HYDROGEN FOR THE ENERGY TRANSITION : WHY ? HOW ?
PART IV : SUBSURFACE

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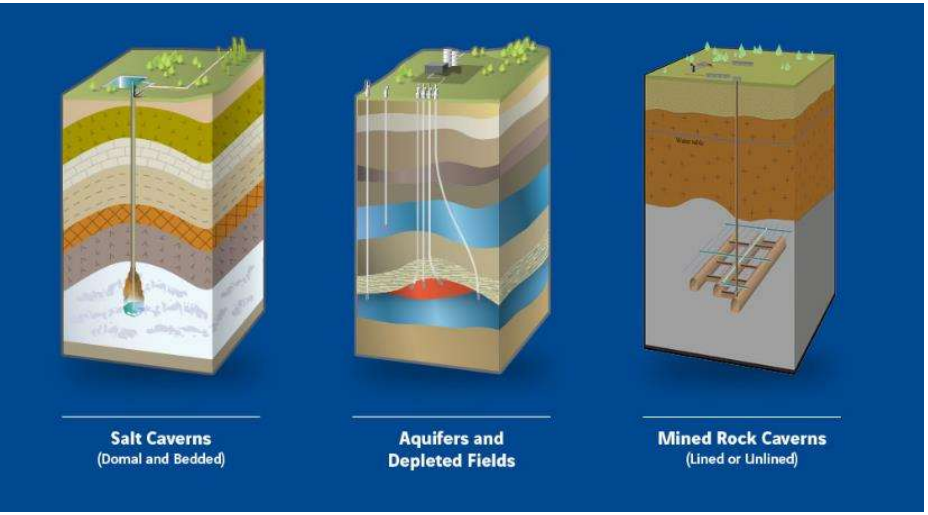
GeoIndia 2022 – Continuing Education Courses October 12th 2022



ifp Energies nouvelles

PROGRAM OF THE COURSE (2/2)

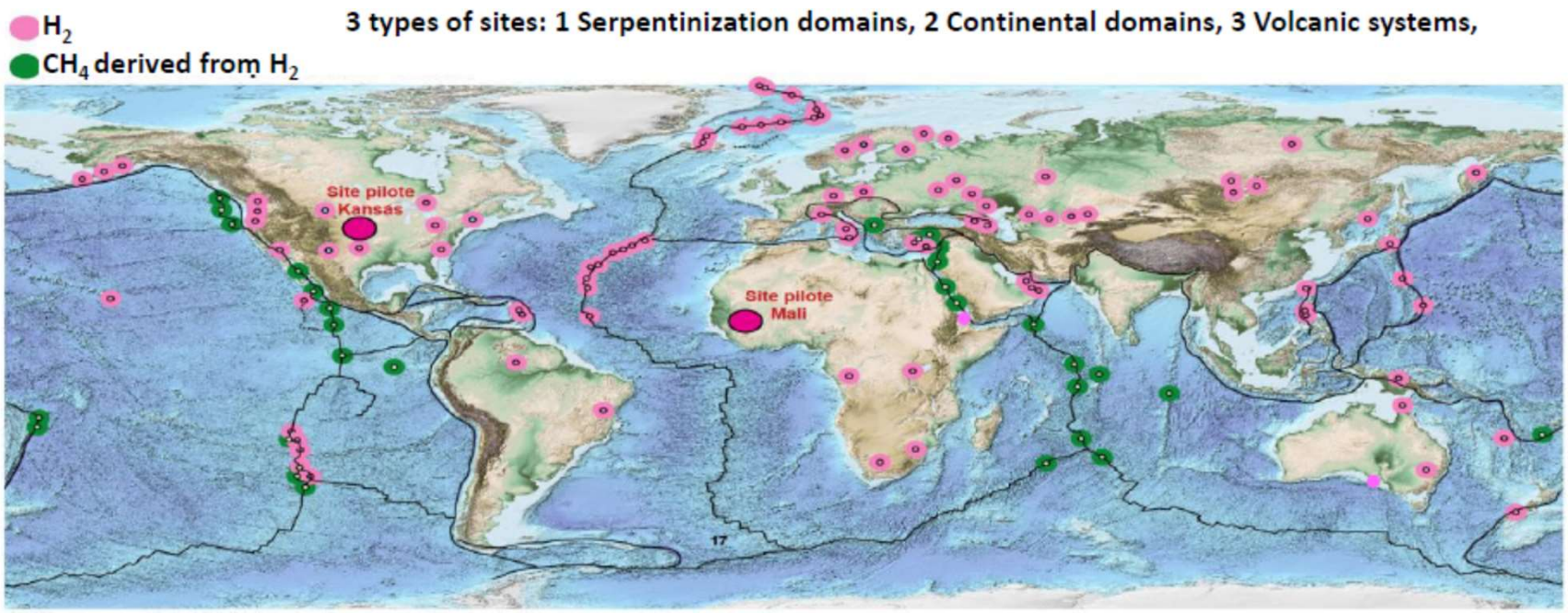
- Part 3 : Toward an hydrogen network
  - Technologies to transport and store hydrogen
  - Safety and quality issues
  - Case study : Your hydrogen strategy for India
- (Tea break)
- Part 4 : Hydrogen underground
  - Underground ressources for hydrogen (native hydrogen and in-situ production)
  - Storing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

PART 4 : HYDROGEN IN THE SUBSURFACE

- Underground ressources for producing hydrogen
  - Natural hydrogen
  - Underground production of hydrogen
- Underground storage
  - Typology of possible geology
  - Technical issues
- No case study this time : open discussion and debate

NATURAL HYDROGEN

NATURAL HYDROGEN : A WORLDWIDE PRESENCE

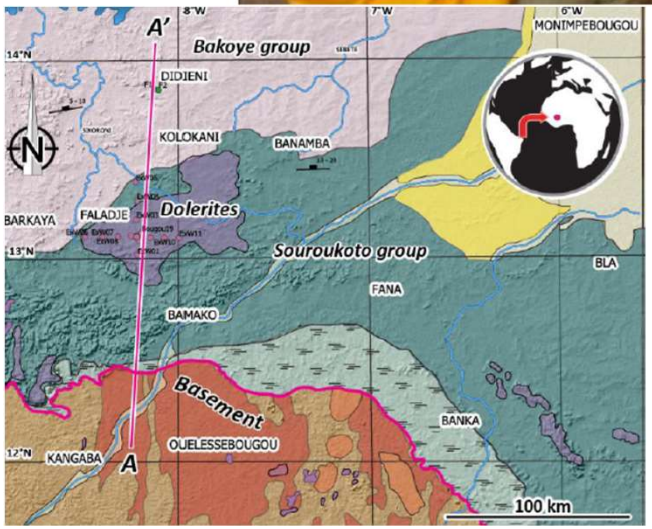


INSTEAD OF A COMMON PREJUDICE:
THEY ARE NUMEROUS ZONES OF EMISSION OF NATURAL H_2 ON EARTH

- While investigations have been far from exhaustive

AND ONE OPERATIONAL PRODUCTION SITE

- In 1987, a well drilled for water was closed due to a gas explosion
- Limited exploitation started in 2011 by HYDROMA
  - Without pressure drop or decrease in flow rate
- Additional drilling in 2018 confirmed the presence of H2
  - But geopolitical context make difficult further progress
- A rarity, or are we just not drilling in the good places ?



NATURAL HYDROGEN CHEMISTRY

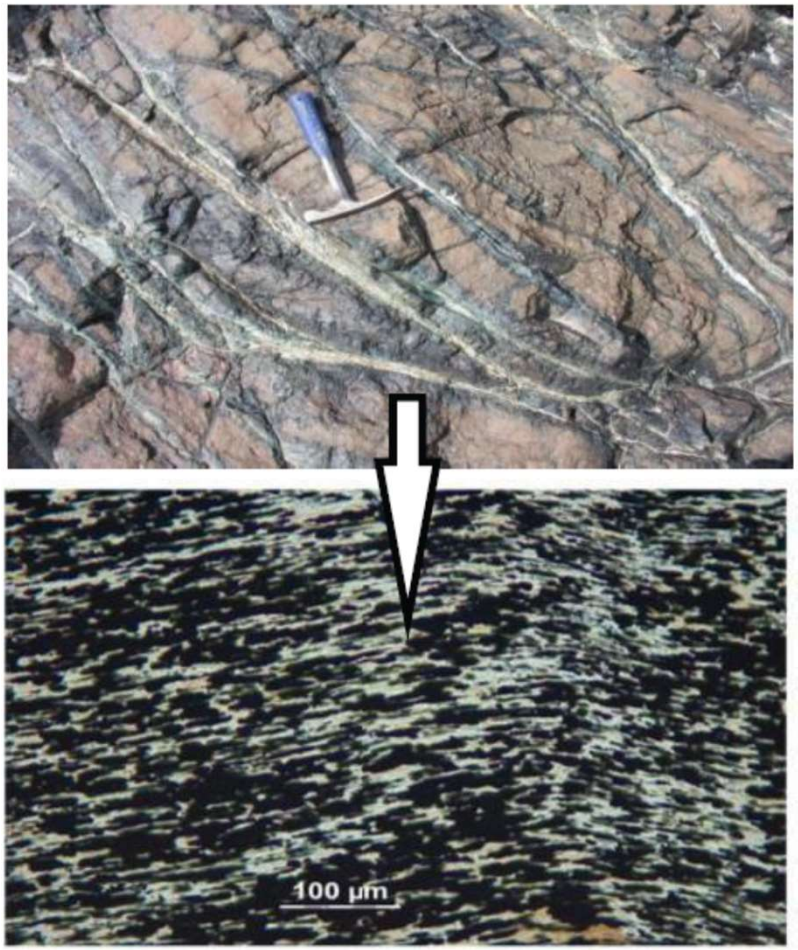
- Reduction of water, like in electrolysis !
- The reductor here being ferrous rock not fully oxydized
- A typical system : olivine → serpentinite

$2\ Mg_2SiO_4 + 3\ H_2O \rightarrow Mg_3Si_2O_5(OH)_4 + 2\ Mg^{2+} + 2OH^-$
Forsterite + water → Serpentine + magnesium + hydroxyde

$3\ Fe_2SiO_4 + 2\ H_2O \rightarrow 2\ Fe_3O_4 + 3\ SiO_2 + 2\ H_2$
Fayalite + water → Magnetite + silica + hydrogen

$3\ Mg_2SiO_4 + 4\ H_2O + SiO_2 \rightarrow Mg_3Si_2O_5(OH)_4$
Forsterite + water → Serpentine

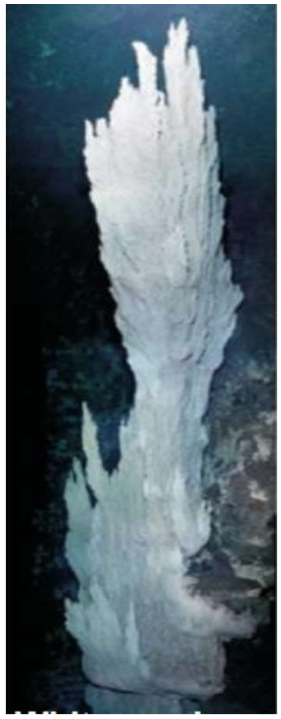
- What you are looking for :
  - Adequate rocks
  - Water circulation
  - Traps/faults system for migration and accumulation

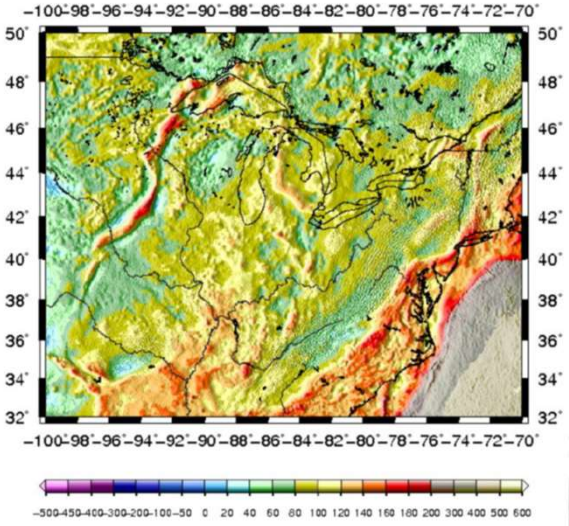


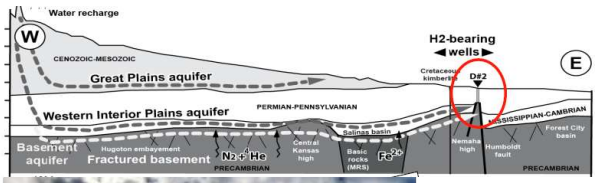
Magnetite $Fe^{2+}Fe^{3+}{}_2O_4$

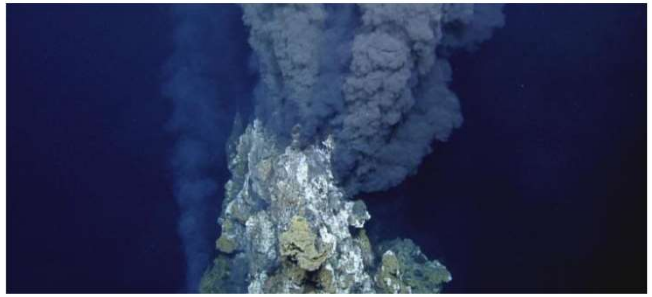
TYPES OF PRODUCTIVE GEOLOGY

- Oceanic lithosphere
  - Crust freshly formed from oceanic dorsal
  - Ophiolites
- Craton
  - Old portions of continental plate, not deformed by tectonic
- Volcanic rocks



