}{P_o}(L-z)\left(\frac{2\pi}{t_{AB}}\right)\sin\left(\frac{2\pi}{t_{AB}}t\right) \qquad \textbf{Equation 1}$$

where L is the total depth to the impermeable lower boundary, ΔP the amplitude of the sinusoidal barometric pressure oscillations, P_o the mean atmospheric pressure, and t_{AB} the period of atmospheric breathing (AB). The resulting subsurface pressure will be attenuated to some degree depending on the permeability of the porous medium and further show some time delay. Eq. (1) is valid when the pressure attenuation is relatively small, and it clearly shows that under those conditions the actual air velocity through the porous medium or "barometric pumping" depends on the relative pressure perturbation ($\Delta P/P_o$) and its period and the depth of the porous medium but not on the physical properties of the porous medium. The Darcy velocity is then calculated as the pore-scale velocity times the porosity (ϕ).

The vertical displacement of air or soil vapor resulting from the barometric pumping can be obtained by integrating Eq. (1) from $t = 0$ to $t = t$ as follows:

$$\begin{aligned}\Delta z &= z(t) - z(0)\\ &\cong \frac{\Delta P}{P_o}(L-z)\cos\left(\frac{2\pi}{t_{AB}}t\right) - \frac{\Delta P}{P_o}(L-z)\cos\left(\frac{2\pi}{t_{AB}}(0)\right) \qquad \textbf{Equation 2}\\ &\cong -\frac{\Delta P}{P_o}(L-z)\left[1-\cos\left(\frac{2\pi}{t_{AB}}t\right)\right]\end{aligned}$$

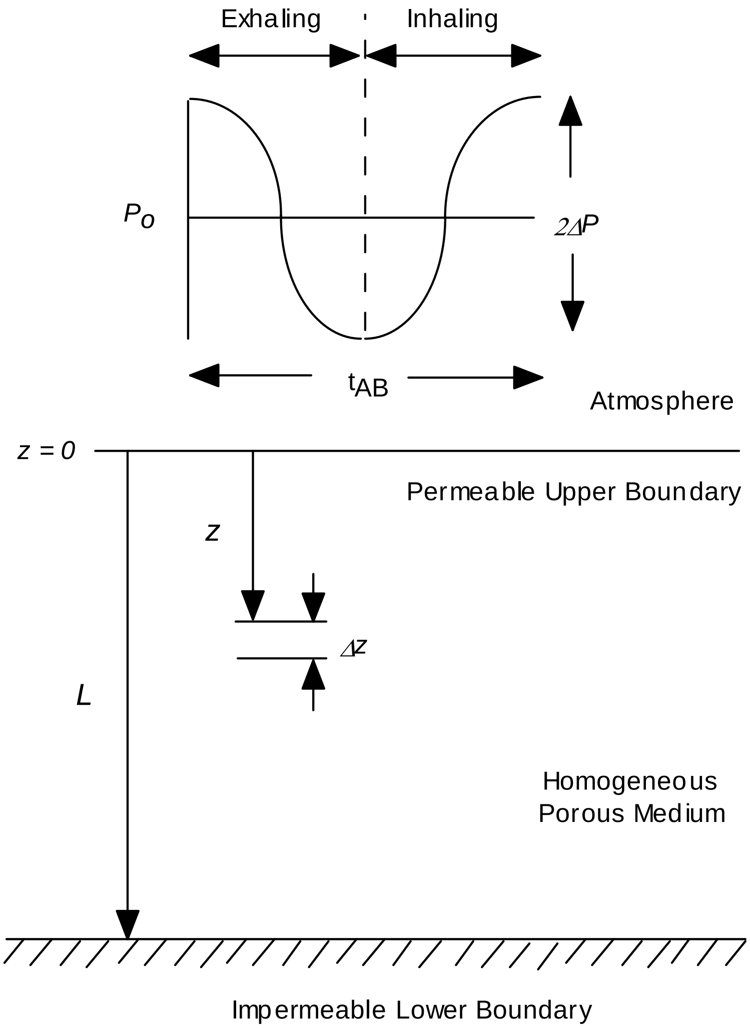

Figure 2. Barometric Pressure Induced Subsurface Transport Studied by Auer et al.[2]

As expected, Eq. (2) shows that at a given time t the displacement is the largest just beneath the surface at $z = 0$ and decreases linearly to zero as the depth is increased to L. Furthermore, the maximum displacement of $-2(\Delta P/P_o)(L-z)$ will occur at $t = t_{AB}/2$, where the negative sign indicates that the displacement is in the upward direction toward the surface. Therefore, the deepest layer of air evacuated during a period of barometric pumping can be calculated by equating the maximum displacement to its corresponding position:

$$z_{mbp} \quad = \quad 2\left(\frac{\Delta P}{P_o}\right)\left(L - z_{mbp}\right) \qquad \textbf{Equation 3}$$

where the subscript mbp stands for the maximum barometric pumping. If the amplitude of the barometric shift is defined as $L_{pump} = (\Delta P/P_o)L$, as was done in Reference 2, and substitute it into Eq. (3), we obtain the following:

$$z_{mbp} = \frac{2L_{pump}}{1+2\dfrac{L_{pump}}{L}}$$ **Equation 4**

Furthermore, we obtain the following equality from the definition of L_{pump}:

$$\frac{L_{pump}}{L} = \frac{\Delta P}{P_o}$$ **Equation 5**

Since $\Delta P/P_o \approx 0.005$ for typical diurnal barometric oscillations, $L_{pump}/L \approx 0$ and Eq. (4) is reduced to:

$$\begin{aligned} z_{mbp} &= 2L_{pump} \\ &= 2\left(\frac{\Delta P}{P_o}\right)L \end{aligned}$$ **Equation 6**

Finally, the average velocity of displacement during an exhaling mode between $t = 0$ and $t = t_{AB}/2$ can be calculated by dividing the total displacement by the duration:

$$\begin{aligned} \bar{v}_{EXH} &= \frac{-2\left(\dfrac{\Delta P}{P_o}\right)L}{\dfrac{t_{AB}}{2}} \\ &= -4\left(\frac{\Delta P}{P_o}\right)\left(\frac{L}{t_{AB}}\right) \end{aligned}$$ **Equation 7**

where the subscript $_{EXH}$ denotes "exhaling," and the negative sign was inserted because the displacement is in the negative z direction toward the surface during an exhaling mode. Likewise, the average velocity of displacement during an inhaling mode between $t = t_{AB}/2$ and $t = t_{AB}$ can be shown as:

$$\bar{v}_{INH} = 4\left(\frac{\Delta P}{P_o}\right)\left(\frac{L}{t_{AB}}\right)$$ **Equation 8**

where the subscript $_{INH}$ denotes "inhaling." It should be noted here that identical expressions for the atmospheric breathing velocities can also be obtained by integrating Eq. (1) directly. For example, the average exhaling velocity can be calculated by integrating from $t = 0$ to $t = t_{AB}/2$:

$$\begin{aligned}\bar{v}_{EXH} &= \frac{\int_0^{\frac{t_{AB}}{2}} -\frac{\Delta P}{P_o}(L-z)\left(\frac{2\pi}{t_{AB}}\right)\sin\left(\frac{2\pi}{t_{AB}}t\right)dt}{\frac{t_{AB}}{2}} \\ &= \frac{\left[\frac{\Delta P}{P_o}(L-z)\cos\left(\frac{2\pi}{t_{AB}}t\right)\right]_0^{\frac{t_{AB}}{2}}}{\frac{t_{AB}}{2}} \\ &= -4\left(\frac{\Delta P}{P_o}\right)\left(\frac{L-z_{mbp}}{t_{AB}}\right)\end{aligned}$$

Equation 9

Substituting Eq. (6) for z_{mbp}, we obtain:

$$\begin{aligned}\bar{v}_{EXH} &= -4\left(\frac{\Delta P}{P_o}\right)\left(\frac{L}{t_{AB}}\right)\left(1-2\frac{\Delta P}{P_o}\right) \\ &\cong -4\left(\frac{\Delta P}{P_o}\right)\left(\frac{L}{t_{AB}}\right)\end{aligned}$$

which is identical to Eq. (7) derived earlier. Likewise, the average inhaling velocity given in Eq. (8) can be obtained by integrating Eq. (1) from $t = t_{AB}/2$ to $t = t_{AB}$. Note that in this approach the signs of respective breathing velocities are automatically taken care of.

2.3 Application to Saltstone Vault

As stated earlier, it can be concluded from the work by Auer et al. that when the attenuation is relatively insignificant, the barometric pumping depends only on the relative pressure perturbation ($\Delta P/P_o$) and its period and the depth or size of the porous medium but not on its physical properties such as permeability.[2] Therefore, the fact that the pressure attenuation in the Saltstone vault vapor space will be negligible should work in favor of further substantiating the applicability of the preceding analysis to the atmospheric breathing in the Saltstone vault.

The additional similarities between the two systems shown in Figure 1 and Figure 2 that justify the application include:

- Both systems are subject to the sinusoidal pressure perturbations.
- Both systems have an impermeable lower boundary.
- Both systems have homogeneous media.
- Vapor transport in both systems can be approximated as one-dimensional.

