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Geologic Considerations for Hydrogen Caverns

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Overview

- Hydrogen versus Natural Gas
- Not all Salt is the Same
- Interbed Permeability
- Product Contamination
- Mineral Reactions
- Microbial Reactions
- References

Hydrogen vs Natural Gas in Salt Caverns (geologic focus)

Geologic concerns regarding both natural gas storage and hydrogen storage in salt caverns are generally the same and are primarily concerned with:

A. characterization of the salt deposit (depth, thickness, distance from edge, internal structure and bedding, salt quality, etc.)
B. product containment
C. managing geologic risk – edge of salt, loss of containment, irregular cavern geometry, etc.

Hydrogen storage in salt caverns differs from natural gas in that H_2 is:

1. Potentially more mobile
2. Leaks 8x times faster than natural gas
3. Is more chemically reactive than natural gas
4. Depending on end use may be more sensitive to product contamination

Laboratory testing, field tests and a 50-year history of hydrogen storage in salt caverns indicate that if a salt cavern is gas tight for nitrogen and natural gas – then it is likely tight for hydrogen. However, certain geologic conditions can negatively impact cavern containment and/or product storage and **every site is unique and has to be evaluated individually**.

Why Salt Caverns for Gas Storage?

Advantages

- Salt is easily mined by solution mining
- Salt is generally impermeable (best geologic seal) and tends to heal fractures, etc.
- Large storage volume (if have thick salt) with minimal surface footprint
- Proven technology to safely store large volumes of volatile products

Potential Concerns (caverns are designed and operated to minimize or avoid)

- Proximity to edge of salt (need to take into account degradation of salt quality and uncertainty defining the edge to maintain sufficient pillar of good salt)
- Excessive salt creep and cavern closure (generally increases with depth and temperature, stress field, water, etc.)
- Anomalous zones of weak and/or permeable salt (potential for leak paths out of salt, connection between caverns or irregular cavern shape)
- Interbeds of non-salt impurities

Long History of Salt cavern Storage – Including H_2 – proven technology

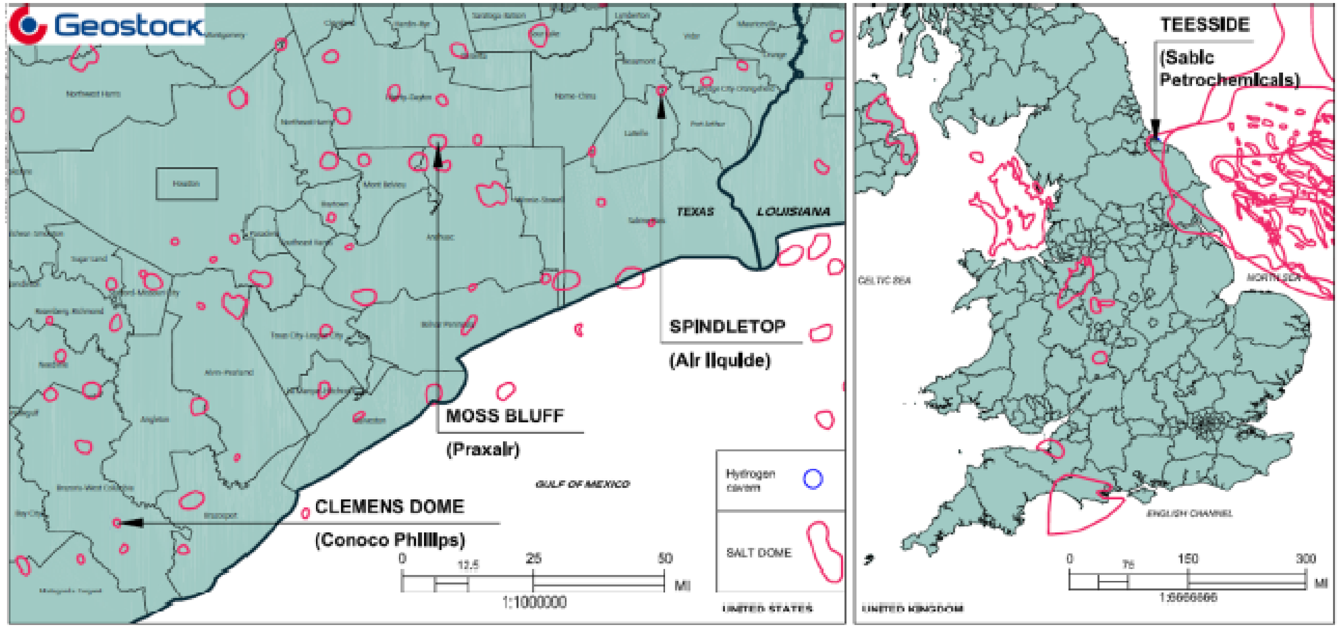
Salt Cavern Storage – North America

- Liquid storage sometime in the late -1940's to early 1950's
- Natural gas storage since -1961 (Marysville, MI – Thoms & Gehle, 2000)