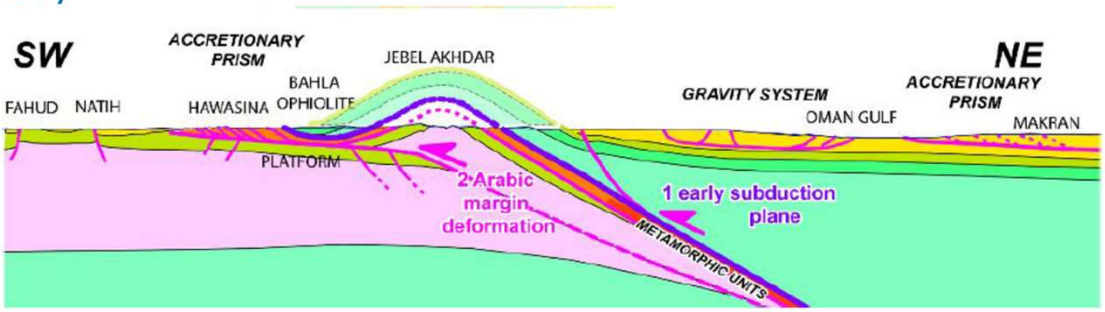


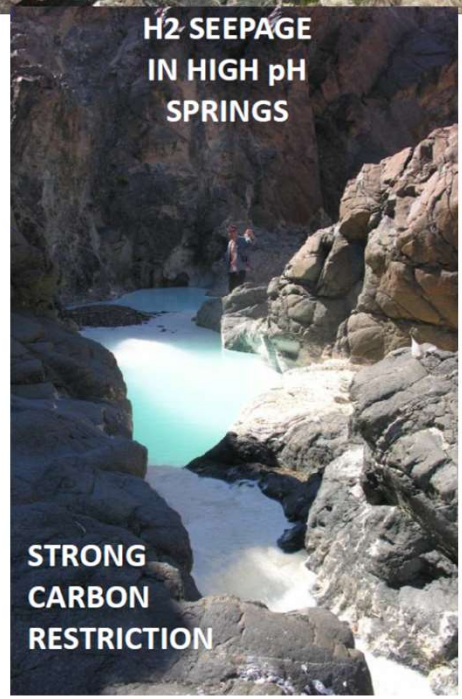




EXAMPLE OF LITHOSPHERIC ORIGIN : OMAN

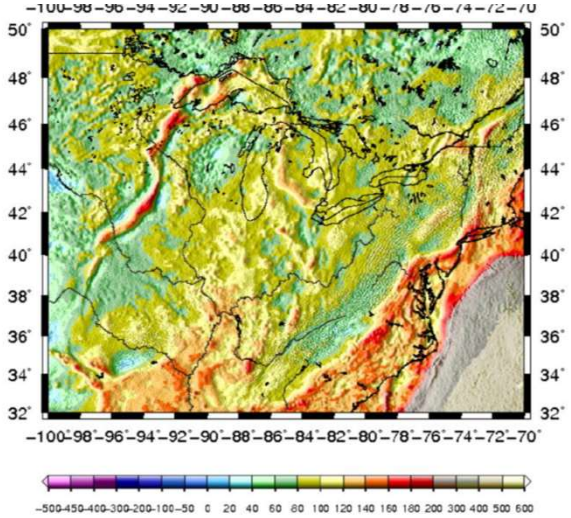
- Obduction phenomenon pushed the ophiolites to the surface
- Peculiar mineralogy
  - (ultrabasic rock)
  - H2 naturally bubbling in some ponds
  - Ultra reactive with CO2
- Other similar cases :
  - New Caledonia
  - Philippines
  - Turkey

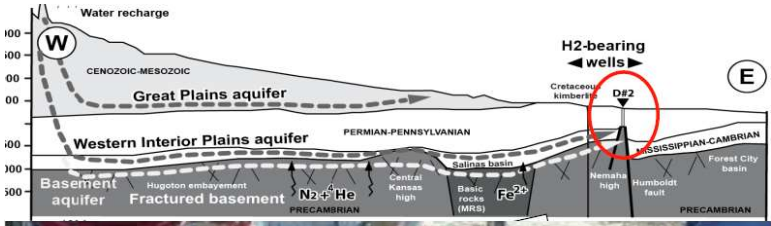


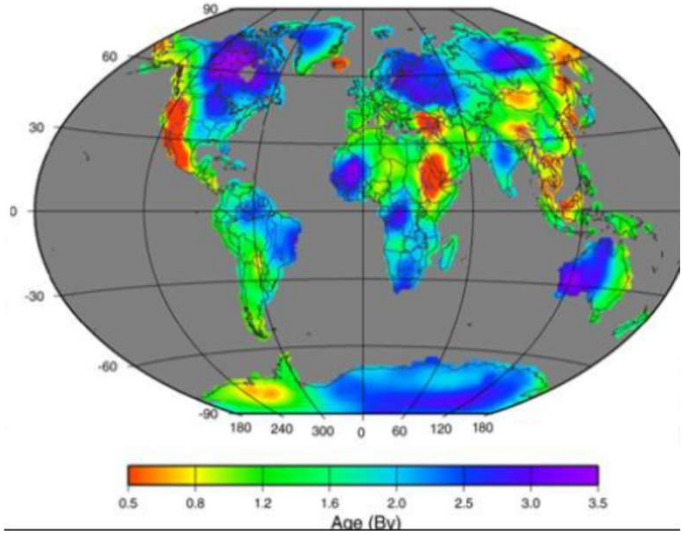


EXEMPLE OF CRATONIC ORIGIN : KANSAS

- Massive potential H2 formation along a large part of North America
- H2 unexepectedly found in several drilling in Kansas
  - The deep H2 forming rocks are locally accessible
- Other similar cases :
  - Russia
  - Mali
  - Australia

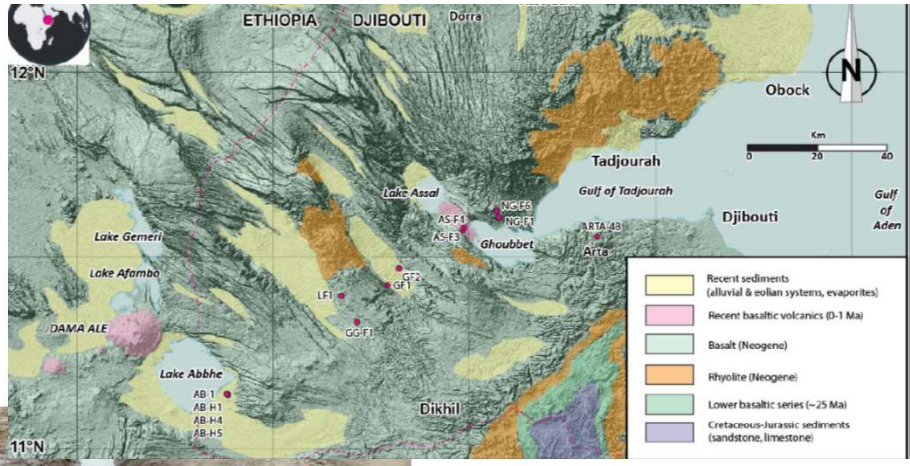


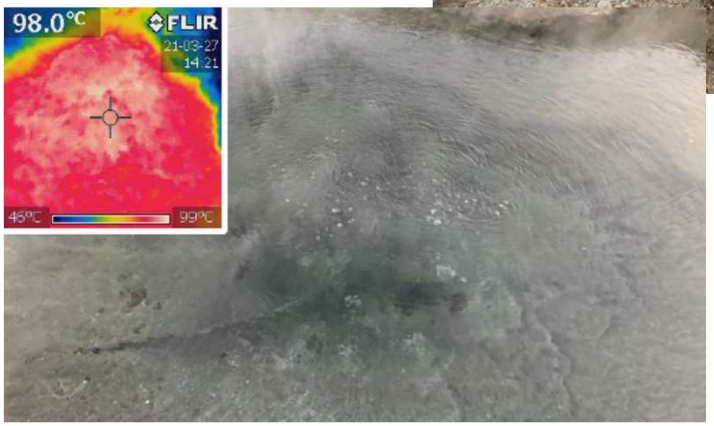


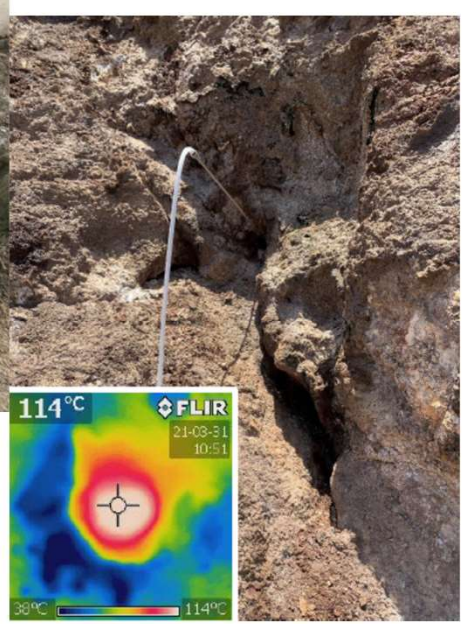


EXEMPLE OF VOLCANIC ORIGIN : DJIBOUTI

- Northern section of the rift valley
  - Basically a oceanic ridge on the continent
- H2 naturally found in volcanic gases
  - An collected in geothermal wells
- Other similar cases :
  - Oceanic ridges
  - Iceland
  - Italy

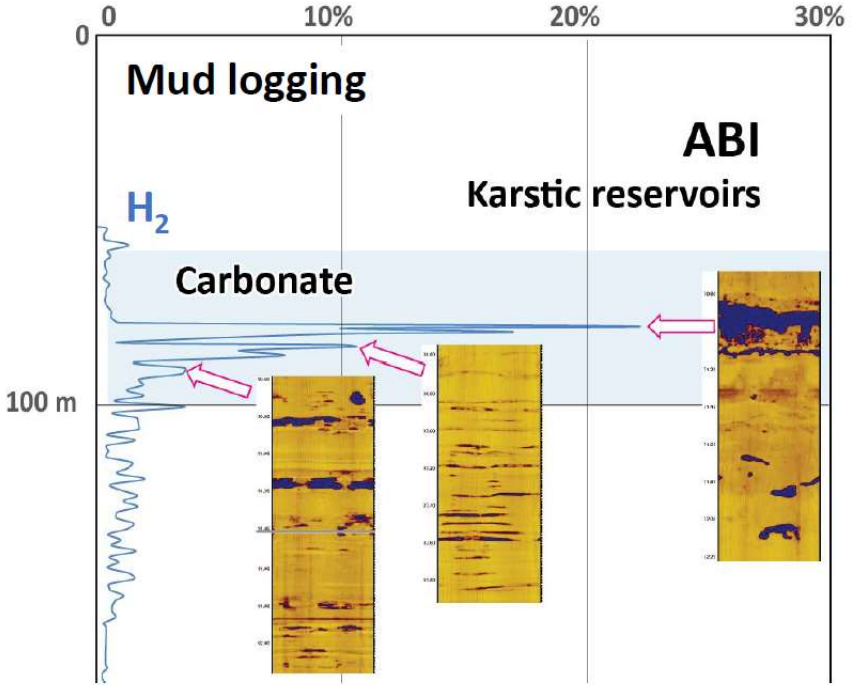


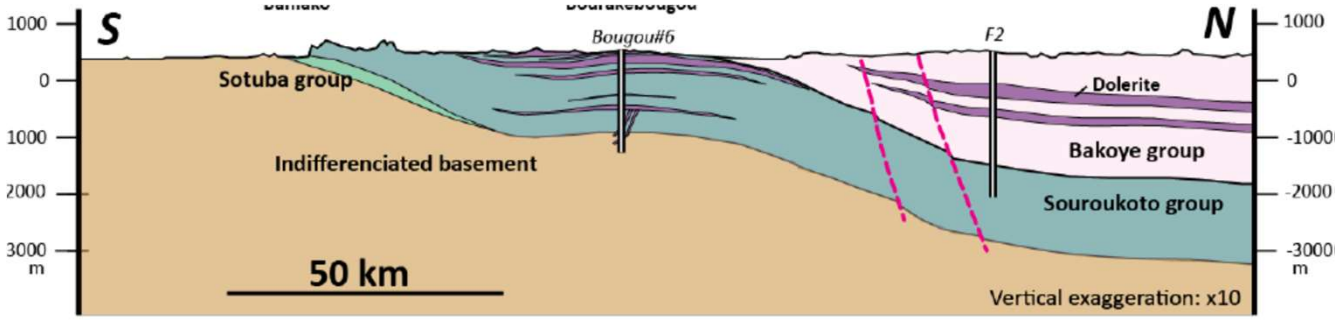




A CONTINUOUS PROCESS OR A RESERVOIR ?

