Sample scale testing method to prevent collapse of plastic liners in composite pressure vessels
Composite pressure vessels
@Air Liquide
Structure of the AL Group

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.

- ASU: Air Separation Unit
- SMR: Hydrogen and carbon monoxide production unit (Steam Methane Reformer)
- On-site: Small local production unit

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AL in the hydrogen value chain

Distribution

Transport

Storage

Production

Applications & Customers

Sample scale testing method to prevent collapse of plastic liners in composite pressure vessels
Composite cylinders for AL supply chain operations

AL in the hydrogen value chain

- Distribution
- Transport
- Storage
- Production

Composite cylinders as customer’s storage to be filled

Applications & Customers

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

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

**Full scale H2 cycling tests = huge costs & duration!**
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...

Solubility $S$  
$mol/(m^3.Pa)$  
Capacity of the material to accept solved gas

Diffusivity $D$  
$m^2/s$  
Capacity of the material to let the gas flow through

Permeability $P_e$  
$mol/(Pa.m.s)$

For a given pressure and temperature condition

700 bar hydrogen permeation test bench
...to allow calculating the pressure at liner-composite interface

Henry’s law to link pressure and concentration:
\[ C_{H2} = S \times P \]

Fick’s law for diffusion:
\[ \frac{\partial C}{\partial t} = D \times \frac{\partial^2 C}{\partial x^2} \]

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

1 h after test – max gap 2.4 mm

1 month after test – max gap 1.86 mm

**No collapse**

Pmax 350bar

Pmax 175bar
What happens to the sample

1. Initial equilibrium

\[ \Delta P = P_i - P_s = 0 \]

\[ \Delta P = P_t - P_i \]

Juste avant l'étape de décompression

\[ P_{ext} = 35 \text{ MPa} \]
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
   \[ 0 \leq P_i - P_s \leq 350 \text{bar} \]

3. Liner/comp. Interface pressure is max
   \[ P_i - P_s = \Delta P_{\text{max}} \]
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 influential parameter** seems to be $\Delta P_{\text{max}}$ (the difference between pressure at liner/composite interface and pressure inside the liner)
  - $\Delta P_{\text{max}} > (\Delta P)^{\text{limit}}$ => collapse
  - $\Delta P_{\text{max}} < (\Delta P)^{\text{limit}}$ => no collapse

- For a given emptying case, $\Delta P_{\text{max}}$ can be calculated using $H_2$ transport parameters obtained from permeation tests

- An idea of $(\Delta P)^{\text{limit}}$ 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 $(\Delta P)^{\text{limit}}$ for a cylinder?
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Tests on cylinders
(2.4 L, 700 bar $H_2$)
Estimation of $\Delta P_{\text{max}}$

<table>
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<th>Emptying rate (MPa/min)</th>
<th>$\Delta P_{\text{max}}$ (MPa)</th>
<th>Emptying rate (MPa/min)</th>
<th>$\Delta P_{\text{max}}$ (MPa)</th>
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Gas diffusion calculations using parameters from permeation tests

$\Delta P_{\text{max}}$ in this calculation, S and D are independent of P and T \textit{(not true!)}

=> the error induced has not been estimated (could be important)
Sample scale testing method to prevent collapse of plastic liners in composite pressure vessels.

- 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 \((\Delta P)_{\text{limit}}\) obtained on plate samples (250-300bar) seems conservative compared to the value on cylinders (300-500bar)

- Once \((\Delta P)_{\text{limit}}\) 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 \(\Delta P\) through emptying

- Cases where liner is not glued to the composite (typically HDPE liners) should be investigated - \((\Delta P)_{\text{limit}}\) may be easier to calculate in such case
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