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Membrane integrated system in the fusion reactor fuel cycle

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Abstract

The future fusion reactor fuel will be a mixture of deuterium and tritium. Deuterium is produced using traditional separation technology. Tritium must be produced by means of a nuclear reaction between neutrons and lithium atoms within the reactor breeder which, in this study, is supposed to be a ceramic lithiated material. The tritium produced in the breeder needs a proper extraction process to reach the required purity level. A conceptual modified version of the tritium recovery plant for the considered ceramic breeder, working with two membrane reactors, each acting as a reaction/separation unit, is studied in this work. The first considered membrane unit is a catalytic ceramic membrane reactor to remove, via oxidation, the hydrogen isotopes from the purge gas (He). The second one is a tritiated water–gas shift reaction. In the latter process unit, the effect of selective hydrogen permeation on the conversion is studied. A detailed description of the experimental equipment, of the material used and some experimental results are presented.

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1. Introduction

The fuel cycle is one of the most interesting problems in fusion technology. Many problems of plasma physics can be simplified by solving technological aspects related to the tritium fuel cycle [1]. Tritium and deuterium will be used in the future as fuel in fusion reactions. The deuterium is commercially available, while the tritium must be produced in-situ by means of a nuclear reaction between neutrons (produced by deuterium–tritium reaction) and lithium atoms [2]. The lithium is contained in the breeder material of the reactor blanket [3,4] as, for example, $LiAlO_2$, Li_4SiO_4, Li_2O, $LiZrO_3$.

The separation of hydrogen isotopes at low concentration levels in gaseous mixtures is a typical problem of the fusion reactor fuel cycle. In fact, the tritium produced in the breeder needs a proper extraction process to reach the required purity level. Molecular sieves or cryogenic traps can be used to separate the hydrogen isotopes.

An alternative method uses a membrane separator to recover hydrogen isotopes at high purity levels. Naito et al. [5] presented an alternative membrane process for the separation of hydrogen isotopes on the basis of an analytical study. Yoshida et al. [6] developed an analysis to evaluate the required exchange area of a Pd/Ag membrane separator to recover tritium from tritiated water with a high conversion ratio at low temperature (450 K). Hsu and Buxbaum [7] studied, from an engineering point of view, the application of a catalytic metallic membrane system in the fusion reactor fuel cycle. Chabot et al. [8] studied the poisoning effects of impurities on a permeation

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process using a Pd/Ag alloy membrane to separate deuterium and tritium from fusion reactor gaseous wastes. Violante et al. proposed [9–11] a conceptual modified version of a plant for the recovery of hydrogen isotopes in the fusion fuel cycle. Among other alternative solutions based on membrane technology, see Latger et al. [12], Glugla et al. [13] and Penzhorn et al. [14] for recovering tritium.

In the present preliminary study, hydrogen has been considered in place of tritium, just to test the feasibility of the proposed process.

2. Description of the process

A simplified flow-sheet of a recovery plant working with a ceramic catalytic membrane reactor (CCMR) has been presented elsewhere [10]. For safety and fuelling efficiency reasons it is desirable to keep the amount of tritium retained by the protective material to a minimum.

The purge gas (pressure: 0.1 MPa) coming out from the reactor blanket is a mixture of He, T_2 (partial pressure: 1–10 Pa) and swamping isotopes (Q_2 = generic hydrogen isotope). T_2 and Q_2 are oxidized and removed from the purge gas as tritiated water by means of a CCMR. The water is separated from the membrane strip outlet stream by cryo-condensation (or by molecular sieves). The tritium and the swamping isotopes are recovered from the water by means of a shift reactor.

2.1. Catalytic membrane reactor and catalytic shift reactor

For the oxidation of the hydrogen isotopes contained in the blanket purge outlet gas a CCMR is used. The reactor is composed of a tubular CCMR obtained by deposition of a thin palladium film ($1 \cdot 10^{-6}$ m). The strip is a mixture of He (0.1 MPa) and O_2 (1–100 Pa). The hydrogen isotopes permeate the ceramic membrane then adsorb on the catalytic palladium layer and are oxidized with oxygen that also adsorbs on the layer. The produced water desorbs and is removed by convection:

$$2\,Q_{2,\mathrm{ads}} + O_2 \rightarrow 2(Q_2O)_{\mathrm{des}}$$

A differential mass balance along the axes of the catalytic membrane reactor (assuming plug flow conditions, perfect gas behaviour and negligible axial diffusion in the gas phase) and of the equivalence at steady state of the molar flux through the membrane with the flux through the film between the feed gas and the membrane internal wall has been considered [10,15,16]. By using the metallic catalytic membrane reactor the NET required exchange area for a pilot scale fusion reactor is > 200 m^2; instead, by using the CCMR, for the same reactor scale, the required area is reduced to 40 m^2.

