Sample scale testing method to prevent collapse of plastic liners in composite pressure vessels

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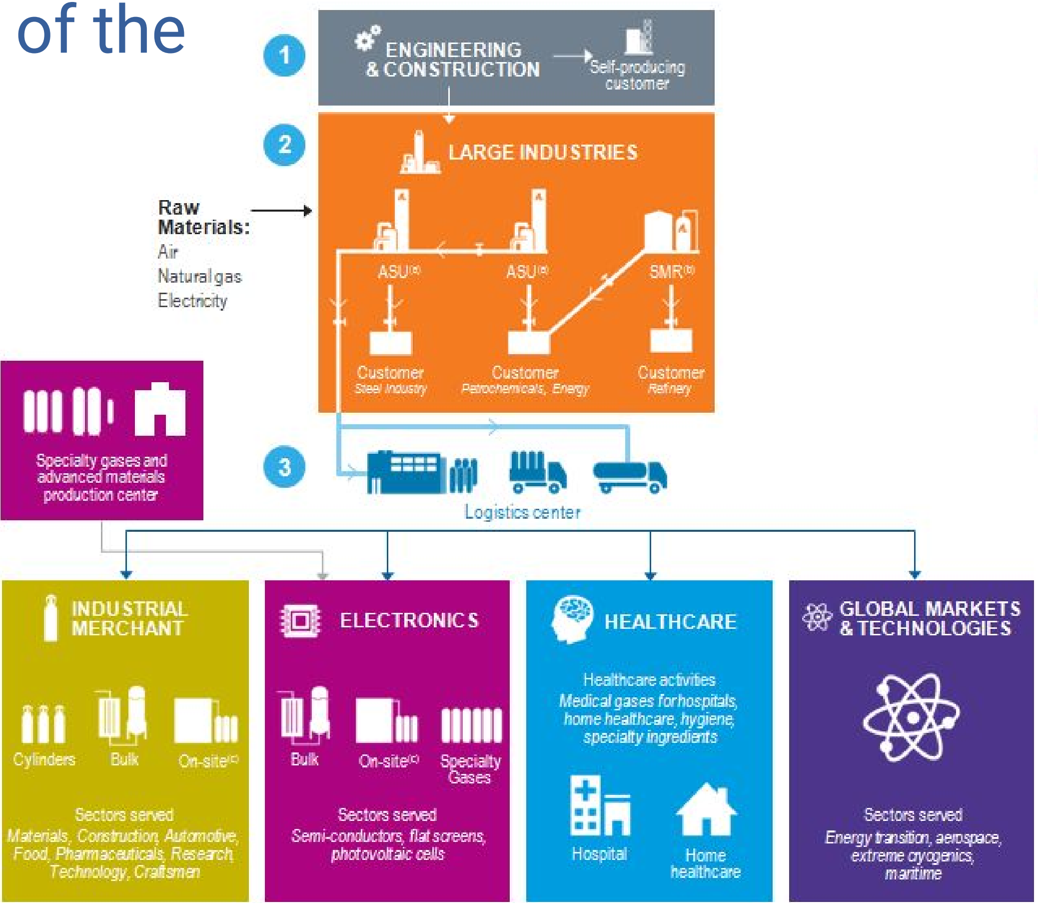
Composite pressure vessels @Air Liquide

Structure of the AL Group



1 **ENGINEERING & CONSTRUCTION** → Self-producing customer

2 **LARGE INDUSTRIES**

Raw Materials:
Air
Natural gas
Electricity

ASU[a] ASU[a] SMR[b]

Customer *Steel Industry*
Customer *Petrochemicals, Energy*
Customer *Refinery*

Specialty gases and advanced materials production center

3 Logistics center

INDUSTRIAL MERCHANT

Cylinders Bulk On-site[c]

Sectors served
Materials, Construction, Automotive, Food, Pharmaceuticals, Research, Technology, Craftsmen

ELECTRONICS

Bulk On-site[c] Specialty Gases

Sectors served
Semi-conductors, flat screens, photovoltaic cells

HEALTHCARE

Healthcare activities
Medical gases for hospitals, home healthcare, hygiene, specialty ingredients

Hospital Home healthcare

GLOBAL MARKETS & TECHNOLOGIES

Sectors served
Energy transition, aerospace, extreme cryogenics, maritime

A three-stage development model

1 **Engineering & Construction**
designing and building state-of-the-art production units for Air Liquide as well as for third-party customers.

2 **Large Industries**
investing long-term to produce large quantities of gases for our customers and to meet the Group's needs.

3 Part of the production capacity of **Large Industries** is used to serve **Industrial Merchant**, **Healthcare**, **Electronics** and **Global Markets & Technologies** within a geographic radius of about 250 km.
Products are distributed in liquid form (in cryogenic trucks driven directly to storage units on the customer's premises) or in gaseous form (in cylinder) depending on the quantities required.
Gas production is actually a local activity, as gases are not transported over long distances, with the exception of some rare and specialty gases used mainly in electronics.