Hydrogen Storage (established 50-year history in salt caverns)

4 existing salt cavern hydrogen storage facilities (Reveillere et al., 2022)

1. Teeside, England (bedded salt) 1972
2. Clemens Dome, TX (domal salt) 1986
3. Moss Bluff, TX (domal salt) 2007
4. Spindletop, TX (domal salt) 2014



	CLEMENS DOME (US)	MOSS BLUFF (US)	SPINDLETOP (US)	TEESSIDE (UK)
Operator	Conoco Phillips	Praxair	Air Liquide	Sabic
Start	1986	2007	2014	1972
Geometrical Volume (m^3)	580 000	566 000	>580 000	3*70000
Geometrical Volume (bbl)	3 648 000	3 560 000	>3 560 000	3*441 000
Pressure range (bar)	70-135	55-152	68–202 bar	45
Pressure range (psi)	1015-1960	800-2200	990–2930 psi	650

	CLEMENS DOME (US)	MOSS BLUFF (US)	SPINDLETOP (US)	TEESSIDE (UK)
Mean Cavern Depth (m)	1000	1200	1340	365
Mean Cavern Depth (ft)	3300	3900	4400	1200
Net energy stored (GWh)	92	120	270	25
Net energy stored (MMBtu)	$3\ 10^5$	$4\ 10^5$	$9\ 10^5$	$0.8\ 10^5$
Working gas (ton H_2)	2400	3700	8200	800
Working gas (MM Sm^3)	27.3	41.5	92.6	9.12

(Reveillere et al., 2022)

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Not all Salt is the Same – Salt Quality can Vary

Rocksalt is typically composed of relatively clean halite - generally has low porosity, is impermeable and tends to heal fractures.

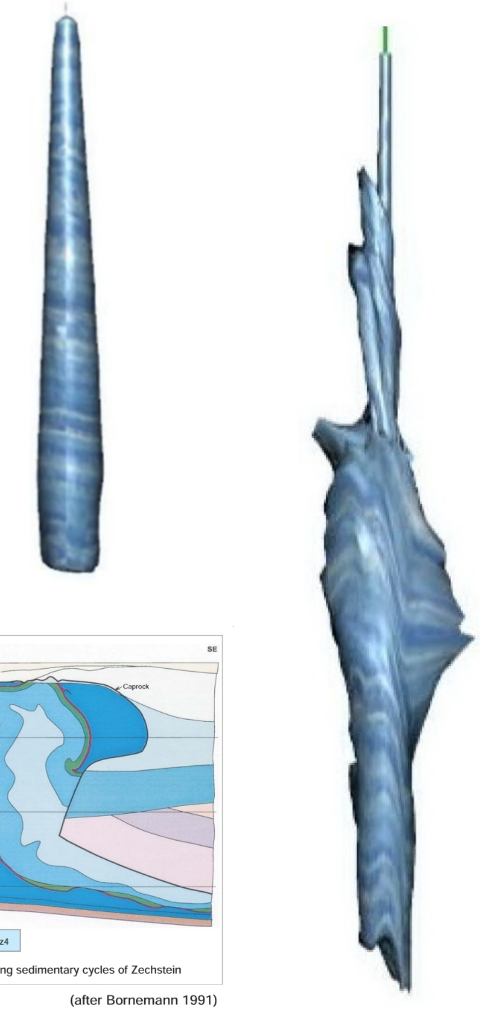
However, the presence of anomalous salt may negatively impact cavern geometry, cavern containment and/or cavern operations by exhibiting

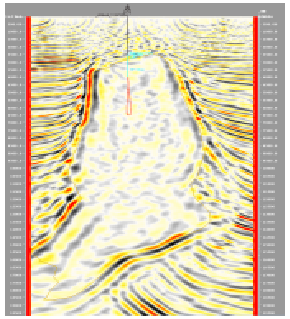
- Increased porosity and permeability in the salt – potential leak paths, irregular leaching, product contamination, etc.
- High insoluble content – increased potential for roof falls, differential leaching, increased sump fill, irregular cavern geometry, etc.
- Highly soluble salts – potential for differential leaching
- Hydrocarbon, brine or gas charged salt - potential for product contamination, preferential leaching, indicates porous salt, possible permeable zone
- Weak, fractured salt or sheared salt – potential for lost containment and/or cavern wings especially during pressure fluctuations associated with gas storage

Domal Salt – structurally more complex

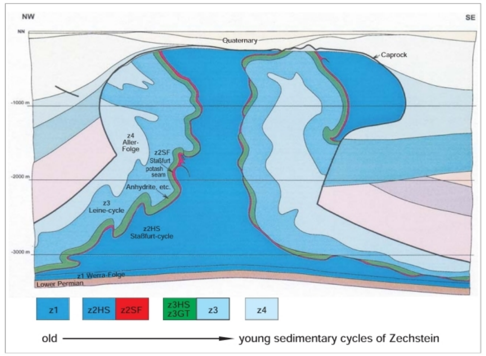
- Complex internal structure.
- Near vertical, highly folded fabric.
- Various degrees of deformed internal bedding or flow banding depending upon:
  - composition of original salt
  - degree of deformation
  - distance salt has migrated vertically from original deposit
- Can rise several thousands to 10's of thousands of feet vertically from original salt bed.
- Usually allows large vertical caverns to be developed.
- Geologically related cavern shape anomalies are generally steeply dipping.

