CACHET II WP1

Pd membrane engineering, development and PDU testing

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[3]IMR

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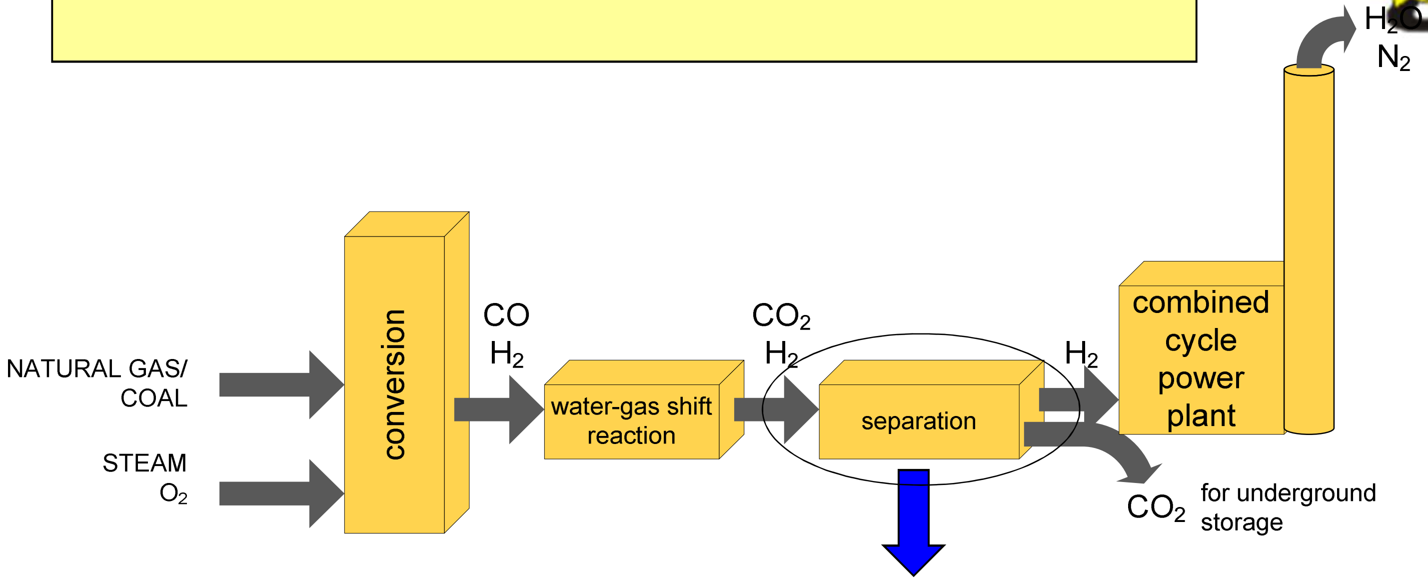
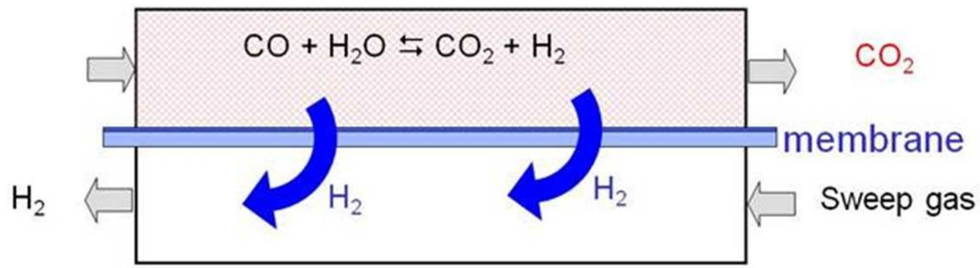
Outline

- Introduction
- Objectives
- Interaction of WP1 with other WP’s
- WP1 approach/structure
- Description and status of activities
- Conclusion

Introduction



Membrane watergas shift (M-WGS)



