SECOND JOINT EUROPEAN SUMMER SCHOOL FOR FUEL CELL AND HYDROGEN TECHNOLOGY

September 17-21, 2012

HYDROGEN STORAGE TECHNOLOGIES: COMPATIBILITY OF NON-METALLIC MATERIALS

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HYDROGEN STORAGE TECHNOLOGIES: COMPATIBILITY OF NON-METALLIC MATERIALS WITH HYDROGEN

AIR LIQUIDE

1. GENERALITIES

   1.1. MATERIALS CONCERNED

   1.2. MAIN INCOMPATIBILITY ISSUES

2. SUMMARY OF HYDROGEN COMPATIBILITY

3. PERMEABILITY OF POLYMERS

4. BLISTERING

1.1. MATERIALS CONCERNED

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- **The most commonly used non-metallic materials for gas cylinders and cylinder valves can be grouped as follows:**

  a) plastics materials
  b) elastomer materials
  c) fluid lubricants

Note: solid lubricants are sometimes used e.g. MoS_2

1.1. MATERIALS CONCERNED

a) Plastics materials

- Polytetrafluoroethylene (PTFE)
- Polychlorotrifluoroethylene (PCTFE)
- Polyvinylidenefluoride (PVDF)
- Polyamide (PA)
- Polypropylene (PP)
- Polyetheretherketone (PEEK)
- Polypropylene sulphide (PPS)
- Polyvinyl chloride (PVC)
- Polyoximetacrylate (POM)

1.1. MATERIALS CONCERNED

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b) Elastomer materials

- Butyl rubber (IIR)
- Nitrile rubber (NBR)
- Chloroprene rubber (CR)
- Fluorocarbon rubber (FKM)
- Methyl-vinyl-silicone rubber (MVQ)
- Ethylene propylene diene monomer (EPDM)
- Polyacrylate rubber (ACM)
- Polyurethane rubber (PUR)
- Methyl-fluoro-silicone rubber (MFQ)

1.1. MATERIALS CONCERNED

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c) Fluid lubricant

- Hydrocarbon (HC)
- Fluorocarbon (FC)

1.2. MAIN INCOMPATIBILITY ISSUES

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A. Explosion and fire (oxidation/burning)

B. Weight loss (W)

B.1. Extraction

B.2. Chemical attack

C. Swelling of material (S)

D. Change in chemical properties (M)

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E. Other compatibility considerations

E.1. Impurities in the gas (I)

E.2. Contamination of the material (C)

E.3. Release of dangerous products (D)

E.4. Ageing (G)

E.5. Permeation (P)

A. Explosion and fire (oxidation/burning)

- Compatibility depends mainly on the operating conditions (pressure, temperature, gas velocity, particles, equipment design and application)

- The risk should particularly be considered with gases such as oxygen, fluorine and chlorine

- Most of the non-metallic materials can be ignited relatively easily when in contact with highly oxidizing gases

A. Explosion and fire (oxidation/burning)

HYDROGEN IS FLAMMABLE consequently risk of violent reactions which flammable solid non-metallic materials cannot occur. However, for liquid hydrogen vessels, if there is a leak of the outer jacket, air will penetrate in the interspace under vacuum, the air will condensate into a liquid mixture composed of about 50 % O_2 and 50 % N_2. Such an oxygen mixture is very oxidizing and can react with non-metallic (or even thin metallic) materials

B. Weight loss (W)

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B.1. Extraction

- Solvent extraction of plasticizers from elastomers can cause shrinkage, especially in highly plasticized products
- Some solvents, e.g. acetone or DMF (Dimethylformamide) used for dissolved gases such as acetylene, can damage non-metallic materials
- Liquefied gases can act as solvents but there are no known materials which can dissolve into liquid hydrogen

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B.2. Chemical attack

- Some non-metallic materials can be chemically attacked by gases. This attack can sometimes lead to the complete destruction of the material, e.g. the chemical attack of silicone elastomer by ammonia

- There is no known reaction of “chemical attack” of commonly used materials with hydrogen

C. Swelling of material (S)

- Elastomers are subject to swelling due to gas (or liquid) absorption. This can lead to an unacceptable increase of dimensions (especially for O-rings) or the cracking due to sudden out-gassing when the partial pressure is decreased, e.g. carbon dioxide and chlorofluorocarbons

C. Swelling of material (S)

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- In standards a swelling of more than approximately 15 % in normal service conditions is marked NR (not recommended); a swelling less than this is marked A (acceptable) provided other risks are acceptable

- Hydrogen gas under pressure may lead to swelling of several elastomer

D. Change in chemical properties (M)

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- Gases can lead to an unacceptable change of mechanical properties in some non-metallic materials. This can result, for example, in an increase in hardness or a decrease in elasticity

- Hydrogen does not create this phenomenon at room temperature

E.1. Impurities in the gas (I)

- **Some gases contain typical impurities which may not be compatible with the candidate materials (e.g. acetone in acetylene, H_2S in methane)**
- **This risk shall be addressed depending on the hydrogen source (electrolytic hydrogen is not likely to contain such contamination except if it is a by-product from chlorine production**

E. Other compatibility considerations

E.2. Contamination of the material (C)

- Some materials become contaminated in toxic gas usage by the toxic gas and become hazardous themselves (e.g. during maintenance of equipment)

- No case known with hydrogen

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E.3. Release of dangerous products (D)

- **Many materials when subjected to extreme conditions (such as elevated temperature) can release dangerous products. This risk shall be considered in particular for breathing gases**
- **No case known with hydrogen**

E. Other compatibility considerations

E.4. Ageing (G)

- Ageing is a gradual change in the mechanical and physical properties of the material due to the environment in which it is used or stored. Many elastomer and plastics materials are particularly subject to ageing; some gases like oxygen can accelerate the ageing process, leading sometimes to brittleness

- No case known with hydrogen at room temperature

E.5. Permeation (P)

- **Permeation is a slow process by which gas passes through materials**
- **Permeation of some gases (e.g. helium, hydrogen, carbon dioxide) through non-metallic material can be significant. For a given material, the permeation rate mainly depends on temperature, pressure, thickness, and surface area of the material in contact with the gas. The molecular weight and the specific formulation of plasticizers and other additives can cause a wide range of permeation rates for a particular type of plastics or elastomers**
- **The risk shall be considered for hydrogen due to the effects to surroundings (e.g. fire potential).**

