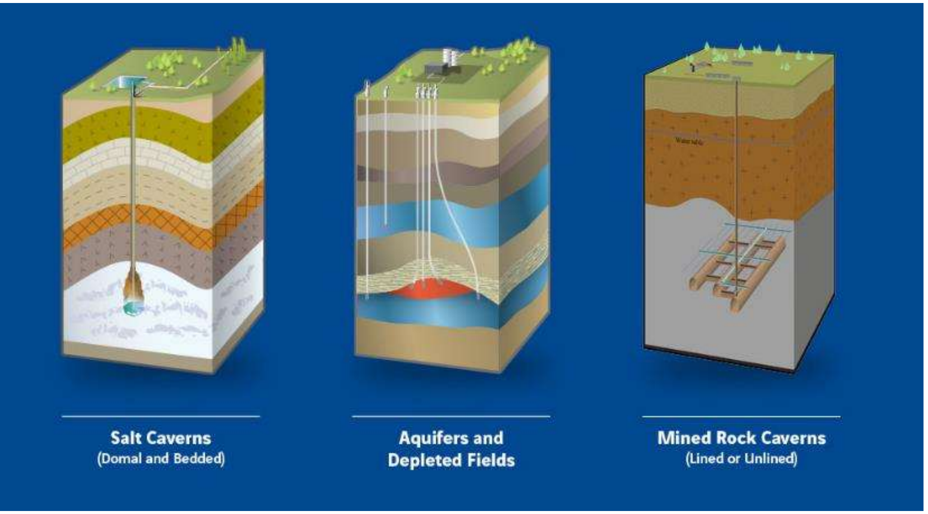
HYDROGEN FOR THE ENERGY TRANSITION : WHY ? HOW ?
PART III : LOGISTICS

Dr Vivien Esnault – IFPEN (France)
GeoIndia 2022 – Continuing Education Courses October 12th 2022



PROGRAM OF THE COURSE (2/2)

- Part 3 : Toward an hydrogen network
  - Technologies to transport and store hydrogen
  - Safety and quality issues
  - Case study : Your hydrogen strategy for India
- (Tea break)
- Part 4 : Hydrogen underground
  - Underground ressources for hydrogen (native hydrogen and in-situ production)
  - Storing hydrogen underground
  - Questions – open debate

PART 3 : TOWARD AN HYDROGEN NETWORK

- Storing hydrogen, at all scale
  - Storing hydrogen in your vehicle
  - Storing hydrogen on a small site
  - Storing strategic quantities of hydrogen
- Transporting hydrogen
  - Today's reality
  - Network needed for the hydrogen economy
- Safety & quality
- Case analysis : your hydrogen strategy for India

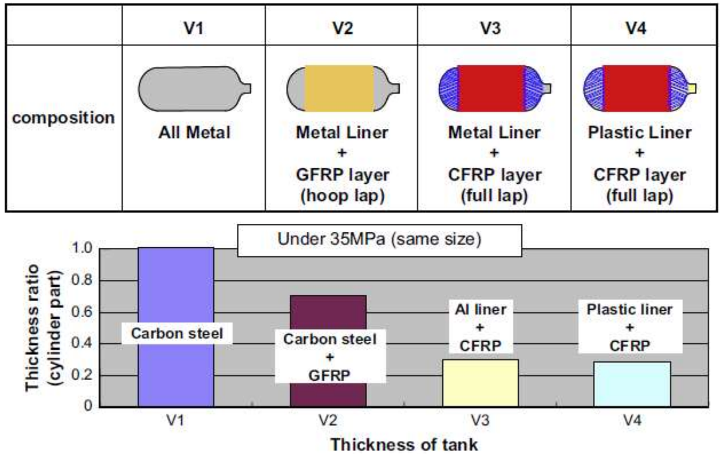
STORAGE

STORING HYDROGEN ON A VEHICLE : A QUESTION OF MASS

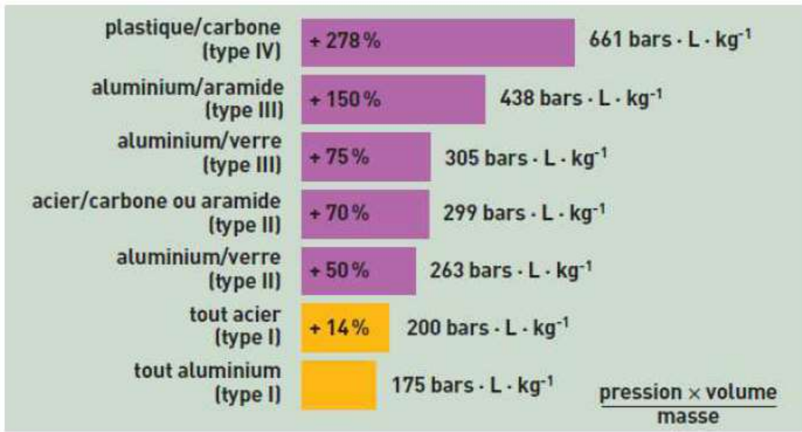
- Hydrogen is light, the resevoir isn't
  - High pressure → demanding reservoir design

- New standard : type 4 reservoir
  - Completely proven at 400 bar, up to 700 bar
  - 100% polymer design
  - >5% of hydrogen mass/ reservoir system mass

Wikipedia (Honda vehicle)



Mori et al. 2009, International Journal of Hydrogen Energy



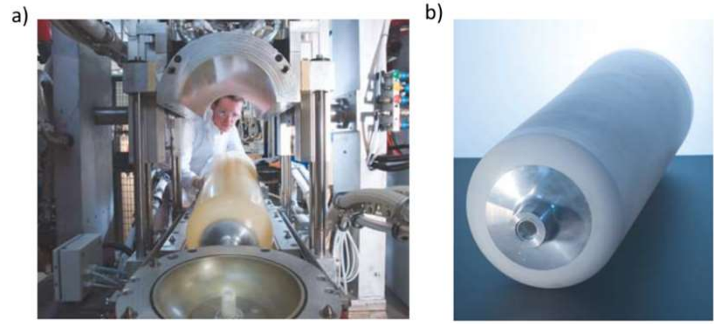
France Hydrogène

TYPE IV RESERVOIR : HOW DOES IT WORK

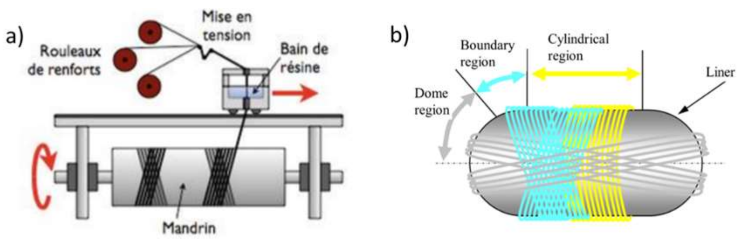
- Liner
  - Molded (ex : rotomolding) in specific thermoplastic
  - Responsible for controling leakage

- Composite enveloppe
  - Woven, carbon-fiber composite
  - Responsible for structural integrity

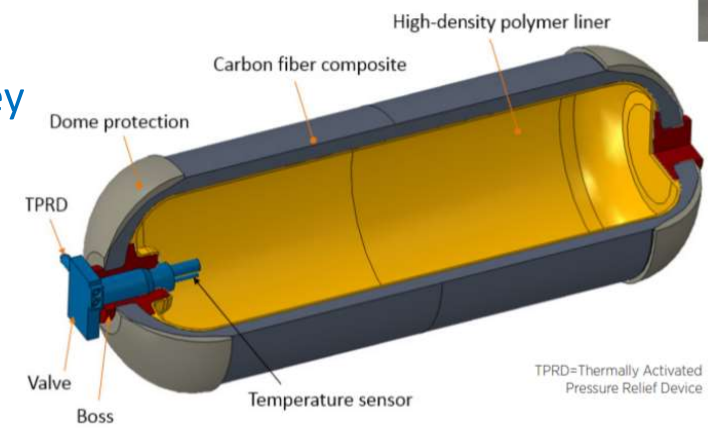
- Boss, valve…
  - Interactions between components is key



CEA



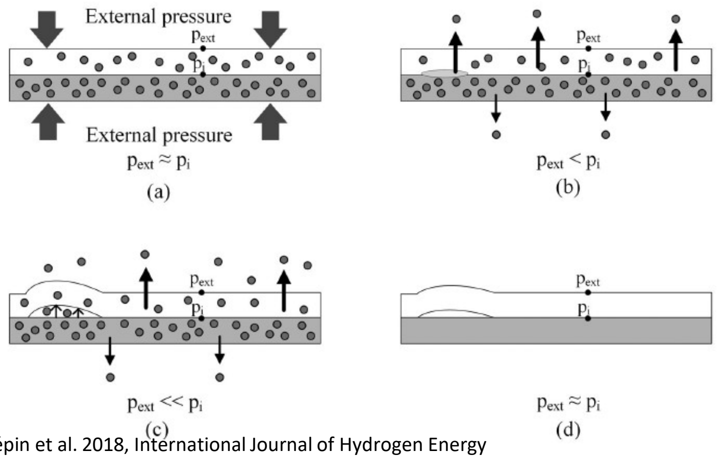
Quantum Technologies



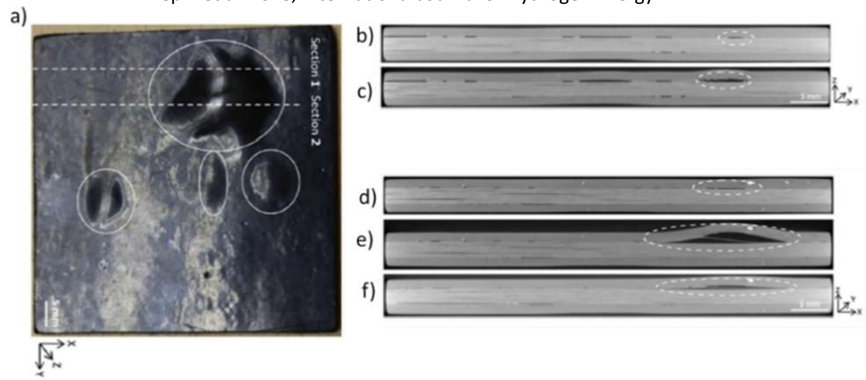
US Department of Energy

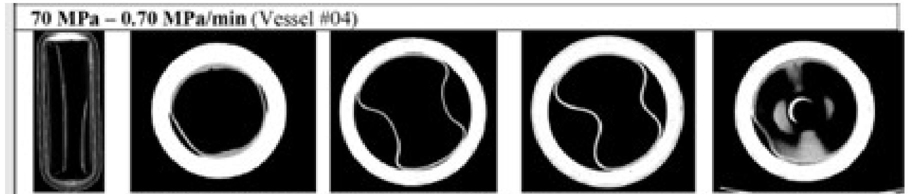
TYPE IV RESERVOIR : LINER INTEGRITY

- Permeability
  - H2 penetrates and migrates (quite) easily in polymers
  - Limit of 10^{-5} loss per hour (order of magnitude) : 1% in a month
- Blistering
  - H2 accumulates at high pressure in the structure
  - If pressure drops, it might not have time to escape
  - Gaseous bubbles form, and eventually blisters
- Collapse
  - Same mechanism as blistering, at the liner/enveloppe interface
  - Liner eventually deform and collapse



Pépin et al. 2018, International Journal of Hydrogen Energy





This vessel exhibits extreme liner collapse with very important permanent deformation. It can be seen on the vertical picture that on one side the buckled shape goes from one dome to the other, whereas on the other side a second collapse stretches along the lower half. ΔP_{max} has not been calculated but is estimated around 68 MPa.

Blanc-Vannet et al. 2019, International Journal of Hydrogen Energy

TYPE IV RESERVOIR : MECHANICAL ENVELOPPE INTEGRITY

- Wild range of tests
  - Burst
  - Impact
  - Bullet shot
  - Bonfire
  - Fatigue
  - …

Washington State University

- Correspond to real life difficult scenario
  - All configurations of car crashes
  - Fire in a confined space (tunnel…)

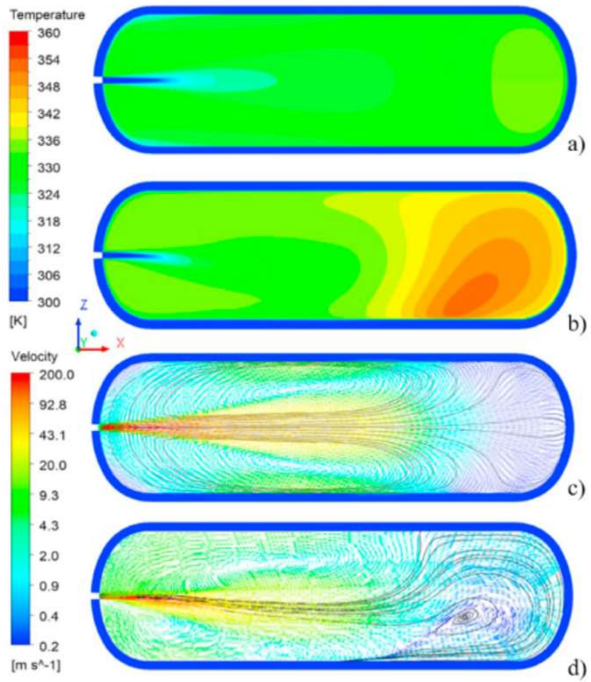
- « Leak before fail »

OSTI

TYPE IV RESERVOIR : REFUELING CONSTRAINTS

- Advantage of hydrogen : fast refueling
  - However, compressing a gas generates heat
  - 100°C of Δ in typical operations
  - Minimal refueling times for light vehicles : 5 min

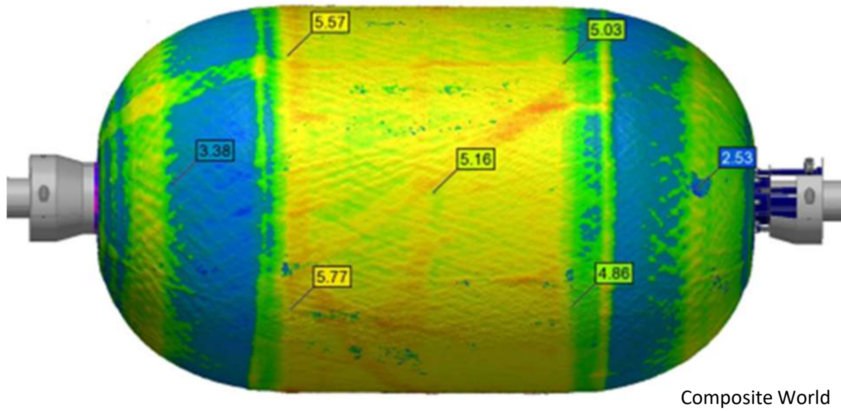
- Important consequences on vehicle and station design
  - Gas is refrigerated to -40°C before injection
  - -40°C to 70°C : very demanding for polymers
  - Cyclical stresses → material fatigue



Li et al. 2021 International Journal of Hydrogen Energy

FUTURE DEVELOPMENT IN RESERVOIRS ?

