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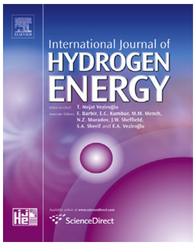

A novel procedure for the preliminary design of dense metal membrane modules for hydrogen separation

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ABSTRACT

The paper introduces a procedure for the preliminary design and optimization of membrane modules made of dense metal permeator tubes for hydrogen separation from gas mixtures. Based on the mass transfer mechanisms of hydrogen into the metal lattice, the design procedure establishes the relationships among the dimensionless parameters related to the geometry (tube diameter, length and wall thickness) and the operating conditions (pressure, temperature, flow rates of feed and permeate streams, etc.).

The concept of maximum hydrogen recovery and its dependence on pressure and dilution of feed stream is introduced and discussed. Similarly, the decrease of the driving force with the increase of the required hydrogen recovery factor is showed. The influence of the operative conditions on the minimum required tube wall thickness is also determined. Particularly, the operation at high temperature reduces significantly the Pd-alloy tensile strength thus increasing the minimum Pd-tube thickness.

Finally, the model is applied to a case study of a Pd-membrane module separating ultra-pure hydrogen from a gas stream coming from the methane reforming. A sensitive analysis is carried out by using the expressions and the graphs of dimensionless parameters defined by the design procedure introduced in this paper.

Introduction

In the last years, the hydrogen has been considered as an energy vector capable to reduce the negative effects on the environment caused by the greenhouse gases emissions due to the large use of fossils [1–3]. When produced from renewable energy sources (solar, wind, biomass) the environmental impact of hydrogen is estimated to be very modest [4] and the possibility to be exploited in distributed energy systems makes it an interesting energy vector [5,6]. However, due to technical and economic reasons, presently most of the hydrogen is produced via reforming of methane or other fossils.

Further diffusion of hydrogen in large-scale applications needs the development of reliable and cheap technologies for its separation, transportation and storage. Among the gas separation technologies, the membranes present several advantages such as continuous operation, reduced costs, modularity and scale-up with possibility of easy integration with other traditional separation processes [7–12].

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Pd-based membranes have the capability of separating selectively hydrogen [13,14]. In the industrial applications the cost of the precious metal is a key issue and therefore several manufacturing technologies have been applied in order to reduce the membrane thickness [14]. Composite membranes are made of thin Pd-alloy layers covered over porous supports [15–17]: these membranes exhibit values of permeance higher than dense self-supported Pd-tubes. In principle, composite membranes achieve complete hydrogen selectivity when the thickness of the metal layer is large enough to close the pores of the support. However, the higher the thickness of the metal layer the higher the shear stress rising at interface metal-support as a consequence of the elongation/contraction of the Pd–Ag hydrogenated/dehydrogenated [18]. Recent literature reports novel composite Pd-membranes characterized by complete hydrogen selectivity and good stability [15]. On the other hand, the dense Pd-membranes of thickness larger than 0.050 mm exhibit an intrinsic infinite selectivity: in order to ensure the stability of such membranes, it is very important to adopt a proper mechanical design avoiding any mechanical stress on the thin-walled Pd-based tubes [23]. Particularly, Pd-based dense membranes have been characterized in long term tests (1 year) demonstrating their compete selectivity [19].

Among metals, the Pd-based alloys maximize a series of properties such as hydrogen permeability, mechanical resistance, electrical resistivity and resistance to H_2 embrittlement [18]. Main applications of thin-walled Pd–Ag tubes have concerned the production of hydrogen from dehydrogenation reactions (reforming of alcohols and hydrocarbons) [14,17,20], alkaline electrolysis [21] and the separation of hydrogen isotopes through detritiation processes [22].

The design of modules made of self-supported tubular membranes has to take into consideration: i) chemical-physical and mechanical criteria, such as hydrogen mass transfer mechanisms and stress analysis, ii) geometry, and iii) operating parameters, such as, pressure, temperature, flow rate, etc. In order to establish the relationships among these main design criteria and parameters, in this work a design procedure is discussed with the aim to provide a tool for the assessment and optimization of membrane modules consisting of dense metal tubes in both single- or multi-tube configuration. The procedure establishes the relationship between the maximum value of the hydrogen recovery, the operative pressure and the dilution of the feed stream.

This study is aimed at providing a tool for the sizing of membrane modules by taking into account a number of parameters related to the operating conditions (P, T, flow rates, gas composition), tube geometry (length, diameter, wall thickness) and material properties (tensile strength, etc.).

Theory

The permeation of hydrogen through a dense metal wall is a mass transfer mechanism consisting of several steps [18]:

- the molecule of hydrogen diffuses through the gas-film over the membrane surface at higher pressure (upstream side),
- the molecule of hydrogen dissociates and is adsorbed over the metal surface,
- the hydrogen atoms diffuse in the metal lattice,
- the hydrogen atoms desorb from the metal surface at lower pressure (downstream side) where they recombine to form molecules,
- the molecule of hydrogen diffuses through the gas-film over the membrane surface at lower pressure (downstream side).

In a simplified way by considering only the mass transfer resistance through the metal, the hydrogen permeation can be obtained by combining the expressions of hydrogen diffusion and solubility into the metal lattice.

The diffusion of hydrogen atoms through the metal lattice is described by the Fick's Law:

$$J = -\delta \frac{\partial c}{\partial z} \tag{1}$$

where J, [mol m^{-2} s^{-1}], is the hydrogen flux, δ, [m^2 s^{-1}], is the diffusivity and c, [mol m^{-3}], the concentration of hydrogen along the abscissa z, [m].

The solubility of hydrogen into the metal is ruled by Sieverts' Law that, under thermodynamic equilibrium conditions, establishes the relationship between the concentration of hydrogen solubilised in the metal lattice and the partial pressure of the hydrogen in the gas phase:

$$c = K\sqrt{P_{H_2}} \tag{2}$$

where K, [mol m^{-3} $Pa^{-0.5}$], is the Sieverts' constant and P_{H_2}, [Pa], the hydrogen partial pressure in the gas phase. The combination of expressions (1) and (2), which is referred to as Sieverts' equation, states that the hydrogen flux through a selective membrane is expressed by:

$$J = \frac{Pe}{s} \cdot \left(P^{0.5}_{H_2,feed} - P^{0.5}_{H_2,perm}\right) \tag{3}$$

where Pe [mol m^{-1} s^{-1} $Pa^{-0.5}$] is the permeability, s [m] the membrane thickness and $P_{H_2,feed}$ and $P_{H_2,perm}$ are, respectively, H_2 partial pressures at the feed side (upstream) and the permeate side (downstream).

Deviations from the Sieverts' equation are mainly due to:

- gas-film resistance,
- surface resistances [23,24],
- presence of poisoning gases such as CO and CO_2 [24],
- permeation through the pores of the support (for membrane composites).

Especially, the Sieverts' equation can be modified by introducing a drop of the hydrogen partial pressures upstream and downstream that accounts for the additional mass transfer resistance due to both surface resistances and the presence of poisoning gases [25]. On the other hand, the mass transfer resistance due to the gas-film and to the permeation through the support's pores is ruled by an expression where the hydrogen partial pressure exponent is 1 instead of 0.5. In order to take into account all these effects, in literature a simplified equation, where the exponent 0.5 of the formula (3) is substituted by $0.5 \le n \le 1$, is proposed [18]:

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