INTERNATIONAL CONFERENCE ON HYDROGEN SAFETY ICHS 2013

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Hydrogen storage – Recent Improvements and Industrial Prospectives

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Hydrogen at Air Liquide

Air Liquide is present worldwide on all segments of the Hydrogen Energy supply chain

H_2 Production → Large Distribution → Secondary Distribution → Markets

Safety/Standards/Regulations

SMR, Electrolysis purification, liquefaction

> 200 plants

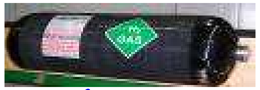
Trucks, trailors

> 1000 trucks

Pipelines

> 1700 km

Refuelling stations



Innovative gas storage & Packaging

Cryogenic tank

Hundred of thousands of 200 bar cylinders

Space propulsion

CRYOSPACE

PEM Fuel Cells

axane

CASE STUDIES AND APPLICATIONS: HYDROGEN STORAGE AND INDUSTRIAL PROSPECTIVE

AIR LIQUIDE

I. COMPRESSED HYDROGEN STORAGE

II. CRYOGENIC VESSELS FOR THE STORAGE OF LIQUID HYDROGEN

I. COMPRESSED HYDROGEN STORAGE

1. INTRODUCTION AND DIFFERENT TYPES
2. SOME HISTORY
3. DESIGN AND MANUFACTURING
4. SUITABLE MATERIALS FOR PRESSURE VESSELS
5. NEW TRENDS DUE TO HYDROGEN ENERGY
6. CONCLUSION

1. INTRODUCTION AND DIFFERENT TYPES OF PRESSURE VESSELS

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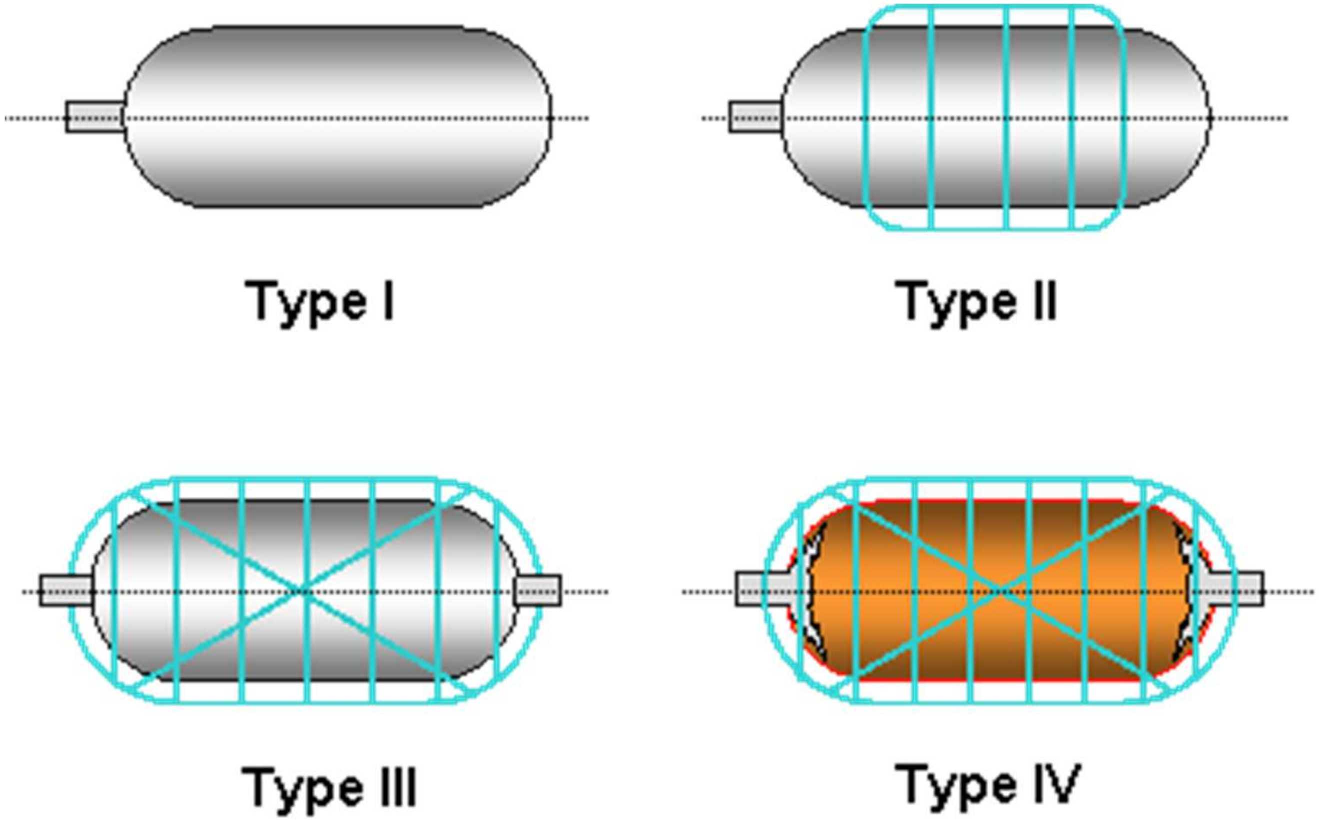
Type I : pressure vessel made of metal

Type II : pressure vessel made of a thick metallic liner hoop wrapped with a fiber resin composite

Type III : pressure vessel made of a metallic liner fully-wrapped with a fiber-resin composite

Type IV : pressure vessel made of polymeric liner fully-wrapped with a fiber-resin composite

