UNIVERSITÀ DEGLI STUDI DI TRIESTE

Dipartimento di Ingegneria e Architettura

HYDROGEN STORAGE

– PART 1 –

LIQUID HYDROGEN STORAGE

Prof. Marco Bogar

A.A. 2023-2024

OUTLINE

1. Hydrogen Storage
2. Liquid Hydrogen Storage

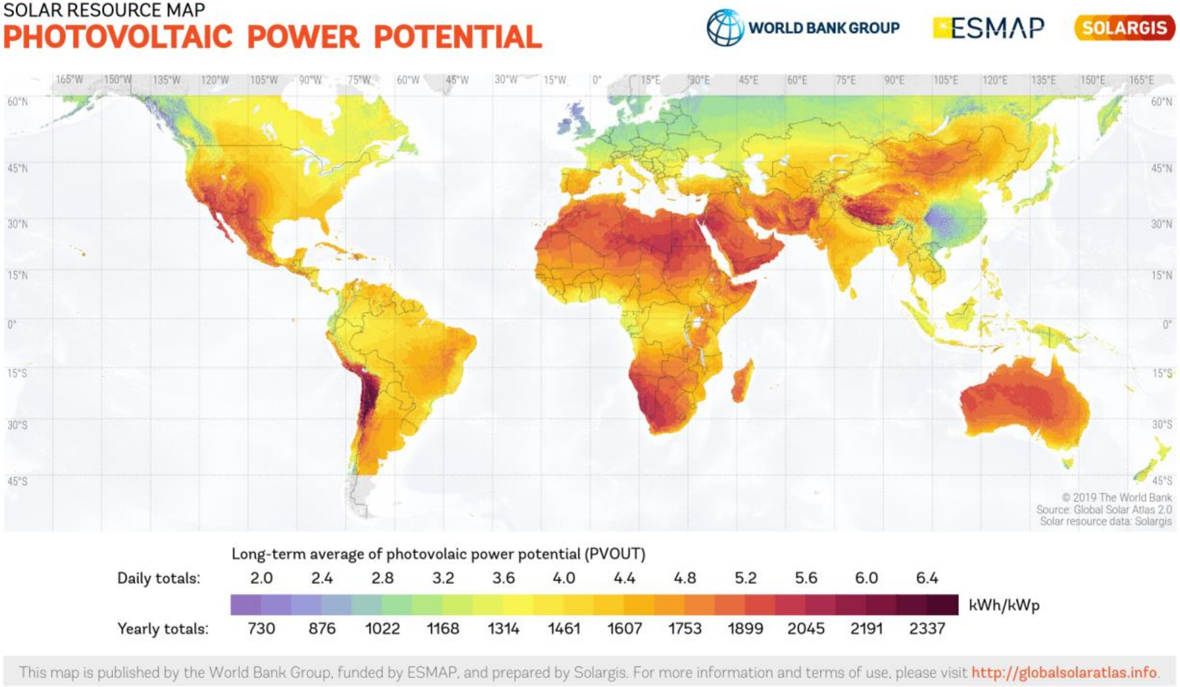
BIBLIOGRAPHY

Reference	Paragraph/Pages
Hydrogen production by electrolysis, Agata Godula-Jopek, 2015 Wiley	Ch. 7

Insights	
R1	Epelle E. et al., Perspectives and prospects of underground hydrogen storage and natural hydrogen, Sustainable Energy Fuels, 2022, 6, 3324; https://doi.org/10.1039/D2SE00618A
R2	Barthelemy H., Hydrogen storage: Recent improvements and industrial perspectives, Internatioanal Journal of Hydrogen Energy, 37, (2012), 17364 – 17372; DOI: http://dx.doi.org/10.1016/j.ijhydene.2012.04.121
R3	Barthelemy H. et al., Hydrogen storage: Recent improvements and industrial perspectives, Internatioanal Journal of Hydrogen Energy, 42, (2017), 7254 – 7262; DOI: http://dx.doi.org/10.1016/j.ijhydene.2016.03.178
R4	Del-Pozo A. et al., Current Trends and Future Developments on (Bio-) Membranes, ch.6: A general overview of hydrogen embrittlement, Elsevier (2020), 139–168; DOI: https://doi.org/10.1016/B978-0-12-818332-8.00006-5
R5	Koyama M., et al., Recent progress in microstructural hydrogen mapping in steels: Quantification, kinetic analysis, and multi-scale characterization, Materials Science and Technology. 2017;33(13):1481-1496, DOI: http://dx.doi.org/10.1080/02670836.2017.129927
R6	Ratankar R.R. et al., Effective thermal conductivity of insulation materials for cryogenic LH2 storage tanks: A review, 48, 21, (2023), 7770 – 7793; DOI: https://doi.org/10.1016/j.ijhydene.2022.11.130

1. HYDROGEN STORAGE

HYDROGEN STORAGE



SOLAR RESOURCE MAP

PHOTOVOLTAIC POWER POTENTIAL

© 2019 The World Bank
Source: Global Solar Atlas 2.0
Solar resource data: Solargis

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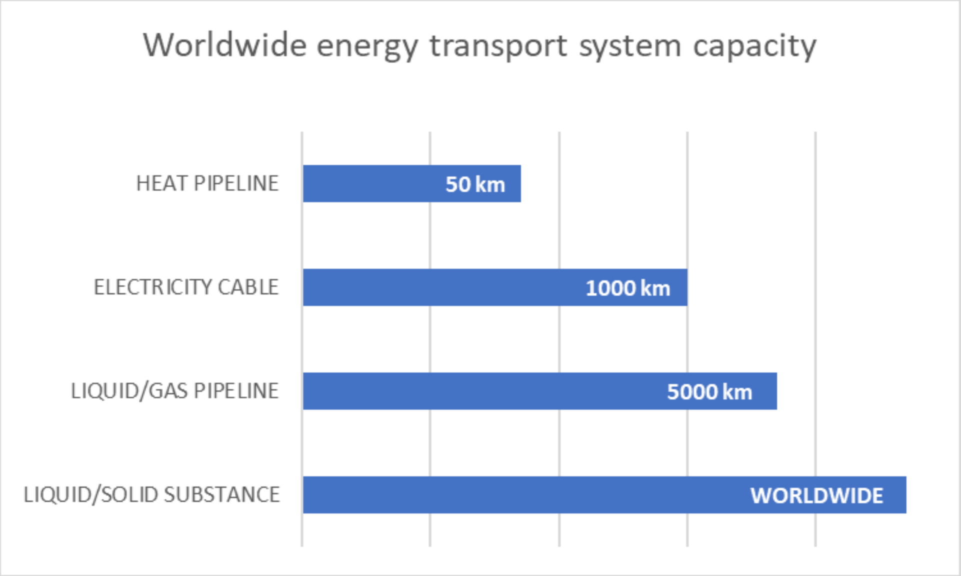
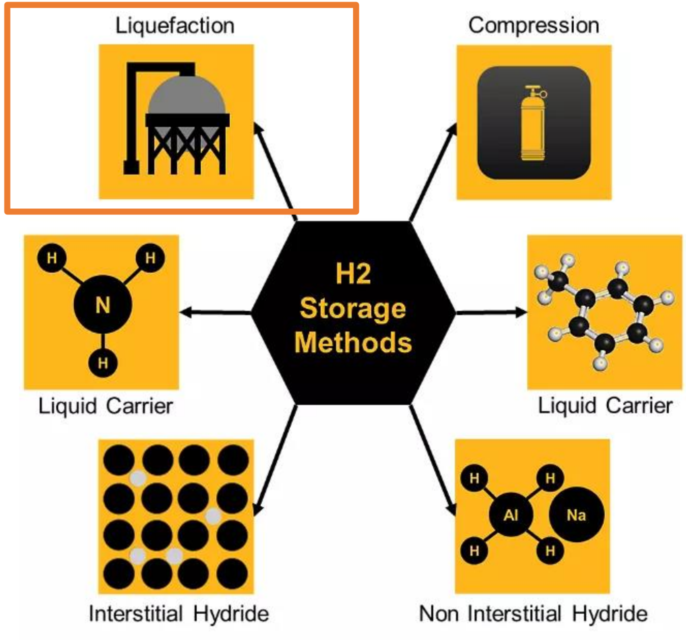
HYDROGEN STORAGE



HYDROGEN STORAGE METHODS

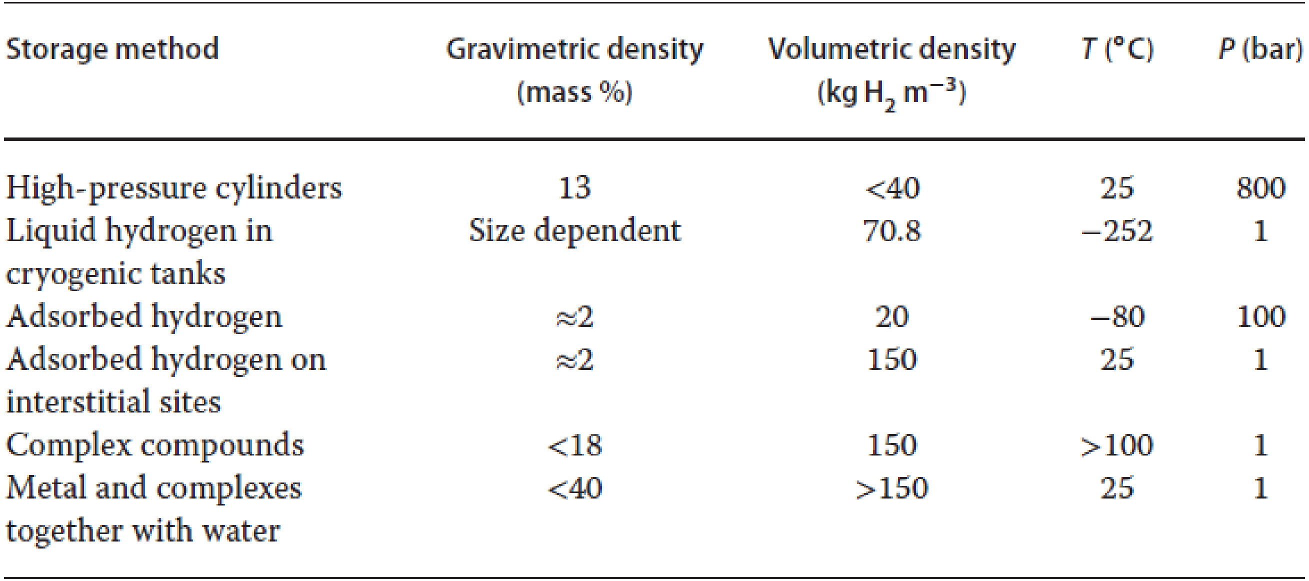


https://wildeanalysis.co.uk/resource/time-right-for-hydrogen/

- high-pressure, compressed in gas cylinders
- liquid, in hydrogen in cryogenic tanks
- adsorbed, on materials with a large specific surface area
- adsorbed, on interstitial sites in a host metal
- chemically bonded, in covalent and ionic compounds
- through oxidation of reactive metals