Removing hydrogen → shift equilibrium

Introduction

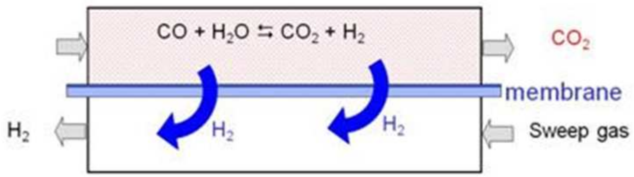
- Critical issues in the field of Pd-membranes:
  - Manufacturing and testing of upscaled membranes up to 1 m
  - Membrane seals and integration into industrial installations
  - Long term performance stability of membrane plus seal
    - H_2-separation and M-WGS

Membrane performance:

$J_{H2} = Q(T)*(p_f^n - p_p^n)$

- High H_2-selectivity
- Stable permeance Q(T,t):
  - Mass transfer
  - Contaminants
  - Inhibition effects

Membrane watergas shift (M-WGS)



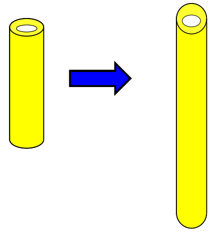
Removing hydrogen → shift equilibrium

In case WGS integrated:
Water gas shift catalyst:

- Stable activity
  - gas composition (inlet → outlet)
- Stable selectivity:
  - no by-products

Objectives

1. Membrane production: Upscaling to 1 m membranes

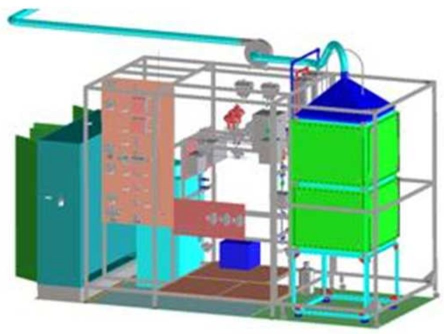


2. Long term separation testing (150 days) with
   5 cm long membranes and different seals at DICP

   - Less than 2% decline in hydrogen flux
   - Selectivity for H_2-separation > 200

3. Scaled down version of a full scale multi-tube M-WGS reactor with 1 m long membranes to be tested over 1000 hours at ECN:

   - Production of at least 95 % pure hydrogen
   - Capture of at least 90% CO_2



Interaction with other workpackages

WP1:
Pd-membrane engineering, and development
(DICP, ECN, IMR)

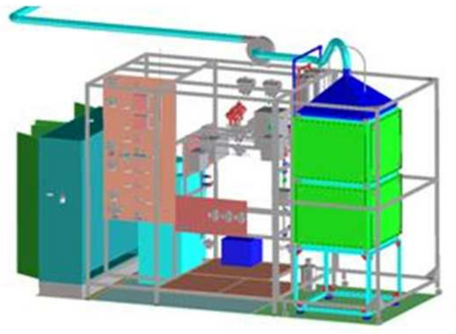
- Membrane operating conditions
- Validation membrane modelling
- Design of benchscale test module

WP4:
Module design, Process integration, Economics

- Robust membrane materials
- Operating conditions under high temperatures or contaminants

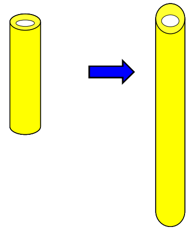
WP2:
High Flux and high stability membrane development