1. INTRODUCTION AND DIFFERENT TYPES OF PRESSURE VESSELS



4 pressure vessels types

1. INTRODUCTION AND DIFFERENT TYPES OF PRESSURE VESSELS

Type I cylinder

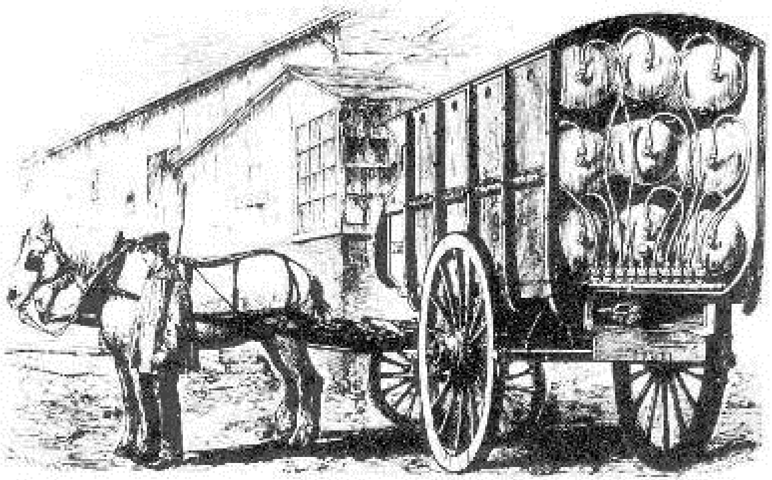
Type II vessel

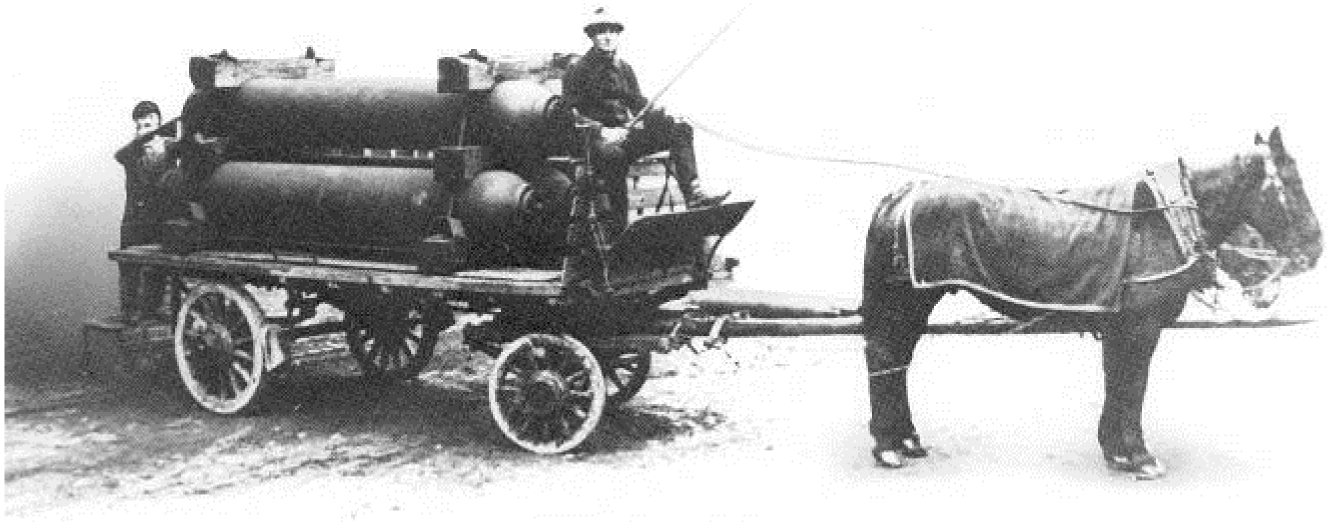
Type III or IV vessel

Toroid composite vessel

Different types of pressure vessels

2. SOME HISTORY





Gas transport - 1857

2. SOME HISTORY

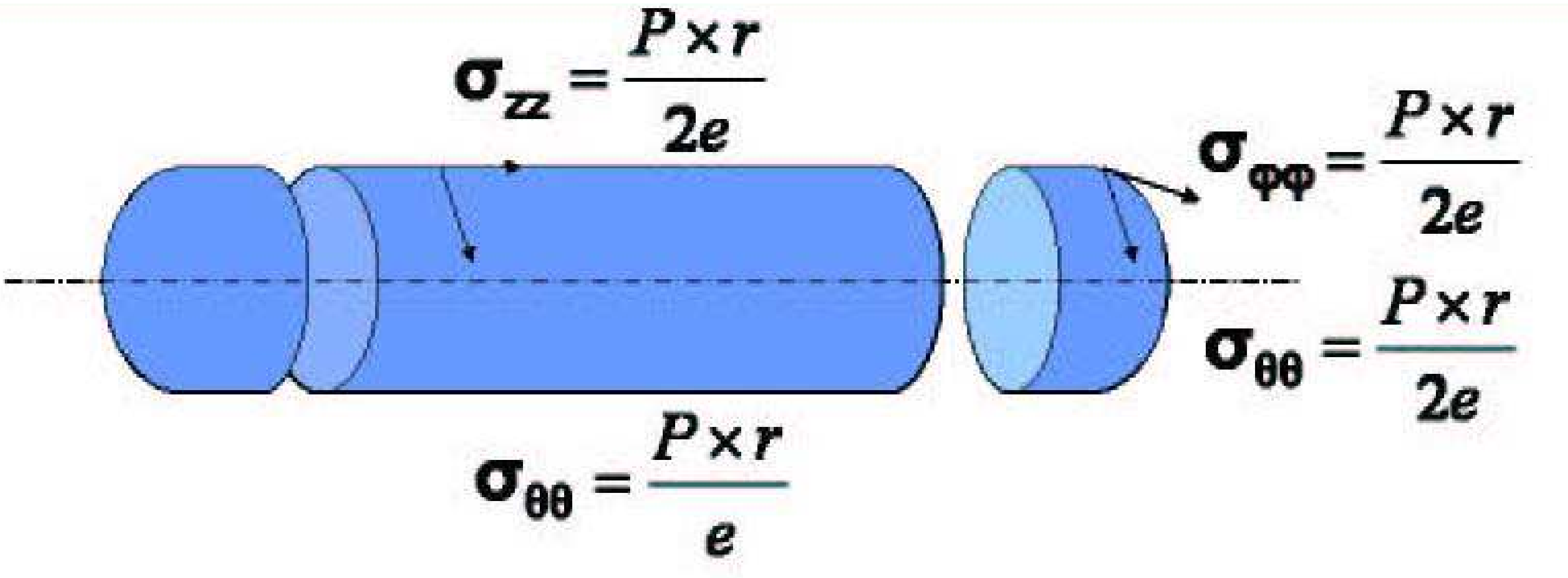
2. SOME HISTORY

AIR LIQUIDE

- **The experimentation of composite vessels started in the 50s**

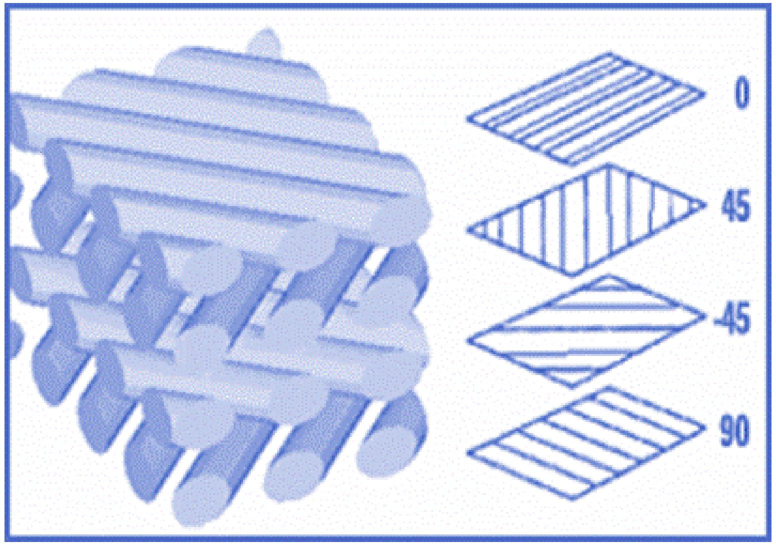
- **Composite vessels were introduced for space and military applications**

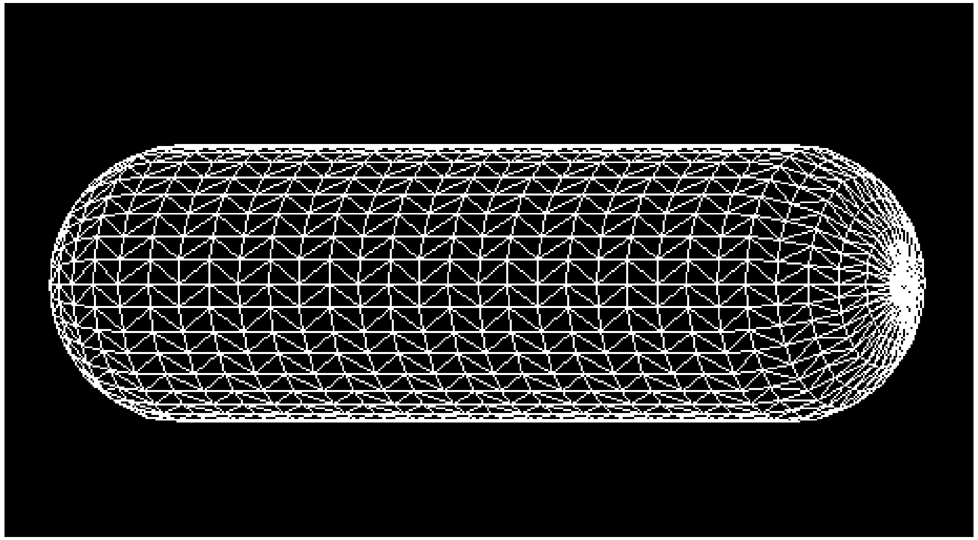
- **Metallic vessels and composite vessels are very different :**
  - **The metal is isotropic, the composite is anisotropic**
  - **The failure modes are different**
  - **The ageing is different**



Main strains considered for the metallic pressure vessels design (type I and metallic liner)