2. SUMMARY OF HYDROGEN COMPATIBILITY OF NON-METALLIC MATERIALS

2. COMPATIBILITY ISSUES WITH NON-METALLIC MATERIALS (Plastic materials)

Name	Formula	PTFE	PCTFE	PVDF	PA	PP
Hydrogen	H_2	AP	A	A	A	AP

Abbrevations for materials

Abbrevations for non-metallic risks

2. COMPATIBILITY ISSUES WITH NON-METALLIC MATERIALS

Name	Formula	POM	PEEK	PPS	PVC
Hydrogen	H_2	A	A	A	A

Abbrevations for materials

Abbrevations for non-metallic risks

2. COMPATIBILITY ISSUES WITH NON-METALLIC MATERIALS (Elastomer materials)

Name	Formula	IIR	NBR	CR	FKM	MVQ	EPDM
Hydrogen	H_2	A	A	A	A	AP	A

Abbrevations for materials

Abbrevations for non-metallic risks

2. COMPATIBILITY ISSUES WITH NON-METALLIC MATERIALS (Lubricants)

Name	Formula	Fluid Lubricant		MoS2
		HC	FC	
Hydrogen	H_2	A	A	A

Abbrevations for materials

Abbrevations for non-metallic risks

3. PERMEABILITY OF POLYMERS

3. PERMEABILITY OF POLYMERS

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3.1. Introduction

3.2. Definition

3.3. Important parameters:

- Temperature
- Pressure
- Material itself
- Type of gas

3.4. Test measurements:

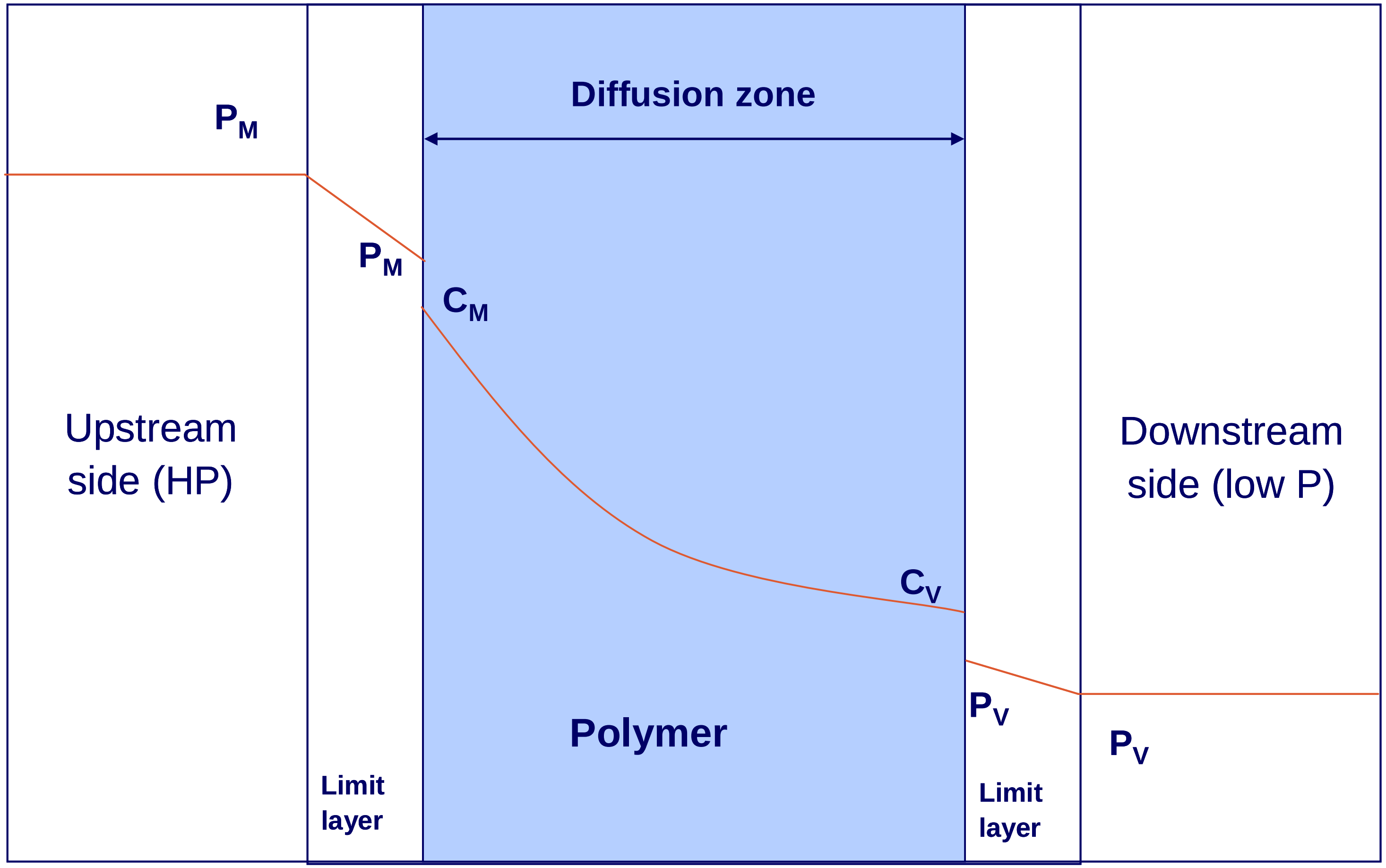
- On samples
- Example on type IV cylinders

3.5. Hydrogen permeability limits

3.1. INTRODUCTION

- Polymers are widely used as gas barriers
- Market: oil industry, car, food, gas applications
- Transport of molecule through polymeric materials will be discussed
- In general, 5 phases can be considered

3.1. INTRODUCTION



Schematic representation of the different resistances encountered by a molecule diffusing through a polymer membrane at fixed temperature

3.2. DEFINITION

- **Permeability is the result of gas solution and gas diffusion**

- **Permeability coefficient is defined as follows :**

$$Pe = S \times D.$$

- **Permeation in polymers is a molecular permeation**

3.2. DEFINITION

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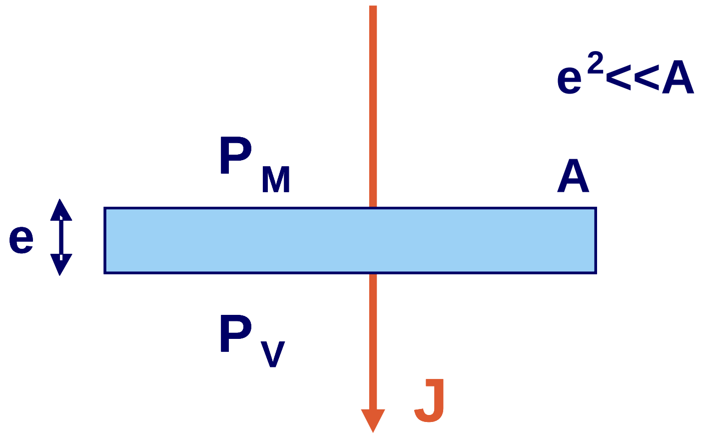
The permeability coefficient is defined as the product of the diffusion and solubility coefficients of the gas for this material. When Henry's law is satisfied, the flow at steady state, for a given temperature, is given by:

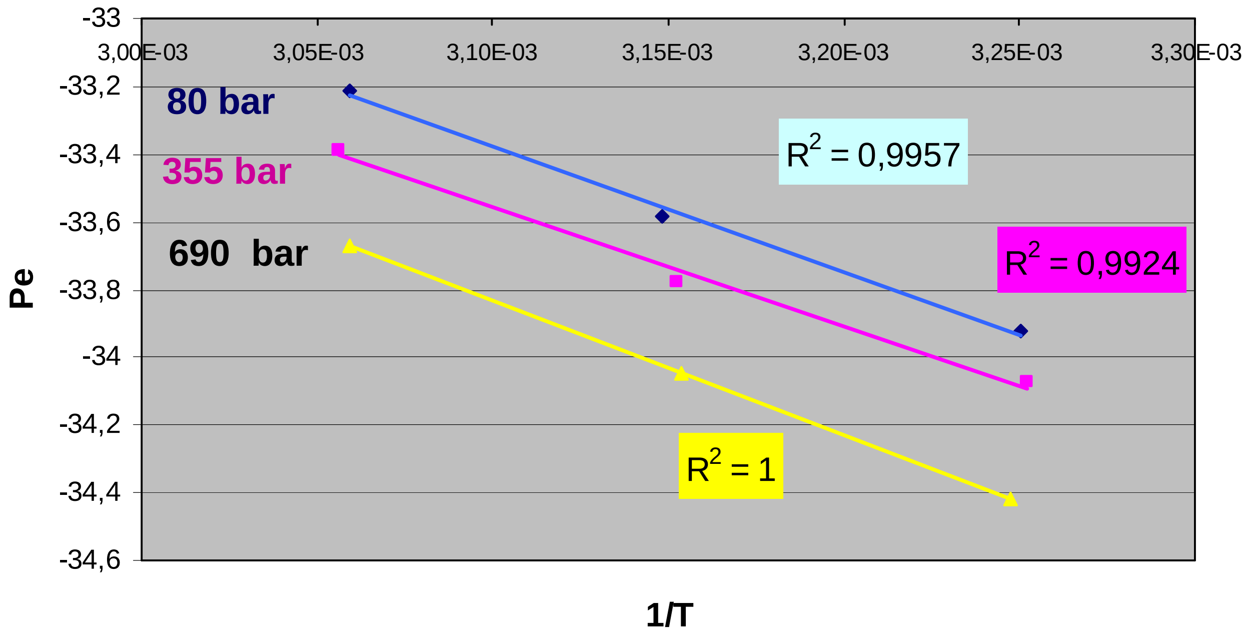
$$J = DS\left(\frac{P_M - P_V}{e}\right) = Pe.\frac{\Delta P}{e}$$



- **J:** flow of molecules going through a surface A, at steady state (permeability flow rate)
- **e:** thickness of the sample
- **PM:** partial pressure of the gas on the upstream side (see slide 27)
- **PV:** partial pressure of the gas on the downstream side (see slide 27)
- **Pe:** permeability coefficient of the gas

3.3. IMPORTANT PARAMETERS: TEMPERATURE

- **According to Arrhenius** $Pe = Pe°(P)\exp(-\frac{Ea(P)}{RT})$
- ***For low P (ΔP <100 bar) : Pe = f(T) only***
- **Example : for natural gas tank at 80, 355 and 690 bar**

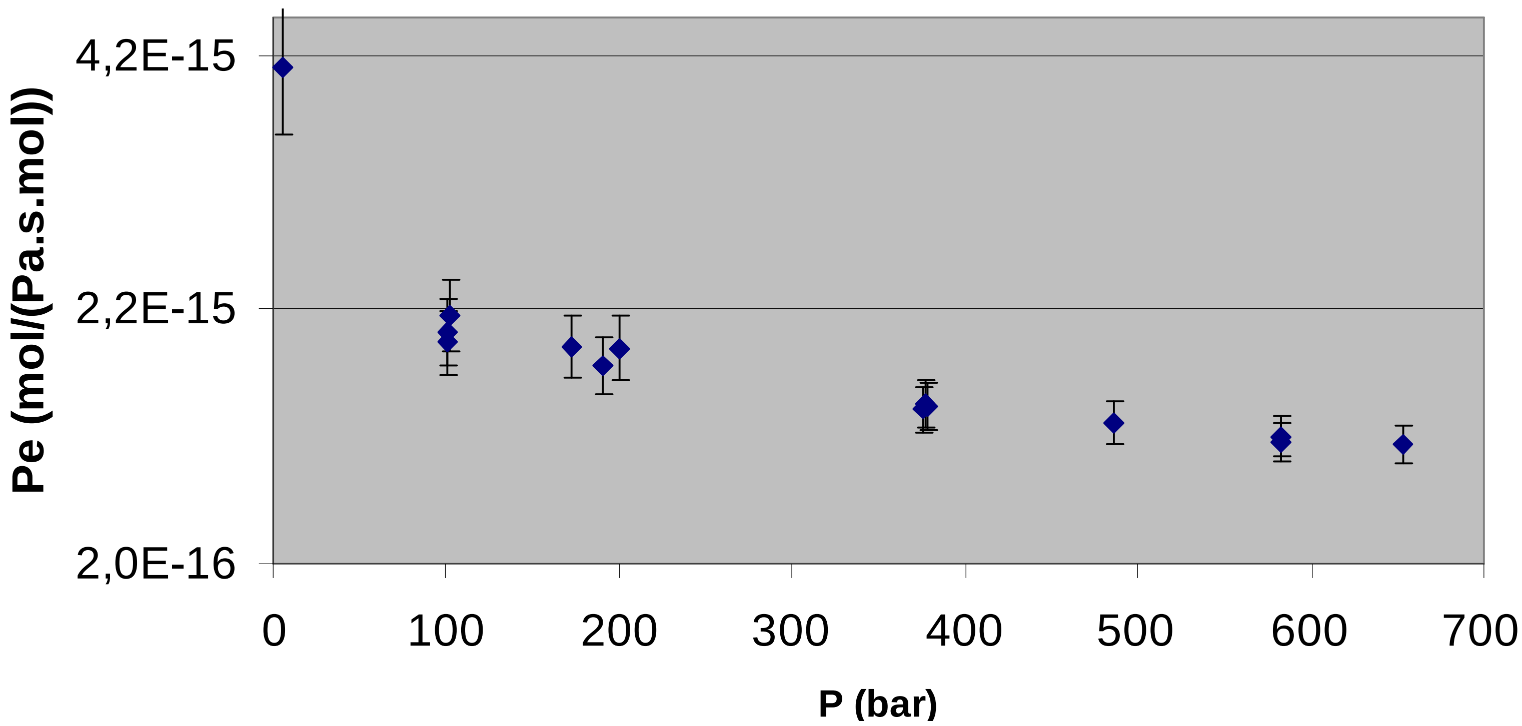


3.3. IMPORTANT PARAMETERS: PRESSURE

- Pe increases when pressure increases
- For HP, Pe decreases when pressure increases (hydrostatic pressure on the polymer)
- This effect is important for HP tanks
- Depends on the polymer
  - For PE, the threshold pressure is 80 bar
  - For PA, the threshold pressure is 300 bar

3.3. IMPORTANT PARAMETERS: PRESSURE

Example for PE used for C_2H_2 tanks



3.3. IMPORTANT PARAMETERS: MATERIAL ITSELF

- Cristallinity
- Orientation
- Reticulation for elastomers

3.3. IMPORTANT PARAMETERS: MATERIAL ITSELF

- Plastifiers
- Additive elements
- Glass transition temperature
- Type of polymer itself not easy to see (because of the influence of the other parameters)

3.3. IMPORTANT PARAMETERS: TYPE OF GAS

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- Molecule size and gas/material interaction
- Example for PE, PA11, PVF_2:
  - **Permeability :** $Pe(CO_2) > Pe(He) > Pe(CH_4) > Pe(Ar) > Pe(N_2)$
  - **Diffusion :** $D(He) >>> D(CO_2) \sim D(Ar) \sim D(CH_4) \sim D(N_2)$
  - **Solubility :** $S(CO_2) >> S(CH_4) >> S(Ar) > S(N_2) >> S(He)$
    - ✓In this case :
      - *small molecules : diffusion is the most important*
      - *large molecules : solubility is the most important*

3.3. IMPORTANT PARAMETERS: TYPE OF GAS

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- **Example : PA11**
  - Permeability : Pe(He) > Pe(CO_2) > Pe(Ar) > Pe(CH_4) > Pe(N_2)
  - Diffusion : D(He) >>> D(CO_2) ~ D(Ar) > D(N_2) ~ D(CH_4)
  - Solubility : S(CO_2) >> S(CH_4) ~ S(Ar) > S(N_2) > S(He)