Scaled-down reactor



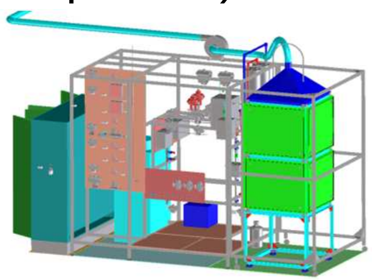
WP1 structure/approach

1. Scaling up Pd membranes (DICP) to a length of 1 m



2. Development of improved sealing technology (IMR, ECN)

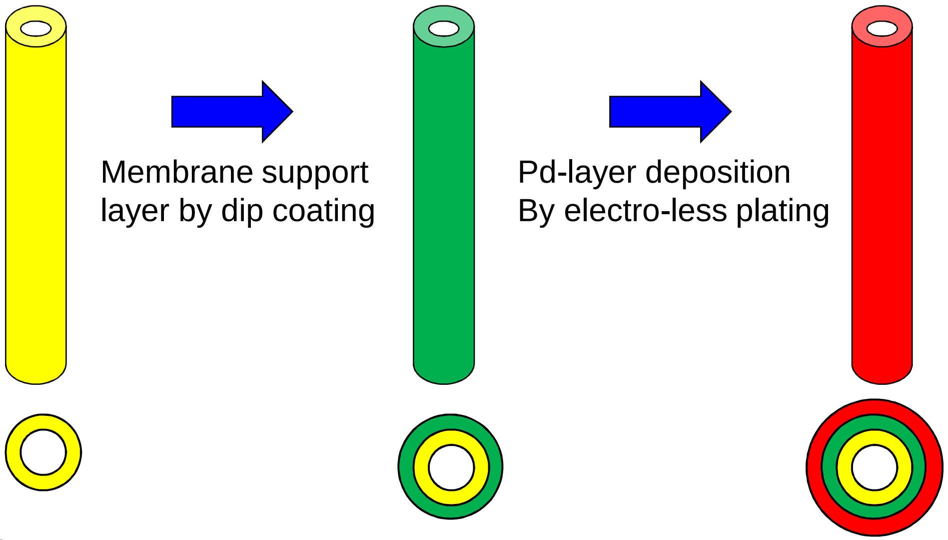
3. Membrane performance testing (ECN, DICP):
   - Long-term stability testing of single Pd membranes (0.05 - 0.5 m) and seals
   - Membrane (0.5 to 1 m) testing at DICP and ECN (multi tube in parallel)
     - Non-integrated/integrated (H_2-separation and M-WGS)



4. Construction and testing of scaled down full scale WGS membrane (1 m) reactor for at least 1000 hours (ECN)

Membrane scale-up and production

- Aim: Scale-up to 1 m membranes
  - ECN supplies porous supports (alumina)
  - DICP will scale up Pd-layer deposition



- Status:
  - 1 m membranes have been manufactured

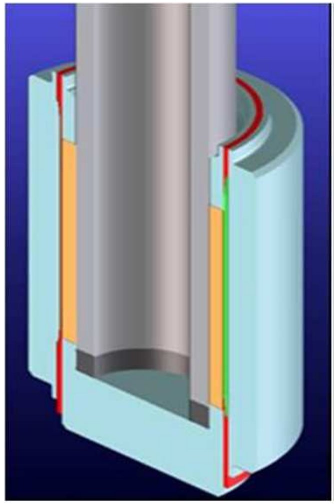
New sealing technologies

- Aim: Improved seal stability and seal dimensions
  - Stability up to 500°C under WGS-conditions
  - Improved seal footprint ensuring mass transfer optimized catalyst bed thickness

- Status:
  - Seals have been developed
  - Seals are in the process of validation

New sealing technologies

1/ Patented ECN compression seal based end-cap



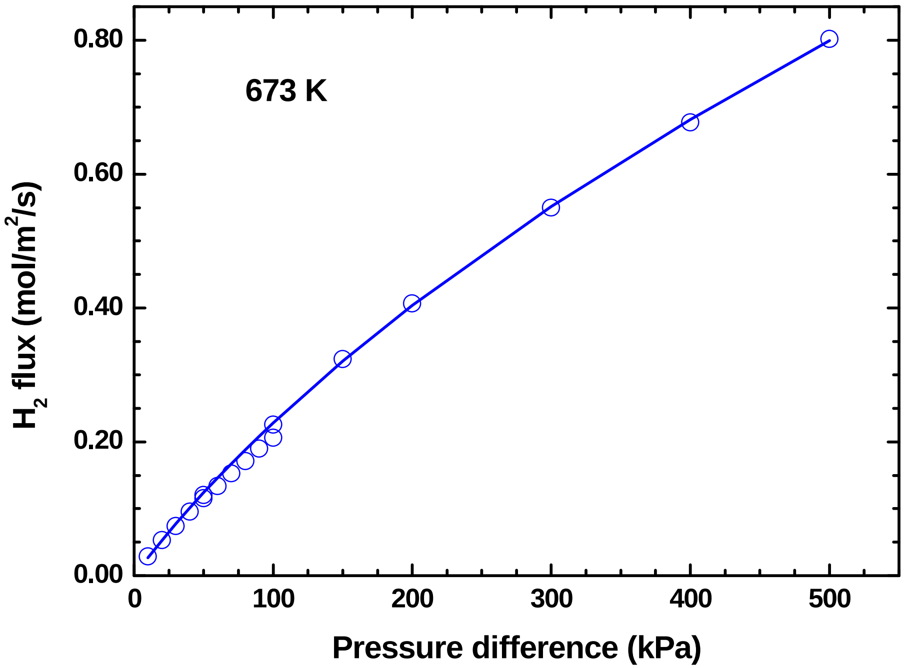
- Sealing material: Graphite
- End-cap: stainless steel
- Design pressure = 38 barg
- Design temperature = 700°C

