ESTIMATION OF AN ALLOWABLE HYDROGEN PERMEATION RATE FROM ROAD VEHICLE COMPRESSED GASEOUS HYDROGEN STORAGE SYSTEMS IN TYPICAL GARAGES; PART 3: MODELLING AND NUMERICAL SIMULATION OF HYDROGEN PERMEATION IN A GARAGE WITH ADIABATIC WALLS AND STILL AIR

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ABSTRACT

The formation of a flammable hydrogen-air mixture is a major safety concern especially for closed space. This hazardous situation can arise when considering permeation from a car equipped with a composite compressed hydrogen tank with a non-metallic liner in a closed garage. In the following paper a scenario is developed and analysed with a simplified approach and a numerical simulation, in order to estimate the evolution of hydrogen concentration. The system is composed of typical size garage and hydrogen car's tank. Some parameters increasing permeation rate (i.e. tank's material, thickness and pressure) have been chosen to have a conservative approach. A close look on the top of tank surface showed that the concentration grows as square root of time, and does not exceed 8.2×10^{-3} % by volume. Also, a simplified comparative analysis estimated that the buoyancy of hydrogen-air mixture prevails on the diffusion 35 seconds after permeation starts, in good agreement with simulation where time is at about 80 seconds. Finally, the numerical simulations demonstrated that across the garage height, the hydrogen is nearly distributed linearly and the difference in hydrogen concentration at the ceiling and floor is negligible (i.e. 3×10^{-3} %).

Nomenclature

a	Acceleration (m·s^{-2})	n	Number of moles (mol)
A_r	Reservoir surface (m^2)	P	Permeability of the material of the tank (mol·s^{-1}·m^{-1}·MPa$^{-1/2}$)
c	Hydrogen concentration in the garage (% vol.)	P_0	Pre-exponential factor of permeability of material of the tank (mol·s^{-1}·m^{-1}·MPa$^{-1/2}$)
D	Diffusion coefficient of hydrogen in air (m^2·s^{-1})	p_r	Reservoir pressure (MPa)
D_0	Diffusivity of hydrogen in air (kg·m^{-2}·s^{-1})	R	Perfect gases universal constant (8.3144 J·mol^{-1}·K^{-1})
E_0	Energy of activation of the material of the tank (J·mol^{-1})	T	Ambient temperature (K).
F	Sum of the forces applied on hydrogen-air mixture	V_g	Volume of garage (m^3)
g	Gravitational force (9.81 m·s^{-2})	V_{m25}	Molar volume at 25 ^{o}C (0.0244 m^3·mol^{-1})
J	Permeation rate of hydrogen (mol·s^{-1}·m^{-2})	V_x	Volume of hydrogen-air mixture
l	Tank thickness (m)	t	Time step (s)
L	Displacement by buoyancy (m)	t_c	Time to reach the concentration c in the whole garage (s)
m	Mass of the hydrogen-air mixture (kg)		

Greek

λ_x	Displacement by diffusion (m)	ρ_{H2}	Density of hydrogen (kg·m^{-3})
ρ_{air}	Density of air (kg·m^{-3})	ρ_{mixt}	Density of hydrogen-air mixture (kg·m^{-3})

Introduction

A work was performed within the framework of the InsHyde internal project of the HySafe NoE, to examine the effect permeation on the distribution of hydrogen in a garage. Indeed, the permeation of hydrogen can be a safety issue for relevant infrastructures and technologies, when considering the phenomena in confined spaces. The released hydrogen could accumulate under the ceiling or in confinements, reach the lower flammability limit (LFL) and either represent a serious safety issue, or be equally distributed in the whole volume at low concentration below the LFL. The research was seperated in 3 parts. The part 1 aimed to define scenarios and an allowable permeation rate [1] while the part 2 focused on the experimental validation of CFD dispersion calculations [2]. The purpose of the present part 3 is to clarify this question by investigating on the behavior of release of hydrogen by permeation. After a description of the phenomena and associated parameters, the case study under consideration (e.g. a hydrogen tank in a closed garage) will be detailed. With an engineering approach, the paper will further evaluate the hydrogen concentration on the surface of the tank and define the interplay between diffusivity and buoyancy. Finally, a numerical simulation is performed to estimate the profile of the distribution of hydrogen within the garage.