  - Similar to PE

- **Example : PVF_2**
  - Permeability : Pe(He) ~ Pe(CO_2) >> Pe(Ar) > Pe(CH_4) > Pe(N_2)
  - Diffusion : D(He) >>> D(CO_2) ~ D(Ar) > D(N_2) ~ D(CH_4)
  - Solubility : S(CO_2) >> S(CH_4) ~ S(Ar) > S(N_2) > S(He)

  - CO_2 : very soluble in PVF_2 $\Rightarrow$ Pe identical to CO_2 even though He diffusion is 50 times bigger

3.4. TEST MEASUREMENTS ON DISC SAMPLE - PRINCIPLE

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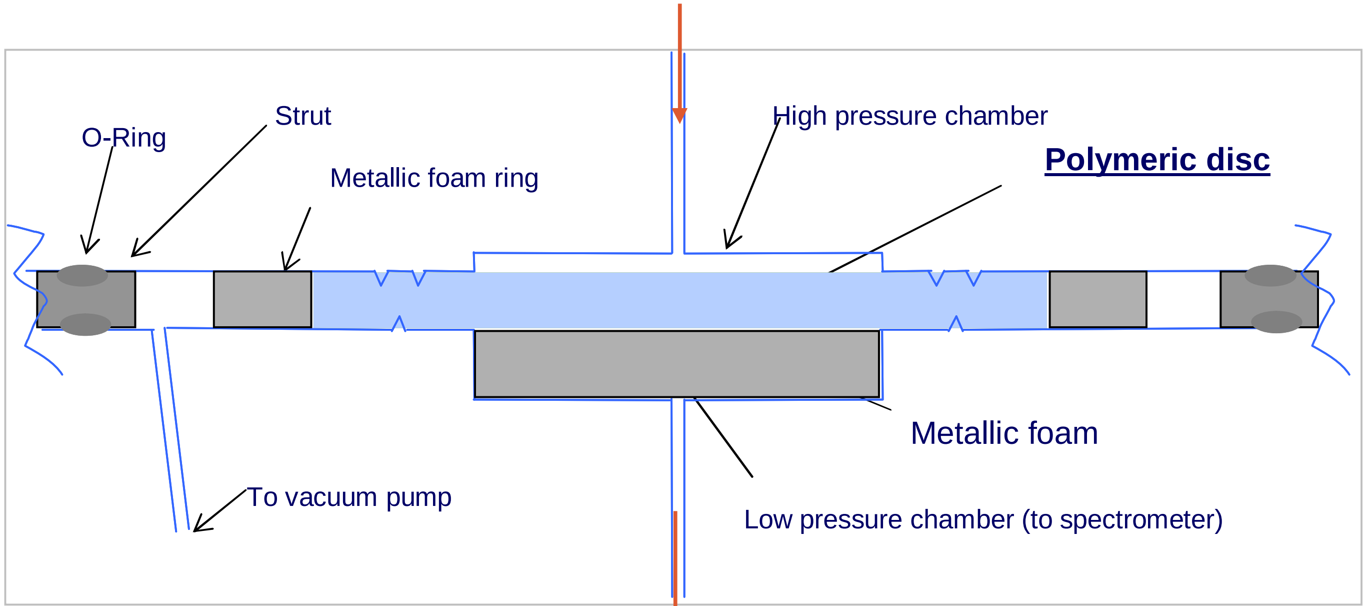
Test bench

Pressure

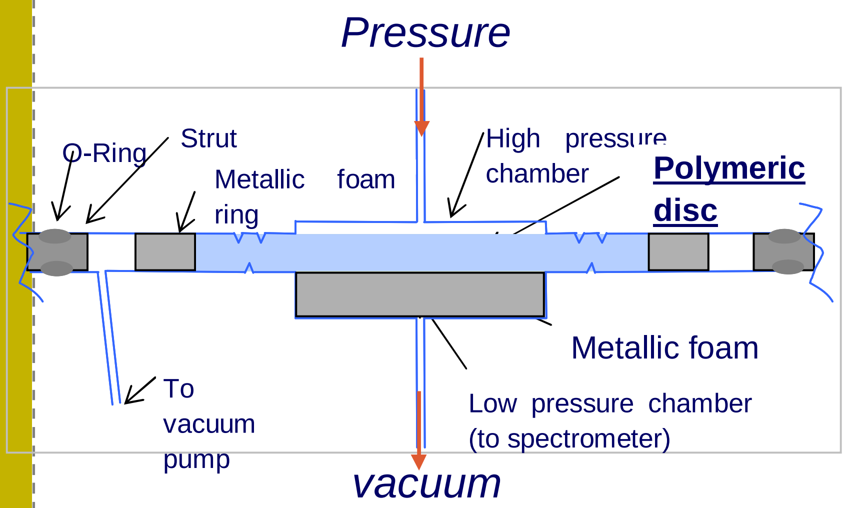


vacuum

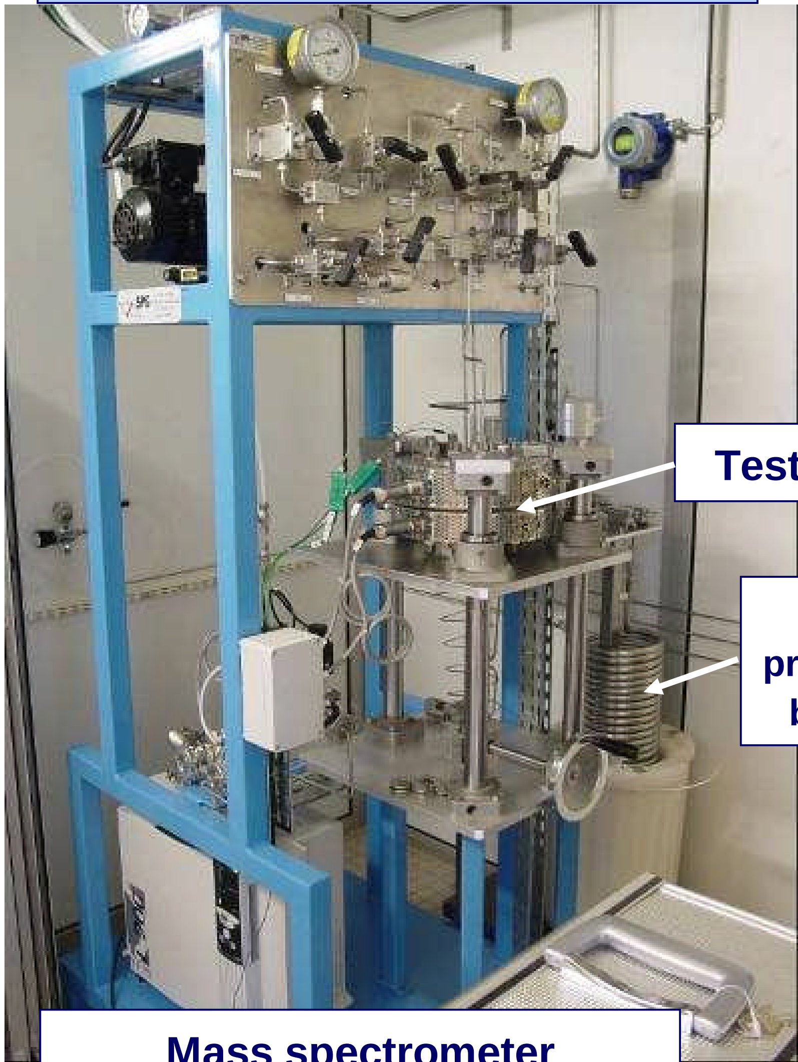
3.4. TEST MEASUREMENTS ON DISC SAMPLE - PRINCIPLE

