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# Heavy water decontamination tests through a Pd-Ag membrane reactor: Comparison of catalysts

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A Pd-Ag membrane reactor has been studied to assess its ability in heavy water decontamination through Isotopic Swamping (IS) and Water Gas Shift (WGS) reactions under different operating conditions (i.e. reactor temperature, lumen pressure, feeding molar ratio and isotopic swamping). The reactor has been installed in a new facility of the ENEA Membrane Laboratory called HyFraMe, by testing two catalysts. The results are reported in terms of decontamination factor or DF (the amount of gaseous deuterium recovered from heavy water). Both catalysts demonstrate, in the WGS reactions, low methane production (1.72 mol.% in the worst case) and high DF, almost 80%, at pressure of 400-500 kPa at 623 K. The IS reaction tests exhibited a lower performance (DF=67% at the best) while no methane production has been observed.

**Keywords:** Water decontamination, Pd-Ag membrane reactor, HCPB blanket

## 1. Introduction

One of the major requirement for future fusion machine (like DEMO) is the ability to guarantee the tritium self-sufficiency, therefore all tritium consumed during the D-T reaction shall be produced inside the blanket and opportunely recovered. In this view, within the WPBB several experimental activities are dedicated to advanced tritium extraction techniques (from both He and PbLi) [1]. Focusing on the Tritium Extraction System (TES) of the solid breeder concept (HCPB), innovative and promising technologies are based on the use of membrane reactors, which have to be deeply investigated under DEMO relevant conditions. These conditions are rather critical essentially for two reasons: firstly, the very low tritium (few ppm) concentration inside the He purge stream and, secondly, the presence of tritium in both molecular and oxidised form, noted Q<sub>2</sub> and Q<sub>2</sub>O respectively (where Q is H, D and T). In particular, according with the results obtained from simulations previously published, [2] the tritium concentration in the He gas stream leaving the HCPB blanket and entering the TES consists of about 10 vppm in form of HT and about 0.3 vppm in form of HTO. Dense Pd-based membranes are able to selectively separate hydrogen isotopes from a gas mixture and, when coupled with a proper catalyst to form a membrane reactor, it is also possible to recover the hydrogen isotopes from a specific molecule (i.e. H<sub>2</sub>O, CH<sub>4</sub>, NH<sub>3</sub>, etc.). Main advantages of such membranes are their high performances in terms of hydrogen selectivity and good permeability, their modularity (easiness of scaling up) and their continuous operation (no need of regeneration) [3]. The Membrane Laboratory of ENEA Frascati has a large experience in the field of Pd-based membranes and recently is investigating the possible application of such device inside TES of the HCPB blanket [3, 4]. This work presents the results of an experimental campaign carried out with a Pd-Ag membrane reactor for heavy (instead of tritiated) water decontamination. The performance of the reactor has been measured by using two different catalysts via two different reactions: Water

Gas Shift (WGS) and Isotopic Swamping (IS). The tests have been performed in a wide range of operating conditions by varying the reactor temperature, the lumen pressure, the feed molar ratio and the isotopic swamping value.

## 2. Experimental

The next paragraphs are dedicated to the description of test facility, the procedure and test schedule adopted for the experimental campaign.

### 2.1 ENEA test facility (HyFraMe)

In the experimental campaign, 68 tests have been carried out by using a dedicated setup called HyFraMe and showed in Fig. 1. In the experiments, a Pd-Ag (25% wt.) single tube having wall thickness of 113 μm, length of 500 mm and diameter of 10 mm has been used.

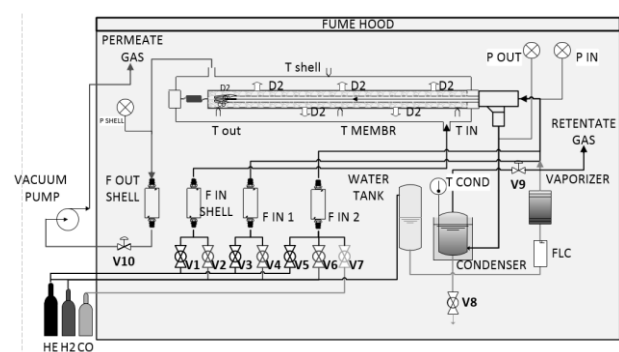


Fig. 1. Simplified HyfraMe facility layout

The HyfraMe apparatus is equipped with several mass flow controllers (F<sub>IN</sub>, F<sub>OUT</sub> and F<sub>SHELL</sub>), K-type thermocouples (T), pressure gauges (P), a water vaporizer, a condenser and a vacuum pump (Adixen ACP15 with ultimate pressure of 0.03 mbar) on the shell side.