2/ Patented IMR-seals:

- Direct metal-ceramic joint
- Thermo-shock stability > 10 cycles (RT – 700°C)
- Smaller footprint
- Design pressure = 50 bar
- Design temperature = 500-700 ° C

Membrane performance

- 0.5 m long DICP Pd membranes with 5-7 μm thick Pd layers and ECN seals



- Typical H_2 permeation rate:

$$1.75\times10^{-2}\ \mathrm{mol/m^2/s/Pa^{0.5}} \times \exp(-12.9\ \mathrm{kJ/mol}/RT) \times (P_{feed}^{0.5} - P_{perm}^{0.5})$$

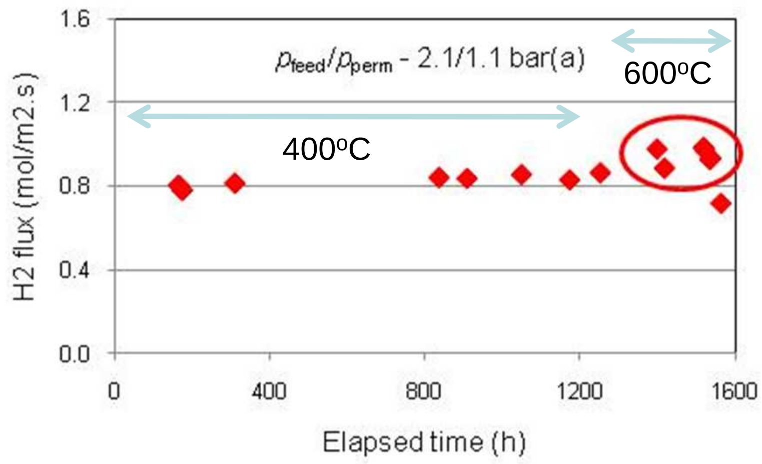
- Typical ideal selectivity at 673 K: ~ 10000 (P_{feed}/P_{perm} = 500/100 kPa)

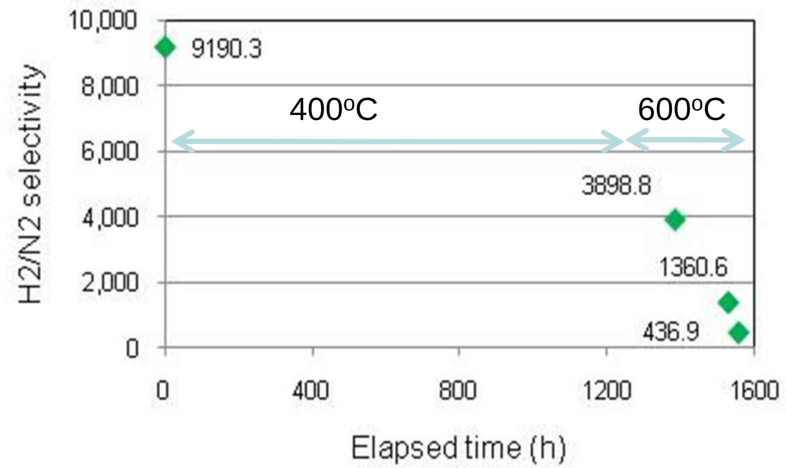
Long term stability testing

- Aim:
  - Demonstration of stability membranes, support and sealing under realistic testing conditions:
    - High pressure 25-40 bar
    - Simulated WGS conditions
    - 150 days testing
- Status:
  - Stable membrane performance demonstrated up to 1200 hours (50 days)