AIR LIQUIDE

Cell

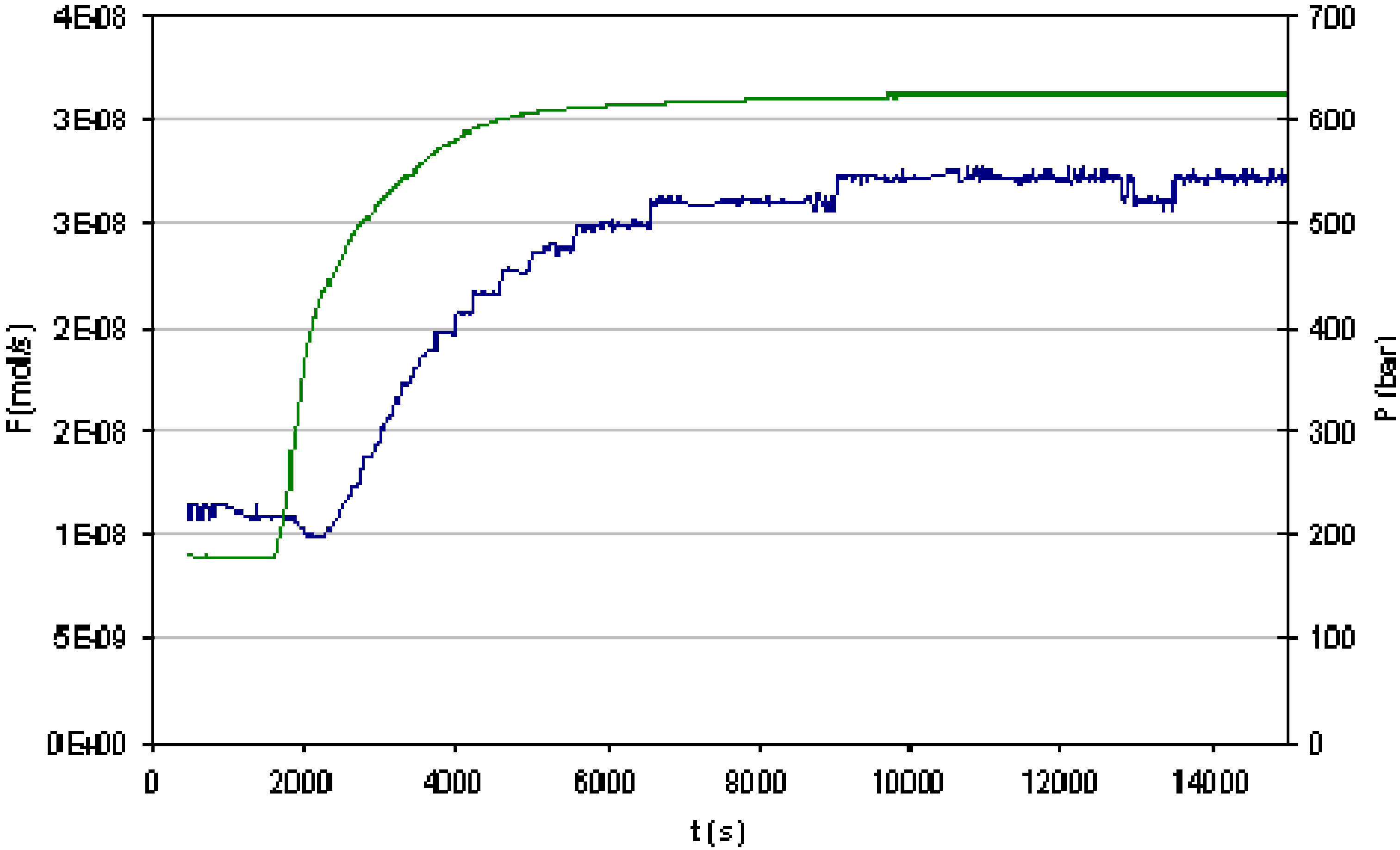


AL-CRCD test bench on disc (High pressure and temperature)



3.4. TEST MEASUREMENTS - PRINCIPLE

AIR LIQUIDE



Hydrogen permeation flow rate (blue curve) and pressure (green curve) as a function of time for a polymer material

3.4. TEST MEASUREMENTS - PRINCIPLE

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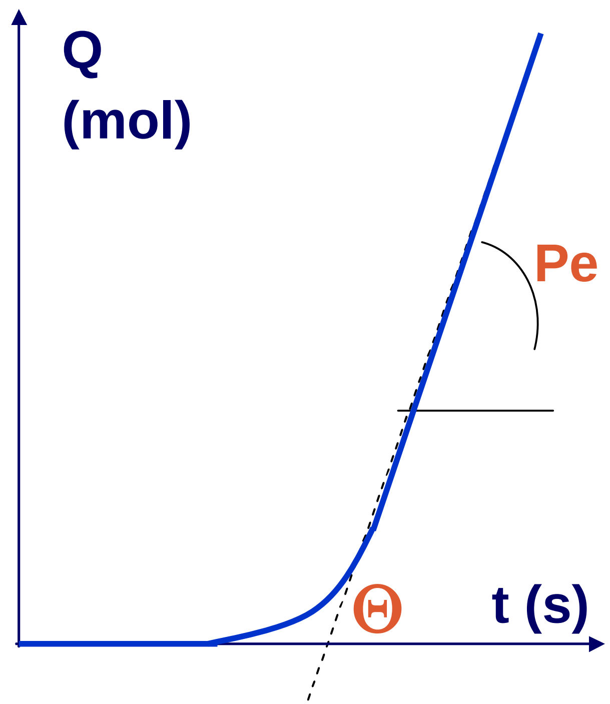
- Steady state (allow to determine S, D and Pe)
- Fick law ($C_2 << C_1$):

$$Q(t) = C1e \times \left(\frac{Dt}{e^2} - \frac{1}{6} - \frac{2}{\pi^2}\sum_{1}^{\infty}\frac{(-1)^n}{n^2} \times \exp\left(-\frac{Dn^2\pi^2 t}{e^2}\right)\right)$$

- For t >> becomes :

$$Q(t) = \frac{DC1}{e} \times \left(t - \frac{e^2}{6D}\right)$$

- Time lag Θ $\Theta = \frac{e^2}{6D}$
- Θ → D
- Slop : Pe
- S can be derived



3.4. TEST MEASUREMENTS – H_2 TEST ON GAS CYLINDERS (TYPE IV)

- **Type IV cylinders at different pressures**
- **Two types of liner : PE and PA**
- **Criteria: e.g. < 1 cm^3/l/h**