1. PERMEABILITY AND PERMEATION

1.1. Engineering correlations

Definition of permeation could be found elsewhere [3]: permeation is the overall process of a fluid crossing a membrane caused by a pressure difference. It is especially pronounced for hydrogen as it is the smallest element with a highest diffusivity.

The permeability of hydrogen for a particular material can be calculated by equation taken from [4] and is expressed in $mol \cdot s^{-1} \cdot m^{-1} \cdot MPa^{-1/2}$,

$$P = P_0 \exp(-E_0 / RT) ,\qquad(1)$$

where P is permeability of a tank material, R is the perfect gases universal constant, and T is ambient temperature. P_0 is a pre-exponential factor of permeability and E_0 is the energy of activation. The permeability strongly depends on the pre-exponential factor and the energy of activation, that are material dependent values. The temperature plays an important role - an increase in temperature leads to a higher permeability.

The permeation rate through a single membrane of a selected material is expressed in moles of hydrogen per second per squared meter of the material. It is calculated using the equation (2)

$$J = P \frac{\sqrt{p_r}}{l} ,\qquad(2)$$

where J is hydrogen permeation rate, p_r is tank pressure and l is tank wall thickness. The permeation rate for a particular material at a defined temperature will depend on an internal pressure and on a membrane thickness. The permeation rate increases with higher pressure and smaller membrane thickness. The equations (1) and (2) are valid for metallic and non-metallic materials and applicable to a single membrane's wall. For serial membranes of different materials like in type IV tanks, the permeation rate can be calculated using other correlations found in literature [5].

1.2. Safety concerns

The economical and technological viability of on-board hydrogen tanks depends on their gravimetric and volumetric capacity [6,7]. The gravimetric capacity is currently improved for types IV tanks with

the use of light, non-metalic materials that are characterized by a strong permeability. While the improvement of the volumetric capacity can be achieved by pressure increase from 350 bar to 700 bar for vehicles [8], which in return increases the permeation rate.

The permeation from onboard hydrogen tanks is a safety issue for enclosures where hydrogen can accumulate over time to create a flammable mixture with air. In well sealed enclosures with low air exchange rates the lower flammability limit of 4% of hydrogen by volume in air can be reached after quite a long time. To estimate the time for reaching LFL it is important to know how hydrogen will be distributed in the enclosure – practically uniformly or a stratified and possibly flammable layer under the ceiling. This study is aimed to clarify this question.

2. EVALUATION OF HYDROGEN PERMEATION

The purpose of this simplified analysis is to estimate how high the hydrogen concentration is on a tank surface as a function of time, and its average concentration in the enclosure based on the assumptions of a fully sealed garage and uniform hydrogen distribution. In order to have a conservative estimate, we used highest practical value currently considered for the tank pressure (1030 bar), and quite small wall thickness of a mock-up pure iron tank (0.5 mm). These choice of initial parameters represent nevertheless *"a hypothetical case since the stress in the wall of such a component would be too high for any practical engineering system"* considered in [4]. The dimensions of the tank were 0.672 m long, and 0.505 m in diameter with two hemispherical volumes at each end with diameter of 0.505 m. This was inspired by the paper [9]. The surface area of the tank is A_r=1.87 m^2. The ambient temperature T is chosen as 298 K. The enclosure considered is a typical size garage (L×W×H=5×3×2.2 m) with a volume V_g=33 m^3.

Pure iron has a very high permeability, two orders of magnitude higher than non-metallic materials. The iron specific pre-exponential factor and energy of activation have been taken from experimental work [10] and are P_0= 5.35×10^{-14} mol·s^{-1}·m^{-1}·MPa$^{-1/2}$, and E_0= 33.6 kJ·mol^{-1} respectively. This represents a permeation rate J=1.40×10^{-6} mol·s^{-1}·m^{-2} or 1.14 NmL·hr^{-1}·L^{-1} water capacity of the tank. This is close to the maximum allowable permeation rate presented in the draft of the UN ECE Regulation for type IV containers (i.e 1.0 NmL·hr^{-1}·L^{-1} of internal volume of container) [11].