However, before we apply Eqs. (7) and (8) to the Saltstone vault, the linear breathing velocities, $\bar{v}_{EXH}$ *and* $\bar{v}_{INH}$, are replaced with the volumetric flow rate Q by substituting the cell vapor space volume V for the depth L as:

$$Q_{AB} = 4\left(\frac{\Delta P}{P_o}\right)\left(\frac{V}{t_{AB}}\right) \qquad \textbf{Equation 10}$$

Eq. (10) represents the average volumetric rates of both exhaling and inhaling modes, and the only difference between the two is in the sign or direction, as shown in Eqs. (7) and (8). The substitution was made possible, since the cell vapor space has a constant cross-sectional area of 98.5 ft by 98.5 ft.

2.4 Derivation of Algorithms

Since the direction of atmospheric breathing reverses twice during a 24-hour period, the mass balance must be performed separately for the exhaling and inhaling modes.

2.4.1 Exhaling _1

Figure 3 shows a schematic of gas flows in and out of the cell vapor space during an exhaling mode as the ambient temperature begins to fall in the evening hours.

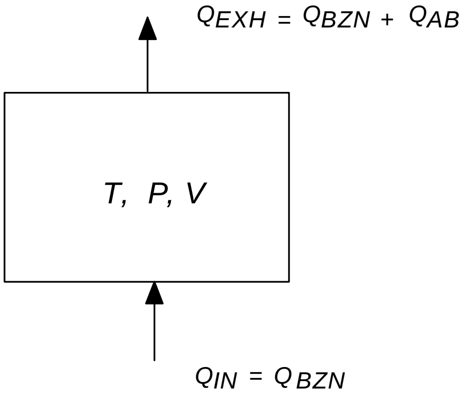

Figure 3. Schematic of Inlet and Outlet Flows during Exhaling_1.

The relevant benzene mole balance equation is:

$$V\frac{dC_{BZN}}{dt} = Q_{BZN}\left(\frac{P}{RT}\right)y_{BZN,IN} - Q_{EXH}\left(\frac{P}{RT}\right)y_{BZN} \qquad \textbf{Equation 11}$$

where C_{BZN} is the molar concentration of benzene in mole/ft^3, Q_{BZN} the benzene generation rate in ft^3/hr, Q_{EXH} the exhaling rate in ft^3/hr, and y the mole fraction. Note that $y_{BZN,IN} = 1$ from Assumption #2. Further applying the ideal gas law, $C_{BZN} = y_{BZN}P/RT$, and substituting the net exhaling flow rate, $Q_{EXH} = Q_{BZN} + Q_{AB}$, Eq. (4) can be re-written as:

$$\frac{dy_{BZN}}{dt} + \frac{Q_{BZN} + Q_{AB}}{V}y_{BZN} = \frac{Q_{BZN}}{V} \qquad \textbf{Equation 12}$$

It is noted in Figure 3 that when $\Delta P = 0$, $Q_{AB} = 0$ and $Q_{EXH} = Q_{BZN}$, as it should to maintain a constant pressure in the cell. Eq. (1) is a first-order linear differential equation and has the following solution:

$$y_{BZN}(t) \quad = \quad (y_{BZN}(o) - QFRC_{BZN\_EXH1})\exp(-\frac{t}{\tau_{EXH1}}) + QFRC_{BZN\_EXH1} \qquad \textbf{Equation 13}$$

where $y_{BZN}(o)$ is the initial mole fraction of benzene in the cell vapor space, $QFRC_{BZN\_EXH1}$ is the volume fraction of benzene in the outlet flow during the exhaling_1 mode defined as:

$$QFRC_{BZN\_EXH1} \quad = \quad \frac{Q_{BZN}}{Q_{BZN} + Q_{AB}} \qquad \textbf{Equation 14}$$

and τ is the first-order time constant for the exhaling_1 mode defined as:

$$\tau_{EXH1} \quad = \quad \frac{V}{Q_{BZN} + Q_{AB}} \qquad \textbf{Equation 15}$$

It should be noted here that the time-dependent atmospheric breathing rate similar to Eq. (1) could have been substituted for Q_{AB} in Eq. (12) instead of the average rate given by Eq. (10). However, although this would have made the resulting solution mathematically more rigorous, it would not necessarily reflect the reality any better, since the actual atmospheric pressure variations are not truly sinusoidal.

2.4.2 Exhaling_2

When $Q_{BZN} > Q_{AB}$, the system could still be exhaling, even though the ambient pressure is rising during the daytime, and the pressure gradient is imposed so as to induce inhaling. This is because the net inhaling flow, $Q_{INH} = Q_{AB} - Q_{BZN}$ is negative. Therefore, as shown in Figure 4, the rate of the net exhaling flow is calculated as $Q_{EXH} = Q_{BZN} - Q_{AB}$.

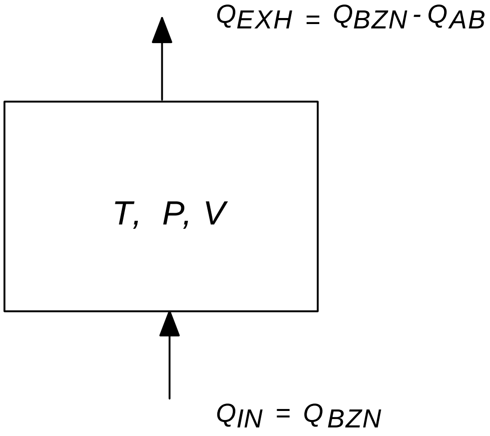

Figure 4. Schematic of Inlet and Outlet Flows during Exhaling_2.

Note that when $\Delta P = 0$, $Q_{AB} = 0$ and Q_{EXH} is again equal to Q_{BZN}, as it should in order to maintain a constant cell pressure. Since the flow directions are identical to those shown in Figure 3, the benzene mole balance equation is also identical to Eq. (11), and the relevant differential equation is:

$$\frac{dy_{BZN}}{dt} + \frac{Q_{BZN} - Q_{AB}}{V} y_{BZN} = \frac{Q_{BZN}}{V}$$ **Equation 16**

The solution to Eq. (16) is identical to Eq. (13) except that $QFRC_{BZN}$ during the exhaling_2 mode is now defined as:

$$QFRC_{BZN\_EXH2} = \frac{Q_{BZN}}{Q_{BZN} - Q_{AB}}$$ **Equation 17**

and τ is defined as:

$$\tau_{EXH2} = \frac{V}{Q_{BZN} - Q_{AB}}$$ **Equation 18**

2.4.3 Inhaling

When $Q_{BZN} < Q_{AB}$, the system will inhale as the ambient pressure rises during the daytime. As shown in Figure 5, the rate of the net inhaling flow is calculated as $Q_{INH} = Q_{AB} - Q_{BZN}$, and note that there are no outlet flows during this period. Furthermore, since Q_{BZN} is assumed to be positive in this study, Q_{AB} cannot be zero or $\Delta P \neq 0$.

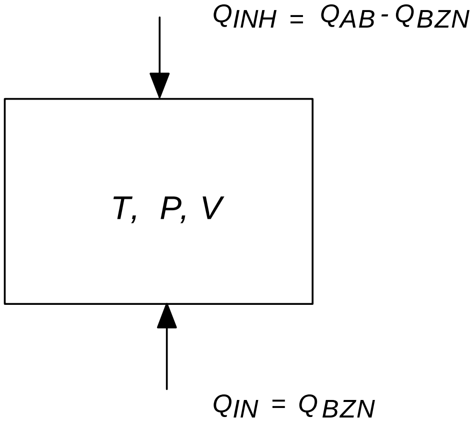

Figure 5. Schematic of Inlet and Outlet Flows during Inhaling.

The relevant benzene mole balance equation becomes:

$$V\frac{dC_{BZN}}{dt} = Q_{BZN}\left(\frac{P}{RT}\right) y_{BZN,IN} + Q_{INH}\left(\frac{P_o}{RT_o}\right) y_{BZN,o}$$ **Equation 19**

where Q_{INH} is the inhaling rate in ft^3/hr, and $y_{BZN,o}$ the mole fraction of benzene in ambient air, which is zero.