[a] **ASU :**	Air Separation Unit
[b] **SMR :**	Hydrogen and carbon monoxide production unit (Steam Methane Reformer)
[c] **On-site :**	Small local production unit

AL in the hydrogen value chain

Distribution

Transport

Storage

Production

Applications & Customers

AL in the hydrogen value chain

Composite cylinders as
customer's storage to be filled

Distribution

Transport

Storage

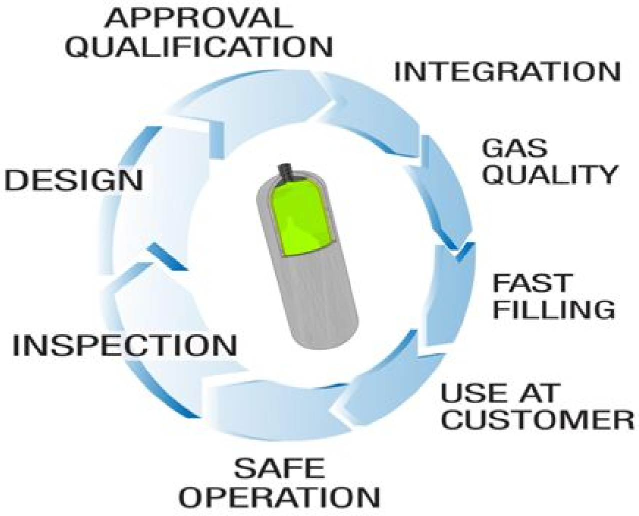
Production

Composite cylinders
for
AL supply chain
operations

Applications & Customers

R&D activity in composite pressure vessels

R&D knowledge covering **all aspects of cylinder's lifetime within AL operations**
Targeting a **safe & efficient use** of composite cylinders

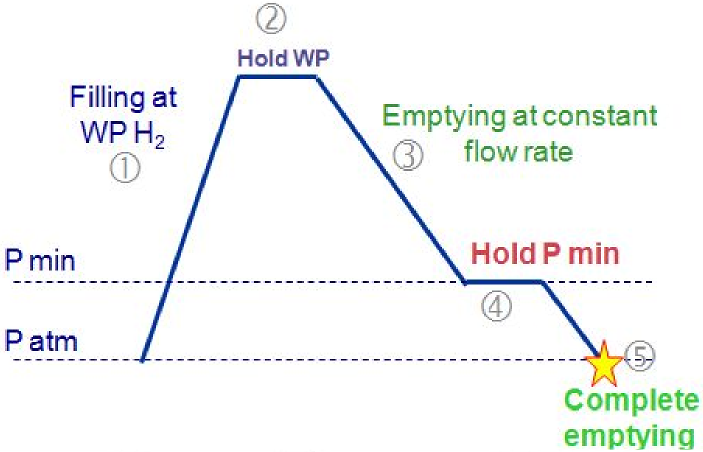


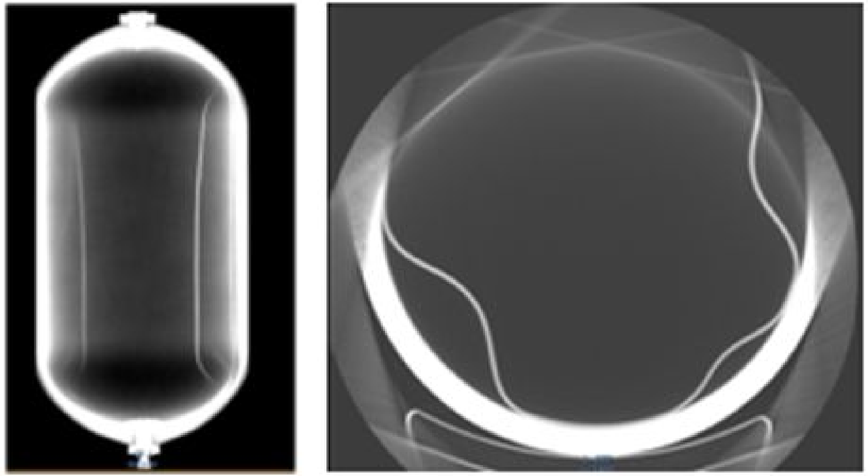
Ensure **structural integrity** of vessels through their lifetime, beyond existing standards

Assess the **consequences** of accidental events and **mitigate** the industrial risk

Reduce the total cost of safely operating
composite pressure vessels
through better understanding

Collapse of plastic liners





1. Hydrogen permeates through plastics
2. Permeation equilibrates, with hydrogen present in porosities and absorbed in the materials
3. Trapped hydrogen desorbing, liner and composite having different permeability

=> Pressure at liner - composite interface

Important deformation of the liner, even when glued to the composite shell

Depending on:
- Pressures
- Emptying flow rate

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Sample scale study in ANR project *Colline*

Current mitigation methods

- Collapse is related to hydrogen desorption
  - Collapse is **linked to high pressure**
  - **Not observed without stabilisation time at high pressure**
- Depending on cylinder design, service pressure & flow rate, collapse appears at different pressure level
  - A **Residual Pressure Valve** (RPV) can be used and qualified for a **maximal flow rate** to avoid collapse in normal operating conditions

- Collapse can not be seen without internal inspection
  - Mandatory only once every 10 years (for transportable cylinders)

Need to define a **liner collapse resistance test**
To prove no collapse happening between WP and RPV pressure

Full scale H2 cycling tests
= huge costs & duration !

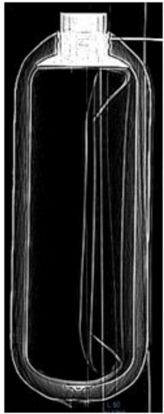
Need to investigate **long-term consequences** of a collapse in case of repeated collapses
(risk = premature leak)

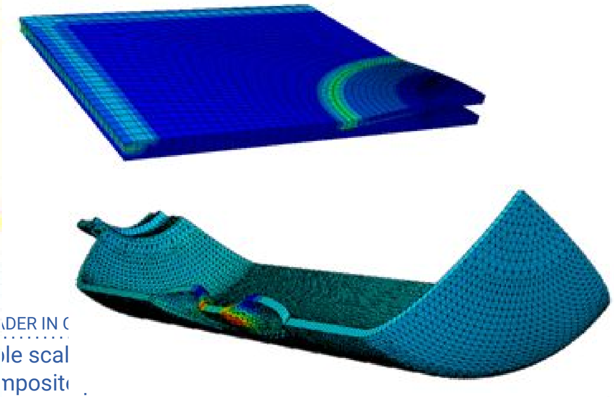
Objectives of the project *Colline*

with funding from French National Research Agency (ANR)