Lock, et al. 1999





(Thompson and Looff, 2021)

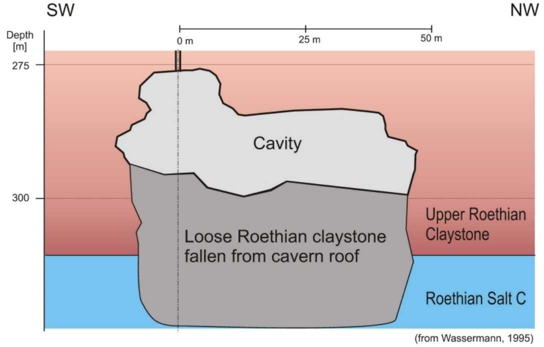


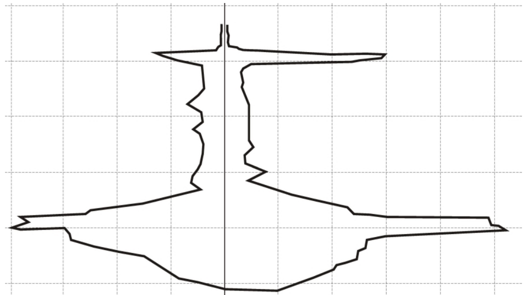
(after Bornemann 1991)

(Gillhaus and Horvath, 2008)

Bedded Salt – interbeds may be problematic

- Horizontally bedded or gently dipping or folded – original layering generally intact
- Contains Interbeds of non-halite (potash, anhydrite, carbonates, shales, etc.) – these may be problematic for product containment or cavern stability
- Cavern size may be limited by bed thickness
- Bulking of large amounts of insoluble material can reduce available storage volume
- Rock falls are common
- Caverns often form bedding parallel wings
- Dissolution fronts, solution chimneys, depositional boundaries, faulting, etc. can form abrupt termination of the salt deposit.





Ft. Saskatchewan, Alberta (Gillhaus et al., 2006)

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Anomalous Salt

Design and regulatory criteria for pillar distance and edge of salt for salt caverns – **assume good salt properties.**

Concept originally developed by Kupfer and others starting in the 1950's through 1970's from conventional mining operations on Gulf Coast salt domes – Five Island Domes. Now applied to other types of salt (Warren, 2017).

Oil Saturated Salt

Weak Friable Salt

Impure Salt

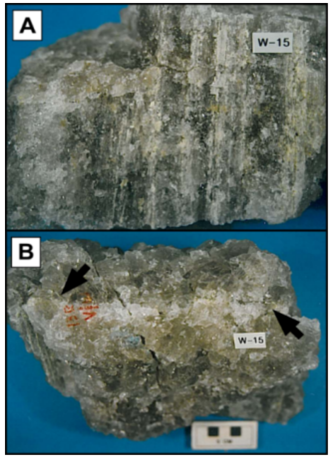
Typical Salt
Avery Island salt

Vein of Recrystallized Salt

Sylvite-rich Halite

Sheared & Dilated Salt

Faulted Salt



Anomalous Salt can negatively impact cavern development and operations

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Anomalous Zones

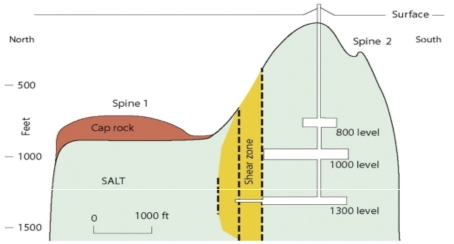
<u>Anomalous Zone (AZ)</u> - a non-genetic term used to describe a linear zone within the salt that contains 3 or more dissimilar anomalous salt features. These zones "although highly variable, lenticular, and discontinuous in detail" are "commonly predictable in trend" (Kupfer, 1990). These zones are common in Gulf Coast Salt Domes.

