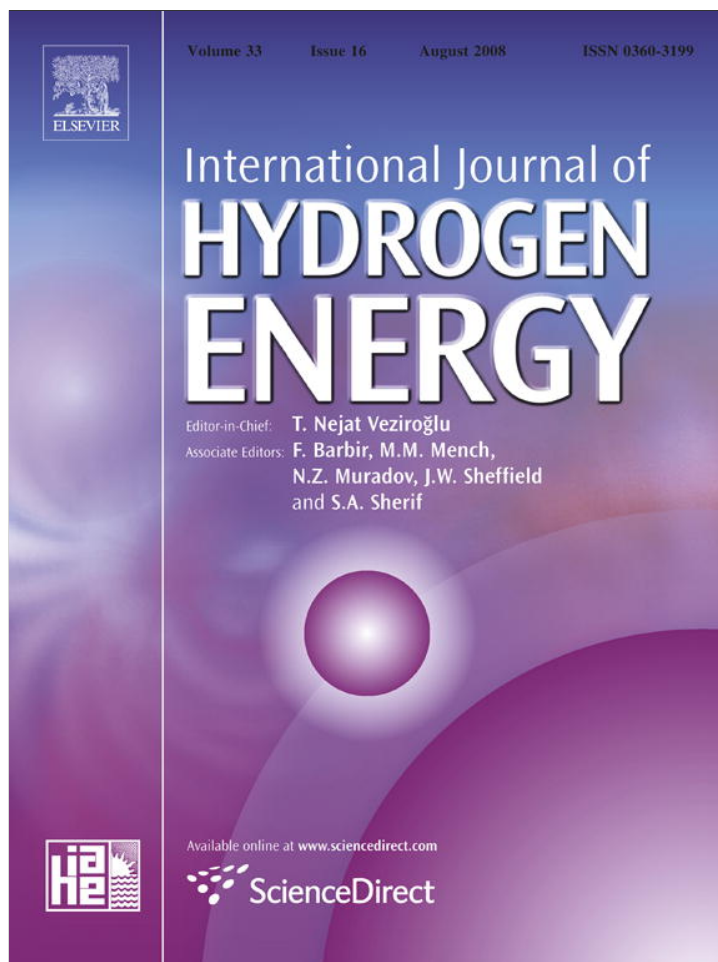


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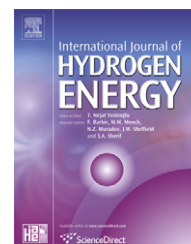


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## Technical Communication

# Material-based hydrogen storage<sup>☆</sup>

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### ABSTRACT

One safety aspect of a material-based hydrogen storage system is the exposure of such system to a high-temperature environment (e.g., a fire) causing an increase in pressure. A simple analysis, based on a material balance, is provided to estimate the effect of temperature on equilibrium storage pressure in a material-based hydrogen storage system. Under certain limited ideal and non-ideal situations and using a linear relationship between the hydrogen in the material phase and vapor phase, simple explicit analytical expression for equilibrium storage pressure at a specified temperature can be easily derived without resorting to complicated numerical techniques.

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## 1. Introduction

One of the main challenges in advancing hydrogen fuel-cell applications to the transportation sector is to improve on-board hydrogen storage to extend driving distance before refueling [1]. In this regard, material-based hydrogen storage, which generally employs absorption, adsorption, or chemical reaction, offers many advantages over conventional storage as high-pressure compressed hydrogen gas or cryogenic liquid hydrogen. The storage system, which is reversible (i.e., rechargeable), can potentially store large quantities of hydrogen at low pressures, can tailor the release of stored hydrogen at low operating temperatures and pressures, and offers significant improvement of gravimetric and volumetric storage capabilities over conventional systems [1]. The material-based storage systems that have been examined include the uses of metal and chemical hydrides, carbon-based

materials, and advanced new-concept materials; however, many scientific technical, and economic challenges remain [1–5].

Although material-based hydrogen storage systems operate at low pressures, the presence of large quantity of hydrogen still poses a safety concern [6]. From a fire hazard and safety standpoint, the final equilibrium storage system's pressure would be an important risk parameter to assess if the storage system on a vehicle was rendered closed due to inoperable, disabled, or malfunctioned flow systems and built-in safety mechanism as a result of a crash event and was exposed to a thermal environment (e.g., a post-crash fire). A change in temperature will perturb the equilibrium hydrogen distributions in the vapor and material phases. Increasing the temperature in general tends to favor the release of hydrogen from the material phase; however, the released hydrogen increases the storage system pressure

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which in turn facilitates the hydrogen transport back to the material matrix until a new equilibrium state is attained. Therefore, in a closed system, complete release of all the stored hydrogen from the material matrix into the bulk vapor phase is not likely due to the equilibrium constraints, which could be considered as an intrinsic safety mechanism to prevent unsafe pressure build-up.

For metal hydride systems, the equilibrium pressure can generally be correlated with temperature using experimental data and the van't Hoff plot [7,8], which is a graph of the logarithm of equilibrium pressure versus the reciprocal of absolute temperature. In this note, a different approach is used to derive the effect of temperature on equilibrium storage pressure based simply on a material balance between the hydrogen contained in the material matrix and the vapor-phase hydrogen. Under certain limited ideal and non-ideal situations, simple explicit analytical expressions for equilibrium storage pressure at a specified temperature can be easily derived with pertinent physical parameters identified and may prove useful for simple safety system engineering analysis.