Long term stability testing

- Test on two parallel ECN Pd membranes 0.5 m with ECN seals
  - 1-2 micron thick Pd-layer
  - Testing condition: P_{feed} / P_{perm} = 2.1 / 1.1 bar(a) pure hydrogen
  - Operating temperature: 400 and 600^{o}C





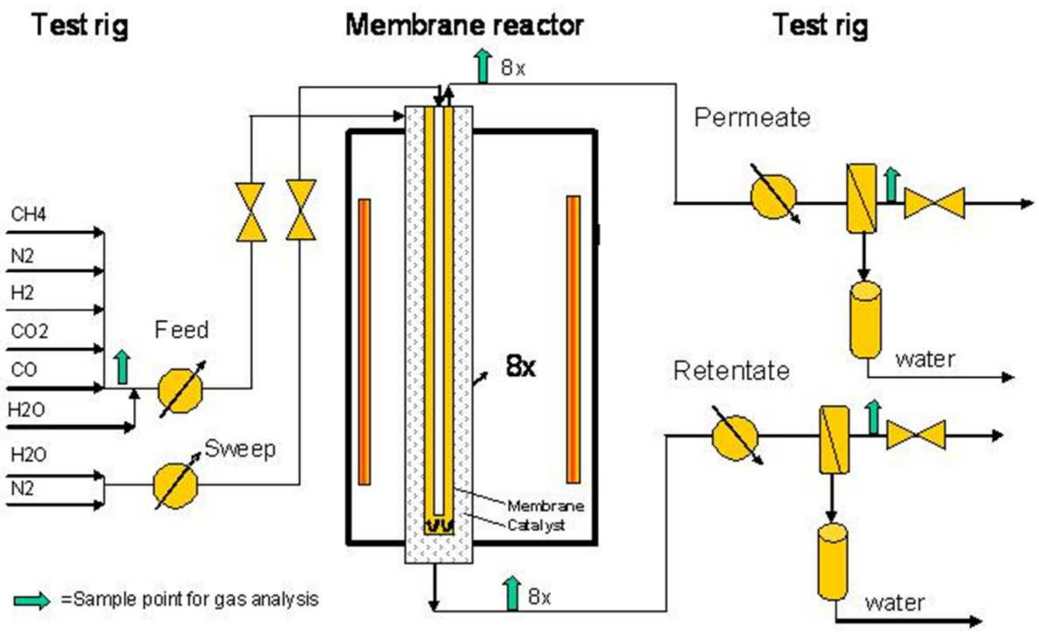
- H_2 flux (400^{o}C, P_{feed} / P_{perm} = 2.1 / 1.1 bar): 0.8 mol/m^2.s
- H_2 permeance stable up to1200 h at 400^{o}C: decrease in selectivity by factor 2.5
- H_2 permeance and selectivity drops after exposure to 600^{o}C
- post test analysis: pinhole/cracks on the membranes and leakage in the seals

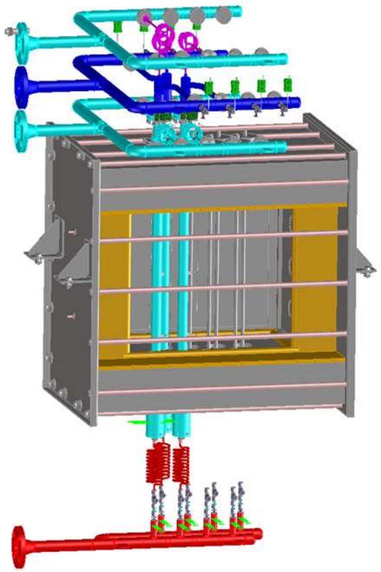
Testing of long membranes

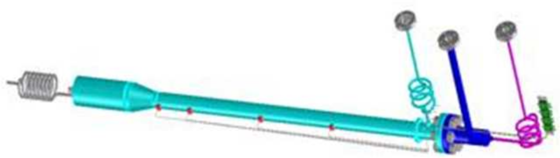
- Aim:
  - Determination of basic permeance data of membranes:
    - Operating temperatures: 400-600 ^{o}C (Accelerated testing)
    - Pressures: around 30 bar
    - Single gases (H_2/N_2), mixtures (H_2 with N_2, CO, CO_2) and syngas.
    - Data will be used as benchmark for reactor model and design tool in WP4
  - Screening commercial WGS catalyst:
    - Stable WGS catalyst performance
    - No by-products

