2nd SECOND EUROPEAN SUMMER SCHOOL HYDROGEN SAFETY
BELFAST
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SAFETY OF HYDROGEN CYLINDERS AND PRESSURE VESSELS

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SAFETY OF HYDROGEN CYLINDERS AND PRESSURE VESSELS

AIR LIQUIDE

1. INTRODUCTION AND DIFFERENT TYPES OF PRESSURE VESSELS
2. SOME HISTORY
3. DESIGN AND MANUFACTURING
4. SUITABLE MATERIALS FOR PRESSURE VESSELS
5. POTENTIAL SOURCES OF INCIDENTS INVOLVING GAS CYLINDERS
6. TESTS APPROVAL & REGULATION
7. NEW TRENDS DUE TO HYDROGEN ENERGY
8. CONCLUSION

1. INTRODUCTION AND DIFFERENT TYPES OF PRESSURE VESSELS

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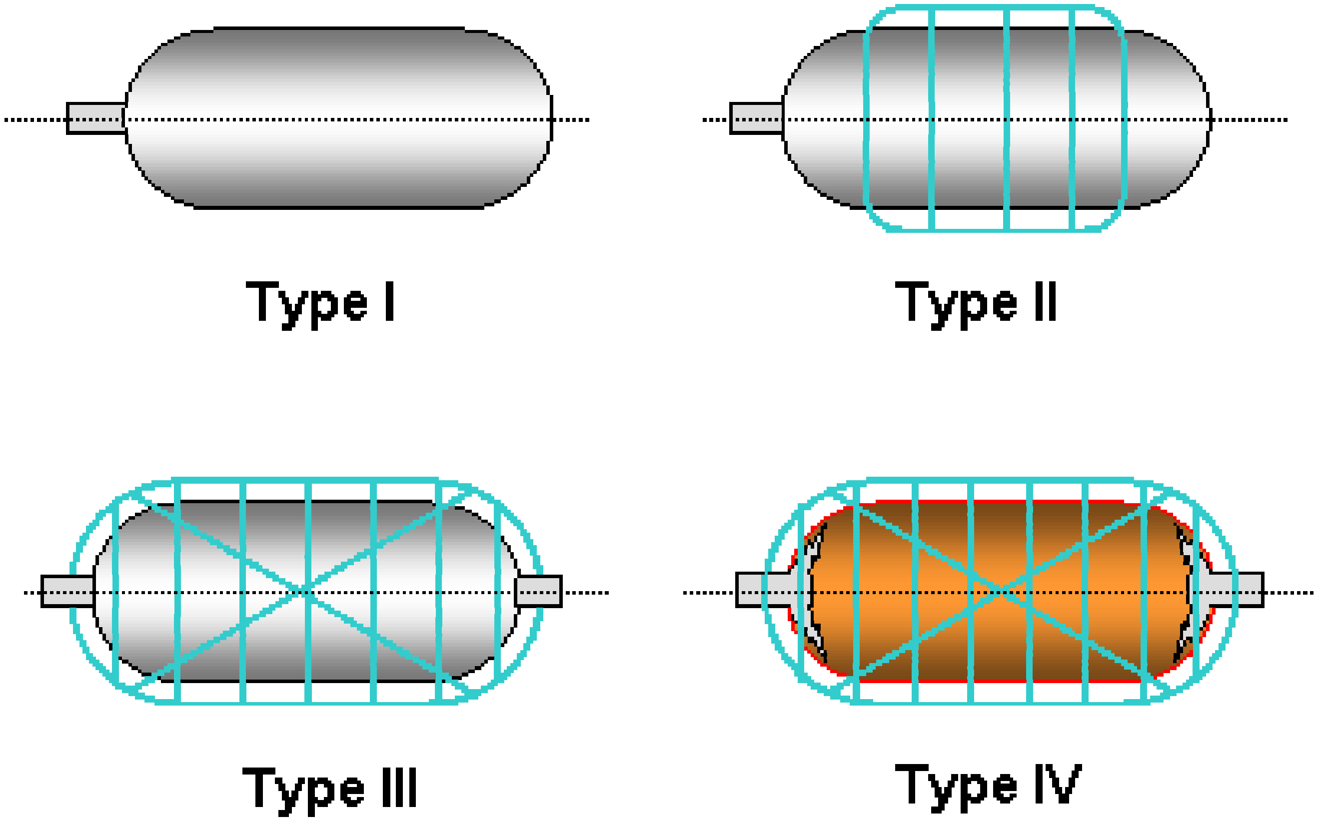
Type I : pressure vessel made of metal

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

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Type I cylinder

Type II vessel

Type III or IV vessel

Toroid composite vessel

Different types of pressure vessels

2. SOME HISTORY

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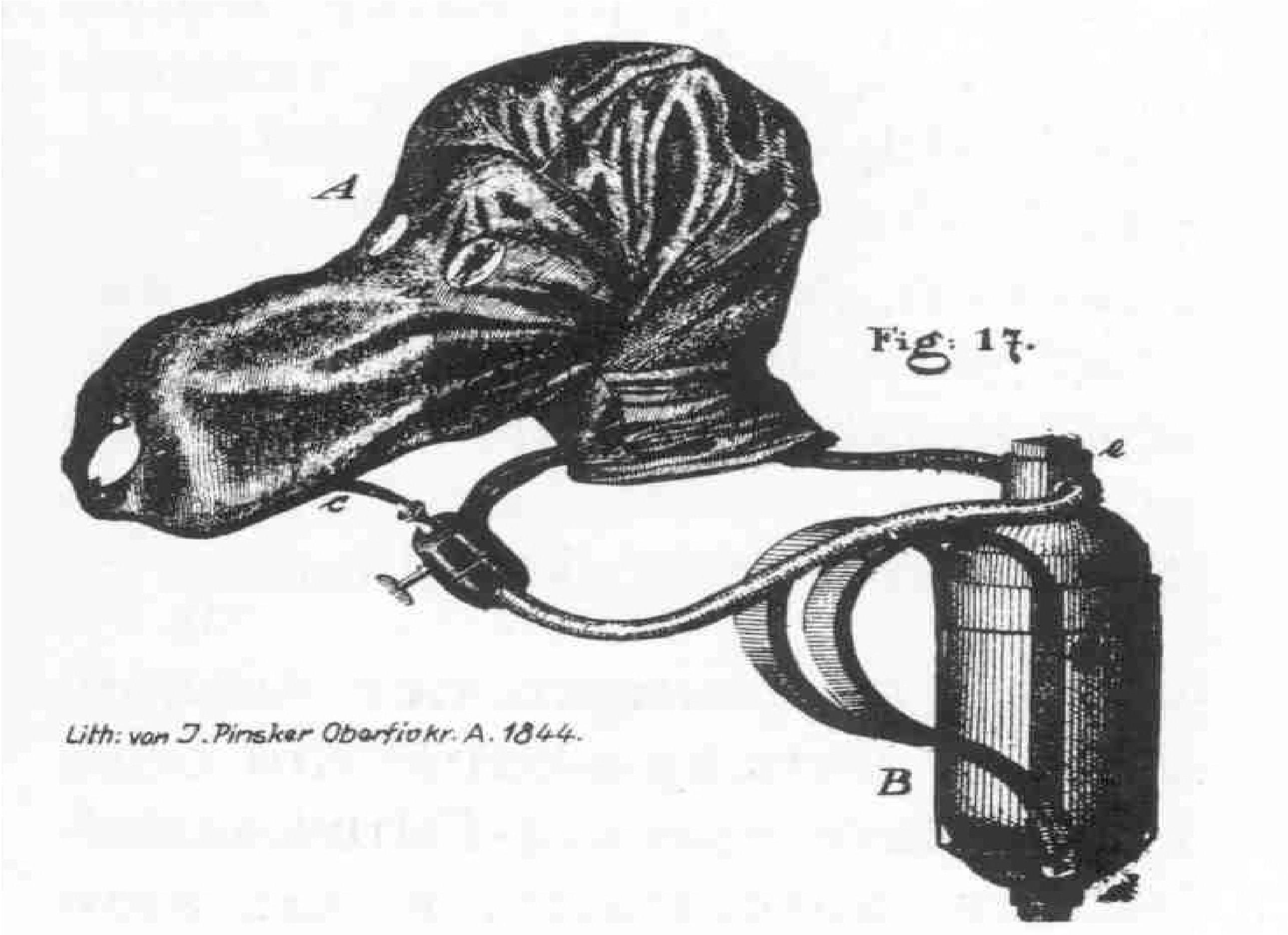
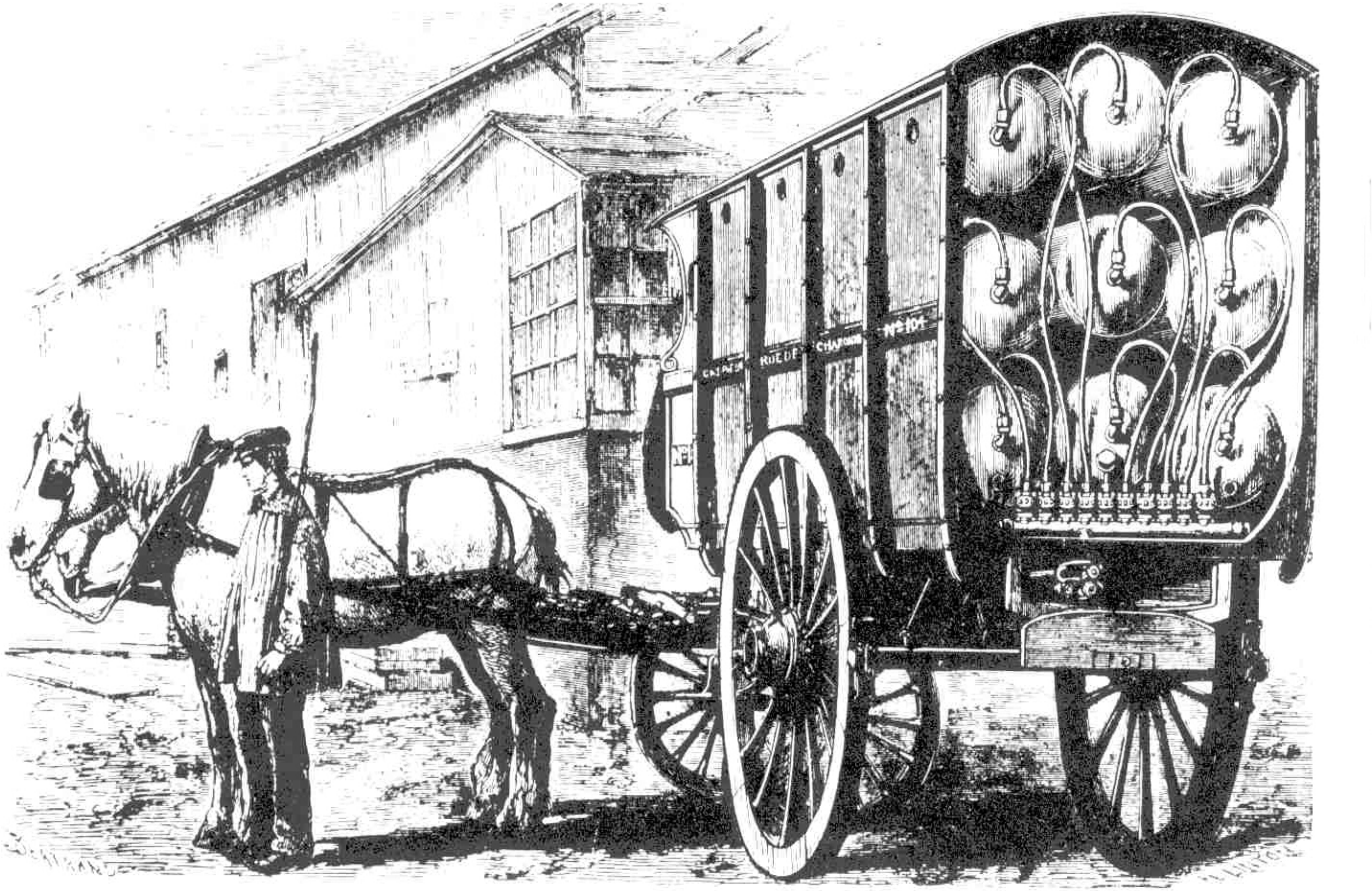


Welded cylinder : test pressure : 60 bar

2. SOME HISTORY

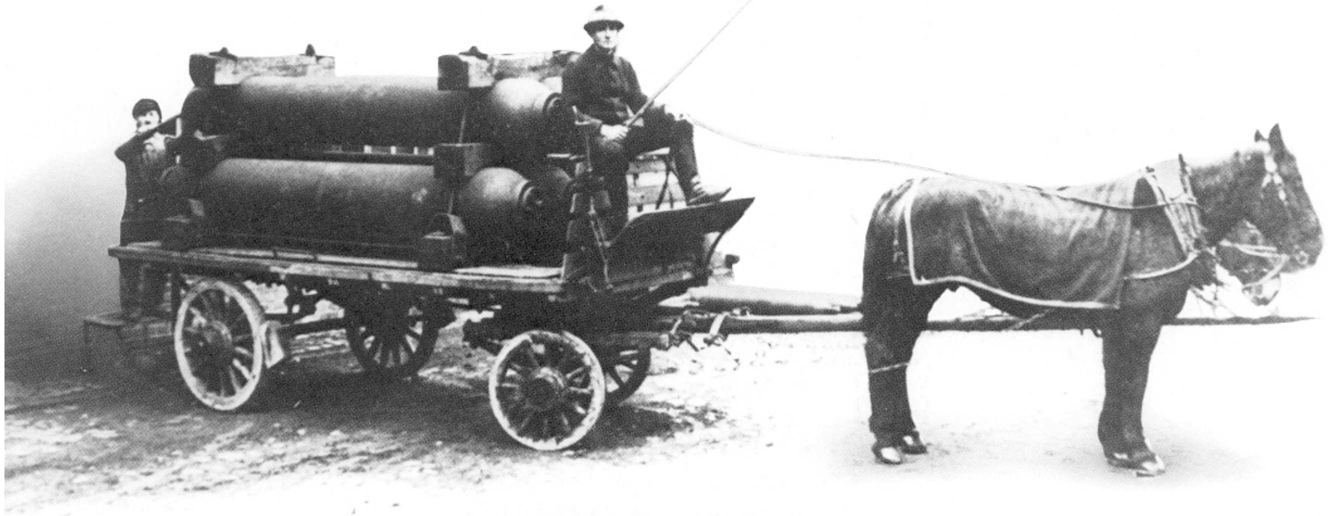
AIR LIQUIDE



Gas transport - 1857

2. SOME HISTORY

AIR LIQUIDE



2. SOME HISTORY

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- The experimentation of composite vessels started in the 50s