- Hydrogen is formed continuously by geothermal processes
  - And migrate through rocks much more easily then oil or even natural gas
- However, natural hydrogen is still going to concentrate mostly in réservoirs
- Order of magnitude in time just not the same
  - 10 000 / 100 000 years, mot millions



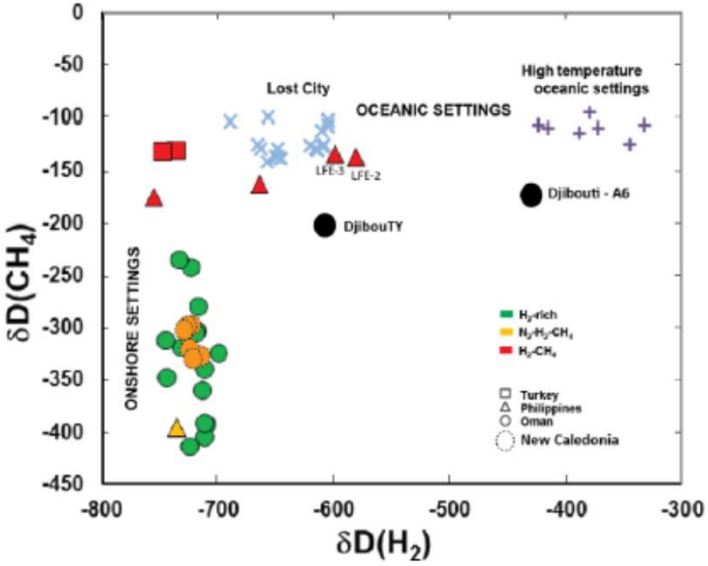


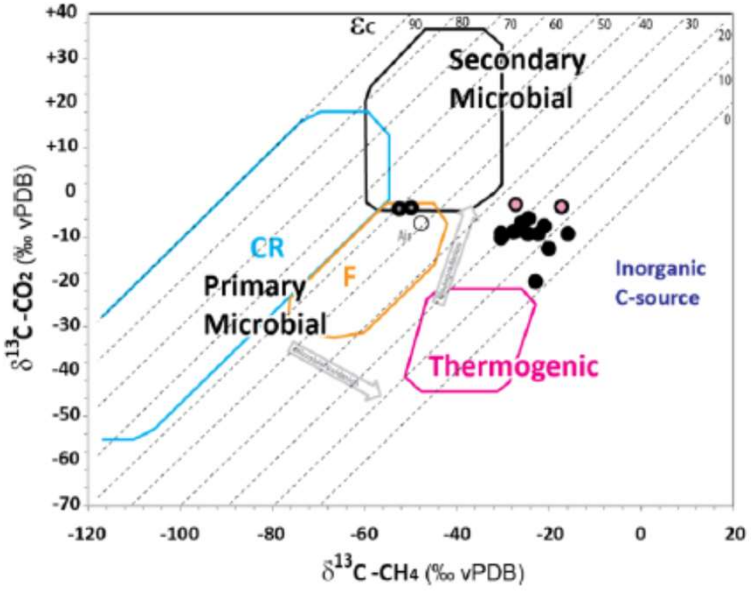
TINY SIGNS ON SURFACE…

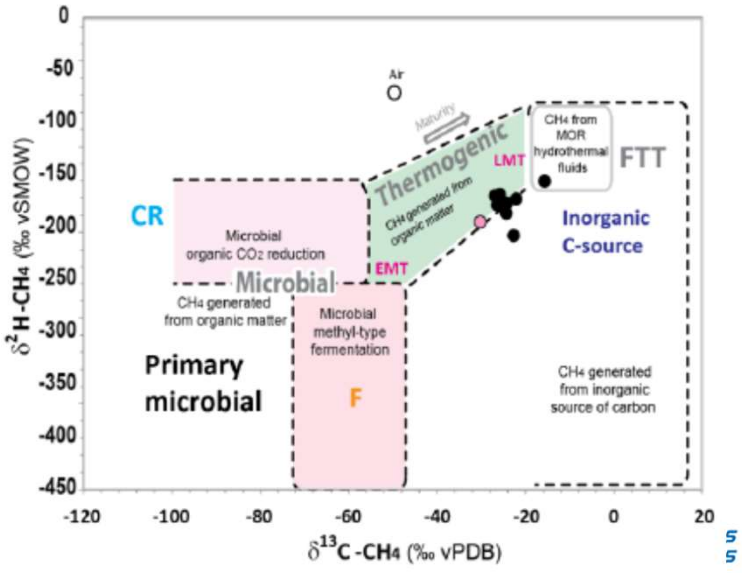
- H2 presence on surface is often disappointing
  - Drilling is better, but expensive, so H2 often found by accident
- But H2 is a very reactive gas
  - Combine with CO2 at temperature (especially in volcanic systems)
  - Microbial activity
  - Pollution with air or other gas flows
- « Witch circles »
  - Plant growth are visibly affected by hydrogen presence
  - An excellent (but not exclusive) sign of H2 seepage, especially in cratons

FOLLOWING GAS SIGNATURE

- H2 will often degrade into methane
- Isotopic signature can discriminate between different origins
  - Hydrogen isotopes
  - Carbon isotopes
  - Comparing carbon in CO2 and CH4







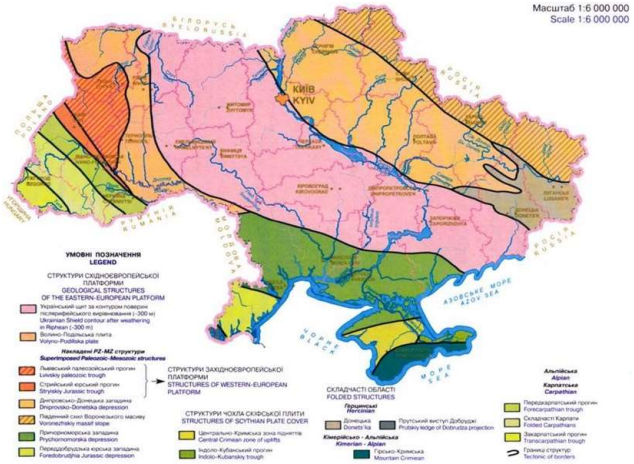
JUMPING IN

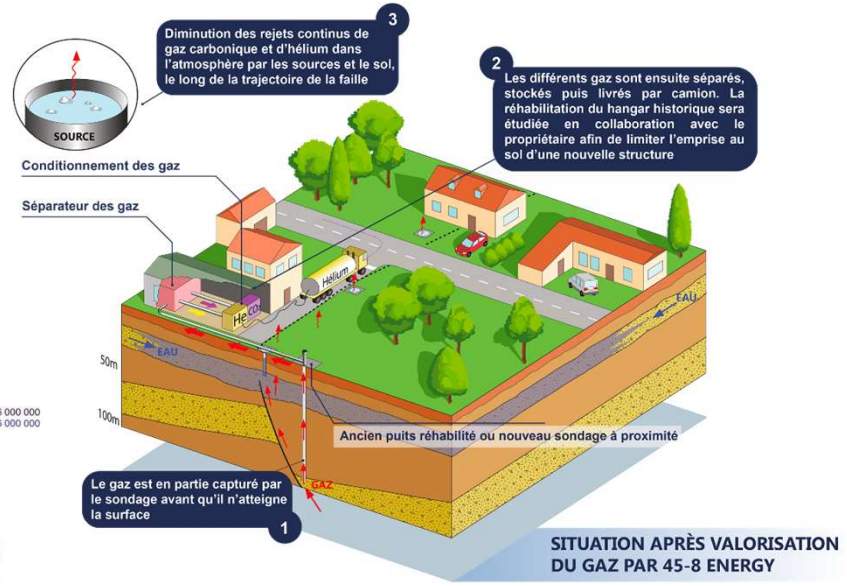
- Surface signature being disappointing, little other choices then exploratory wells
  - But expensive
  - Discovery often accidental
- Very little insight on profitability due to the near zero experience
  - Production costs ?
  - Logistics in isolated area ?
- Possible co-exploitation could help bridge the gap
  - H2 is often found in volcanic fluids exploited for geothermy
  - Often discovered together wit Helium which has a better business model

START DIGGING ! 45.8

45-8 energy

- French startup, primarily dedicated to Helium
  - With a strong side interest for natural hydrogen
- First small scale permit and exploitation in Eastern France
- Promising permit for H2/He exploration in a European country…

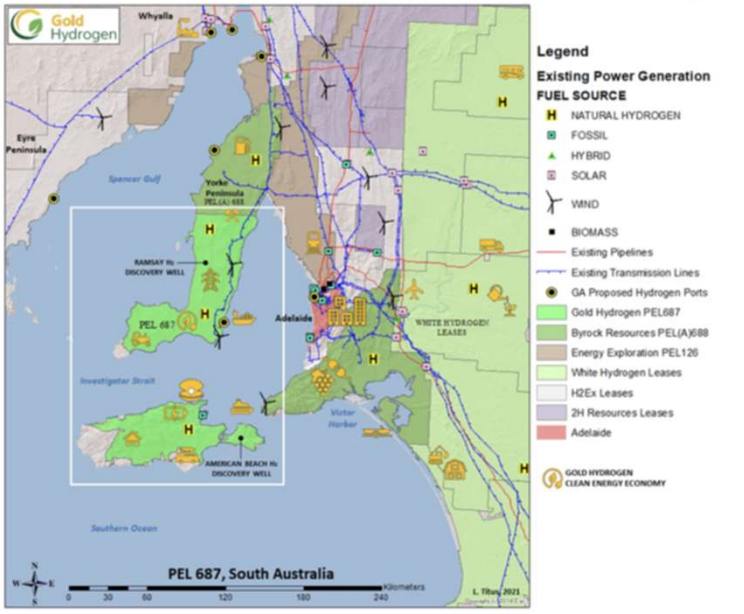




IFP Energies nouvelles

START DIGGING ! AUSTRALIA

- Australia has a promising geology (cratons), and many promising surface signs
- A promising ecosystems of startups brings a businesss mentality
  - Gold Hydrogen
  - H2EX
- Exploration permits granted at an unprecedent scale



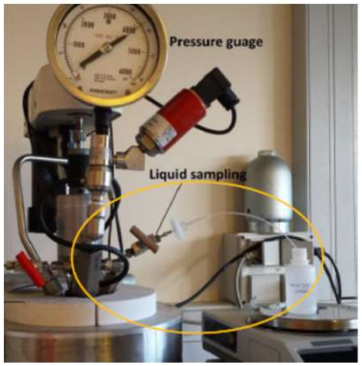
UNDERGROUND PRODUCTION

MINE TAILINGS

- Formation chemistry is known…
  - It can be tempting to activate it
- In New Caledonia, a lot of olivine containing rocks
  - Wich happen to be dug for nickel mining
  - Could mine tailing be treated with water to form hydrogen?
- Formation of H2 observed in the lab
  - Quantities are probably too small to justify the manipulation of large quantities of minerals