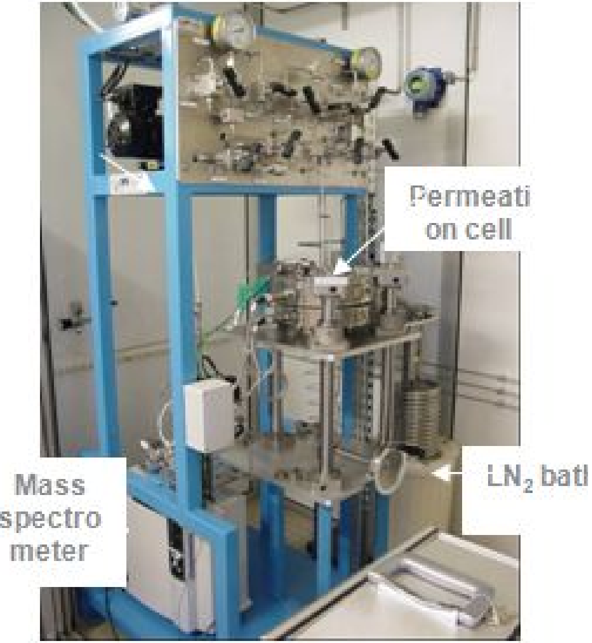
- Better understand the **conditions leading to a collapse** of the plastic liner
  - Emptying tests on 2.4 L 700 bar cylinders
  - Definition of representative samples for parametric study
  - Identification of the influence factors
    - Maximum pressure
    - Decompression rate
    - Residual pressure

- Investigate the impact of a collapsed liner on the **durability** of a pressure vessel
  - Hydrogen cycling tests on tanks with collapsed liner
  - Development of a multi-physics numerical model to predict the fatigue behaviour of a collapsed liner

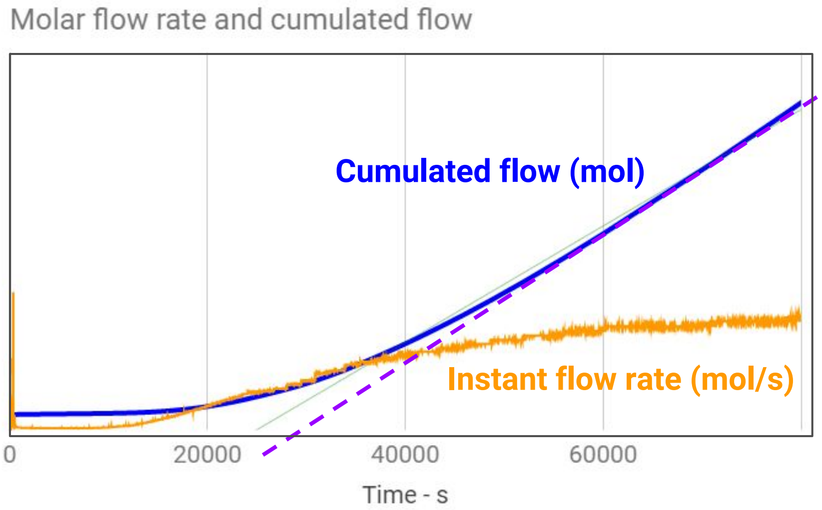




Permeation tests - to get gas transport parameters... *@AL*



700 bar hydrogen permeation test bench



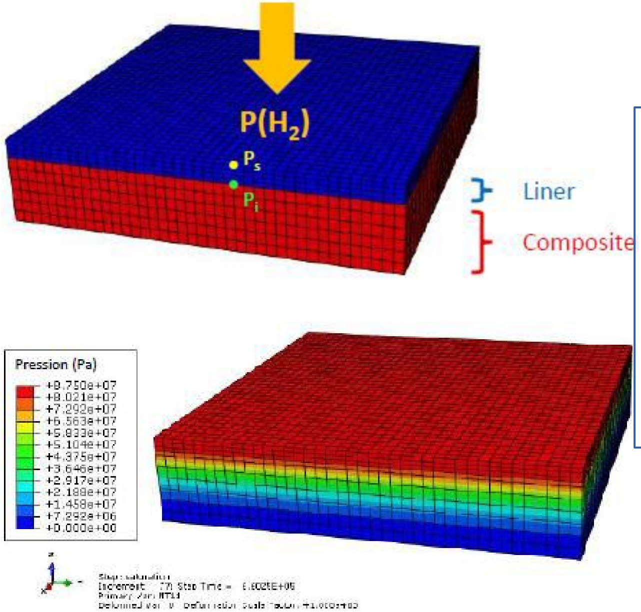
Solubility S
mol/(m3.Pa)
Capacity of the material to accept solved gas

Diffusivity D
m²/s
Capacity of the material to let the gas flow through

Permeability Pe = S*D
mol/(Pa.m.s)