Genetic terminology:

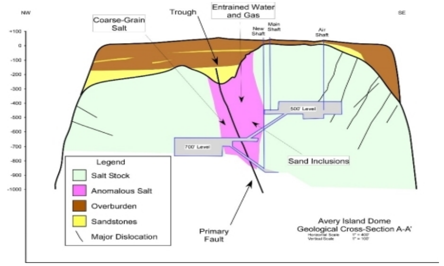
- <u>Edge Zone</u> – near edge of structure – applies to all salt structures especially domal
- <u>Boundary Shear Zones (BSZ)</u> – internal shear zones between differentially moving salt spines that is mostly applied to Gulf Coast salt domes

BSZ – Gulf Coast Salt Domes

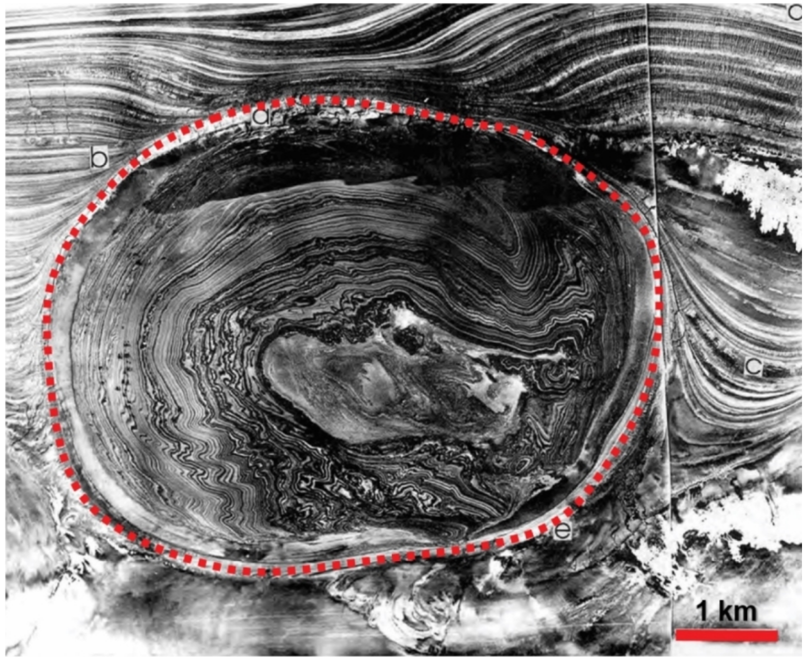
Jefferson Island Dome (Modified from Kupfer as per Warren, 2016)



Avery Island Dome (Modified from Jacoby, 1977)



Edge Zone



(Modified by Duffy et al., 2022, original from Jackson, 1990)

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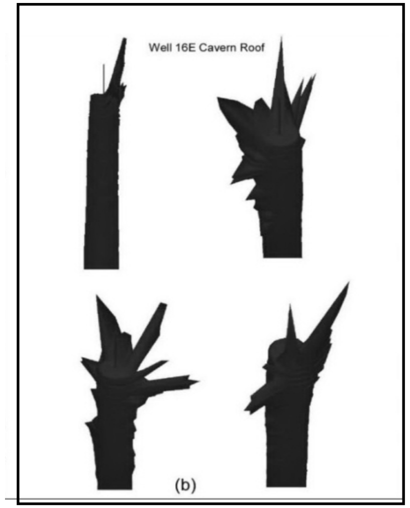
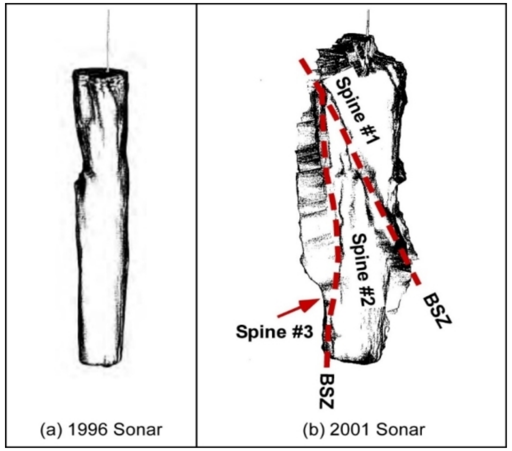
Anomalous Salt – cavern geometry irregularity

Anomalous salt can result in geometric irregularities created by differential solution mining that can result in wings, attic spaces (trapped product) , etc. In some cases, can result in communication between caverns or permeability pathways to the edge of salt.

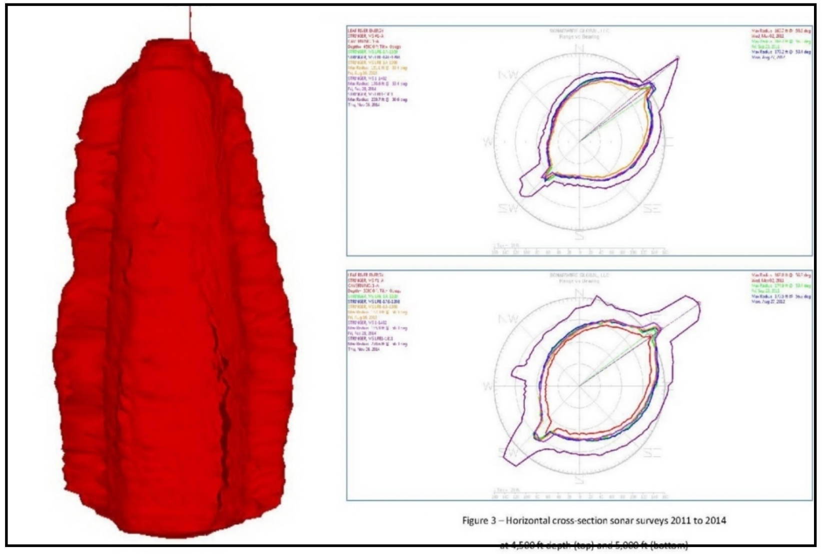
(Looff et. al., 2010a)