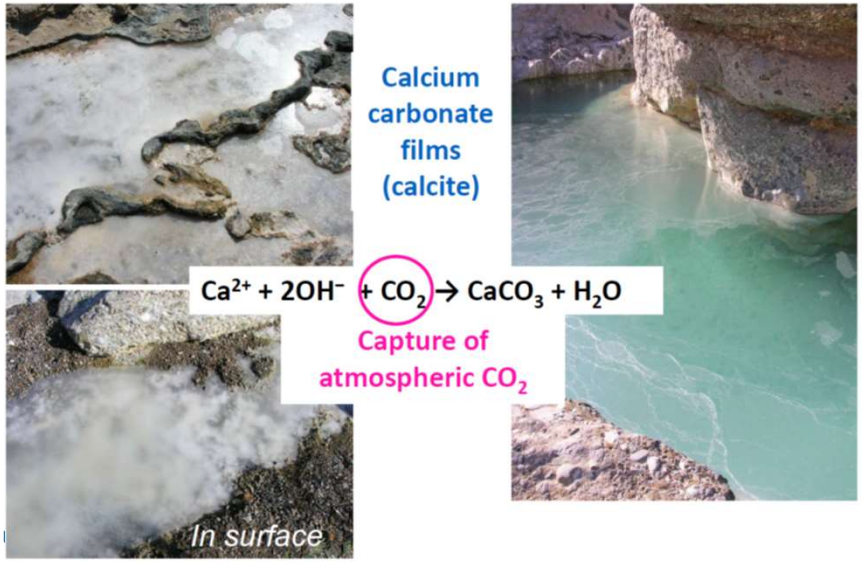
Mine waste after Ni extraction

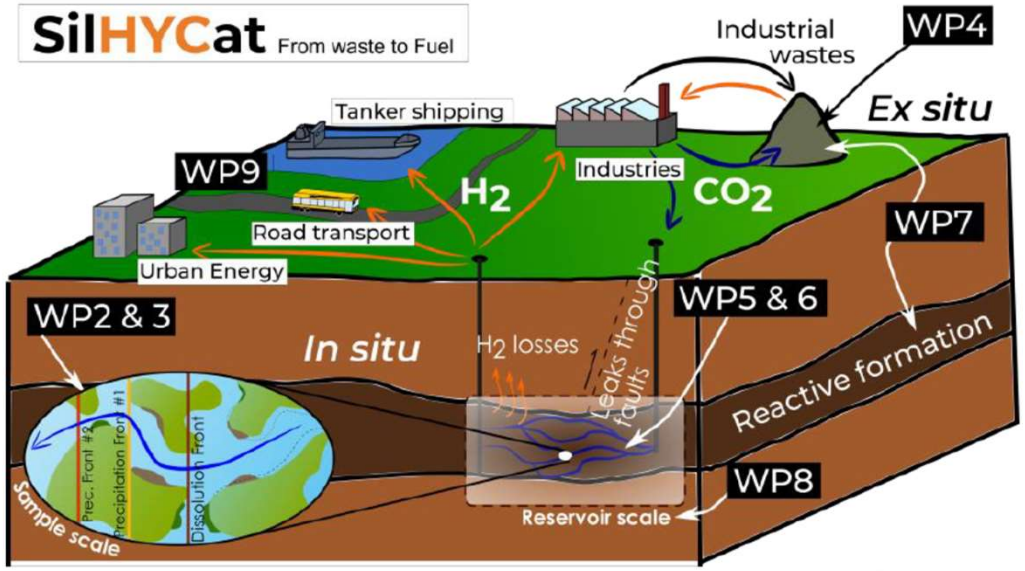
Olivine $(Mg,Fe)_2SiO_4$



IN-SITU STIMULATION OF H2 PRODUCTION

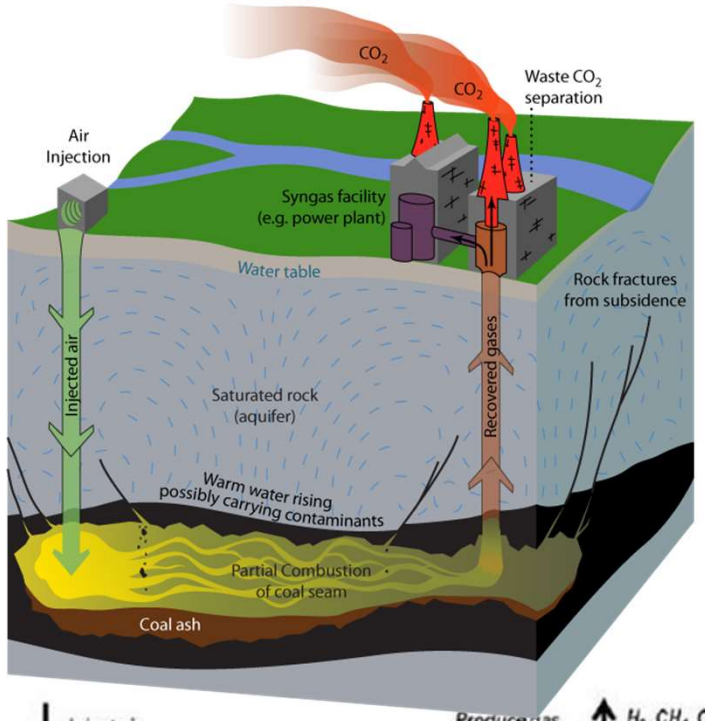
- Concept of the SilHYCat project
  - Inject water underground to stimulate naturally reactive formation
  - As the formation is reactive to CO2, load the water with CO2 to do CCUS as a premium
  - Actualy mimick the reactions actually going on in places like Oman
- We even have a color ready : orange hydrogen

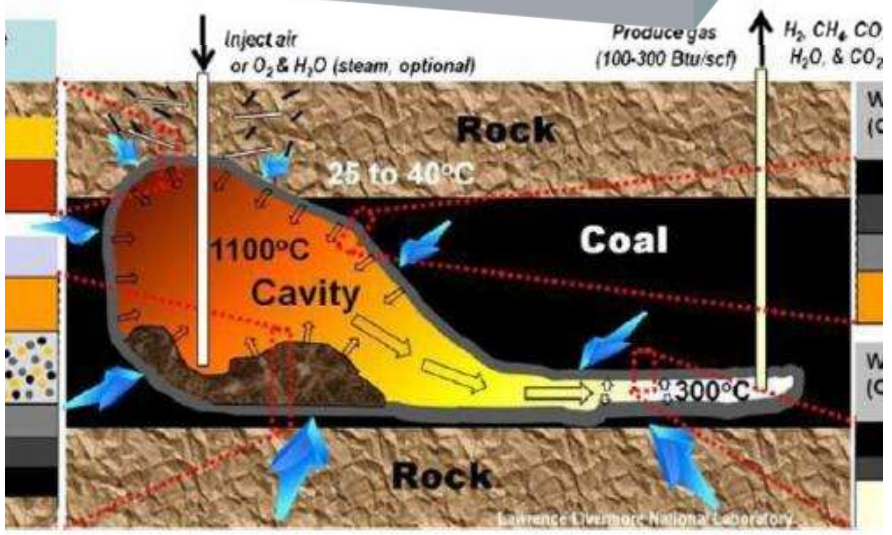




IN-SITU GASIFICATION OF COAL

- Coal gasification, using the seam as a reactor
  - Inject air and possibly water
  - Let the downhole pressure and T° do the job
- Low impact exploitation of coal ?
  - No surface mining
  - Ash and possibly CO2 stored underground
  - A way to exploit difficult to access seams
- A potential avenue for low carbon H2 ?





A QUESTION OF IMPACT

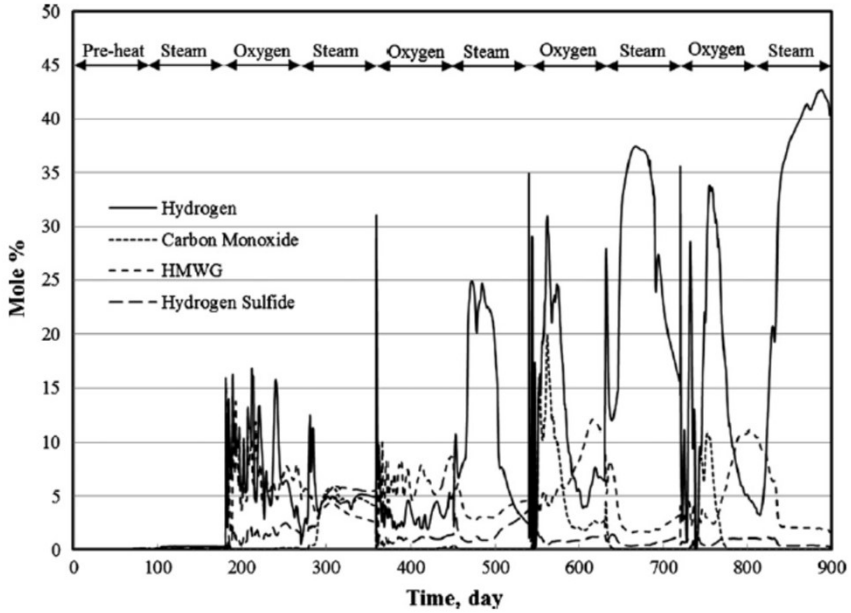
- No real control of emmitted gas
  - Little guarantee the CO2 will stay underground
  - Possibly nasty gases formed on top (Nox, SO2…)
- Aquifer pollution ?
  - Potentially catastrophic if volatile products from the gasification reach the water table
- Most recent attempts in Australia were blocked due to environmental concerns
  - But demonstrations continue in China or South Africa…

Cougar's plant problems escalate

Cougar Energy's difficulties with its flagship underground coal gasification project near Brisbane have escalated after the Queensland Environment Department rejected the company's environmental report for the plant.

IN-SITU GASIFICATION OF BITUMEN

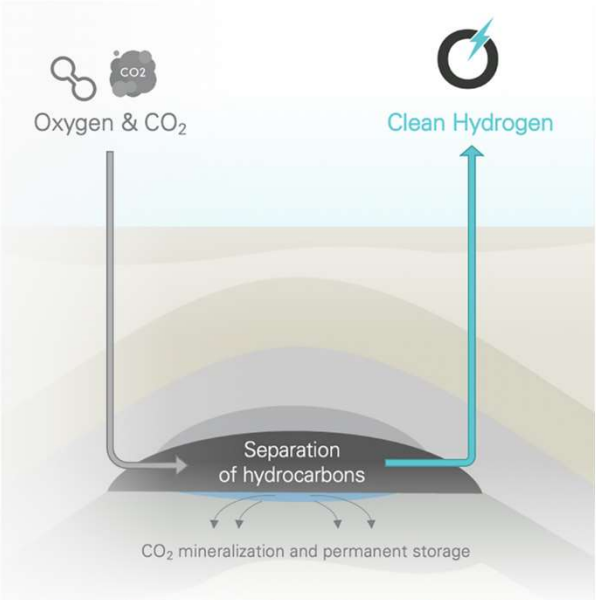
- Same idea as for coal, with difficult to exploit bitumen
- Mainly explored in Canada (sand bitumen)
  - First pilot attempts in 1983
  - Mixtures of syngas and fluidized oil exploited
- A better potential for limiting impact
  - Geology more naturally prone to trap gases



THE PROMISES OF PROTON TECHNOLOGIES

PROTON

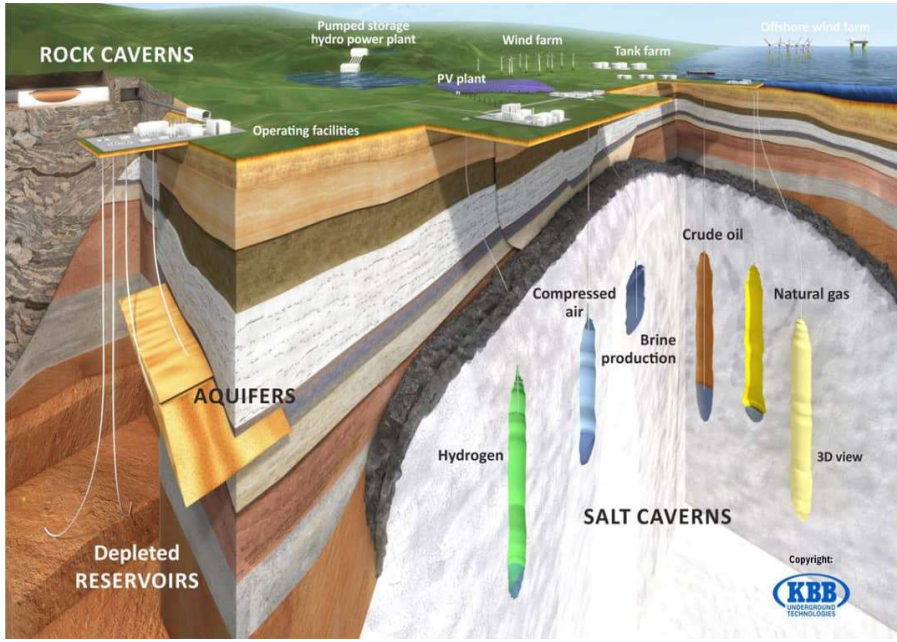
- Canadian company
  - Acquired in 2017 permit to try in-situ gasification in Saskatchewan
- Originality : focus on low-carbon hydrogen
  - H2 is spearated from other flue gas, which are einjected in the reservoir
  - Ultimately, a downwell filter could allow to bring only the hydrogen to the surface
- Spectacular claims, both on economy and footprint
  - Cost at 0.3 $/kg
  - Carbon footprint below $1t_{CO2}/t_{H2}$
  - « Extraordinary claims require extraordinary evidence » Carl Sagan