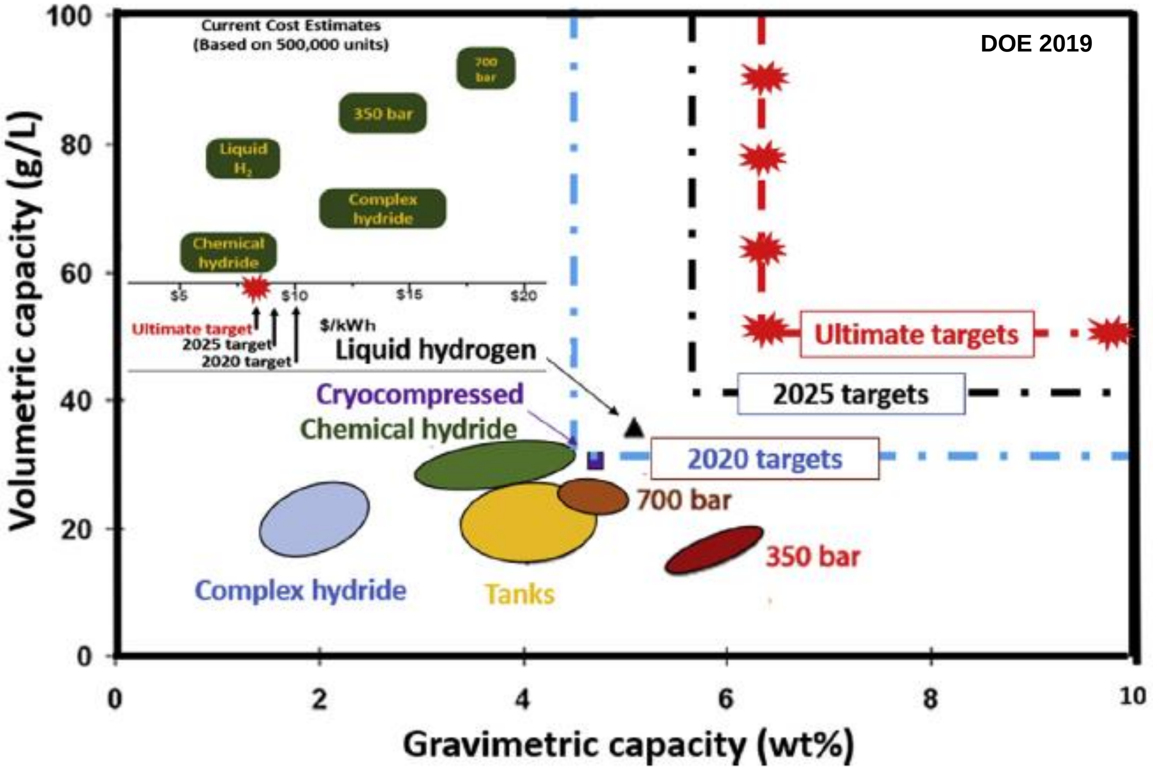
HYDROGEN STORAGE

Hydrogen volumetric density in standard conditions: 0.083 kg m^{-3}



Storage method	Gravimetric density (mass %)	Volumetric density (kg H_2 m^{-3})	T (°C)	P (bar)
High-pressure cylinders	13	<40	25	800
Liquid hydrogen in cryogenic tanks	Size dependent	70.8	−252	1
Adsorbed hydrogen	≈2	20	−80	100
Adsorbed hydrogen on interstitial sites	≈2	150	25	1
Complex compounds	<18	150	>100	1
Metal and complexes together with water	<40	>150	25	1

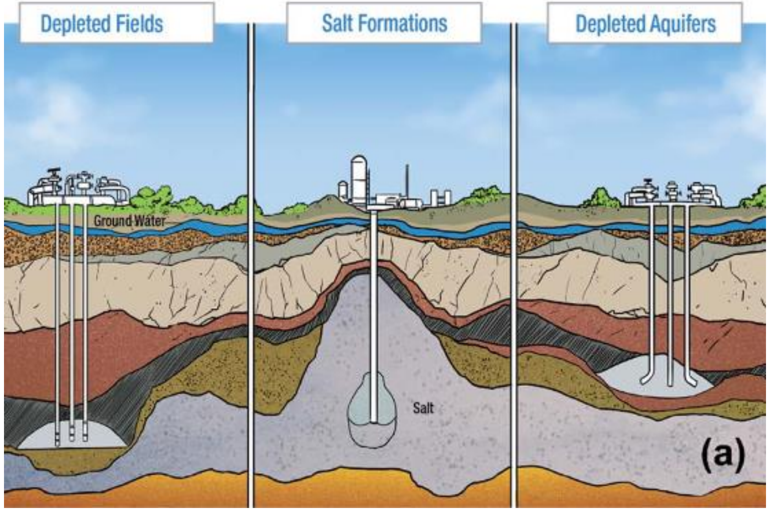
HYDROGEN STORAGE

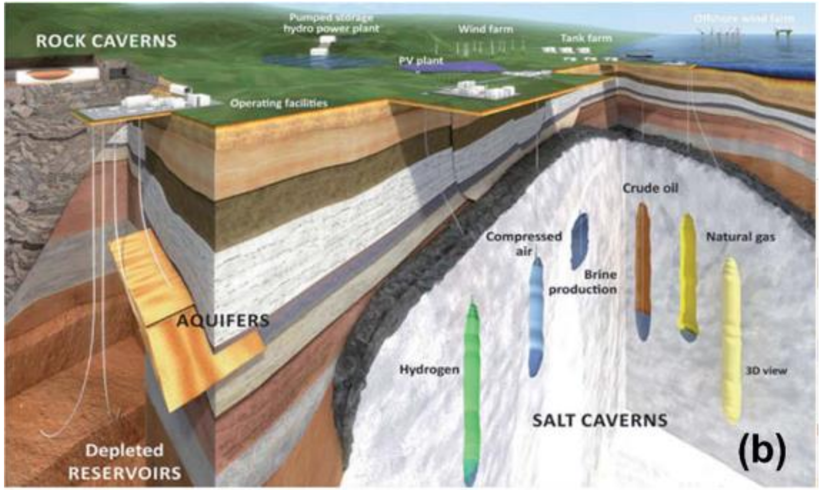


E. Boateng, A. Chen / Materials Today Advances 6 (2020) 100022

UNDERGROUND HYDROGEN STORAGE

Underground hydrogen storage is a promising route to addressing the demand-supply gap caused by the characteristic fluctuations of renewable energies.





UNDERGROUND HYDROGEN STORAGE

Underground hydrogen storage is attractive because characterized by:

- Good gas tightness
- High wall (sealing) thicknesses compared to tanks for conventional storage
- Extensive subsurface depths, which can minimize the risks posed to safety
- It is a mature technology, already used for storing natural gas and carbon dioxide in carbon capture and storage systems.
- Safe way of storage, as limits the hydrogen contact with atmospheric oxygen
- Long-term storage is guaranteed (estimated: 40 ÷ 50 years, pressurized at over than 200 bar)
- High energy storage density (up to 250 Wh L^{-1}).

UNDERGROUND HYDROGEN STORAGE

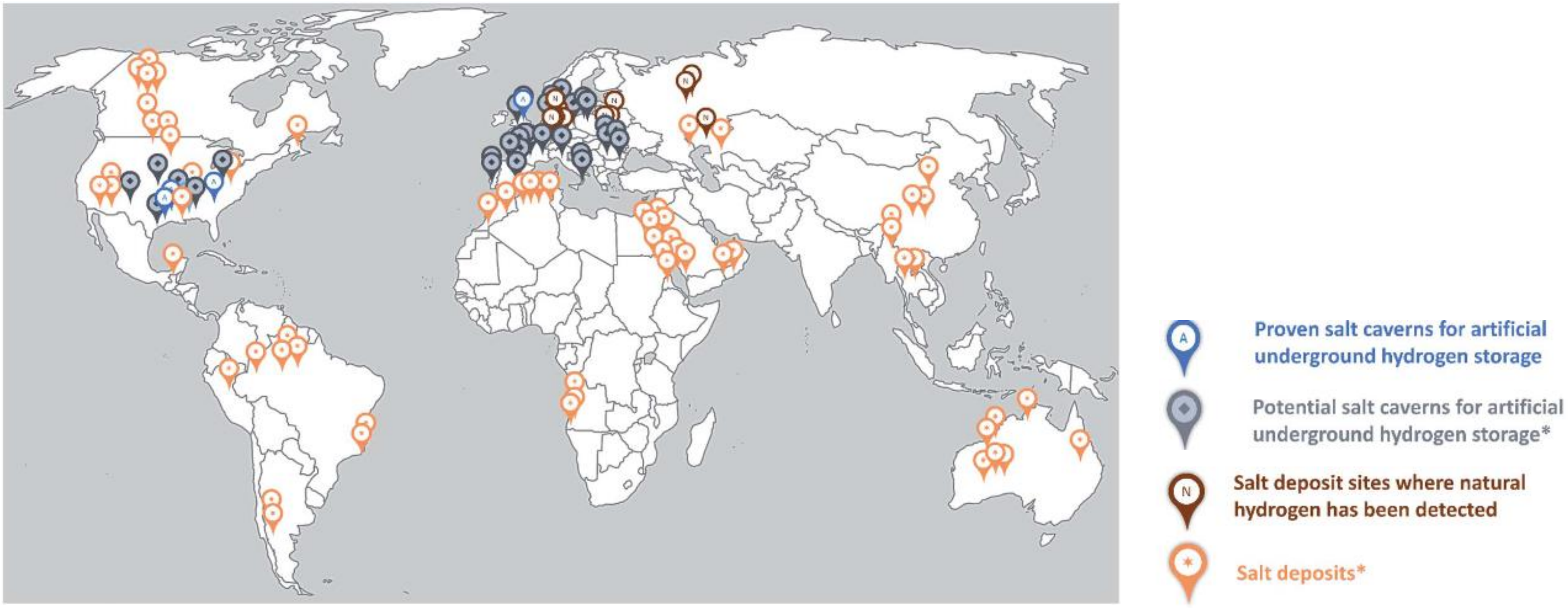
Nonetheless some aspects are still unclear, as:

- Interaction of hydrogen with rock/salt walls are not known (is gas poisoning possible due to unknown reactions? Do walls embrittle in long term storage? Can hydrogen-consuming reactions take place?)
- Can eventual residuals or rock materials poison hydrogen? (in this extent presence of sulphur should be avoided)
- Effects of frequent hydrogen withdraw (way of use not common for actual technology)
- Risks of hydrogen leak and dispersion in atmosphere (what might it happen if the concentration of dissolved hydrogen in the atmosphere would largely increase?)
- Technological maturity needs to be adapted to hydrogen (in example in terms of the equipment to be employed, as well as to the characteristics of the cushion gas to be used)

Some useful insights might arrive form the analysis of natural hydrogen cavities

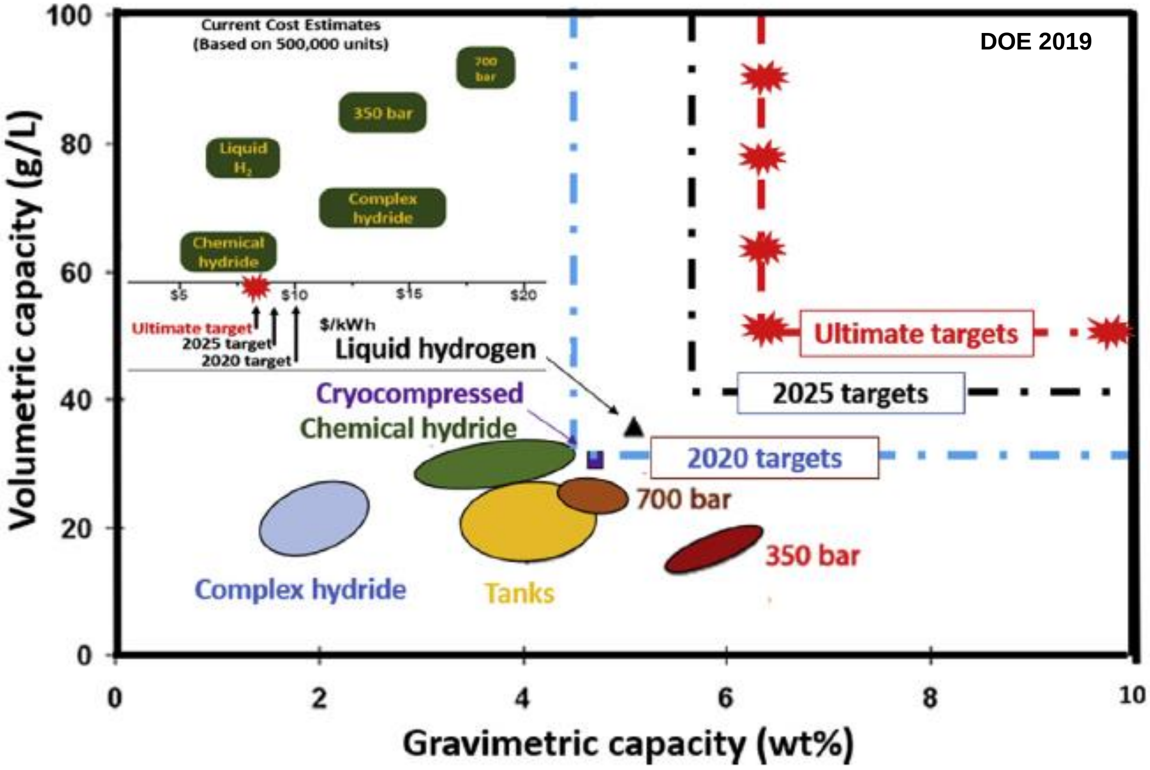
UNDERGROUND HYDROGEN STORAGE

R.1



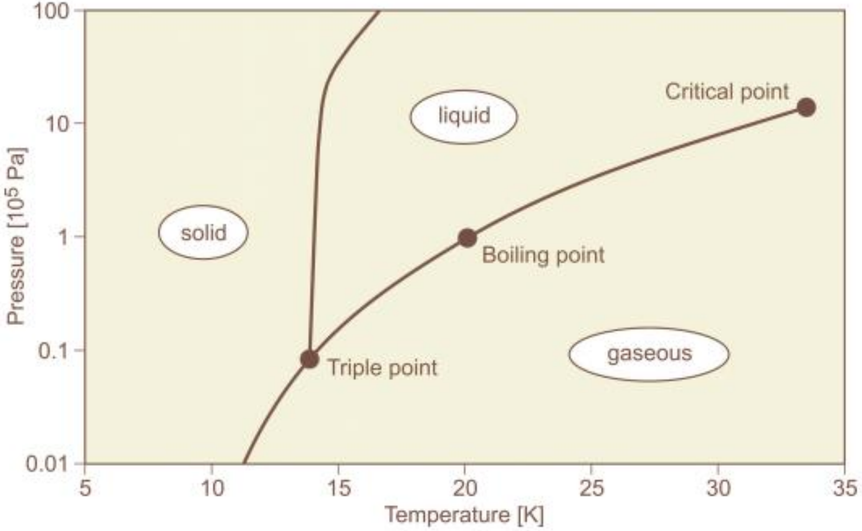
2. LIQUID HYDROGEN STORAGE

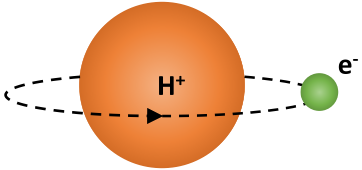
OVERVIEW



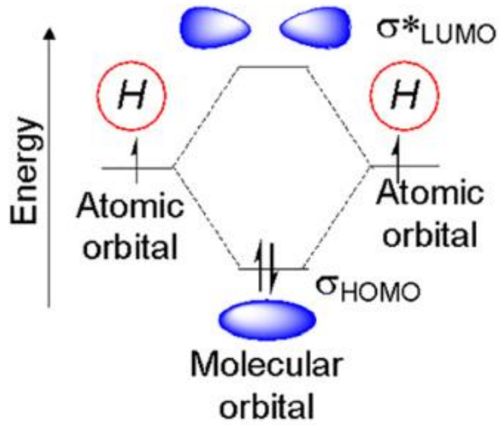
E. Boateng, A. Chen / Materials Today Advances 6 (2020) 100022

HYDROGEN PROPERTIES





$$s = (\pm)\frac{1}{2}$$



Luscombe C.K., Chemistry Teacher International 2021; 3(2): 169–183

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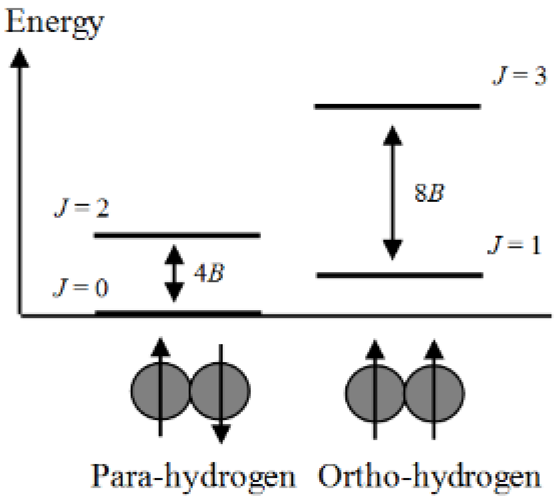
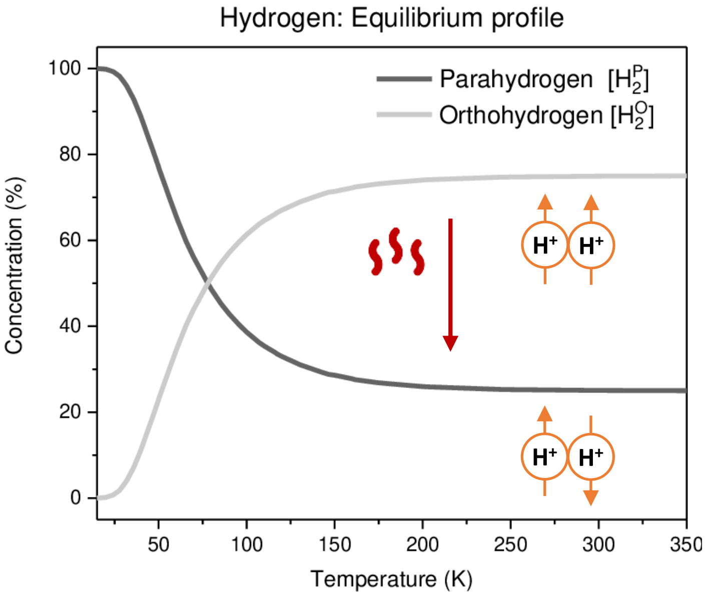


http://jascoinc.com/docs/application-notes/Determination%20of%20ortho%20and%20para%20hydrogen%20ratio%20by%20using%20Raman%20spectroscopy%201112.pdf

Hydrogen form	Spin number, s	Rotational energy level, J
o-H_2	1	1
p-H_2	0	0

- The *ortho*-hydrogen is the molecule characterized by the higher energy level
- Temperature defines the ratio among ortho-to-para-hydrogen concentration within the gas.

HYDROGEN PROPERTIES

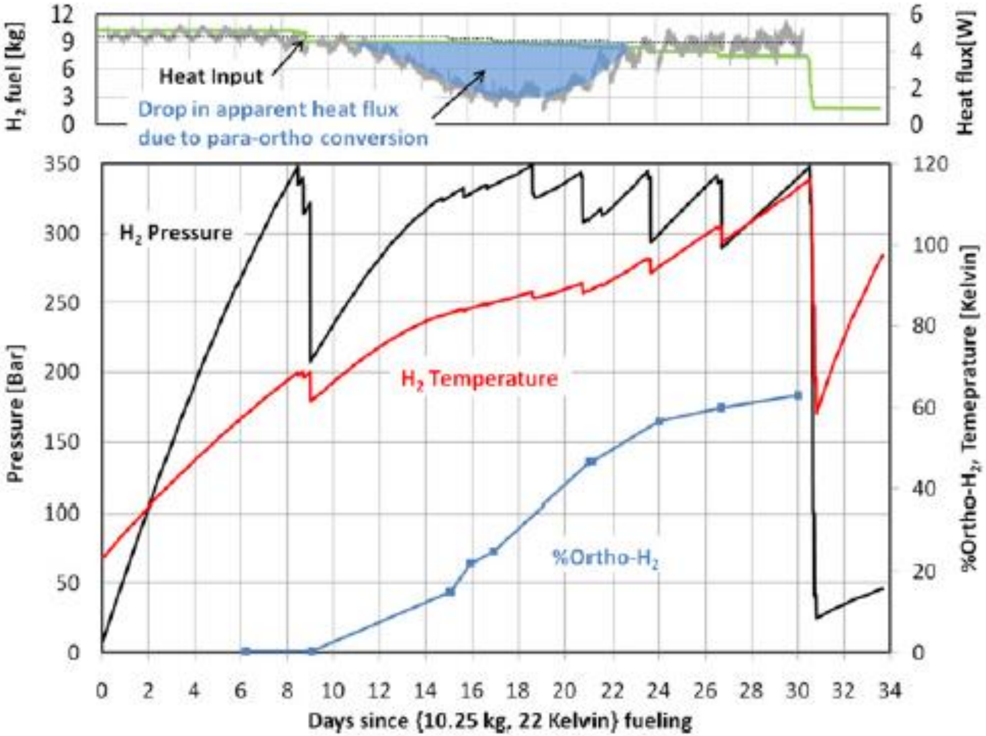


Karlsson, E. (2017). Catalytic ortho- to parahydrogen conversion in liquid hydrogen.