3.4. TEST MEASUREMENTS – PRINCIPLE

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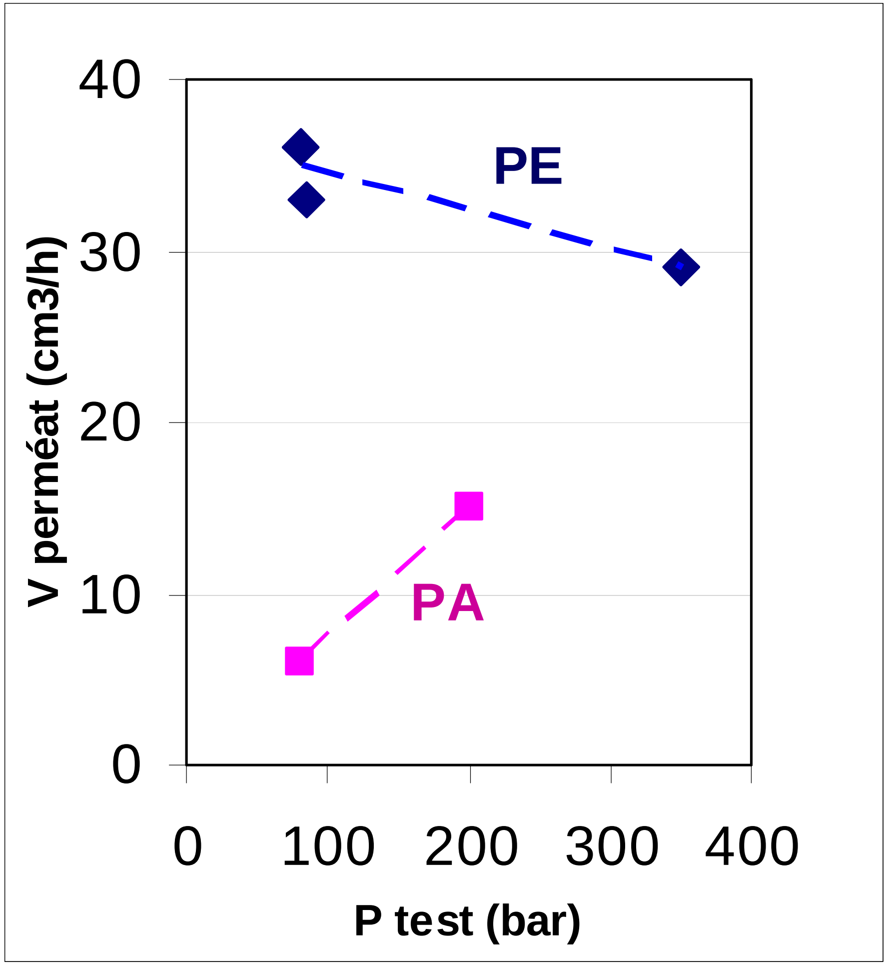
1. Place the cylinder in a sealed test chamber, either purged with a neutral gas or under vacuum
2. Fill the cylinder with hydrogen at working pressure
3. Close the valve
4. Regulate test chamber and detector temperature (for instance 27[1] ± 2 °C)
5. Measure hydrogen leak rate until steady state is reached and continue the measure for at least 4 days at steady state
6. Empty the cylinder

[1] As permeability limits are defined for 15°C, having a higher test temperature will be more severe

3.4. TEST MEASUREMENTS – SOME RESULTS



H_2, T = 22°C

3.4. TEST MEASUREMENTS – SOME RESULTS ON DISC SAMPLES

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COEFFICIENT OF PERMEABILITY

	Test on tanks	Test on disc samples
T:22°C, P:85bar, gas:H_2	8.10^{-16}	1.10^{-15}
T:18°C, P:80bar, gas:H_2	8.10^{-16}	8.10^{-16}
T:18°C, P:350bar, gas:H_2	1.10^{-16}	8.10^{-16}

3.5. HYDROGEN PERMEABILITY LIMITS – LITERATURE REVIEW

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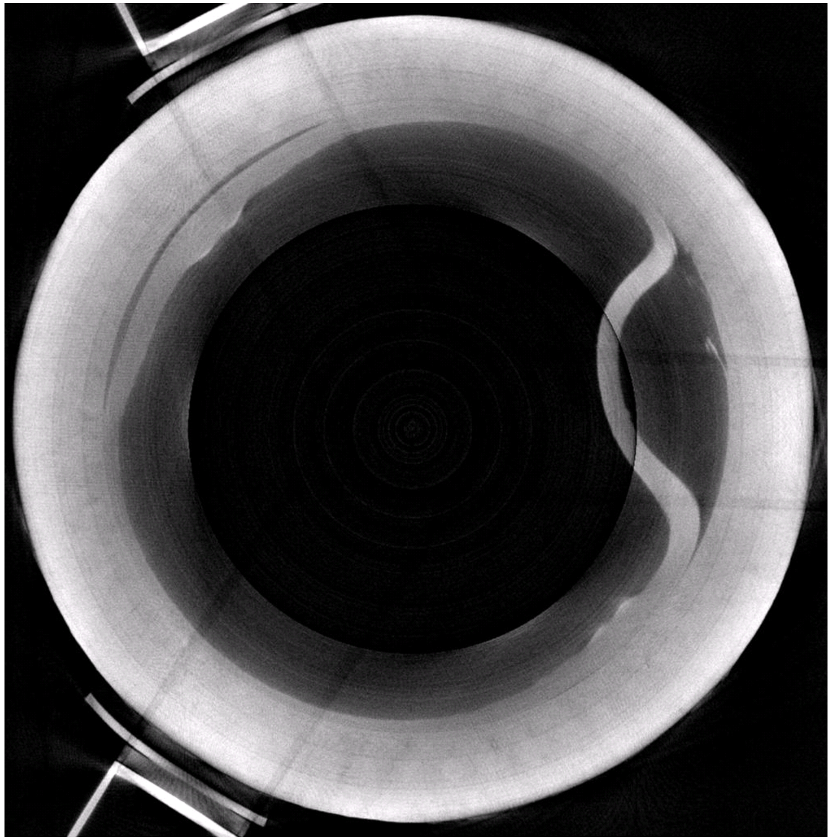
Reference	Scope	Permeability rate	Temperature
EIHP II European project [2]	On board H_2 storage in vehicles	1 $Ncm^3/h/L$-tank	Room temperature
ISO/TS 15869 [3]	On board H_2 storage in vehicles	2.8 $cm^3/h/L$-tank at 700 bar and 2 at 350 bar	15°C
European regulation for on-board storage in vehicles (R79/2009) [4]	On board H_2 storage in vehicles according to [5]	6 $Ncm^3/h/L$-tank	15°C
Hysafe European project [5]	Risk analysis on a vehicle in a garage with on board storage	6 $Ncm^3/h/L$-tank	15°C
Department of Energy study [6]	Risk analysis on a vehicle in a garage with on board storage (540 L @ 350 bar)	10 $cm^3/h/L$-tank	15°C