Testing of long membranes

- Equipment:
  - Process development unit (PDU) at ECN;
    - 8 membrane reactors in parallel







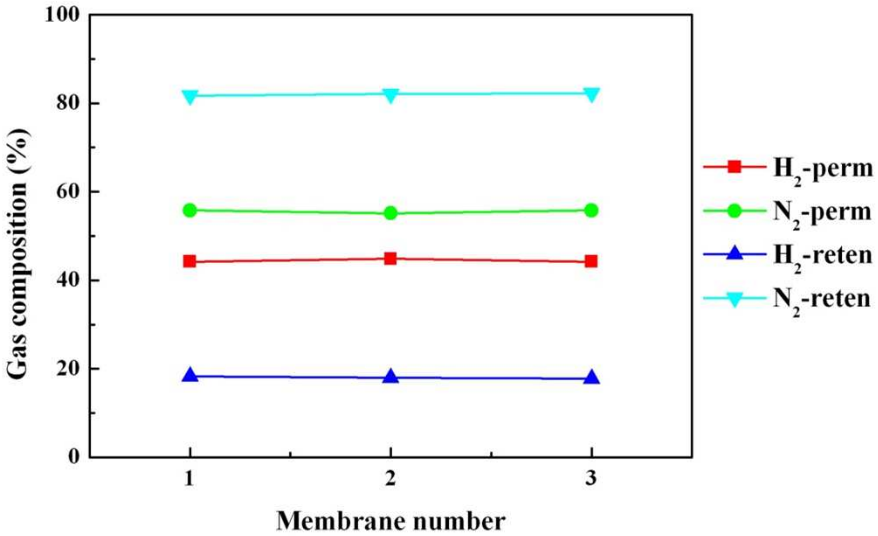
Testing of long membranes

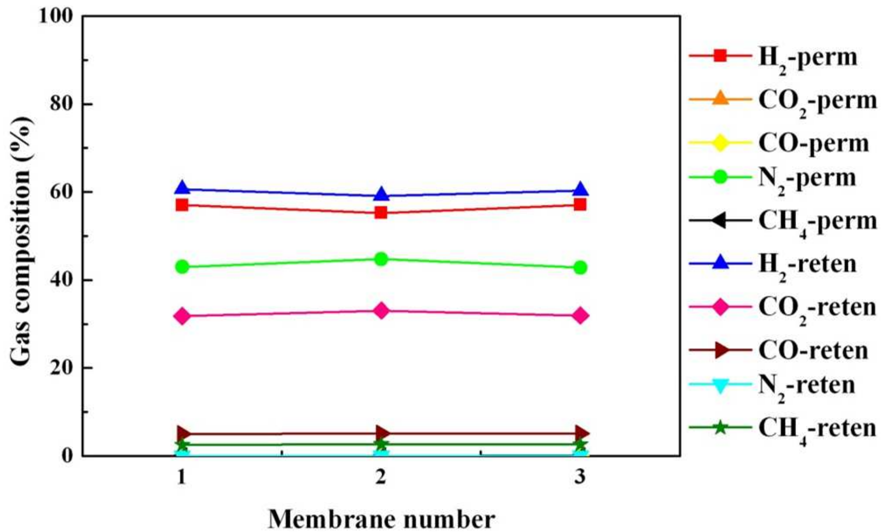
- Validation Process Development Unit (PDU):
  - Flow distribution over 3 different DICP membranes (0.5 m long)