- Composite vessels were introduced for space and military applications

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- 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

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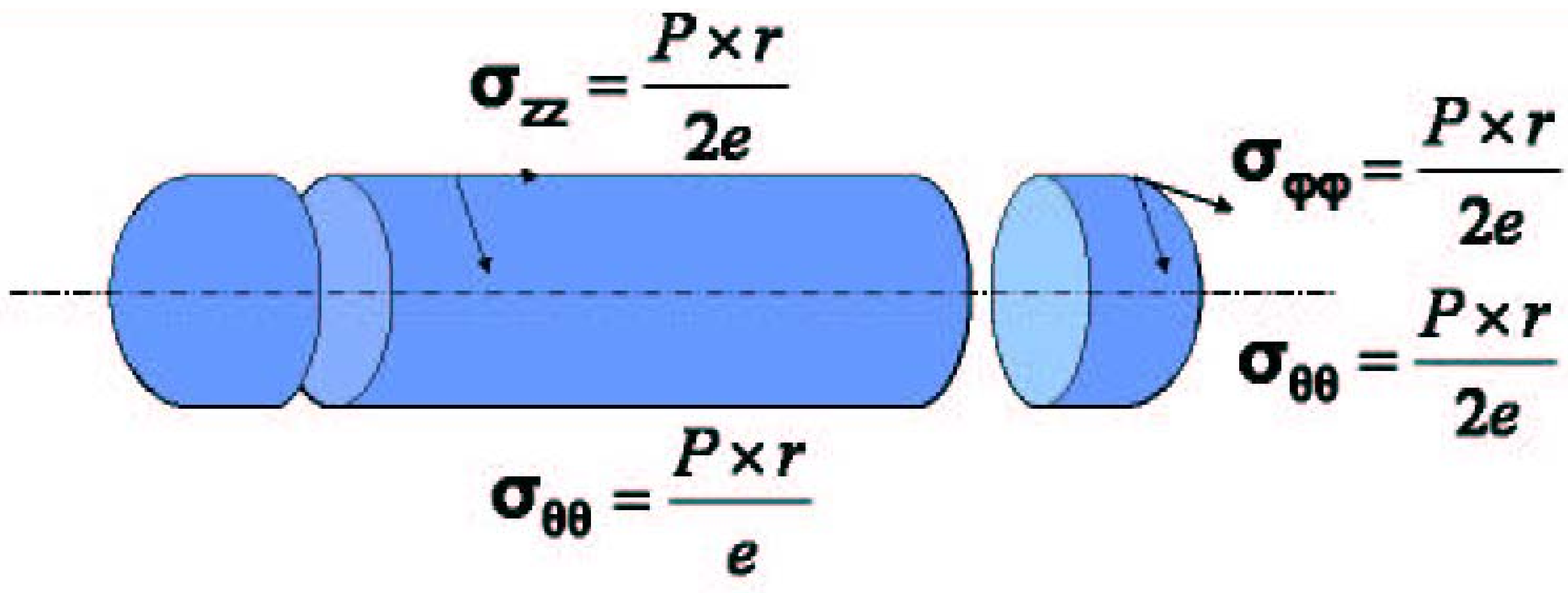
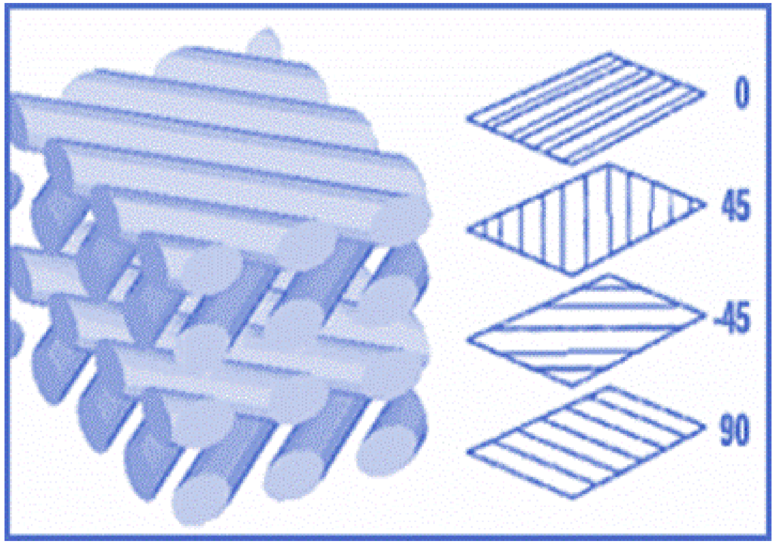
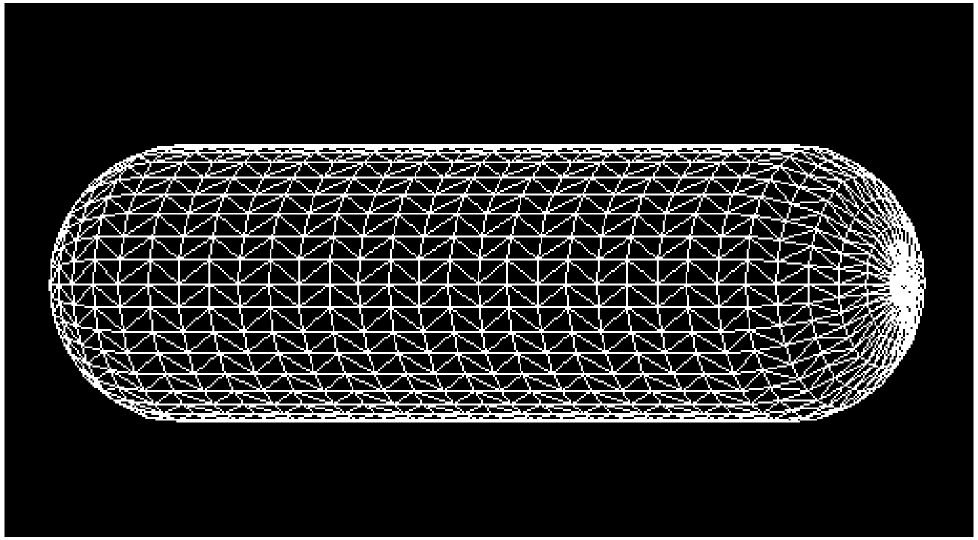


Main strains considered for the metallic pressure vessels design (type I and metallic liner)

3. DESIGN AND MANUFACTURING





Multi-layered element and vessel meshes example

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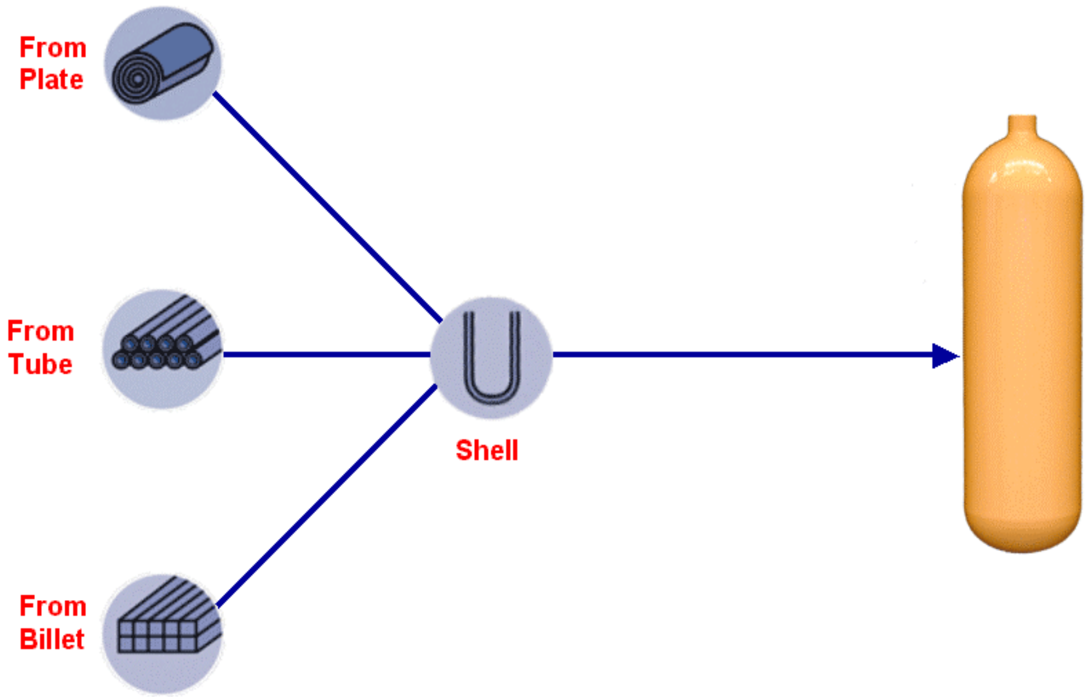
- **Type I :**

3 different manufacturing processes

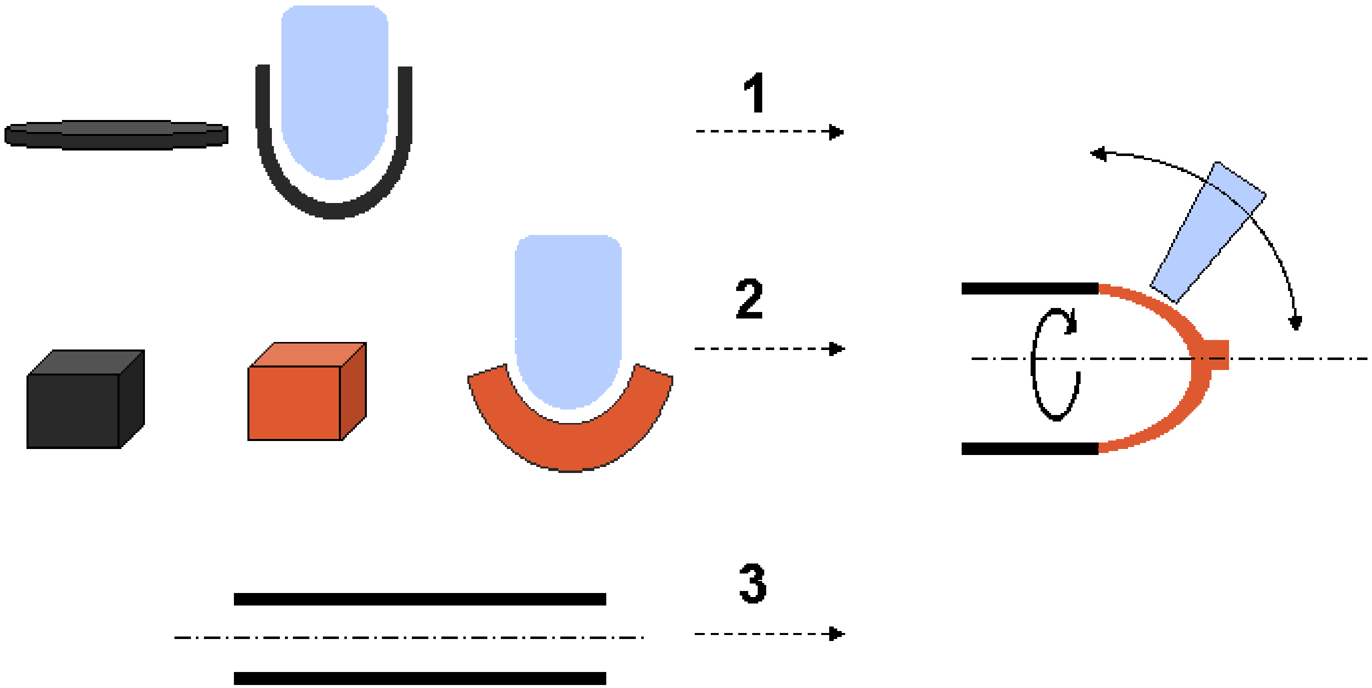
- **From plates**
- **From billets**
- **From tubes**

3. DESIGN AND MANUFACTURING



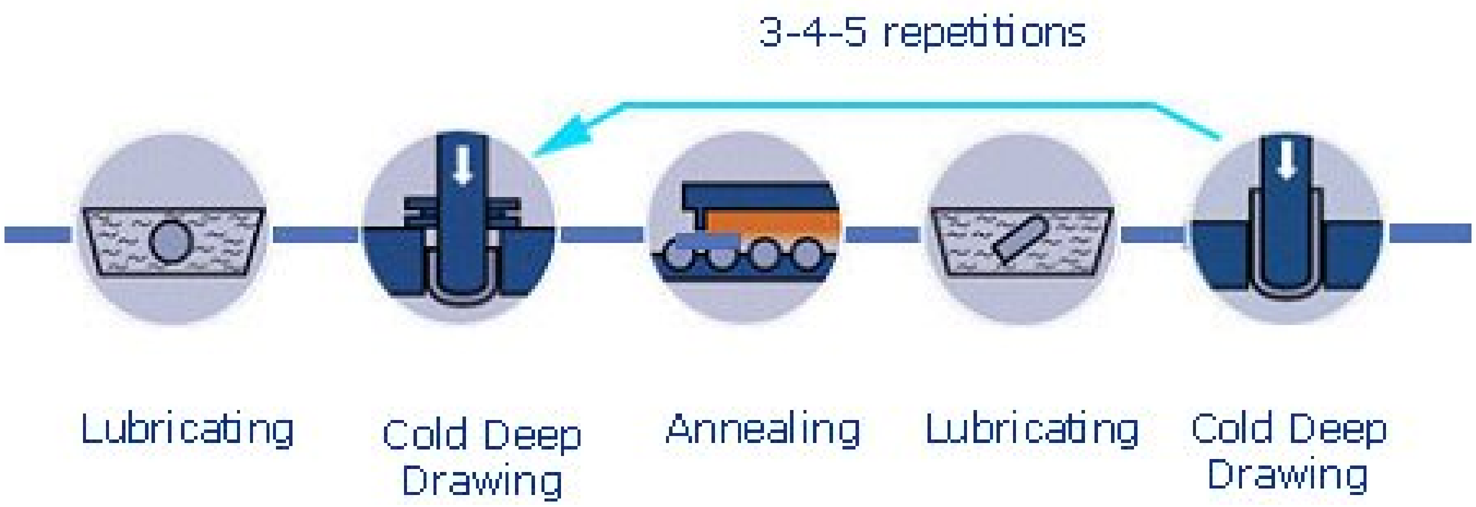
Different production methods

AIR LIQUIDE



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

3. DESIGN AND MANUFACTURING



Production process from steel plate

3. DESIGN AND MANUFACTURING

Production process from steel plate

3. DESIGN AND MANUFACTURING

Manufacturing from plate

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Stock of steel bars for cylinders made from billets