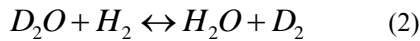
## 2.2 Test and operational procedures

During WGS reaction tests, a mixture of CO and D<sub>2</sub>O (steam) has been sent to the reactor. The WGS reaction occur with a resulting deuterium production, according to formula (1).



The retentate, or the non-permeated steam coming out the reactor, is driven into a condenser to collect the un-reacted water. Then, the dried gas composition is investigated via batch Gas Chromatographic (GC) analysis carried out at the end of each test once steady-state conditions were reached. A needle valve downwards the condenser allows to regulate the pressure in the lumen side. On the shell side, the turbo-pump guarantees a low vacuum pressure. The flowmeter located downwards the reactor measures the permeated hydrogen flux. The dried gas stream mainly consists of CO<sub>2</sub>, small amount of D<sub>2</sub>O vapour, un-reacted CO, un-permeated D<sub>2</sub> and methane impurities. In particular, the presence of methane should be as low as possible because, otherwise, additional efforts are required in tritium treatment due to the good stability of CQ<sub>4</sub> molecule [6, 7].

In the IS reaction tests the heavy water vapour is fed in the reactor lumen together with a carrier gas (He) while the shell side is flushed with hydrogen whose pressure (about 3-6 kPa) is regulated by means of a needle valve upstream the vacuum pump. The reaction, enhanced by the catalyst, is an isotopic exchange between the deuterium and the hydrogen as shown in the formula (2).



On the lumen side, the condenser separates the water from the He carrier; water is gathered at the end of each test through the V8 valve in a phial, for Infrared analysis.

## 2.3 Experimental Schedule

The tests have been carried out as shown in Tables 1 (for the WGS) and 2 (for the IS). In all the experiments, heavy water (*Cambridge isotopes laboratory Inc*, purity 99.9%) has been fed in the membrane lumen.

Table 1. List of WGS experiments ( $P_{shell} \sim 3-10$  kPa)

| D <sub>2</sub> O/CO feed ratio | D <sub>2</sub> O, mol h <sup>-1</sup> (g h <sup>-1</sup> ) | CO, mol h <sup>-1</sup> (sccm) | T <sub>reactor</sub> , K | P <sub>lumen</sub> , kPa |
|--------------------------------|--|--------------------------------|--------------------------|--------------------------|
| ~1                             | 0.25 (5)   | 0.25 (93)                      | 573-623-673              | 100-200-300-400-500      |
| ~1.5                           | 0.25 (5)   | 0.16 (62)                      | 623                      | 300                      |
| ~0.75                          | 0.25 (5)   | 0.33 (125)                     | 623                      | 300                      |

In case of IS reactions, a small amount of He has been also send as carrier gas (0.08 mol h<sup>-1</sup> equivalent to 30 sccm), while in WGS reaction tests, the CO worked as a carrier.

Table 2. List of IS experiments ( $P_{shell} \sim 10$  kPa)

| H <sub>2</sub> /D <sub>2</sub> O swamping ratio | D <sub>2</sub> O, mol h <sup>-1</sup> (g h <sup>-1</sup> ) | H <sub>2</sub> shell, mol h <sup>-1</sup> (sccm) | T <sub>reactor</sub> , K | P <sub>lumen</sub> , kPa |
|---|--|--|--------------------------|--------------------------|
| ~1  | 0.25 (5)   | 0.25 (93)  | 573-623-673              | 100-200-300-400-500      |
| ~2  | 0.25 (5)   | 0.50 (186)                                       | 673                      | 200                      |
| ~4  | 0.25 (5)   | 1 (372)  | 673                      | 200                      |

At the end of each experiment and before the cleaning loop, a sample of the retentate stream has been picked for post-analysis. In case of WGS tests, the retentate gas is analysed by a micro-GC in order to measure the CO<sub>2</sub> and CQ<sub>4</sub> concentration. In case of IS tests, the condensed water of the retentate consisting of a mixture of heavy and light water is analysed to assess the D<sub>2</sub>O/H<sub>2</sub>O composition, through a FTIR (Fourier transform infrared spectroscopy) analysis that measures the bending and stretching signal of the OD bond. A calibration of the Infrared spectrometer SHIMADZU IRAffinity-1S has been performed by testing the OD stretching (at about 2500 cm<sup>-1</sup> wavenumber frequency) and bending signal (at about 1200 cm<sup>-1</sup> wavenumber frequency) in different mixture of H<sub>2</sub>O / D<sub>2</sub>O.

