Hydrogen Diffusion Through Multiple Packaging Layers

John E. McAllister, Ph.D., Abrar Mohiuddin
URS-Safety Management Solutions
2131 South Centennial Avenue
Aiken, SC 29803-7680
(803) 502-9870, Fax (803) 502-9775
(john.mcallister@wsms.com)

Introduction

For this scenario, hydrogen is generated in a container that is eventually stored within a drum or some type of long range storage container. When preparing for long-term storage, the hydrogen container (HC) is placed in a plastic bag (PB1). The PB1 is then placed inside an inner drum (ID). The ID is placed inside a plastic bag (PB2) which is then placed within an outer drum (OD). One or more ODs are then storage is a large container (LC). Filtered vents or vent holes are located on all the container barriers to prevent pressurization and allow gases to flow in and out of the HC. The LC is vented to the atmosphere with four vent paths for this example.

The source of hydrogen generation for this study is not important. Any source that generates hydrogen in elemental form (i.e., H_2) is a candidate for the purposes of this generic evaluation. The released hydrogen accumulates inside the waste packaging. Depending on the permeability of the packaging layers, some of the accumulated hydrogen may diffuse out of the packaging layers and into the space surrounding the drums. Since the drums are confined in the LC, the hydrogen accumulates in the LC as it did inside the drums if venting of the LC does not occur. If accumulation in the LC is allowed without venting, the confinement is eventually breached or the hydrogen is consumed by reaction with other chemical species. One possible reaction is combustion with oxygen. Such a reaction can be explosive, and from this possibility arises the safety concern.

This hypothetical packaging configuration is modeled with six regions, and a seventh designating the environment. The regions are:

Region 1: Inside HC - void region inside the HC
Region 2: Between HC and PB1 - volume inside inner plastic bag and outside of the HC
Region 3: Between PB1 and ID - volume defined by the outside of the innermost bag and the inside of the ID
Region 4: Between ID and PB2 - volume inside the outermost bag and outside of the ID
Region 5: Between PB2 and drum (OD) - volume defined as outside the outer most bag and the inside of the OD

Region 6: Between the four drums and LC - volume of the interior of the LC minus the
volume of the four drums
Region 7: Outside the LC.

Analytical Methods and Computations

Inputs

Table 1 provides a summary of the input information for the calculation. It is assumed that there is no resistance across the enclosure of PB1. The values for k_{12}, k_{34}, k_{45}, and k_{56} are representative values for NFT and HEPA filters and do not represent any specific filter. The value for k_{67} is where the four 0.5-inch diameter vent holes in the walls of the LC holes are modeled as a diffusion coefficient. By using a diffusion coefficient for the vent holes, the diffusion model is simplified.

Analytical Method

Equations 1 and 2 are the governing equations for hydrogen diffusion

$$q_{ij} = k_{ij} \cdot \left(mf_i - mf_j \right) \qquad (1)$$

where q_{ij} = molar flow by diffusion from region i to region j, moles/sec
k_{ij} = diffusion coefficient between regions i and j, moles / (sec – molefrac)
mf_i = hydrogen mole fraction in region i

$$\frac{d}{dt} \cdot \left(\frac{V_{Di} \cdot c_{Di}}{V_{Mi}} \right) = S_{Hi} - q_{ij} + q_{i\_1j\_1} \qquad (3)$$

where V_{Mj} = volume per mole of gas at the assumed pressure and temperature in region i, L/mole
V_{Dj} = void (gas) volume in region i, L
c_{Di} = hydrogen mole fraction in a region i
S_{Hi} = hydrogen generation in a region i, moles/sec
q_{ij} = molar flow by diffusion from region i to region j, moles/sec
$q_{i\_1\ j\_1}$ = molar flow by diffusion from region i_1 to region j_1, moles/sec

Table 1.

Variable Name and Symbol	Value
Diffusivity regions 1 to 2, k_{12}	6.25E-05 mole/s
Diffusivity regions 2 to 3, k_{23}	1.00E+00 mole/s
Diffusivity regions 3 to 4, k_{34}	1.65E-04 mole/s
Diffusivity regions 4 to 5, k_{45}	3.14E-04 mole/s
Diffusivity regions 5 to 6, k_{56}	1.65E-04 mole/s
Diffusivity regions 6 to 7, k_{67}	6.31E-06 mole/s
Molar volume region 1, VM1	24.5 L/mole
Molar volume region 2, VM2	24.5 L/mole
Molar volume region 3, VM3	24.5 L/mole
Molar volume region 4, VM4	24.5 L/mole
Molar volume region 5, VM5	24.5 L/mole

Variable Name and Symbol	Value
Molar volume region 6, VM6	24.5 L/mole
Region 1 volume, VD1	10 L
Region 2 volume, VD2	5 L
Region 3 volume, VD3	5 L
Region 4 volume, VD4	100 L
Region 5 volume, VD5	100 L
Region 6 volume, VD6	2000 L
Hydrogen generation region 1, SH1	5.00E-08 moles/s
Hydrogen generation regions 2-6, SH2 through SH6	0 mole/s

Input Information for the Calculation.