HYDROGEN UNDERGROUND STORAGE

WHY DO WE STORE GAS (AND HYDROGEN) UNDEGROUND

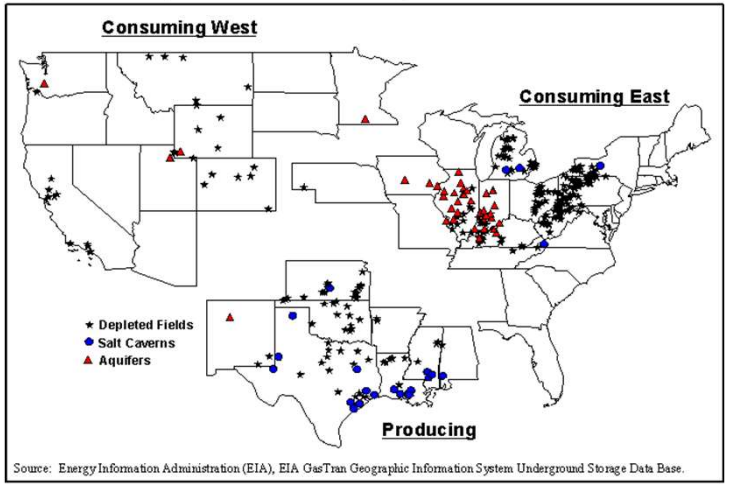
- Old and proven technology
- Huge capacities
  - 1 storage can fill 1 000 000 individual cars
  - Or 10 000 tube trailers trucks
- Ultra competitive cost
  - 300 time less expensive then a type IV reservoir
- Safe
  - There is hundreds of meters of rock between hydrogen and oxygen
- Limited surface footprint



STORING GAS UNDERGROUND, AN OLD STORY

- Main solution for the storage of methane around the world
  - In Europe, 124 sites with a total capacity of 10^{11} Nm^3
  - 415 sites in the USA (which is also a gas producer)
  - EU countries are required to have 15 % of their consumption in storage capacity
- Hydrogen
  - Underground storage of hydrogen is rare but not unknown
    - Exactly 4 in operation (all salt caverns)
  - More experience if you count syngas
    - But not all happy experience

Figure 2. Underground Natural Gas Storage Facilities in the Lower 48 States

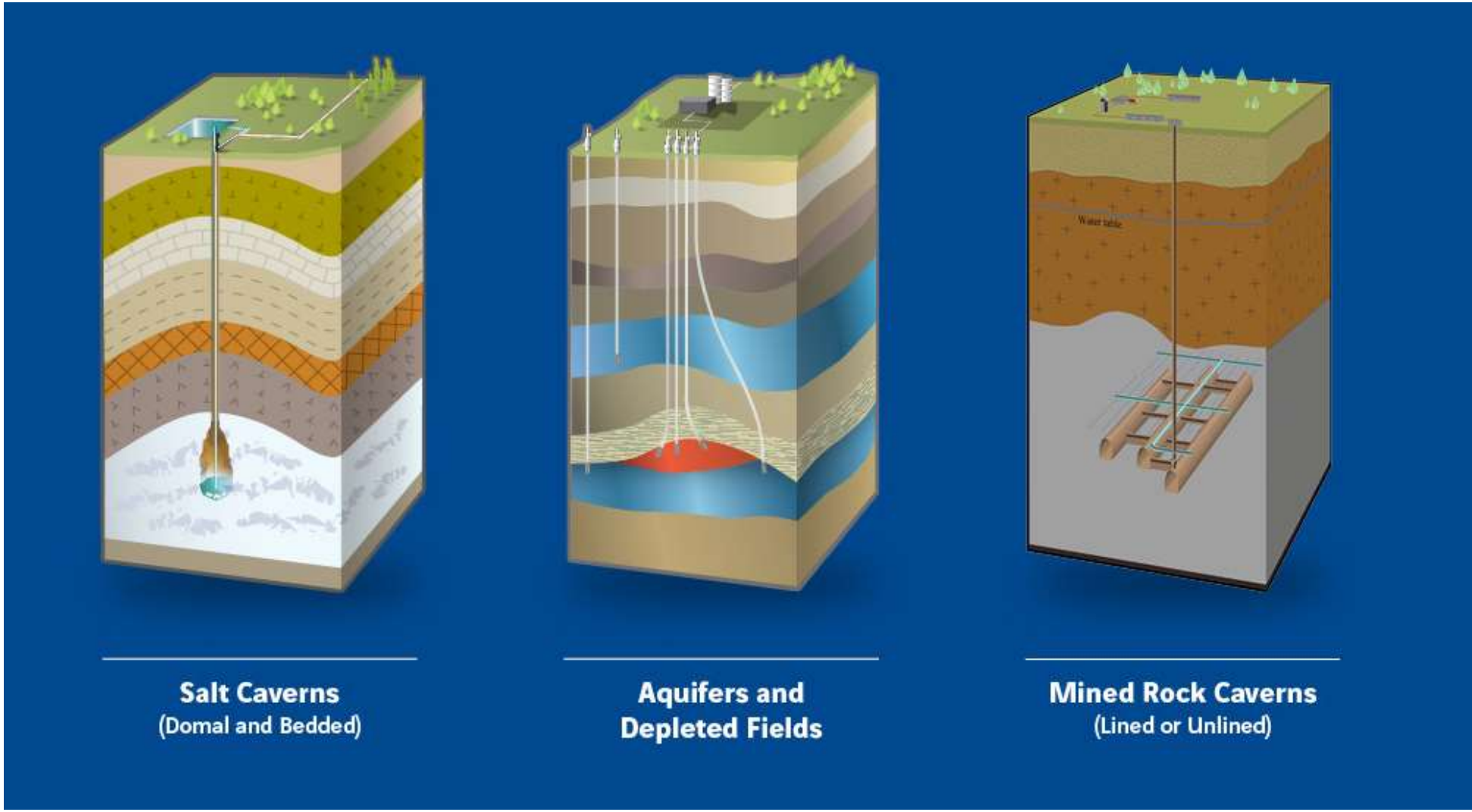


Source: Energy Information Administration (EIA), EIA GasTran Geographic Information System Underground Storage Data Base.

	Teeside (UK)	Clemens Dome (Texas)	Moss Bluff (Texas)	Spindletop (Texas)
Salt formation	Bedded Salt	Salt dome	Salt dome	Salt dome
Operator	Sabic Petrochem.	Chevron Phillips Chem. Comp.	Praxair	Air Liquide
Commissioned	1972	1986	2007	Information not available
Geometrical volume [m^3]	210 000	580 000	566 000	906 000
Mean cavern depth [m]	365	1 000	1 200	1 340
Pressure range [bar]	45	70-135	55-152	68-202
Net energy stored [GWh]	27	81	123	274
H_2 mass [ton]	810	2 400	3 690	8230
Net volume [m^3] (std)	9.12×10^6	27.3×10^6	41.5×10^6	92.6×10^6

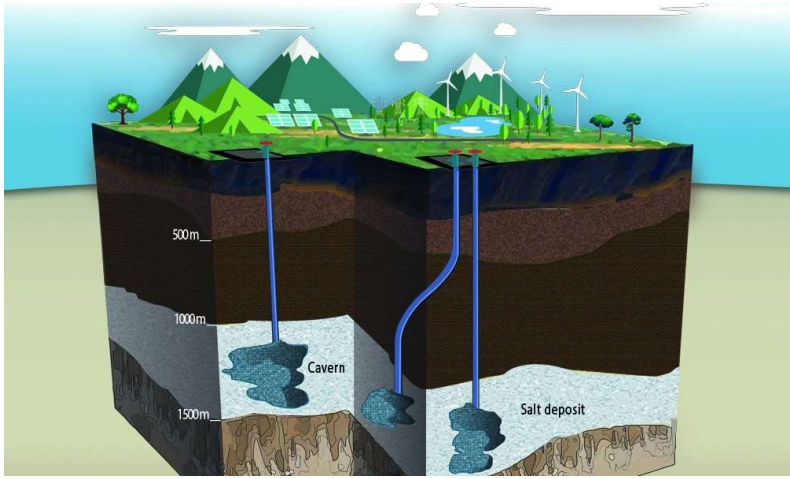
DIFFERENT TYPE OF GEOLOGY

Geostock

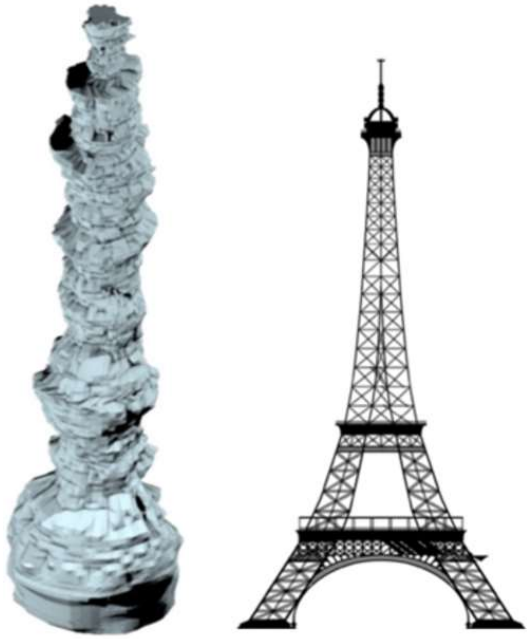


SALT CAVERN

- Some essential difference with say, an oil reservoir
  - Free volume, not a porous media saturated with gas
  - Entirely artificial
- Mind-boggling size and capacity. Data from a german cavity
  - Height : 600 m
  - Volume : 400 000 m^3
  - Pressure : 200 bar
  - Up to 4 TWh of energy stored on the year



