

RELEVANCE OF CONCENTRATION POLARIZATION ON HYDROGEN FLUX THROUGH A THIN, HIGHLY SELECTIVE Pd₈₀-Ag₂₀ CERAMIC SUPPORTED MEMBRANE

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Abstract

Permeation experiments using pure hydrogen and several mixtures of hydrogen, nitrogen, and methane were performed on a Pd-based membrane deposited on a ceramic support. In particular, the permeance of pure hydrogen as well as binary and ternary mixtures containing also nitrogen and methane was measured using different feed flow-rates and H₂ concentrations, in a custom-built, tube-in-shell apparatus. The membranes, supplied by NGK Insulator Ltd Japan, consisted of a 2.5 μm Pd-Ag layer deposited on a tubular ceramic support. They showed extremely high hydrogen permeance and practically infinite selectivity toward hydrogen. Permeability and permeance were calculated from the linear regression of pure hydrogen data, according to Sieverts' law; permeability at 673 K is $3.08 \times 10^{-6} \text{ mol s}^{-1} \text{ m}^{-1} \text{ bar}^{-0.5}$.

Surprisingly, experiments showed that hydrogen permeability is much lower for gas mixtures experiments than for the pure hydrogen case, and also that the hydrogen flux for mixture experiments deviates significantly from Sieverts' law. The above features reveal the presence of a significant mass transfer resistance in the external gas phase; that is also clearly confirmed by the increase in hydrogen permeability obtained with increasing the feed flow-rate of the gas mixtures.

The data collected were then used to calculate the average mass transfer coefficient in different experimental conditions. The gas phase mass transfer coefficient follows closely a correlation of boundary-layer type, proportional to the square root of the Reynolds number and to the cubic root of the Schmidt number.

Introduction

The idea of a hydrogen economy related to the use of this gas as a clean energy carrier has gained much attention in the last years giving new interest to researches aimed at improvements of the production of pure hydrogen. Thus palladium and palladium based membranes, which are theoretically able to completely purify hydrogen from other gases, have been widely studied in the last years with the focus on the fabrication of stable and long lasting membranes, with high flux and selectivity.

Nowadays, even if not yet at an industrial level, palladium based membranes can be produced, providing a high permeate flux and ultra-pure hydrogen[1,2]. The attention is then progressively moving from the production and characterization to the study of the membrane behavior inside the separation modules or membrane reactors in order to have valuable information for the development of pilot scale processes and for the system scale up. Indeed the peculiar characteristics of these membranes, with high rates of hydrogen permeation, can lead to accumulation of non permeable gases and depletion of hydrogen on the boundary layer close to the membrane[3,4,5]; concentration polarization phenomena have, therefore, to be taken into account for a proper description of the module behavior.

In this study the analysis of such phenomena is considered testing hydrogen permeation behavior of highly permeable and highly selective Pd₈₀Ag₂₀ membranes in different operative conditions; different mixture compositions as well as different feed flow-rates were considered in

order to reveal the presence, if any, of concentration polarization in the module and to understand their influence on the membrane efficiency as a function of the different operating conditions.

Materials and equipment

The membranes used in the present work were provided by NGK Insulators Ltd. and consist of a dense, 2.5 μm thick, Pd-Ag layer, with silver content of about 20% by weight, deposited via electroless plating on the external surface of a tubular asymmetric α -alumina support[1].

The membranes used have an external diameter of about 1 cm, a total length of 9 cm, and are sealed, on one end, with a stainless steel plug and endowed, on the other end, with a VCR fitting for coupling with the permeation module. The latter was a custom-built stainless-steel shell-in-tube module connected to the gas reservoirs through different pressure and flow controllers which allow to feed the module with mixtures of desired compositions and flow-rates.

The different streams leaving the module were also endowed with pressure controllers and mass flowmeters on both permeate and retentate sides in order to maintain the desired pressure difference across the membrane and to measure the permeating flow. A gas chromatograph connected to all the different streams in the system gave a direct measurement of their compositions.

The module was located inside a tubular furnace and an additional heating element, as well as a thermocouple, were inserted close the membrane to obtain an accurate temperature control, during the experiments[1].