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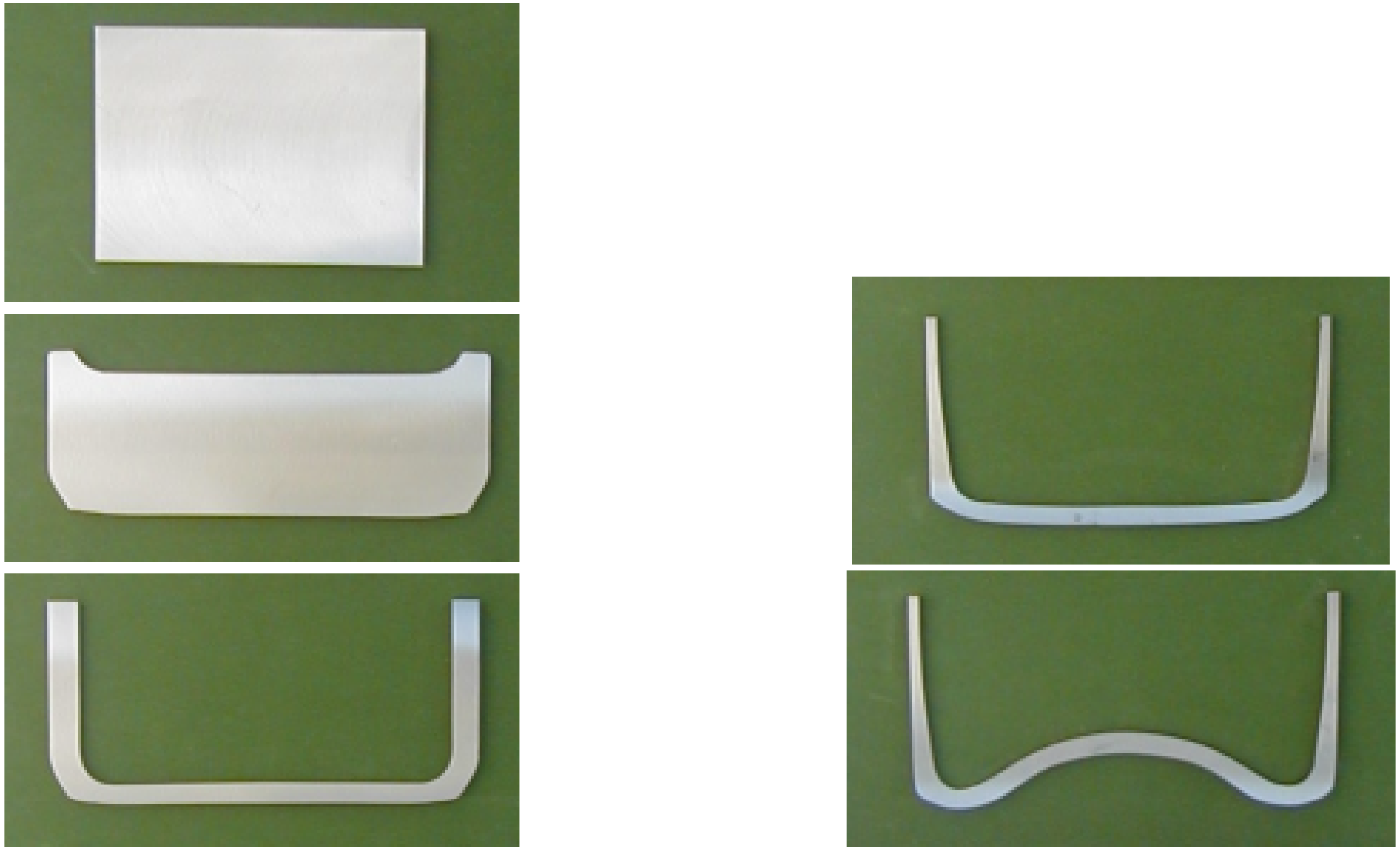
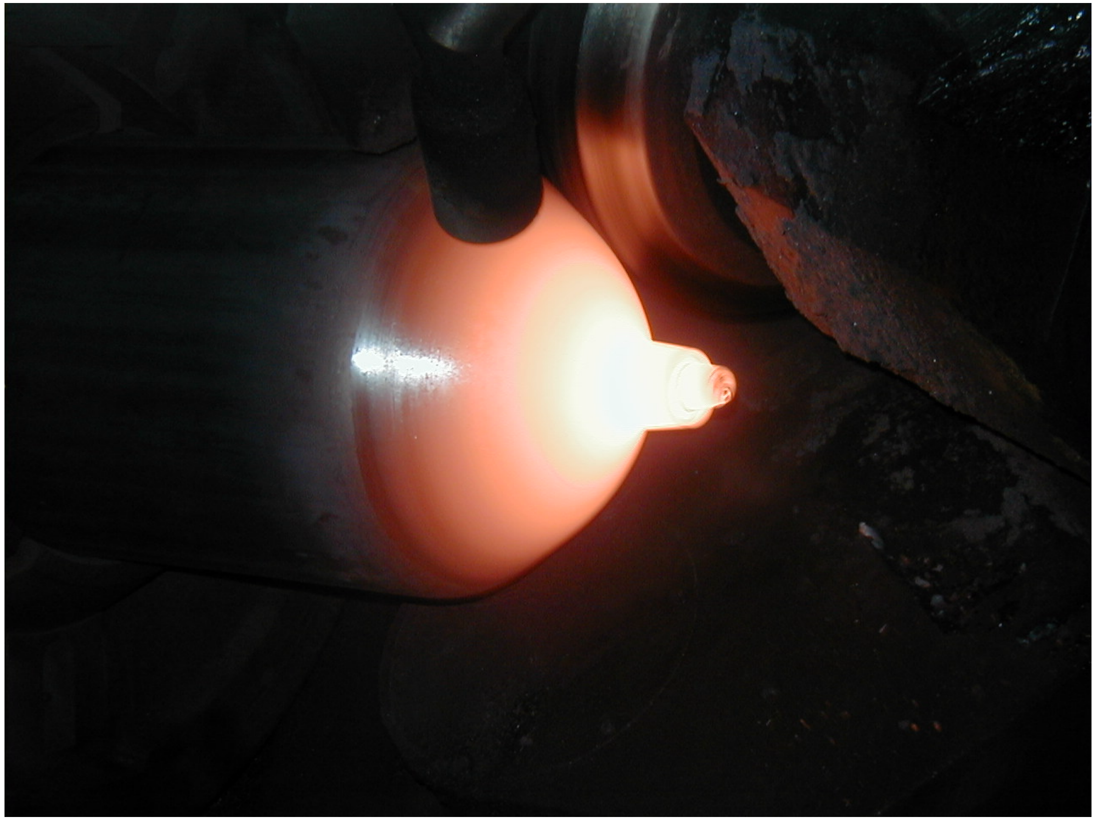


Cylinders made from billets
Different forging steps



Steel cylinders spinning process

3. DESIGN AND MANUFACTURING

Stock of aluminium billets

3. DESIGN AND MANUFACTURING

Aluminium cylinders made from cold extrusion

3. DESIGN AND MANUFACTURING

Aluminium cylinders made from hot extrusion

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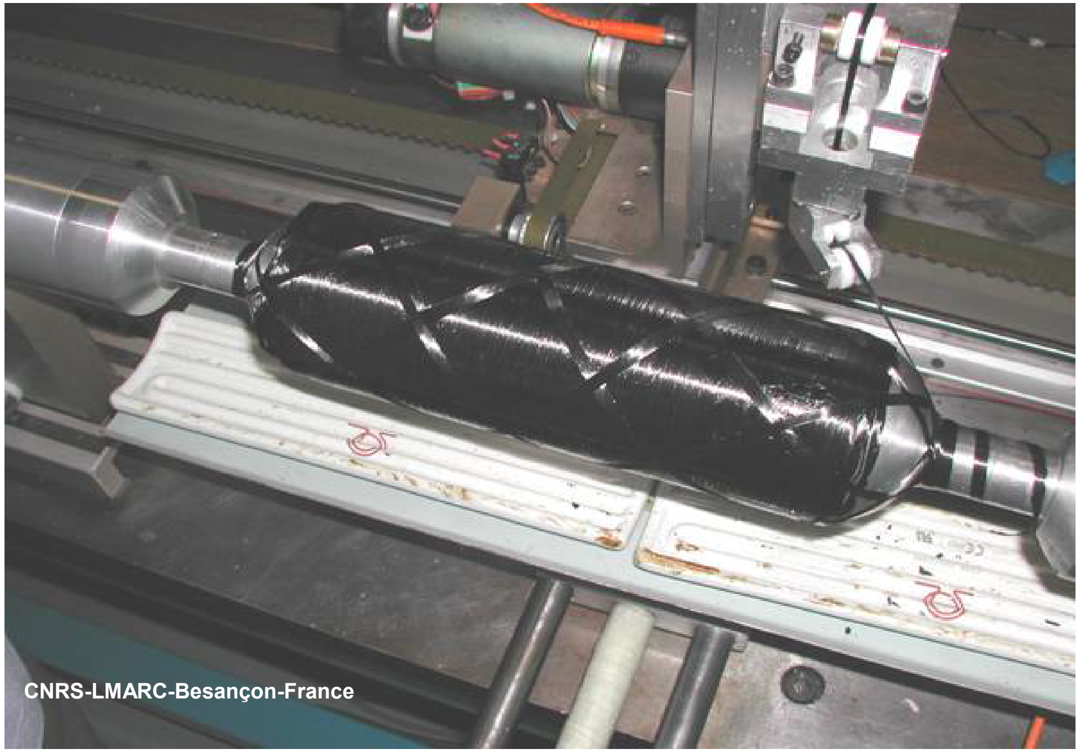
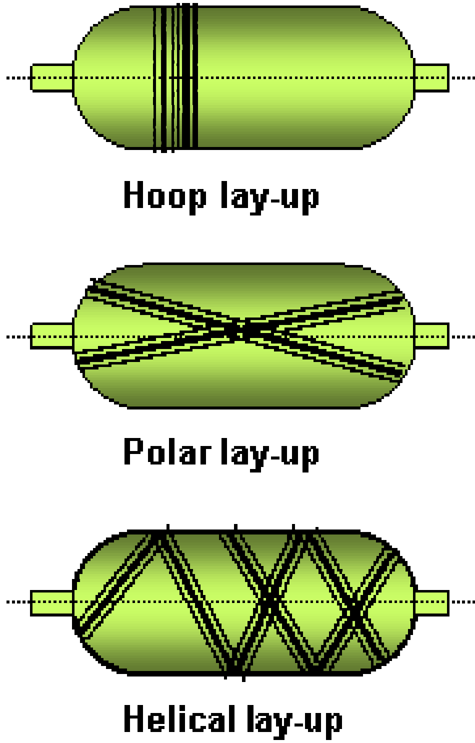
Polymers liners :

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





Winding machine and the 3 winding possibilities

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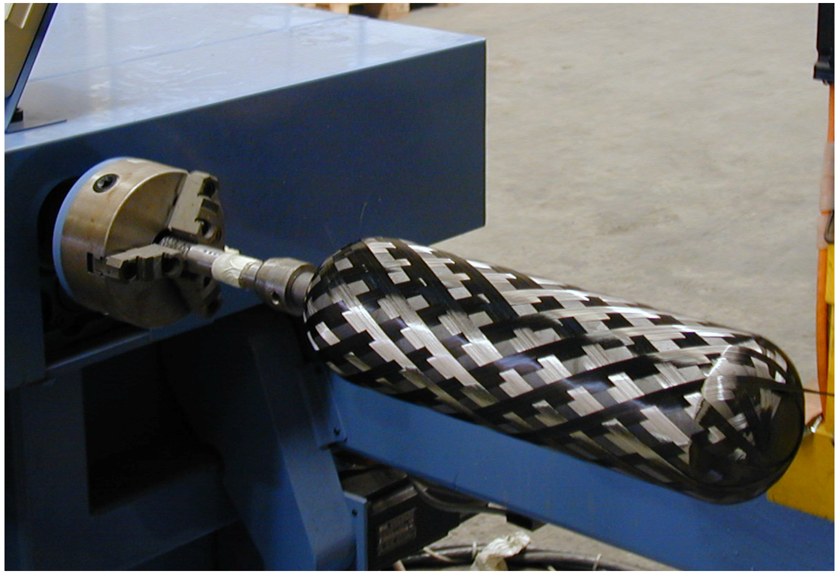
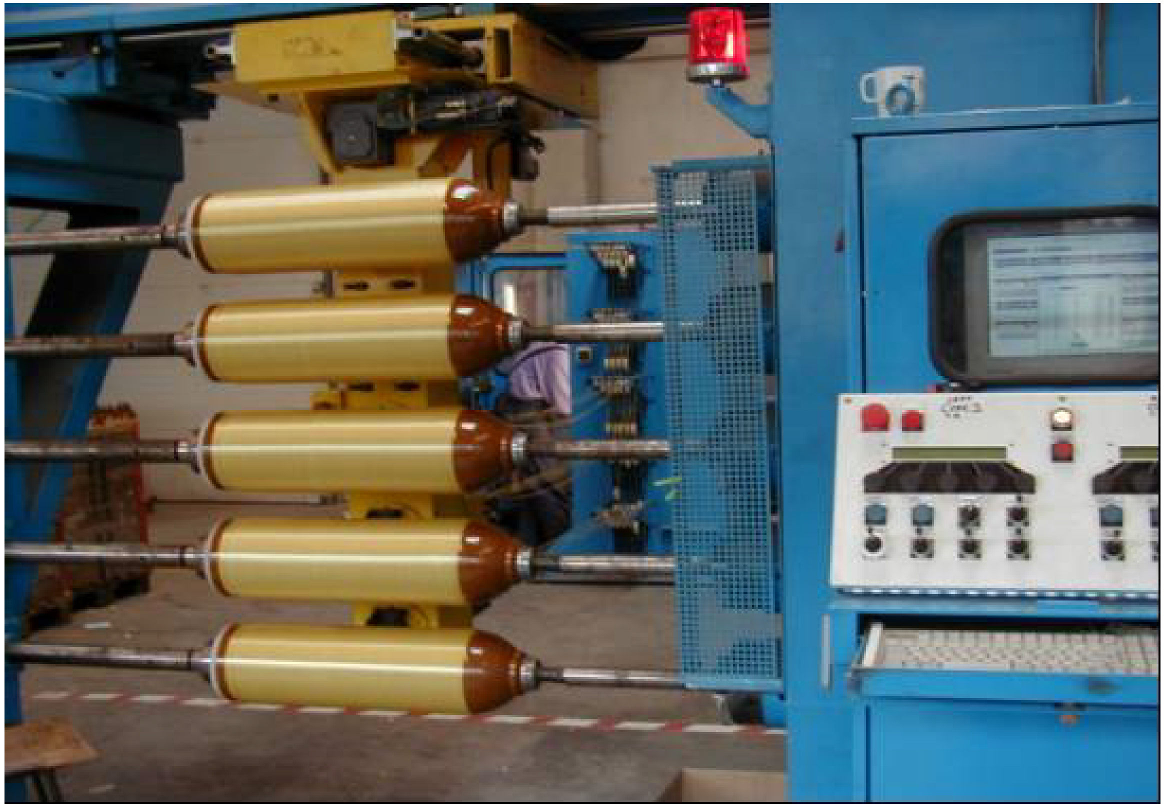