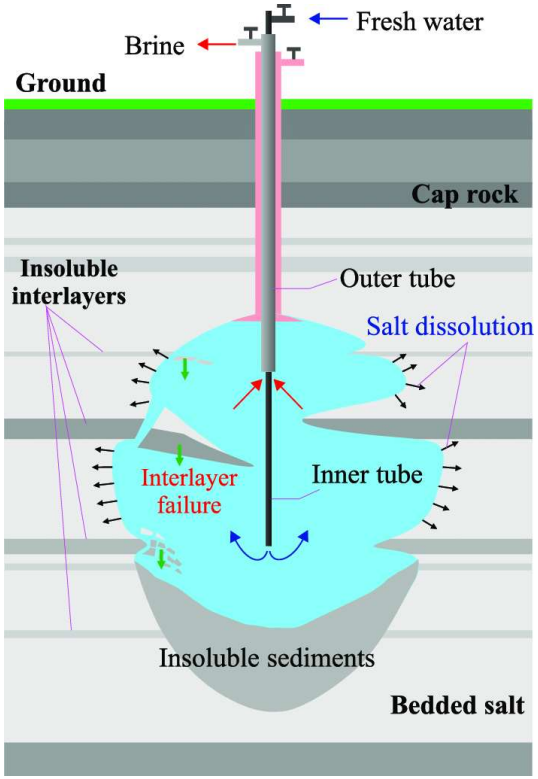
AS-Schneider

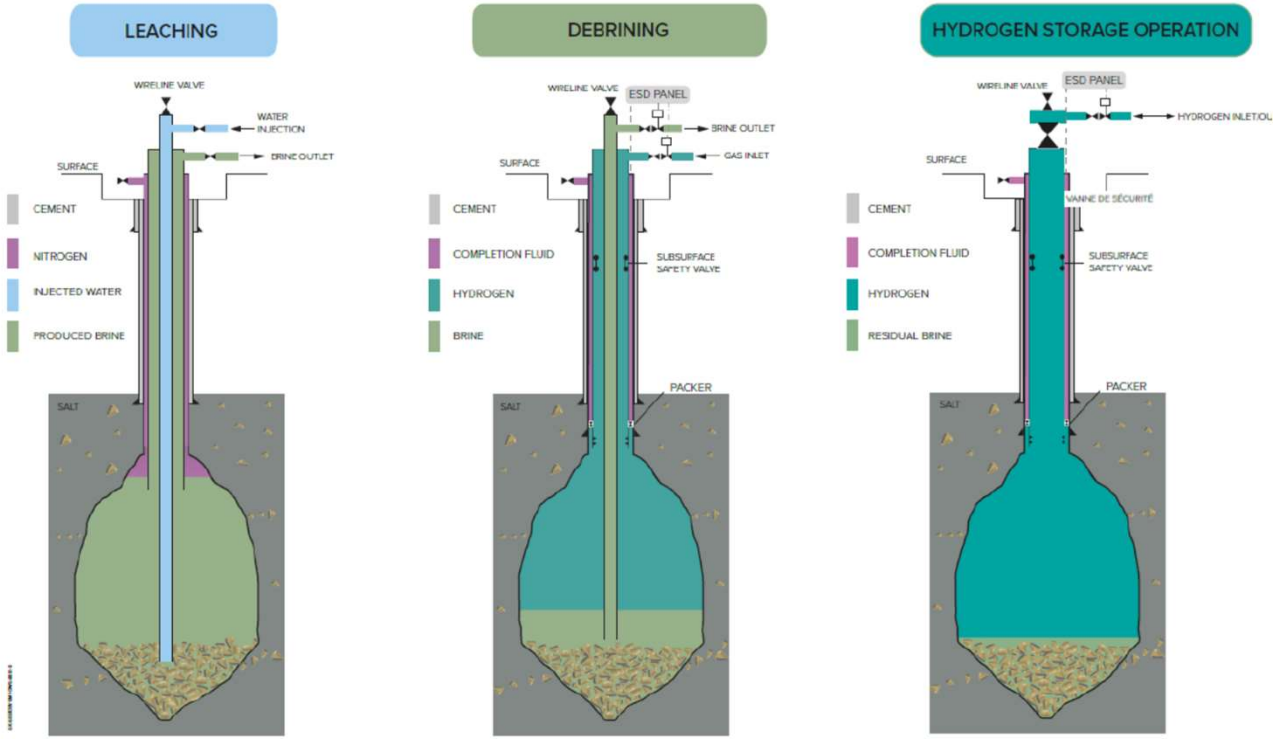


Geosel

BUILDING A SALT CAVERN

- Inject water to dissolve the salt, extract the brine, replace with gas
  - And find some way to dispose of the large quantities of brines

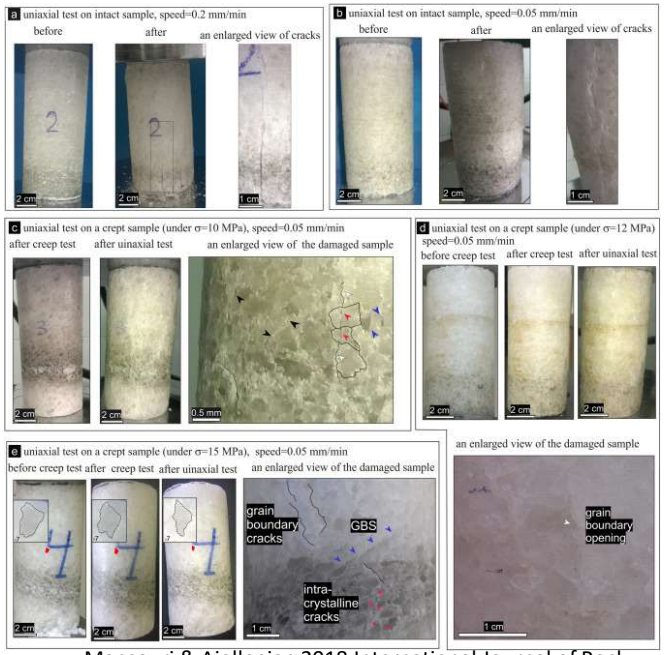




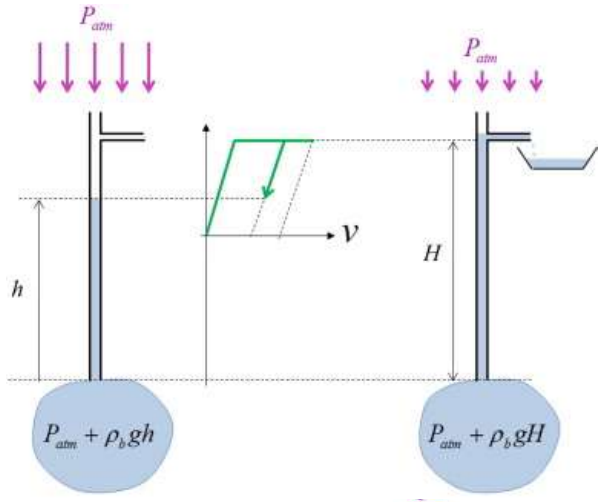
Geostock

A QUESTION OF CREEP

- Salt is a viscoplastic material
  - It tends to deform other time when submitted to pressure
- One adversial consequence
  - The cavity is not entirely stable
  - It can deform or close even without dramatic pressure drop
    - Very slow for common conditios
- But one very beneficial !
  - Cracks close, making the formation as a whole very tight



Mansouri & Ajolloeian 2018 International Journal of Rock Mechanics and Mining Science



Brouard et al 2013 International Journal of Rock Mechanics and Mining Science

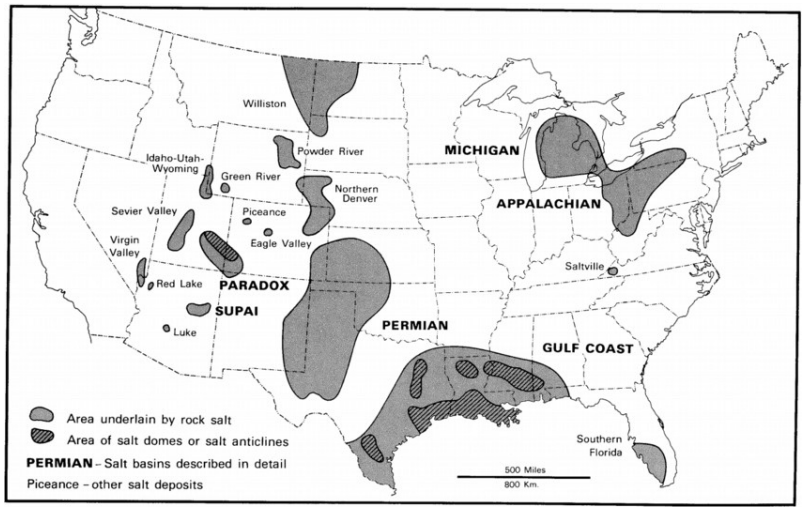
WHAT MAKES SALT CAVERN SUCH SUPERIOR OPTIONS FOR HYDROGEN

- Almost perfect tightness (self-sealing through creep)
- Limited issue with microbial activities (gas pollution during storage)
- Superior cyclability
- Cushion gas limited to a minimum

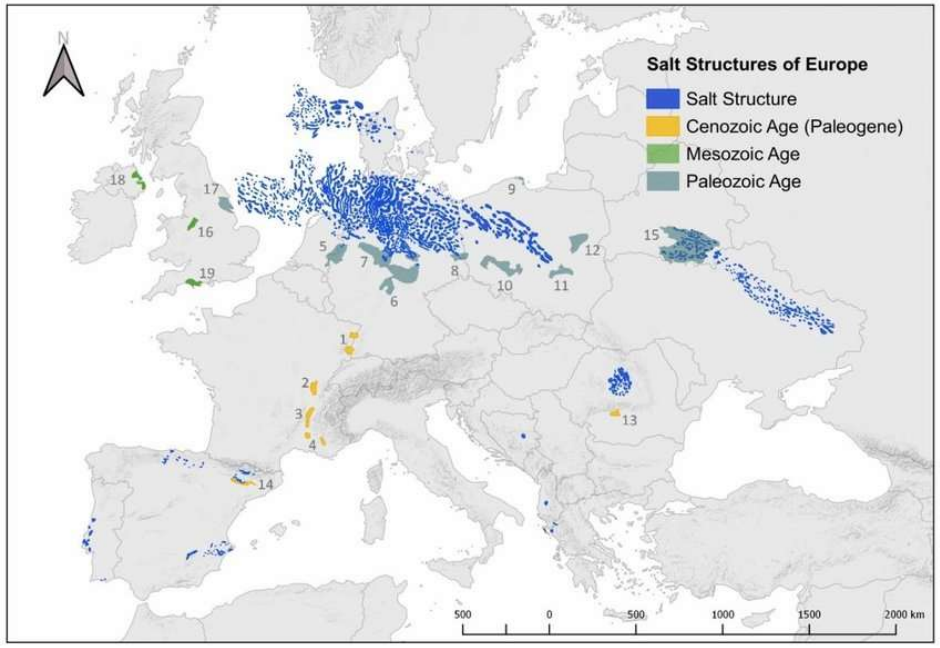
- Explain why salt cavern are the geology considered for current demo projects

hypster Hydrogen Storage

POSSIBILITIES LIMITED BY GEOLOGY



Oklahoma geological survey



Source : Caglayan et al. 2019 Internation Journal of Hydrogen Energy

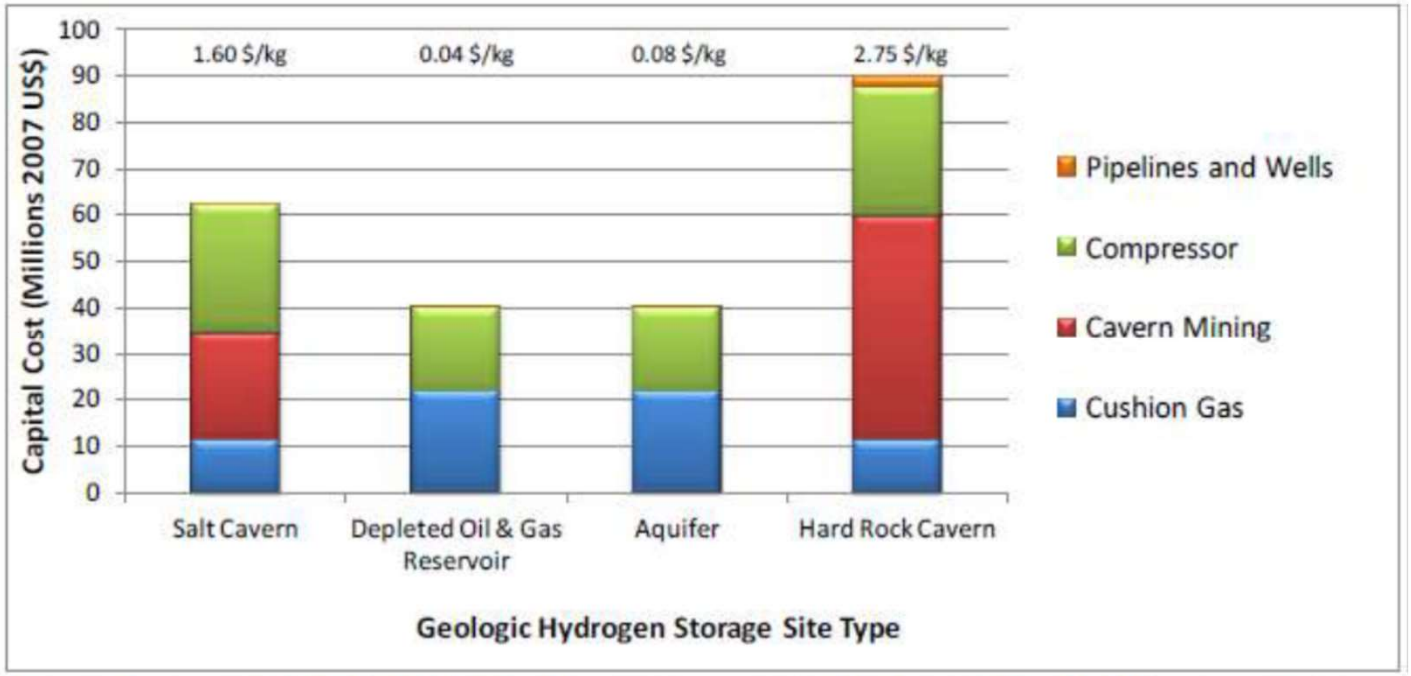
King et al. 2021 Renewable and sustainable energy reviewq