The resulting mole balance equation is then:

$$V\frac{dC_{BZN}}{dt} = Q_{BZN}\left(\frac{P}{RT}\right) \qquad \textbf{Equation 20}$$

It should be noted that the cell pressure was assumed to remain constant in the previous two exhaling modes, since the amplitude of diurnal barometric pressure variations is small, i.e., less than 0.5%. If the cell pressure is also assumed to remain constant during the inhaling mode, the solution to Eq. (20) is then simply:

$$y_{BZN}(t) = \frac{Q_{BZN}}{V}t + y_{BZN}(o) \qquad \textbf{Equation 21}$$

The implication of Eq. (21) is that the benzene concentration will increase linearly with time and the entire vapor space will be eventually filled with pure benzene. However, this scenario is not feasible because during the inhaling mode ambient air will infiltrate at a higher rate than that of the benzene generation, resulting in continuous dilution of the benzene concentration instead of concentrating it. To overcome this difficulty, the cell pressure was allowed to vary in this case, as there are no outlet flows unlike the exhaling modes. The relevant total mole balance equation is then:

$$\frac{dn_t}{dt} = Q_{BZN}\left(\frac{P}{RT}\right) + Q_{INH}\left(\frac{P_o}{RT_o}\right) \qquad \textbf{Equation 22}$$

where the subscript o denotes the ambient conditions. Since the degree of the cell pressure variations will be still relatively insignificant compared to the ambient pressure, it is assumed that $P_o \approx P$ and $T_o \approx T$. Upon further substituting $Q_{INH} = Q_{AB} - Q_{BZN}$, Eq. (22) is reduced to:

$$\frac{dn_t}{dt} = \frac{Q_{AB}}{V}n_t \qquad \textbf{Equation 23}$$

whose solution is simply:

$$n_t(t) = n_t(o)\exp(\frac{Q_{AB}}{V}t) \qquad \textbf{Equation 24}$$

where $n_t(o)$ is the total number of moles in the vapor space at $t = 0$. After substituting $C_{BZN} = n_t y_{BZN}/V$ in Eq. (20) followed by differentiation and further substitution of Eq. (24) for n_t, we have:

$$\frac{dy_{BZN}}{dt} + \frac{Q_{AB}}{V}y_{BZN} = \frac{Q_{BZN}}{V} \qquad \textbf{Equation 25}$$

whose solution is of the same form as Eq. (13) except that $QFRC_{BZN}$ for the inhaling mode is now defined as:

$$QFRC_{BZN\_INH} = \frac{Q_{BZN}}{Q_{AB}} \qquad \textbf{Equation 26}$$

and τ is defined as:

$$\tau_{INH} = \frac{V}{Q_{AB}} \qquad \textbf{Equation 27}$$

In summary, since the relevant differential mass balance equations are of the same form for both exhaling and inhaling modes, the general form of their solutions is also of the same form as Eq. (13); they only differ in the definitions of $QFRC_{BZN}$ and τ, as shown below:

Table 1. Volumetric Flow Fraction of Benzene and First-Order Time Constant.

Breathing Mode	$QFRC_{BZN}$	τ (hr)
Exhaling_1	$\frac{Q_{BZN}}{Q_{BZN}+Q_{AB}}$	$\frac{V}{Q_{BZN}+Q_{AB}}$
Exhaling_2	$\frac{Q_{BZN}}{Q_{BZN}-Q_{AB}}$	$\frac{V}{Q_{BZN}-Q_{AB}}$
Inhaling	$\frac{Q_{BZN}}{Q_{AB}}$	$\frac{V}{Q_{AB}}$

3.0 CASE STUDIES

It is important to note that each atmospheric breathing cycle can occur in pairs of either (*Exhaling_1 + Exhaling_2*) or (*Exhaling_1+ Inhaling*), depending on the relative magnitudes of the atmospheric breathing rate Q_{AB} and the benzene generation rate Q_{BZN}. The breathing pair (*Exhaling_2 + Inhaling*) is not physically feasible, since it would mean that ambient air never cools down.

In this work, four different breathing modes, including no atmospheric breathing, were considered at two different fill heights for a total of eight cases in all. The values of $QFRC_{BZN}$ and τ defined in Table 1 need to be determined first to simulate the cyclical variations of atmospheric breathing for each case. Table 2 summarizes the operating data used for the baseline case, including the diurnal barometric pressure change of 5 mbar or ±2.5 mbar about the mean value of 1,013 mbar.[1] The goal was to estimate the equilibrium benzene concentrations in the cell vapor space using the algorithms derived in the preceding section. The cell dimensions used in the case studies were given earlier in this report.

Table 2. Saltstone Vault Operating Data Used in Baseline Case.

Parameter	Value
Benzene generation rate, $\dot{m}_{BZN}$ (g/hr)	3.4
Maximum fill height, H_{max} (ft)	25
Minimum fill height, H_{min} (ft)	17
Maximum vapor space temperature, T_{max} (°C)	95
Period of atmospheric breathing, t_{AB} (hr)	24
Amplitude of barometric pressure oscillation, ΔP (mbar)	2.5
Mean barometric pressure, P_o (mbar)	1,013

3.1 No Atmospheric Breathing

This case was run to quantify the relative impact of atmospheric breathing on the equilibrium benzene concentration and the time to LFL. In the absence of atmospheric breathing, the cell vapor must be discharged to the atmosphere at the same volumetric rate as that of benzene entering from the grout matrix. Therefore, the mode of gas flows is identical to that of Exhaling_1 shown in Figure 3, except that $Q_{EXH} = Q_{BZN}$. The concentration of benzene is then given as:

$$y_{BZN}(t) \quad = \quad (y_{BZN}(o) - 1)\exp(-\frac{t}{\tau_{NAB}}) + 1 \qquad \textbf{Equation 28}$$

where $\tau_{NAB} = V/Q_{BZN}$ and the subscript $_{\text{NAB}}$ denotes no atmospheric breathing. It is noted that Eq. (28) is obtained from Eq. (13) simply by letting $Q_{AB} \to 0$. Since the LFL of benzene is at $y_{BZN} = 0.012$, the time to LFL is calculated as:

$$t_{LFL,NAB} \quad = \quad -\frac{V}{Q_{BZN}}\ln(1 - 0.012) \qquad \textbf{Equation 29}$$

The vapor space volume V is calculated as:

$$\begin{aligned} V &= V_{cell} - V_{grout} \\ &= L_{eff}{}^{2}\left(H_o + \frac{(H_i - H_o)}{2} - H\right) \end{aligned} \qquad \textbf{Equation 30}$$

where L_{eff} is the effective cell length, which is given as 98.5 ft after taking into account the vault wall thickness.[1] After substituting the values for H_o, H_i, and L_{eff} in Eq. (30), the volume of the cell vapor space in ft^3 is calculated as:

$$\boxed{V \quad = \quad 9{,}702.25\,(27 - H)} \qquad \textbf{Equation 31}$$

At $H = H_{max} = 25\,ft$, the vapor space volume is calculated to be 19,404.5 ft^3.

The baseline volumetric rate of benzene generation is calculated from the mass generation rate as:

$$
\begin{aligned}
Q_{BZN} &= \frac{\overset{\bullet}{m}_{BZN}}{MW_{BZN}}\left(\frac{RT}{P}\right) \\
&= \frac{3.4\,\frac{g}{hr}}{78\,\frac{g}{gmole}}\,\frac{\left(0.00294\,\frac{bar\;ft^3}{gmole\,K}\right)(273.15+95)\,K}{1.013\,bar} \\
&= 0.046552\,\frac{ft^3}{hr}
\end{aligned}
$$

Therefore, the time to LFL in the absence of atmospheric breathing is:

$$
\begin{aligned}
t_{LFL} &= -\frac{19{,}404.5}{0.046552}\ln(1-0.012) \\
&\approx 5{,}032\ \ hr \\
&\approx 210\ \ days
\end{aligned}
$$

Likewise, the time to 25% of the LFL in the absence of atmospheric breathing is:

$$
\begin{aligned}
t_{25\%\,LFL} &= -\frac{19{,}404.5}{0.046552}\ln\bigl(1-(0.012)(0.25)\bigr) \\
&\approx 1{,}252\ \ hr \\
&\approx 52\ \ days
\end{aligned}
$$

At the fill height $H = H_{min} = 17\,ft$, the vapor space volume is calculated to be $97{,}022.5\ ft^3$ from Eq. (31). By repeating the same calculations above, it can be shown that the corresponding times to 100% and 25% LFL at 17 ft fill height are:

$$
\begin{aligned}
t_{LFL} &= 1{,}048\ \ days \\
t_{25\%\,LFL} &= 261\ \ days
\end{aligned}
$$

These results show that it would take five times longer to reach the threshold LFL points at 17 ft fill height than at 25 ft fill height, since the vapor space volume of the former case is five times larger than that of the latter. It can also be shown from Eq. (28) that in the absence of atmospheric breathing the maximum concentration of benzene will eventually reach $y_{BZN} = 1$ or pure benzene at both fill heights.

3.2 Atmospheric Breathing with Baseline Benzene Rate

The algorithm for estimating the atmospheric breathing rate in ft^3/hr is obtained by substituting $t_{AB} = 24\ hr$ and Eq. (31) for V in Eq. (10):

$$\boxed{Q_{AB} \quad = \quad 1{,}617.042(27 - H)\frac{\Delta P}{P_o}} \qquad \textbf{Equation 32}$$

At the given amplitude of barometric pressure oscillations of $\Delta P = 2.5\ mbar$, the rate of atmospheric breathing Q_{AB} is calculated to be ~8.0 and 39.9 ft^3/hr at 25 and 17 fill heights, respectively. Since $Q_{BZN} << Q_{AB}$,, the relevant breathing pair for the baseline case is (*Exhaling_1* + *Inhaling*). The calculated values of $QFRC_{BZN}$ and τ are tabulated in Table 3:

Table 3. Values of Solution Parameters at 3.4 g/hr Benzene Generation Rate.