Different permeation experiments were performed testing the membranes at $400\text{ }^\circ\text{C}\pm 2\%$ and using different pressures (total differential pressures ranging between 0.2 and 6 bar), and different feed flow-rates (1, 2, and 3 NL min^{-1}). Tests were performed with pure hydrogen as well as mixtures with nitrogen and methane; in particular H_2/N_2 mixtures (50 and 88 % $_{\text{vol}}$ of H_2), H_2/CH_4 mixtures (50% $_{\text{vol}}$ of H_2) and the ternary mixtures $\text{H}_2/\text{N}_2/\text{CH}_4$ (50/25/25 % $_{\text{vol}}$) were used for the experiments. All gases used in the experiments were gascromatographic grade with purity of 99,99% and were available at 11 bar.

During permeation experiments the pressure in the shell side was increased by subsequent steps, measuring the permeate flux and the concentration of the different streams leaving the module until constant steady state was reached, and the permeate, retentate and feed streams remained unchanged for at least one hour.

Theoretical Background

Hydrogen transport through Pd-based membranes is commonly represented by Sieverts' law, which results from the coupling of two processes: i) the hydrogen adsorption and dissociation onto Pd surface ($\text{H}_2 \rightarrow 2\text{H}$) and ii) the subsequent atomic hydrogen diffusion in the metallic lattice [7, 8]; when the reaction is fast enough for the diffusion to be the controlling step of the process, the hydrogen flux, \mathbf{N}_{H_2} , can be written as:

$$\mathbf{N}_{\text{H}_2} = \frac{D_{\text{H}} K_{\text{S}}}{2} \cdot \frac{(p_{\text{H}_2, \text{ret}}^{0.5} - p_{\text{H}_2, \text{per}}^{0.5})}{\delta} \quad (1)$$

where D_{H} is the average diffusivity of atomic hydrogen in the Pd-Ag alloy, p_{H_2} is the partial pressure of hydrogen at the retentate (*ret*) or permeate (*per*) side, δ is the membrane thickness and K_{S} is the Sieverts' constant which represents the equilibrium constant of the adsorption/dissociation reaction considered above.

Consistently with the solution diffusion model for transport in dense membrane an hydrogen permeability, $\bar{\mathbf{P}}_{\text{H}_2}$, [$\text{mol m}^{-1} \text{s}^{-1} \text{bar}^{-0.5}$ or $\text{NL m}^{-1} \text{s}^{-1} \text{bar}^{-0.5}$] and permeance, $\bar{\mathbf{K}}_{\text{H}_2}$, [$\text{mol m}^{-2} \text{s}^{-1} \text{bar}^{-0.5}$ or $\text{NL m}^{-2} \text{s}^{-1} \text{bar}^{-0.5}$] through the Pd based membrane can be defined as :

$$\bar{K}_{H_2} = \frac{\bar{P}_{H_2}}{\delta} = \frac{N_{H_2}}{(P_{H_2,ret}^{0.5} - P_{H_2,per}^{0.5})} \quad (2)$$

which can be used to characterize the transport properties of the membranes under consideration.

Eq (2) hold for hydrogen which is undergoing dissociation at the Pd surface, but not for other gases that follow the solution diffusion mechanism and thus, in view of their negligible solubility and diffusivity values in the metallic lattice, cannot practically permeate in the dense palladium layer, giving to this kind of membranes a virtually infinite selectivity.

Due to the presence of other resistances to mass transport, as those related to the porous support or to concentration profile in the gas phase, experimental data often deviate from Sieverts' law and are usually described by modifying the relationship as follows:

$$N_{H_2} = \bar{P}_{H_2} \frac{(P_{H_2,ret}^n - P_{H_2,per}^n)}{\delta} \quad (3)$$

where n is now an empirical exponent which usually takes values between 0.5 and 1 depending on the dominant resistance in the system.

Such an approach indeed does not give any physical insight to the system behavior and better results are easily achievable considering the different process in series; such a problem was originally treated and solved by Ward and Dao[9] which referred to the works done by Holleck[8] and by King and Wells[10] for the modeling of hydrogen transport in Pd membranes. In particular these authors considered the transport as the result of the following processes:

- Hydrogen transport in the gas phase from the bulk to the membrane surface in the high concentration (and vice versa in the permeate side);
- Adsorption (desorption) and dissociation (formation) of atomic (molecular) hydrogen at the high (low) Pd surface;
- Atomic hydrogen diffusion in the metallic layer.

The transport in the porous support was not included in the list because only unsupported membranes were considered in the study but it is easily understood that in the case of supported membranes also the support resistance has to be considered in principle[11].