3. DESIGN AND MANUFACTURING



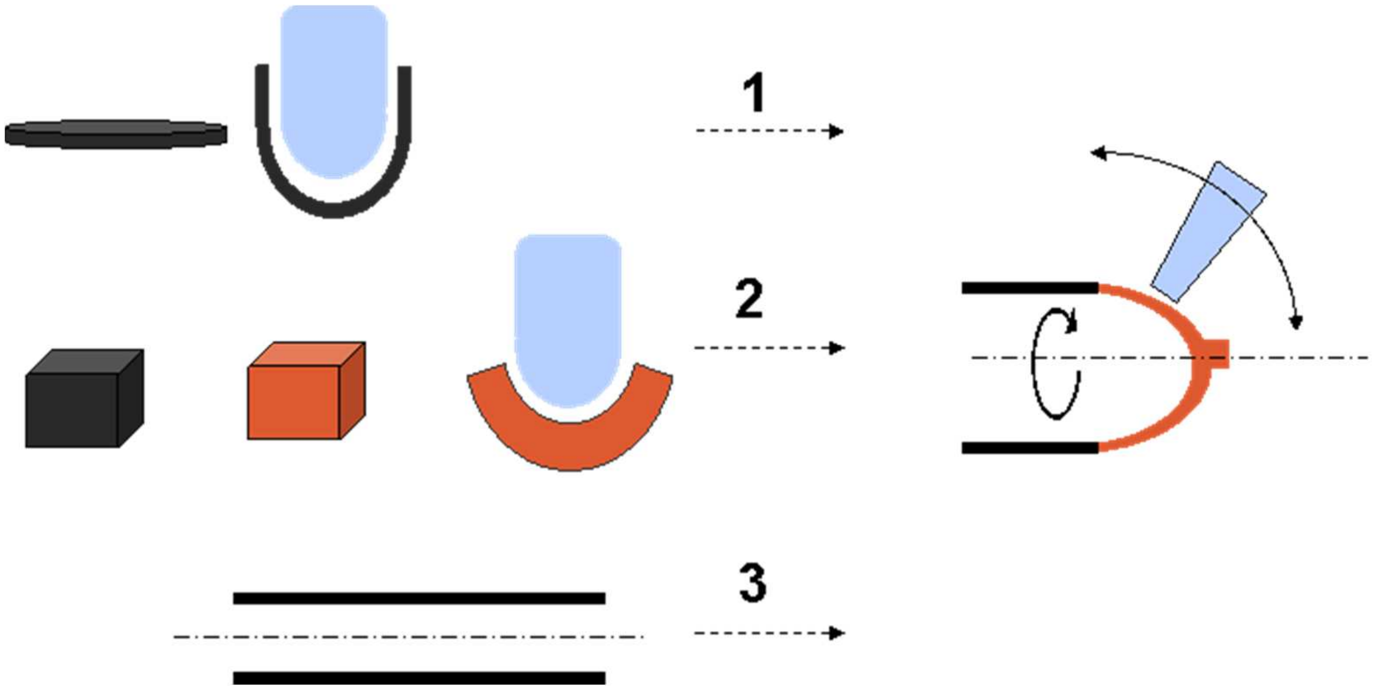


Multi-layered element and vessel meshes example

- **Type I :**

3 different manufacturing processes

- **From plates**
- **From billets**
- **From tubes**

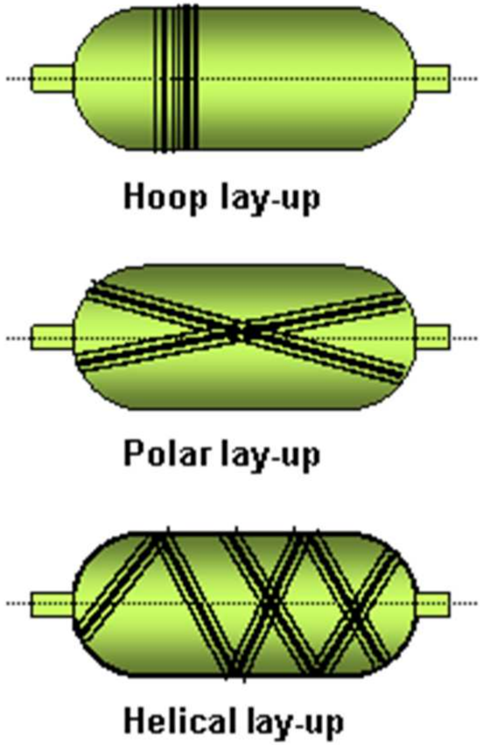


Principle of metallic tank manufacturing processes (1 : from plates / 2 : from billets / 3 : from tubes

Polymers liners :

- From the polymer or the monomers by the rotomolding process
- From tubes : polymeric tubes (made by extrusion blow moding)

3. DESIGN AND MANUFACTURING



Winding machine and the 3 winding possibilities

4. SUITABLE STEELS FOR HYDROGEN HIGH PRESSURE VESSELS

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- **Risk of hydrogen embrittlement :**
  - **Environment**
  - **Material**
  - **Design and surface conditions**

4. COMPOSITE CYLINDERS – SUITABLE MATERIALS

AIR LIQUIDE

- **Permeation rate through the polymeric liner :**

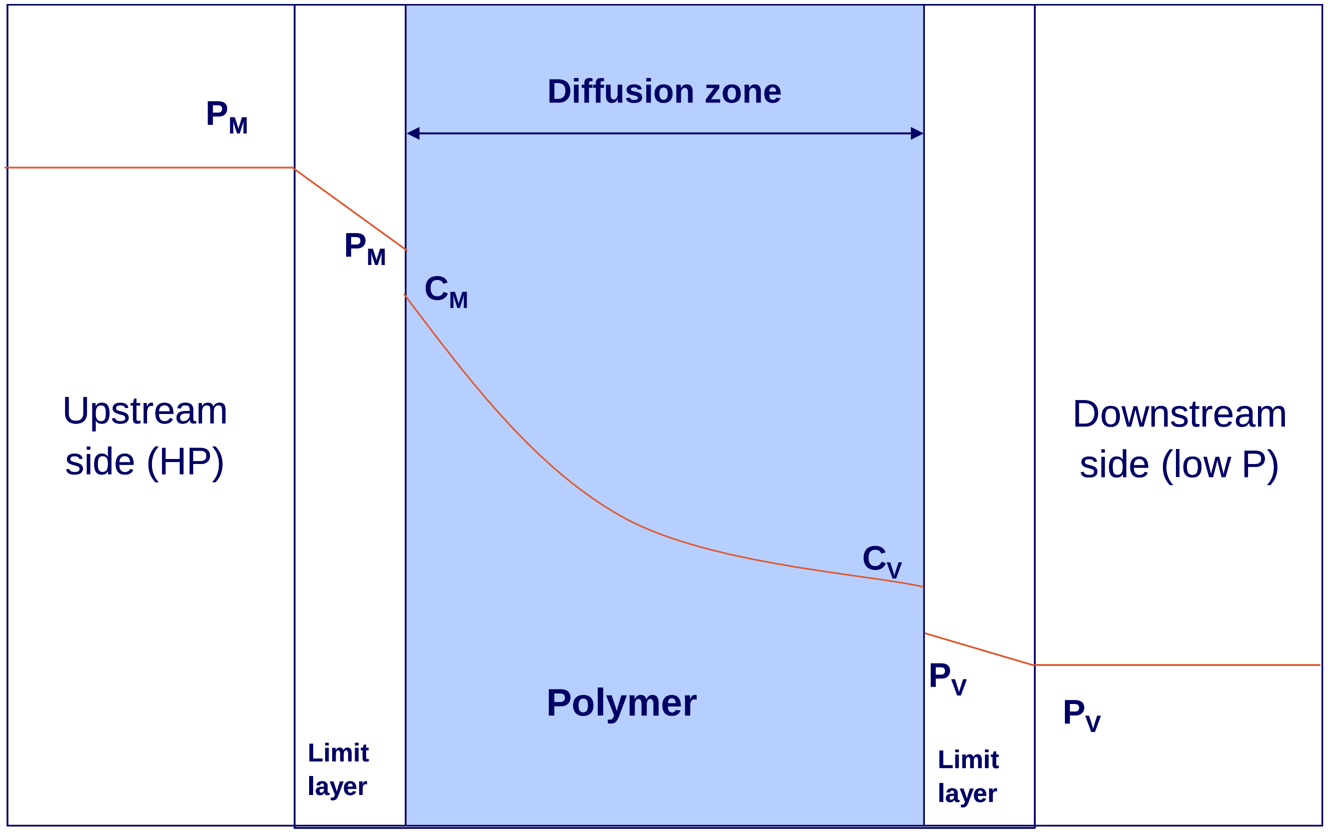
  - ✓ **Permeation is specific of type IV vessels. It is the result of the H_2 gas dissolution and diffusion in the polymer matrix**

  - ✓ **H_2 is a small molecule, and thus the permeation is enhanced. This leads to the development of special polymers**