2.1. Hydrogen concentration on the surface

The hydrogen that slowly permeates through a tank's wall, is ejected on the outer surface of the material. From a safety point of view, it is important to know if this hydrogen would quickly evacuate from the surface or if it would accumulate. In the later case, a dangerous built up in concentration could lead to the formation of a flammable hydrogen-air mixture close to tank's wall.

Molecules permeated from the tank are subject to Brownian motion. It describes the random movement of molecules suspended in a liquid or a gas [12]. The chaotic movement is influenced by collisions between molecules of hydrogen and other molecules in the air. Using the Brownian Motion described by Einstein's law [13] *"the displacement in direction of the x-axis that a particle experiences on the average, or, to be more precise, the root-mean-square displacement"* λ_x is

$$\lambda_x = \sqrt{\overline{\Delta x^2}} = \sqrt{2Dt} ,$$ (3)

where D is the diffusion coefficient of hydrogen in air at 25°C (i.e. 7.79 ×10^{-5} m^2·s^{-1}) and t is time.

Considering time t after start of the permeation the maximum displacement of molecules would be $\sqrt{2Dt}$. Hence, the volume V_x comprising all already permeated hydrogen molecules is calculated by

$$V_x = A_r \sqrt{2Dt} ,$$ (4)

where A_r is the tank surface. The number of moles of hydrogen n in this volume is

$$n = JtA_r . \tag{5}$$

Assuming the uniform distribution of hydrogen molecules in V_x, the hydrogen concentration $[H_2]_t$ after time t, is the ratio of the volume of hydrogen, on the total volume, where V_{m25} is the molar volume at $25^{\circ}C$ (i.e. 0.0244 m$^3\cdot$mol^{-1}), can be calculated by formula

$$[H_2]_t = 100\frac{nV_{m25}}{V_X} \tag{6}$$

By combining equations (4), (5) and (6), we obtain

$$[H_2]_t = 100\frac{JtA_rV_{m25}}{\sqrt{2Dt}\,A_r} = 100\frac{JV_{m25}}{\sqrt{2D}} \times \frac{t}{\sqrt{t}} . \tag{7}$$

Because the number of moles n will be proportional to t, and the volume will be proportional to $\sqrt{t}$, the concentration on the surface will increase with time as $[H_2]_t \propto \sqrt{t}$ until the buoyancy will overcome diffusion transport of hydrogen. It is clear that buoyancy effect increases with increase of hydrogen concentration. The second Newton's Law for buoyant motion of hydrogen-air mixture of density ρ_{mixt} in air of density ρ_{air} can be written as $F = ma = (\rho_{air} - \rho_{mixt})g$. From mechanics we know that distance passed by a body moving with acceleration a is $L = at^2/2$. Hence, the first formula could be rewritten as

$$\rho_{mixt}V_{mixt}a = \rho_{mixt}\frac{2L}{t^2} = (\rho_{air} - \rho_{mixt})g . \tag{8}$$

Finally we can calculate the displacement of mixture by buoyancy with time

$$L = \left(\frac{\rho_{air}}{\rho_{mixt}} - 1\right) \cdot \frac{gt^2}{2} , \tag{9}$$

where the density of the mixture can also be expressed by

$$\rho_{mixt} = \frac{[H_2]_t}{100} \cdot \left(\rho_{H_2} - \rho_{air}\right) + \rho_{air} . \tag{10}$$

We can now calculate a time t, when a characteristic displacement of hydrogen by buoyancy is of the same order as the displacement of hydrogen by diffusion, $\lambda_x = L$. By combining equations (7), (9) and (10)

$$\sqrt{2Dt} = \left(\frac{\rho_{air}}{\frac{JtV_{m25}}{\sqrt{2Dt}}\left(\rho_{H2} - \rho_{air}\right) + \rho_{air}} - 1\right) \cdot \frac{gt^2}{2} . \tag{11}$$

By this relationship one can estimate that after a characteristic time of about 34 seconds the displacement by buoyancy equals the displacement by diffusion and buoyancy effect prevails after that.