For liquid hydrogen storage ortho-to-para conversion is one of the main aspects limiting the storage time of hydrogen: in fact, the conversion from ortho- to para-hydrogen is exothermic and inversely proportional to temperature.

T (K)	Heat of conversion (kJ/kg)
300	270
77	519
< 77	523

LIQUID HYDROGEN STORAGE – PRESSURE LOADING EVALUATION



Acevas S.M., et al., International journal of hydrogen energy , 38, (2013), 2480 – 2489

Month-long dormancy experiment of a 10 kg tank 96% full with saturated LH2 at 2 bar.

Losses can be observed already after one week of inactivity. Long periods of inactivity can thus lead to loss of fuel from the tank.

Within the same experiment it was shown as driving about 8 km/day (that is extracting about 2.5 kg of H_2 in one month), helps in avoiding evaporative losses, due to the fact that hydrogen extraction induces isentropic expansion, helping in further cooling down the reservoir.

HYDROGEN EMBRITTLEMENT

Hydrogen embrittlement constitutes one of the main problems in materials in contact with hydrogen. It consists in a premature crack of the steel due to hydrogen atom dissolution and trap in the material crystallites.

In hydrogen embrittlement, the hydrogen enters through the process of diffusion in the grain boundaries and combines with the carbon found in the alloy with iron, which generates the formation of methane gas. Due to the formation of methane gas, a huge increase in pressure is generated, which reduces ductility and strength, and promotes the initiation of the cracks.

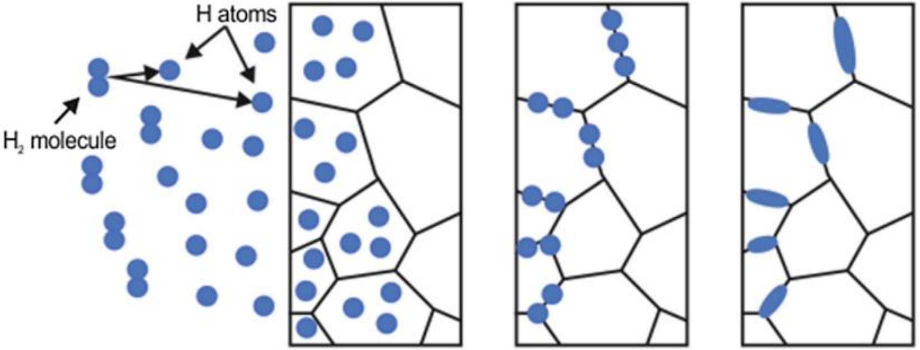


Figure 6.6 Absorbed hydrogen atoms by carbon steel alloys.

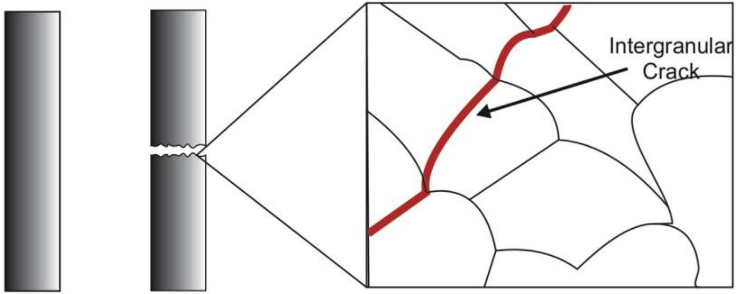


Figure 6.7 Example of failure due to hydrogen embrittlement.

$$HE\ index = \alpha\, P^{-n}$$

HYDROGEN EMBRITTLEMENT

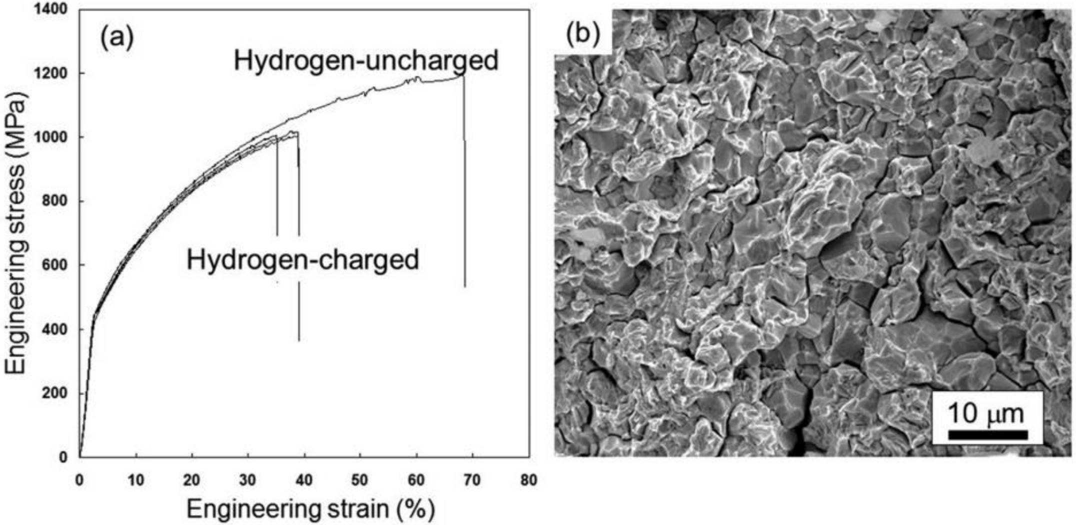


Fig. 2 – (a) Ductility degradation in a hydrogen-charged Fe-18Mn-0.6C TWIP steel. (b) Scanning electron micrograph showing an intergranularly fractured surface [24]. The initial strain rate is 5.1 × 10^{-5} s^{-1}. Alloy composition is in weight %. "Reproduced with permission from *Corros. Sci.*, 54, 1 (2012). Copyright 2011, Elsevier."

Koyama M. et al., Int. J. Hydr. En., 42, (2017), 12706–12723

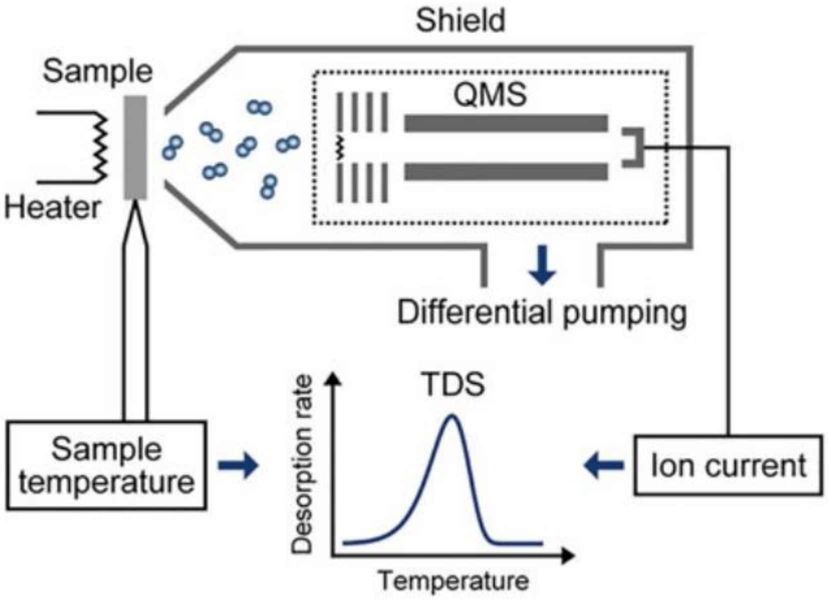
HYDROGEN EMBRITTLEMENT – DETECTION METHODS

At a research degree, to investigate the most proper materials to face hydrogen embrittlement, several techniques can be used to detect the presence of hydrogen inside materials. Three of them will be highlighted, able to measure different aspects of hydrogen absorption.