This diffusion model assumes that a volume is modeled as a single region. The configuration assumes that four drums are placed inside an LC. The LC is able to communicate with the surrounding atmosphere by four vent holes, one hole on each vertical side of the LC.
This analysis divides the drum into five separate regions. The hydrogen is generated inside the HC. The HC has a vent hole that allows the hydrogen generated inside the HC to diffuse into the void volume inside the PB1. Region 1 in the hydrogen diffusion model is the region inside the HC. There is a HEPA filter that provides the flow path for the hydrogen to diffuse from the inside of the HC to the region outside the HC.

The HC is wrapped inside a plastic bag and placed inside the ID. This bag is considered the innermost bag in the drum model. The void region between the HC and ID is divided into two regions due to the plastic bag for the hydrogen diffusion model. The volume inside the bag and outside of the HC is Region 2. Region 3 is the volume defined by the outside of this innermost bag and the inside of the ID.

The ID is wrapped inside a second plastic bag (PB2) and is placed inside the drum. This bag is the outermost bag in the model. The void region between the ID and drum (OD) is divided into two regions due to this bag. The volume inside the bag and outside of the ID is Region 4. Region 5 is the volume defined by the outside of this outermost bag and the inside of the OD.

Four drums are placed inside the LC. The volume of the interior of the LC minus the volume of the four drums is Region 6 in the model.
Equation 2 is integrated to give Equation 3.

$$c_{Dit\Delta t} = c_{Dit} + \left(\frac{V_{Mi}}{V_{Di}}\right)\cdot\left(S_{Hi} - q_{ij} + q_{i\_1j\_1}\right)\cdot\Delta t \qquad (3)$$

where $c_{Dit\Delta t}$ = hydrogen mole fraction in a region i at the end of the time step
c_{Dit} = hydrogen mole fraction in a region i at the start of the time step
Δt = time step, sec

A modification is needed for Equation 1. The variables in Equation 1 are evaluated as average values over a time step. With this interpretation, Equation 1 is rewritten as Equation 5.

$$q_{ij} = k_{ij} \cdot \left(\frac{c_{Dit\Delta t} + c_{Dit}}{2} - \frac{c_{Djt\Delta t} + c_{Djt}}{2} \right) \quad (4)$$

where the variables are defined as in the previous equations.

Equations 3 and 4 exist for each region in this analysis. Table 2 shows the particular notation for each equation for each region in this analysis. The comments column notes any potential simplification/change to Equation 3. For example for region 1, there is no q_{i_1,j_1} term as there is no region inside of region 1. The equation for region 6 reflects the four drums inside the LC and the assumption that there is no hydrogen concentration in the atmosphere surrounding the LC.

The transient solution is solved from the equations shown in Table 2. For each time step, the 12 equations are solved. The unknowns are the hydrogen molar flows, q_{ij}, for each region and the final hydrogen concentrations, $c_{Dit\Delta t}$, for each region at the end of the time step. The initial hydrogen concentrations, c_{Dit}, at the beginning of each time step are known from the concentrations at the end of the previous time step.

Hydrogen loss from Region 6 is modeled in the equations given in Table 2 by an effective diffusivity from the four vent holes in the LC. An additional mechanism for hydrogen loss from the vent holes is due to wind and barometric pressure variations outside the LC. The fractional loss of hydrogen per day when wind and barometric pressure variations are considered is 0.0089. Once a hydrogen concentration is determined in Region 6 from the equations in Table 2, the final concentration is reduced due to the impact of wind and barometric pressure variations. The 0.0089 fractional reduction per day is converted to the reduction for a given time step by Equation 5.

Table 2.