## 2.4 Parameters

The experimental procedure is finalized to measure the Decontamination Factor (DF) interpreted as the amount of gaseous deuterium recovered from heavy water. The aim is to identify the catalyst that minimizes the methane production in the WGS reaction. The DF<sub>WGS</sub> has been calculated as the percentage molar ratio between the D<sub>2</sub> recovered in the shell side and the D<sub>2</sub>O fed (3).

$$DF_{WGS} = \frac{D_{2Fshellout}}{D_{D2O}} \times 100 \quad (3)$$

Where DF<sub>WGS</sub> is the decontamination factor in WGS experiments (%), D<sub>2Fshellout</sub> is the flow rate of deuterium collected in the shell side (mol h<sup>-1</sup>) and D<sub>D2O</sub> is the heavy water feed flow rate (mol h<sup>-1</sup>).

In the IS experiments, since the experimental set up does not allow to directly measure the D<sub>2</sub> in the H<sub>2</sub>/D<sub>2</sub> gas mixture of the shell side, the DF<sub>IS</sub> has been obtained as the ratio between the D<sub>2</sub>O concentration in the condensed water of retentate D<sub>2</sub>O<sub>out</sub> (mol/mol) and the D<sub>2</sub>O concentration in the water fed D<sub>2</sub>O<sub>in</sub> (mol/mol) according to (4).

$$DF_{IS} = \frac{D_{2O_{out}}}{D_{2O_{in}}} \times 100 \quad (4)$$

In all the IS experiments pure heavy water has been fed (D<sub>2</sub>O<sub>in</sub> equal to 1).

## 3. The catalysts

Two different catalysts have been tested for the WGS and IS reactions. In both cases, 16 g of catalyst has been filled

inside the Pd-Ag membrane lumen. The first catalyst (CAT1) has been synthesized by the Instituto de Investigaciones en Catálisis y Petroquímica (FIQ, UNL-CONICET), Santa Fe, Argentina. It is in form of pellets with irregular dimensions (from 1x1x1 mm to 4x2x1 mm). A complete description and characterization of the catalyst can be found in [5]. Its composition has been checked by using X-Ray Fluorescence analysis (XRF) (model Shimadzu-720): Pt (0.62 wt.%), SiO<sub>2</sub> (56.32 wt.%) and La<sub>2</sub>O<sub>3</sub> (43.06 wt.%). The activation of this catalyst has been done in two steps: the first consisted in a thermal activation at 673 K (heating ramp of 1.5 K min<sup>-1</sup>) in Ar atmosphere for 30 minutes; the second has been performed inside the membrane reactor in H<sub>2</sub> atmosphere at 673 K for 2 h.

The second catalyst (CAT2) tested is a commercial one produced by BASF. It consists of a Pt-based dry unreduced catalyst (Pt 1 wt.% on alumina support, SP-01 T) in regular small pellets cylindrically shaped 1.5 mm x 1.5 mm. The activation has been performed by reducing it in the membrane reactor through flowing H<sub>2</sub> at 573K for about 2 h.

## 4. Results

All the tests discussed have been carried out by following the procedure previously described. In order to have a benchmark concerning the methane production trend in the WGS tests, a thermodynamic simulation has been also carried out through the software AsTher [8].

### 4.1 WGS Results

Fig. 2 shows the results of the WGS tests carried out with the catalysts CAT1 (on the left) and CAT2 (on the right). All the results are reported in terms of DF vs. pressure and temperature. Looking at CAT 1 results, by increasing the temperature of the reactor from 573 to 623 K, the DF<sub>WGS</sub> factor considerably increases (more than 10 percentage points) while, at higher temperature (from 623 K to 673 K) there is not an appreciable difference in term of decontamination capability. Otherwise, the temperature does not affect significantly the CAT2 performance.