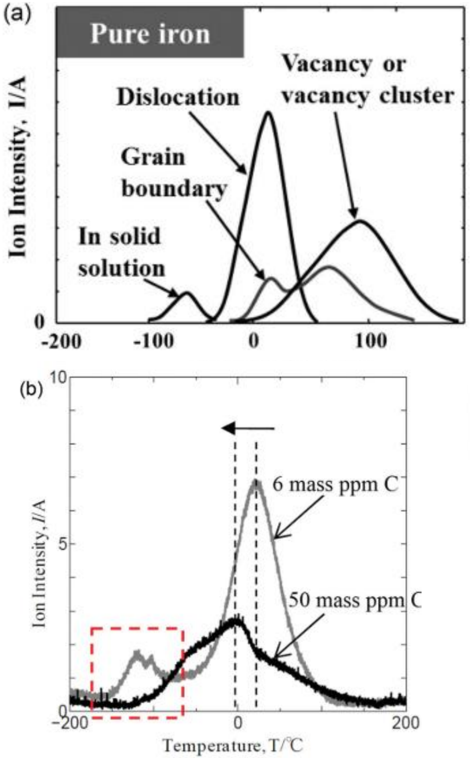
1. Thermal desorption spectroscopy

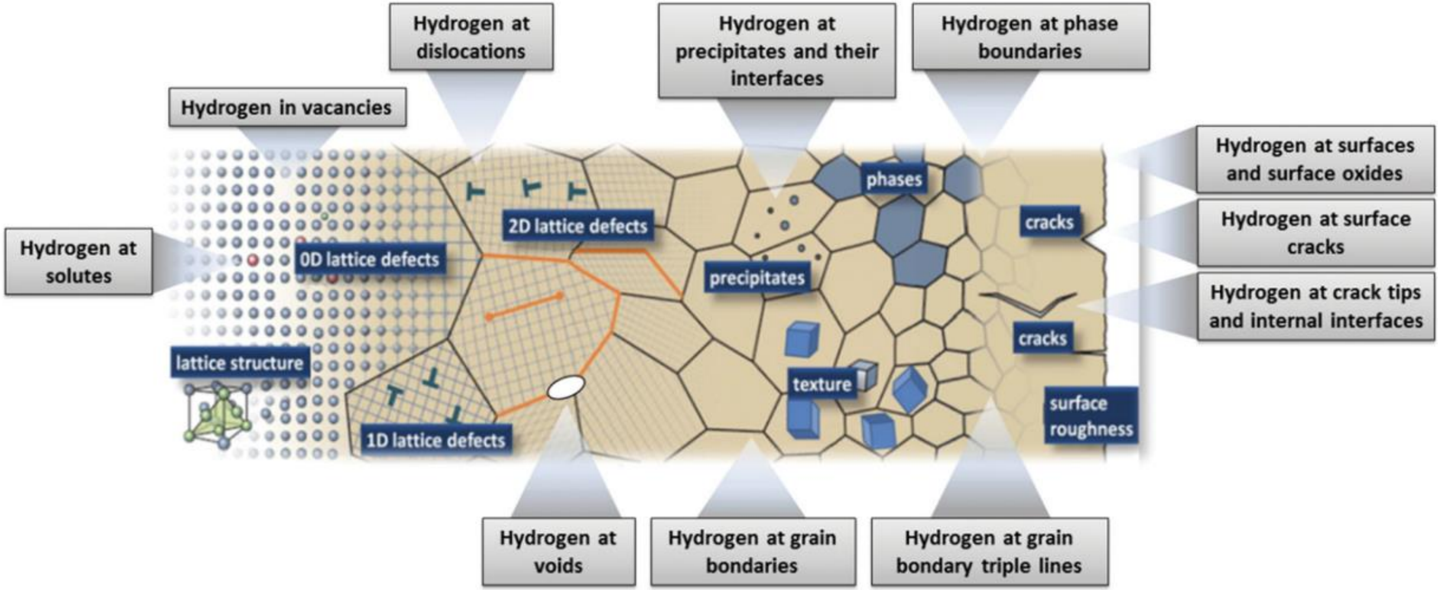
The material to be tested is inserted in a vacuum chamber. Material temperature is scanned: by increasing the temperature, molecules bound to the surface are released into vacuum and discriminated via a Quadruple Mass Spectrometer according to their mass-to-charge ratio (m/z).

Ogura, S., Fukutani, K. Thermal Desorption Spectroscopy. (2018). Springer.



HYDROGEN EMBRITTLEMENT – DETECTION METHODS

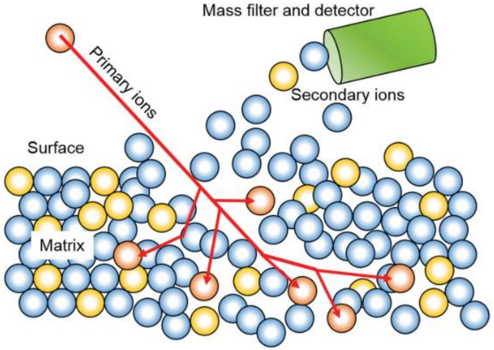


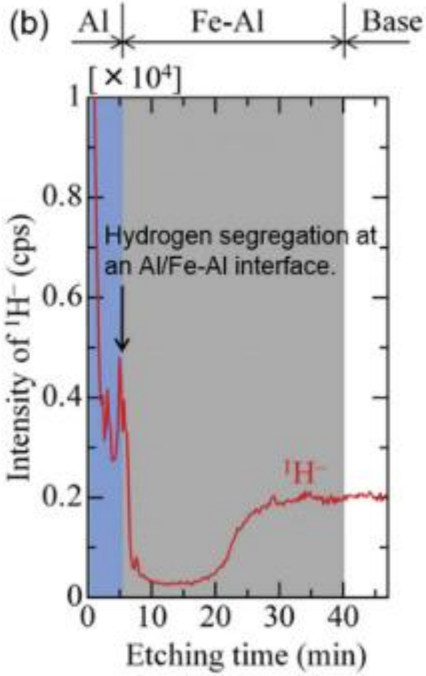


HYDROGEN EMBRITTLEMENT – DETECTION METHODS

2. Secondary ion mass spectroscopy

It is a surface sensitive chemical probing method which allows to perform both spatially-resolved as well as cross-sectional analysis. But results can be contaminated by: (i) hydrogen present on moisture or hydrocarbons deposited on the sample surface, (ii) background hydrogen in ion chamber since (hydrogen exists even under excellent ultra high vacuum conditions), (iii) diffusion and desorption of hydrogen during the measurement in steels, (iv) effects associated with sputter direction, crystallo- graphic texture and surface topology (also referred to as matrix effects).

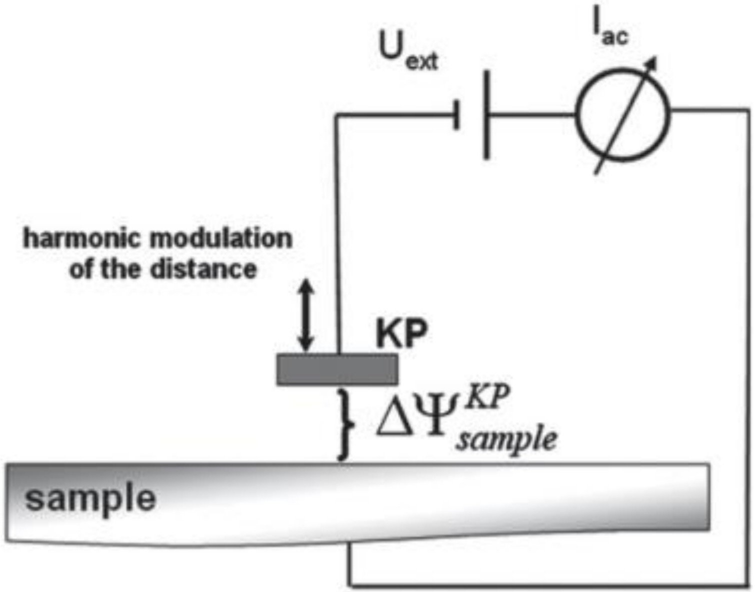




HYDROGEN EMBRITTLEMENT – DETECTION METHODS

3. Kelvin probe microscopy

It is a surface sensitive technique which constitutes in scanning the material surface and measuring the surface potential, which decreases when hydrogen atoms are embed in the structure. The main advantage relies in combining spatially-resolved and temporal-resolve analyses, allowing to monitor both adsorption and release.



HYDROGEN EMBRITTLEMENT – DETECTION METHODS

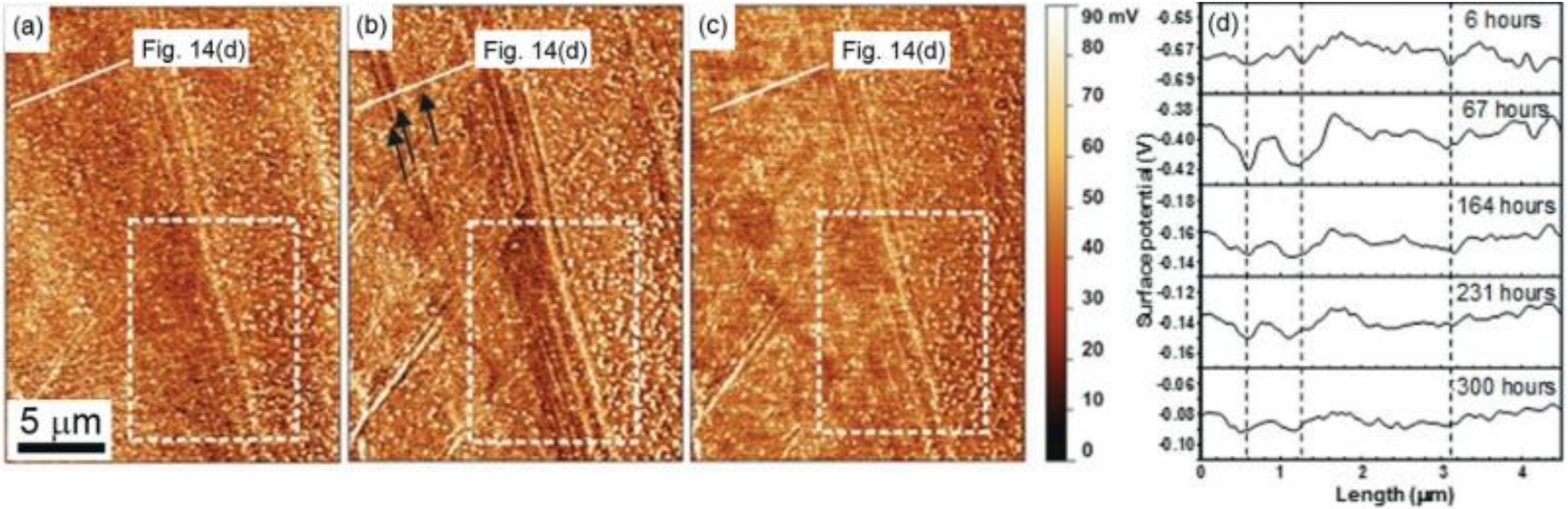
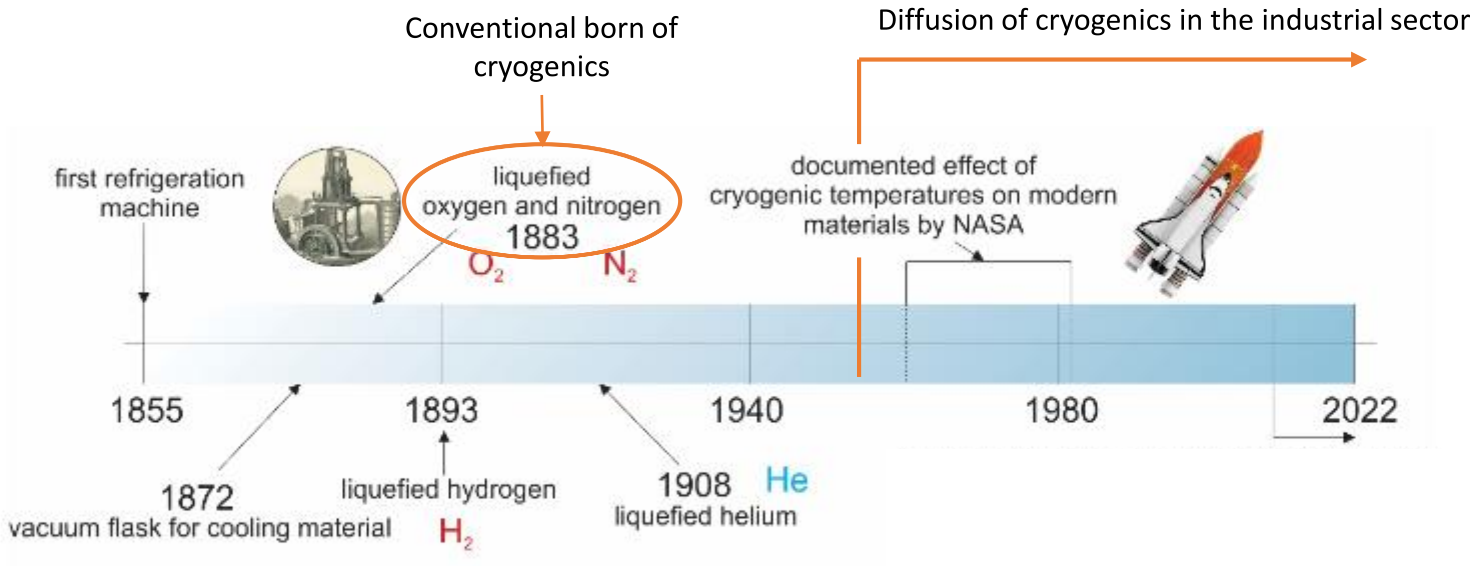