- No need for more pressure
  - 300-400 bar might be enough for a lot of applications
- Type 5 reservoirs ?
  - Get rid of liner, full composite
  - No additional capacity, but easier process
- Simplify process
  - Current process is very time and ressource consuming
  - Partially responsible for FCEV high prices
- Adaptable shapes for the reservoir
  - Would ease vastly vehicle integration
  - Good luck to come out with anything else then a cylinder, though

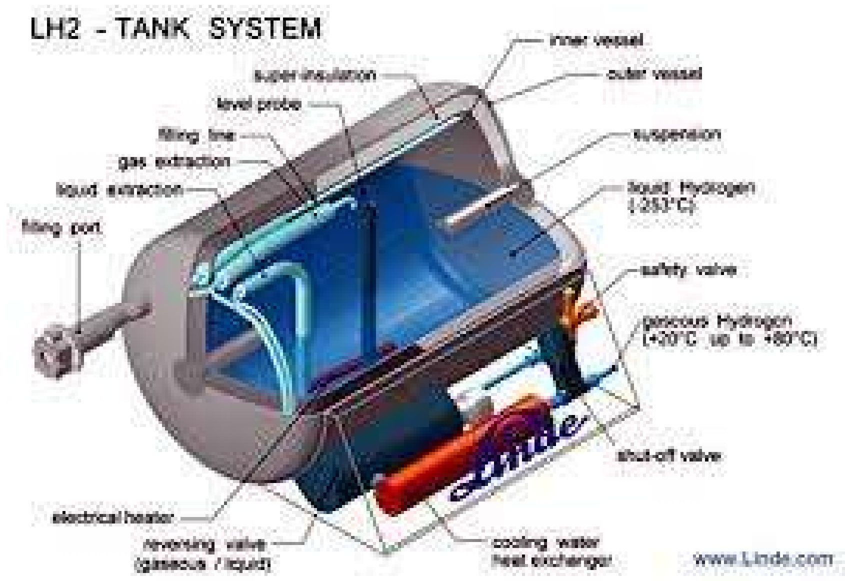


Composite World

LIQUID HYDROGEN STORAGE

- Denser then 700 bar gaseous
  - Not so much, on a physic point of view (x1.7)
  - Very much so, taking into account the reservoir which is lighter

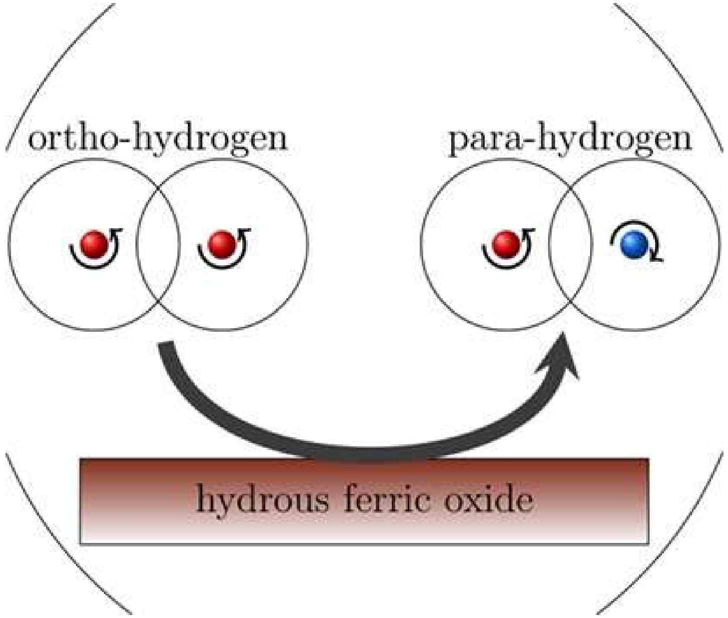
- -253°C…
  - LNG -160°C, liquid nitrogen -196°C, absolute zero -273°C
  - Relatively unknown levels of cold (except niche industries)
  - Energy consumption : +20% (33% of energy yield)



- Who will need it ?
  - Airplanes : certainly
  - Heavy trucks, naval vessels : perhaps
  - Long range transport ? (road, naval)

LIQUID HYDROGEN : BOIL-OFF ISSUES

- The ortho/para issue
  - « Ortho » and « para » are two quantum-spin related state of hydrogen
  - At low temperature, hydrogen transitions from ortho to para, generating heat
  - Liquid hydrogen needs to forced into para beforehand



Donaubauer et al. 2019 Chemical Engineering Technology

- Nevertheless, partial boiling can't be avoided
  - In the 1% order of magnitude
  - Depends of vessel size

- What do you do with boiled-off hydrogen ?
  - Large vessels : keep the pressurized gas
  - Small ones : vent it (safety ? carbon footprint?)

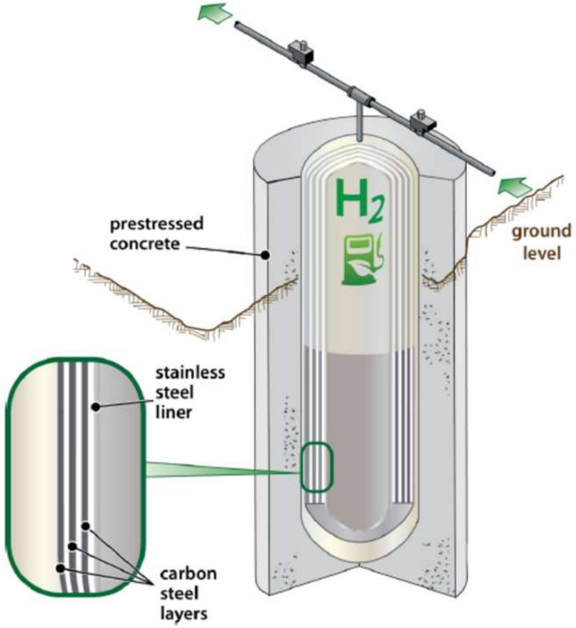
FACILITY-SIZED, STATIONNARY STORAGE

- Less demanding then mobile applications
  - Density requirements not as important
  - More cost-sensitive

- No rocket technology needed
  - Working pressure : 100-200 bar ?
  - Additional pressure for mobility ?: only in a small buffer
  - All steel vessels mainstream
  - Buried, concrete vessels an interesting possibility

- Large quantities of gaseous hydrogen: a good idea ?
  - As hydrogen leaves industrial areas to urban areas ?
  - Already tensions about regulations in Europe

Idesa

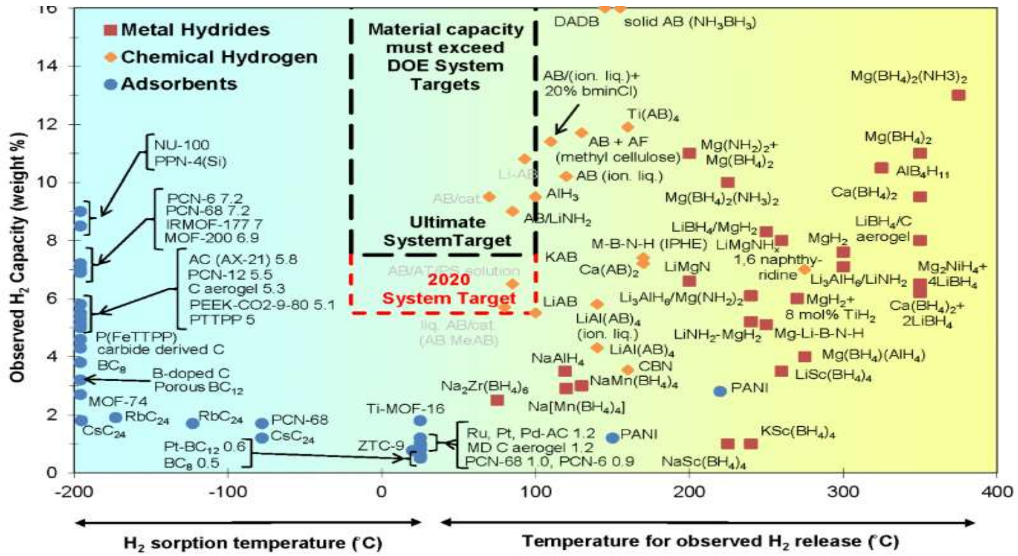


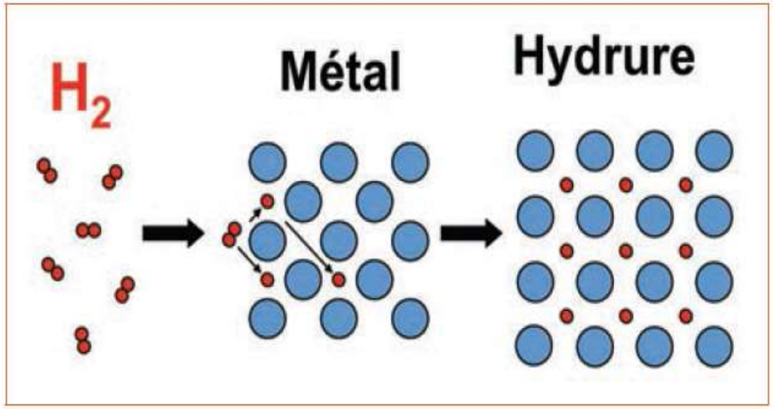
US Department of Energy

STORING HYDROGEN AS A SOLID ?

- Metal hydrides
  - Hydrogen can form complexes with a wide variety of metals
  - Hydrogen stored in a dissociated form

- Complex to reach the targets
  - Difficult to reach high levels of mass %
  - The best systems only works at high T°
  - Other issues, such as reaction speed, durability of cycling





Dissociation de l'hydrogène en surface, diffusion dans le métal et formation de l'hydrure métallique.

McPhy

METAL HYDRIDES : A FORMER GOOD IDEA ?

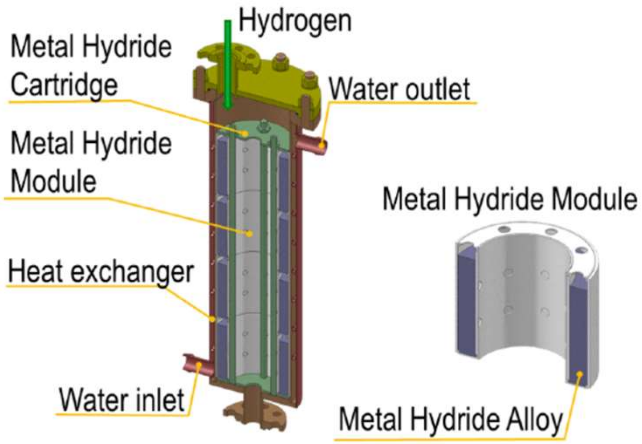
US Department of energy

Mobility usage : a lost battle ?

- Main drawback : heavy, and slow
- In the meanwhile, pressured gas options made dramatic improvement

Still an interest for stationary applications ?

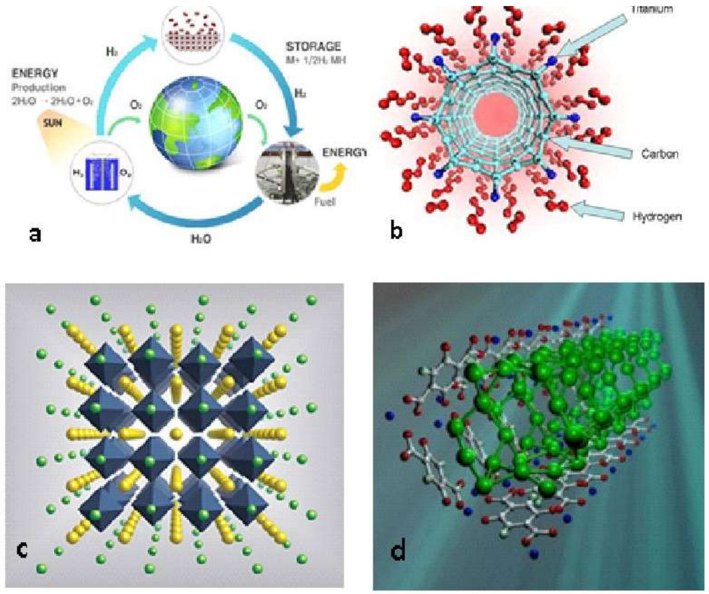
- Cycling speed issues and speed not so important
- Stability of the hydride could be very important for safety



Blinov et al. Energy System Research

Pictures: VONEN MH Storage charged with H_2, placed in fire.