## 2. Analysis

The storage system is assumed to be closed and at a uniform temperature, and the total charged amount of hydrogen in the storage system is known.

Assuming a storage system with a total volume  $V_t$  containing a hydrogen-storage medium with volume  $V_{ads}$  and mass,  $m_{ads}$  and the total moles of hydrogen,  $n_t$ , in the system (see Fig. 1), the hydrogen mole balance is

$$n_t = n_a + n_v \quad (1)$$

where  $n_a$  and  $n_v$  are the total moles of hydrogen in the material and bulk vapor phase, respectively. For a given storage system, the left-hand side of Eq. (1) is known. Under equilibrium conditions,  $n_a$  and  $n_v$  are related as

$$n_a = F(n_v) \quad (2)$$

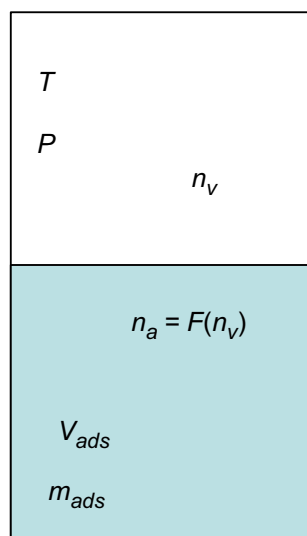


Fig. 1 – Schematic of an idealized storage system used for the analysis.

where the function  $F$  is, in general, temperature dependent and is determined by correlating experimental measurements. In the case of adsorption, Eq. (2) corresponds to an adsorption isotherm. At equilibrium and using Eq. (2), there is only one unknown parameter in Eq. (1), namely  $n_v$ . Having solved for  $n_v$ , the equilibrium pressure in the storage system can be derived with the help of an equation of state.

As an illustration, a linear functional form of  $F$  is used in order to obtain an explicit analytical expression for equilibrium system pressure. This functional form has been used in the adsorption literature [9–11] and may be approximated in material-based hydrogen storage systems under low-hydrogen loadings [12,13].

$$b_a = k_L c_a \quad (3)$$

where  $b_a$  is the concentration of hydrogen in the material phase in mole/kg of material,  $k_L$  is an equilibrium constant and is a function of temperature, and  $c_a$  is the concentration of hydrogen in the bulk vapor phase in mole/m<sup>3</sup> of vapor phase.

In this communication, the bulk vapor phase will be treated as either an ideal or a non-ideal gas. Ideal gas assumption greatly simplifies the analysis and may be a reasonable approximation for low-pressure material-based hydrogen storage systems. For the case of non-ideal gas, the truncated pressure form of the virial equation is used to render the analysis tractable so that a simple analytical expression for pressure can also be obtained.

### 2.1. Ideal gas

From the ideal gas law,

$$c_a = \frac{P}{RT} \quad (4)$$

where  $P$  is the pressure in the vapor phase,  $R$  is the universal gas constant, and  $T$  is the temperature.

From Eqs. (1), (3), and (4),

$$n_t = m_{ads} k_L \frac{P}{RT} + \frac{P(V_t - V_{ads})}{RT} \quad (5)$$

Solving for  $P$ ,

$$P_{ideal} = \frac{n_t RT}{m_{ads} k_L + (V_t - V_{ads})} \quad (6)$$

### 2.2. Non-ideal gas

The truncated pressure form of the virial equation to represent non-ideality, which is usually adequate and acceptable when  $P_r \leq 0.5T_r$  [14], is:

$$Z = \frac{P}{RTc_a} = 1 + B'P \quad (7)$$

where  $P_r$  and  $T_r$  are the reduced pressure and temperature, respectively,  $Z$  is the compressibility factor, and  $B'$  is the second virial coefficient. From Eq. (7),

$$c_a = \frac{P}{RT(1 + B'P)} \quad (8)$$

From Eqs. (1), (3), and (7), and solving for  $P$ ,

$$P_{\text{non-ideal}} = \frac{n_t RT}{m_{\text{ads}} k_L + (V_t - V_{\text{ads}}) - n_t RT B'} \quad (9)$$

Note that Eq. (9) reduces to Eq. (6) if the gas is ideal ( $B' = 0$ ).

Combining Eq. (6) and Eq. (9),

$$\frac{P_{\text{non-ideal}} - P_{\text{ideal}}}{P_{\text{non-ideal}}} = B' P_{\text{ideal}} \quad (10)$$

In this particular case, the ideal gas assumption results in the under-prediction of the non-ideal equilibrium storage pressure by  $B' P_{\text{ideal}} \times 100$  percent.

### 3. Concluding remarks

The above analysis indicates that the total amount of hydrogen charged, the free (ullage) space of the storage system, the amount of material used for hydrogen storage, and the amount of hydrogen in the material phase are important parameters to determine the equilibrium pressure at a specified temperature. If the vessel is breached, rendered closed, and compressed due to impact, the pressure build-up in a potential post-crash fire could be substantial from a reduction in vessel volume according to Eqs. (6) and (9). The approach described above is applicable to a closed storage system characterized by a complex nonlinear equilibrium relationship (e.g., Langmuir-type adsorption isotherms [9,10]) and a non-ideal equation of state (e.g., [15]); however, numerical techniques are needed to solve for the attainable pressure at a prescribed temperature.

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