Figure 14. Time-dependent variation of the hydrogen distribution analysed by SKPFM in a Fe–18Mn–1.2C twinning-induced-plasticity steel (wt-%) covered with a palladium buffer layer [25]. Surface potential images taken at exposure times of (a) 6, (b) 67, (c) 300 h, respectively. (d) Line profiles of the detected surface potential corresponding to the white lines in (a–c). The black arrows indicate hydrogen segregation at deformation twins. 'Reproduced with permission from *J. Electrochem. Soc.*, **160**, C643 (2015). Copyright 2015, The Electrochemical Society'.

CRYOGENICS



Adapted from: Patricia Jovičević-Klug, PhD thesis, Mechanisms and Effect of Deep Cryogenic Treatment on Steel Properties, 2022

CRYOGENICS

To date there are only few companies manufacturing cryogenic vessels on a large scale

CRYOGENIC VESSELS FOR LIQUID HYDROGEN STORAGE

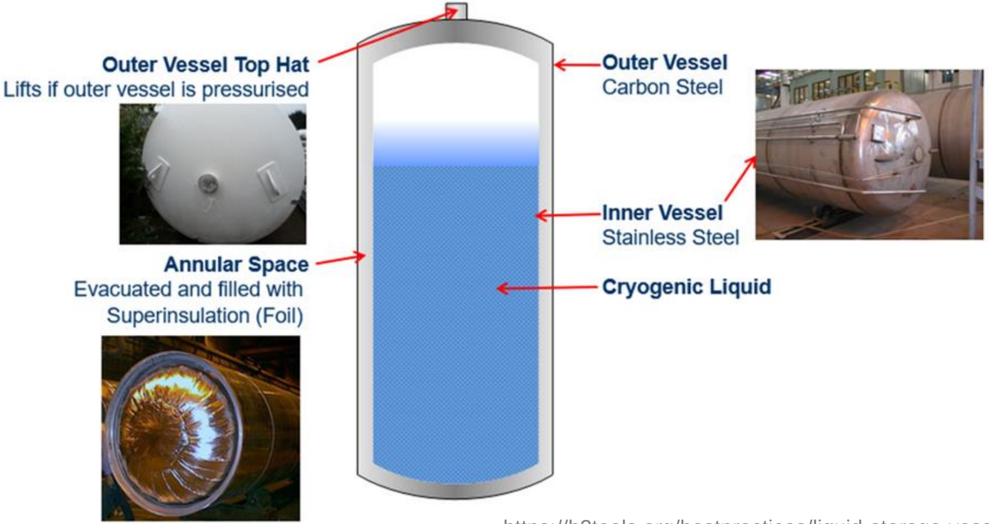
Cryogenic vessels can be either classified according to the type of insulation provided or depending on their application:

- trailers for large scale transportation (by road, railroad or sea)
- vessels for small scale transportation (<1000 L, used for industrial or medical supply to the end users)
- storage on production site
- storage at end-user site

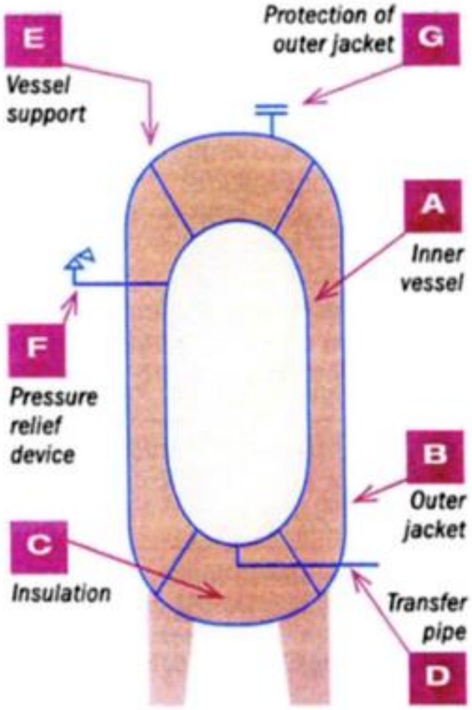
CRYOGENIC VESSELS FOR LIQUID HYDROGEN STORAGE

R.2, R.3

Liquid hydrogen needs to be kept at about 20 K. For this sake vessels are normally vacuum-insulated and composed of an inner pressure vessel and an external protective jacket. As thermal insulators, perlite (powder structure) or super insulation (wrapping with layers of aluminium films) can be also used.



https://h2tools.org/bestpractices/liquid-storage-vessels



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THERMAL INSULATION IN LIQUID HYDROGEN VESSELS

The significant temperature difference among liquid hydrogen and the surrounding environment, is another source for the boil-off phenomenon.

Gas boil off induces an increase of hydrogen pressure within the tank, and the evaporated hydrogen needs to be vented at the outside, producing a loss.

Thus maximizing thermal insulation is mandatory in order to reduce heat leakages .

Category	Active	Passive
Approach	A refrigerator is used to re-condense the evaporated hydrogen gas	Use insulating materials designed in order to reduce as much as possible the heat transfer
Characteristics	Low efficiency, expensive (also in terms of design, and overall for large volumes)	They don’t require external energy supply. They can be further classified into: multilayer, spray on foam, fibrous, and powder insulators

Nowadays thermal insulators are characterized by a thermal conductivity about $10^{-6} \div 10^{-5}$ W m^{-1} K^{-1}.

THERMAL INSULATION IN LIQUID HYDROGEN VESSELS

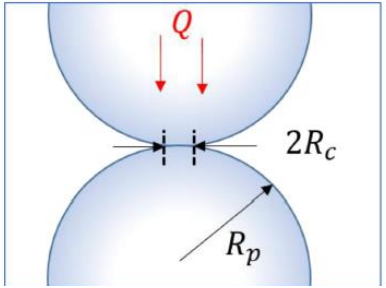
Powder Insulation

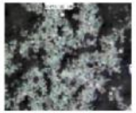
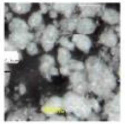
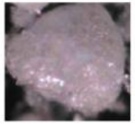
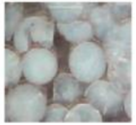
Powder fillings often used for cryogenic application include perlite, aerogel powder/beads and glass bubbles/microspheres.

It is hard to have a complete and uniform geometric description of powder conductivity due to the variation in particle size (R_P) distribution and packing structure:

$$k_{SE}(T) \cong \frac{R_C}{R_P} k_s(T) \rightarrow k_{SE}(T) = \frac{4}{\pi^2}(1-\phi)C\xi\frac{R_C}{R_P}k_s(T)$$

Where: R_C: radius of the contact area, C: coordination number, ξ: particle surface roughness, ϕ: porosity, k_S: conductivity of the solid material.

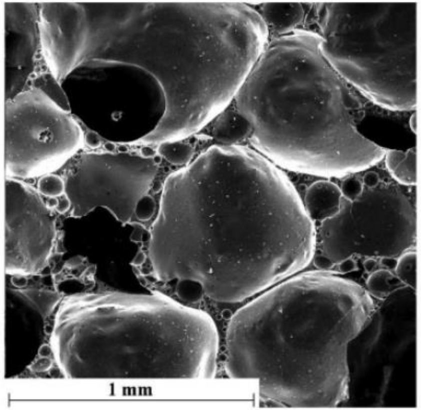


	10x	100x
Glass Bubbles ~65µm		
Perlite Powder ~600µm		
Aerogel Beads ~2000 µm		

AIP Conference Proceedings 985, 152–159 (2008)

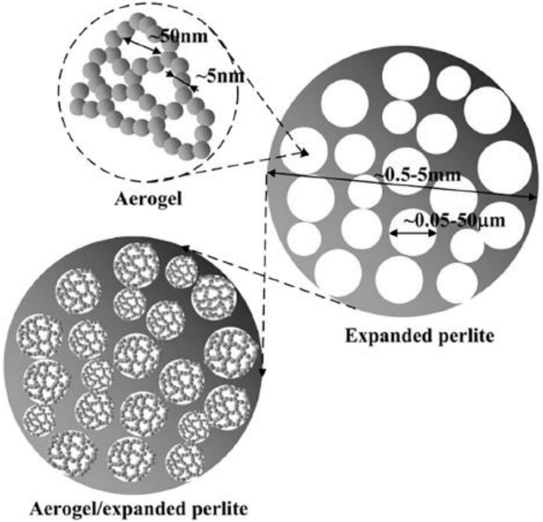
LIQUID HYDROGEN STORAGE – APPROACHES OF THERMAL INSULATION