Breathing Mode	Q_{AB} (ft^3/hr)		$QFRC_{BZN}$		τ (hr)	
	$H = 25\ ft$	$H = 17\ ft$	$H = 25\ ft$	$H = 17\ ft$	$H = 25\ ft$	$H = 17\ ft$
Exhaling_1	7.9814	39.9072	0.00580	0.00117	2,417	2,428
Inhaling	7.9814	39.9072	0.00583	0.00117	2,431	2,431

The calculated benzene concentration profiles at 25 and 17 ft fill heights are shown in Figure 6 and Figure 7, respectively. These profiles were obtained by alternating the solutions for the exhaling_1 and inhaling modes each with a 12-hour period. For example, the value of y_{BZN} obtained at the end of an exhaling mode was used as the initial value for the next 12-hour inhaling solution and vice versa. An illustration of this discrete solution approach will be given later in the report.

The final equilibrium concentration of benzene is calculated as the average of those for the exhaling and inhaling modes as t → ∞. For example, the equilibrium benzene concentration at 25 fill height is calculated as:

$$\begin{aligned} y_{BZN}^{eq} &= \frac{y_{BZN,EXH}(\infty) + y_{BZN,INH}(\infty)}{2} \\ &= \frac{QFRC_{BZN,EXH1} + QFRC_{BZN,INH}}{2} \\ &= \frac{0.00580 + 0.00583}{2} \\ &\approx 0.0058 \end{aligned} \qquad \textbf{Equation 33}$$

which means that atmospheric breathing would prevent the cell vapor from ever reaching the LFL. Furthermore, it is estimated to take 1,758 hours or 73 days to reach the 25% of the LFL or $y_{BZN} = 0.003$ at the *25 ft* fill height and the baseline benzene generation rate of 3.4 g/hr. As a comparison, it was estimated earlier that in the absence of atmospheric breathing it would take 1,252 hours or 52 days to reach 25% of the LFL. Therefore, it can be concluded that under the assumptions made in this work atmospheric breathing effectively increases the time to reach 25% of the LFL by ~40% over the non-breathing case.

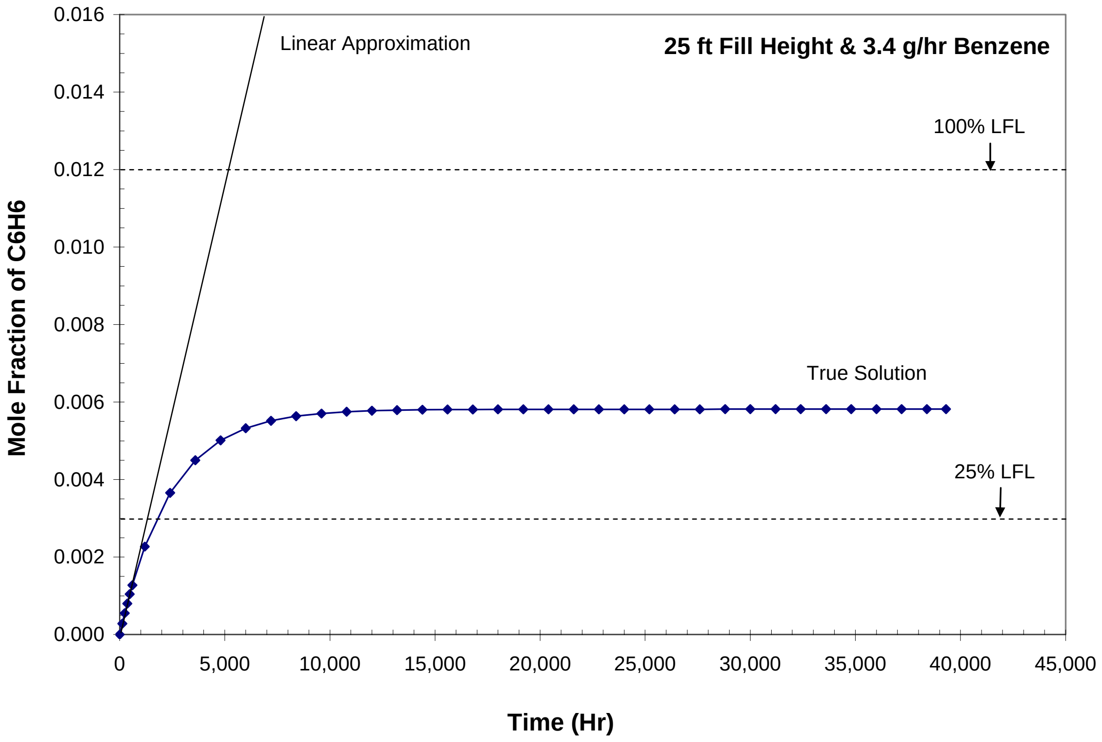

Figure 6. Benzene Concentration Profile in Cell Vapor Space at 25 ft Fill Height.

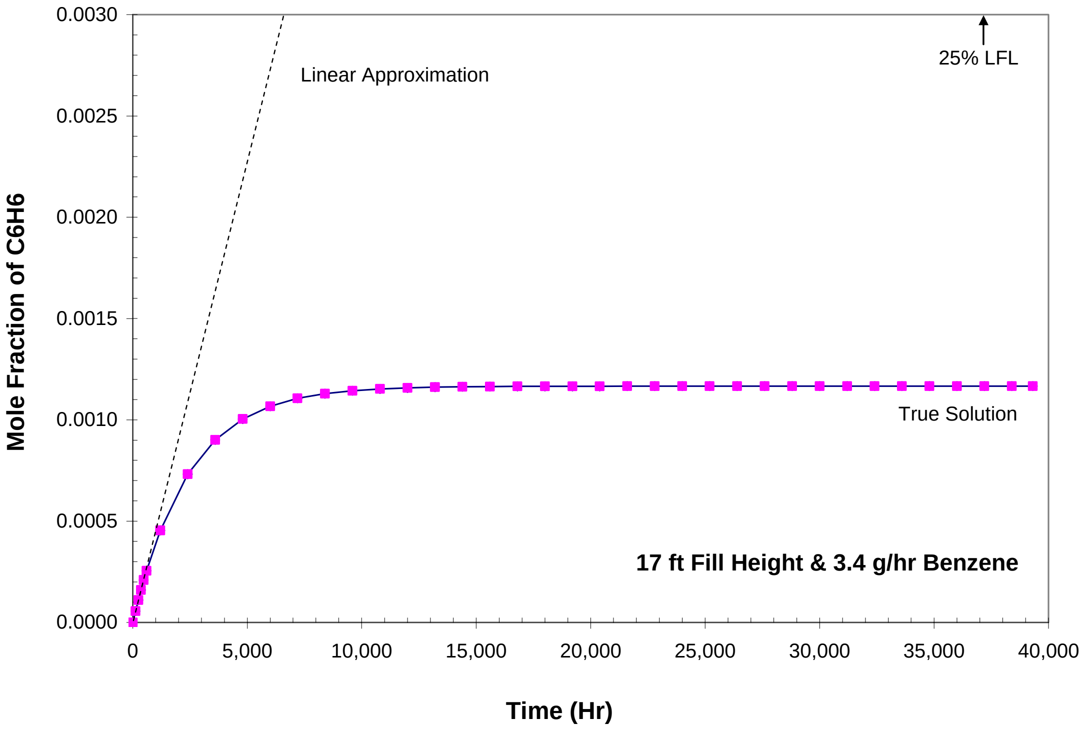

Figure 7. Benzene Concentration Profile in Cell Vapor Space at 17 ft Fill Height.

When the fill height was lowered to 17 ft, Figure 7 shows that the final equilibrium benzene concentration is reduced to $y_{BZN} = 0.0012$, i.e., by the same factor of ~5 over that at 25 ft fill height. Therefore, it can be concluded that under the assumptions made in this work the potential for flammability in the cell vapor space is highly unlikely at the 17 ft fill height and the baseline benzene generation rate of 3.4 g/hr.

The overall first-order time constant for the 25 ft fill height is also calculated as the average of those for the exhaling and inhaling modes:

$$\begin{aligned}\tau &= \frac{\tau_{EXH} + \tau_{INH}}{2} \\ &= \frac{2{,}417 + 2{,}431}{2} \\ &= 2{,}424 \ hr\end{aligned}$$

At the 2,424th hour, the calculated concentration of benzene is:

$$\begin{aligned}y_{BZN} &= 0.003676 \\ &= 63.2\% \ \ of \ \ y_{BZN}(\infty)\end{aligned}$$

which was expected for this first-order system.

It can be seen from Eq. (33) that the final equilibrium concentration of benzene at t → ∞ depends on the value of $QFRC_{BZN}$ but not on the initial value, $y_{BZN}(0)$. It is, however, important to note that the initial benzene concentration strongly impacts the time to LFL and that it was assumed in this work that there is no benzene in the vapor space initially after the grout is filled to any height (Assumption #3). Since this is not a realistic assumption, the results presented here should be treated cautiously until suitable initial values are added to the solution algorithms. Nevertheless, the positive impact of atmospheric breathing has been clearly shown by the results, as summarized in Table 4.

Table 4. Impact of Atmospheric Breathing at 3.4 g/hr Benzene Generation Rate.