OTHER SOLID STORAGE OPTIONS



- Adsorption storage
  - Hydrogen stored in nanoporous structure
    - Zeolites, MOFs, nanotubes
  - Hydrogen stored in its molecular form
  - Dense only with high pressure or low T°

- Hydrogen hydrates
  - H_2 like CH_4 can form ice-like structures with water
  - Once again : forms significatively at extremely low T° and high pressure

Wikipedia

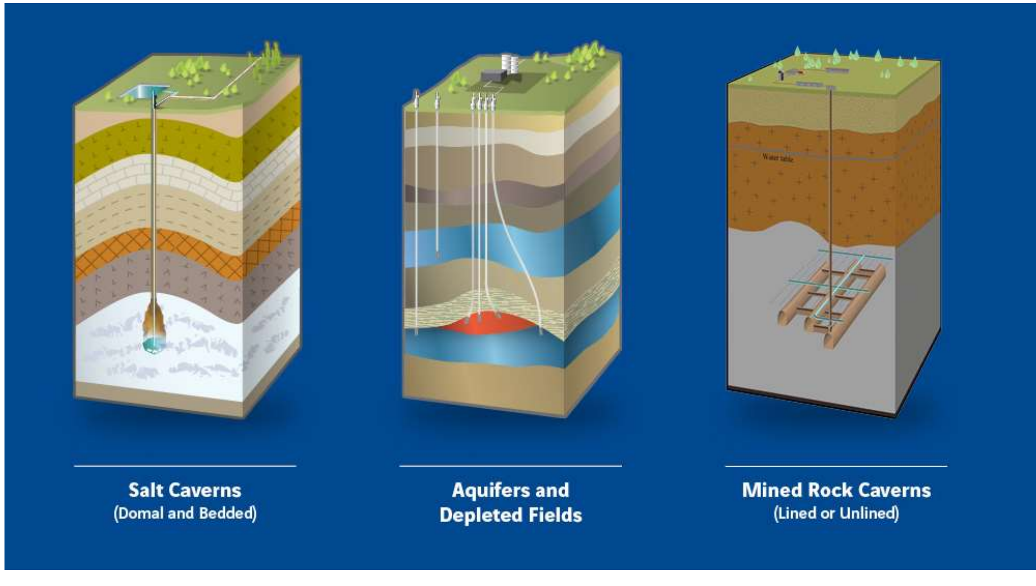
- Liquid Organic Hydrogen Carriers
  - Hydrogen stored in liquid organic molecules
  - Speak about it later for transport applications

STORAGE WRAP-UP

- Vehicle level storage
  - Dramatic breakthrough of gaseous storage under pressure
  - Liquid hydrogen an (expensive) option for denser storage

- Station level storage
  - Technology ready, robust, and not very complex
  - Potential interest for solid options, for safety ?

- Large-scale, strategic storage ?
  - Underground storage of course
  - Will be discussed in part IV of the course

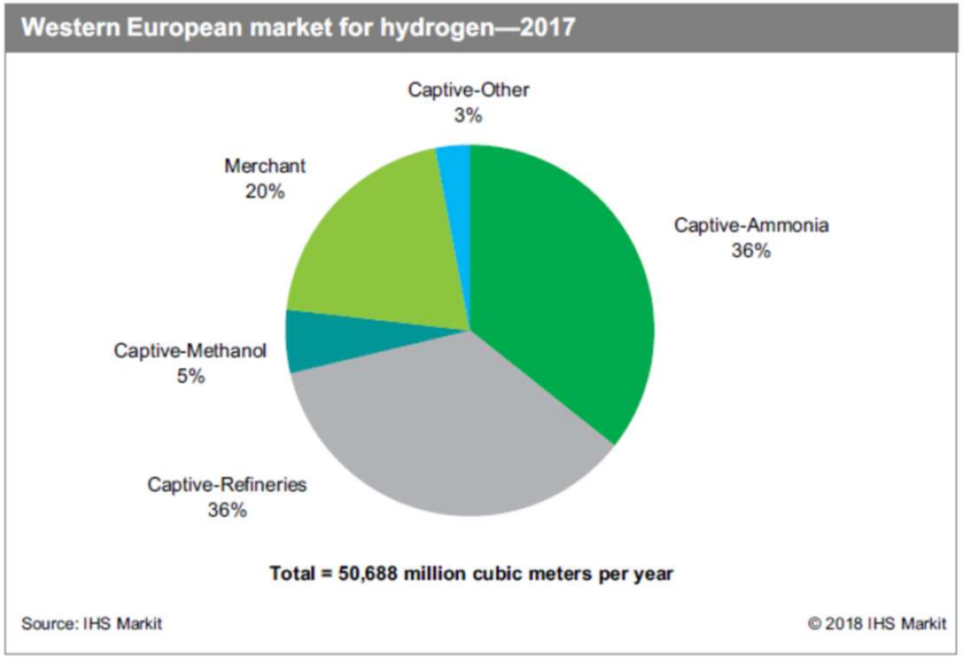


Geostock

TRANSPORT

WHY TRANSPORT HYDROGEN, AGAIN ?

- Wen you can produce it onsite ?
  - Today, 80% of H2 production is «captive»
  - Coherent for large industrial users, using methane as a commodity
- Future usage
  - Large industrial users are still going to be a thing
  - Mobility usage are much more decentralized
- Future of production
  - Premium to large production farms
  - Driven by access to cheap green electricity, not proximity to an industrial site



Future hydrogen economy will see important transport of hydrogen

TRANSPORTING HYDROGEN : TRUCKS

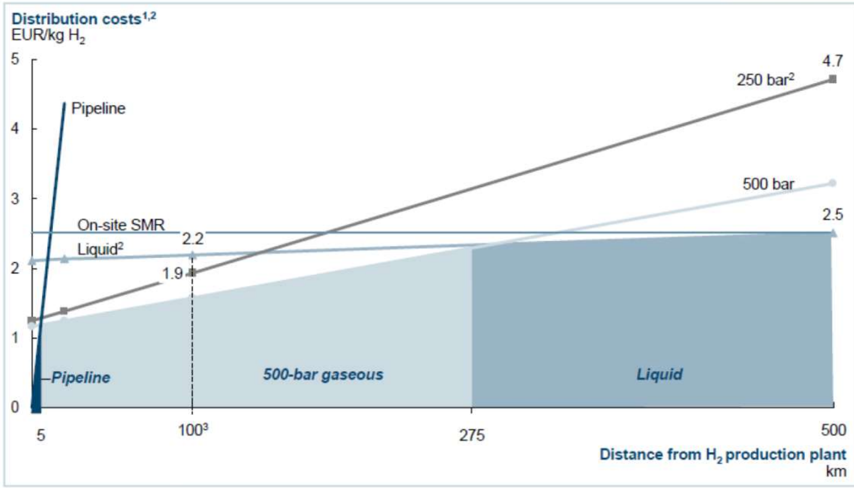
- Often the only solution to deliver hydrogen today

- Progressive increase of capacity per truck
  - Steel tubes : 380 kg per truck
  - Composite tube trailers : 560-900 kg per truck
  - Liquid hydrogen trucks : around 3 t per truck

- A compromise to be found
  - Longer range : strong interest in larger capacity
  - CAPEX rise sharply with more demanding transport

THE ECONOMY OF TRUCK TRANSPORT

- Compressed gas trucks : short distance
  - Relatively low CAPEX
  - Sharp increase of cost per km
- Liquid hydrogen truck
  - Costly CAPEX and liquefaction OPEX
  - Low cost per km
- Anyway : too expensive for the H2 economy
  - Current delivery price in station is 10$/kg
  - Technology not compatible with a 2$/kg world



	Gaseous tube trailers		Liquid tankers	
Capacity	450 kg/day	1,000 kg/day	450 kg/day	1,000 kg/day
Hydrogen delivery and dispensing cost	$9.46/kg	$8.17/kg	$11.35/kg	$8.31/kg

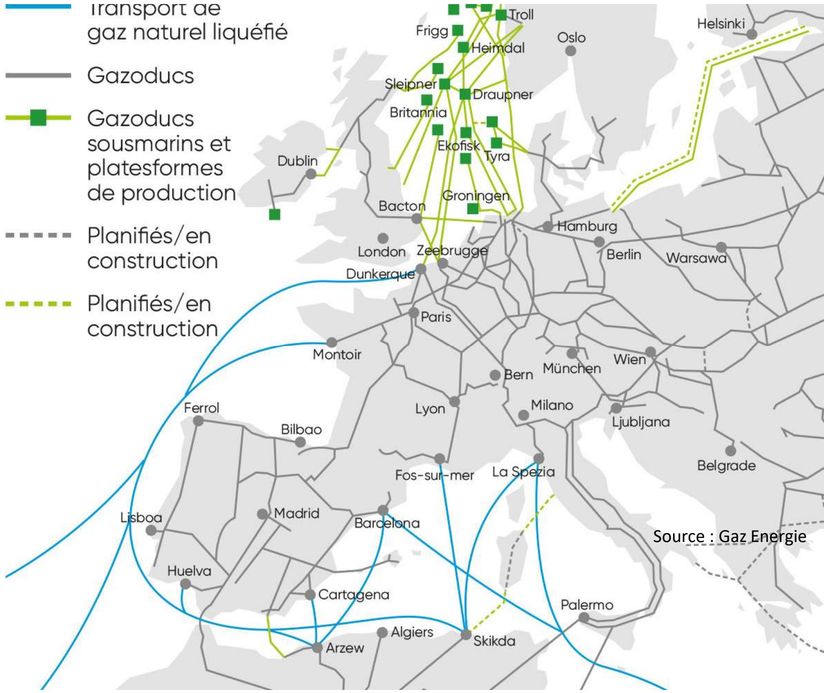
US Department of Energy

GAS IS BEST TRANSPORTED IN PIPE

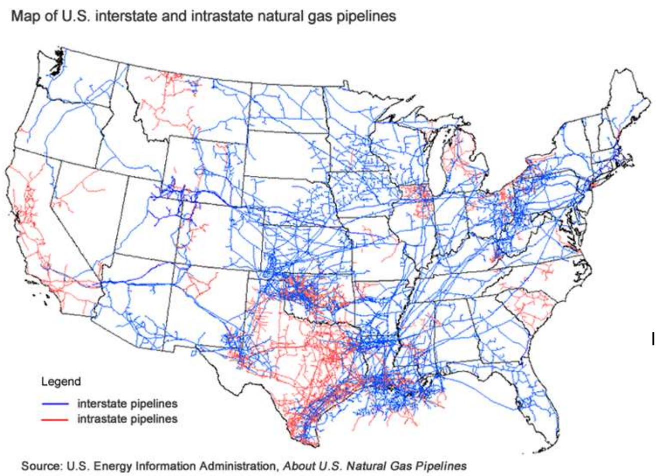
- The natural gas benchmark

- A few figures for the USA :
  - 4.5 millions km of pipelines
  - 70 millions households delivered
  - Several thousands of billions $ of investment

- More then a benchmark, an opportunity
  - The gas industry has a strong interest in recycling its assets



Gaz Energie



IEA

HYDROGEN TRANSPORT IN PIPELINE

- Infrastructures are similar to natural gas pipeline
  - Typical diameter: 300 mm
  - Pressure : 10-100 bar
  - Flow velocity up to 40 km/h
  - Meaning 65 kg/s with methane…
  - … but only 7 kg/s with hydrogen !
- Mostly underground pipeline: buried for safety issue
- Key equipments:
  - Boosting stations : recompress gas every 200 km
  - Maintenance valves : every 8 to 30 km
  - Distribution stations…

Source : euractiv.org

Source : loe.org

H2 PIPE NETWORKS HAVE EXISTED FOR A LONG TIME

- Rare, because rarely needed
  - But operated for decades is some very dense industrial regions

Northern Europe Air Liquide network :
First segment built: 1938
Length : 240 km
Capacity : 25 000 t/year