Experimental tests have been carried out on a CCMR [17,18] under the following conditions: reactor feeds of Ar + 1% H_2 and Ar + 1% O_2; feed pressure fixed at 100 and 103 kPa; strip pressure: 100 kPa; flow rate: $1.0 \cdot 10^{-6}$–$1.5 \cdot 10^{-6}$ m^3/s (in both sides). By increasing the temperature, the conversion increases because of the reduction of the kinetic resistance.

Comparison between theoretical and experimental results shows that the difference between the experimental and the theoretical curves can be explained in terms of palladium coating defects producing a short circuit of a fraction of the permeating hydrogen that is not adsorbed on the Pd layer and does not react.

The tritium and the swamping isotopes are recovered from the water by a catalytic shift reactor coupled with a membrane permeator. The water–gas shift reactor is a well known reaction, exothermic, with equilibrium constant increasing as temperature decreases:

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

Extracting H_2 from the reaction mixture, by using a palladium membrane, shifts the reaction toward the products, giving higher conversion than obtained in an equilibrium system.

A modelling study has been carried out to evaluate the performance of a composite membrane

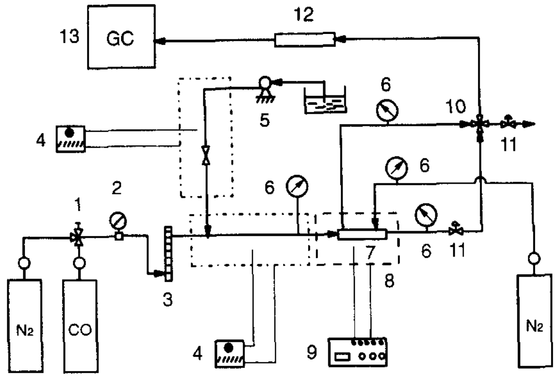

Fig. 1. Schematic diagram of apparatus for the water–gas shift reaction.

reactor for the catalytic water–gas shift reaction [19]. It has been divided in *n* elements (about 500 steps) each one representing a tubular reactor in which the parameters (film resistance, gas velocity, gas properties, etc.) are assumed to be constant. The analysis has been developed considering both isothermal and adiabatic conditions and by assuming a typical Langmuir–Hinselwood rate expression. A similar approach has been used in a computer simulation of the system described hereinafter.

2.2. Experimental apparatus

The experimental apparatus used to study conversion in the water–gas shift reactor is shown in Fig. 1. A micropump (5) (Ismetec-SA) is used to send bi-distilled water, pre-heated (4) and mixed with CO gas (purity 99.95%, 0.05 N_2), through a membrane module (7). The permeate gas and residue gas were analysed separately by a gas chromatograph (Carlo Erba, integrator Shimadzu) using a Carboxen$$$ 1000 column. Ar was used as carrier gas. The module, rolled up in glass wool, is kept at constant temperature by a temperature controller (9) (Digi-Sense).

The module consists in a stainless steel shell in which is located a ceramic membrane. N. 4 ($2.8 \cdot 10^{-3}$ kg/each) graphite rings (Gee Graphite ltd., England) ensure that permeate and residue gas do not mix with each other. Each graphite ring is composed of 99.53% C and 0.47% S. The ceramic membrane, supplied by S.C.T. (France), is $2.5 \cdot 10^{-1}$ m length ($1 \cdot 10^{-2}$ m was vitrified at both ends), I.D. is $6.7 \cdot 10^{-3}$ m and O.D. $1.2 \cdot 10^{-2}$ m, nominal average pore diameter is $5.0 \cdot 10^{-9}$ m. From inside to outside the ceramic membrane there are four layers: γ-Al_2O_3 (thickness: $2.5 \cdot 10^{-6}$–$3.0 \cdot 10^{-6}$ m) and three α-Al_2O_3 with higher pore diameter.