Fill Height (ft)	*25*		*17*	
Mode of Breathing	*Atmospheric Breathing*	*No Atmospheric Breathing*	*Atmospheric Breathing*	*No Atmospheric Breathing*
Equilibrium y_{BZN}	0.0058	1.0000	0.0012	1.0000
Time to LFL (day)	∞	210	∞	1,048
Time to 25% of LFL (day)	73	52	∞	261

The following algorithm for estimating the equilibrium benzene concentration for the (*Exhaling_1* + *Inhaling*) breathing pair can be obtained from Eq. (33) by substituting appropriate $QFRC_{BZN}$'s:

$$\boxed{y_{BZN}^{eq} = \frac{Q_{BZN}\left(Q_{BZN} + 2Q_{AB}\right)}{2Q_{AB}\left(Q_{BZN} + Q_{AB}\right)}} \qquad \textbf{Equation 34}$$

3.3 Atmospheric Breathing at 10X Baseline Benzene Generation

In the 3rd case, the benzene generation rate was set at 10 times the baseline rate or 34 g/hr and the corresponding volumetric rate Q_{BZN} is calculated to be 0.46552 ft^3/hr. Since $Q_{BZN} < Q_{AB}$ at both fill heights, the relevant breathing pair is still (*Exhaling_1 + Inhaling*). The calculated values of $QFRC_{BZN}$ and τ are tabulated in Table 5:

Table 5. Values of Solution Parameters at 34 g/hr Benzene Generation Rate.

Breathing Mode	Q_{AB} (ft^3/hr)		$QFRC_{BZN}$		τ (hr)	
	H = 25 ft	*H = 17 ft*	*H = 25 ft*	*H = 17 ft*	*H = 25 ft*	*H = 17 ft*
Exhaling_1	7.9814	39.9072	0.05511	0.01153	2,297	2,403
Inhaling	7.9814	39.9072	0.05833	0.01167	2,431	2,431

The calculated benzene concentration profiles at 25 and 17 ft fill heights are shown in Figure 8 and Figure 9, respectively, for the benzene generation rate of 34 g/hr. It is projected to take 562 hours or 23 days to reach the LFL at 25 ft fill height, and the final equilibrium concentration of $y_{BZN} = 0.0567$ or 4.7 times the LFL is ~10 times that at the baseline benzene generation rate. As a comparison, the projected equilibrium benzene mole fraction at 17 ft fill height is *0.0116*, still a tad below the LFL due to 5 times higher atmospheric breathing rate. It is shown in Table 6 that the positive impact of atmospheric breathing as evidenced by the increased time to LFL for the baseline case (Table 4) over the non-breathing case has diminished significantly at 25 ft fill height when the benzene generation rate is increased by a factor of 10 to 34 g/hr.

Table 6. Impact of Atmospheric Breathing at 34 g/hr Benzene Generation Rate.

Fill Height (ft)	*25*		*17*	
Mode of Breathing	*Atmospheric Breathing*	*No Atmospheric Breathing*	*Atmospheric Breathing*	*No Atmospheric Breathing*
Equilibrium y_{BZN}	0.0567	1.0000	0.0116	1.0000
Time to LFL (day)	23	21	∞	105
Time to 25% of LFL (day)	5.3	5.2	30	26

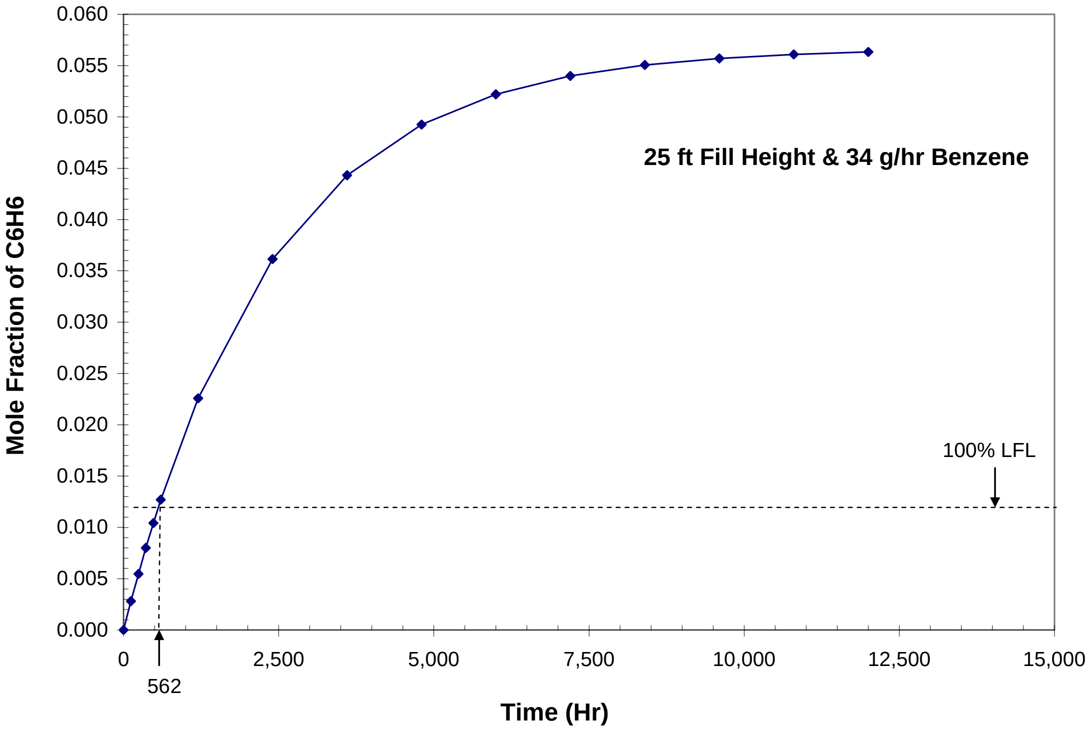

Figure 8. Benzene Concentration Profile at 34 g/hr Benzene Rate & 25 ft Fill Height.

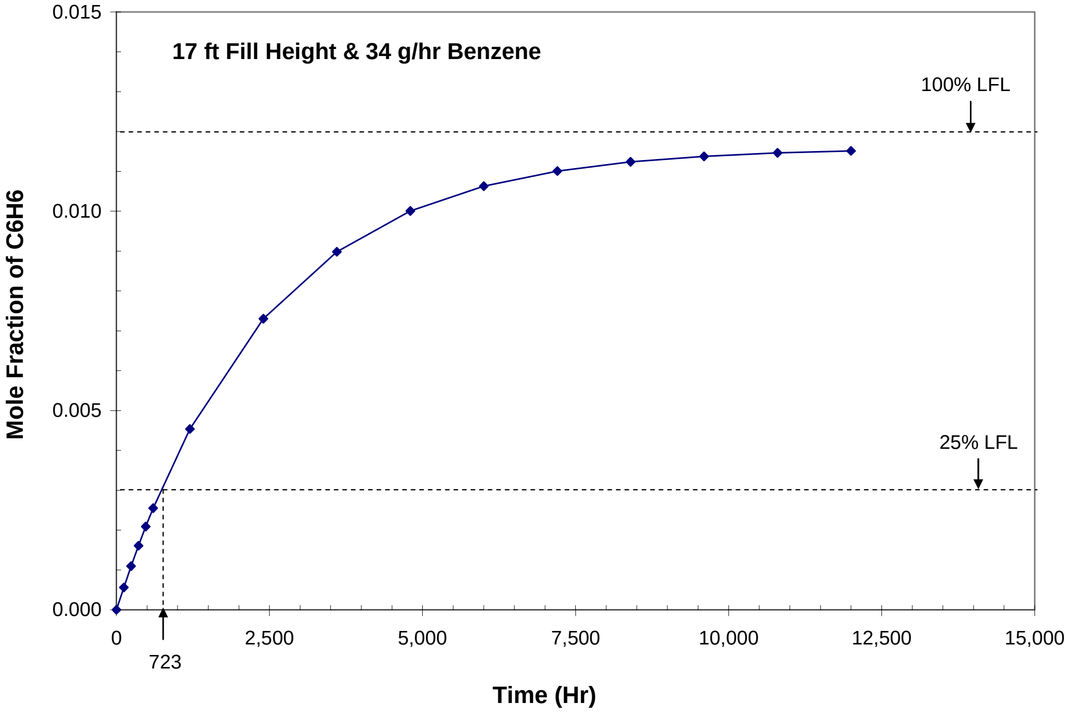

Figure 9. Benzene Concentration Profile at 34 g/hr Benzene Rate & 17 ft Fill Height.

3.4 Atmospheric Breathing at 100X Baseline Benzene Generation

In the 4th case, the benzene generation rate was set at 100 times the baseline rate or 340 g/hr and the corresponding volumetric rate Q_{BZN} is calculated to be 4.6552 ft^3/hr. Since $Q_{BZN} < Q_{AB}$ at both fill heights, the relevant breathing pair is still (*Exhaling_1 + Inhaling*). The calculated values of $QFRC_{BZN}$ and τ are tabulated in Table 7:

Table 7. Values of Solution Parameters at 340 g/hr Benzene Generation Rate.