In the present work the interest was focused on the possible presence of external transport resistances which are responsible of the differences in hydrogen permeability observed between pure hydrogen and mixture experiments. Such resistances indeed are usually neglected for metallic membranes, but different authors have already pointed out that for highly permeable and selective membranes they can have not negligible effects on the separation performances[3,4,5]. The resistance of the gas phase can be easily accounted for through the introduction of an external mass transport coefficient, k_G ; the hydrogen flux can therefore be described as:

$$N_{H_2} - x_{H_2,int} N_{tot} = k_G (x_{H_2,ret} - x_{H_2,int}) \quad (4)$$

where N_{tot} is the total permeate flux and x_{H_2} is the average hydrogen molar fraction at the retentate side (subscript *ret*) and at the interface between the gas phase and the Pd-Ag membrane (subscript *int*).

When the Sieverts' law can be used to describe the transport in the membrane the combination of Eqs. (1) and (4) allows to calculate the interfacial hydrogen concentration and to determine the importance of the mass transport resistance in the gas phase. The relevance of such term depends obviously on the value of k_G which depends on both the material properties and system fluid dynamics, and is related to Schmidt (Sc) and Reynolds (Re) numbers through a general relationship of the following form[12]:

$$Sh = \frac{k_G l}{cD} = \alpha Re^a Sc^b \quad (5)$$

where Sh represents the Sherwood number l is a characteristic length of the system, a and b are constants that depend on the system geometry and fluid dynamics and c and D represent respectively the molar concentration and the diffusion coefficient of hydrogen in the gas phase.

Results

The membrane behavior was studied extensively considering three different feed flow-rates (1, 2 and 3 NL min⁻¹) at 400 °C, both for the pure hydrogen tests as well as for hydrogen mixtures of different compositions.

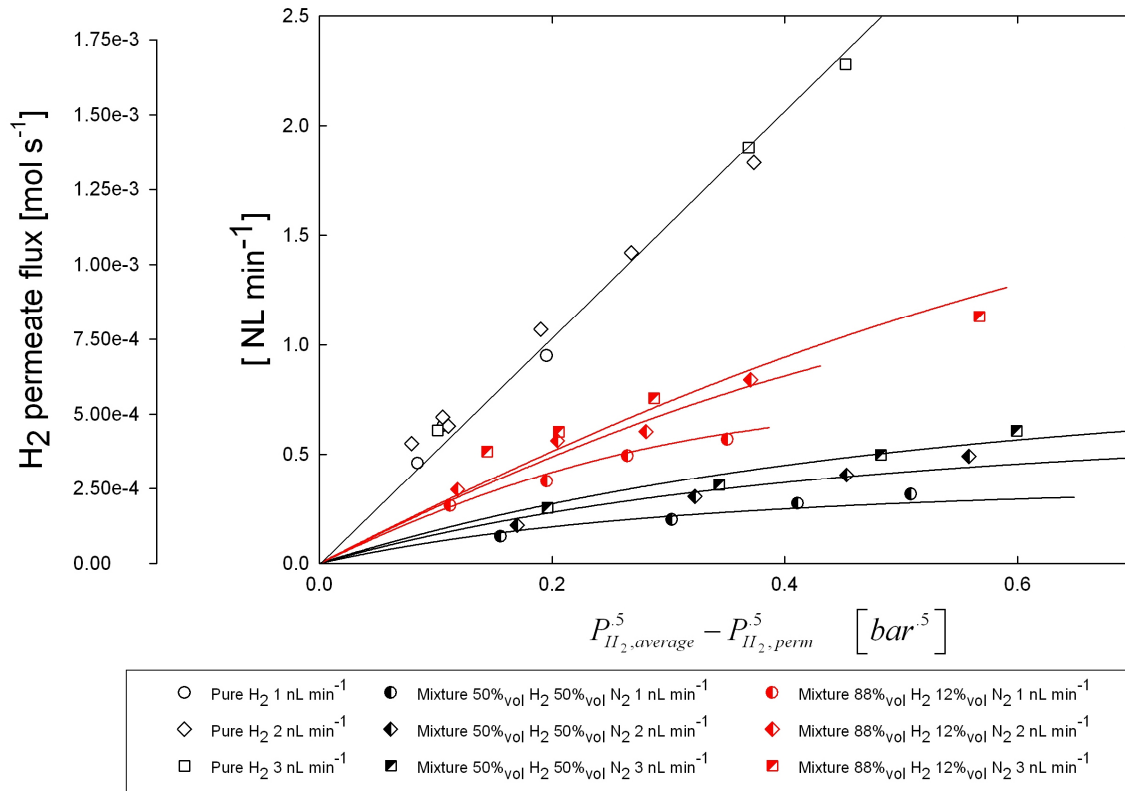


Figure 1 Experiments performed at 400°C at three different flow-rates. Shaded symbols represent pure hydrogen tests, semi-shaded N₂-H₂ mixtures: black symbols 50%_{vol} H₂-50%_{vol} N₂, red 88%_{vol} H₂-12%_{vol} N₂.

