

A EVOLUÇÃO DO MERCADO DE HIDROGÊNIO VERDE H2V NO BRASIL



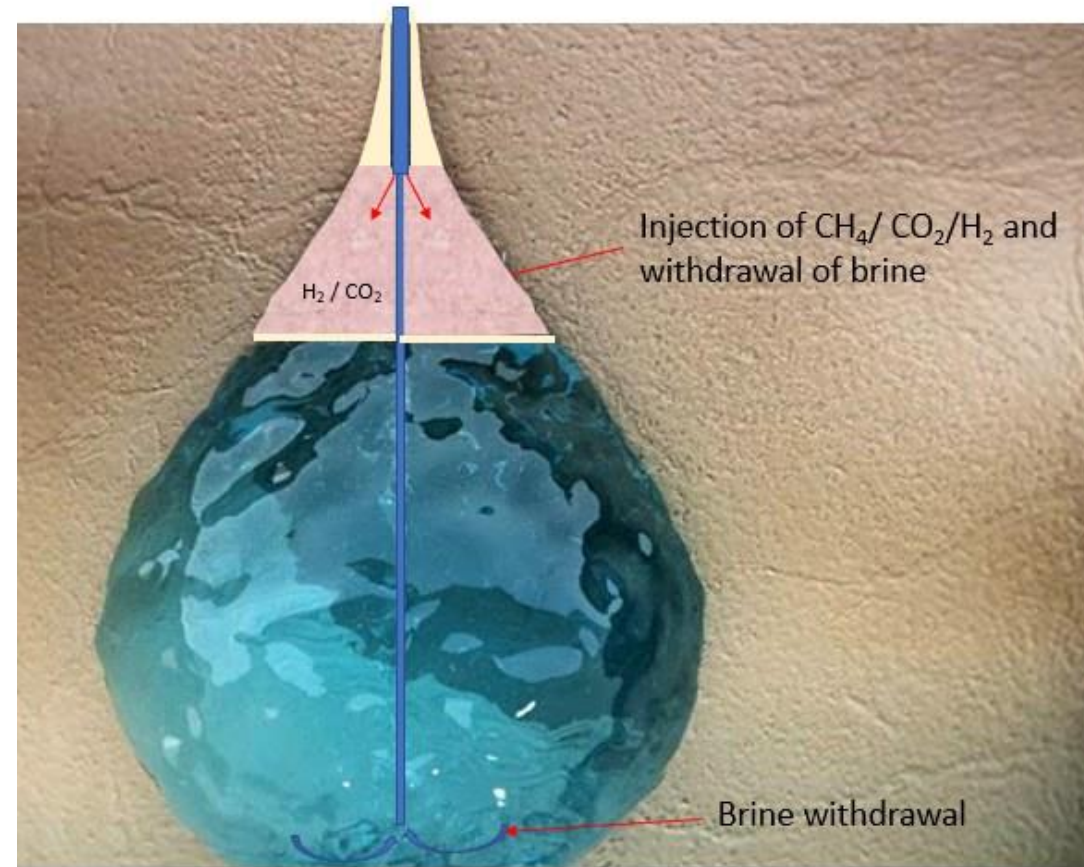
Large-scale of Hydrogen underground storage in salt caverns: the future of sustainable energy storage