For a given pressure and temperature condition

...to allow calculating the pressure at liner-composite interface



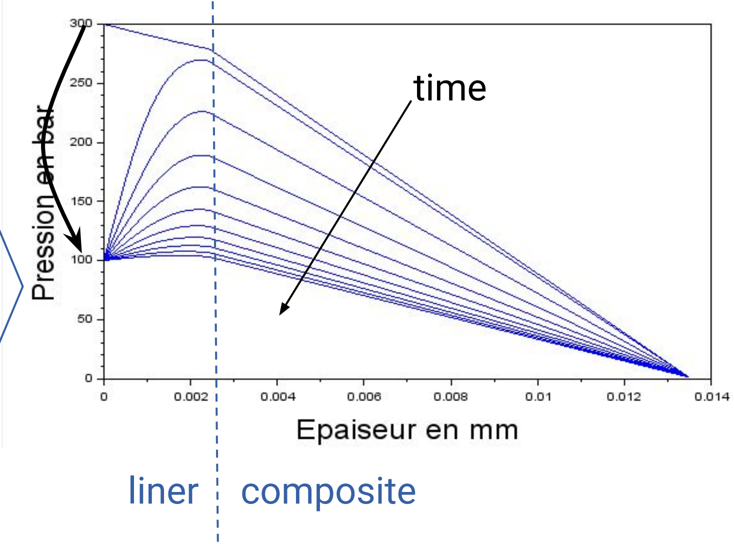
Henry's law to link pressure and concentration

$$C_{H2} = S * P$$

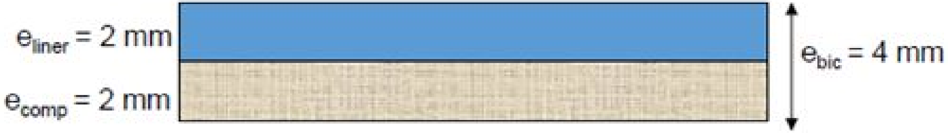
Fick's law for diffusion

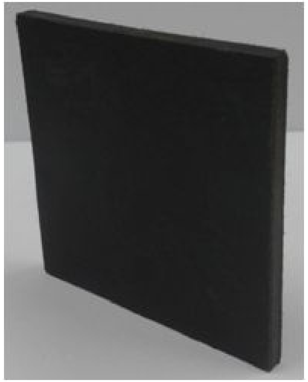
$$\frac{\partial C}{\partial t} = D * \frac{\partial^2 C}{\partial x^2}$$

Sudden inner pressure drop 300 to 100 bar



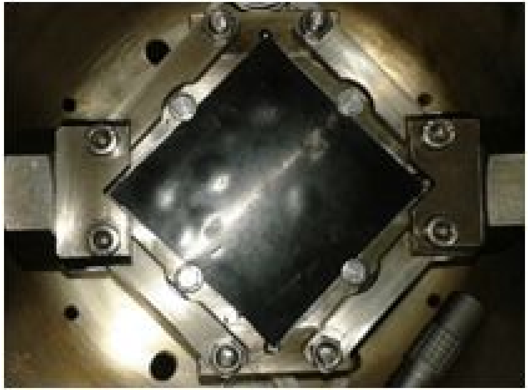
Decompression tests on liner/composite plates @Pprime





Samples representing cylinder wall:
2mm thermo-compressed polyamide
2mm carbon/epoxy composite

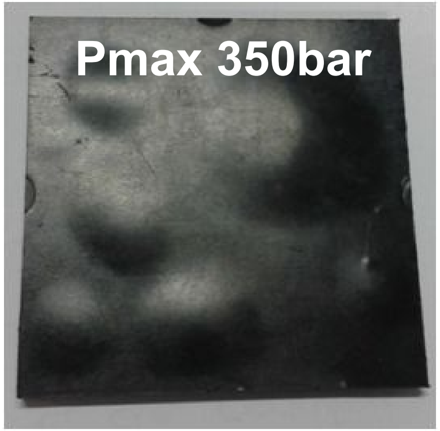
Traction machine with hydrogen chambre
Mechanical stress on the edges
to reproduce the liner stress state
Temperature control - 25 °C or 65 °C
to study the influence of temperature on collapse
Maximal **pressure 350bar** of hydrogen
long hold before rapid decompression
CT Scan observation
before and moments after decompression



A sample scale study is possible

Conditions
Temperature 65°C
Decompression speed 50 bar/min

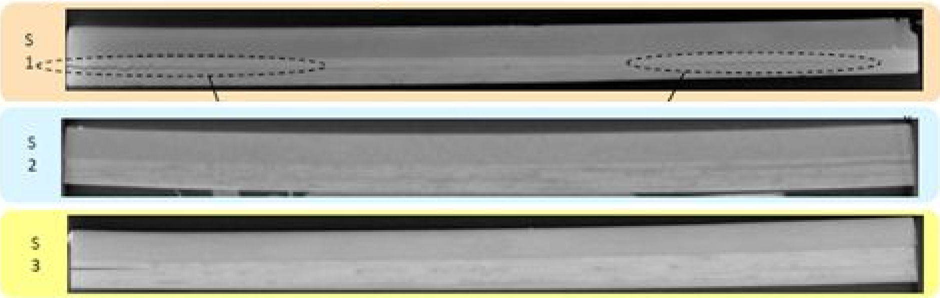
Strong collapse, small decrease over time