AN EXPENSIVE ALTERNATIVE : HARD ROCK CAVERN

- Direct excavation in a rock formation
- Favorable geology can be found pretty much everywhere
- For gaseous hydrogen, no need for a liner
  - If deep enough, water will flow toward the cavity
- Smaller, more expensive

MINED CAVITIES : A DIFFERENT COST STRUCTURE

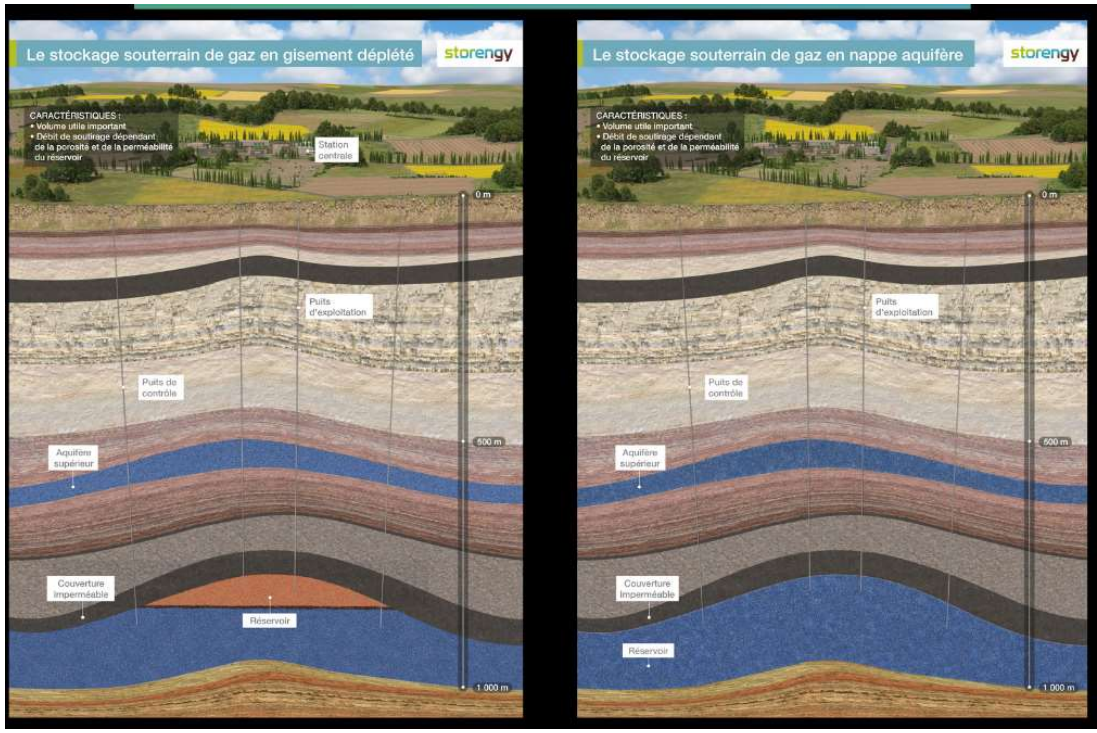
- Salt cavern (or porous) : CAPEX are not proportional to size
  - Lot of expensive equipments and to get started, but marginal cost for additional volumes are small
- Hard rock cavern costs are more proportional to volume
  - Making the solution relevant for smaller cavities



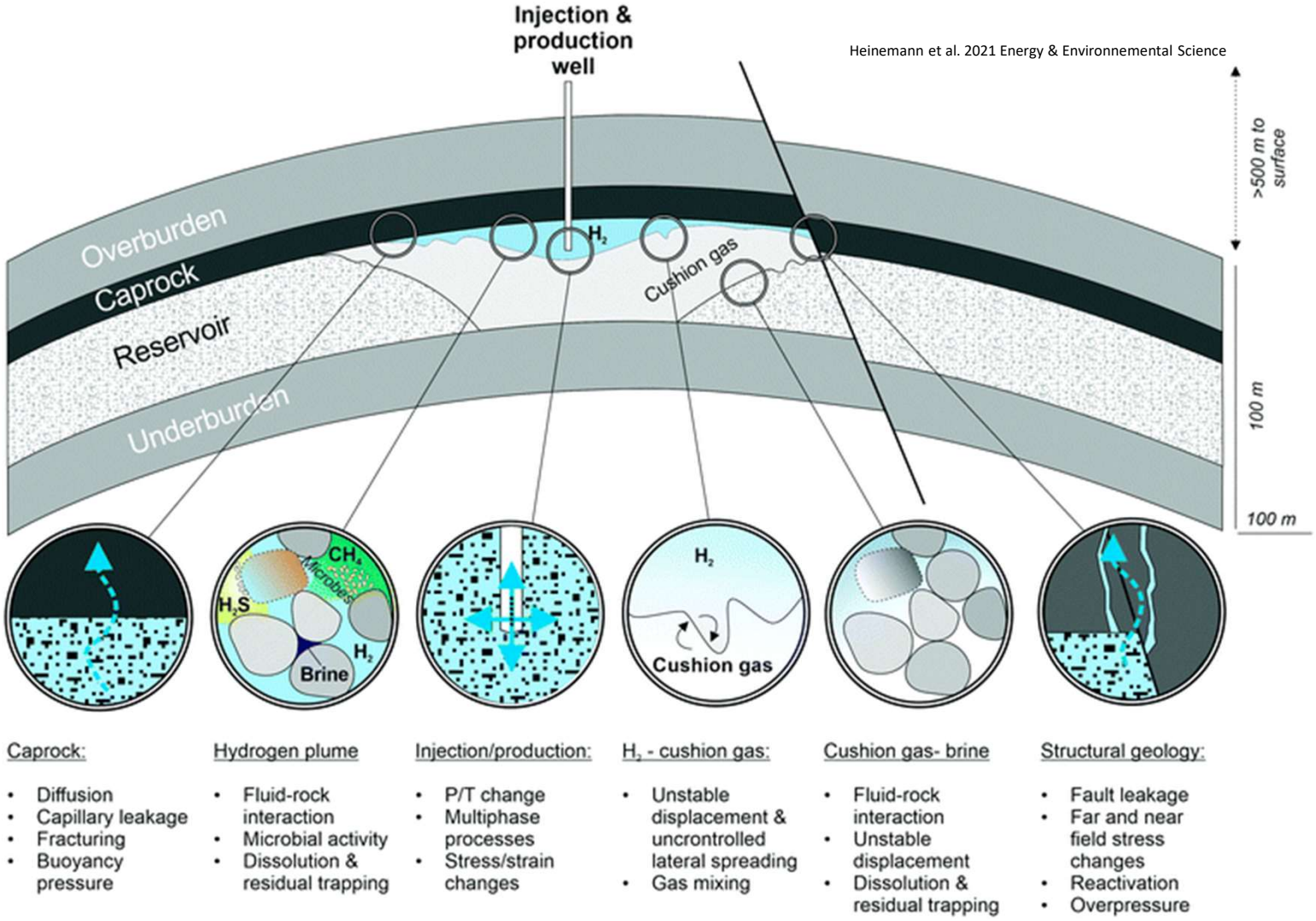
Source : DoE

POROUS STORAGE TYPES

- Regroup two types of geologies
  - Depleted O&G field
  - Deep aquifers
- But technical characteristics are similar
  - Main difference : depleted field have proven they were tight
- Capacities absolutely huge
  - Individual site coud typically hold x100 the quantity of a salt cavern
  - Geology much more common then salt formation

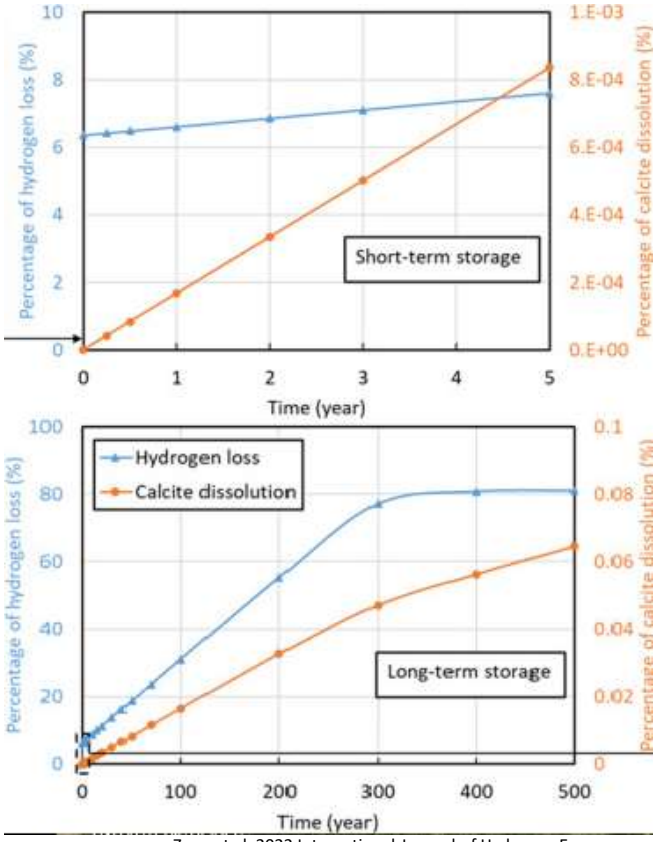


A FEW POSSIBLE ISSUES…



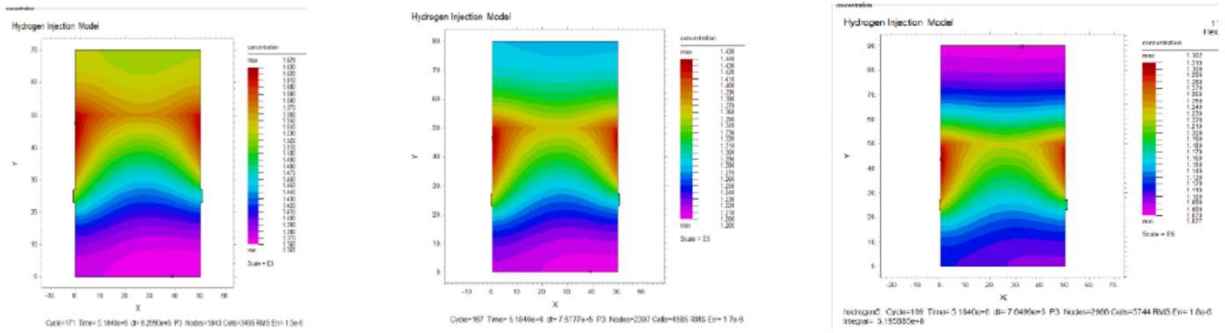
CAPROCK AND FORMATION INTEGRITY

- If it was tight for gas, it will be for hydrogen
  - Hydrogen is a bit more leaky, but not by order of magnitudes
- What to llok for : unstable geochemical modifications by H_2
- Dissolution of cement of sandstone caprock
- Dissolution of carbonates in the reservoir



Zeng et al. 2022 International Journal of Hydrogen Energy

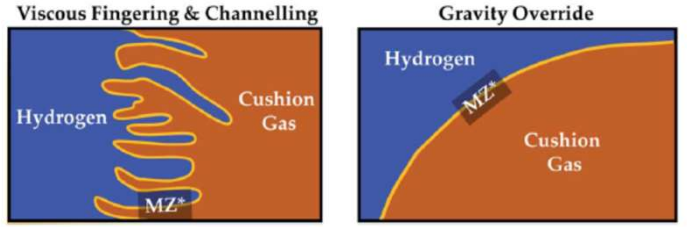
Hydrogen saturation variation in caprock with 20, 30, and 40 meter thickness