Figure 4 – Réseau de gazoducs Air Liquide au Texas et en Louisiane

Figure 2 - Réseaux pipelines d'Air Liquide en Allemagne

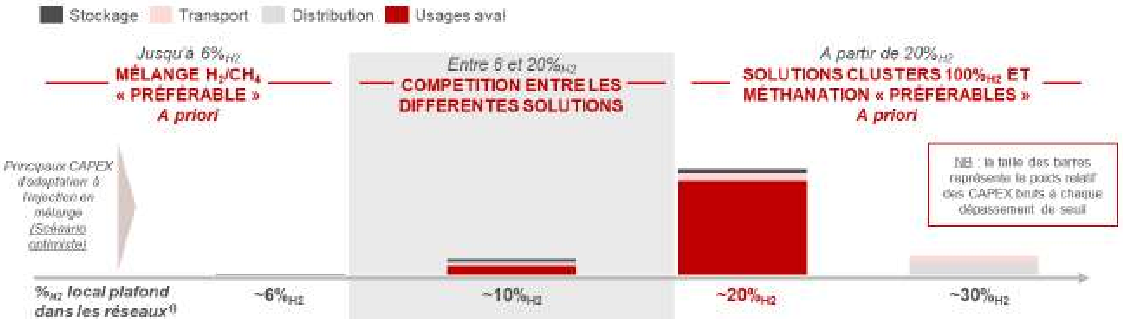
France Hydrogène

GRT Gaz

FIRST OPTION : INJECTING HYDROGEN ON THE GAS GRID

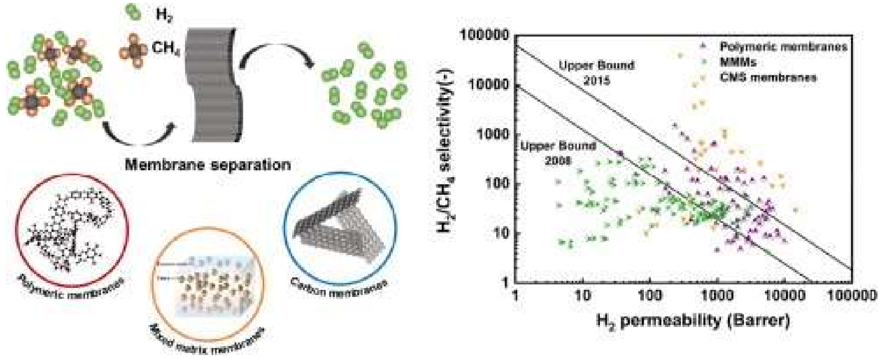
- Injecting H_2 on the methane network can be seen as a transition technology
  - Could solve issues of disconnection between supply and demand in early H_2 economy
  - A storage potential of up to 40 TWh/year in France, according to the operators

- Adaptation costs hinder the profitability of the solution beyond a 20% vol. load
  - Main issue : adapting end users installations



Source : « Conditions techniques et économiques d'injection d'hydrogène dans les réseaux gaz naturel », juin 2019

THE ISSUES WITH THE H2/CH4 MIX



- The presence of H_2 is a hassle for the CH_4 users
  - Especially the industrials
  - Extracting H_2 before sensitive CH_4 user is compulsory

- Doesn't mean you can easily use this hydrogen…
  - Extraction needs to focus on producing pure CH_4 or H_2, can't do both efficiently
  - Standards for fuel cell usage are very, very pure

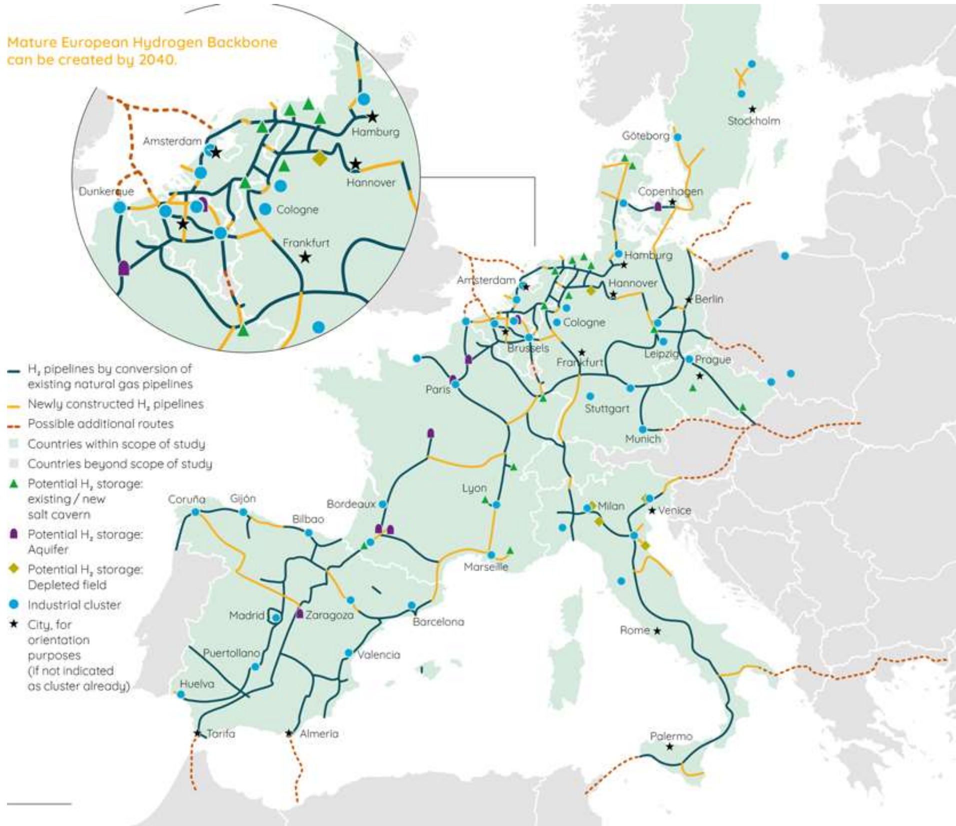
- Most of hydrogen will burn with methane
  - Which, in the general case, is a nonsense economically

GRT Gaz

TOWARD A 100% HYDROGEN NETWORK

- Example of the EU Hydrogen backbone
  - Will ramp from 2030 to 2040
  - 80% of existing recommissioned pipes

- Very attractive cost
  - Pipe transport is almost % CAPEX and very scale dependant
  - Transport costs as low as 0.1 or 0.2 $/kg/1000 km
  - Compatible with an hydrogen economy and balancing offer/demand balance at continental scale

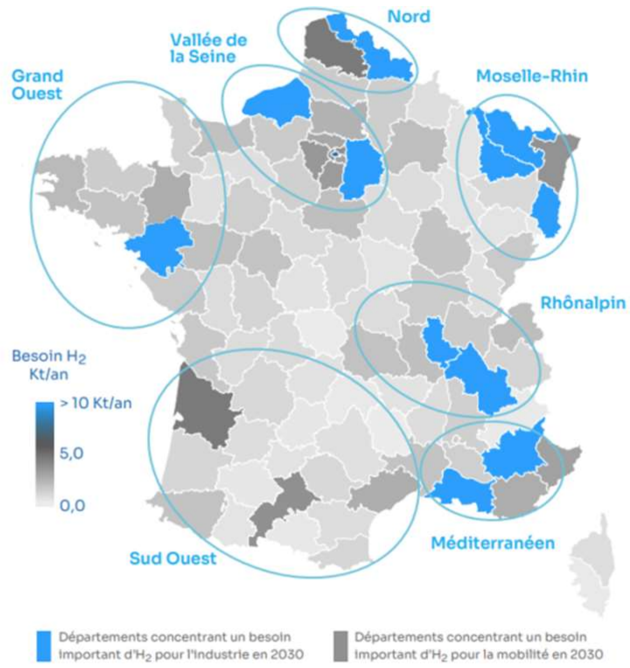


Hydrogen Backbone Consortium

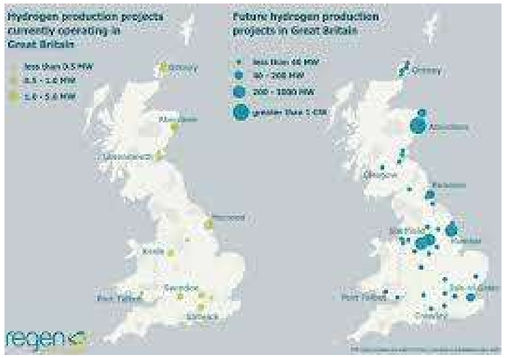
NOT SO FAST ! THE HUB STRATEGY

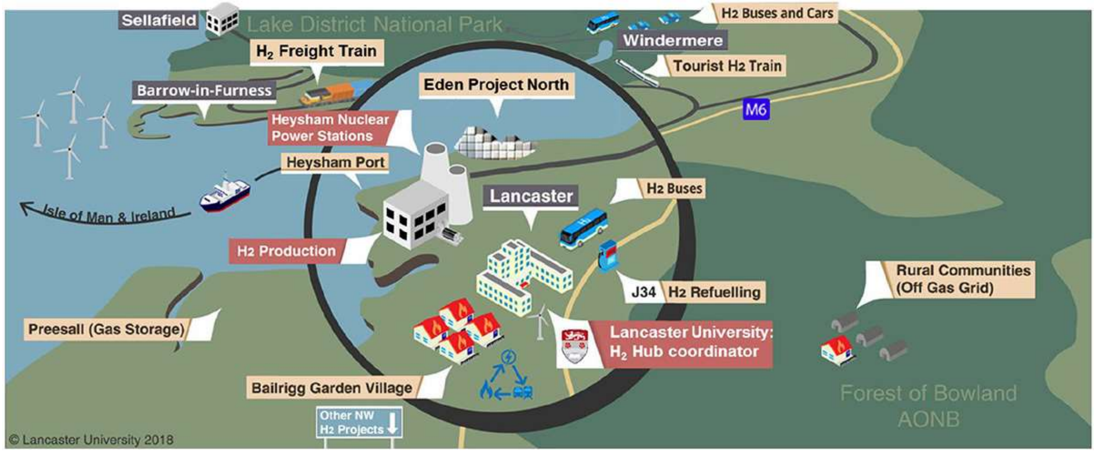
- What’s a Hub ?
  - An identified hotspot, for demand and potential offer
  - Work on an independant, self-sufficient regional ecosystem
  - Plan the logistics accordingly
    - Trucks to start with, but local pipes an option

- Connect the dots to create a global network



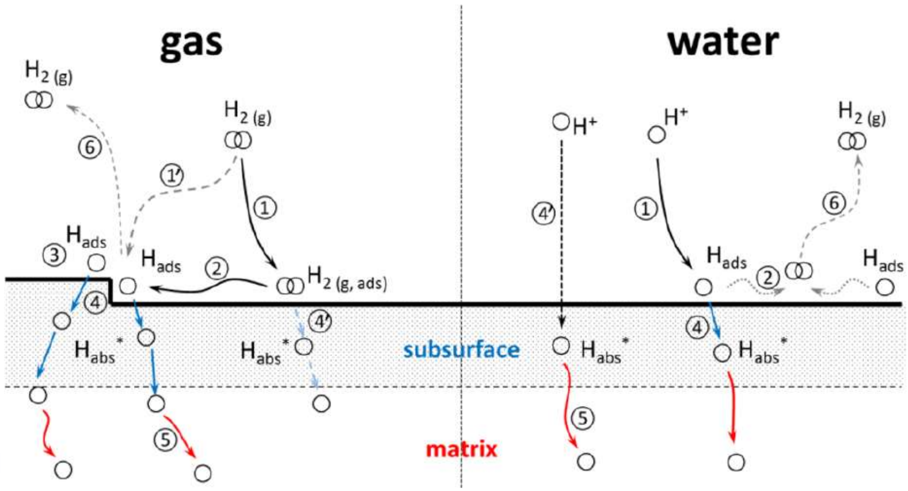
In France, 90% of potential needs identified in 7 key regions

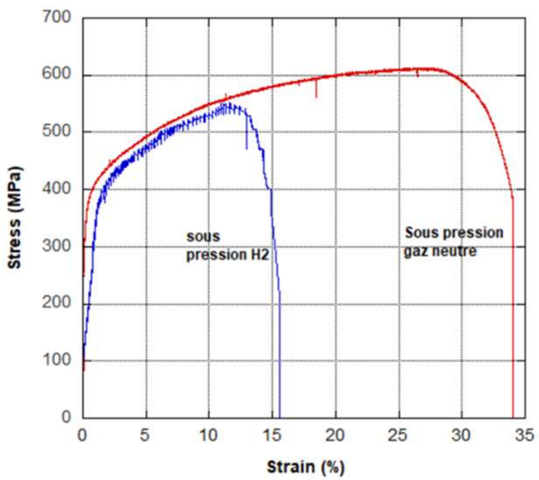


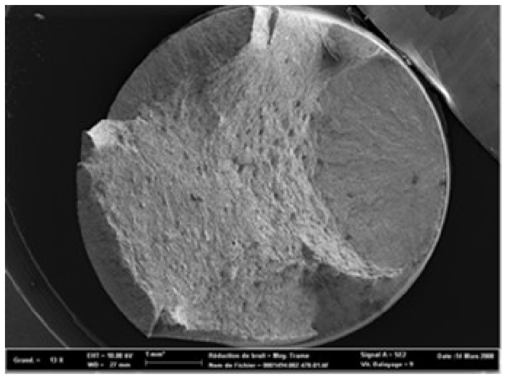


THE PROBLEM OF STEEL ENBRITTLEMENT

- Hydrogen will dissociate on steel surface and penetrate the structure
  - Hydrogen will interact with the steel microstructure an degrade properties
  - Less plasticity, decreased fatigue properties and tenacity
- Nothing new under the sun, but…
  - New pipes : no issue adequate grade can be used, conditions not so severe
  - But old gas pipelines were not designed to handle hydrogen





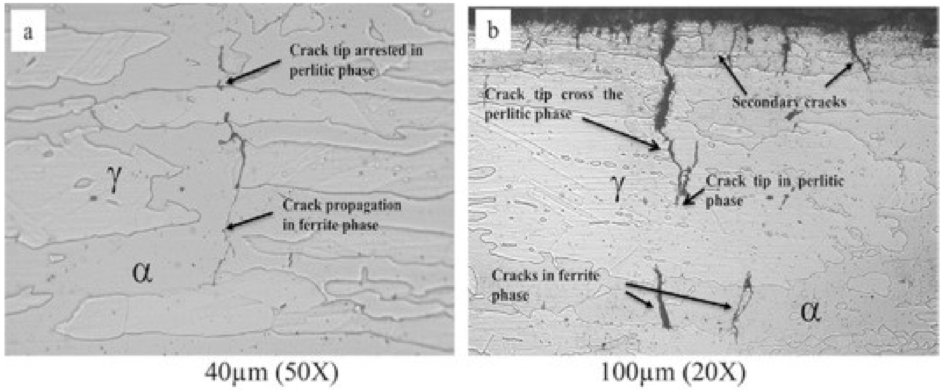


THE PROBLEM OF STEEL ENBRITTLEMENT

- Current focus of research by the gas industry
  - First results not catastrophic
  - Careful to influence of pipe age, impurities

- Solutions ?
  - Be careful : avoid older tubings, reconsider dates for end of life
  - Inner coating of the pipes as an ultimate solution ?