The results, reported in compact form in figure 1, show that for pure hydrogen permeation tests permeability follows the Sieverts' law, confirming that the diffusion in the Pd alloy is still controlling the hydrogen transport in the membrane, even if the membranes are very thin. The permeate flux is independent of the feed flow-rate. Permeability and permeance values are calculated through a linear regression of experimental data, according to Eq. (2), in particular hydrogen permeability at 400 °C is $3.08 \times 10^{-6} \text{ mol s}^{-1} \text{ m}^{-1} \text{ bar}^{-0.5}$ and is consistent with the many experimental data reported in previous works[13-19]; on the other hand, due to the small thickness of the metallic layer, the permeance is $1.23 \text{ mol s}^{-1} \text{ m}^{-2} \text{ bar}^{-0.5}$ at 400 °C and is among the highest values found in the literature for similar membranes as it can be observed in table 1.

The hydrogen flux permeating from different gaseous mixtures is also reported in figure 1; it is apparent that hydrogen permeance in pure gas experiments is definitely higher than that measured in the case of mixtures at the same hydrogen partial pressure. In mixture experiments the hydrogen flux across the membrane shows a rather different dependence on the driving force, since it depends

on both hydrogen concentration in the feed and on feed flow-rate; it decreases drastically when the feed concentration decreases and increases when the feed flow-rate is increased.

Table 1. Permeante values at several temperatures, nominally 400, 450, and 500 °C and comparison with selected literature data.

Authors	Ref.	Pd μm	T $^{\circ}C$	\bar{K}_{H_2} $mol\ s^{-1}\ m^{-2}\ bar^{-0.5}$
This study		~2.5	400	1.232
Pizzi et Al. (2008).	[6]	~2.5	400	0.853
A. Basile et al. (2001)	[14]	70	400	0.054
S. Uemiya et al (1991)	[15]	5.8	400	0.659
N. Itoh et al.(1993)	[16]	20	400	0.204
L. Yang (2006)	[17]	20	400	0.264
E. Gobina et al(1994)	[18]	6	400	0.017
Y. Guo et al(2003)	[19]	8.6	400	0.864

In addition clear deviations from Sieverts' law are visible since the permeate flux is not linear with the difference of the square root of hydrogen partial pressure at the two sides of the membrane but shows a well defined downward concavity. In any event, the G.C. analysis showed that no nitrogen, or methane, was present in the permeate stream, in all the tests performed, so that the selectivity of the membrane can be assessed to be larger than 10000 (estimated from the accuracy of the gascromatograph) confirming the existence of a continuous, dense and defect free Pd-Ag layer on the external surface of the tested membranes. Thus the behavior observed for mixtures cannot be attributed to the presence of defects on the membrane surface.