2.2. Homogeneous hydrogen concentration in the garage

By considering the garage as perfectly sealed, we can estimate the time t_c necessary for hydrogen to reach a homogenous volumetric concentration of the lower flammability limit of c=4% by volume

$$t_c = \frac{V_g c}{V_{m25} J A_r},$$ (12)

i.e. about 240 days.

3. NUMERICAL SIMULATIONS OF PERMEATED HYDROGEN DISTRIBUTION IN THE GARAGE

Permeation is essentially different physical phenomena compared to classical plumes (buoyancy controlled flows) and jets (momentum controlled flows). Hydrogen "releases" in very small amounts equally along the surface of high pressure storage tank. Then hydrogen diffuses to areas with smaller concentration and buoyancy affects the flow pattern at some stage. This numerical study was performed to clarify the interplay between hydrogen diffusion and buoyancy and its joint effect of distribution of permeation from a typical car tank hydrogen within a typical size garage with still air. Dimensions are identical to the one described in the engineering approach but there was a small squared orifice (0.2 m × 0.2 m) at the floor to undertake simulations at constant pressure and use assumption of incompressible flow. The small area of the vent and constant H2 supply in the garage ensured pure outflow conditions in the vent. The velocity of the descending hydrogen layer is in average about 0.012 m·s⁻¹.

The CFD model was based on solution of three dimensional, incompressible Navier-Stokes equations, energy, continuity, and hydrogen mass concentration conservation equations for laminar flow. The calculation domain represented quarter of the garage with a hydrogen storage cylinder located in the centre of the garage with a clearance 0.5 m above the floor.

The hydrogen permeation J in pure iron at 25°C was modelled using a tiny volumetric source of hydrogen in a thin layer (thickness 1 mm) around the cylinder surface. This is different from modelling of permeation by artificial plumes or jets with a momentum and mass fraction Y_{H2}=1 of hydrogen at "release orifice" (simulation demonstrated that there is no a layer with Y_{H2}=1 on tank's surface). To match the specified permeation rate, the hydrogen volumetric source term for hydrogen mass was equal just S_{H2}=2.61×10⁻⁸ kg·m⁻³·s⁻¹. The minimum control volume (CV) size was on tank's surface and equal to Δx=0.5 mm, so the hydrogen was released in a layer of two CV thickness along the surface. The total number of CVs in the calculation domain was 194,464. It is understood that the use of a smaller thickness for the volumetric source would tend to increase the hydrogen concentration of the source to 1 at the limit. Nevertheless, in the case of permeation, the source is not a continuous flow of pure hydrogen but more a discontinuous desorption of hydrogen, molecule per molecule, through wall's gaps. The CFD model formulation tried to represent this particular feature of permeation. Theoretically, the permeation rate used in this study does not release enough hydrogen to cover the whole surface of the tank to form a single layer of pure hydrogen. Indeed the diffusion process displaces quickly the hydrogen molecules away from the tank's surface.

SIMPLE algorithm was used for pressure-velocity coupling with 3ʳᵈ order MUSCL discretisation scheme for convective terms, central difference for diffusion terms, and 2ⁿᵈ order implicit time stepping. The time step, Δt=0.05 s, was kept as constant and corresponds to the maximum cell Reynolds number of about 100 and maximum CFL number 0.06. It is a common practice to use implicit SIMPLE-similar procedure for incompressible flows. Slow flow velocities and low hydrogen mass fractions in the calculation domain required high precision of calculations, and the time step Δt was chosen to minimize the numerical error.