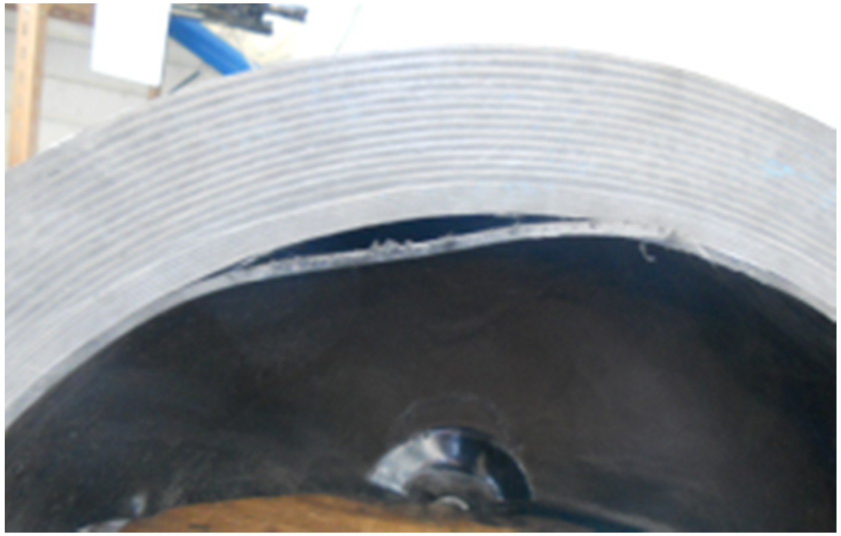
  - ✓ **Polyethylene and polyamide are the most used liners for type IV tanks**

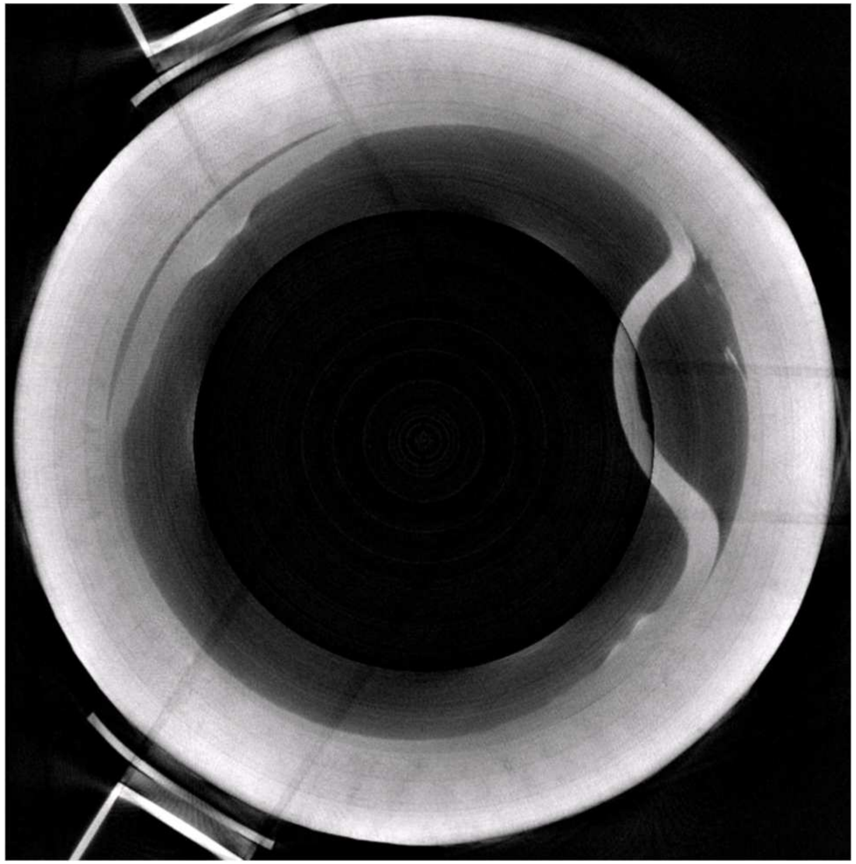
  - ✓ **One phenomena to avoid is the blistering of liner collaps**

4. SUITABLE PLASTIC MATERIALS FOR HYDROGEN HIGH PRESSURE VESSELS



4. SUITABLE PLASTIC MATERIALS FOR HYDROGEN HIGH PRESSURE VESSELS

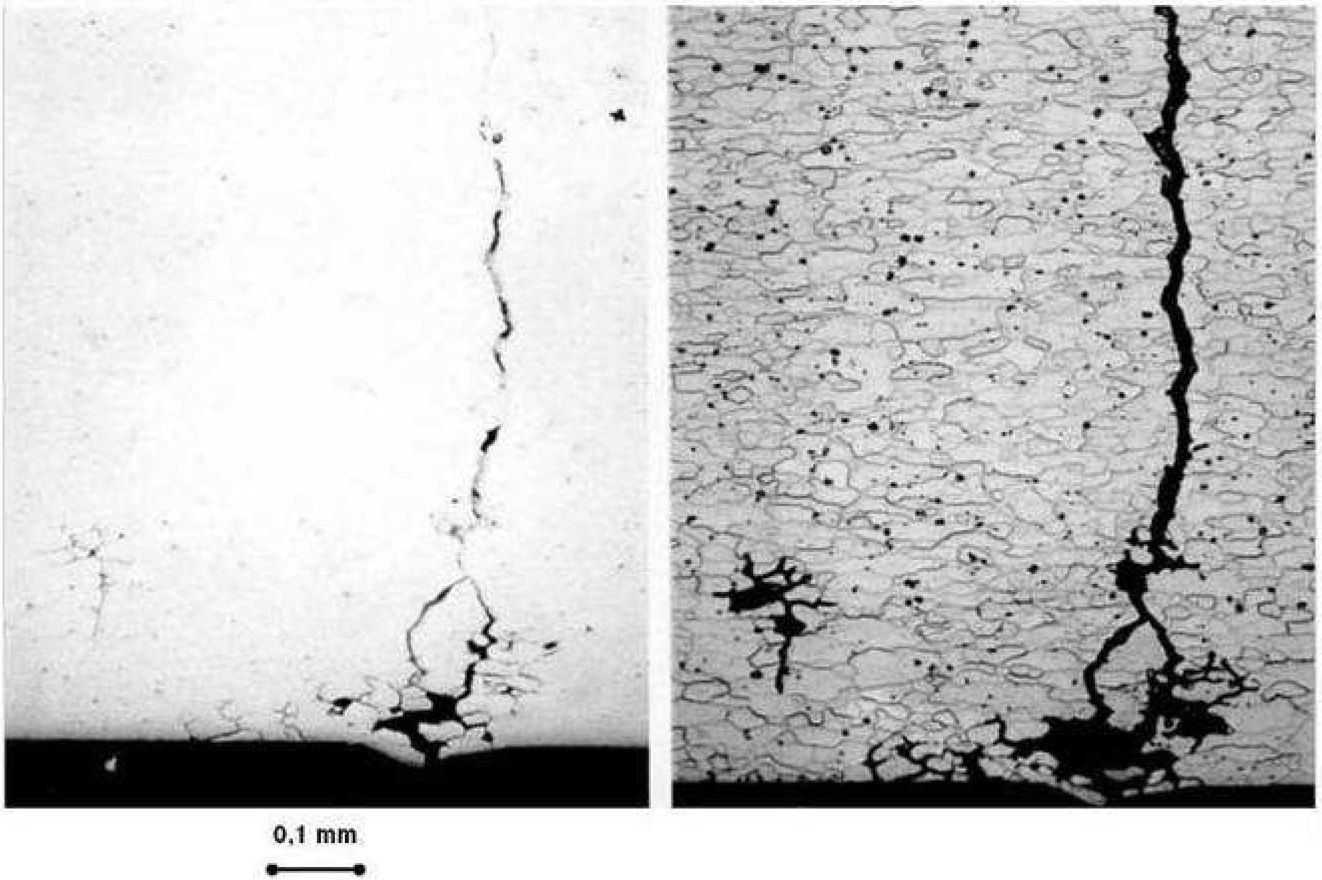




4. SUITABLE MATERIALS FOR ALUMINIUM ALLOY

- **Specific issues:**
  - ✓ **Presence of mercury into H_2**
  - ✓ **Influence of tap water which reduces significantly the pressure cycling life**