(Cartwright and Ratigan, 2005)



(Looff et. al., 2014)



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Salt Porosity

- Porosity generally +/-1% appears to be typical in halite rocksalt and the porosity is generally isolated - but porosity can be higher and connected under certain circumstances.
- Porosity occurs as fluid inclusions, at grain boundaries, cleavage planes, micro-cracks, and possibly with some non-salt stringers.
- Gas & brine pockets can be common in salt domes and bedded salts
- Fluids at grain boundaries may prevent healing.

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Evidence of fluids bleeding from grain boundaries

Oil Impregnated Salt (Weeks Island)

Crackle Salt with gas-rich fluid inclusions

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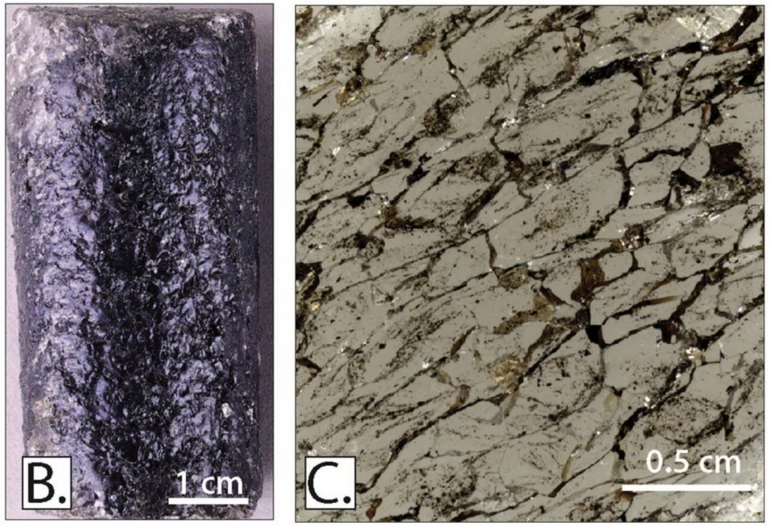
Salt Permeability

- Rock salt is generally considered impermeable and is used to safely store liquid and gaseous products in underground salt caverns.
- Permeability in rock salt generally ranges from 10-4 mD to 10-7 mD (Donadio, 2017) – but can be higher under certain conditions.
- Gas & brine pockets are generally isolated zones of trapped fluid.
- Active and unhealed faults/shear zones can provide permeability conduits.
- Active shearing (differential movement) creates permeability by grain dilation, grain boundary sliding and rotation, microcracking and fracturing.
- Salt will tend to heal and re-seal over time, however, active shear or fluids trapped at grain boundaries may prevent healing of fractures and grain boundaries

Warren (2017)