Mass-weighted mixing law was chosen for calculation of hydrogen-air mixture viscosity, where viscosity of both components (air and hydrogen) was calculated according to the Sutherland law. Diffusivity coefficient for hydrogen in air at $T=25^0$C was estimated as $D_{H2}=7.79\times10^{-5}$ kg·m^{-2}·s^{-1}. The permeation process and hydrogen distribution in the garage were simulated for 133 min (8000 s) of real time. Simulation showed that the maximum volumetric hydrogen concentration on the top of the tank surface has reached negligible concentration of about 8.2×10^{-3} % by volume (mole fraction 0.000082 compared to lower flammability limit 0.04) at this stage. A visible distortion of the symmetrical hydrogen layer on the surface at the top of the tank, at 80 s as shown in Figure 1, indicates the buoyancy starts acting on the hydrogen-air mixture.
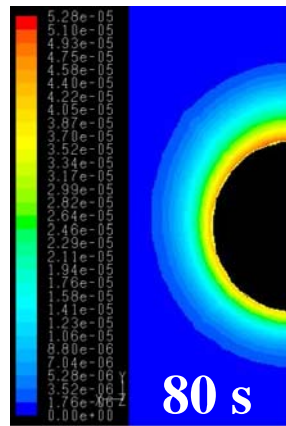

Figure 1. Hydrogen concentration (vol. %) on the tank's surface after 80 s.

Profiles of the hydrogen concentration distribution across the garage height (obtained from a vertical line situated in the middle between the cylinder and the garage walls) are shown in Figure 2. The hydrogen is distributed practically linearly across the garage height with a negligible difference in concentration of just 3×10^{-3} % of hydrogen by volume, i.e. three orders of magnitude smaller than the lower flammability limit of 4% by volume. The hydrogen concentration increases simultaneously both at the top and at the bottom of the garage with time preserving linear distribution of hydrogen concentration. It is the indication that with time the transport of hydrogen by diffusion downwards and hydrogen transport upwards by buoyancy are balanced. It would suggest that the flammability limit is reached identically in the whole volume, after about 240 days as calculated in our case study.
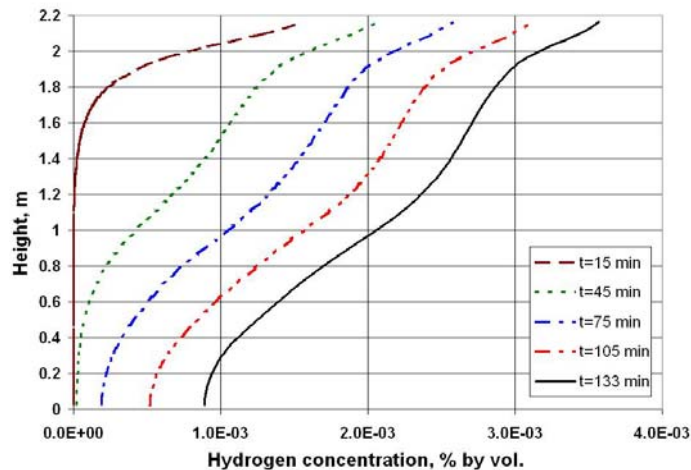

Figure 2. Hydrogen concentration profile across the garage height with time.