Composite cylinders

3. DESIGN AND MANUFACTURING



Composite cylinders being wrapped with amaride fiber

4. SUITABLE MATERIALS FOR HYDROGEN HIGH PRESSURE VESSELS

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Risk of hydrogen embrittlement :

- Environment
- Material
- Design and surface conditions

4. SUITABLE STEELS

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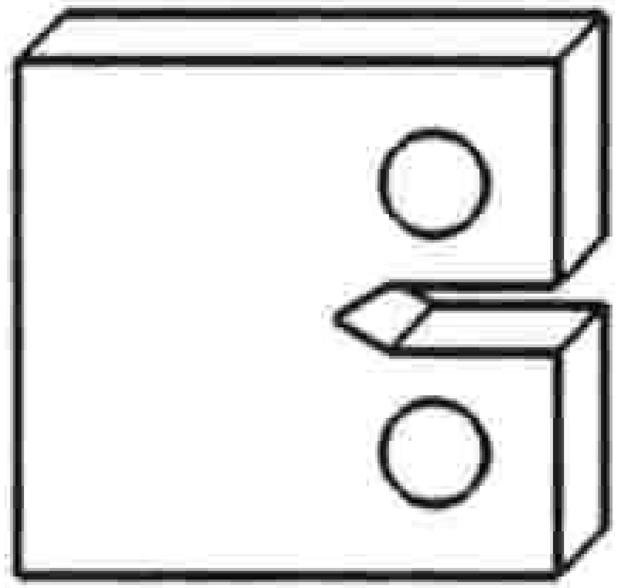
Type of steel	Note
Normalized and carbon steels	Embrittlement to be assessed if (C + Mn/6) high
Quenched and tempered steels	More used (ex. : 34CrMo4) ; Embrittlement to be assessed if Rm > 950 Mpa.
Stainless steels	Some of them can be sensitive to embrittlement (ex. : 304)

Steels acceptable for hydrogen pressure storage (ISO 11114-1)

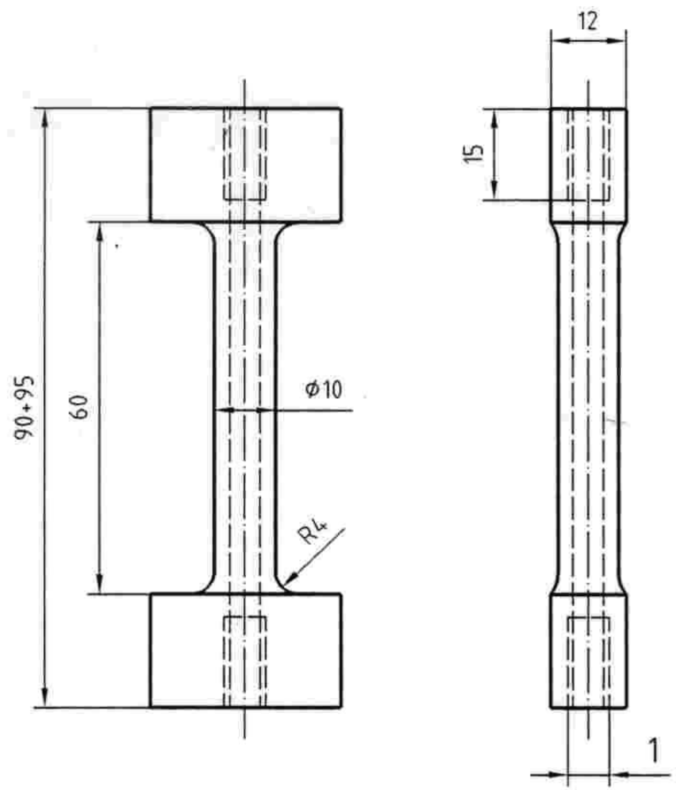
4. TEST METHODS

AIR LIQUIDE



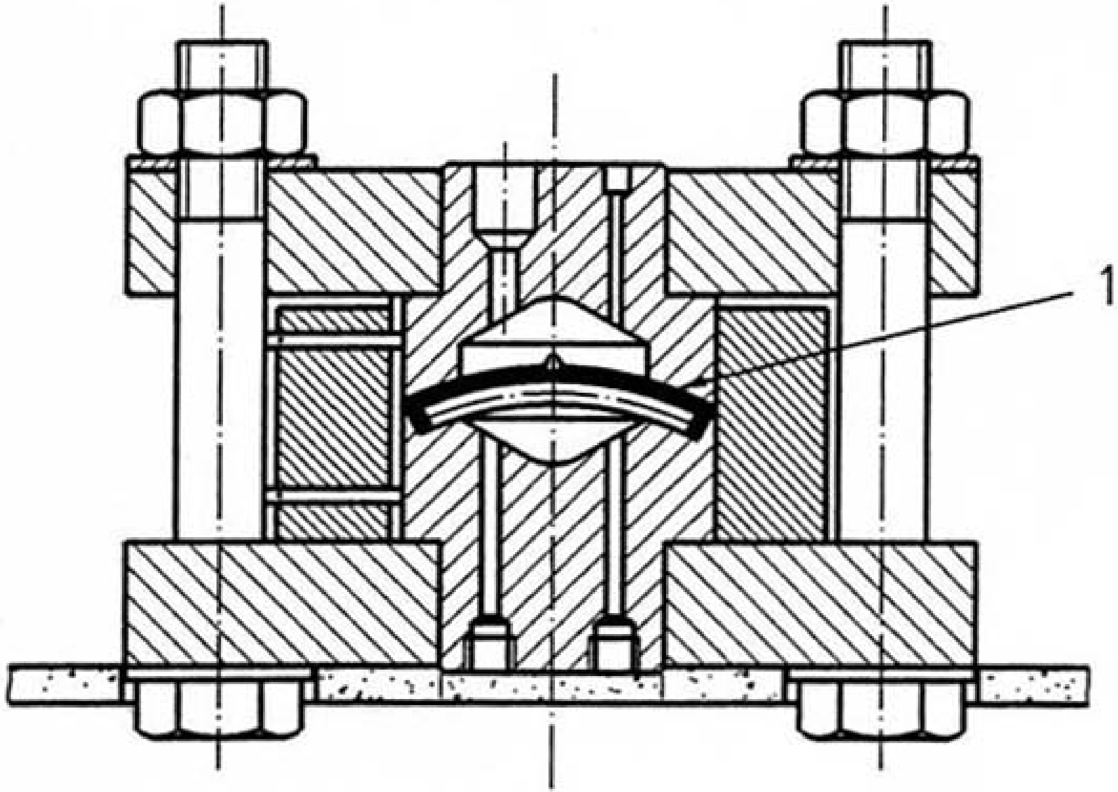
Specimens for compact tension test

4. TEST METHODS



Tensile specimen for hydrogen tests (hollow tensile specimen) (can also be performed with specimens cathodically charged or with tensile spencimens in a high pressure cell)

4. TEST METHODS

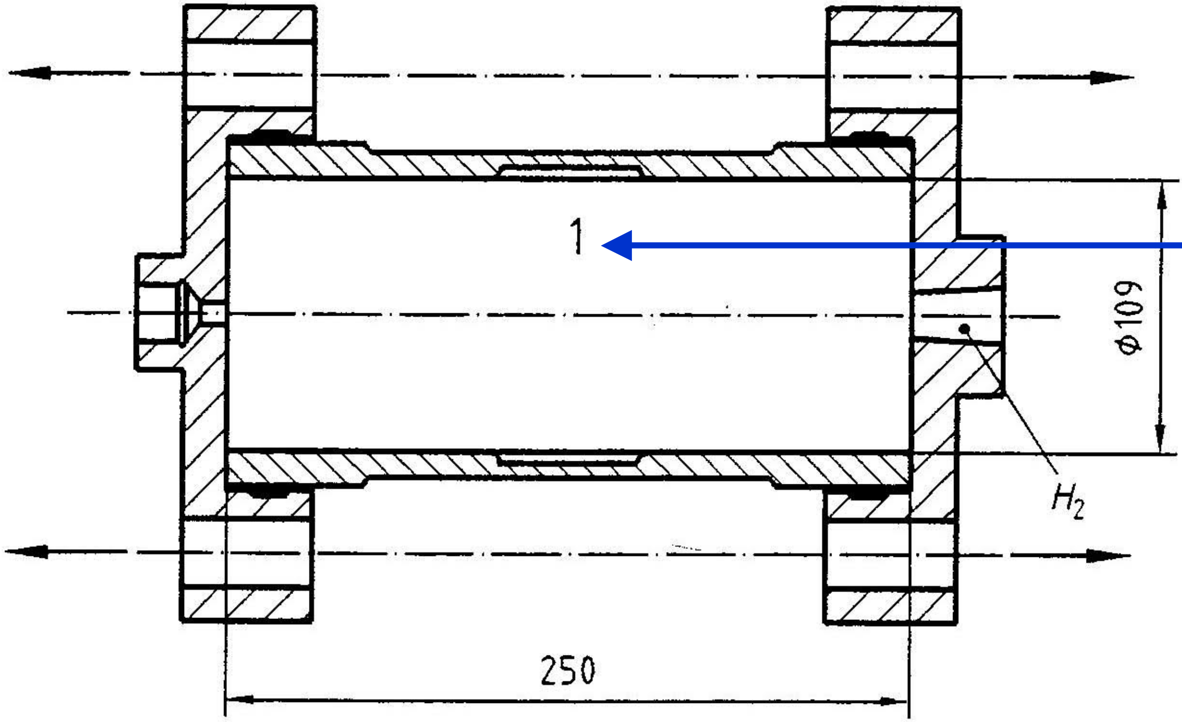


Pseudo Elliptic Specimen

Cell for delayed rupture test with Pseudo Elliptic Specimen

4. TEST METHODS

AIR LIQUIDE

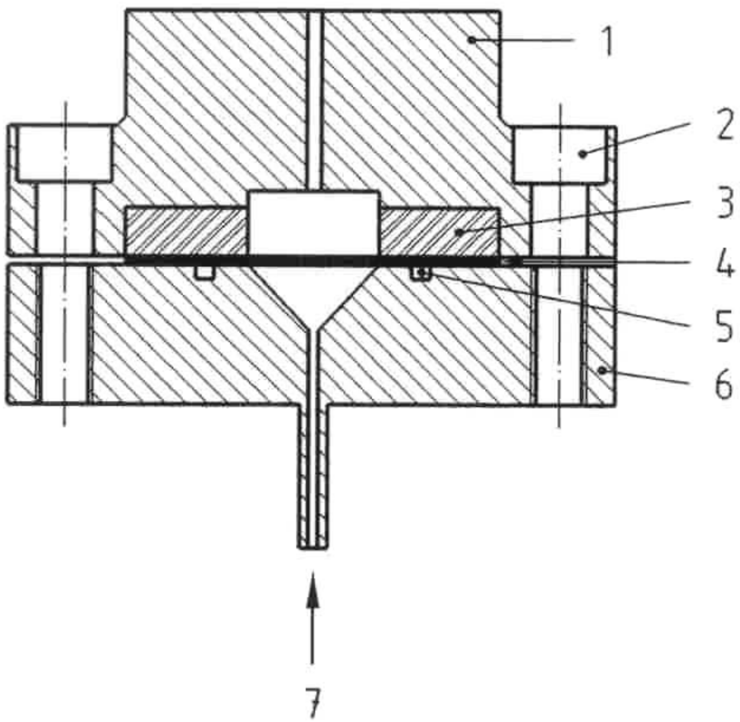


Inner notches with elongation measurement strip

Tubular specimen for hydrogen assisted fatigue tests

4. TEST METHODS

AIR LIQUIDE

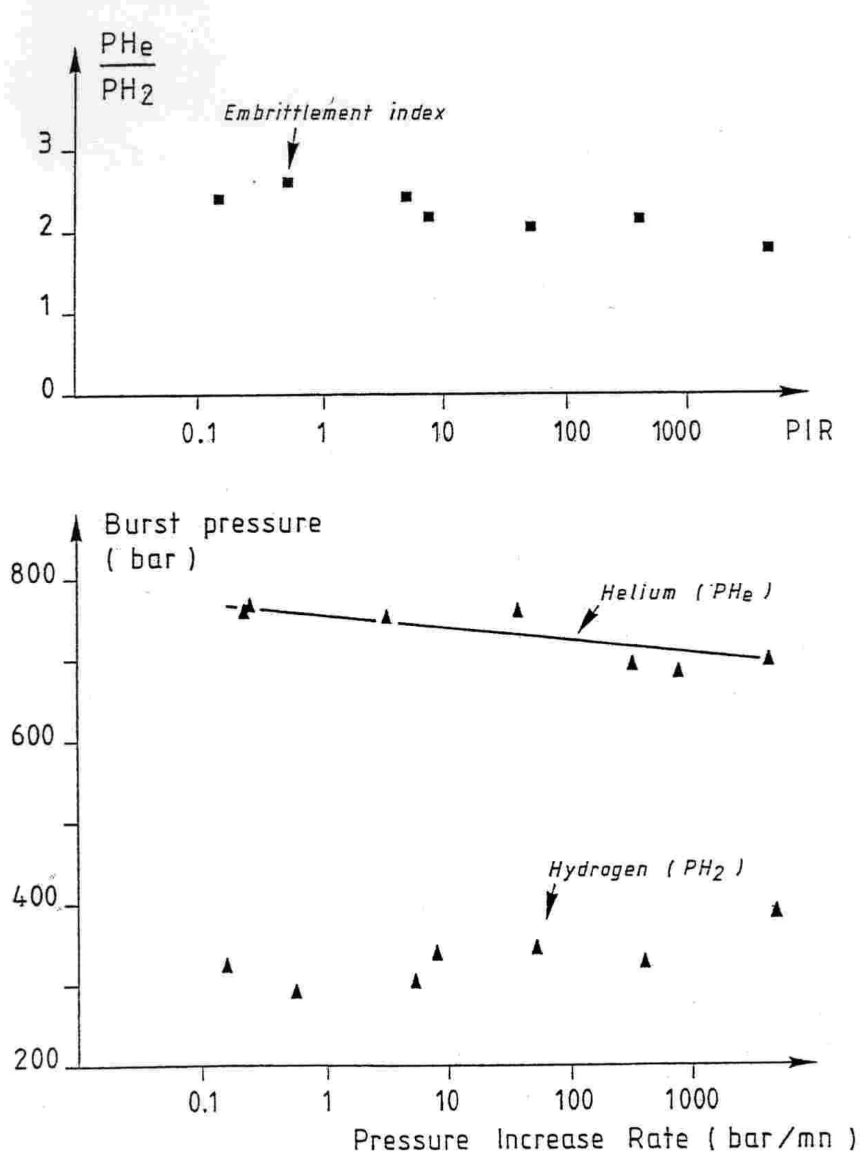


1. Upper flange
2. Bolt Hole
3. High-strength steel ring
4. Disk
5. O-ring seal
6. Lower flange
7. Gas inlet

Disk testing method – Rupture cell for embedded disk-specimen

4. TEST METHODS

AIR LIQUIDE



Example of a disk rupture test curve

4. H_2 EMBRITTLEMENT - RECOMMENDATION

1) The influence of the different parameters shall be addressed.