Region	Specific Equations	Comments
1	$q_{12} - \frac{k_{12}}{2}\cdot c_{D1t\Delta t} + \frac{k_{12}}{2}\cdot c_{D2t\Delta t} = \frac{k_{12}}{2}\cdot c_{D1t} - \frac{k_{12}}{2}\cdot c_{D2t}$ $\frac{V_{M1}\cdot\Delta t}{V_{D1}}\cdot q_{12} + c_{D1t\Delta t} = c_{D1t} + \frac{V_{M1}\cdot S_{H1}\cdot\Delta t}{V_{D1}}$	The $q_{i-1\ j-1}$ term is zero for Region 1. There is no region inside of Region 1 to supply a hydrogen molar flow.
2	$q_{23} - \frac{k_{23}}{2}\cdot c_{D2t\Delta t} + \frac{k_{23}}{2}\cdot c_{D3t\Delta t} = \frac{k_{23}}{2}\cdot c_{D2t} - \frac{k_{23}}{2}\cdot c_{D3t}$ $\frac{V_{M2}\cdot\Delta t}{V_{D2}}\cdot q_{23} - \frac{V_{M2}\cdot\Delta t}{V_{D2}}\cdot q_{12} + c_{D2t\Delta t} = c_{D2t} + \frac{V_{M2}\cdot S_{H2}\cdot\Delta t}{V_{D2}}$	None
3	$q_{34} - \frac{k_{34}}{2}\cdot c_{D3t\Delta t} + \frac{k_{34}}{2}\cdot c_{D4t\Delta t} = \frac{k_{34}}{2}\cdot c_{D3t} - \frac{k_{34}}{2}\cdot c_{D4t}$ $\frac{V_{M3}\cdot\Delta t}{V_{D3}}\cdot q_{34} - \frac{V_{M3}\cdot\Delta t}{V_{D3}}\cdot q_{23} + c_{D3t\Delta t} = c_{D3t} + \frac{V_{M3}\cdot S_{H3}\cdot\Delta t}{V_{D3}}$	None
4	$q_{45} - \frac{k_{45}}{2}\cdot c_{D4t\Delta t} + \frac{k_{45}}{2}\cdot c_{D5t\Delta t} = \frac{k_{45}}{2}\cdot c_{D4t} - \frac{k_{45}}{2}\cdot c_{D5t}$ $\frac{V_{M4}\cdot\Delta t}{V_{D4}}\cdot q_{45} - \frac{V_{M4}\cdot\Delta t}{V_{D4}}\cdot q_{34} + c_{D4t\Delta t} = c_{D4t} + \frac{V_{M4}\cdot S_{H4}\cdot\Delta t}{V_{D4}}$	None
5	$q_{56} - \frac{k_{56}}{2}\cdot c_{D5t\Delta t} + \frac{k_{56}}{2}\cdot c_{D6t\Delta t} = \frac{k_{56}}{2}\cdot c_{D5t} - \frac{k_{56}}{2}\cdot c_{D6t}$ $\frac{V_{M5}\cdot\Delta t}{V_{D5}}\cdot q_{56} - \frac{V_{M5}\cdot\Delta t}{V_{D5}}\cdot q_{45} + c_{D5t\Delta t} = c_{D5t} + \frac{V_{M5}\cdot S_{H5}\cdot\Delta t}{V_{D5}}$	None
6	$q_{67} - \frac{k_{67}}{2}\cdot c_{D6t\Delta t} = \frac{k_{67}}{2}\cdot c_{D6t}$ $\frac{V_{M6}\cdot\Delta t}{V_{D6}}\cdot q_{67} - \frac{V_{M6}\cdot\Delta t}{V_{D6}}\cdot 4q_{56} + c_{D6t\Delta t} = c_{D6t} + \frac{V_{M6}\cdot S_{H6}\cdot\Delta t}{V_{D6}}$	There is no c_{D7t} term as the ambient region outside the LC has no hydrogen concentration. The "4" coefficient on the q_{56} term accounts for the four drums in the LC.

Governing Equations.

$$c_{Dfinal} = c_{D6t\Delta t} \cdot \left(1 - \frac{0.0089}{24 \cdot 3600} \cdot \Delta t\right) \qquad (5)$$

where c_{Dfinal} = final hydrogen concentration in Region 6
$c_{D6t\Delta t}$ = hydrogen concentration in Region 6 at the end of a time step as calculated from the equations in Table 2
Δt = time step, sec

In Equation 5, the fractional reduction in hydrogen on a per day basis is converted to the fractional reduction for the time step in the solution. The reduction is very small.

The equations in Table 2 can be characterized as a set of linear algebraic equations of the form.

$$A * X = B \qquad (7)$$

where A = coefficient matrix
X = matrix of unknown variables
B = column matrix representing the non-homogenous solution for the equations.

The solution to Equation 7 is Equation 8.

$$X = A^{-1} * B \qquad (8)$$

where A^{-1} = inverse of the coefficient matrix

Solution Technique

The solution technique solves the equations at each time step. The hydrogen concentrations at the end of the time step are set equal to the concentrations at the beginning of the next time step.

The solution technique is implemented within an Excel macro. The matrix operations are completed using Excel functions for matrix inverse and matrix multiplication.