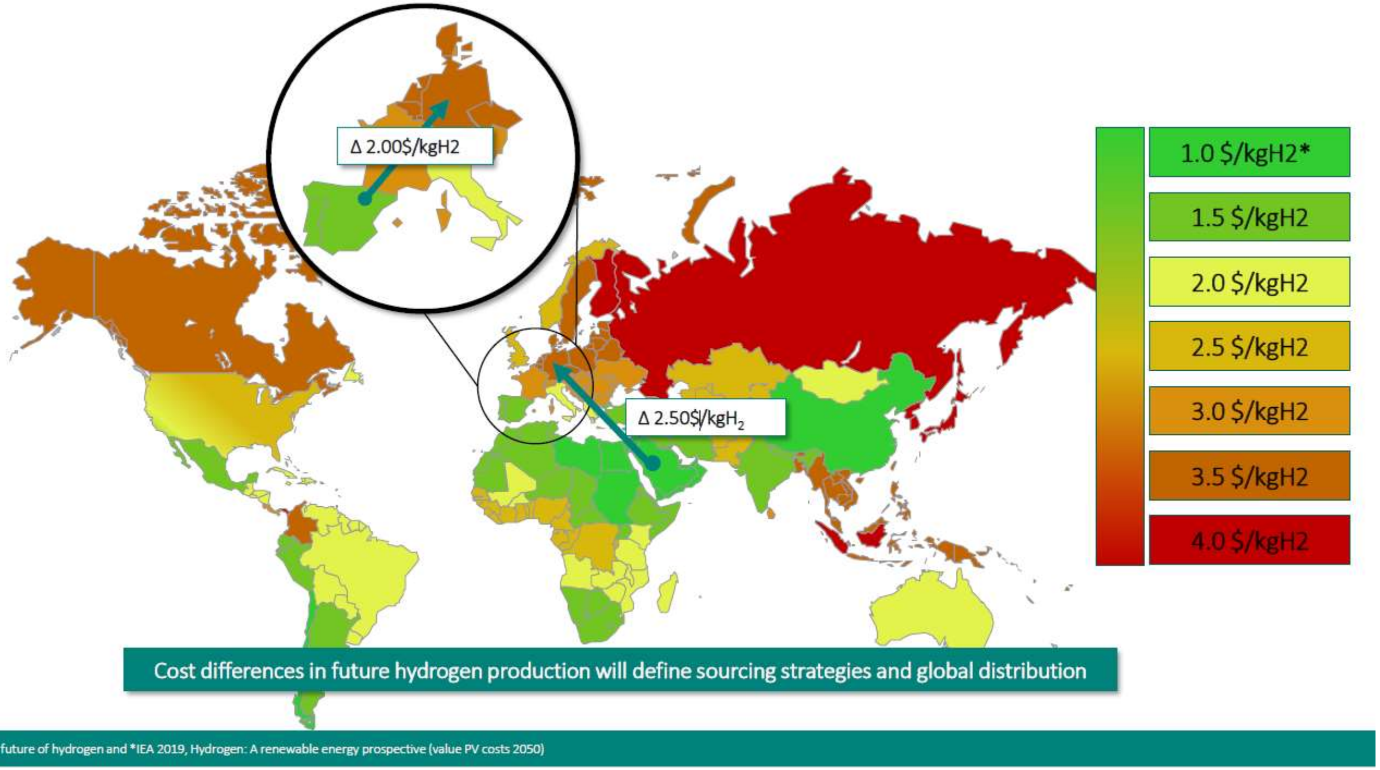
Arcelor Mittal



Bourkoot et al. 2019 International of Hydrogen Energy

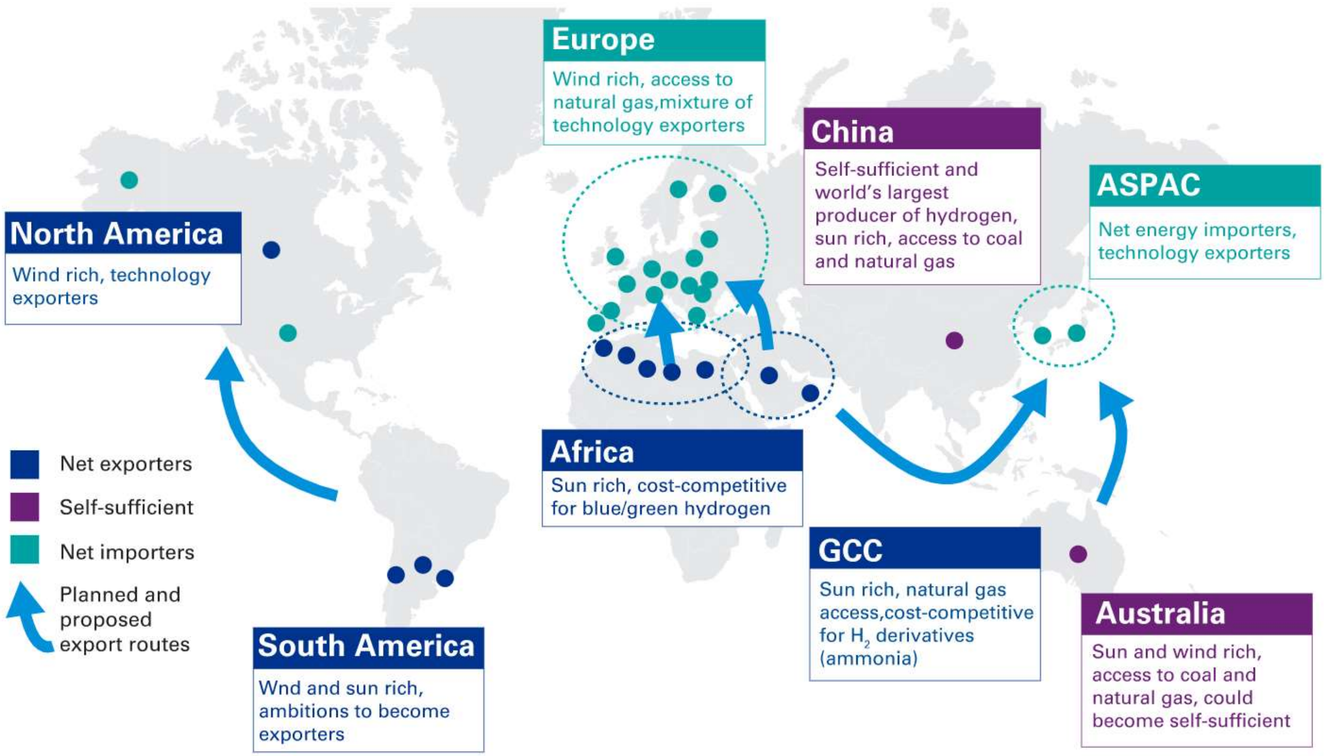
INTERNATIONAL MARITIME HYDROGEN TRANSPORT. WHY ?

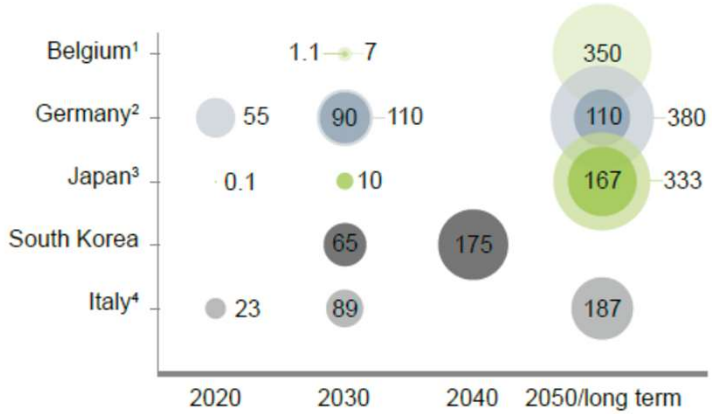
- Exploiting disparities in production costs of H2
  - Driven by the productivity of renewables
  - Up to 2-3 $/kg gradients



INTERNATIONAL MARITIME HYDROGEN TRANSPORT. WHY ?

- Can potentially correspond to durable discrepancies between offer and demand
  - Japan could import the equivalent of1/3 of its electricity





GUideHouse

© Global hydrogen hot spots and distribution corridors (not exhaustive).

KPMG

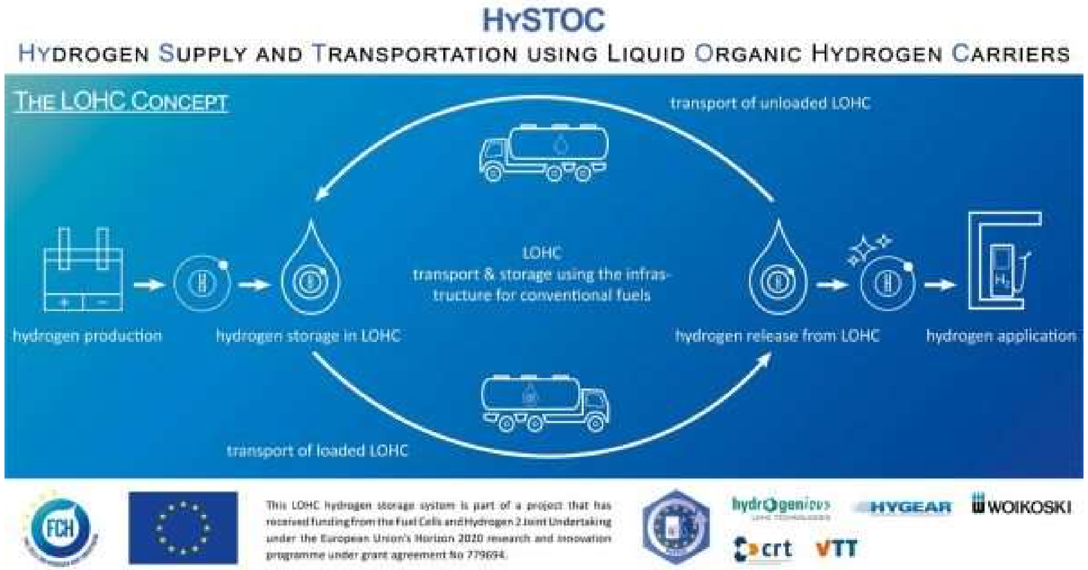
OPTIONS FOR NAVAL TRANSPORT

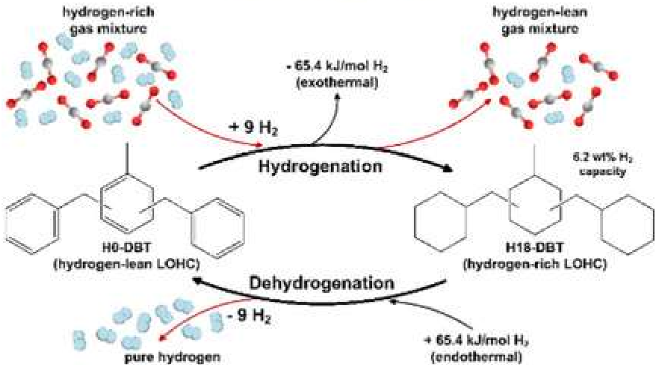
- Direct transport of liquid hydrogen

- Liquid Organic Hydrogen Carriers

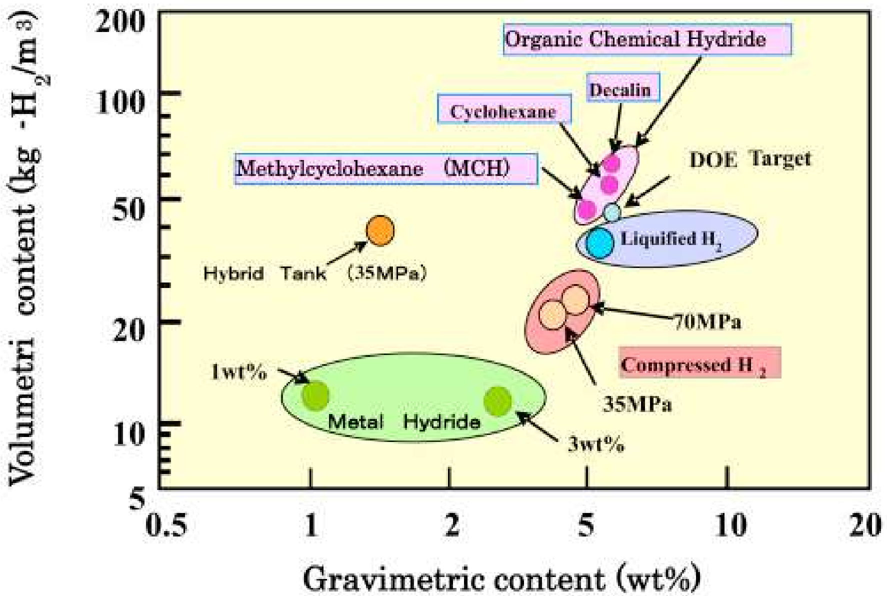
- Don’t transport hydrogen, but e-fuels or ammonia