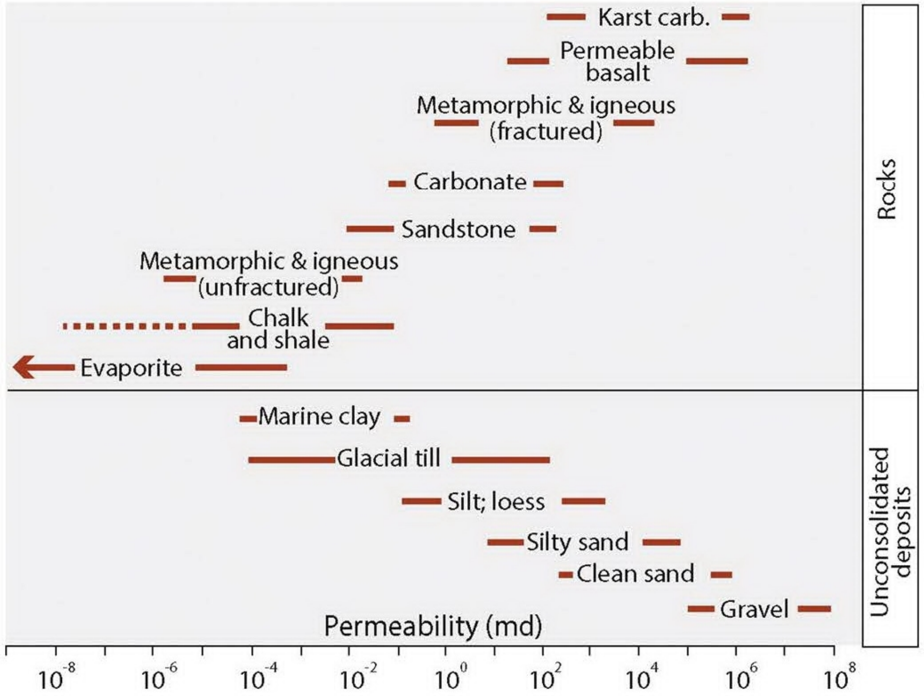


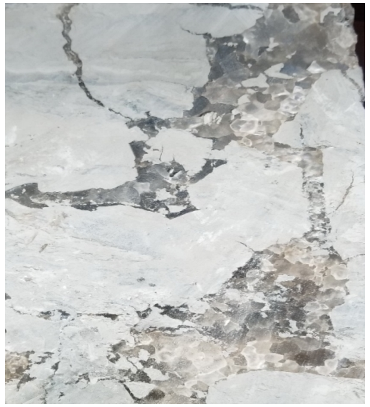
Interbed Permeability

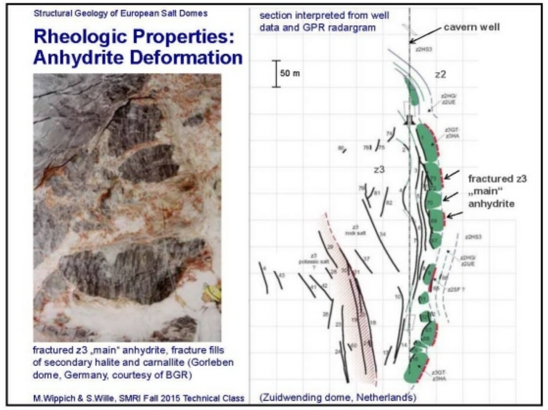
Salt is the best geologic seal – permeability generally ranges from nano-Darcy or less (10^{-6} mD or 10^{-22}m^2) with some tighter halite being 10^{-7} to 10^{-9} mD (10^{-23} to 10^{-25} m^2). As a rule of thumb in the oil industry 2m (6.6 ft.) of good halite is considered a seal (Warren, 2017). In some cases of anomalous salt – permeability can equal that of sandstones approaching the Darcy level ($9.87e^{-13}$ m^2) range (Warren, 2017).

Shale generally has a permeability of 10^{-1} to10^{-5} mD (10^{-14} to 10^{-21} m^2) with an extreme value of 10^{-8} mD (10^{-24} m^2).

Massive anhydrite has a permeability of 10^{-5} mD (10^{-21} m^2). As a rule of thumb in the oil industry 10 m (32.8 ft.) of anhydrite is considered a seal (Warren, 2017).







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Interbed Permeability II

Every site is different.

Numerous caverns including interbeds are considered gas tight.

Fractures or faults can be permeability pathways.

Fractures and porosity in non-salt interbeds often sealed by reprecipitated secondary salt.

Based upon helium diffusion testing pure salt crystals are basically impermeable (Yuan 2017).

Microfractures and crystal boundaries promote helium diffusion (Yuan, 2017).

Recent field well testing, NMR log data and helium core testing shows carbonate mudstone often with some salt filled fractures exhibits permeabilities in the nano-darcy range. Gas storage caverns currently are operated in these rocks at a different site supporting the premise that they will be gas tight to H_2.

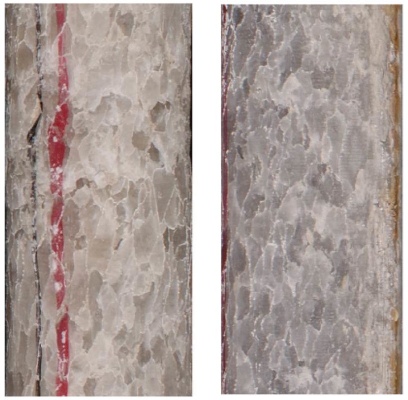
Product Contamination (impurities entrained in salt)

Large quantities of impurities of gas and liquid hydrocarbons are known to exist in salt deposits that can bleed into a cavern – i.e., gas or liquids released as a salt cavern is leached that could contaminate stored H2 (ie., Sorrento Dome, Louisiana) (Looff & Evans, 2016)

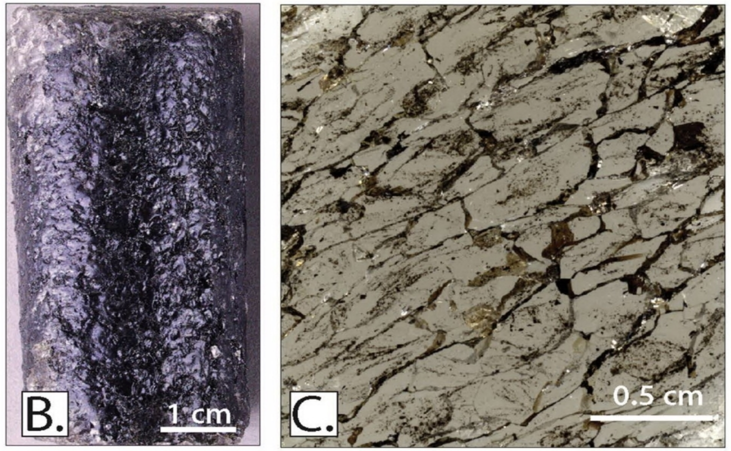
Looff 2010b

Looff 2010b

Evidence of fluids (gas or brine) bleeding from grain boundaries



Oman salt – Warren, 2107)



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Chemical and Microbial Reactions

H2 is more reactive than natural gas.