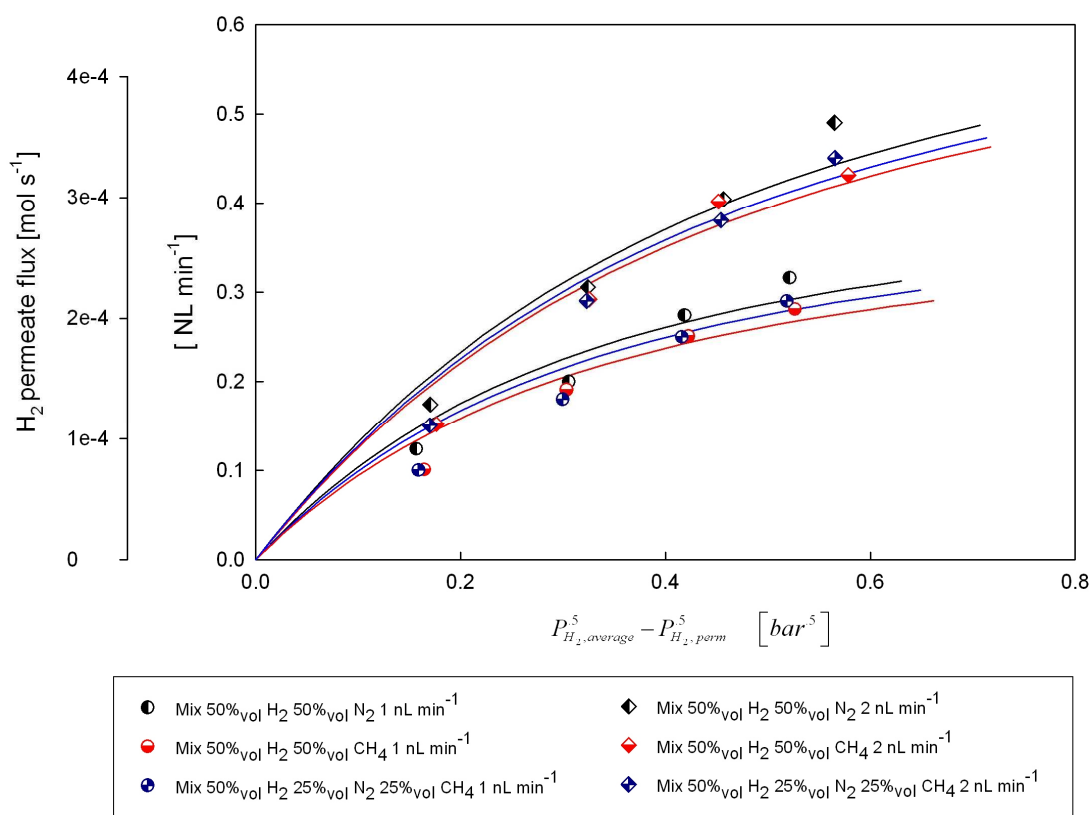


Figure 2. Effect of different non permeable gas in the hydrogen permeation. Tests were carried out with 50%_{vol} H₂ feed content for three different mixtures at 1 and 2 NL min⁻¹ feed flow rate.

The same behavior observed for H₂/N₂ mixtures is shown also when hydrogen-methane mixture as well as ternary mixture of the three gases are considered; the data, reported in figure 2, show indeed the general qualitative behavior of the other mixtures with just a slight decrease in the permeate flux when nitrogen was substituted by methane, as the non-permeable gas, in the feed. In mixture permeation tests the clear difference with respect to the pure hydrogen experiments is not directly related to the type of non penetrating gas present in the mixture.

Discussion

The results show that the membranes considered are endowed with an extremely high selectivity towards hydrogen suggesting the presence of a defect free Pd-Ag layer deposited on the porous substrate.

Permeate flux from pure hydrogen feeds follows Sieverts' law, while when mixtures are used in the feed the hydrogen flux shows a different trend and increases when the feed flow-rate increases. Such deviations, observed for gas mixture, can be explained considering the existence of additional resistance to mass transport in the gas phase. Other possible explanations, such as competitive absorption or surface poisoning, which has been reported in some cases[20,21,22], also for inert gas like nitrogen, do not appear applicable to the present case, since two different non permeable gases (methane and nitrogen) lead to very similar behaviors despite of their different chemical nature. Furthermore, surface effects cannot explain the permeate flux dependence on the feed flow-rate shown for gas mixtures.

In order to confirm the role of concentration polarization in the gas phase, the behavior of the system can be described by using Eqs. (2) and (4), thus obtaining the value of k_G as well as of the average interfacial pressure of hydrogen on the membrane surface, for all the experimental conditions inspected. The gas transport coefficient has been considered as the only fitting parameter of the procedure and was used to minimize the deviation between the model predictions and the experimental data. The curves, calculated through such approach are reported, as solid lines in figures 1 and 2, from which the rather good agreement with experimental values is self-evident.

In order to further support the interpretation offered for the behavior of hydrogen flux from gas mixtures, it is important to show that the k_G values obtained have a clear physical meaning and that k_G is not a mere fitting parameter. To that aim Eq. (5) has been used as a guideline to derive a relationship among the Sherwood number, calculated through the fitted k_G values, and Reynolds and Schmidt numbers corresponding to the different operating conditions examined.

The relationship obtained is reported in figure 4, which clearly indicates that there is a nice linearity between the calculated Sherwood number and the product $Re^{0.5}Sc^{0.33}$, showing a dependence very similar to that derived by the well known boundary layer theory over a flat surface; the proportionality constant is different and is about 1.89, nonetheless the existence of such a typical relationship strongly confirms the physical consistence of the interpretation offered. Thus we can conclude that the presence of concentration polarization phenomena cannot be neglected and must be considered in order to simulate and design properly the separation modules.