OPTIONS FOR NAVAL TRANSPORT : LOHC



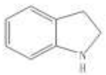
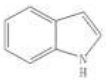
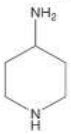
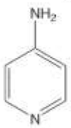


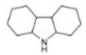
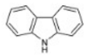
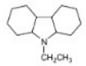
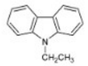
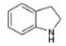
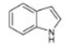
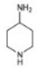
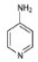
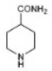
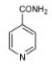
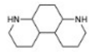
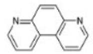
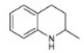
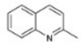
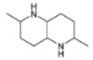
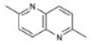
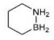
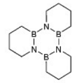
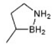
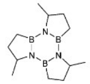
- The best of two worlds :
  - The energy density of hydrocarbons
  - With actual H_2 for use

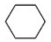
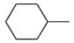
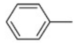
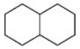
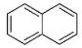
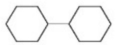
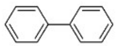


OPTIONS FOR NAVAL TRANSPORT : LOHC

- What to look at ? :
  - H_2 content
  - (De-)hydrogenation energy
  - Carrier loss per cycle
  - Viscosity
  - Toxicity of either forms

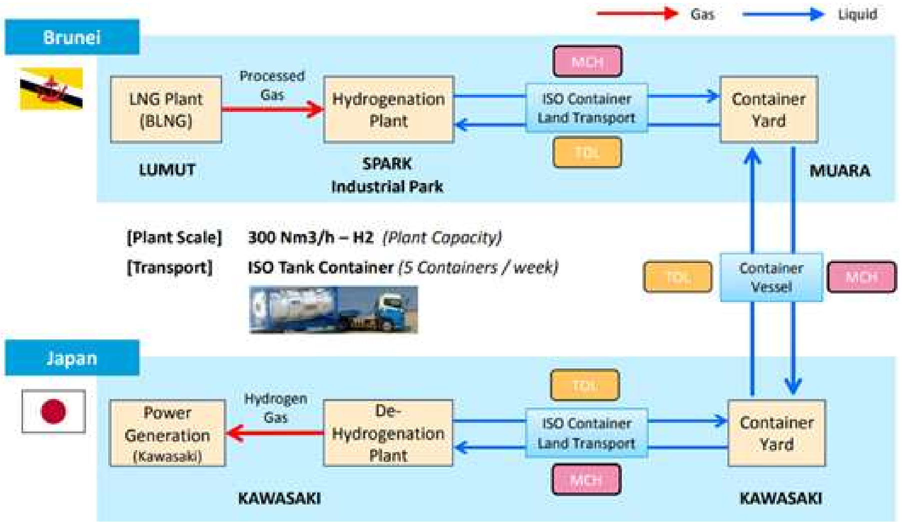
	Products of dehydrogenation	Hydrogen capacity (wt%)	Calculated ΔH (kJ/mol$_{H_2}$)	Catalyst and activity	Ref.
Indoline 	indole 	1.7	51.9	5% Pd/C: 110 °C, conversion 100% 5% Ru/C: 110 °C, conversion 100%	[47] [47]
4-Aminopiperdine 	4-aminopyridine 	6.1	56.7	10% Pd/SiO$_2$: 170 °C, conversion 66%	[48]
Dodecahydrocarbazole 	carbazole 	6.7	51.1	5% Pd/C: 170 °C, conversion 100%	[19]
Dodecahydro-N-ethylcarbazole 	N-ethylcarbazole 	5.8	50.6	5% Pd/C: 170 °C, conversion 100% 4% Pd/Lithium aluminate: 197 °C 5% Pd/SiO$_2$: 170 °C IrH$_2$[2,6-C$_6$H$_3$-(OPBu^t)$_2$]$_2$: 200 °C	[19] [46] [52] [53]

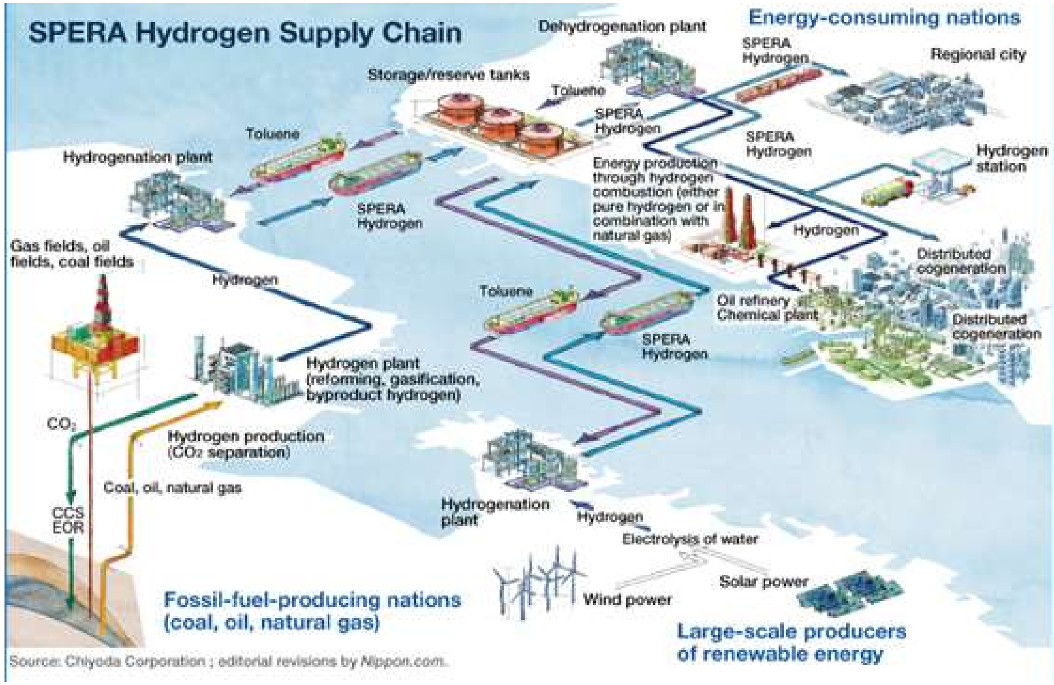
Entry	Storage media	Hydrogenated form	Dehydrogenated form	Density (g mL^{-1})	(and experimental) $\Delta H^0_{H_2}$ (kcal mol^{-1})	wt%	g L^{-1}
N-substituted heterocycles							
5	Dodecahydrocarbazole			1.298	12.2	6.7	87
6	Dodecahydro-*N*-ethylcarbazole			0.931	12.1 (12.4)[a]	5.8	54
7	Indoline			1.063	12.4	1.7	18.1
8	4-Aminopiperidine			0.945	13.3	6.0	57
9	Piperidine-4-carboxamide					4.7	
10	Perhydro-4,7-phenanthroline			0.958		7.2	69
11	2-Methyl-1,2,3,4-tetrahydroquinoline					2.7	
12	2,6-Dimethyldecahydro-1,5-naphthyridine					6.0	
1,2-BN-heterocycles							
13	1,2-BN-cyclohexane			1.011		4.7	48
14	3-Methyl-1,2-BN-cyclopentane			0.894		4.7	42

media	Hydrogenated form	Dehydrogenated form	Density (g mL^{-1})	Calculated (and experimental) $\Delta H^0_{H_2}$ (kcal mol^{-1})	Hydrogen content wt%	g L^{-1}
:ane			0.779	15.6 (16.42)	7.2	56.0
:clohexane			0.770	16.3	6.2	47.4
			0.896	(*cis*-) 15.1 (15.29) (*trans*-) 15.8 (15.91)	7.3	65.3
exyl			0.883	16.0	7.3	64.2

OPTIONS FOR NAVAL TRANSPORT : LOHC

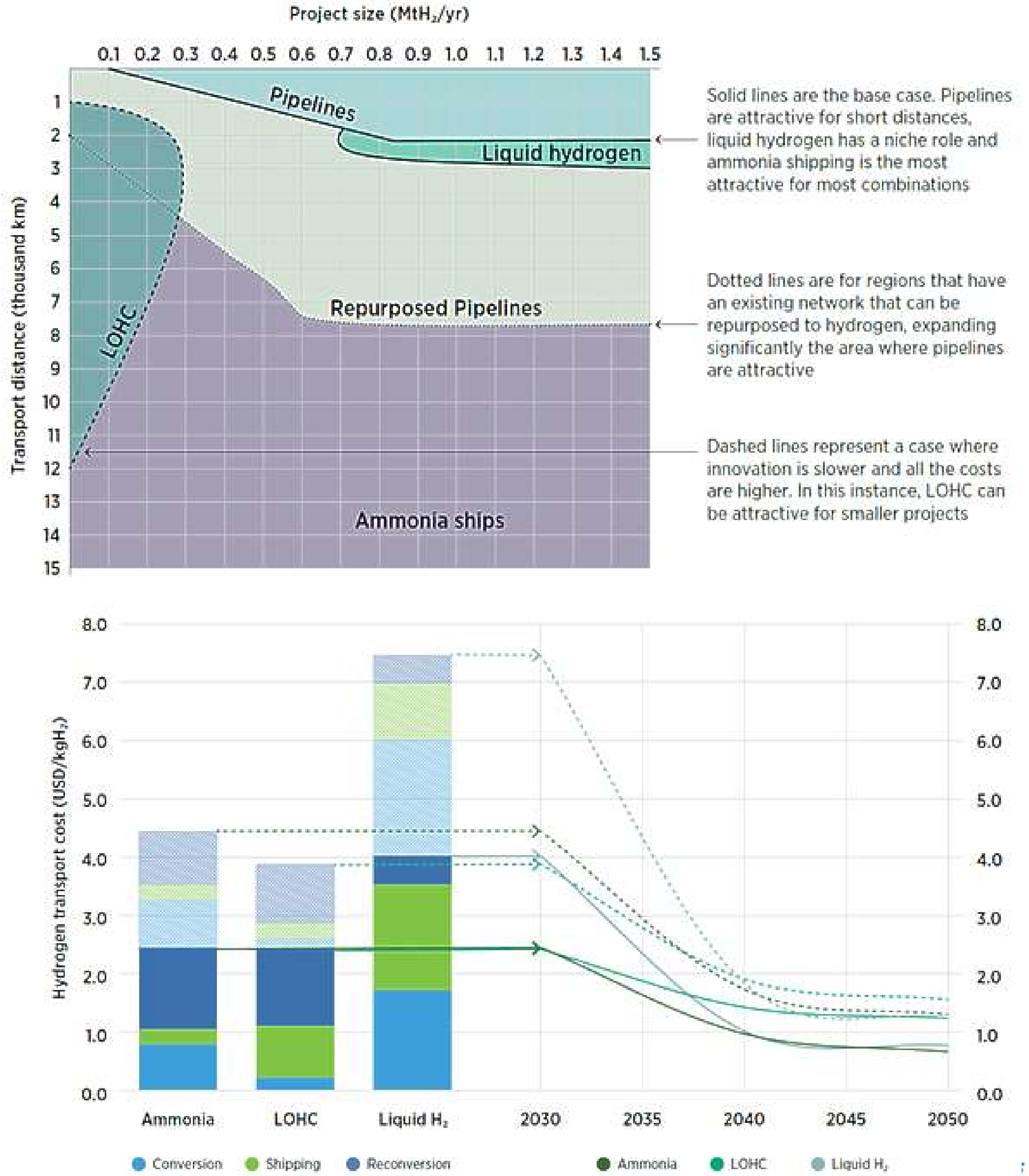
- Logistics is heavy
  - Tankers circulate loaded in AND out
  - Petrochemical installations at both end
- But technologies are quite mature
  - Mostly adaptations of existing refining technologies





ECONOMY : A CLOSE CALL

- Liquid hydrogen seems expensive
  - But is directly usable at reception
- LOHC and ammonia competes closely…
  - Around 2 or 3 $/kg, compatible with anticipated contrasts in production costs
- Ammonia wins if used directly
  - But it is still a horrible molecule
- Require engaging decision, on a permanently evolving field