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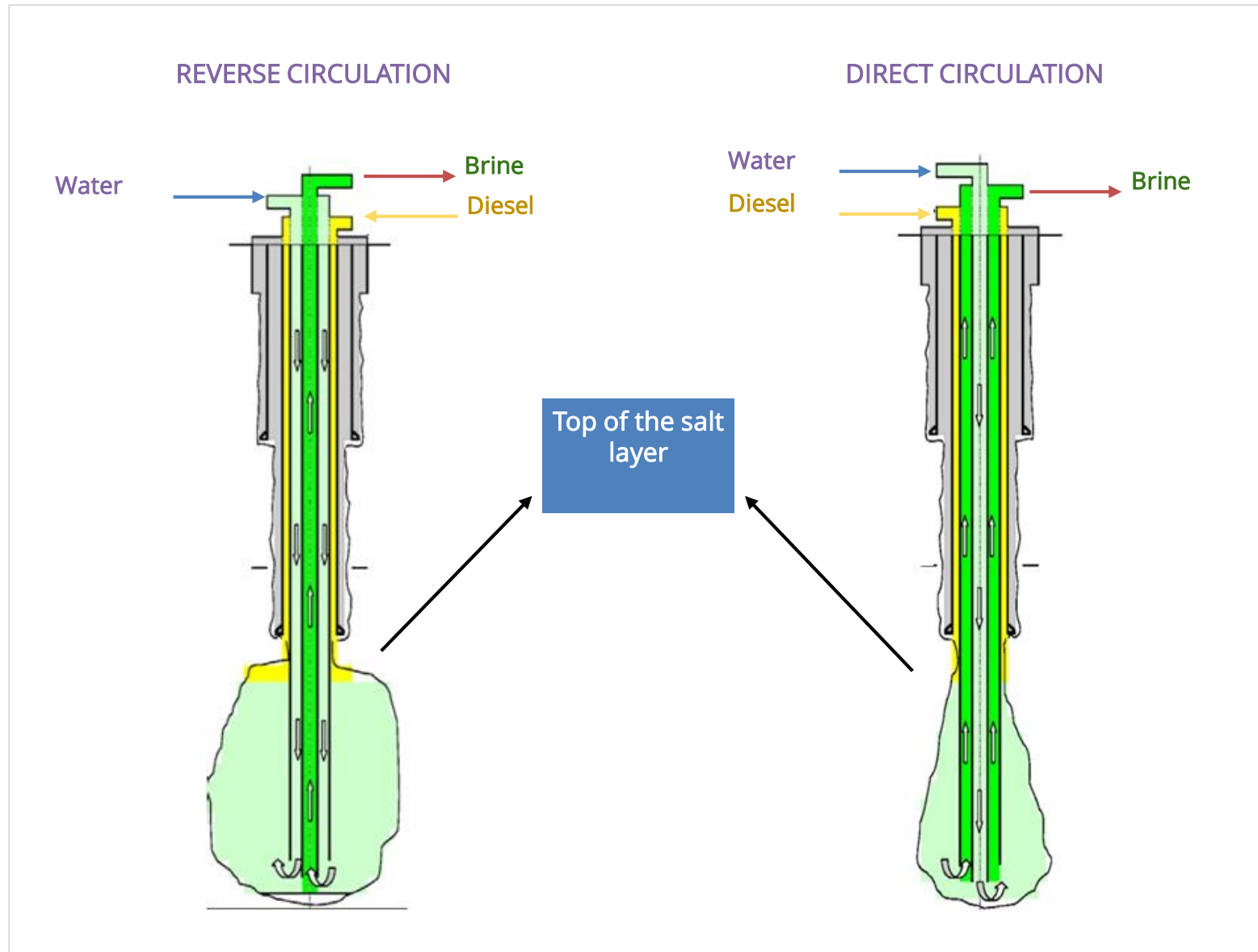
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Compared to other gases, hydrogen has the lowest molecular weight (2.016 g/mol), a low density (0.08375 kg/m³), that is, high compressibility at the normal conditions of pressure and temperature (101,325 kPa a 25°C), very low solubility in water and a low dynamic viscosity. Hydrogen has a high mass-energy density (120 MJ/kg) with a very low volumetric energy density (0.01079 MJ/L), which requires large volumes to be stored. These parameters will affect underground storage differently, and the low viscosity of hydrogen and the associated rate of gas movement carry a higher risk of leakage from underground storage in depleted oil & gas reservoirs and saline aquifers.

In this context geological storage in salt caverns stands out as the most promising technology. Salt caverns mined by leaching have unique physicochemical characteristics such as: negligible permeability under high gas pressures (avoiding leakage), self-healing, higher levels of stability, and stress safety shield due to the phenomenon of creep. Also, it allows higher injection and withdrawal ratios of hydrogen, meeting cycles between demand and production, a smaller need for cushion gas, and more controllable construction from the point of view of monitoring and tightness certification. At the end of the operational life of the storage system, the cushion hydrogen can be extracted just by injecting brine into the cavern.