Breathing Mode	Q_{AB} (ft^3/hr)		$QFRC_{BZN}$		τ (hr)	
	H = 25 ft	*H = 17 ft*	*H = 25 ft*	*H = 17 ft*	*H = 25 ft*	*H = 17 ft*
Exhaling_1	7.9814	39.9072	0.3684	0.1045	1,536	2,177
Inhaling	7.9814	39.9072	0.5833	0.1167	2,431	2,431

The calculated benzene concentration profiles at 25 and 17 ft fill heights are shown in Figure 10 and Figure 11, respectively, for the benzene generation rate of 340 g/hr. At 25 ft fill height, it is projected to take 51 hours to reach the LFL on its way to the final equilibrium concentration of $y_{BZN} = 0.4758$. As a comparison, it is projected to take 265 hours to reach the LFL at 17 ft fill height and the projected equilibrium benzene mole fraction is *0.1106*. It is also shown in Table 8 that the positive impact of atmospheric breathing as evidenced by the increased time to LFL for the baseline case (Table 4) over the non-breathing case has pretty much vanished for both fill heights when the benzene generation rate is increased by a factor of 100 to 340 g/hr.

Table 8. Impact of Atmospheric Breathing at 340 g/hr Benzene Generation Rate.

Fill Height (ft)	*25*		*17*	
Mode of Breathing	*Atmospheric Breathing*	*No Atmospheric Breathing*	*Atmospheric Breathing*	*No Atmospheric Breathing*
Equilibrium y_{BZN}	0.4758	1.0000	0.1106	1.0000
Time to LFL (hr)	51	50	265	252
Time to 25% of LFL (hr)	13	13	63	63

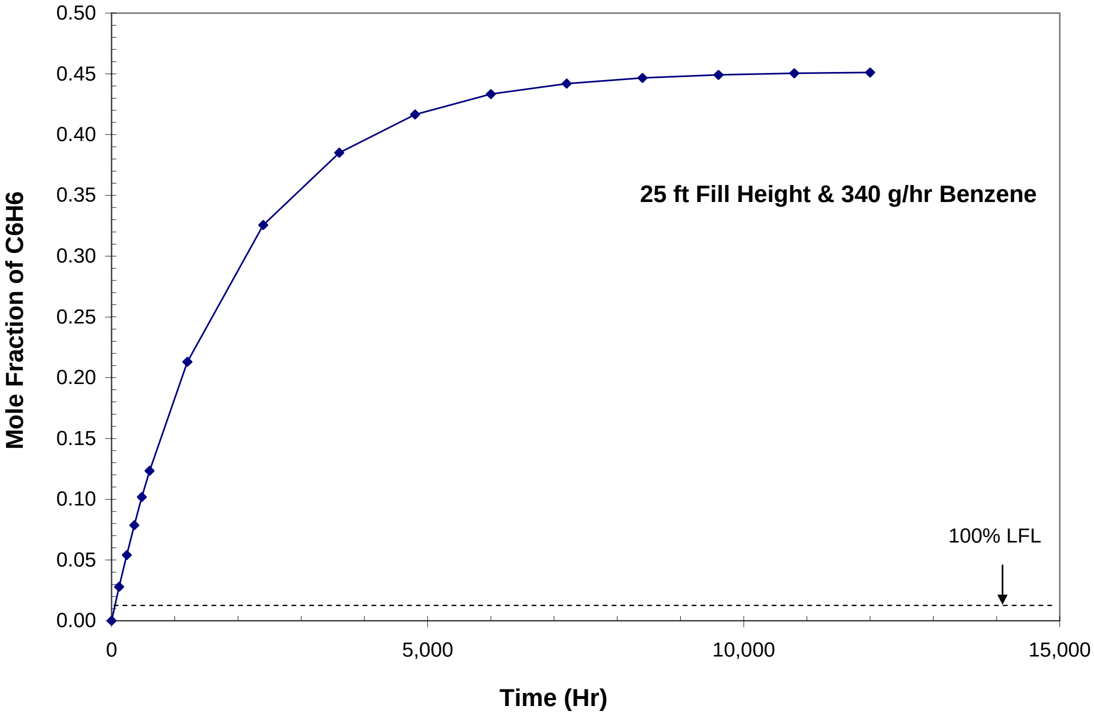

Figure 10. Benzene Concentration Profile at 340 g/hr Benzene Rate & 25 ft Fill Height.

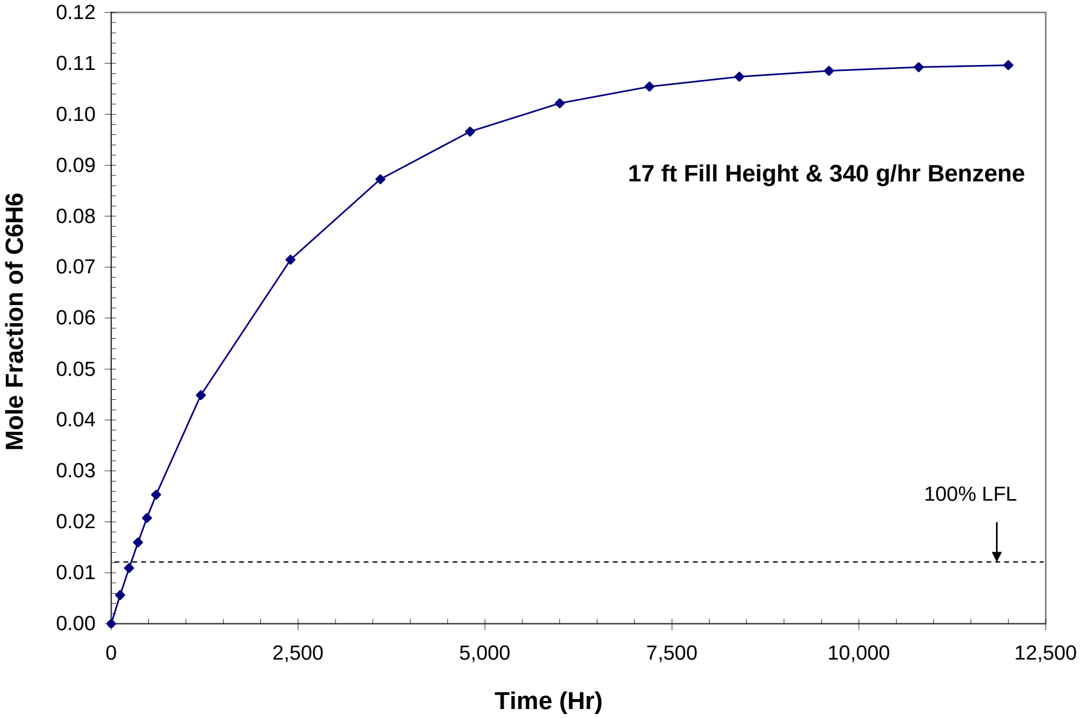

Figure 11. Benzene Concentration Profile at 340 g/hr Benzene Rate & 17 ft Fill Height.

3.5 Atmospheric Breathing at 1000X Baseline Benzene Generation

In the last case considered, the benzene generation rate was set at 1,000 times the baseline rate or 3,400 g/hr, and the corresponding volumetric rate Q_{BZN} is calculated to be 46.552 ft^3/hr. At both fill heights, the benzene generation rate Q_{BZN} is now higher than the atmospheric breathing rate Q_{AB} and the relevant breathing pair is (*Exhaling_1* + *Exhaling_2*). The calculated values of $QFRC_{BZN}$ and τ are tabulated in Table 9:

Table 9. Values of Solution Parameters at 3,400 g/hr Benzene Generation Rate.

Breathing Mode	Q_{AB} (ft^3/hr)		$QFRC_{BZN}$		τ (hr)	
	H = 25 ft	*H = 17 ft*	*H = 25 ft*	*H = 17 ft*	*H = 25 ft*	*H = 17 ft*
Exhaling_1	7.9814	39.9072	0.8536	0.5384	356	1,122
Exhaling_2	7.9814	39.9072	1.2069	7.0022	503	14,593

The calculated benzene concentration profiles at 25 and 17 ft fill heights are shown in Figure 12 and Figure 13, respectively, for the benzene generation rate of 3,400 g/hr. At 25 ft fill height, it is projected to take only 5 hours to reach the LFL and fill the entire vapor space with pure benzene after ~2,500 hours. As a comparison, it is projected to take 25 hours to reach the LFL at 17 ft fill height and also eventually fill the entire vapor space with pure benzene. It is shown in Table 10 that at either fill height the atmospheric breathing no longer has any positive impact on either the time to LFL or the final equilibrium concentration of benzene, compared to the non-breathing case.

Table 10. Impact of Atmospheric Breathing at 3,400 g/hr Benzene Generation Rate.