2) To safely use materials in presence of hydrogen, an internal specification shall cover the following :

- The « scope », i.e. the hydrogen pressure, the temperature and the hydrogen purity
- The material, i.e. the mechanical properties, chemical composition and heat treatment
- The stress level of the equipment
- The surface defects and quality of finishing
- And the welding procedure, if any

4. COMPOSITE CYLINDERS – SUITABLE MATERIALS

- **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**

4. COMPOSITE CYLINDERS – SUITABLE MATERIALS

- **No specific issue with aluminium alloys (except if presence of mercury or water)**

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 (specified rate < 1 $cm^3/l/h$).

5. POTENTIAL SOURCES OF INCIDENTS

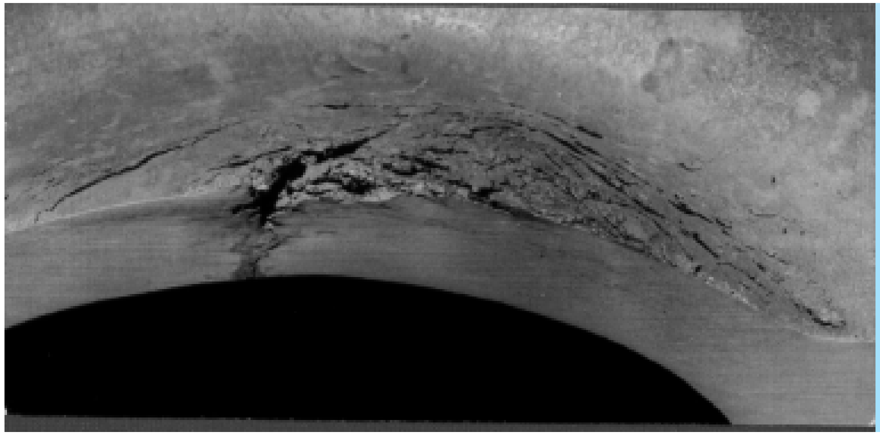
5.1. Type I cylinders

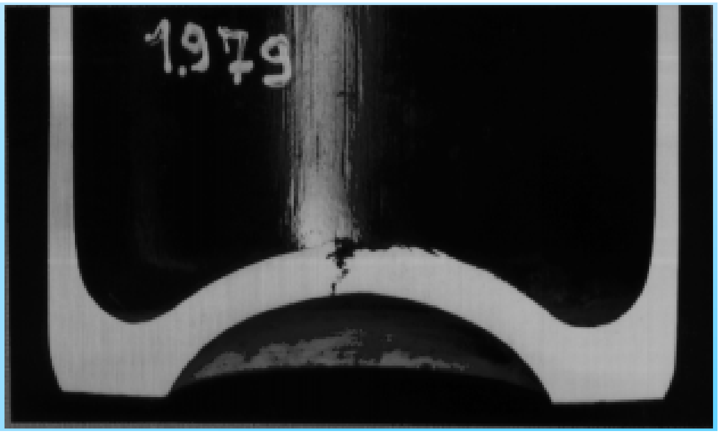
5.2. Composite cylinders

MANUFACTURING DEFECTS

From the original materials

Defect of the billet (continuous casting)



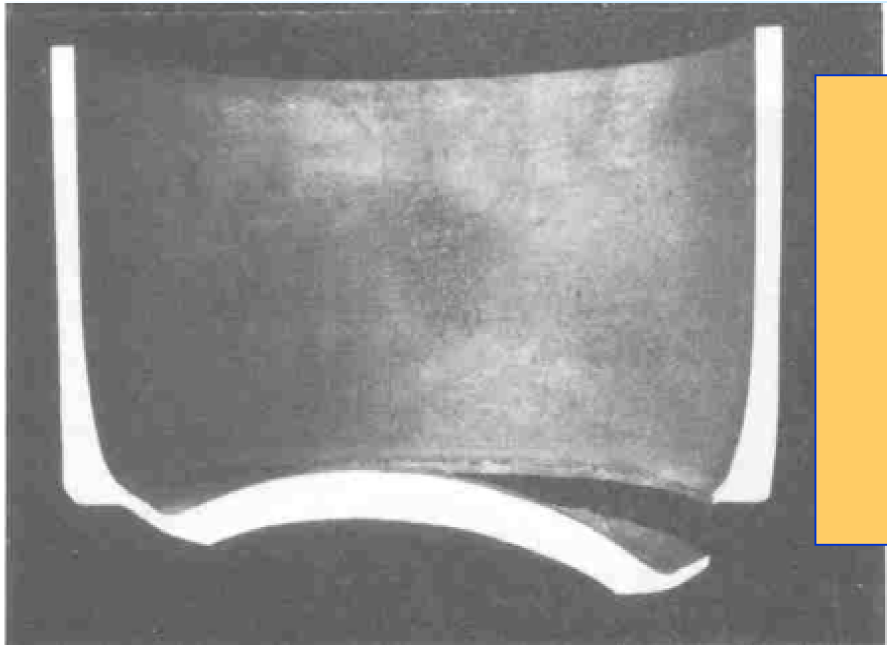


AIR LIQUIDE

MANUFACTURING DEFECTS

During forging

Billet : eccentricity – excessively thin cylinder base



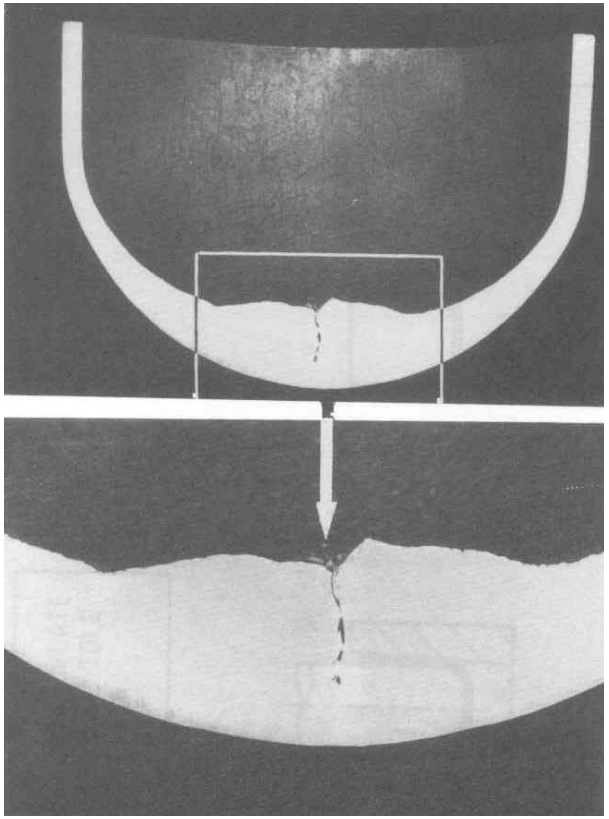
Cross section showing thickness remaining at bottom

AIR LIQUIDE

MANUFACTURING DEFECTS

During forging

Tube : leak at cylinder base



MANUFACTURING DEFECTS

During forging

Plate : crack resulting from extremely severe deformation

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MANUFACTURING DEFECTS

Shoulder shaping

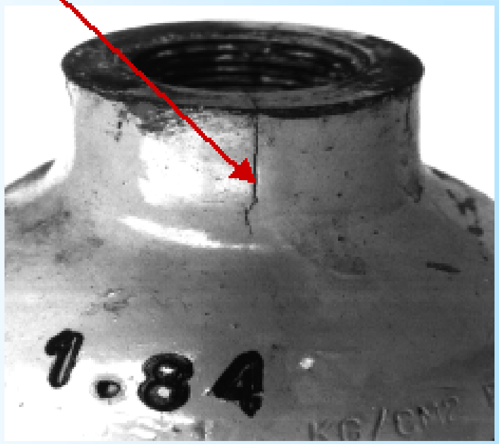
- Pre-existing defects

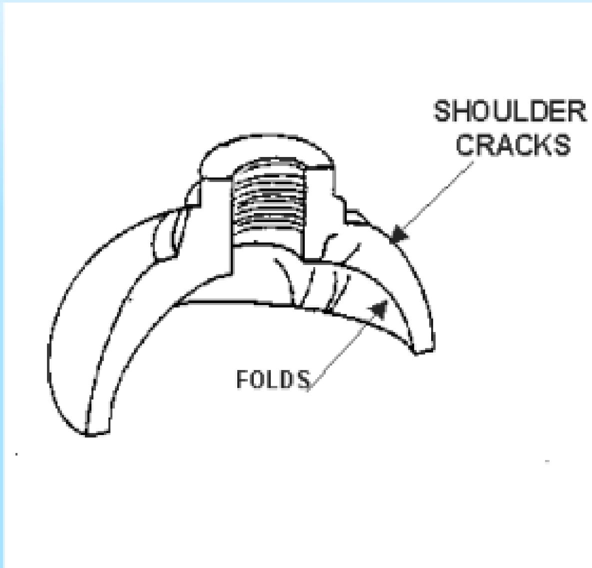
- Improper preheating

AIR LIQUIDE

MANUFACTURING DEFECTS

Neck crack





Neck and shoulder cracks due to sustained load cracking

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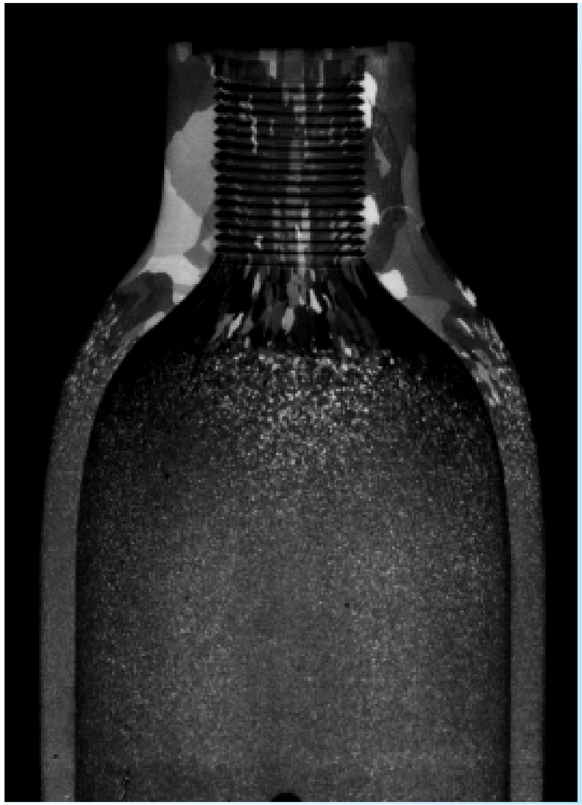
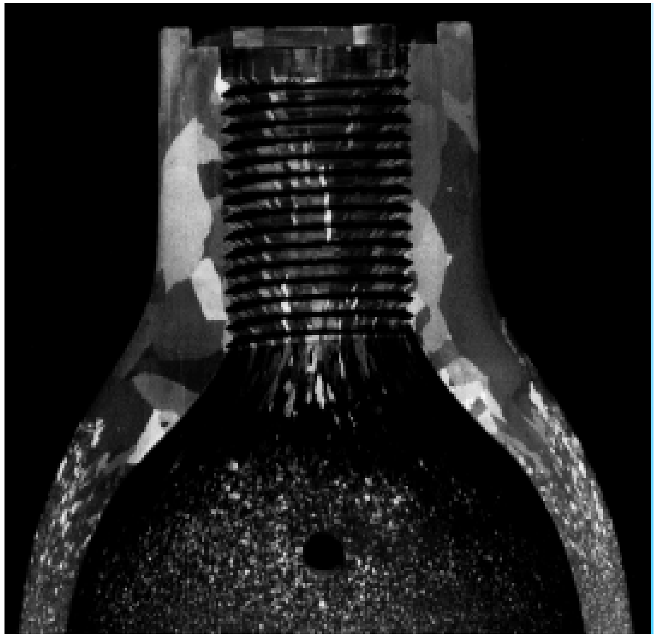
MANUFACTURING DEFECTS





Aluminium cylinders with coarse grain structure in the neck / shoulder region

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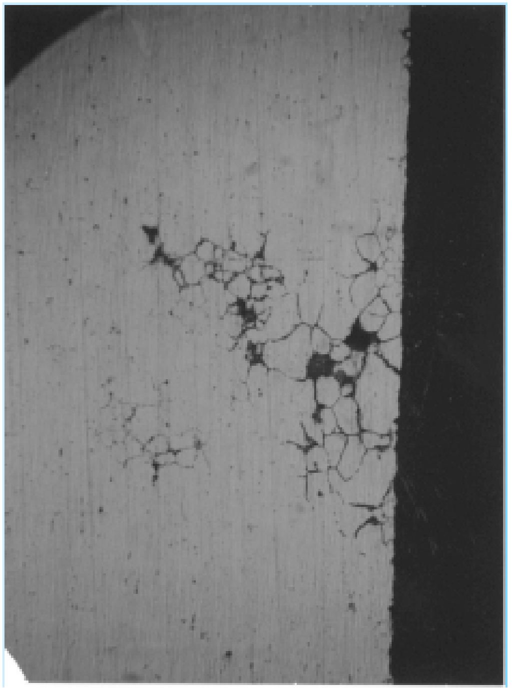
MANUFACTURING DEFECTS

Heat treatment

- Steel : improper treatment may lead to brittleness at low temperature
- Aluminium alloys : some materials may become sensitive to intercrystalline or stress corrosion