4. SUITABLE PLASTIC MATERIALS FOR HYDROGEN HIGH PRESSURE VESSELS



Without attack Internal surface Keller attack

4. COMPOSITE CYLINDERS – SUITABLE MATERIALS

Fiber category	Tensile modulus (GPa)	Tensile strength (MPa)	Elongation (%)
Glass	~ 70 - 90	~ 3300 - 4800	~ 5
Amarid	~ 40 - 200	~ 3500	~ 1 - 9
Carbon	~ 230 - 600	~ 3500 - 6500	~ 0,7 – 2,2

Range of fiber mechanical properties

4. MATERIALS SUITABLE FOR HYDROGEN HIGH PRESSURE VESSELS

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Hydrogen requires special attention for the choice of :

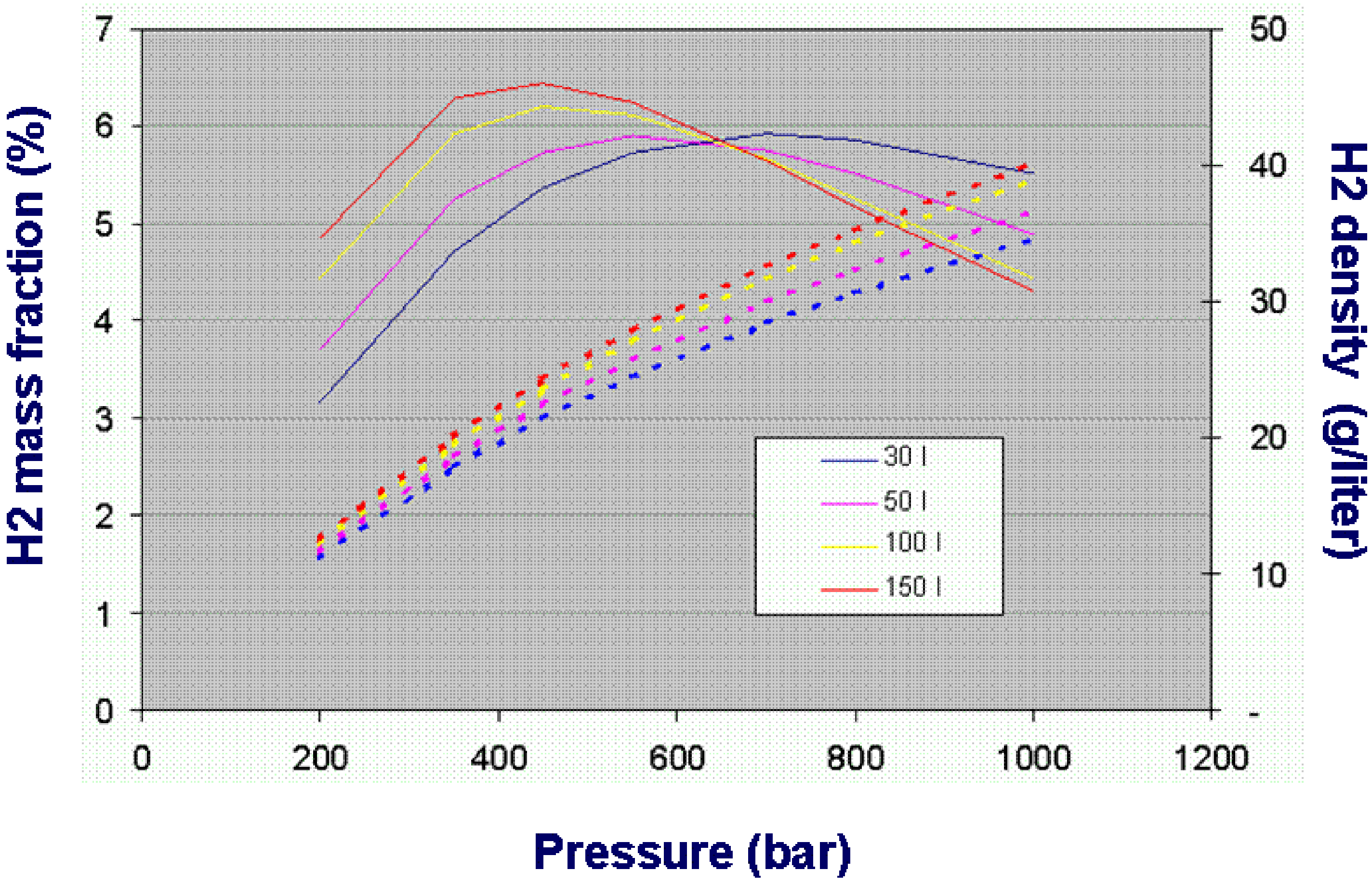
- **the steel (types I, II and III tanks)**
- **the polymer (type IV tanks)**

Material test generally requested to check "H_2 embrittlement"

For type IV, permeation measurement is required (e.g. specified rate < 1 cm^3/l/h).

5. TYPES I AND II CYLINDERS FOR STATIONARY APPLICATIONS

5. TECHNICAL PERFORMANCES OF COMPOSITE CYLINDERS



Cm : weight performance : mass of H_2 stored divided by the mass of the vessel (% wt)
Cv : volume performance : mass of H_2 stored divided by the external volume of the vessel (g/l)

Cm and Cv as a function of the pressure (types III and IV)

6. COMPRESSED GAS STORAGE - CONCLUSION

	Technology mature	Cost performance	Weight performance
Type I	++ *Pressure limited to 500 bar (⇒ density : –)*	++	–
Type II	+ *Pressure not limited (⇒ density : +)*	+	0
Type III	For P ≤ 350 bar; *(difficulty to pass pressure cycling requirement for 700)*	–	+
Type IV	For P ≤ 350 bar; *(700 bar under development)*	–	+

Main features for H_2 pressure vessel types in 2006

II. CRYOGENIC VESSELS FOR THE STORAGE OF LIQUID HYDROGEN

AIR LIQUIDE

1. INTRODUCTION (COMPARISON OF EFFICIENCY/GROWS STORAGE)
2. DIFFERENT TYPES OF CRYOGENIC VESSELS
3. REDUCING THE WALL THICKNESS OF THE VESSELS
4. TRANSPORT OF LIQUID HYDROGEN
5. MATERIAL ISSUES

1. INTRODUCTION – EFFICIENCY & STORAGE CAPACITY

AIR LIQUIDE

Cryogenic vessels have been commonly used for 40+ years to store and transport industrial and medical gases

- **Advantage of storing in cryogenic vessels**
  - ✓ **1 liter of liquide ≃ 800 liters of gas stored**

- **Advantage of transporting in cryogenic vessels vs. in compressed form**
  - ✓ **More gas stored per volume unit**
    Compressed form: 200-300 bar (less gas per volume unit)
  - ✓ **Cylinders storing gas can be lighter (thinner walls)**
    Compressed form: Heavy vessels (thick walls) to resist high pressure

1. INTRODUCTION – EFFICIENCY & STORAGE CAPACITY

AIR LIQUIDE

Cryogenic vessels have been commonly used for 40+ years to store and transport industrial and medical gases

- **Disadvantages of cryogenic vessels:**
  - ✓ **Gases (especially H_2) must be refrigerated down to very low temperatures to be in liquid form**

    See gas/liquid temperature equilibrium for different gases at atmospheric pressure on slide 32)

  - ✓ **At such low temperatures, gases must be stored in high efficiency (vacuum) insulated vessels**

1. INTRODUCTION (COMPARISON OF EFFICIENCY/GROWS STORAGE)

BOILING TEMPERATURES (°C) AT ATMOSPHERIC PRESSURE OF DIFFERENT GASES

Gases	Kr	O_2	Ar	Air	N_2	Ne	H_2	He
Boiling Temperature	- 153	- 183	- 186	- 191	- 196	- 246	- 253	- 269

2. DIFFERENT TYPES OF CRYOGENIC VESSELS

AIR LIQUIDE

Cryogenic vessels used for gases requiring low temperature for liquefaction are normally:

- **Vacuum-insulated**

  and
- **Composed of an inner pressure vessel and an external protective jacket**

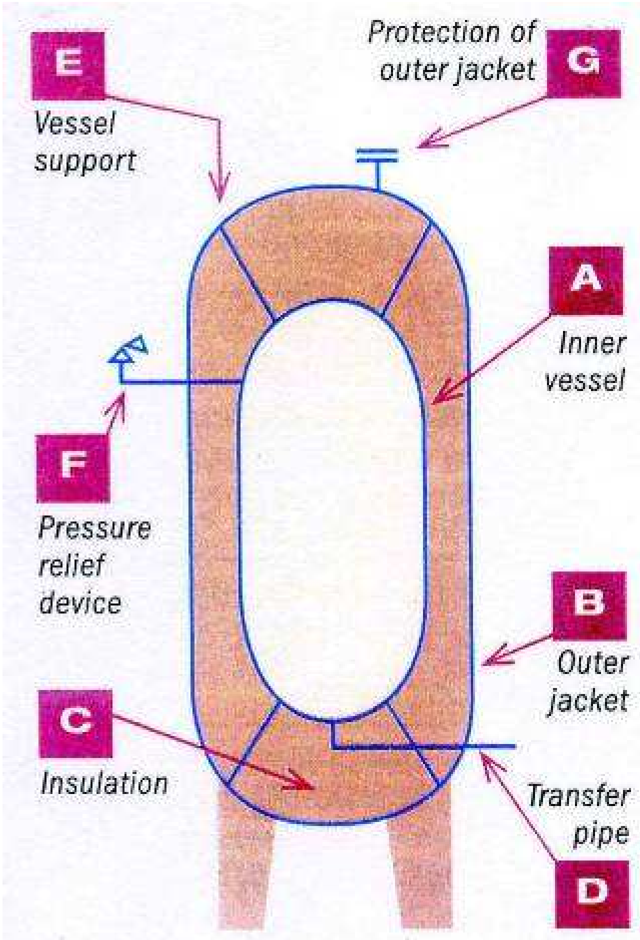
Thermal conductivity of the space between the inner vessel and the outer jacket is reduced by using either:

- **Perlite (powder structure)**

  or
- **Super insulation (wrapping with layers of aluminum film)**

2. DIFFERENT TYPES OF CRYOGENIC VESSELS

SCHEMATIC SHOWING THE MAIN COMPONENTS OF A CRYOGENIC VESSEL



2. DIFFERENT TYPES OF CRYOGENIC VESSELS

- CO_2 and N_2O (and other gases with relatively high liquefaction temperature)

  ✓ Non-vacuum insulated vessels are used
  ✓ Vessel insulation is normally a thick layer of polyurethane

- Gas storage

  Cryogenic vessels are used to store gases at production sites and end-user sites.

2. DIFFERENT TYPES OF CRYOGENIC VESSELS

- **Large transportable cryogenic vessels are used to fill and/or transport gases**

  ✓**Cryogenic trailers: Refilling stationary vessels at end-user sites.**

  ✓**Large containers: Road, railroad and sea transportation**

2. DIFFERENT TYPES OF CRYOGENIC VESSELS

AIR LIQUIDE

- **Small cryogenic vessels (< 1 000 liters water capacity) are filled and transported by suppliers of industrial or medical gas to end-users**

- **A large number of cryogenic vessels are in use worldwide**

2. CRYOGENIC VESSELS USED FOR STORAGE OF LIQUID HYDROGEN

2. DIFFERENT TYPES OF CRYOGENIC VESSELS

2. DIFFERENT TYPES OF CRYOGENIC VESSELS

NUMBER OF DIFFERENT TYPES OF VESSELS BEING USE IN THE WORLD

Type of vessels	Units					
	Vacuum insulated			Non vacuum insulated		
	Australia	Europe	USA	Australia	Europe	USA
Static vessels	2 000	40 000	50 000	200	20 000	20 000
Small transportable vessels (no more than 1000 L)	3 000	100 000	250 000	-	-	-
Large transportable vessels	200	5 000	5 000	40	1 000	1 000

3. REDUCING VESSEL WALL THICKNESS

- **Modern methods based on cold stretching (use of cold properties) are widely used in Europe but are still not fully accepted in North America and Japan.**
- **These methods considerably reduce vessel wall thickness in stationary cryogenic vessels.**
- **Design and manufacturing improvements limit the quantity of expensive materials (e.g. stainless steel) used and thus reduce vessel price.**

3. REDUCING THE WALL THICKNESS OF THE VESSELS

- **The principle and detail information on the cold stretching method is given in paper "An overview of RCS for hydrogen pressure vessels"**

- **All efforts were made to produce efficient ISO standards for stationary cryogenic vessels in an expedient manner. ISO 21009-2, Cryogenic vessels – Static vacuum insulated vessels – Part 2: Operational requirements, is already available, while ISO 2 1009-1, Cryogenic vessels – Static vacuum-insulated vessels completed and waiting to be issued in the coming months**

4. TRANSPORT OF LIQUID HYDROGEN

AIR LIQUIDE

- In order to reduce the volume required to store a useful amount of hydrogen - particularly for vehicles - liquefaction may be employed. Since hydrogen does not liquefy until it reaches - 253° C (20 degrees above absolute zero), the process is both time consuming and energy intensive demanding. Up to 40 % of the energy content in the hydrogen can be lost (in comparison with 10 % energy loss with compressed hydrogen).

4. TRANSPORT OF LIQUID HYDROGEN

AIR LIQUIDE

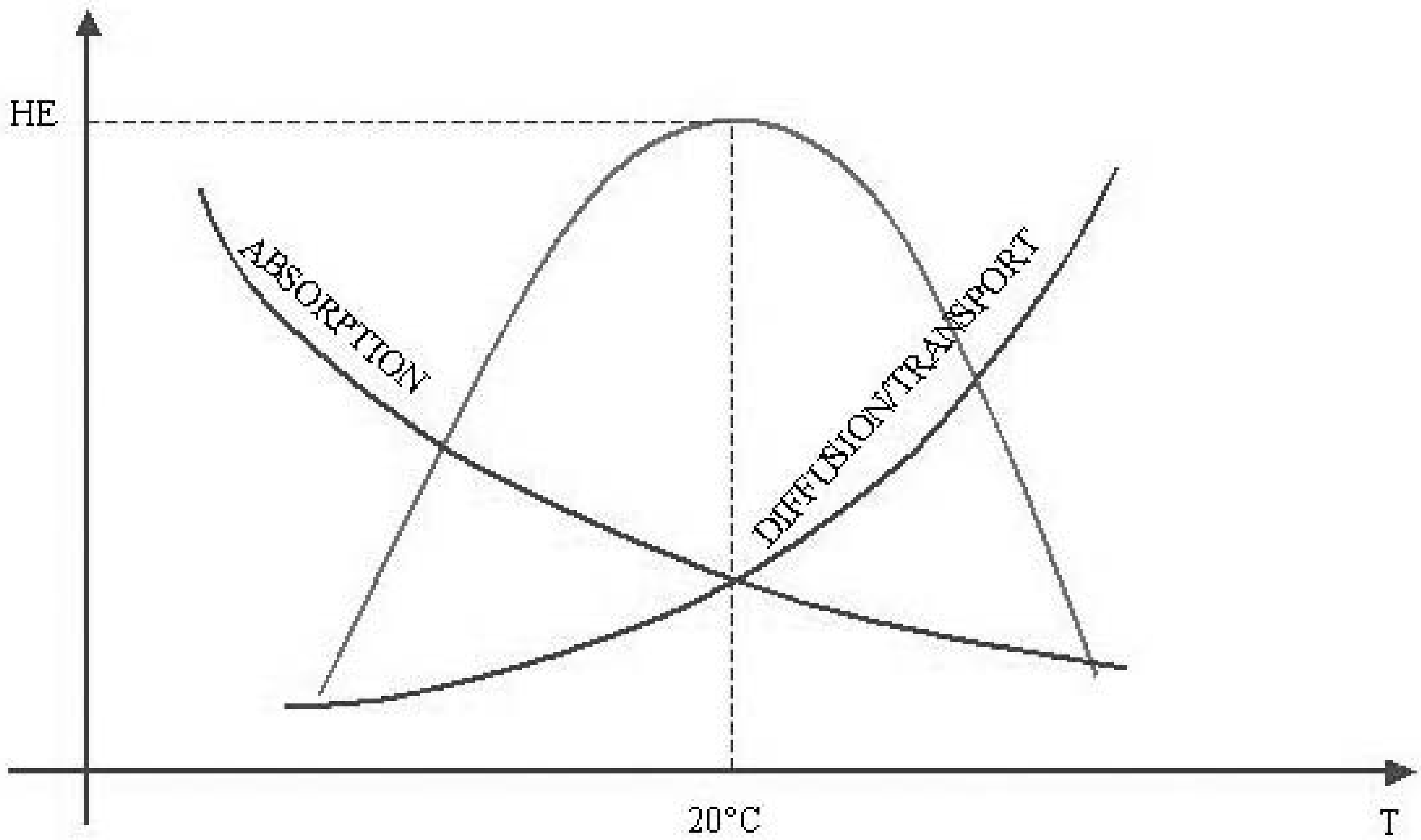
H2, the most energy-dense fuel in use* is employed in all space programs