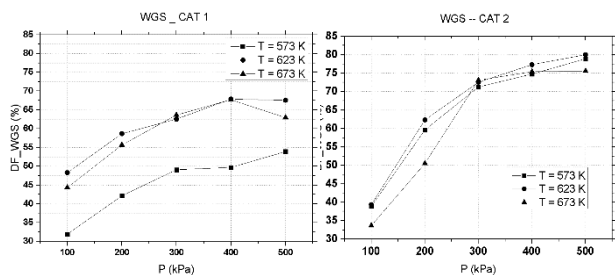


Fig. 2. WGS results for CAT1 (on the left) and CAT2 (on the right) at different lumen pressure (100-500 kPa) and reactor temperature (573-673K), constant CO/D<sub>2</sub>O feeding molar ratio equal to 1.

This result is reasonably coherent with literature [9] because the DF<sub>WGS</sub> is influenced by both the hydrogen formation and its permeation through the membrane. The permeation is enhanced at high temperature while the WGS reaction, and then the hydrogen production, is

promoted at lower temperature. Then it is reasonable that at 623 K there is the best balance between the membrane permeation and WGS reaction yield. In general, the DF factor increases by raising the lumen pressure.

Concerning the CAT2, the performances are a little bit lower at low pressure (between 33% and 39% at 100 kPa), while they are higher between 300 kPa and 500 kPa (between 71%-73% at 300 kPa and 75%-80% at 500 kPa) compared to CAT1 performances. Otherwise, the temperature affects very modestly the DF<sub>WGS</sub> when using the CAT2.

As known by literature [4], the most critical drawback of the WGS is the methane formation. Especially in the fusion fuel cycle processes, the methane production must be seriously avoided [6]. This could be done by adopting specialized catalysts that are methane hinder and by operating in particular conditions of pressure and temperature. The figure 3 (left side) collects all simulations performed with AsTher; these give indication about the operational field in which operate in order to reach low methane formation. The simulations suggest operating at low pressure and temperature. It is mandatory to clarify that AsTher calculates the methane production under thermodynamic equilibrium; these simulations are therefore far from the test conditions because the membrane reactor operates in a non-equilibrium conditions as a consequence of the continuous hydrogen removal through the membrane. In fact, thermodynamically the methane yield increases vs. the pressure while in a membrane reactor with the increase of the pressure more hydrogen permeates thus shifting to right the methanation reactions.

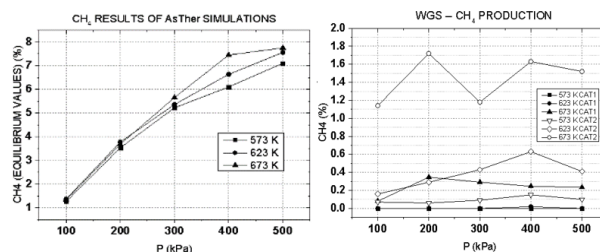


Fig. 3. On the left: results (CH<sub>4</sub>, mol.%) of AsTher simulation at different pressures and temperatures. On the right: CH<sub>4</sub> (mol.%) amount in the retentate stream of the WGS experiment for both catalysts at different temperatures and pressures.

Anyway, both catalysts demonstrate very good performances in term of methane production. In particular, it is important to underline that using the non-commercial catalyst (CAT1) the methane production at 573 K and 623 K is below the GC detection limit, while vs increasing the temperature to 673 K, the methane production reaches its maximum value at 200 kPa (0.35%). Regarding the CAT2, a higher methane production has been measured but always less than 1% at 573 K and 623 K while it reaches the maximum value of 1.72% at 673 K and 200 kPa.

Lastly, the influence of the feeding molar ratio (D<sub>2</sub>O/CO) on the decontamination factor has been investigated. And it was evident that the CAT2 DF<sub>WGS</sub> was always higher.