Fill Height (ft)	*25*		*17*	
Mode of Breathing	*Atmospheric Breathing*	*No Atmospheric Breathing*	*Atmospheric Breathing*	*No Atmospheric Breathing*
Equilibrium y_{BZN}	1.0000	1.0000	1.0000	1.0000
Time to LFL (hr)	5.0	5.0	25	25
Time to 25% of LFL (hr)	1.3	1.3	6.3	6.3

The following algorithm for estimating the equilibrium benzene concentration for the (*Exhaling_1* + *Exhaling_2*) breathing pair can be obtained from Eq. (33) by substituting appropriate $QFRC_{BZN}$'s:

$$\boxed{y_{BZN}^{eq} = \frac{Q_{BZN}^{2}}{Q_{BZN}^{2} - Q_{AB}^{2}}} \qquad \textbf{Equation 35}$$

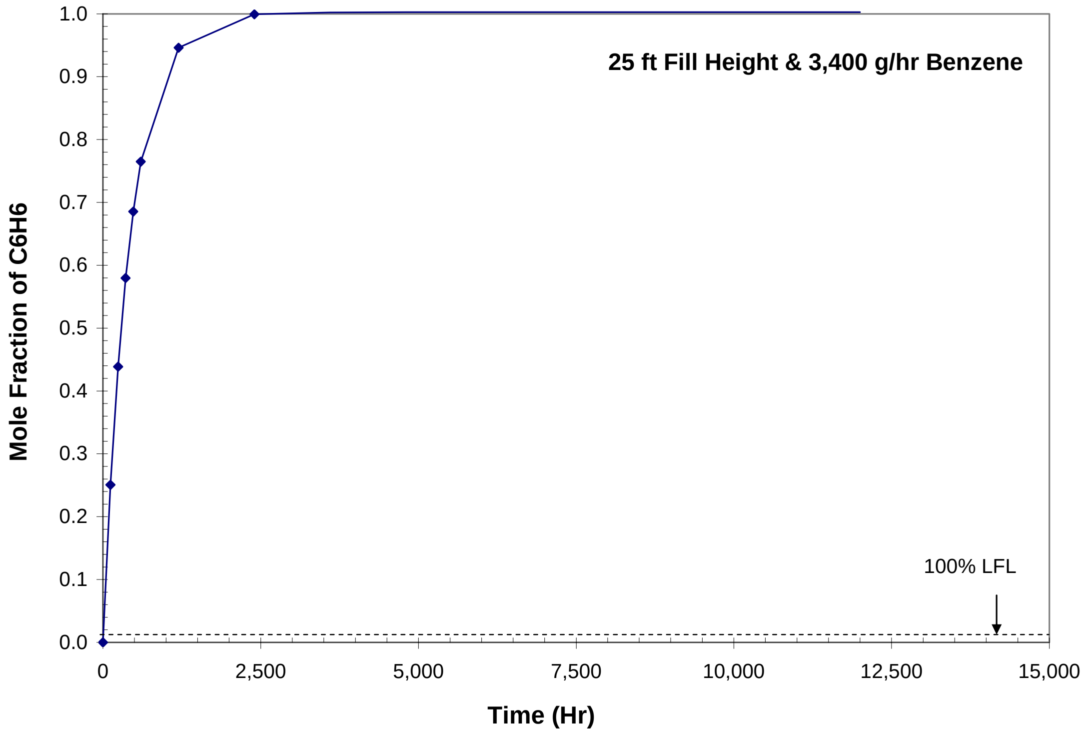

Figure 12. Benzene Concentration Profile at 3,400 g/hr Benzene Rate & 25 ft Fill Height.

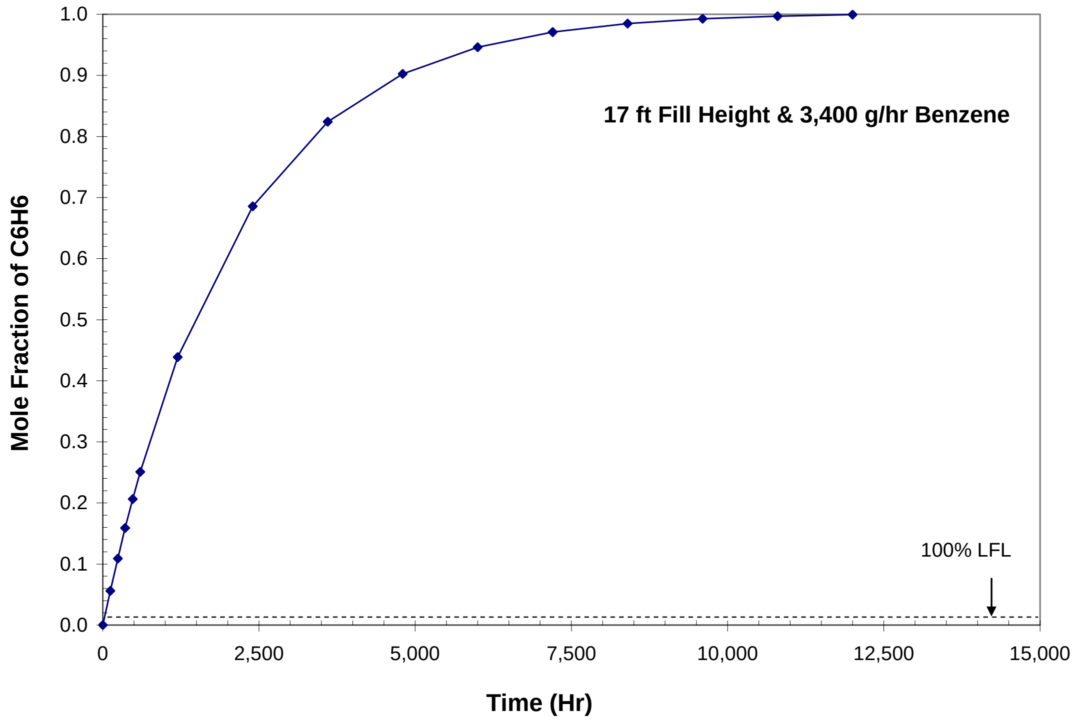

Figure 13. Benzene Concentration Profile at 3,400 g/hr Benzene Rate & 17 ft Fill Height.

If we were to re-plot the benzene concentration profiles shown earlier on a finer time-scale, we would find that they are not smooth. Instead, they would look zigzagged especially at larger times, as shown by the "overall" breathing curve in Figure 14. The reason for zigzagging is that these profiles were obtained by alternating the average solutions of the *Exhaling_1* and *Exhaling_2* at a 12-hour interval; the value of y_{BZN} at the end of the Exhaling_1 mode was used as the initial value for the next 12-hour Exhaling_2 solution or vice versa. The two dotted curves in Figure 14 represent the discrete solutions to the *Exhaling_1* and *Exhaling_2* equations obtained using the cumulative time scale instead of the fresh 12-hour duration for each breathing cycle. The two curves are dotted or discontinuous, since each 12-hour breathing cycle occurs only once in a 24-hour period. And the zigzagging of the "overall" breathing curve results when the two dotted curves are averaged.

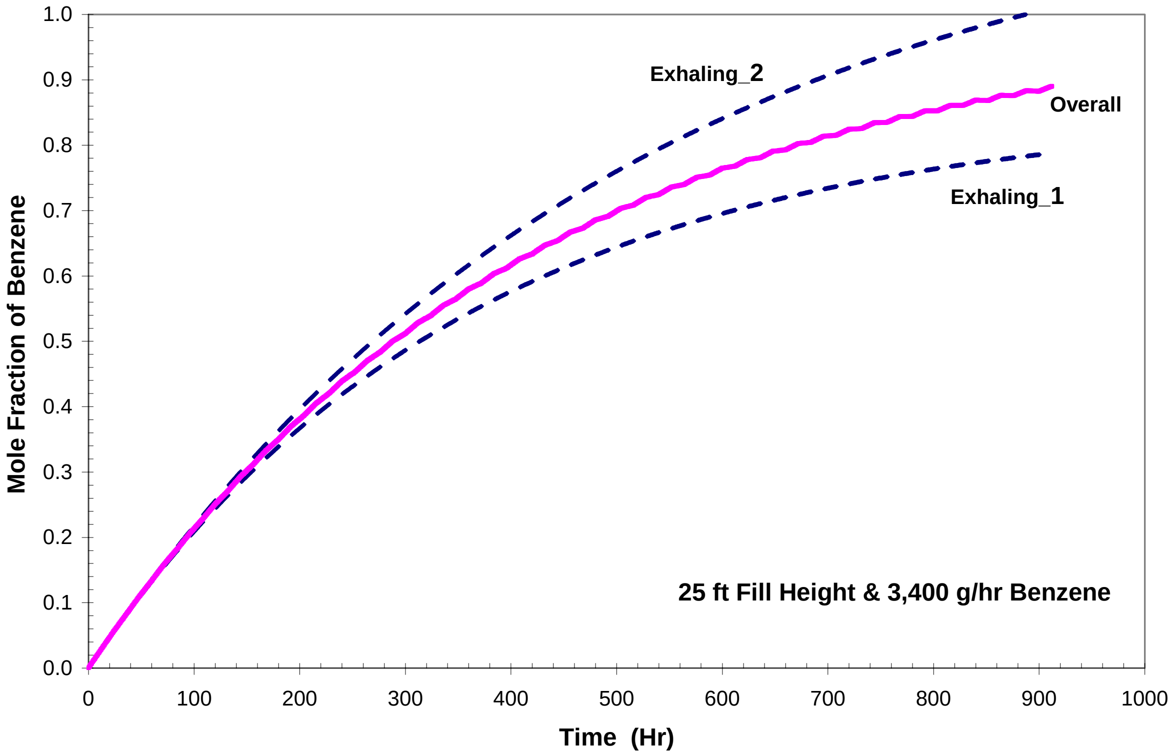

Figure 14. Components of Benzene Concentration Profile at 3,400 g/hr Benzene Rate.