WGS-reaction test

H_2/N_2 mixture, 30/19.57 l/min, 31/15 bara

WGS mixture, 90/19.57 l/min, 27/15 bara





H_2/N_2 mixture **WGS-mixture**

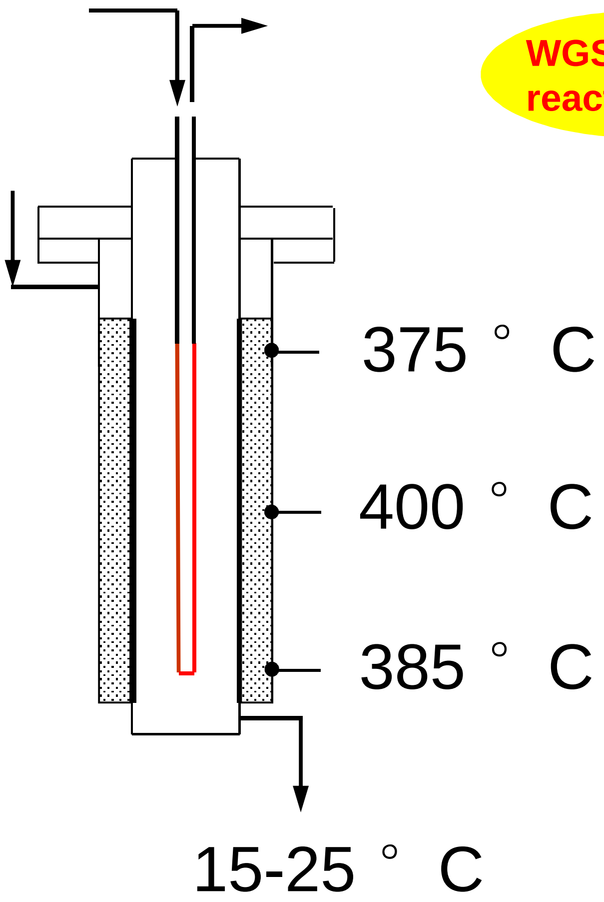
Flow distribution: Relative difference <6%

Testing of long membranes

- Validation Process Development Unit (PDU):
  - Temperature distribution over membrane length