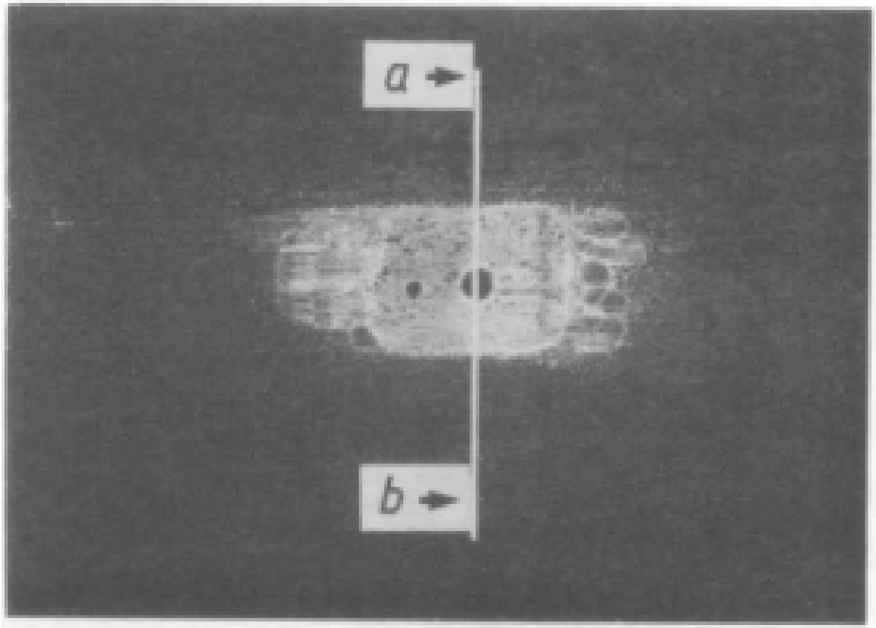


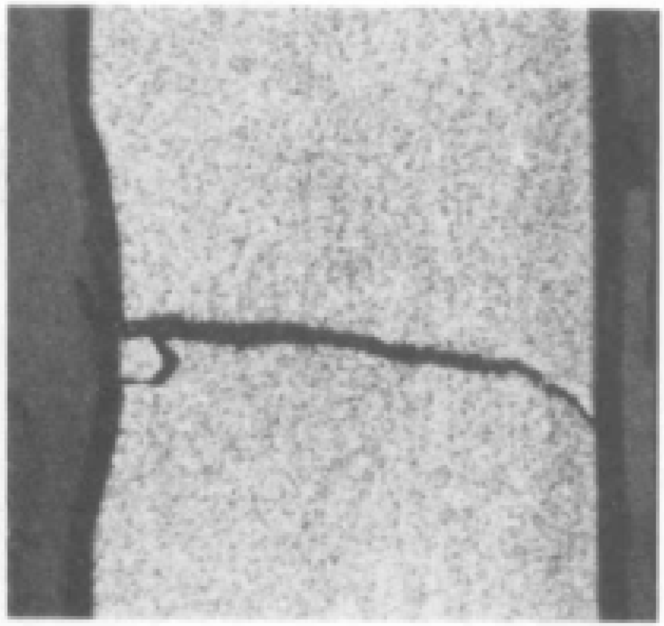
AIR LIQUIDE

MANUFACTURING DEFECTS

Marking - Stampmarking

Surface defects





AIR LIQUIDE

IN SERVICE DEFECTS

Overfilling

- Relevant for HP liquefied gases – Use of bursting disc
- Excessive pressure (or stress)
- CO / CO_2 / H_2O stress corrosion cracking

AIR LIQUIDE

IN SERVICE DEFECTS

Gas material compatibility

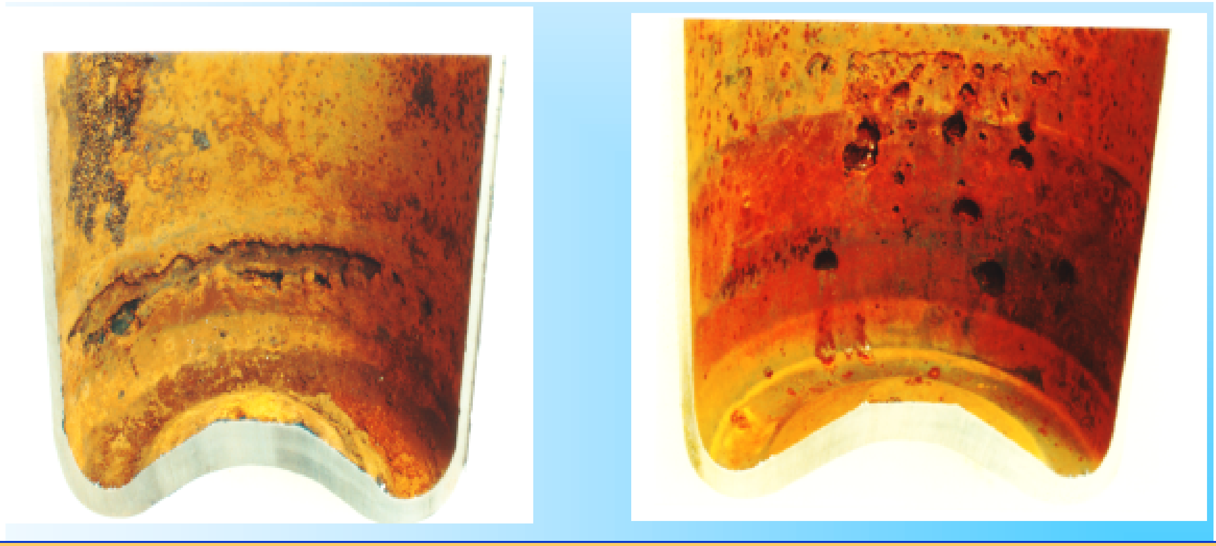
H_2 embrittlement

Other gases : see ISO 11114

IN SERVICE DEFECTS

Corrosion

- External : severe environment (seaside…)
- Internal :
  - O_2, CO_2 with water ingress



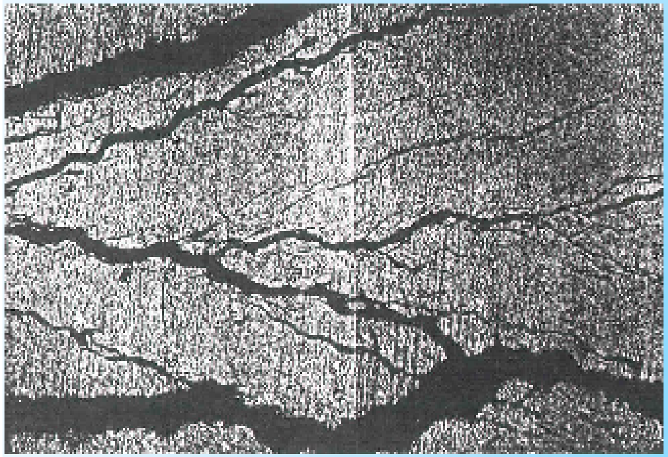
Steel cylinders – Internal corrosion

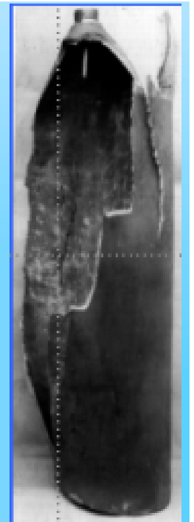
AIR LIQUIDE

IN SERVICE DEFECTS

Corrosion

- Internal :
  - CO / CO_2 / H_2O stress corrosion cracking





Steel cylinders – Stress corrosion

AIR LIQUIDE

IN SERVICE DEFECTS

Corrosion

- Internal :

  - Corrosion of AA 6061 with tap water. Reduction of fatigue life for composite cylinders

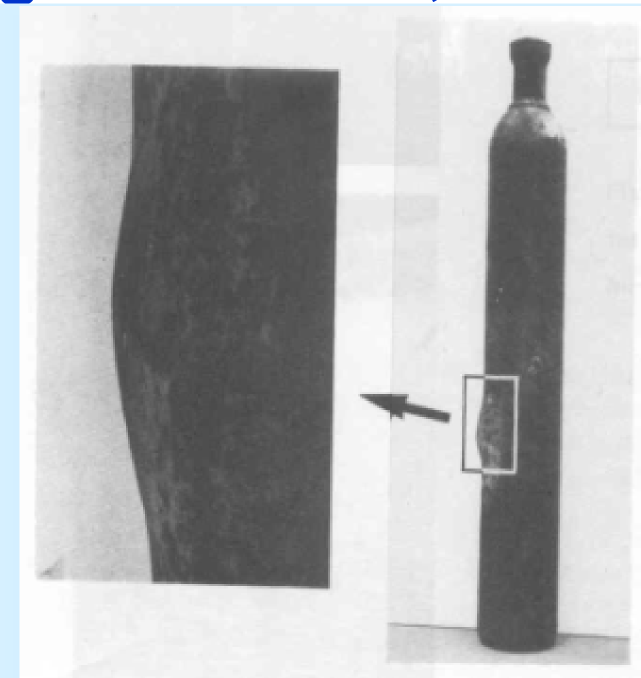
External impact

AIR LIQUIDE

IN SERVICE DEFECTS

Fires

- Local : (local reduction of mechanical proper-ties, thinning of the wall, local swelling)



Swelling and leak following applications of torch

IN SERVICE DEFECTS

Fires

- Arc burns

Swelling and leak following applications of torch

AIR LIQUIDE

IN SERVICE DEFECTS

Foreign bodies (internal)

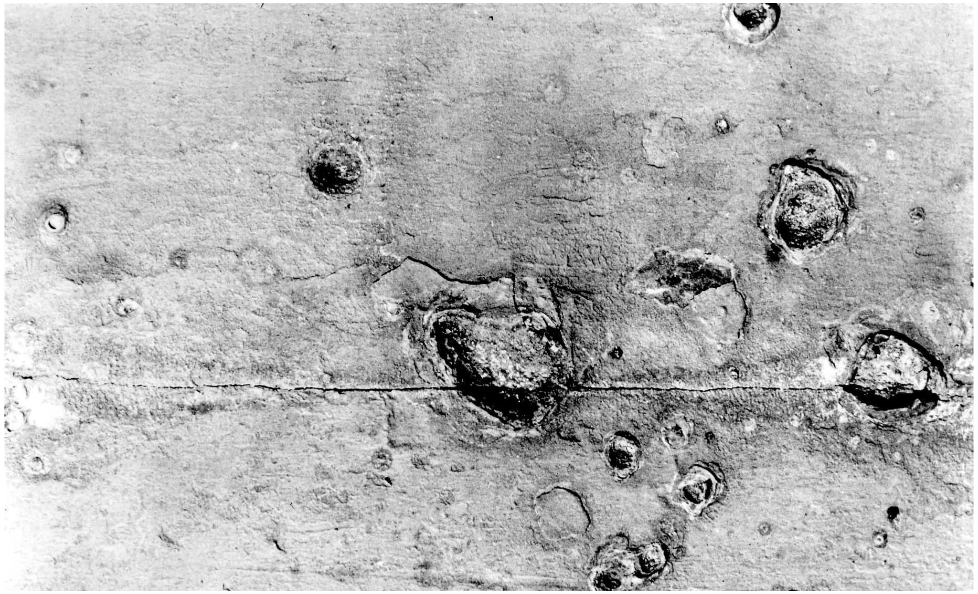
Risk of violent reactions with O_2 and other oxidising gases