4.0 CONCLUSIONS

Under the assumptions made in this study, it can be concluded that:

- At 3.4 g/hr benzene generation rate, passive breathing induced by the diurnal oscillations of atmospheric pressure is sufficient enough to limit the maximum benzene concentration below 50% of the LFL, thus mitigating potential flammability in the Saltstone vault vapor space without installing any active ventilation system.

- At 34 g/hr benzene generation rate, it is estimated to take 23 and 5 days to reach 100% and 25% of the LFL, respectively, at 25 ft fill height. At 17 ft fill height, it is estimated to take 30 days to reach 25% of the LFL with the maximum equilibrium concentration of benzene just below the LFL.

- At 34 g/hr benzene generation rate, the advantage of atmospheric breathing over the non-breathing case becomes only marginal at 25 ft fill height.

- At benzene generation rates higher than 340 g/hr, the atmospheric breathing no longer has any positive impact on the time to LFL at both 17 and 25 ft fill levels.

As specified in the Technical Task Request (TTR) for this work,[1] the following algorithms have been developed to support scoping analysis:

- Cell vapor space volume (*ft*^{3}): $\boxed{V = 9{,}702.25\,(27 - H)}$

- Atmospheric breathing rate (*ft*^{3}*/hr*): $\boxed{Q_{AB} = 1{,}617.042\,(27 - H)\frac{\Delta P}{P_o}}$

- Equilibrium benzene concentration (*mole fraction*):
  - *Exhaling_1* + *Inhaling*: $\boxed{y_{BZN}^{eq} = \frac{Q_{BZN}\,(Q_{BZN} + 2Q_{AB})}{2Q_{AB}\,(Q_{BZN} + Q_{AB})}}$
  - *Exhaling_1* + *Exhaling_2*: $\boxed{y_{BZN}^{eq} = \frac{Q_{BZN}^{\;2}}{Q_{BZN}^{\;2} - Q_{AB}^{\;2}}}$

The following algorithms also have been developed for a quick estimation of the equilibrium benzene mole fraction as a function of benzene generation rate in *g/hr* by curve-fitting the calculated values as shown in Figure 15 and Figure 16:

- At 25 ft fill height: $\frac{1}{y_{BZN}} = 0.37627 + \frac{586.581}{\dot{m}_{BZN}}$

- At 17 ft fill height: $\frac{1}{y_{BZN}} = 0.46973 + \frac{2{,}915.163}{\dot{m}_{BZN}}$

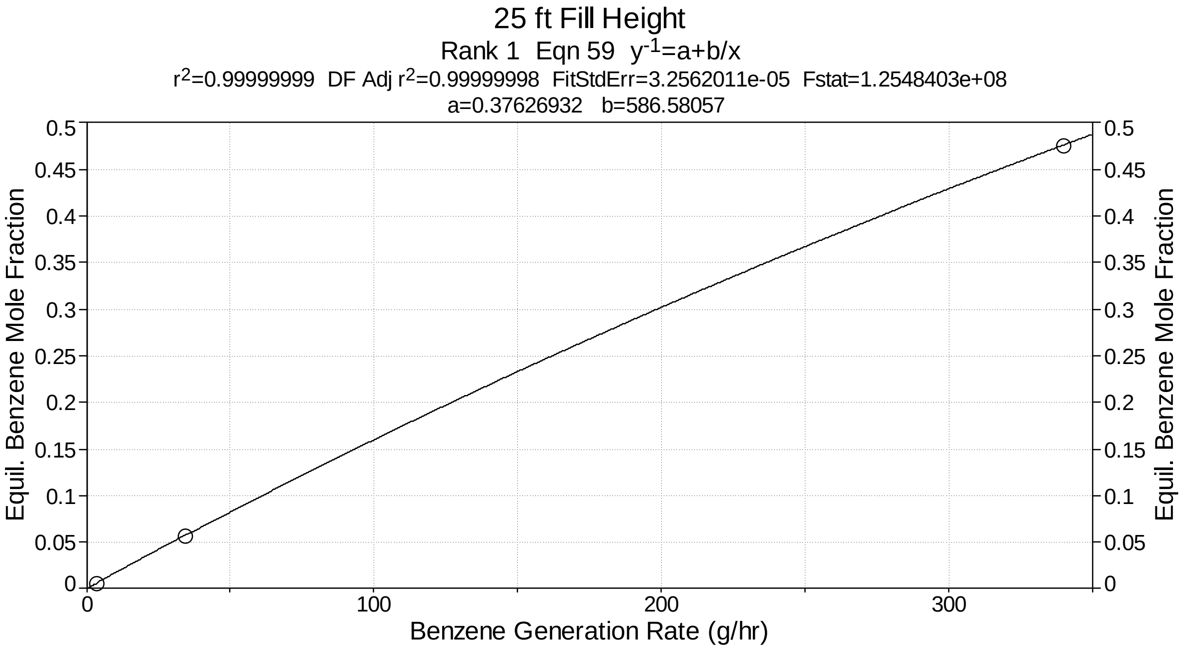

Figure 15. Equilibrium Benzene Concentration Profile at 25 Ft Fill Height.

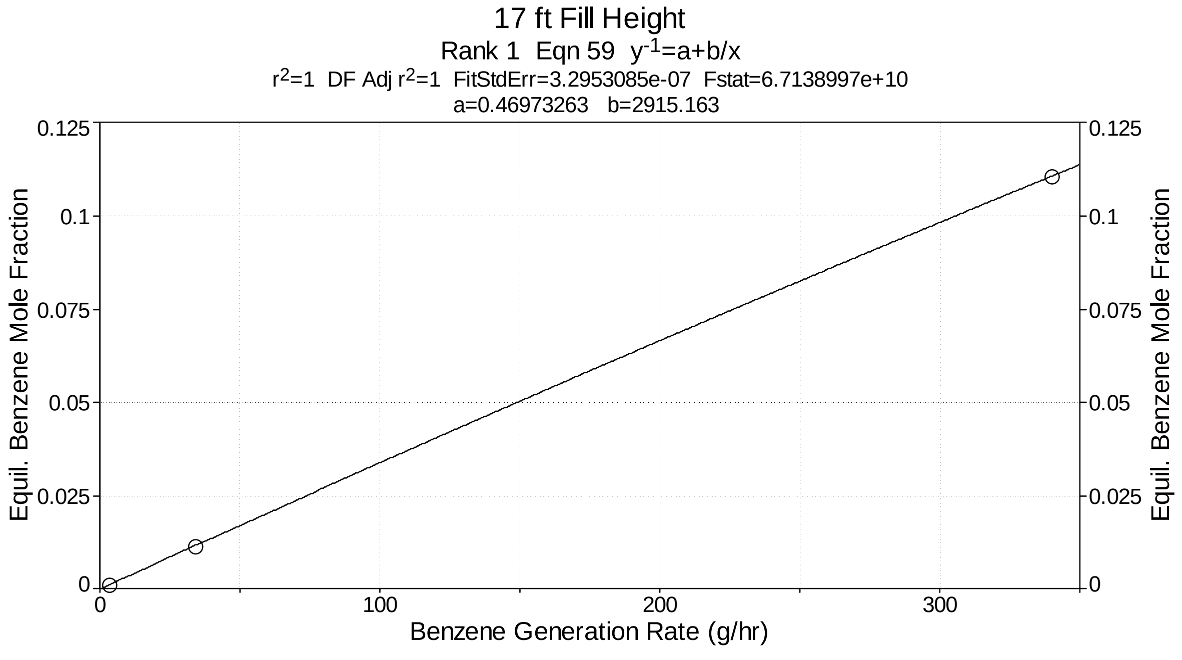

Figure 16. Equilibrium Benzene Concentration Profile at 17 Ft Fill Height.

5.0 RECOMMENDATIONS/PATH FORWARD

As stated in the TTR,[1] the purpose of this work was to develop the algorithms that can be used for scoping purposes to quantify the impact of atmospheric breathing on the benzene concentration that is expected to build up in the cell vapor space during the curing process. As a result, several simplifying assumptions were made but some were not necessarily bounding.

Specifically, it is recommended that

- The assumed "zero" initial benzene concentration in the cell (Assumption #3) be replaced with some bounding value.

- The assumed perfect-mixing in the vapor space (Assumption #5) be supplemented by looking into the effects of gas layering or partitioning.

- Convective flows induced by the heat emitted from the grout and the solar heating of the roof during the day and cooling at night be added to the analysis.

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6.0 REFERENCES

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3. Nilson, R. H., Peterson, E. W., Lie, K. H., Burkhard, N. R., and Hears, J. R., “Atmospheric Pumping: A Mechanism Causing Vertical Transport of Contaminated Gases Through Fractured Permeable Media,” **J. Geophys. Res.**, **96**, No. B13, pp 21933-21948 (1991).