Mineral and microbial reactions mostly based upon laboratory analysis

Additional work needed on how it upscales to cavern scale and conditions (Buzogany, et al., 2023)

Product Containment and Contamination

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Hydrogen induced abiotic reactions in non-salt layers

Impact – H_2 trap and loss, mineral dissolution and precipitation, H_2S and CO_2 generation, change of mechanical and transport properties, etc.

Studies (1) H_2-brine-shale → rapid increase in pH → mineral dissolution
(2) H_2-brine → calcite dissolution
(3) H_2-brine → no chemical or morphological change with calcite

- K. Labus and R. Tarkowski (2022) Modeling hydrogen – rock – brine interactions for the Jurassic reservoir and cap rocks from Polish Lowlands, International Journal of Hydrogen Energy, 47, no. 20, pp. 10947-10962
- J. P. Bensing, D. Misch, L. Skerbisch, and R. F. Sachsenhofer (2022) Hydrogen-induced calcite dissolution in Amaltheenton Formation claystones: Implications for underground hydrogen storage caprock integrity, *International Journal of Hydrogen Energy,* 47, no. 71, pp. 30621-30626
- O. Gelencsér et al. (2023) Effect of hydrogen on calcite reactivity in sandstone reservoirs: Experimental results compared to geochemical modeling predictions, Journal of Energy Storage, 61, p. 106737

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Product Containment and Contamination

Hydrogen induced physisorption in non-salt layers

Impact: Adsorb H_2 onto mineral surface

Study (1) Indicated significant retention of H_2 (0.06 – 0.11%) to clay and claystone (shale) and also reducing Fe^{3+} to Fe^{2+}.

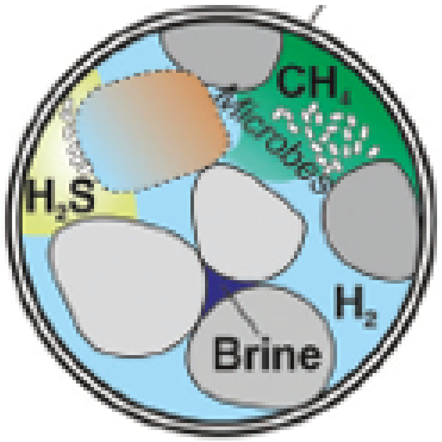
- M. Didier, L. Leone, J.-M. Greneche, E. Giffaut, and L. Charlet (2012) Adsorption of Hydrogen Gas and Redox Processes in Clays, Environmental Science & Technology, 46, no. 6, pp. 3574-357.

Hydrogen induced microbial reactions – H_2S, methane, CO_2, Fe reduction

Impact: H_2 consumed by microbes, H_2S generation, change of mineral compositions

- Lovely, D. R. & Chapelle, F. H. (1995) Deep subsurface microbial processes. Rev Geophys., 33(3), 365-81.
- Kotelnikova S. (2002) Microbial production and oxidation of methane in deep subsurface, Earth Sci. Rev., 58(3–4), 367–95.

Mineral Interactions



Hydrogen induced mineral reactions and its effect on pore space connectivity - impacts containment

Phase transition → mechanical property changes

Need to understand
- site mineralogy
- brine composition

- Dissolution
- Precipitation
- Potential to produce H_2S

Mineral Reactions – Bedded Salt Study

H_2 Adsorption

(test at 10 MPa and 55C)