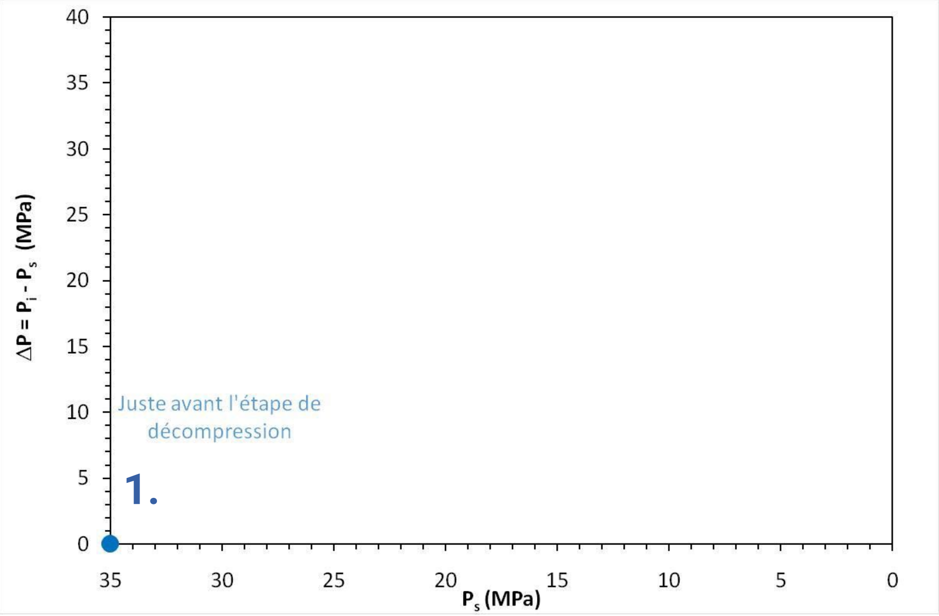
No collapse

1 h after test – max gap 2.4 mm

1 month after test – max gap 1.86mm



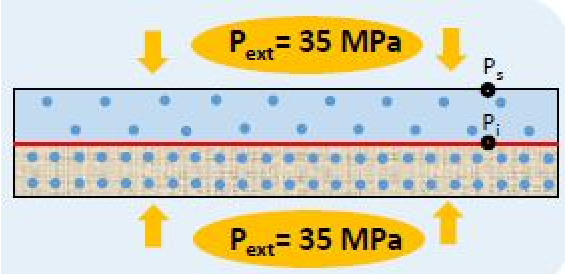
What happens to the sample



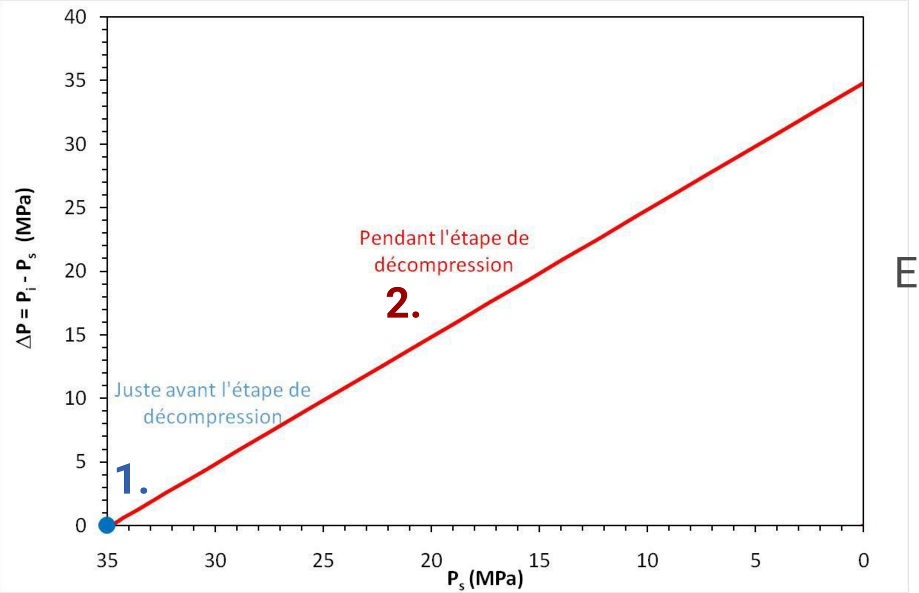
1.

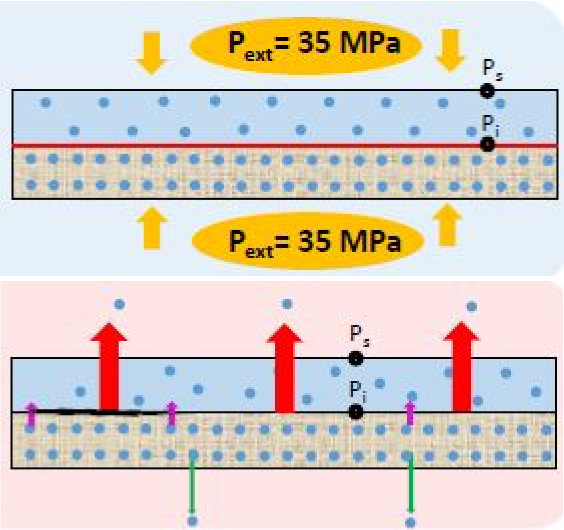
Initial equilibrium

$\Delta P = P_i - P_s = 0$



What happens to the sample





1.

Initial equilibrium

$\Delta P = P_i - P_s = 0$

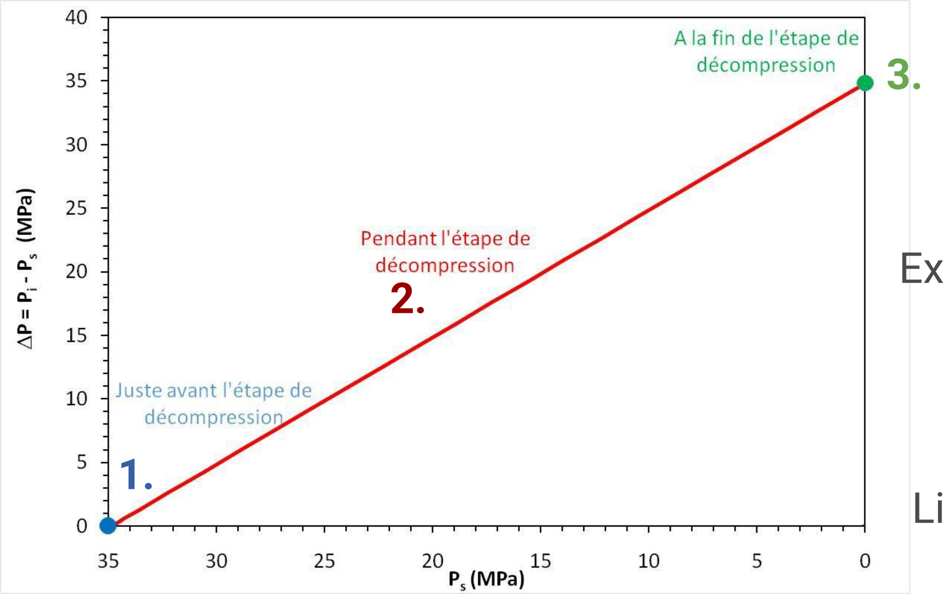
2.