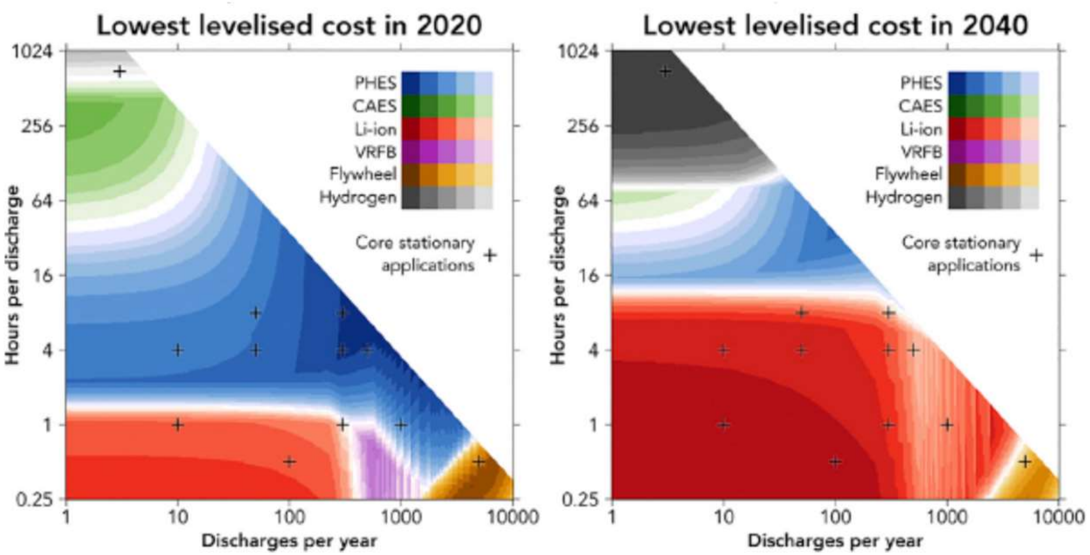
Energypost.eu

BEYOND HYDROGEN : BALANCING THE ELECTRICITY GRID

- If intermittence is high on electric production, you need to store energy
  - Intermittence increasing drastically with renewables
  - Produce hydrogen during peak production, use it to generate during peak demand

- Except H2 is a terrible way of storing electricity !
  - Only relevant for long term, seasonal storage, and far in the future
  - 30% efficiency of the power-to-gas-to-power chain

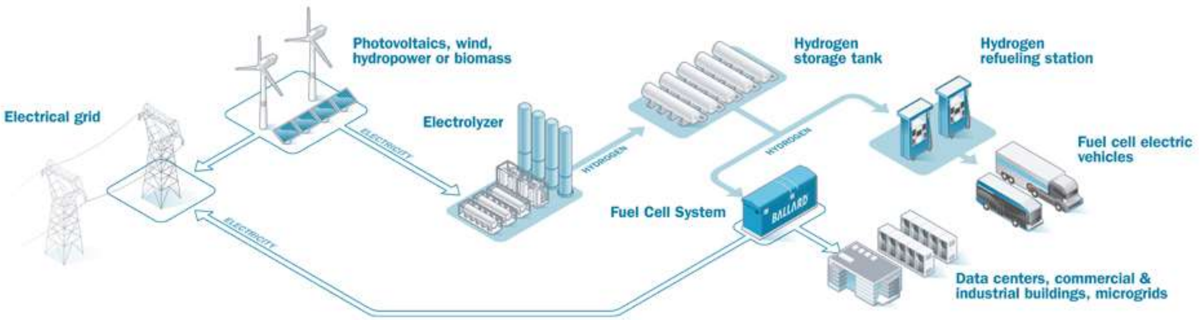
- Far better to insert hydrogen in a global strategy of your energy needs
  - Produce H2 during peaks, ok, but use it as hydrogen
  - Could actually works even with a high proportion of renewables



Schmidt et al. 2019 Joule

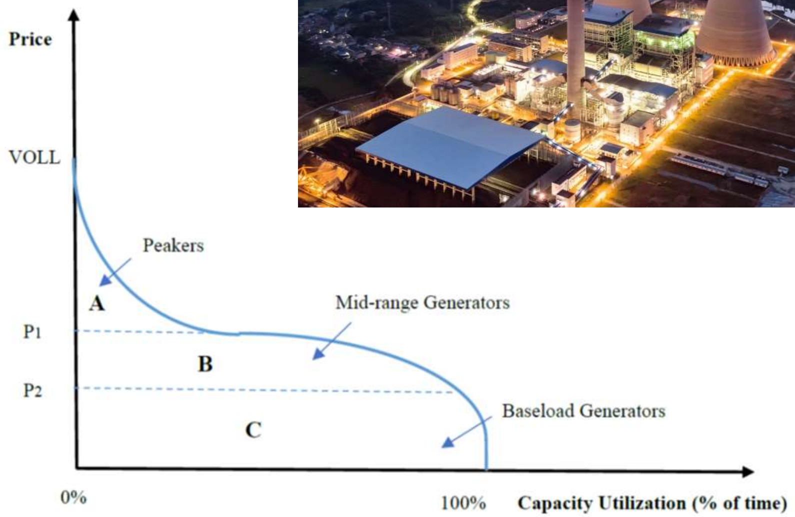
YOU REALLY WANT H2-ELECTRICITY ? WHAT'S YOUR OPTIONS ?

- Large scale fuel-cells
  - Most efficient
  - Huge CAPEX



- Converted thermal powerplant
  - Not as efficient as fuel-cell
  - Could aslo burn ammonia, biomethane…
  - Option to use existing (adapted) power plants

- Thermal plants are better peaker systems
  - Using even a very expensive fuel make sense
  - Starts on demand
  - Low CAPEX very important for peakers



Future importing countries (Japan, Germany) bet on converting their power plants

GERMAN CASE : GEOGRAPHIC UNBALANCE

- German energy geography
  - Potential for renewables (wind) and naval imports are in the North
  - Industry concentration in the South
- Hydrogen transfer to balance ?
  - Electric infrastructure not up to the task for North/South transfers
  - Hydrogen pipes could do the job
  - And import through pipes could come from the South

APSIS

SAFETY AND QUALITY

VERY DEMANDING REQUIREMENTS ON PURITY

- A very demanding list
  - It's long !
  - Some very low values here : sulphur, water , oxygen…
  - Some complex to define : « total sulphur compounds »
- Justified by aging problems on fuel cell
  - No problem for chemical or combustion usage
- Challenging to even measure
  - Techniques are making progress, but at a point complete characterization was almost impossible
    - Now it would still cost 20 000 $
  - No total online quality control possible !
  - You have to guarantee no pollution can happen

Maximum concentration of individual contaminants	
Water (H_2O)	5 µmol mol^{-1}
Total hydrocarbons (methane basis)[b]	2 µmol mol^{-1}
Oxygen (O_2)	5 µmol mol^{-1}
Helium	300 µmol mol^{-1}
Total Nitrogen (N_2) and Argon	100 µmol mol^{-1}
Carbon dioxide (CO_2)	2 µmol mol^{-1}
Carbon monoxide (CO)	0.2 µmol mol^{-1}
Total sulphur compounds (H2S basis)[c]	0.004 µmol mol^{-1}
Formaldehyde (HCHO)	0.01 µmol mol^{-1}
Formic acid (HCOOH)	0.2 µmol mol^{-1}
Ammonia (NH_3)	0.1 µmol mol^{-1}
Total halogenated compounds[d] (Halogenate ion basis)	0.05 µmol mol^{-1}
Maximum particulates concentration	1 mg kg^{-1}

Bacquart et al. 2018 International Journal of Hydrogen Energy

ORIGIN OF POLLUTIONS

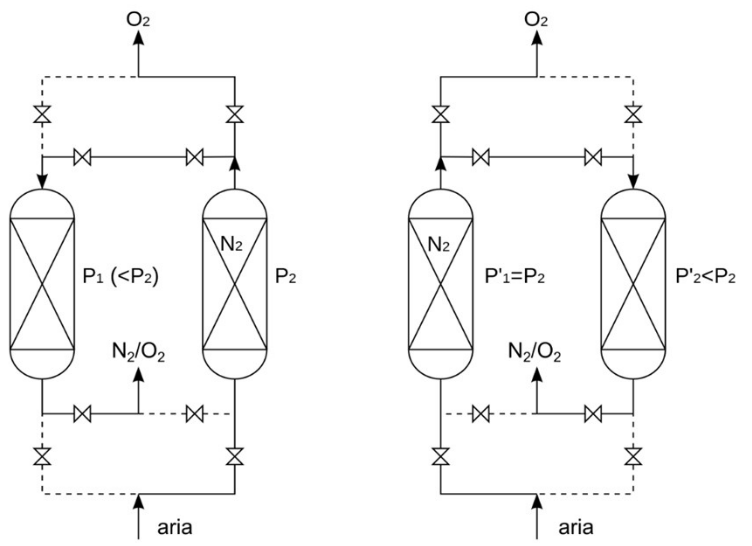
- SMR production
  - Sulphur, CO, CO_2…
  - Actually well handled by refineries massive purification systems
- Electrolysis
  - Water, O_2…
  - Less problematic impurities, but standards still to be built
- But the problems don’t end at production
  - Keeping the hydrogen pure is a problem at those standards
  - Transport ?
    - A 50 years-old methane pipeline is not going to be mirror-clean…
  - Compression ?
    - Need to develop lubricant-less technologies

AICHE

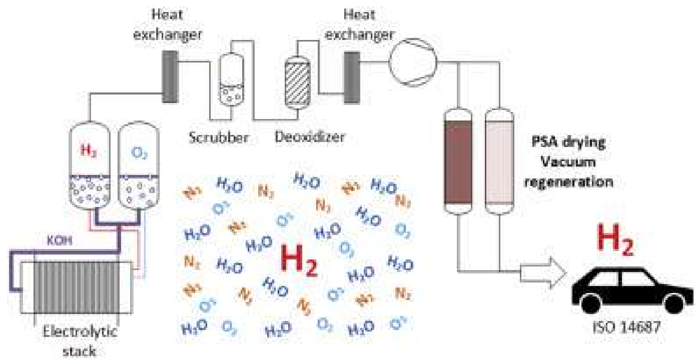
Peric

PURIFICATION METHODS AND STRATEGY

- Option 1 : Keep it clean, at all cost !
  - Current strategy for commercial H_2
  - Large-scale, centralized purification at the plant
  - Perfect control of downstream conditions
- Option 2 : Guarantee purity at the consumer end
  - You can (somehow) tolerate degrading purity in transport
  - Last step of purification just before consumer delivery
  - Small purifiers on eack delivery points
  - Don’t bother with users who don’t use a fuel cell
- Important, because purification techniques are scale dependant
  - Massive PSA/TSA units in large plants
  - Small, limited purifiers still to be optimized



WIkipedia



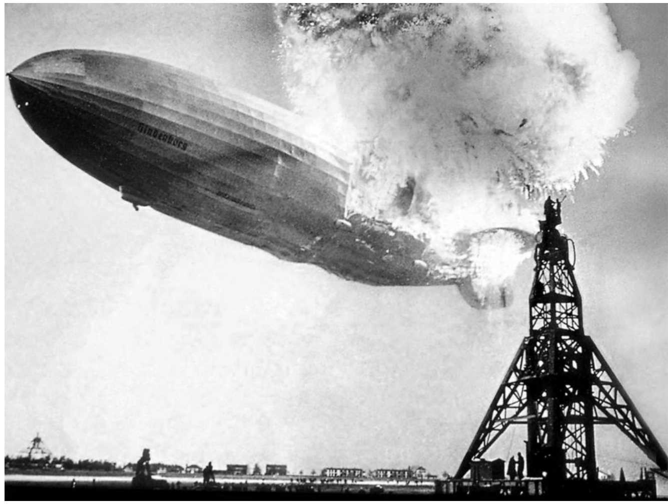
Ligen et al. 2020 International Journal of Hydrogen Energy

SAFETY : AN EXPLOSIVE GAS

- Flamability, explosivity
  - Flamability range : 4%-75% at ambiant pressure and T°
    - Methane : 5-15%
  - Detonation range : 11%-59% (supersonic shockwave)
  - Ignition energy 17 µJ/mole
    - 15 times less then methane (290 µJ/mole)
  - Any mix of hydrogen and oxygen can burn, with barely a spark

- Hydrogen flame is often too hot to be visible
  - 2000°C… mostly in the ultraviolet range

- A leaky gas…
  - Small molecule, will permeate tiny cracks and many materials
  - Known adverse effect on steels



Imagesensors.org

SAFETY : SENSORS

- Hear it : leak detector
  - Leaking gas make a distinctive sharp gas
    - Even more specific in ultrasound
  - Huge progress using AI to isolate the noise specific signature

MSA

- Smell it : gas detector
  - Detect the presence of the gas in the atmosphere
    - Catalyst, infrared
  - 1/10 of the inferior explovisity range

- See it : flame detector
  - Detect the light emmited by a flame
  - Huge progress again in discrimination capacity

SAFETY : ON THE ROAD

- A safety challenge
  - Vehicles are disseminated in a free environment
  - Wide variety of protentIal problems

- Hydrogen disseminate quickly
  - Can make the situation less dangerous then with liquid fuels
  - Won't save you in a confined environment

- Two main design principle
  - Maintain mechanical integrity of the reservoir box
    - On the model of deforming the structure to preserve the passengers
  - « Leak before break », especially in a fire situation
    - Because breakage most likely lead to an explosion
    - Thermal pressure release systems

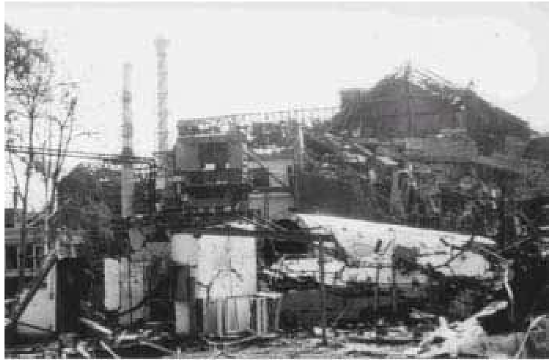
Hyundai

U.S. Department of Energy

SAFETY : STATIONNERY STORAGE AND SOCIAL ACCEPTANCE

- Most serious accidents implied stationnary storage
  - More hydrogen stored
  - Confined space
  - Industrial handling of hydrogen is an old story, though