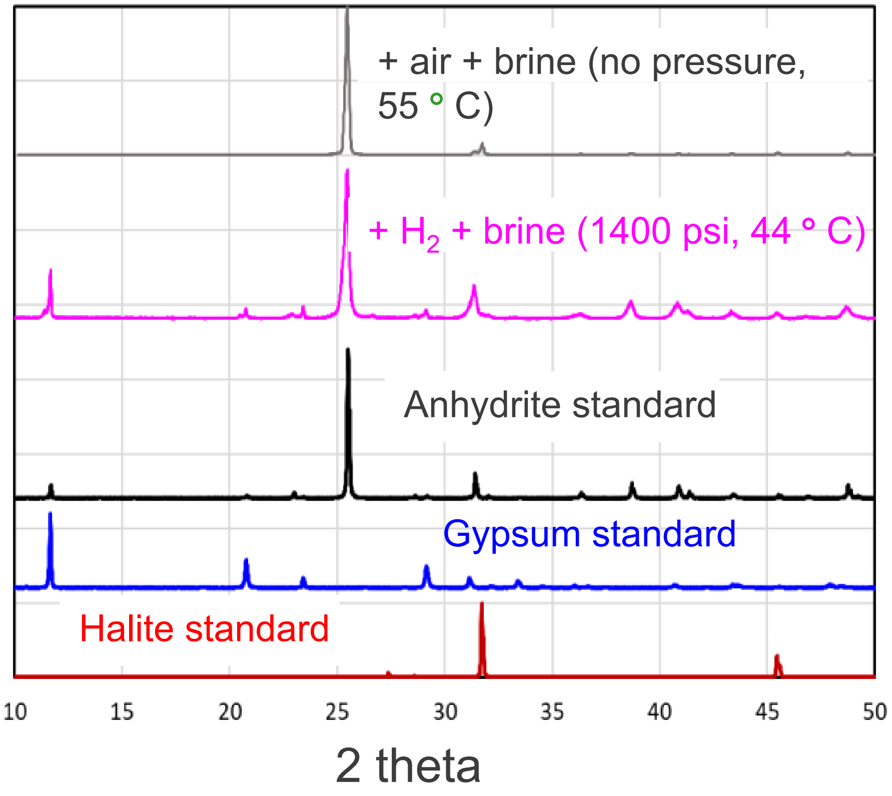
- H_2 adsorption **minimal** and **reversable** with pressure change

H_2 Inducted reactions

(test at 9.6 MPa @ 44C, powdered samples with saturated brine)

- **Solubility of carbonate and sulfates not enhanced**, no phase transitions
  - H_2 inhibited phase transition between anhydrite and gypsum.
  - Phase transition seen with exposure to both air and N_2
- **No H_2S generated** from anhydrite and sulfate.
- There is no mineral source for H_2S (no pyrite present)

9.5% Halite + 60% **anhydrite** + 30.5% **gypsum**



XRD plot

Salt is relatively "inert"

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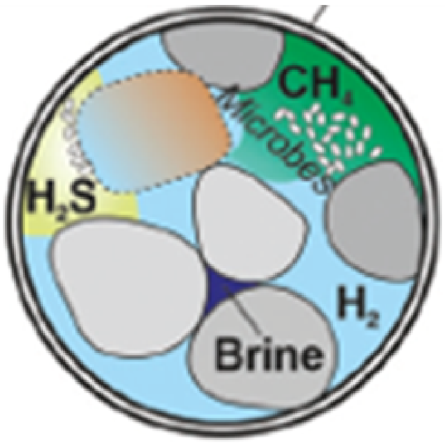
Microbial Reactions



Bio-chemical reactions have the potential to consume and produce associated byproducts

Need to understand

- Type of microbes present
- Source of microbes
- Potential to consume H_2

Produce VOC's via

- ferric iron reduction
- sulfate reduction
- methanogenesis

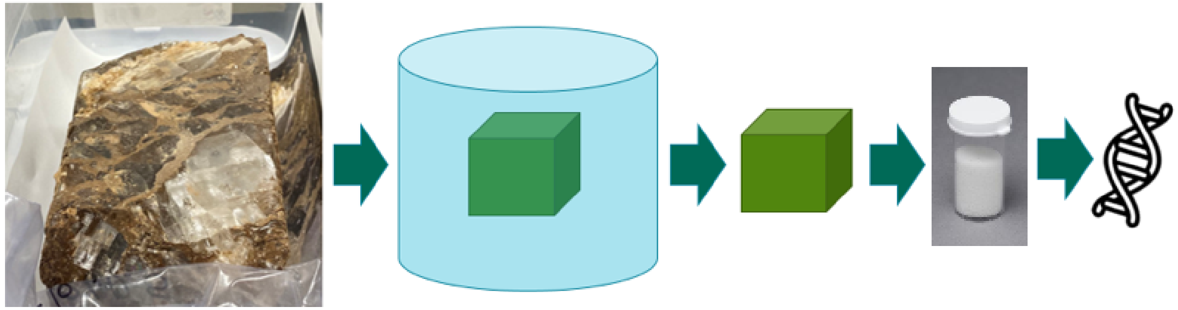
$H_2 + 2Fe(OH)_3 \rightarrow 2Fe(OH)_2 + 2H_2O$

$4H_2 + H^+ + SO_4^{2-} \rightarrow HS^- + 4H_2O$

$4H_2 + H^+ + HCO_3^- \rightarrow CH_4 + 3H_2O$

Microbial – Bedded Salt study

DNA Extraction



H2 Exposure Incubations

From microbial species identified, H_2 gas oxidizing microbial species were further classified.

H_2 exposure incubations (50°C, 1 month, 100% H_2)

- H_2 exposure found very little change in microbial abundance

Risk

Introduce microbial species from surface water or soils through drilling and cavern development

Outer core

- Microbial species most likely from **surface water** or **soil** and introduced through the **fluids**

Center core

- **Low abundance of genetic material**
- Microbial species not found on outer core
- microbial profiles differed across center core samples and replicates

Biological reactions limited due to lack of organic C and Fe. No Pyrite present.

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Questions?

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