Ext. pressure removed

Gas desorption

$0 \leq P_i - P_s \leq 350\text{bar}$

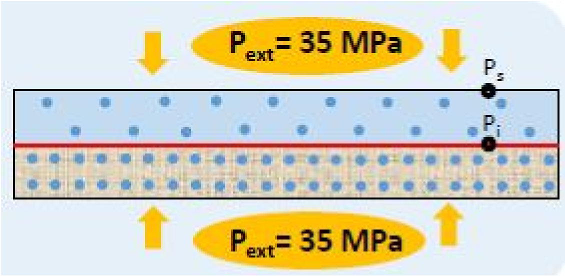
What happens to the sample



1.

Initial equilibrium

$\Delta P = P_i - P_s = 0$

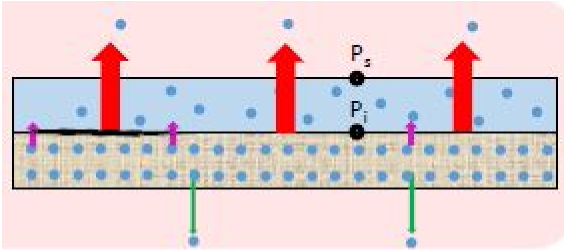


2.

Ext. pressure removed

Gas desorption

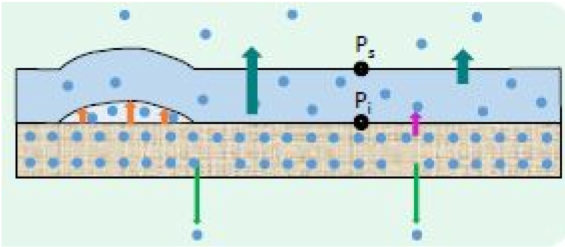
$0 \leq P_i - P_s \leq 350$bar



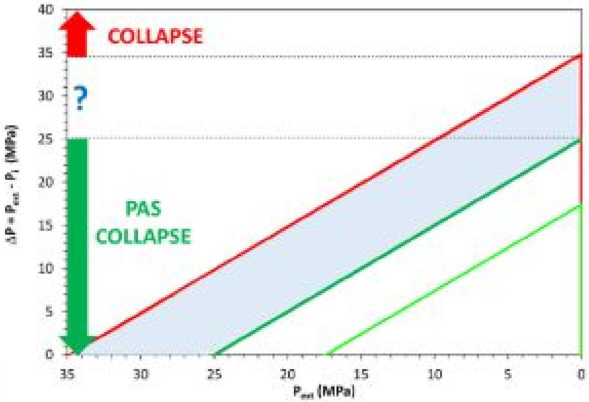
3.

Liner/comp. Interface pressure is max

$P_i - P_s = \Delta P_{max}$

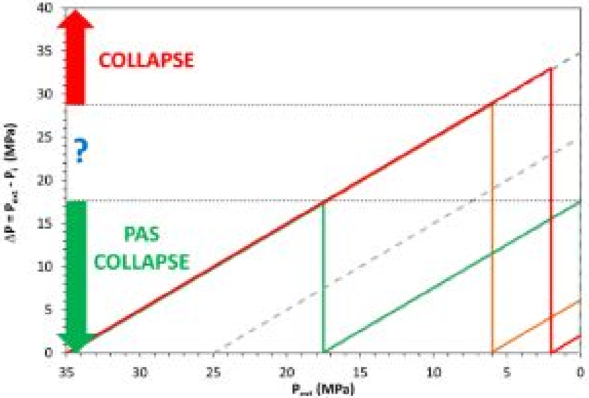


Influent parameters



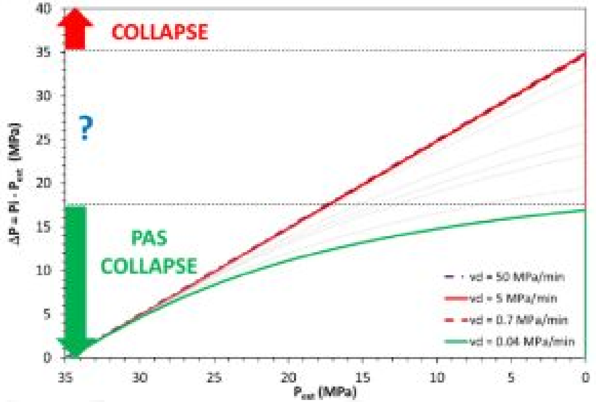
Pressure

Initial pressures:
- 350 bar (collapse)
- 250 bar (no collapse)
- 175 bar (no collapse)