5.1. H_2 REPORTED ACCIDENTS

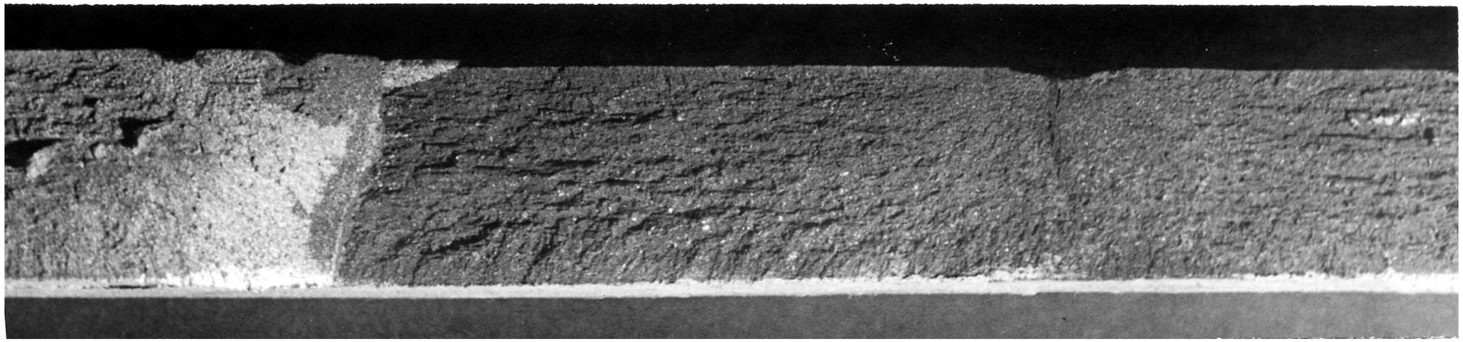
AIR LIQUIDE

FAILURE OF A HYDROGEN TRANSPORT VESSEL IN 1980

5.1. H_2 REPORTED ACCIDENTS

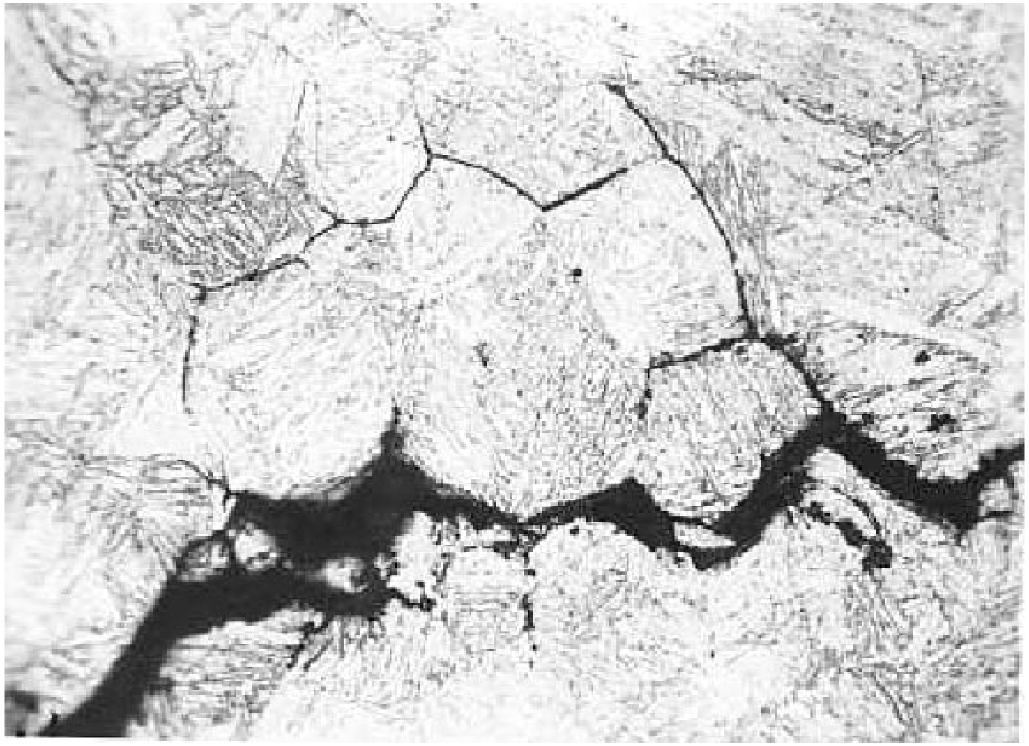


FAILURE OF A HYDROGEN TRANSPORT VESSEL IN 1983. HYDROGEN CRACK INITIATED ON INTERNAL CORROSION PITS



5.1. H_2 REPORTED ACCIDENTS

AIR LIQUIDE



HYDROGEN CYLINDER BURSTS
INTERGRANULAR CRACK

5.1. H_2 REPORTED ACCIDENTS

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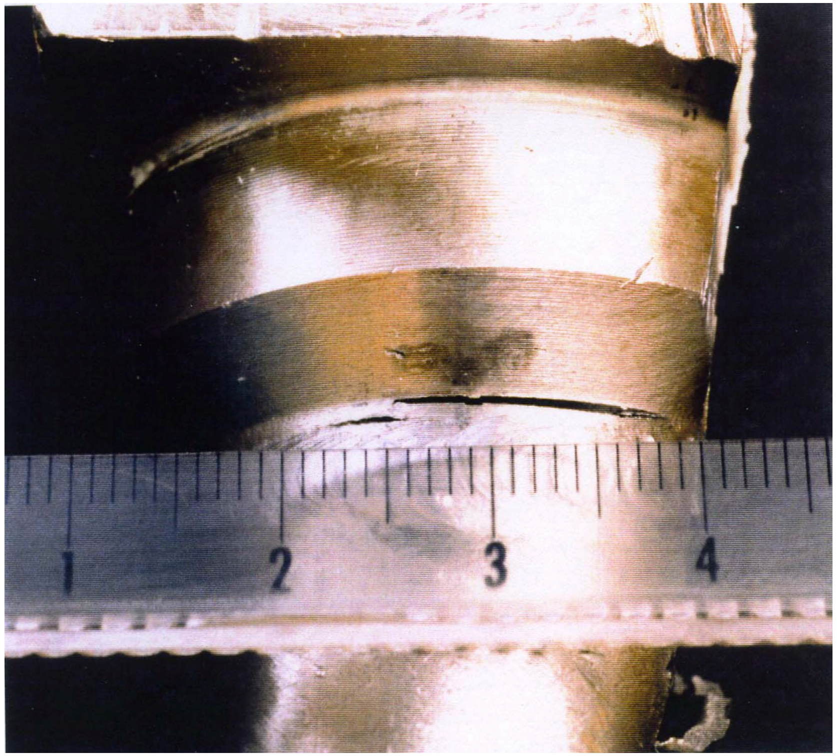
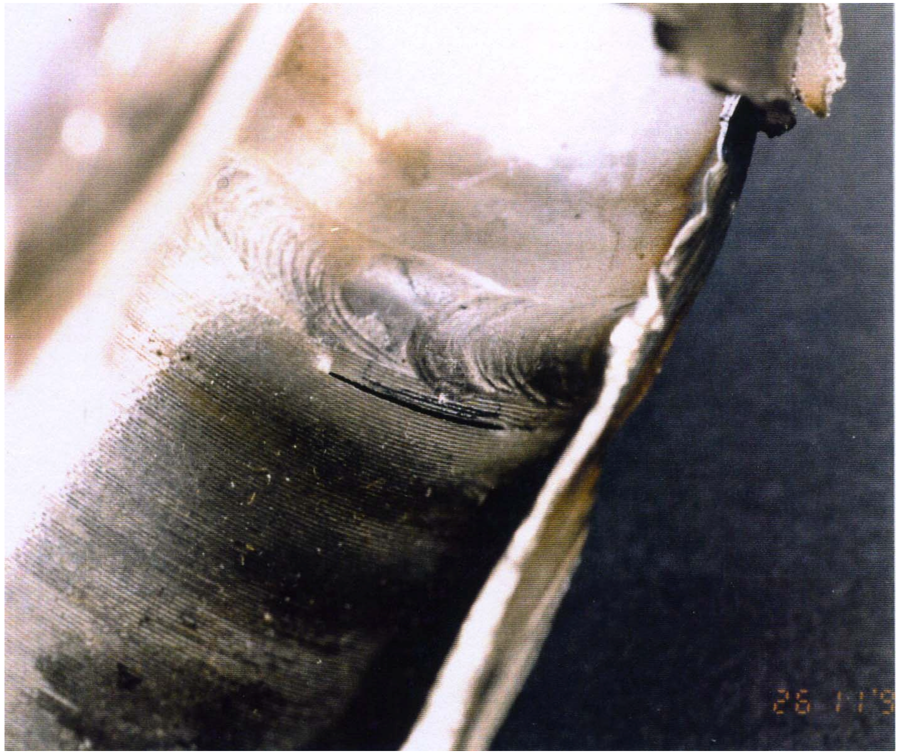
VIOLENT RUPTURE
OF A HYDROGEN STORAGE VESSEL

5.1. H_2 REPORTED ACCIDENTS





H2 VESSEL. HYDROGEN CRACK ON STAINLESS STEEL PIPING

5.2. COMPOSITE CYLINDERS

AIR LIQUIDE

No real experience of accidents because this is new types of cylinders, but :

- **For metallic liner, see 5.1**
- **For fiber and matrix risk of :**
  - **- Delamination**
  - **- Resistance to fire**
  - **- Resistance to impact**
  - **- « Blistering » for plastic liner**
  - **- Leak and/or permeation for plastic liner**

- **Cylinders used to transport gases :**
  - **The Transportable Pressure Equipment Directive (TPED) which relies on the ADR/RID and the standards**
  - **At international level, a similar regulation is being prepared by the United Nations (ISO standards)**

6. TESTS APPROVAL & REGULATION

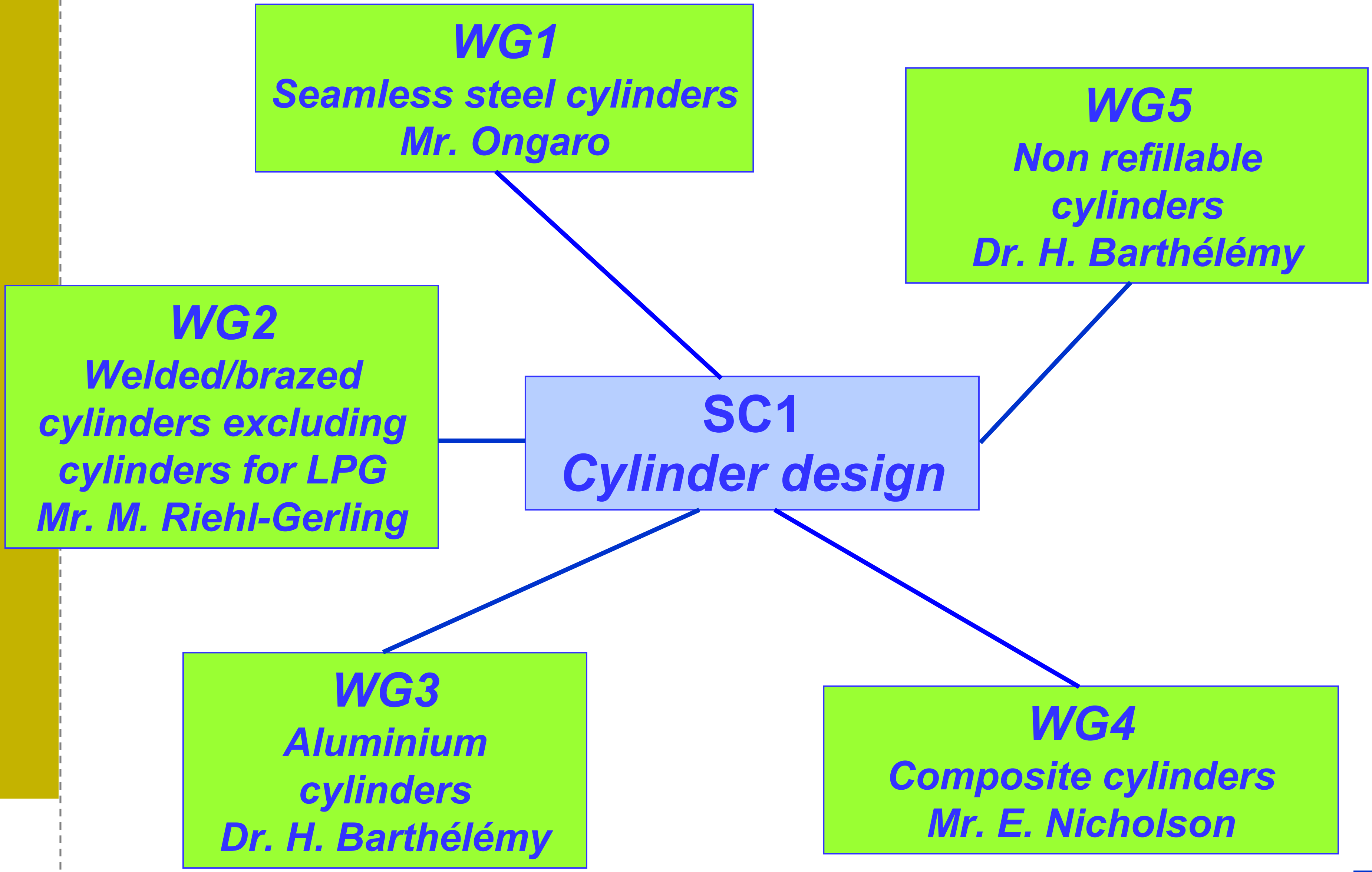
AIR LIQUIDE

- Hydrogen stations :
  - The Pressure Equipment Directive (PED) in Europe
  - ASME code in North America
- Hydrogen tanks used on vehicles (no yet any regulation in place, the exemption often based on ISO TC 197 (ISO DIS 15869)

AIR LIQUIDE

STRUCTURE CEN/TC 23 – Gas cylinders
Dr. C. Jubb

- **SC1**
  Cylinders design
  Dr. R. Irani
- **SC2**
  Fittings
  Dr. H. Barthélémy
- **SC3**
  Operational requirements
  Mr. K. Markhoff


WG1
Seamless steel cylinders
Mr. Ongaro
WG5
Non refillable cylinders
Dr. H. Barthélémy
WG2
Welded/brazed cylinders excluding cylinders for LPG
Mr. M. Riehl-Gerling
SC1
Cylinder design
WG3
Aluminium cylinders
Dr. H. Barthélémy
WG4
Composite cylinders
Mr. E. Nicholson

6. TESTS APPROVAL & REGULATION

AIR LIQUIDE

WG1
Filling conditions
Dr. Karl

WG5
Manifold receptacles
Mr. P. Thomas

SC3
Operational requirements

WG2
Inspection and periodic testing
Dr. R. Irani

WG3
Identification of cylinders and contents
Dr. H. Barthélémy

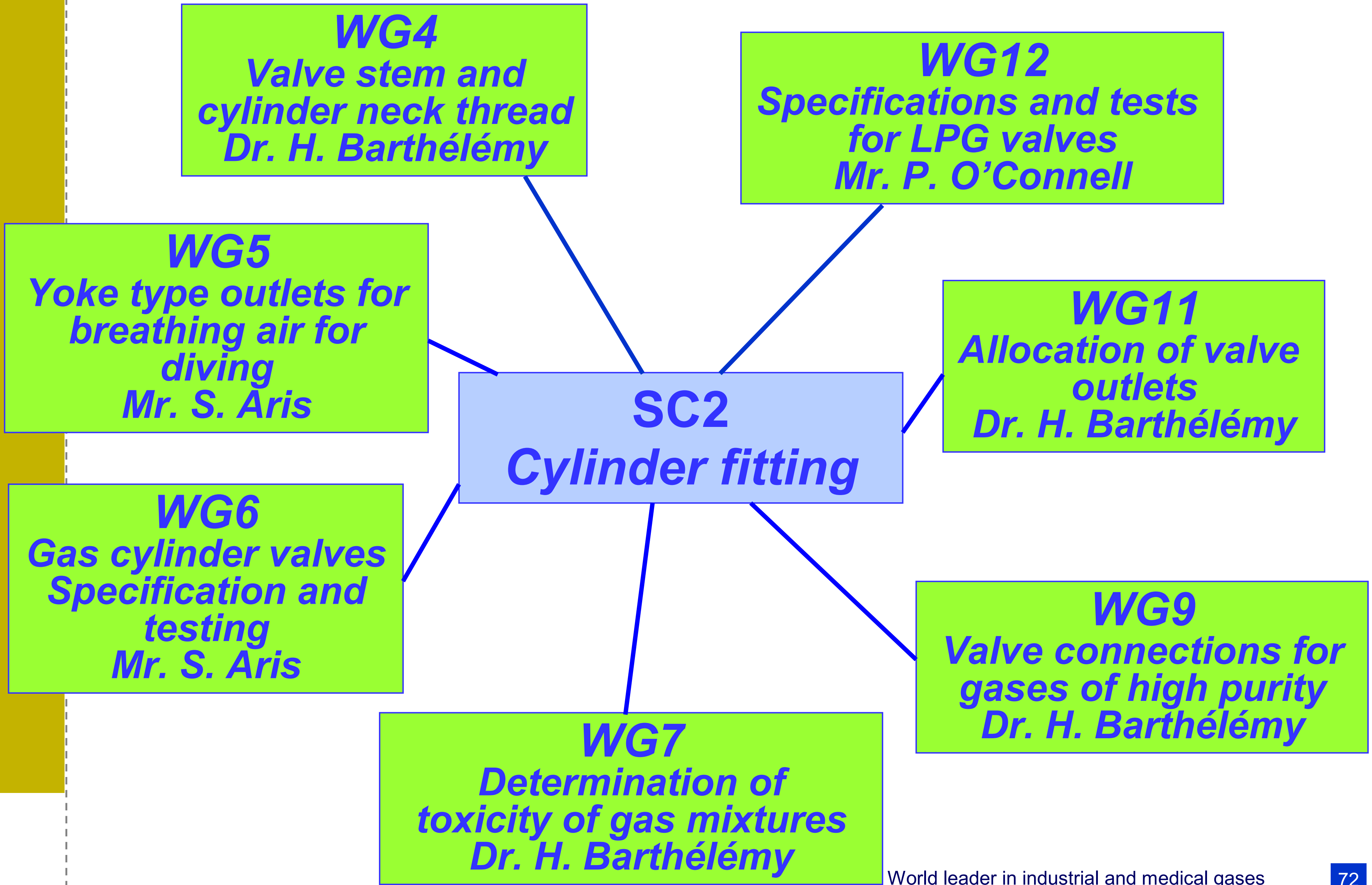
AIR LIQUIDE

STRUCTURE ISO/TC 58 – Gas cylinders
Dr. C. Jubb

- **WG7** – Compatibility between gases and materials – Dr. H. Barthélémy
- **WG10** – Fitting of valves to gas cylinders – Dr. H. Barthélémy
- **SC2** – Cylinders fittings – Dr. H. Barthélémy
- **SC3** – Cylinder design – Dr. W. Hepples
- **SC4** – Operational requirements – Mr. R. Smith