The macro within the Excel workbook is composed on a main function and several other functions. The program is very simple as separate functions are used to complete a unique activity.

Results

Hydrogen Concentrations in the Packaging Layers

The transient variation in the hydrogen concentrations in the six regions is shown in Figure 1. The results in this figure used the nominal input values in Table 1 and a time step of 1800 sec. As shown in Figure 1, there are no spikes in the hydrogen concentration during the transient.

Sensitivity Study on Region 1 Hydrogen Concentration

The resultant hydrogen concentration in Region 1 after 20,000 hrs is 3.26%. Sample calculations were run to evaluate the effect of uncertainties within the various packaging layers. The different cases and their results are shown in Table 3.

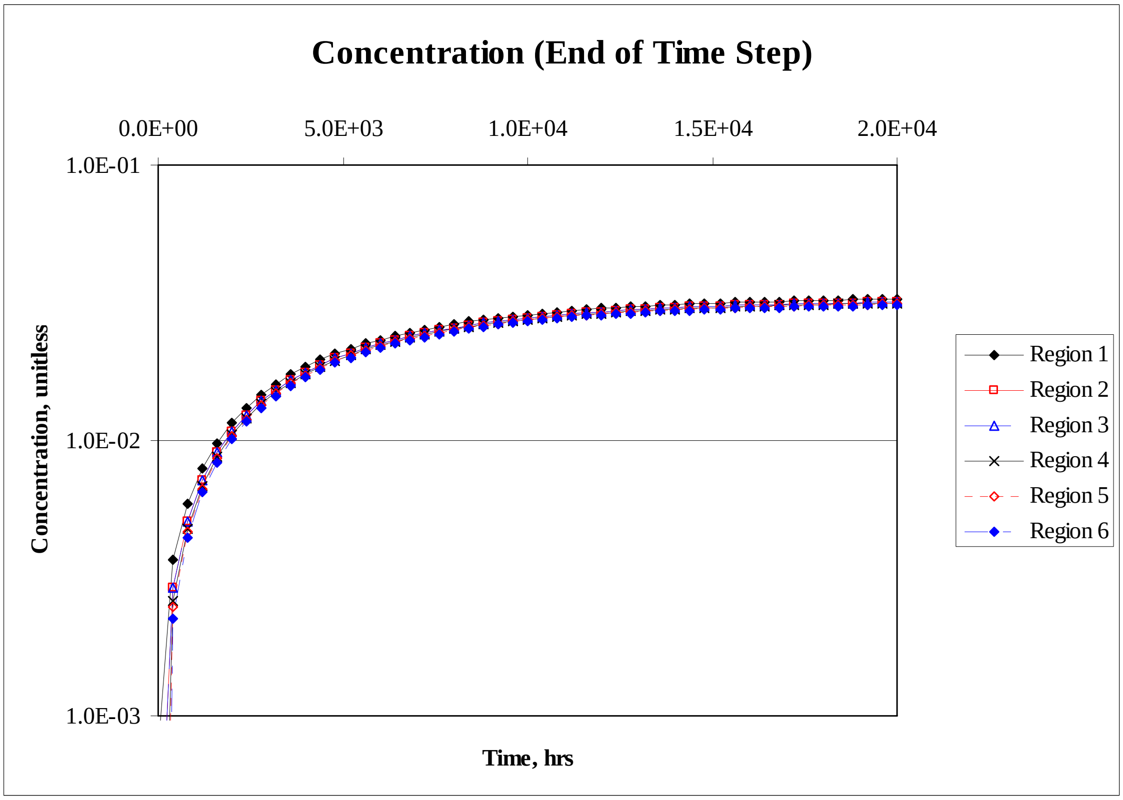

Figure 1. Hydrogen Concentration in the Various Regions.

Table 3.

Case Number	Case	Final H_2 Concentration of Region 1 (%)
1	Base	3.26
2	k_{12} / 10	3.98
3	10 * k_{12}	3.19
4	VD2 = 1 L, VD3 = 9 L	3.26
5	VD2 = 9 L, VD3 = 1 L	3.26
6	VD4 = 5 L, VD5 = 195 L	3.26
7	VD4 = 195 L, VD5 = 5 L	3.26
8	k_{34} / 10	3.53
9	10 * k_{34}	3.23
10	k_{67} / 10	10.3
11	10 * k_{67}	0.48

Sensitivity Study Cases.

Conclusions

It is concluded that the hydrogen concentration in Region 1 is not affected by adjusting the volumes of any of the plastic bags. However, the concentration in Region 1 is influenced by variation in the diffusion coefficients between any of the packaging layers. Region 1 is affected the most when the diffusivity between the LC and the surrounding atmosphere is altered.