Glass foam

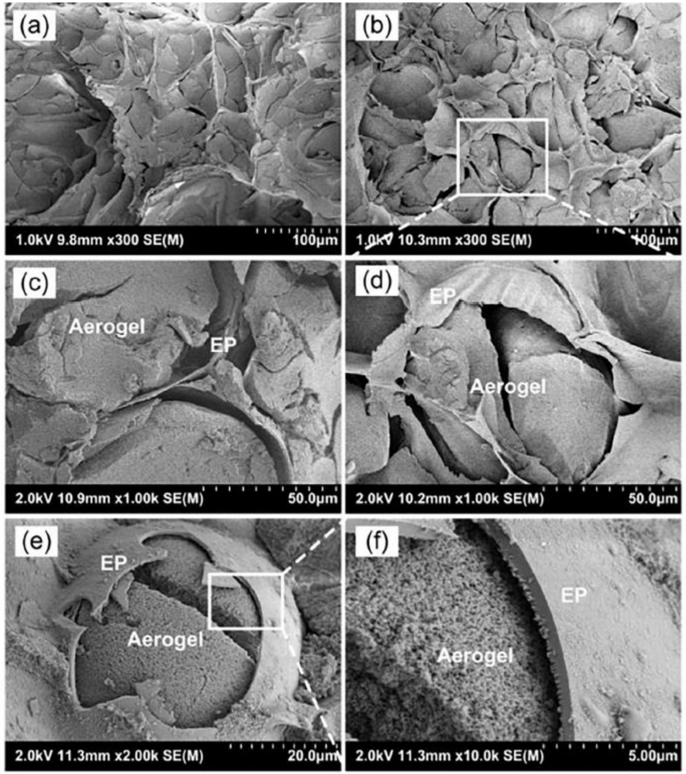


Yatsenko E.A. Et al., Int J. Hydr. Ener. 47 (2022) 41046-41054

Aerogel



Jia G., et al., Journal of Non-Crystalline Solids 482 (2018) 192–202

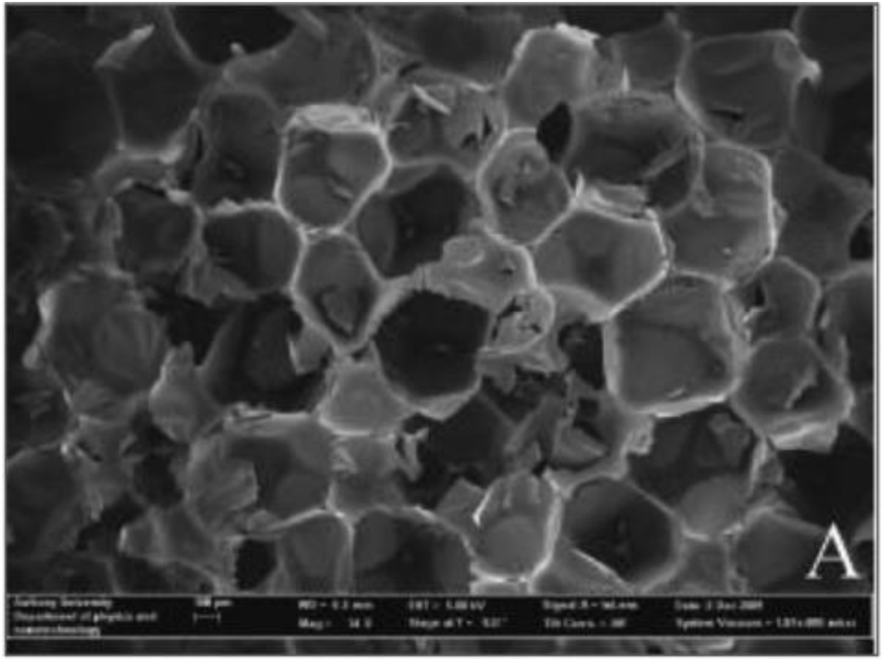


THERMAL INSULATION IN LIQUID HYDROGEN VESSELS

R.6

Spry-On Foam Insulation

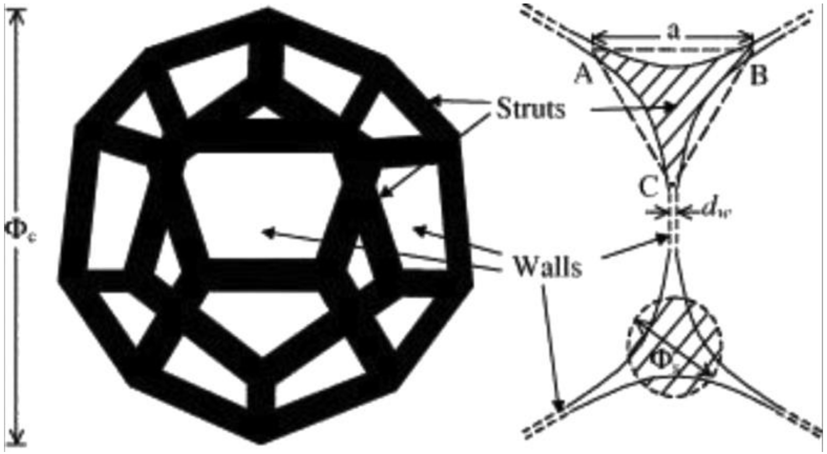
SOFI systems are generally produced by gaseous expansion of organic solids, creating a highly porous, but continuous solid structure, and is characterized by low cost and ease of fabrication. The low bulk density of foam insulation is helpful in reducing solid phase heat conduction, but removing the residual gas can be difficult and time-consuming, and the resulting. Polymer materials such as polyurethane, polystyrene and polyimide are popular solids for foam insulation.



THERMAL INSULATION IN LIQUID HYDROGEN VESSELS

Foam thermal conductivity depends on the structure of the cell, the size of struts and walls, in particular is dependent on the bulk (ρ) and solid (ρ_S) material densities, the conductivity of the solid material (k_S), and the mass or volumetric fraction of the structure (f_S):

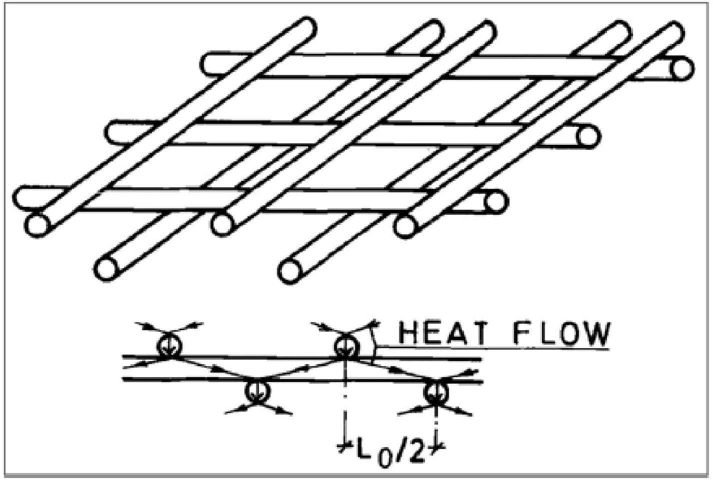
$$k_{SE}(T) = \left(\frac{2 - f_s}{3}\right)\frac{\rho}{\rho_s} k_s(T), \qquad f_s = \frac{m_{structures}}{m_{structures} + m_{walls}}$$



LIQUID HYDROGEN STORAGE – APPROACHES OF THERMAL INSULATION

Fibrous Insulation

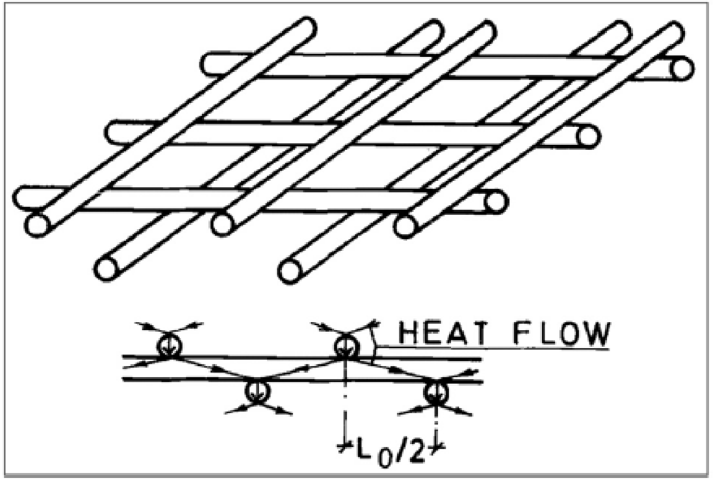
Combine flexibility and easy handling with vibrations and shocks could be transmitted to the cryogenic system. They can be viewed as crossing fibres arranged regularly in layered planes perpendicular to the heat flow direction. Typically, the fibre layers are oriented randomly, while the fibre rods in each layer may have uniformed distance: $L = \pi D/[4(1-\phi)]$, with ϕ porosity and D fibre diameter.



LIQUID HYDROGEN STORAGE – APPROACHES OF THERMAL INSULATION

Heat transfers through fibre rods contacting points. In absence of deformation the conductibility can be modelled in function of

$$k_{SE}(T) = \frac{32(1-\phi)^2}{\pi\left[3 + \frac{\pi}{4(1-\phi)}\right]} k_s(T)$$



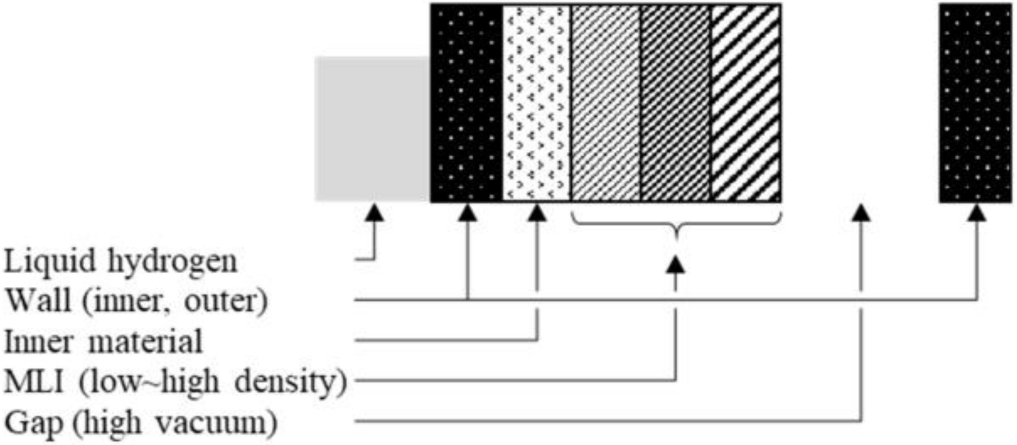
For elastic materials the model can be refined including the fibre elasticity, the Poisson ratio and the external pressure applied to the fibre layer:

$$k_{SE}(T) = f(E, \upsilon, \phi, P) k_s(T)$$

LIQUID HYDROGEN STORAGE – APPROACHES OF THERMAL INSULATION

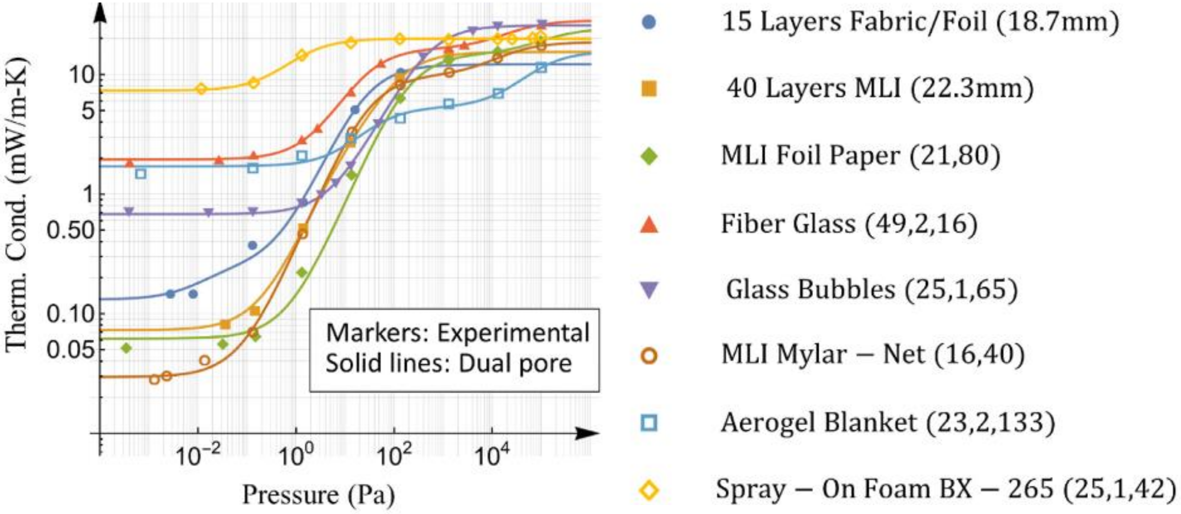
Multilayer insulation

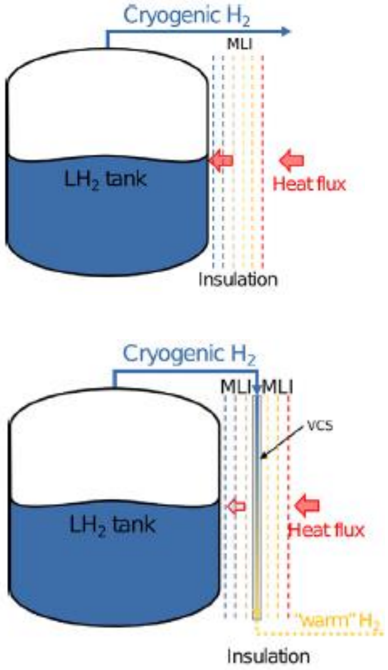
It offers the best performances, but it is subjected to vacuum changes. As a consequence, on the long-term, as the vacuum gradually deteriorates, thermal insulation performance drops significantly. The shields are typically made by alternating materials with high reflectance and spacers.



Kang, D. et al., Energies 2022, 15, 4357.

LIQUID HYDROGEN STORAGE – APPROACHES OF THERMAL INSULATION





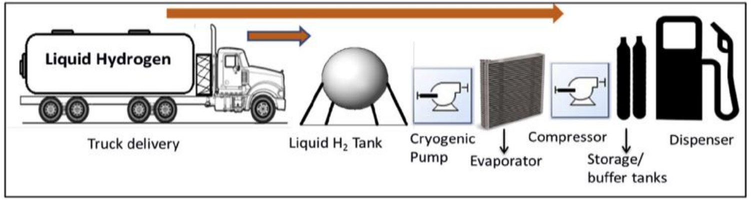
Jiang W. et al., Int. J. Hydr. En., 47 (2022) 8000-8014

LIQUID HYDROGEN STORAGE – SOME PROPOSALS FOR THE MARKET

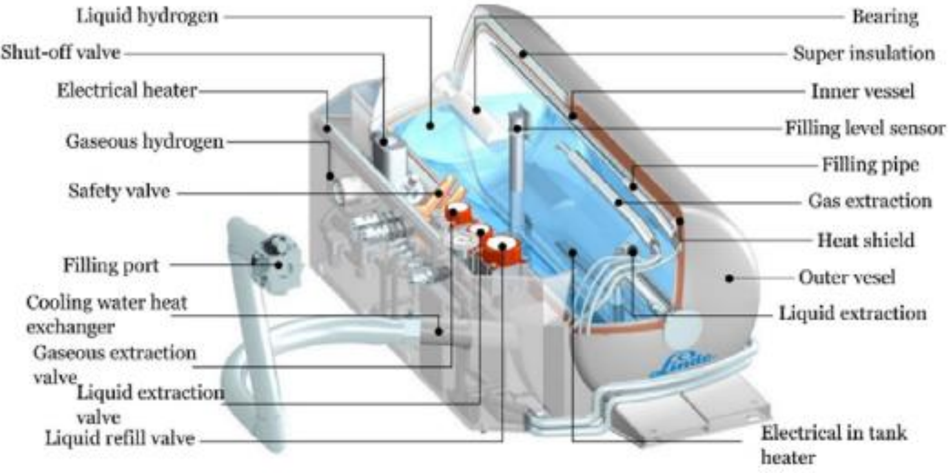
Figure 7.5 Linde hydrogen refuelling station in Munich. (Reprinted by kind permission of Linde AG, Germany.)

Figure 7.4 Linde mobile refuelling unit. (By kind permission of Linde AG, Germany.)

LIQUID HYDROGEN USE



Mayyas A., Mann M., International Journal of Hydrogen Energy 44 (1029) 9121 – 9142



Schematic of a cryogenic hydrogen tank (source: Linde®)

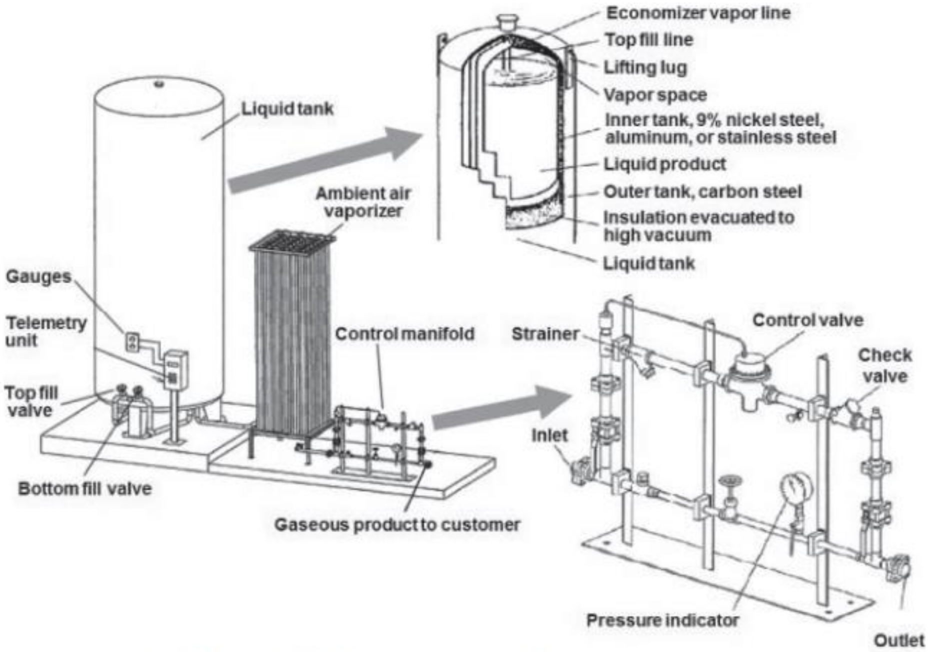
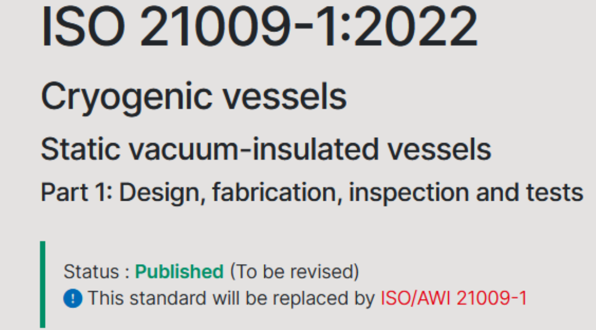


Figure 32.4 Typical bulk liquid storage system with cryogenic storage tank, ambient air vaporizer, and control manifold [23].

Stolten D., Scherer V., Transition to Renewable Energy Systems Wiley, 2013

CRYOGENIC VESSELS FOR LIQUID HYDROGEN STORAGE – STANDARDS



ISO 21009-1:2022

Cryogenic vessels

Static vacuum-insulated vessels

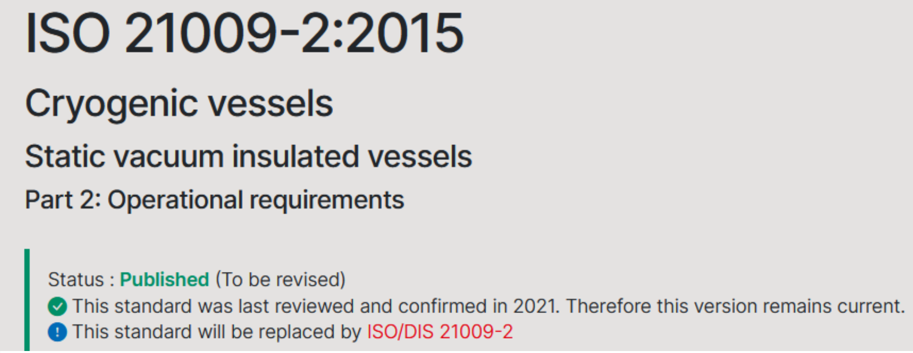
Part 1: Design, fabrication, inspection and tests

Status : **Published** (To be revised)

This standard will be replaced by ISO/AWI 21009-1

Main target:

Specify the requirements for the design, fabrication, inspection and testing of static vacuum-insulated cryogenic vessels designed for operating at $P_{max} > 50$ kPa.



ISO 21009-2:2015

Cryogenic vessels

Static vacuum insulated vessels

Part 2: Operational requirements

Status : **Published** (To be revised)

✓ This standard was last reviewed and confirmed in 2021. Therefore this version remains current.

This standard will be replaced by ISO/DIS 21009-2

Main target:

Specify the operational requirements for static vacuum insulated vessels ($P_{max} > 50$ kPa).

LIQUID HYDROGEN STORAGE – ADVANTAGES AND DRAWBACKS

Technical specifications	Advantages	Disadvantages / Limitations
• Convenient for large storage volumes (> 60000 L). • During hydrogen refill and withdraw is mandatory to avoid air entering the system to avoid the formation of an explosive mixture (nitrogen purge of the system is required). • Downstream conversion plant to cryogenic or compressed gas is needed before use.	• Efficient (in terms of mass of hydrogen stored).	• Difficult to store over long periods due to evaporation losses. • Challenging to be handled from the materials point of view: few materials (Austenitic steel, aluminium, brass) can be used for handle cryogenic hydrogen (polymers have bigger glass transitions, below which they lose elasticity). • Discharge kinetics have still to be improved

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