- Advantages of H_2
  - ✓ High energy/mass ratio (3x more than gasoline)
- Disadvantages of H_2
  - ✓ Low energy/volume ratio
  - ✓ Liquid H_2
    - Difficult to store over a long period (product loss by vaporization)
    - Insulated tank required may be large and bulky

* (excluding nuclear reaction fuels)

5. MATERIAL ISSUES – HYDROGEN EMBRITTLEMENT

- **At room temperature,**



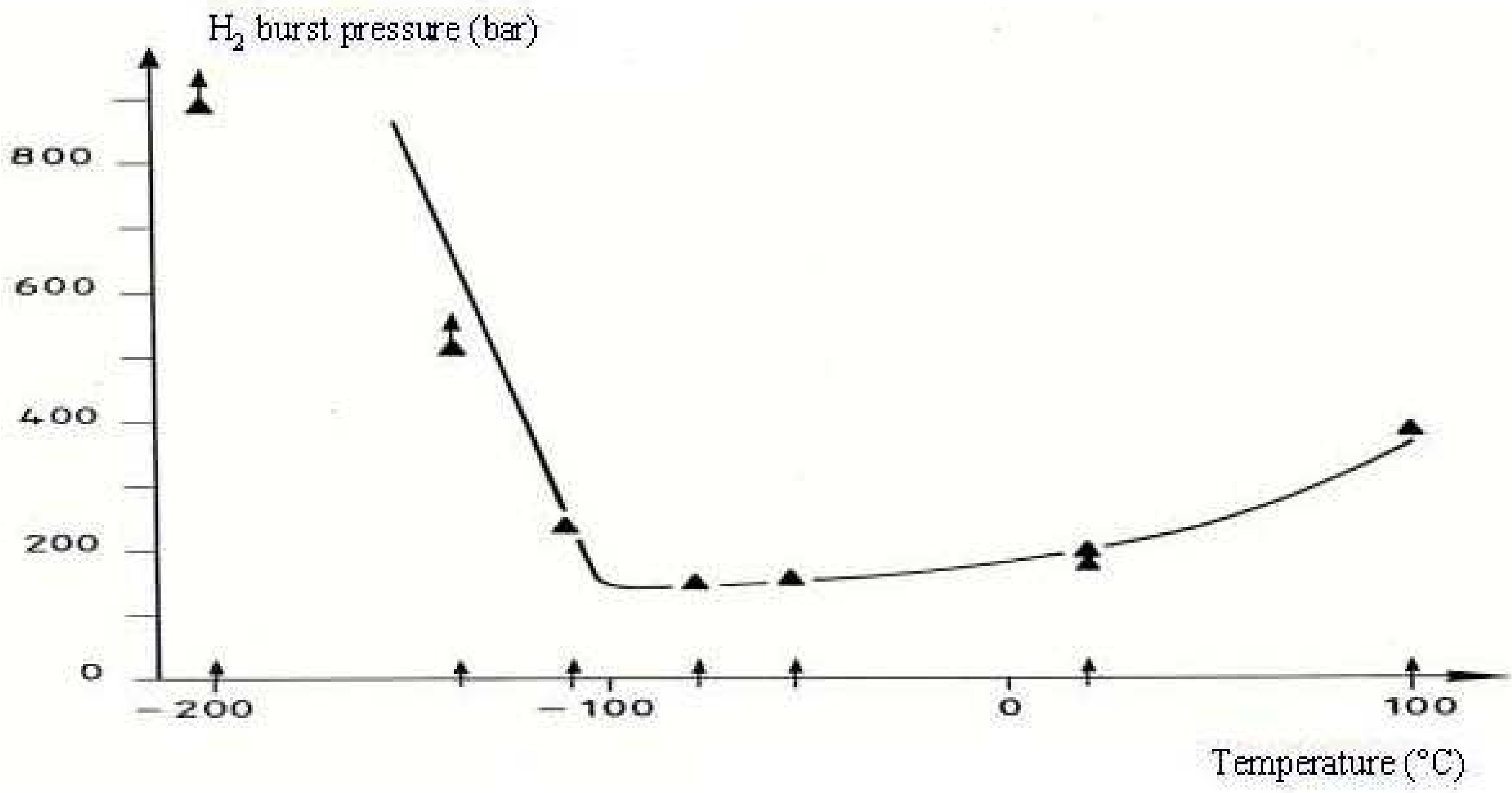
INFLUENCE OF TEMPERATURE - PRINCIPLE

5. MATERIAL ISSUES – HYDROGEN EMBRITTLEMENT

- HE effect normally occurs at ambient temperatures and is often negligible for temperatures above +100°C.

- Unstable austenitic stainless steels (commonly used for cryogenic vessels)
  Maximum HE effect occurs at - 100°C, but is negligible for temperatures below - 150°C

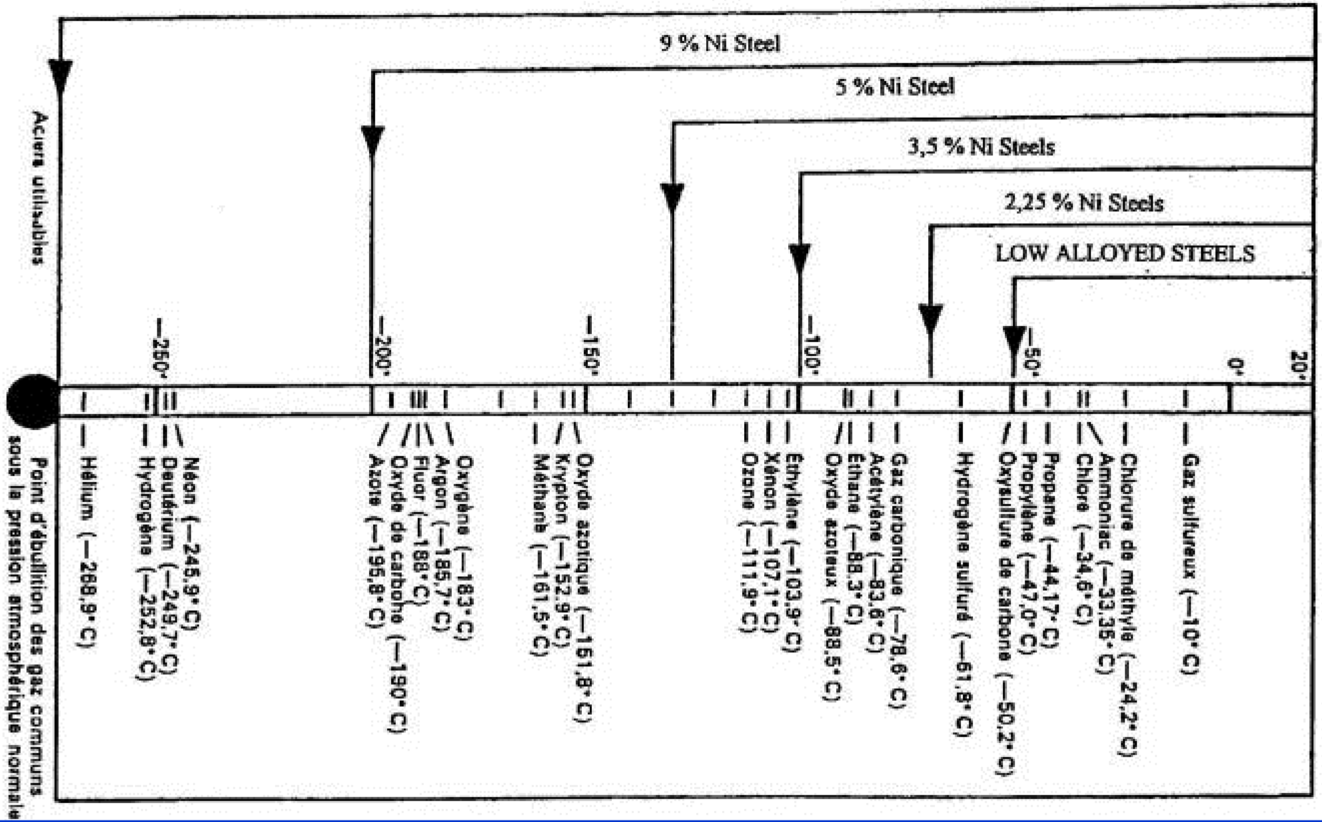
5. MATERIAL ISSUES – HYDROGEN EMBRITTLEMENT