4. BLISTERING

4. LINER COLLAPSE/BLISTERING DEFINITION AND OCCURENCE

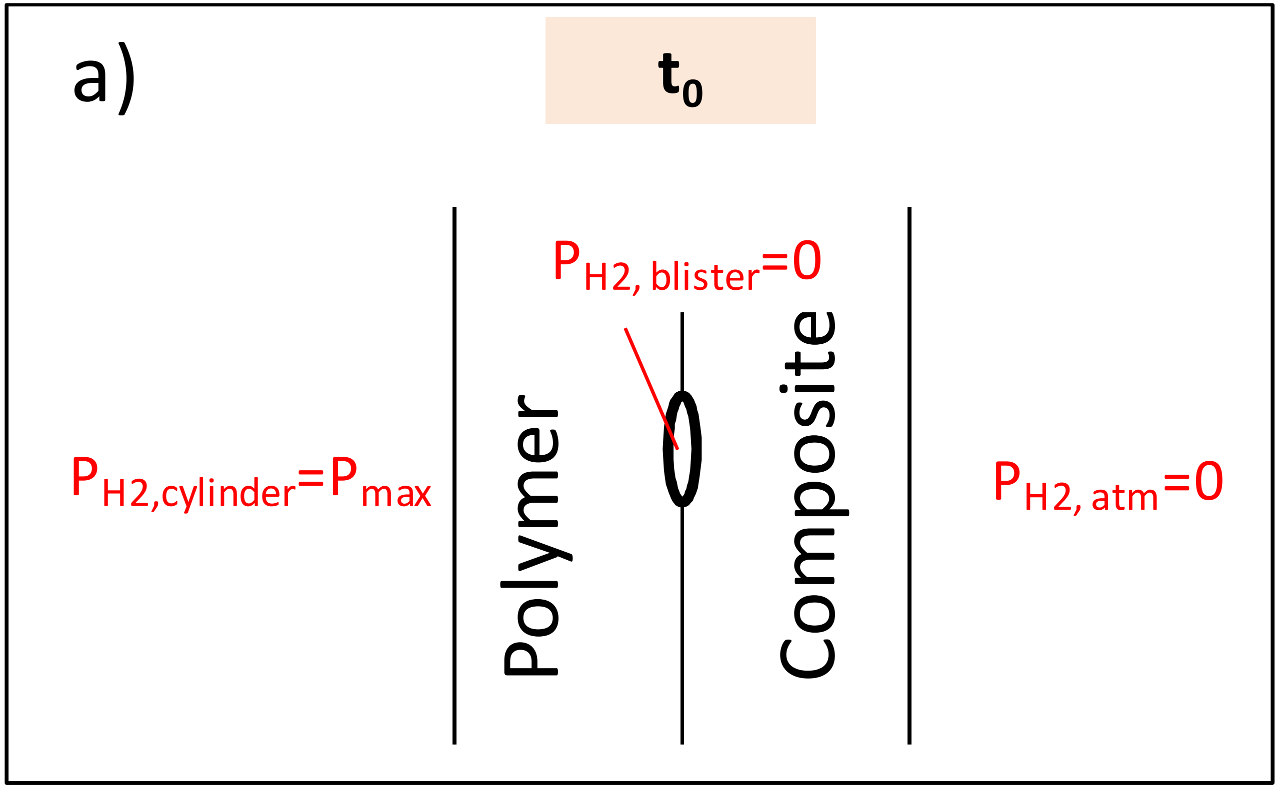
High pressure hydrogen filling-emptying tests on composite cylinders have shown that a permanent deformation of the liner can occur under certain conditions