Conclusions

Permeation experiments have been performed on thin Pd-Ag membranes for hydrogen purification at different feed flow-rates and feed mixture compositions.

The membranes resulted to be extremely selective towards hydrogen and to possess very high permeance values, among the highest found in the open literature for similar membranes. The pure hydrogen data showed excellent agreement with the Sieverts' law while significant deviations from Sieverts' law were found in mixtures experiments, where the permeate flux is lower than for the pure hydrogen case, at a given value of hydrogen partial pressure in the feed side. For gas mixtures, in addition, the hydrogen permeate flux increases both with increasing feed hydrogen concentration

and feed flow-rate, indicating the presence of a significant concentration polarization in the separation module.

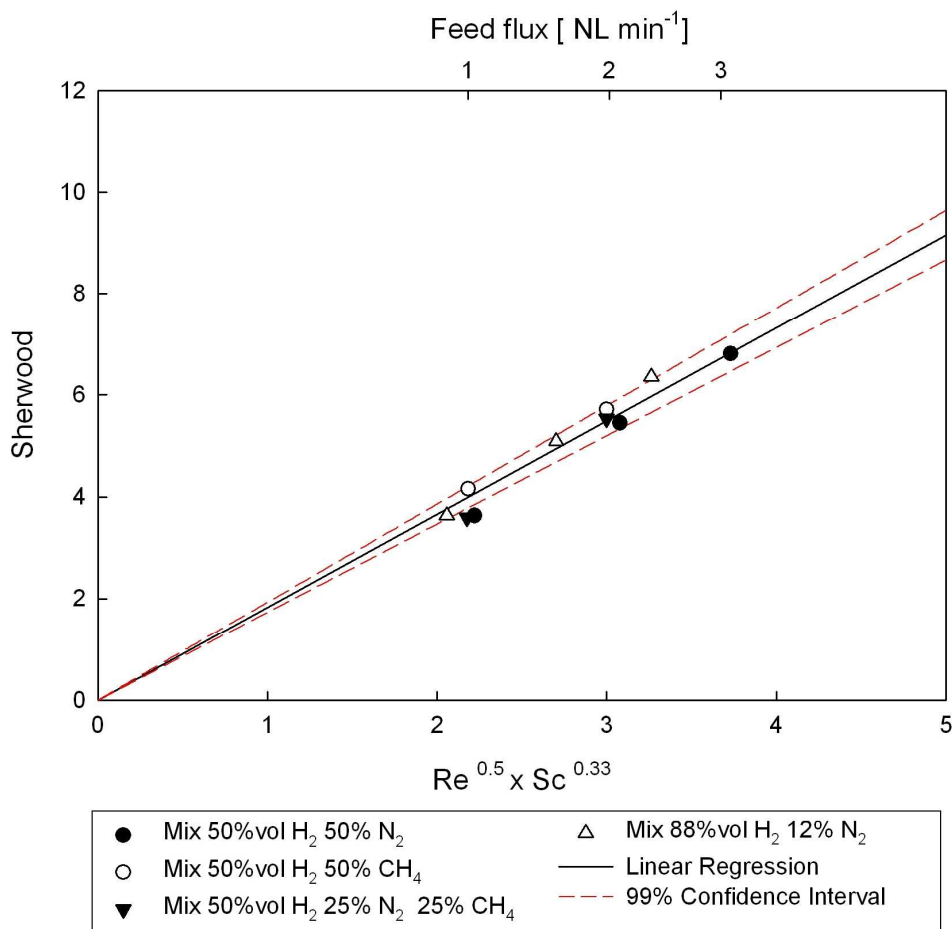


Figure 4. Calculated Sherwood number versus a boundary layer type correlation.

The data collected in the different experimental conditions were modeled accounting for the existence of this additional resistance to mass transport in the gas phase and using the average mass transfer coefficient as a fitting parameter.

The model results are in very good agreement with the experimental data and the Sherwood numbers obtained are related to Reynolds and Schmidt numbers through a boundary layer type correlation, showing the physical consistence of the interpretation offered.

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Progetto: Idrogeno puro da gas naturale mediante reforming a conversione totale ottenuta integrando reazione chimica e separazione a membrana”.

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