At the CNR CSMSOA (Pisa, Italy), an homogeneous film (mono-or bi-layers) of palladium was deposited on the γ-Al_2O_3 layer by using the same technique developed by Capannelli et al. [20] to deposit Pt film on the same membrane. Palladium vapour, mesitylene and hexene-1, were co-condensed at 77 K in a glass reactor. The solid matrix produced was heated up to 233 K yielding a solution stable at low temperature which was used to fill the ceramic tube. The system was heated at room temperature. The thickness of the Pd layer is $1.0 \cdot 10^{-7}$ m. (G. Vitulli and P. Salvadori, CNR CSMSOA Pisa, Italy (unpublished results)).

The lumen of the composite palladium membrane was packed with particles of a low temperature shift catalyst (including a type designated LK-821-2) provided by Haldor Topsoe A/S (Copenhagen, Denmark) ($9.5 \cdot 10^{-3}$ kg, pellet diameter $1.0 \cdot 10^{-3}$ m).

2.3. Operation

At first, H_2 and N_2 pure gas permeation tests were carried out: at 595 K, 615 K and 625 K. Afterwards, the water–gas shift reaction was carried out at 595 K and 615 K varying the total flow rate of the feed ($9.5 \cdot 10^{-5}$ mol/s, $1.183 \cdot 10^{-4}$ mol/s, $1.333 \cdot 10^{-4}$ mol/s, $1.483 \cdot 10^{-4}$ mol/s), H_2O/CO molar ratio (1.04, 1.54, 1.86, 2.19), and pressure (102 kPa, 104 kPa).

After the temperature of the CO gas reached the desired level (550 K), and water vaporized at 473 K, both CO and water were mixed and kept at 550 K. The mixture then entered the reactor.

3. Results and discussion

H_2 and N_2 pure gas permeation tests at 595 K, have shown α (H_2/N_2) $= \infty$, with a mole flux of hydrogen 0.4772 $mol/m^2 \cdot s$, in good agreement with results presented in literature [21]. After 20 h of experimental tests, the membrane seems to be microporous, with α (H_2/N_2) = 74 and a mole flux of hydrogen 0.7304 $mol/m^2 \cdot s$.

It has been verified at three different temperatures (595 K, 615 K, 625 K) that the permeation of pure H_2 through the composite palladium membrane results in a rate of hydrogen permeation that follows the Sievert law (Fig. 2). An Arrhenius plot of log *P*, where *P* is the permeability of pure H_2 through the composite palladium membrane, versus $1/T$ gives a linear relationship (Fig. 3). The activation energy from these data is between 0.41 and 0.44 kJ/mol · K, while the pre-exponential factor is between $5.04 \cdot 10^{-7}$ and $5.06 \cdot 10^{-7}$ $mol \cdot m/m^2 \cdot s \cdot kPa^{0.5}$.

In Fig. 4 is shown the conversion of CO versus the feed flow rate of CO at $H_2O/CO = 1.04 \div 1.15$ and $T = 595$ K. At higher CO molar flow rate a lower conversion is observed. In particular, at $CO = 8.3 \cdot 10^{-5}$ mol/s, the conversion is less than for an equilibrium at the same conditions; at $CO = 2.5 \cdot 10^{-5}$ mol/s, the conversion (0.94) is higher than for equilibrium (0.86) at the same conditions.

Fig. 5 shows the results of some experimental tests in terms of conversion of CO and in terms of the modelling of the catalytic membrane reactor versus different values of the H_2O/CO ratio, at 595 K and molar flow rate of $CO = 4.7 \cdot 10^{-5}$ mol/s. Both experimental results and simulation curve have a higher degree of CO conversion compared to the equilibrium system, due to the permeation of H_2 through the composite palladium membrane. The difference between experimental results and simulation curve is observed because of the hypothesis assumed in the modelling work; in particular the rate equation of Langmuir–Hinselwood does not correlate closely with experimental results.