4. LINER COLLAPSE/BLISTERING DEFINITION AND OCCURENCE

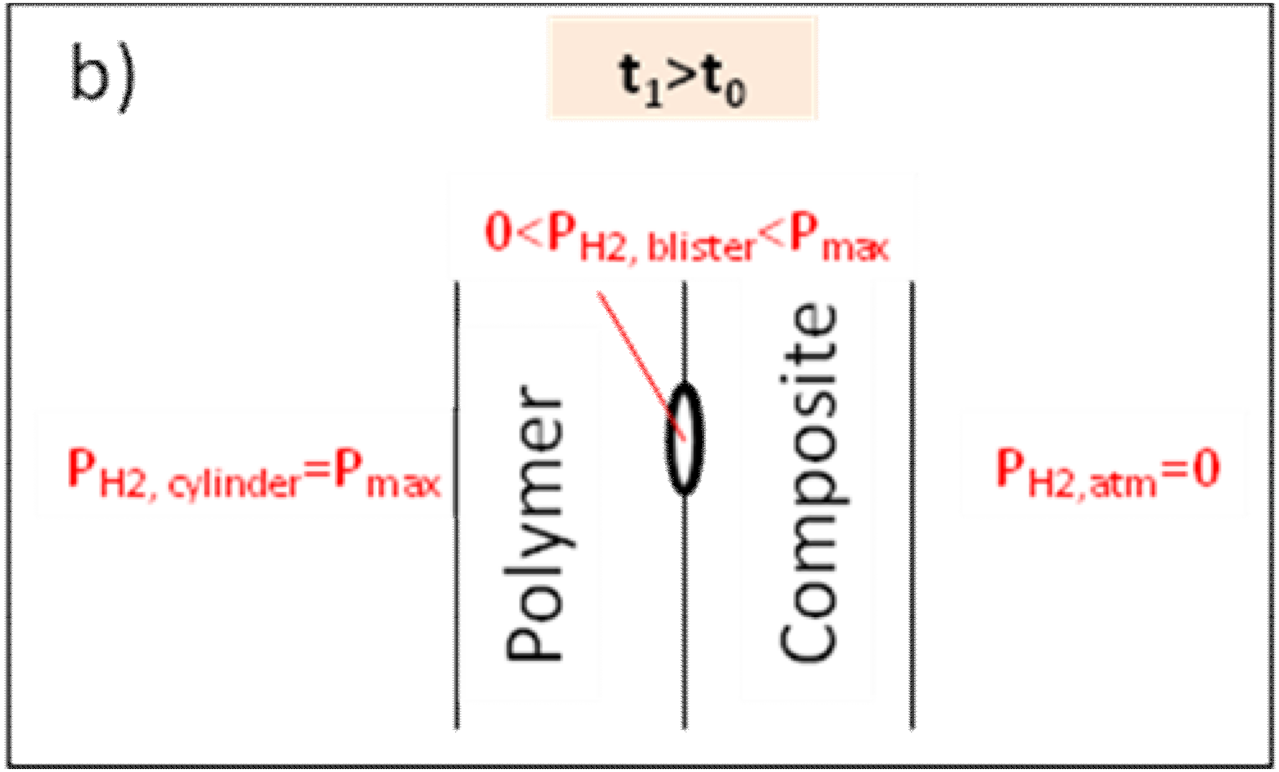


Picture (left) and XRay tomography (right) of a liner collapse

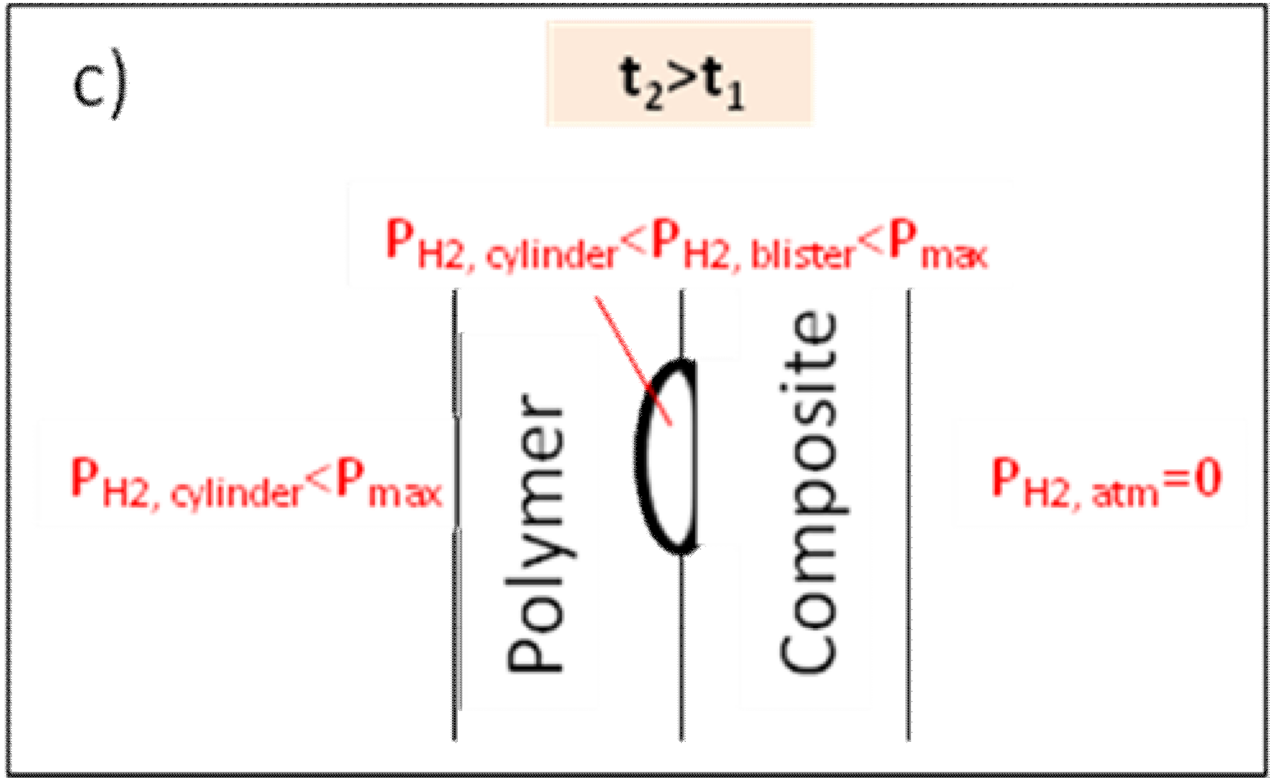
4. LINER COLLAPSE/BLISTERING PRINCIPLE



4. LINER COLLAPSE/BLISTERING PRINCIPLE



4. LINER COLLAPSE/BLISTERING PRINCIPLE



4. LINER COLLAPSE/BLISTERING DEFINITION AND OCCURENCE

Liner collapse is related to gas accumulation in the materials (solubility, swelling) and at the interface between the liner and the composite (in voids, adhesion defects, etc). When already present, collapses tend to propagate with pressure release. Indeed, pressure release decreases mechanical load on the liner and allow it to relax. Collapse expansion also allows equilibrating the pressure in the collapse and in the cylinder.

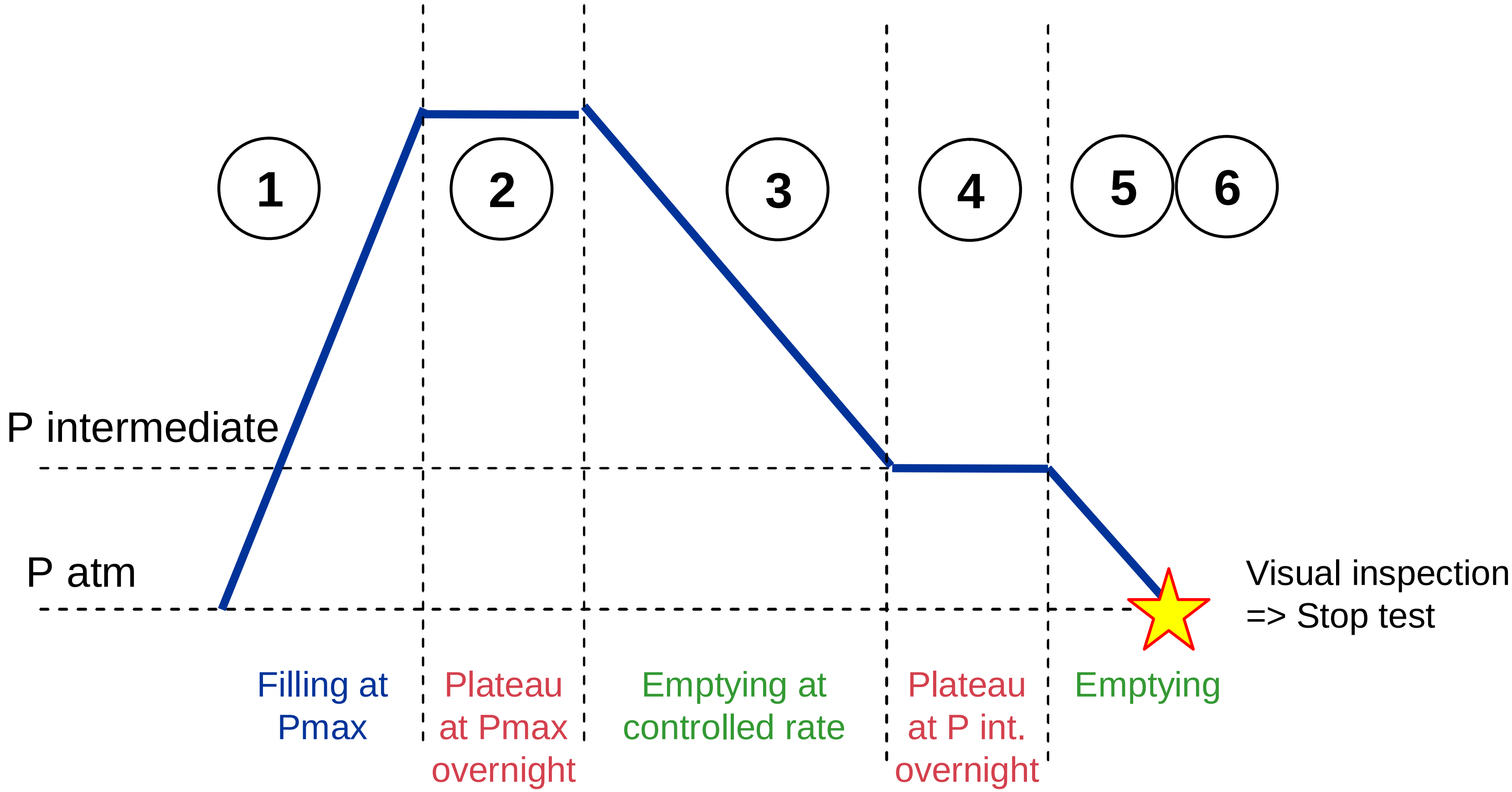
4. LINER COLLAPSE/BLISTERING DEFINITION AND OCCURENCE

The exact mechanism governing the initiation and propagation of liner collapse is still under study. The occurrence of liner collapse depends on the nature of the gas and of the liner (solubility and diffusion effects), maximum pressure in the cylinder, emptying speed and minimum pressure in the cylinder (i.e. use of a RPV). Having a "high" minimum pressure in the cylinder contributes to mitigate the phenomenon.

4. LINER COLLAPSE/BLISTERING DEFINITION AND OCCURENCE

It is also likely to depend on the liner mechanical properties (polyamide-6 only tested). A numeric study started with an academic partner showed the high impact of the maximum and minimum pressure in the cylinder on the occurrence of the phenomenon.

4. LINER COLLAPSE/BLISTERING TEST PROCEDURE



Schematic representation of the liner collapse test procedure