Separation only

WGS-reaction test

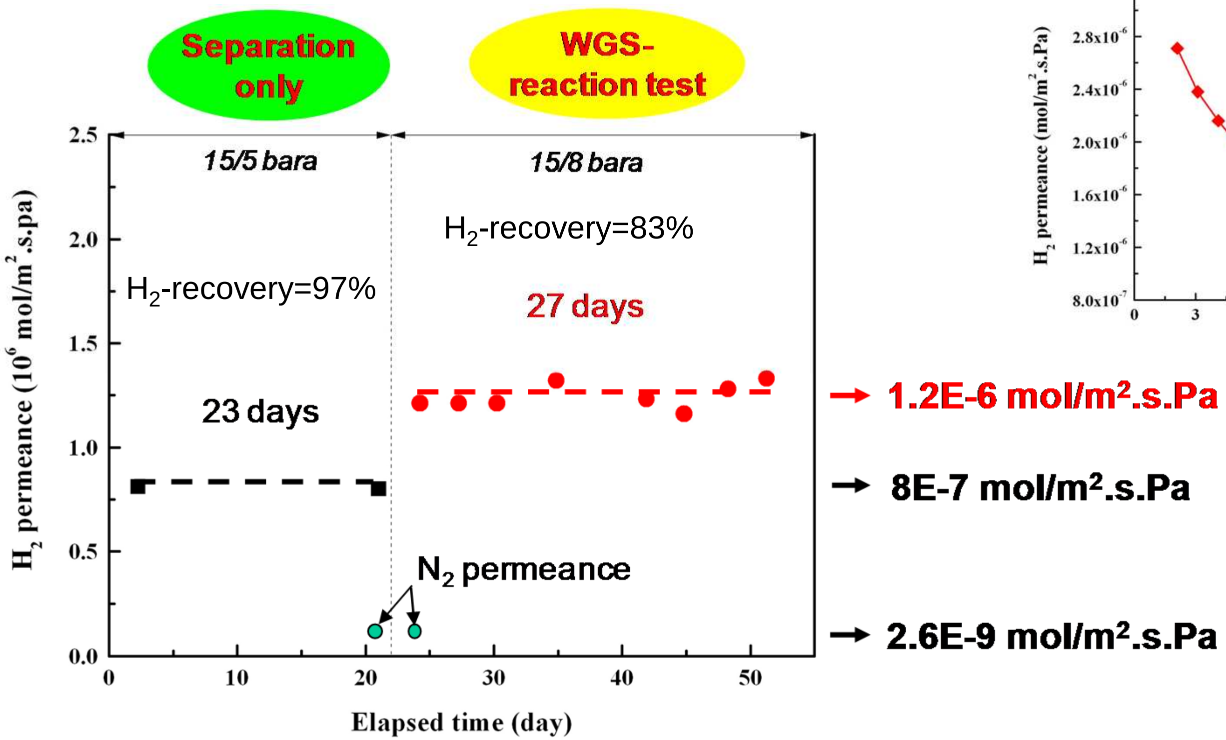


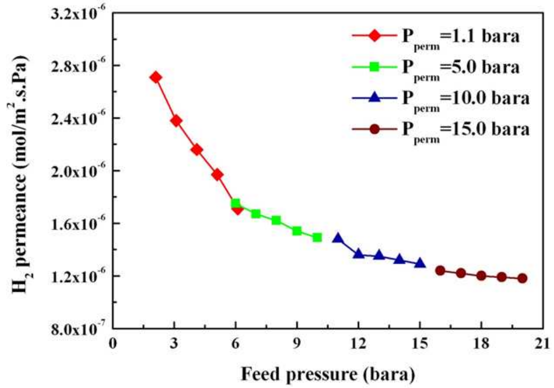
44 cm effective length

→ 3 membranes same T-distribution

Testing of long membranes

- PDU-testing of 3 DICP Pd membranes 0.5 m with ECN HTTP seals
  - Pure H_2/Pure N_2 permeance, separation and shift test (NGCC)





➡ Stable membrane performance for both non-integrated and integrated for a total period of 50 days

Testing of long membranes

- Choice of WGS catalyst (non expensive base metal catalyst):
  - Two commercial catalyst (A (Fe-Cr) and B (alternative)) have been examined
    - Watergas shift stability as function of H_2O/H_2 and H_2O/CO-ratio

- Resulting gas composition for stability catalyst performance:
  - Cat A (Fe-Cr): $H_2O/H_2 > 0.5$* (high H_2O/H_2, prevent reduction) and $H_2O/CO > 2$
  - Cat B: low H_2O/H_2 allowed* and safe operation at $H_2O/CO \leq 2$: vulnerable to H_2S

NGCC	**Low H_2O/H_2**	**High H_2O/H_2**
S/C ratio in ATR	1.4	1.4
Efficiency, %	**45.09**	**44.41**
CO_2 capture, %	99.9	99.9
Net Electricity, MW	437.4	431.2
H_2 recovery, %	98.23	98.27
Membrane area, m^2	**4560**	**5900**
H_2 permeated, kmol/hr	11083	11100
Membrane flux, $mol/m^2.s$	0.6751	0.5226

*vendor spec

➡ Non expensive commercial catalyst available for M-WGS

Reactor testing

- Aim:
  - Reactor design for 1 m membranes based on scaled down full scale WGS membrane reactor design from WP4
  - 1000 h test with 1 m DICP Pd membranes using ATR gas and/or coal gas
  - No test with H_2S
  - The reactor will be tested under different conditions, temperatures between 350 and 500 ^oC, different pressure level for feed and outlet.

- Status:
  - Design of reactor in progress
  - This test will be performed at the end of the project (Q3 and 4 2012)

Overall conclusions

What has been achieved:

- Membrane upscaling to 1 m length
- Membrane stability proven for 1200 hours at 400^{o}C:
  - Integrated and non-integrated
- Non-expensive commercial WGS catalysts identified

Overall conclusions

What has <u>not</u> been achieved <u>yet</u>:

- Demonstration of seals with lower footprint, no slip:
  - Seals in validation process
  - 150 days testing
- Long term M-WGS testing
- Benchscale 1 m long membrane WGS reactor testing

Future activities

Next logical steps within CACHET2:

- Demonstration stability membrane plus improved seal in 150 days testing
- Long term M-WGS testing
- Benchscale 1 m long membrane WGS reactor testing