Dynamics of the hydrogen distribution within the garage is shown in Figure 3. It is seen, that during the whole simulated period there is no stratification of hydrogen in practical sense and formation of layer beneath the ceiling.
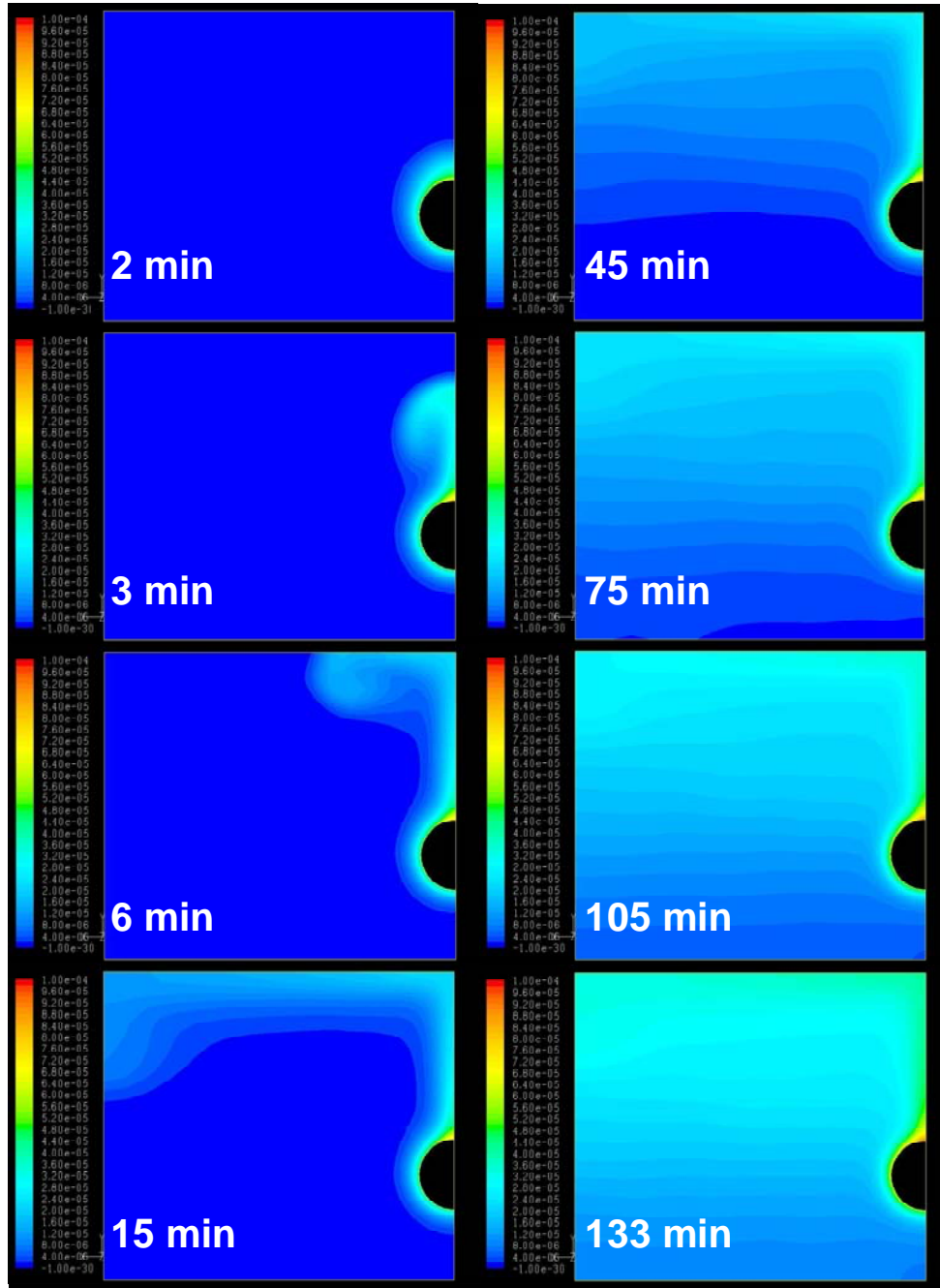

Figure 3. Permeated hydrogen distribution in space and time.

4. CONCLUSIONS

The permeation rate can be calculated by relationships available in literature based on the selection of material and its thickness, storage pressure and temperature.

During the initial stage of permeation the concentration of hydrogen at the surface grows as square root of time. Simulation showed that the maximum volumetric hydrogen concentration on the top of the tank is about 8.2×10^{-3} % by volume. The simplified comparative analysis of diffusion and buoyancy processes close to the surface during permeation shows that the buoyancy overcomes the diffusion in about 34 seconds after start of the process and then buoyancy prevails. Numerical simulations confirmed this result. Indeed, at time of about 80 s the buoyancy distortion of "cylindrical" symmetry of hydrogen propagation by diffusion is clearly seen.

This particular scenario simulated over a period of 133 minutes, showed that during the permeation process from the tank in a "closed adiabatic" garage with still air, the difference in concentration of hydrogen at the ceiling and floor is negligible. Further investigations would be needed to consider the permeation in a more realistic scenario i.e. a whole compressed hydrogen car parked in a garage.

Acknowledgment

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