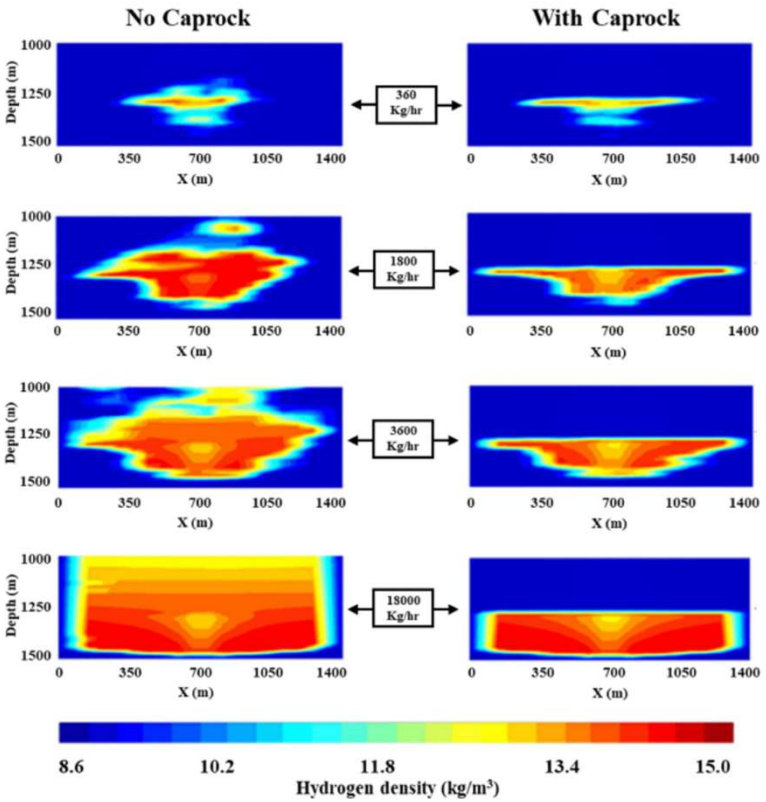
Bahar & Rezae 20221 APPEA Journal

MIXING AND PURITY

- Losing H2 in the other fluids downwell
  - In particular, remaining methane in depleted reservoirs
  - Understanding H2 diffusion in the reservoir and its mixing is key to evaluate recovery and losses
  - Losses can escalate if H2 migrates beyond the caprock cover
- And extracting more then H2 at recovery
  - When purity of H2 is a known issue
  - At minimum, saturated with water (in salt cavern too)
  - Purification facilities necessary



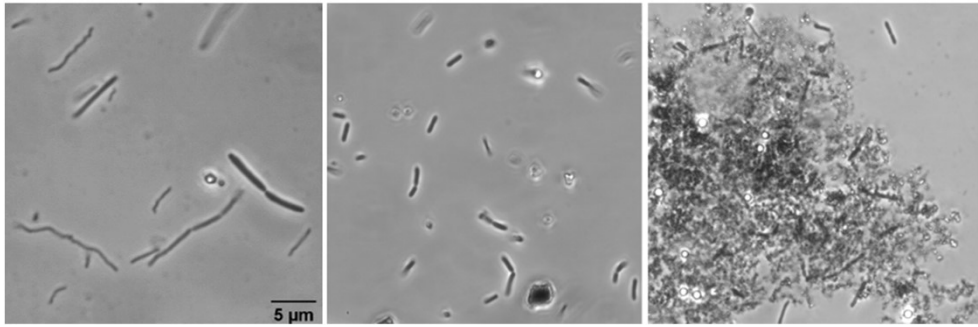
Epelle et al. 2022 Sustainable Energy and Fuels



Mahdi et al. 2021 Advances in Geo-Energy research

MICROBIAL ACTIVITY : POSSIBLE METABOLISM

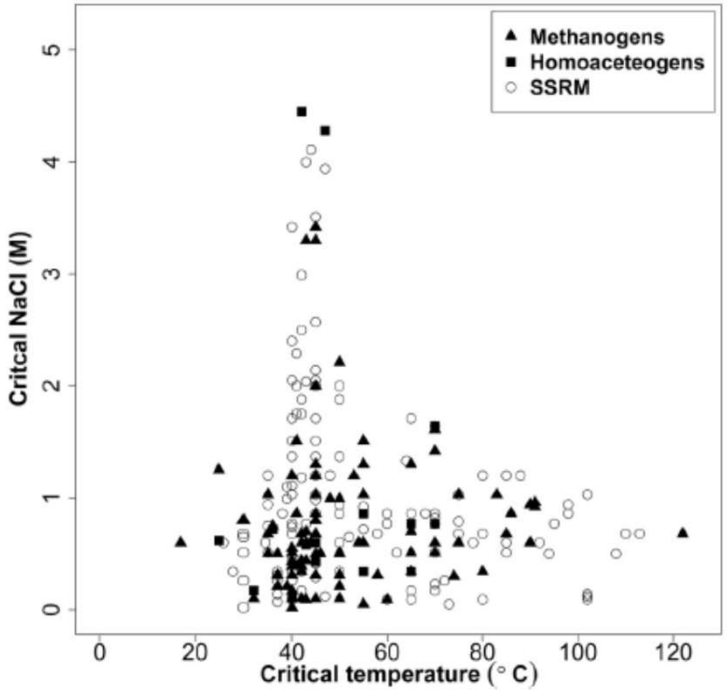
- Humans are not the only species that noticed the energy potential of H2…
  - Plenty of micro-organisms will extracts its energy
  - Can be classified by reaction path (and oxydizer)
- CO2 based metabolism
  - Methanogenesis → CH4
  - Acetogenesis →acetic acid
  - Consume H2 subtantially
- Sulfate-reductor metabolism
  - Consume sulfate
  - Less volume, but form toxic, corrosive H2S…



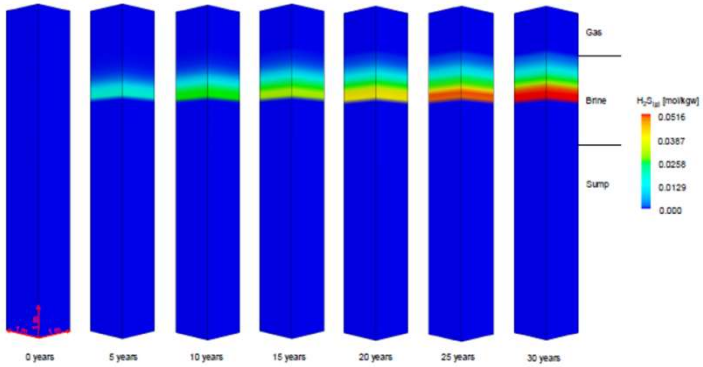
Hystories

MICROBIAL ACTIVITY : PREVIOUS EXPERIENCE

- A classical example in Lobodice (Czech Republic)
  - Syngas storage
  - 53 to 37% H2 in the mix… in 7 months !
  - But different field far less problematic
  - Main factors could be T° and salinity
- Is there an issue with salt caverns
  - Supposed sterile due to very high salinity
  - But recent studies suspect possible sulfate-based extremophile activity



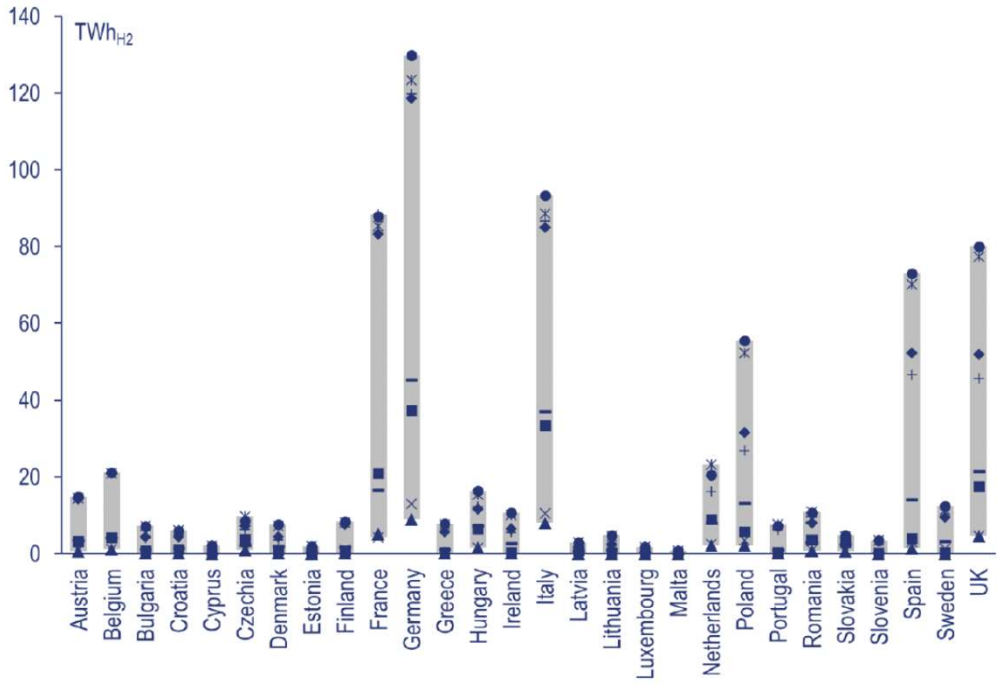
Source : Thaisen et al. 2021 Renewable and Sustainable Energy Review



Source : Hemme & Van Berke 2017 Journal of natural gas science and engineering

DO WE NEED THIS ? UNCERTAINTIES IN STORAGE PATTERN

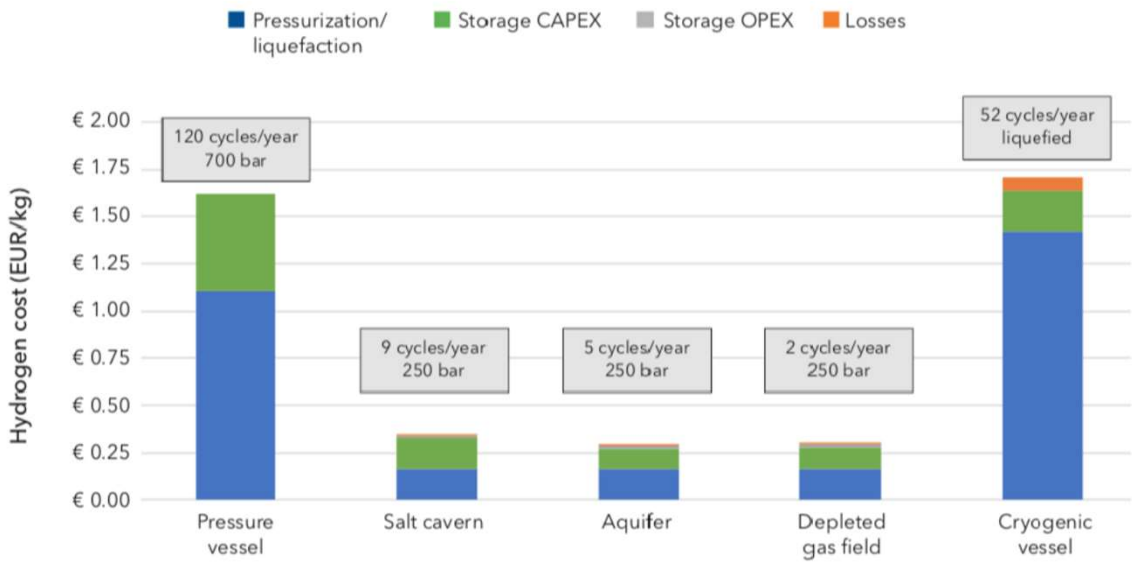
- A recent EU study tried to predict storage need based on various usage patterns
- Variations up to x 10 according to the scenarios !
- Storage possibilities are going to make impossible some options relying too much on hydrogen



Hystories

DO WE NEED THIS ? CONSERVATIVE ASSUMPTIONS

- Conservative estimates, based on 10% of annual consumption in storage capacities
  - Benchmark on natural gas
  - Requires 100's, if not 1000's of dedicated storage capacities
- Complementary role of salt caverns and porous storage
  - Based on cycling speed
  - Dayly variation in surface storage
  - Weekly variation dealt by salt caverns
  - Seasonal storage in porous storage



GLOBAL COURSE WRAP-UP

PART 1 : DEMAND

- Current industrial usage are substantial, and not going away
- Emerging industrial usage (steel, combustion) are important, but will struggle to ramp up due to short term cost issue
- Mobility usage : focus on heavy ground transport, at least when H2 is directly used

PART 2 : OFFER

- Focus on footprint, not color !
- Hydrocarbon based production challenge : availability of CCUS, issues with methane sourcing and environmental footprint
- Electrolysis production challenge : decrease electrolyzer cost, access to cheap enough green electricity

PART 3 : LOGISTICS

- Handling pressurized hydrogen is now effficient enough to put it into vehicles. Only the most demanding applications will require liquid hydrogen
- Pipe transport is probably necessary if we want cheap enough hydrogen. Ships might transport LOHC or ammonia on long distance
- We will not all die in an hydrogen explosion (if we are professional enough)

PART 4 : UNDERGROUND

- Natural hydrogen occurs around the world. Its potential for energy production is still vastly unknown
- Salt cavern is a mature, almost immediately available option to store vast quantities of hydrogen
- Porous storage can hold even more important quantities, but has technical issues which needs to be more systematically adressed

THANK YOU !

Innovating for energy

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