## IS Results

Differently from the WGS experiments, the IS performances (Fig. 4) seem to be not considerably influenced by the lumen pressure, especially in the CAT2 tests. Otherwise, the temperature is clearly one of the crucial parameter for the  $DF_{IS}$  that increases at the higher temperatures when the hydrogen isotopes permeability is maximum. For CAT2, by increasing the temperature from 573 K to 673 K, the  $DF_{IS}$  raise of 8-10 percentage points, while, in the CAT1 tests at 100 kPa, the performances are rather similar. Considering the same increasing of temperature from 573 K to 673 K at 300 kPa, the values of the  $DF_{IS}$  vary between 38% and 43% for the CAT1 and between 28% and 42% for the CAT2. This demonstrates that the CAT1 is more suitable for IS reaction than the CAT2 especially at low temperatures and pressures. Several tests at different  $H_2/D_2O$  swamping ratio have been carried out as shown in the Fig. 5. Both catalysts show the same trend even though the CAT1 has the best performances in all cases. As expected, the DF increases by working with an excess of swamping hydrogen.

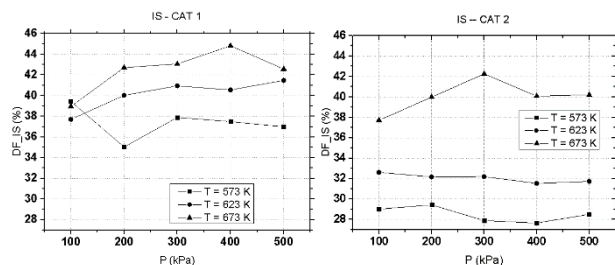


Fig. 4. IS results for CAT1 (on the left) and CAT2 (on the right) at different pressure (100-500 kPa) and temperature (573-673K), at constant  $H_2/D_2O$  swamping ratio of 1 and shell pressure of 10 kPa.

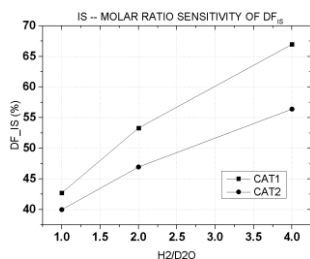


Fig. 5. Experimental result and comparison of IS reaction for both catalyst at  $T = 673$  K,  $P = 200$  kPa at different  $H_2/D_2O$  swamping ratios.

In general, in both the tested catalysts there is an increasing of the decontamination factor of 8-percentage points, at least, by doubling the hydrogen swamping molar flow rate and 16-percentage points, by increasing by four times the hydrogen swamping ratio.

## 5. Discussion and comparison

The results clearly show that both the catalysts tested reach good performances in WGS and, especially, low methane formation. Regarding this last point, by using CAT1 in all the experiments performed, the measured methane was always under the 0.40 mol.%. At 573 K and 623 K, the methane production is under the detection limit of the micro-GC analyser. Anyway, with CAT2 the amount of methane produced is barely appreciable (at

maximum 1.72 mol.% of methane was measured at 673 K and 400 kPa).

On the other hand, the  $DF_{WGS}$  using CAT1 is lower than CAT2 experiments. The  $DF_{WGS}$  reaches values above 80% at 623 K, 500 kPa.

Working with CO excess does not univocally benefit the water decontamination: just using CAT2, the increasing of performance is slightly appreciable.

Conversely in the IS, the  $DF_{IS}$  (CAT1) is about 67% and 43% with a swamping ratio  $H_2/D_2O=4$  and  $H_2/D_2O=1$ , respectively. The best value for CAT2 is 56% ( $H_2/D_2O=4$ ) against 39.98% ( $H_2/D_2O=1$ ). These values were measured at 673 K at 200 kPa.

In practice, although the operation at higher pressure increases the promotion of decontamination capability, feasibility and safety reasons suggest to work at low pressure (around 100-200 kPa). It is noteworthy that increasing the  $H_2/D_2O$  swamping ratio, better decontamination performances can be achieved but a deeper and more expensive isotopic separation of  $T_2$  from  $H_2$  will be needed.

Focusing on the application of this technology in the HCPB breeding blanket, one of the issue is to understand if, by adopting the WGS reaction, the methane produced is tolerable for the further processing. In such a case, the WGS can be preferred because of its higher DF values.

In conclusion, in view of a DEMO HCPB breeding blanket, 0.28 ppm of tritiated water in He, that correspond to a flow rate of  $9.03 \times 10^{-4} \text{ Nm}^3 \text{ h}^{-1}$  (0.81 g  $\text{h}^{-1}$ ) of HTO, will be produced. Therefore the membrane reactor tested in this work (diameter 10 mm and length 500 mm) could be suitable to recover the tritium from the DEMO HCPB by considering a DF of 40% at ambient pressure and 623 K.

## Acknowledgement

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