INFLUENCE OF TEMPERATURE FOR SOME STAINLESS STEELS

5. MATERIAL ISSUES – COMPATIBILITY OF METALS AND ALLOYS WITH LOW TEMPERATURE

- **Main materials employed:**



POSSIBILITY OF USING STEEL FOR THE DIFFERENT CRYOGENIC GASES

5. MATERIAL ISSUES – COMPATIBILITY OF METALS AND ALLOYS WITH LOW TEMPERATURE

AIR LIQUIDE

- **Use of metal at low temperatures entails special problems which must be resolved, in particular:**

  ✓ **Changes in mechanical characteristics,**
  ✓ **Expansion and contraction phenomena**
  ✓ **Thermal conduction of materials**

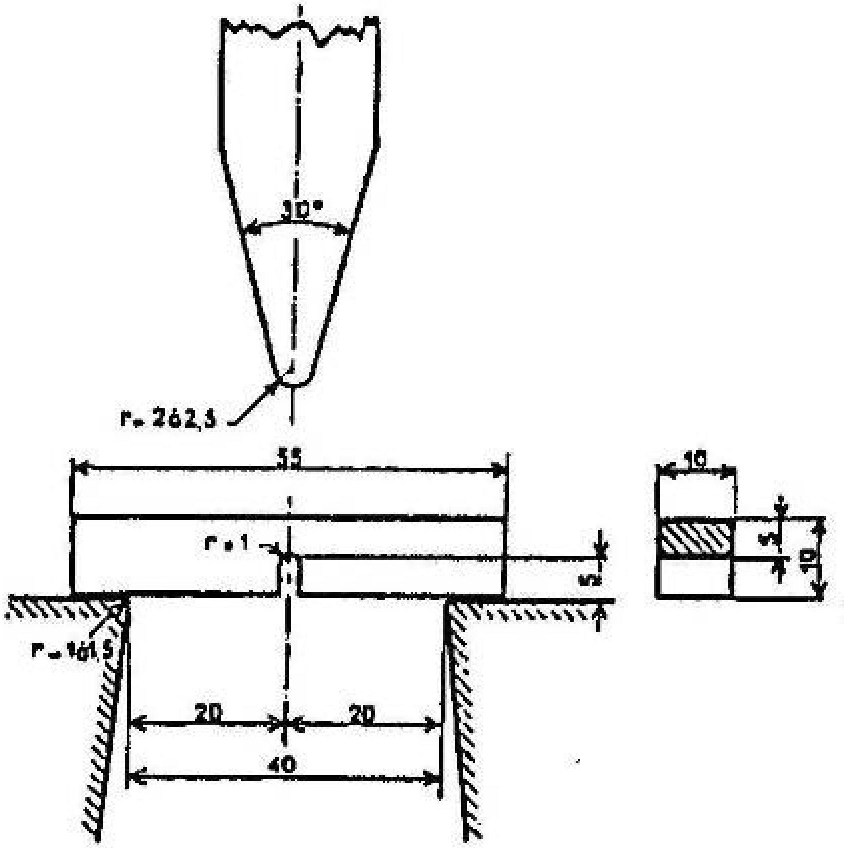
- **Brittleness – The most critical problem**
  It can effect certain metallic equipment used at cryogenic temperatures

5. MATERIAL ISSUES – COMPATIBILITY OF METALS AND ALLOYS WITH LOW TEMPERATURE

AIR LIQUIDE

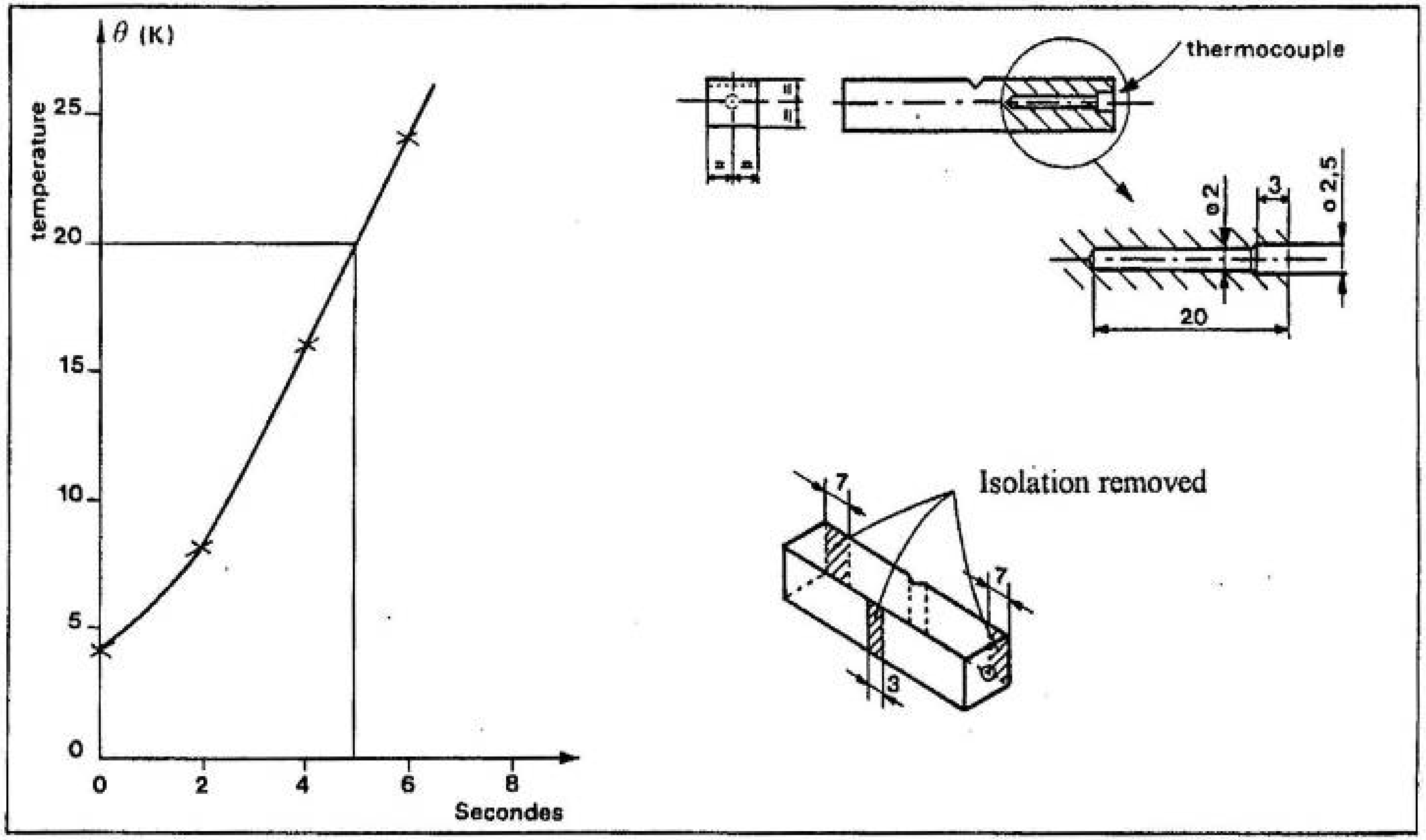
- In what follows, we shall only deal ferritic steels, stainless steels and aluminium alloys, which are the main materials used at low temperatures

5. MATERIAL ISSUES – COMPATIBILITY OF METALS AND ALLOYS WITH LOW TEMPERATURE



CHARPY TEST

5. MATERIAL ISSUES – COMPATIBILITY OF METALS AND ALLOYS WITH LOW TEMPERATURE



CHARPY TEST AT LIQUID HELIUM TEMPERATURE – TEMPERATURE VERSUS TIME