2-steps decompression

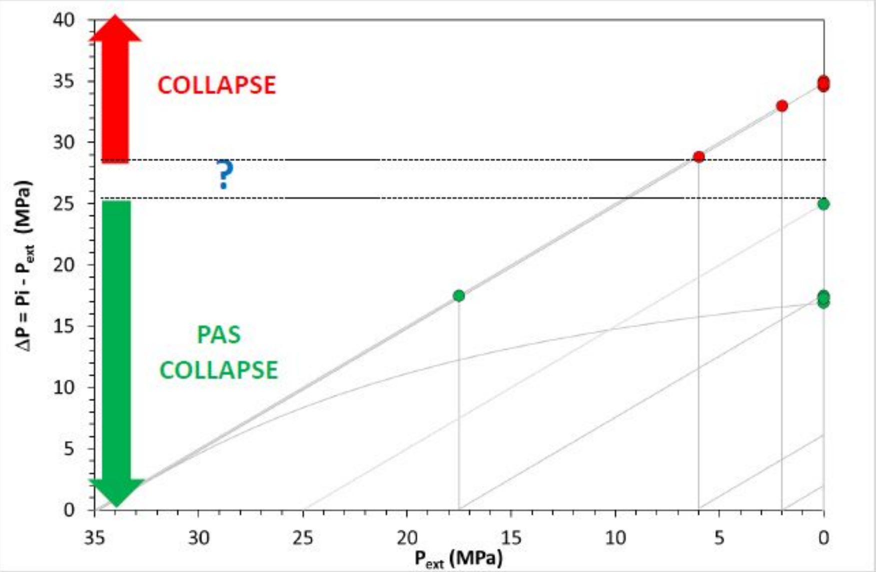
Residual pressure hold:
- at 20 bar (collapse)
- at 60 bar (collapse)
- at 175 bar (no coll.)



Low flow rate

Emptying flow rates:
- 7, 50, 500 bar/min (collapse)
- 0.7 bar/min (no coll.)

Conclusions



- The **most influent parameter** seems to be **ΔP_{max}** (the difference between pressure at liner/composite interface and pressure inside the liner)
  - ○ $\Delta P_{max} > (\Delta P)^{limit}$ => collapse
  - ○ $\Delta P_{max} < (\Delta P)^{limit}$ => no collapse

- For a given emptying case, ΔP_{max} can be calculated using **H_2 transport parameters** obtained from **permeation tests**

- An idea of $(\Delta P)^{limit}$ can be obtained using **decompression tests on liner/composite plates**
  - ○ A maximal flow rate can be calculated to remain in the “no collapse” zone

Open question: how to predict $(\Delta P)^{limit}$ for a **cylinder** ?

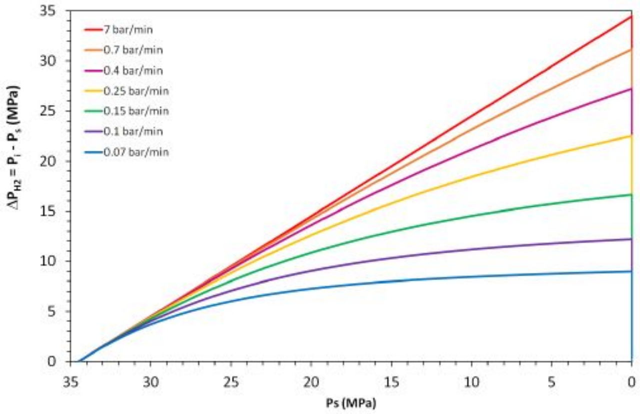
3

Tests on cylinders

(2.4 L, 700 bar H_2)

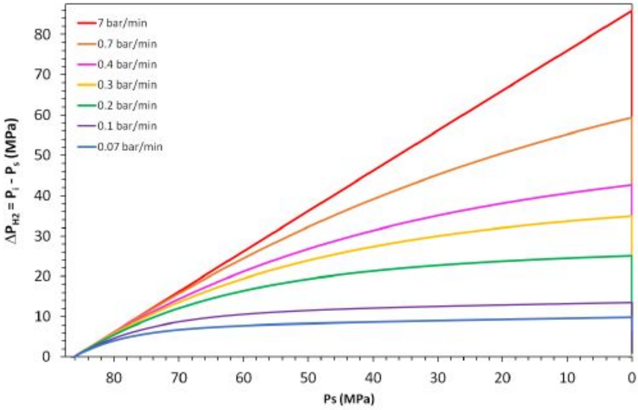
Estimation of ΔP_{max}

Initial pressure 35 MPa		Initial pressure 87.5 MPa	
Emptying rate	ΔP_{max}	Emptying rate	ΔP_{max}
0.007 MPa/min	9.0 MPa	0.007 MPa/min	10.0 MPa
0.01 MPa/min	12.4 MPa	0.01 MPa/min	12.7 MPa
0.015 MPa/min	16.5 MPa	0.02 MPa/min	24.8 MPa
0.025 MPa/min	22.5 MPa	0.03 MPa/min	34.6 MPa
0.04 MPa/min	27.1 MPa	0.04 MPa/min	42.4 MPa
0.07 MPa/min	31.1 MPa	0.07 MPa/min	59.4 MPa
0.7 MPa/min	34.2 MPa	0.7 MPa/min	85.9 MPa