- Pressure from industrial to relax constraints on stored hydrogen
  - Limits that were sent for a niche chemical are very constraining for mobility applications
  - But those limits were set for a reason…
  - Growth of the sector is very fast, actor's skills a real issue



- Social acceptance
  - Public image of hydrogen is generally very good, and projects easily accepted
  - One serious accident can change this reputation rapidly

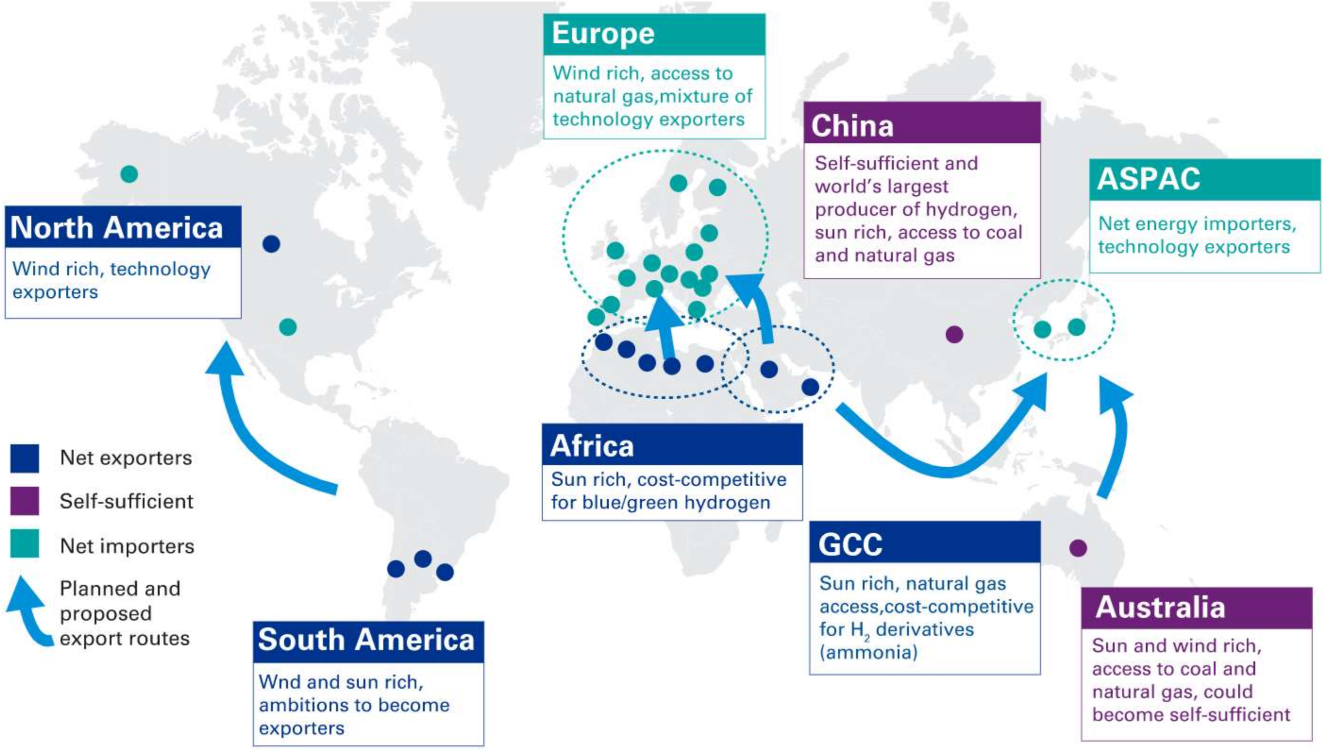
CASE STUDY

YOUR TIME TO WORK !

- India’s hydrogen strategy: global
  - How do you think India will use hydrogen to balance its energy needs
    - Hubs ? Transport ?
    - Import-export ?

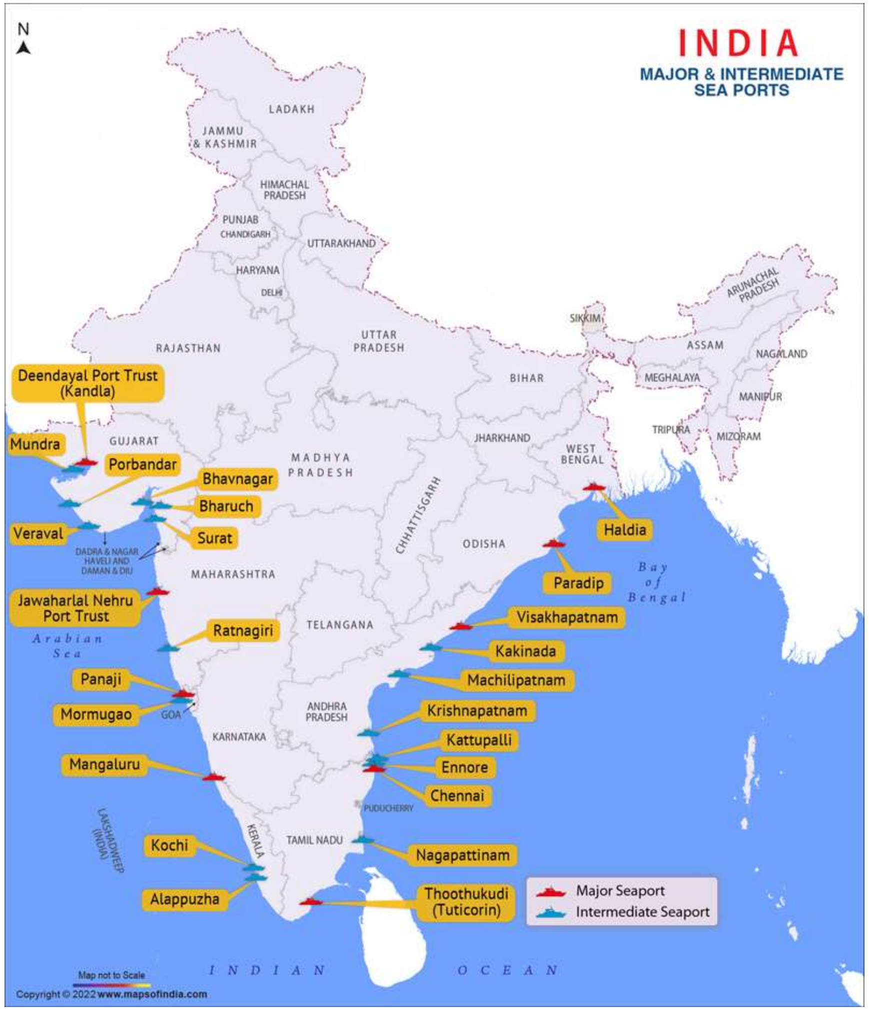
- I don’t have a correction !
  - You are the experts concerning India, not me…
  - But I have a few éléments and we can debate

BOTH A MASSIVE PRODUCER AND A MASSIVE CONSUMER

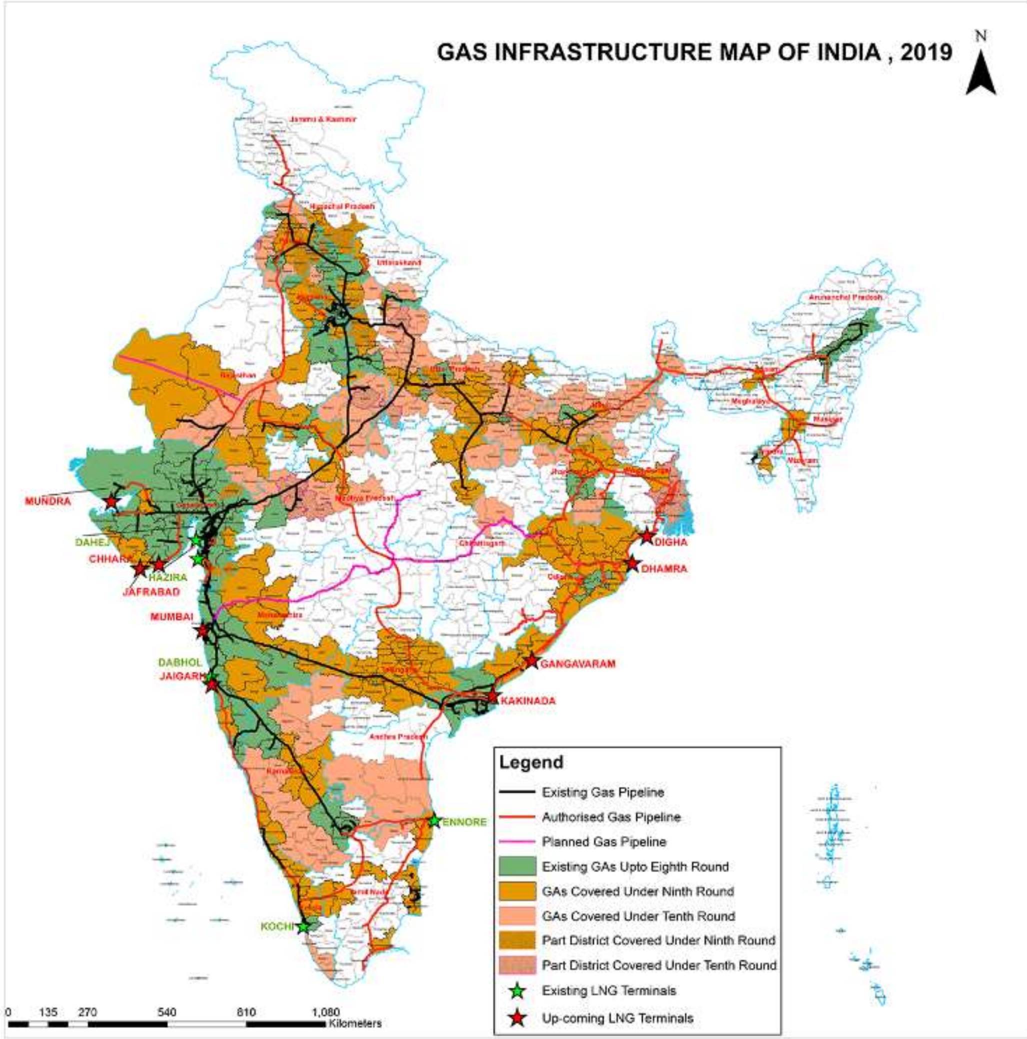


Global hydrogen hot spots and distribution corridors (not exhaustive).

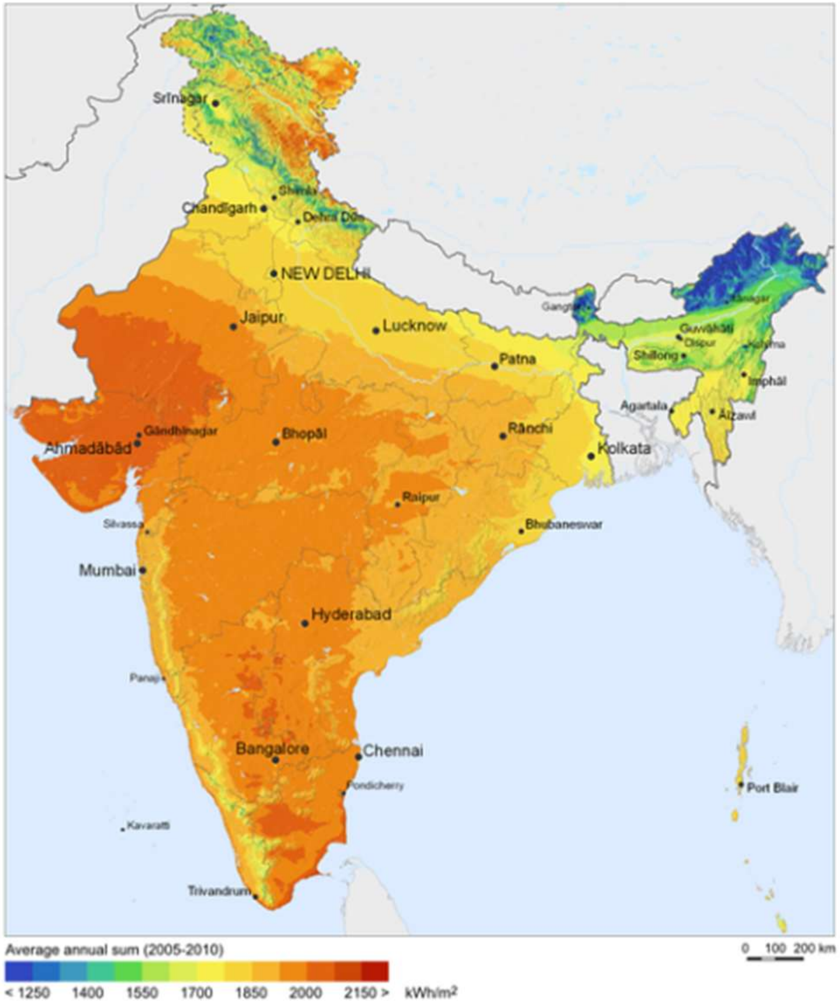
PORTS AS POTENTIAL HUBS



A RESPECTABLE GAS GRID



WEST-EAST UNBALANCE ?



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