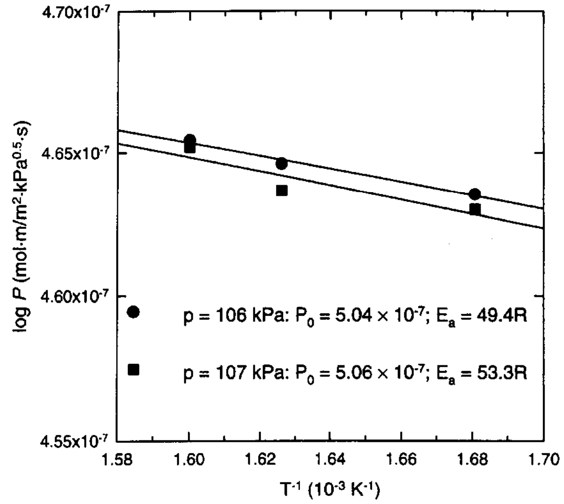

Fig. 3. Arrhenius plot of H_2 permeability through the composite palladium membrane.

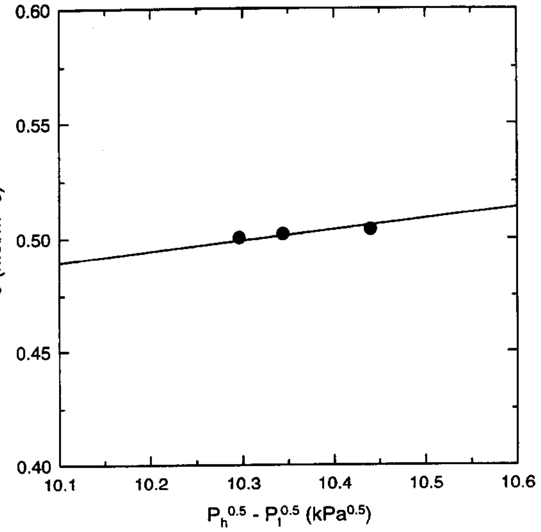

Fig. 2. Pressure dependence of H_2 permeation flux at 595 K.

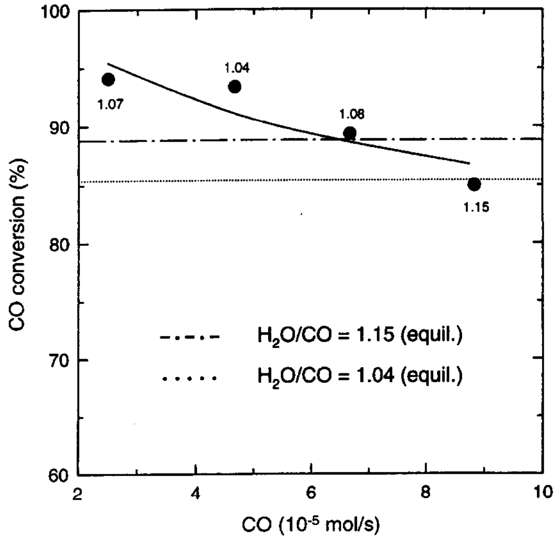

Fig. 4. Plot of CO conversion versus CO feed at 595 K.

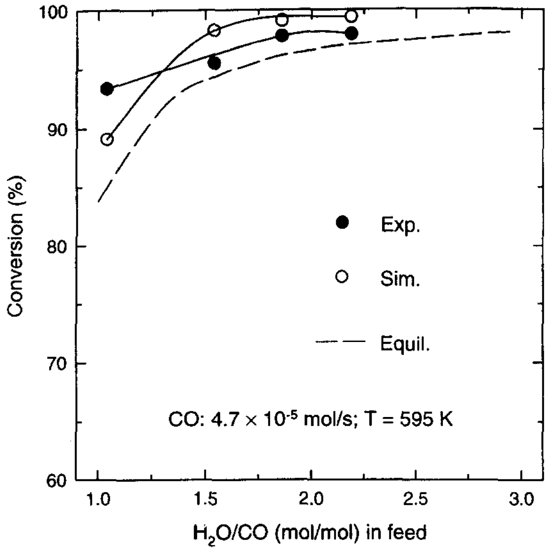

Fig. 5. Effect of H_2O/CO on conversion of carbon monoxide.

4. Conclusions

The preliminary results obtained with the theoretical models and with experimental results, in which hydrogen has been considered in place of tritium, show that the proposed membrane process units can be considered as a real alternative for the recovery plant for the tritium produced within a solid blanket.

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