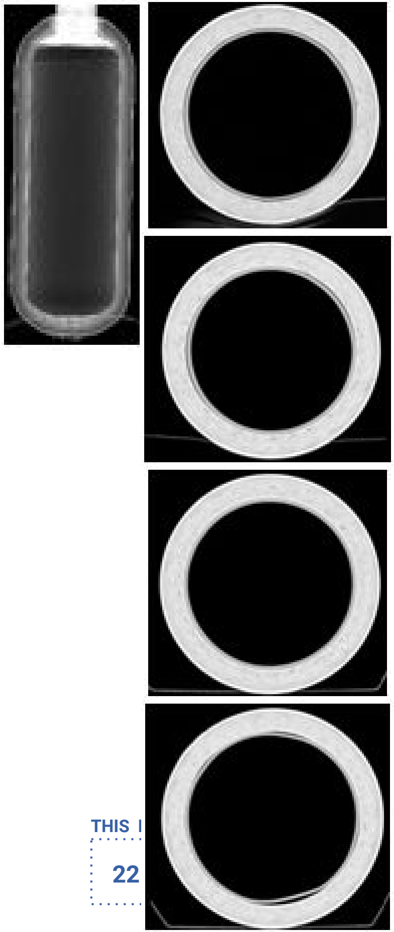
Gas diffusion calculations using parameters from permeation tests

/!\ in this calculation, S and D are <u>independent of P and T</u> *(not true!)* => the error induced has not been estimated (could be important)



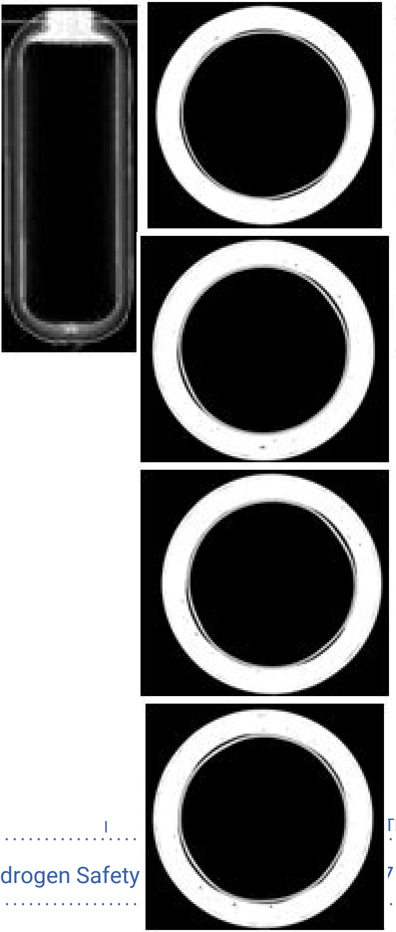
700bar - 0.1bar/min

ΔP_{max} **200 bar**



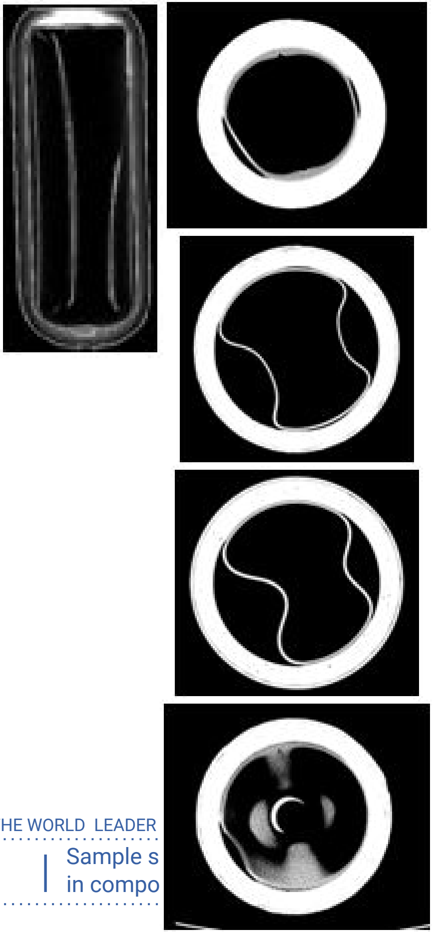
700bar - 0.7bar/min

ΔP_{max} **500 bar**

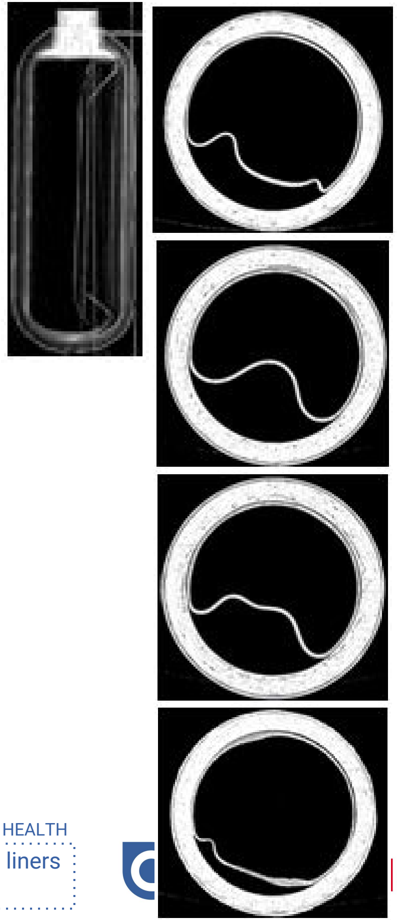


700bar - 7bar/min

ΔP_{max} **680 bar**



700bar - 7bar/min - Defueling paused at 20 bar for 72 hours - ΔP_{max} **650 bar**



Conclusions

- The value of $(\Delta P)^{limit}$ obtained on plate samples (250-300bar) seems conservative compared to the value on cylinders (300-500bar)
- Once $(\Delta P)^{limit}$ is known, a maximal flow rate can be calculated

=> Permeation and decompression tests could provide a method for preventing the formation of liner collapse by adapting operational flow rates

- The effect of pressure and temperature on transport coefficients (S and D) should be assessed to refine the calculation of ΔP through emptying
- Cases where liner is not glued to the composite (typically HDPE liners) should be investigated - *$(\Delta P)^{limit}$ may be easier to calculate in such case*

Thank you for your attention.