6. TESTS APPROVAL & REGULATION

AIR LIQUIDE



6. TESTS APPROVAL & REGULATION

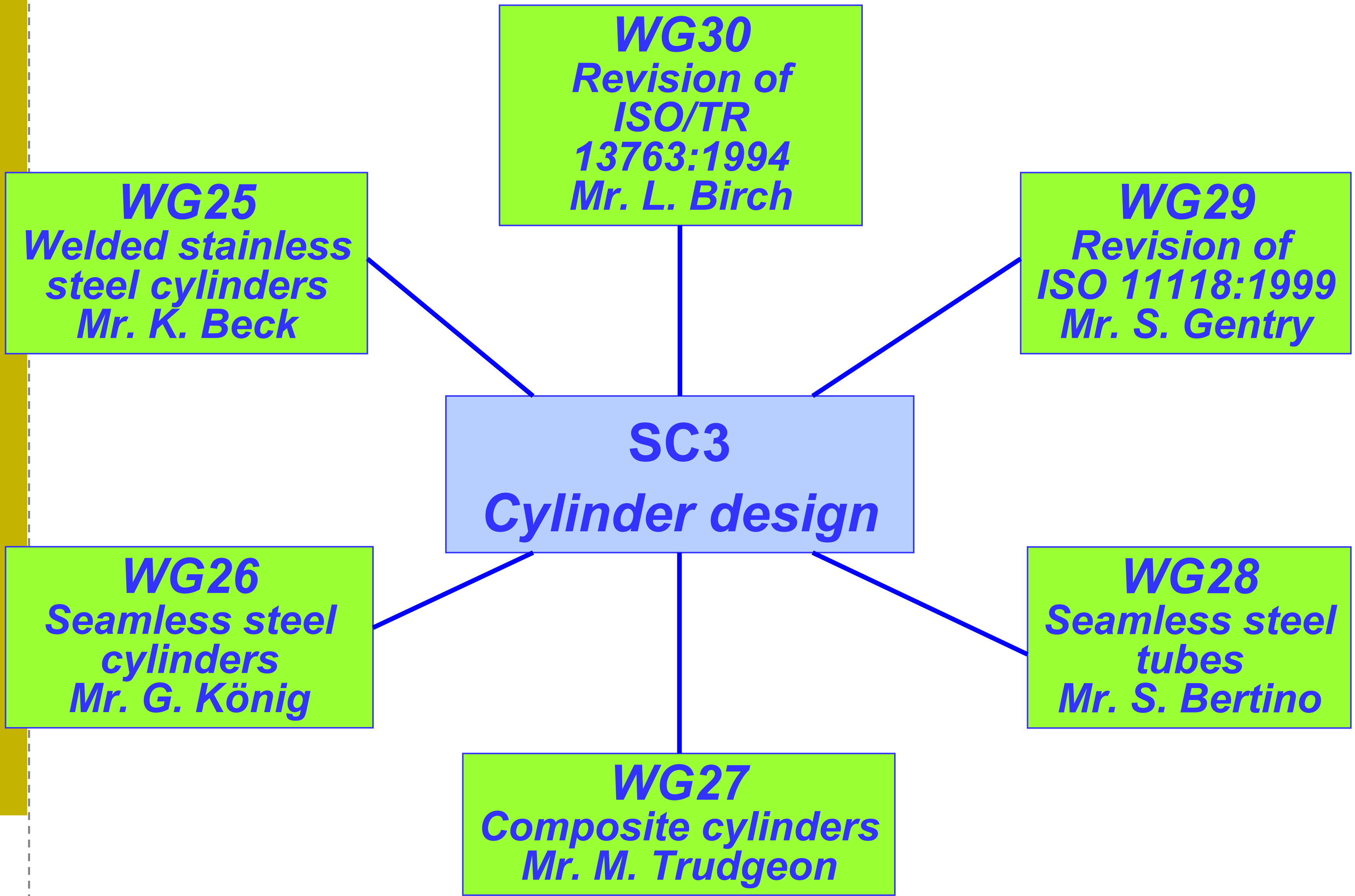
AIR LIQUIDE

SC3
Cylinder design

- **WG17** – Compressed natural gas cylinders for road vehicles – Mr. C. Webster
- **WG24** – Factory of safety for composite cylinders – Mr. N. Newhouse
- **WG18** – Welded aluminium alloy cylinders – Dr. H. Barthélémy
- **WG23** – Welded steel pressure drums – Mr. A. Fouet
- **WG19** – Test methods on fracture performance for high strength aluminium – Mr. L. Birch
- **WG21** – Refillable welded steel gas cylinders – Mr. S. Gentry

6. TESTS APPROVAL & REGULATION

AIR LIQUIDE



6. TESTS APPROVAL & REGULATION

AIR LIQUIDE

SC4
Operational requirements

WG1
Rejection criteria for Materials gas cylinders
Dr. R. Irani

WG8
Bundles
Mr. K. Markhoff

WG2
Acoustic emission
Dr. H. Barthélémy

WG7
Valve removal
Dr. W. Dörner

WG6
Cylinder identification
Dr. H. Barthélémy

AIR LIQUIDE

LIST OF DESIGN STANDARDS

SEAMLESS STEEL

EN ISO 9809 : 1999

Seamless steel

Part 1 : with tensile strength < 1 100 MPa

Part 2 : with tensile strength > or equal to 1 100 MPa

Part 3 : Normalized steel cylinders

Part 4 : with a R_m value of < 1 100 MPa

LIST OF DESIGN STANDARDS

SEAMLESS ALUMINIUM

EN ISO 7866 : 1999 — Seamless aluminium Design, construction and testing

WELDED STEEL

ISO 4706 : 1989 — Welded steel

Part 1 : Test pressure 60 bar and below

Part 2 : Test pressure > 60 bar

LIST OF DESIGN STANDARDS

WELDED STAINLESS STEEL

ISO FDIS 18172	Welded stainless steel Part 1 : Test pressure 6 MPa and below Part 2 : Test pressure > 6 MPa

WELDED ALUMINIUM

ISO 20703 : 2006	Welded aluminium Design, construction and testing

LIST OF DESIGN STANDARDS

COMPOSITE

ISO 11119 : 2002 Composite

Part 1 : Hoop wrapped

Part 2 : Fully wrapped fibre reinforced composite gas Cylinders with load-sharing metal liners

Part 3 : Fully wrapped fibre reinforced composite gas cylinders with non load-sharing metallic or non-metallic liners

AIR LIQUIDE

LIST OF DESIGN STANDARDS

NON-REFILLABLE

ISO 11118 : 1999
Non-refillable
Specification and test methods

LIST OF DESIGN STANDARDS

TUBES

ISO 11120 : 1999	Refillable seamless steel Design construction and testing

LIST OF DESIGN STANDARDS

DRUMS

ISO/CD 21172 — **Part 1 : Capacities up to 1 000 liters**

Part 2 : Capacities up to 3 000 liters

AIR LIQUIDE

LIST OF DESIGN STANDARDS

VEHICLE TANKS

ISO 11439 : 2000	High pressure cylinders for the on-board storage of natural gas as a fuel for automative vehicles

ISO/DIS 15869	Hydrogen vehicle tanks

7. NEW TRENDS DUE TO HYDROGEN ENERGY

Consumption (Nm^3/h)	Type of supply
< 100 Nm^3/h	200 or 300 bar cylinders
From 1 to several hundreds Nm^3/h	200 or 300 bar trailers - 20 K Liquid tank – small on site production (electrolyser/ reforming etc…)
A few thousands Nm^3/h	Pipelines – on-site production

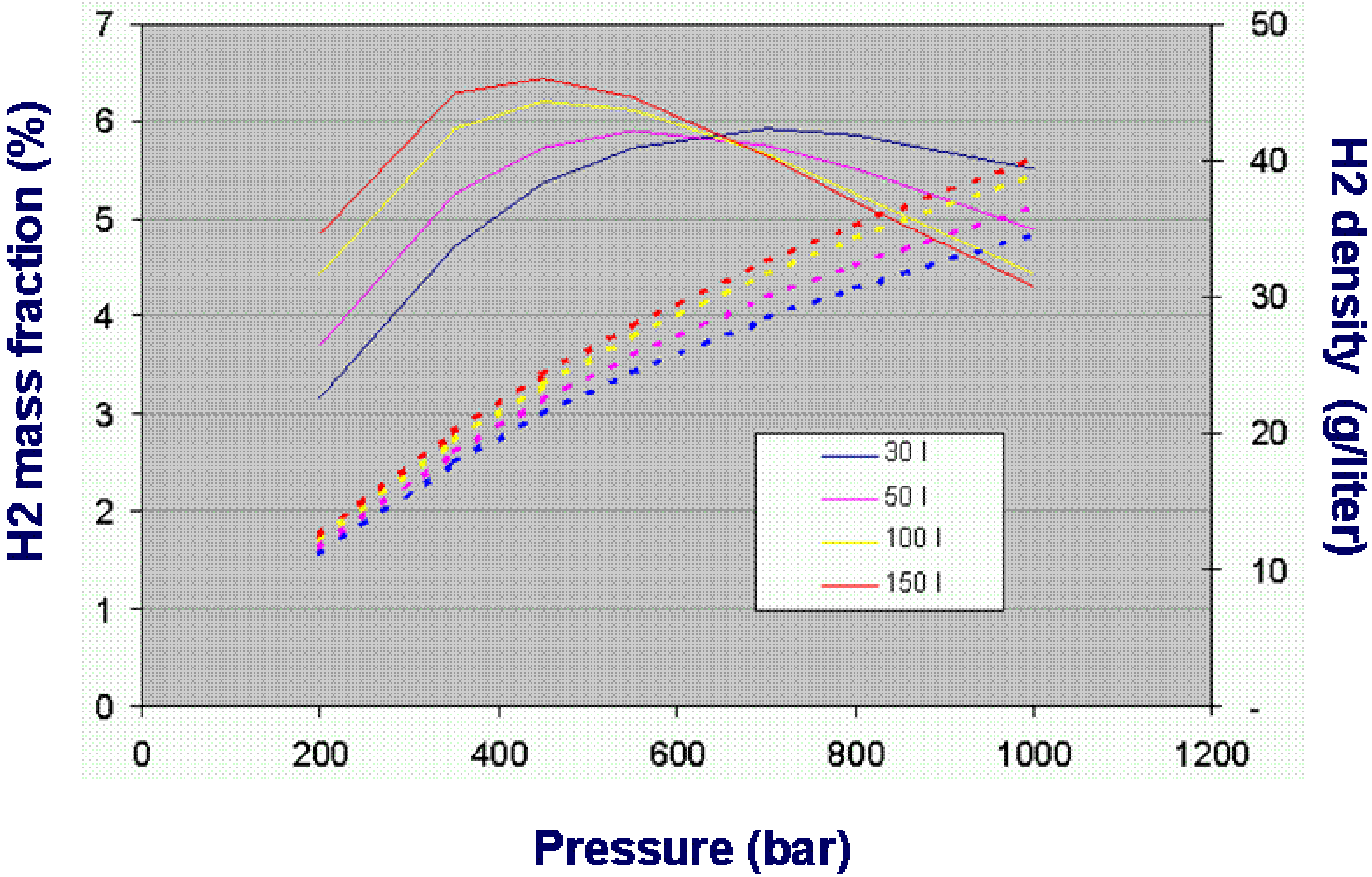
Industrial hydrogen conventional delivery in 2006

7. NEW TRENDS DUE TO HYDROGEN ENERGY

AIR LIQUIDE

- Compared to industrial gas, hydrogen energy has brought new constraints :
  - Fuel for transportation : weight and volume savings
  - Stationary applications (back-up power supply or power generator for residential) : cost
  - Portable applications (computers, mobile phone, etc…) : weight and volume savings

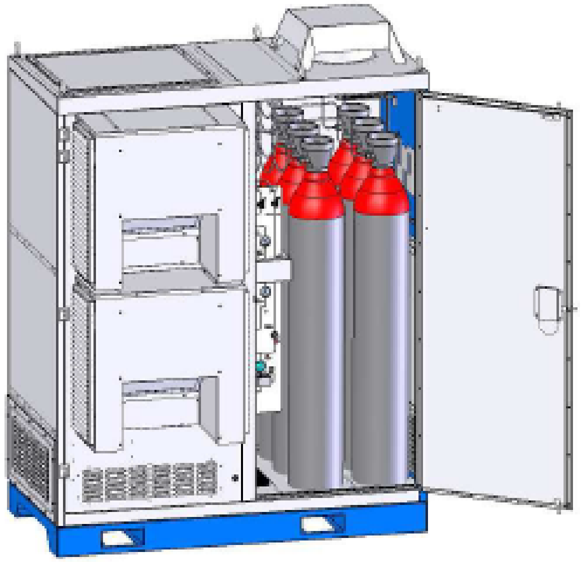
7. NEW TRENDS DUE TO HYDROGEN ENERGY



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)

7. NEW TRENDS DUE TO HYDROGEN ENERGY



Stationary fuel cell power supply equipped with conventional 200 bar type I vessels (Axane technology)

7. NEW TRENDS DUE TO HYDROGEN ENERGY

AIR LIQUIDE

Fast filling station with type II buffers

7. NEW TRENDS DUE TO HYDROGEN ENERGY

AIR LIQUIDE

	2005	2010	2015
System gravimetric density (kWh/kg) (% wt)	1,5 4,5	2 6	3 9
System volumetric density (kWh/kg) kgH_2/100 l)	1,2 3,6	1,5 4,5	2,7 8,1

DoE requirements for transportation

8. CONCLUSION

AIR LIQUIDE

	Technology mature	Cost performance	Weight performance
Type I	++ *Pressure limited to 300 bar (⇒ density : –)*	++	–
Type II	+ *Pressure not limited (⇒ density : +)*	+	0
Type III	For P ≤ 350 bar; *(700 bar under development)*	–	+
Type IV	For P ≤ 350 bar; *(700 bar under development)*	–	+

Main features for H_2 pressure vessel types in 2006