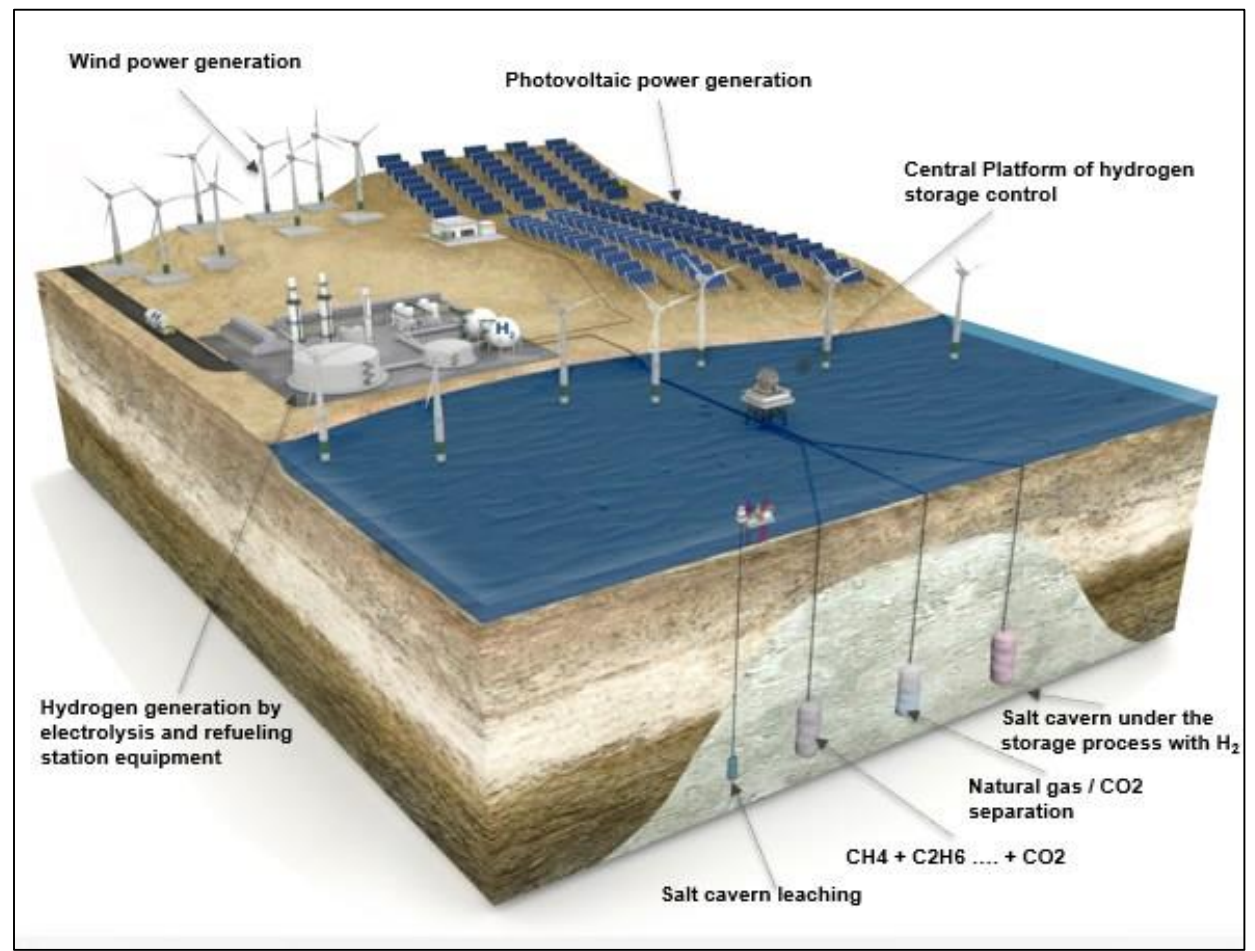
SALT CAVERN CONSTRUCTION BY LEACHING



POSSIBLE SITES FOR THE CONSTRUCTION OF THE HYDROGEN STORAGE IN SALT CAVERNS

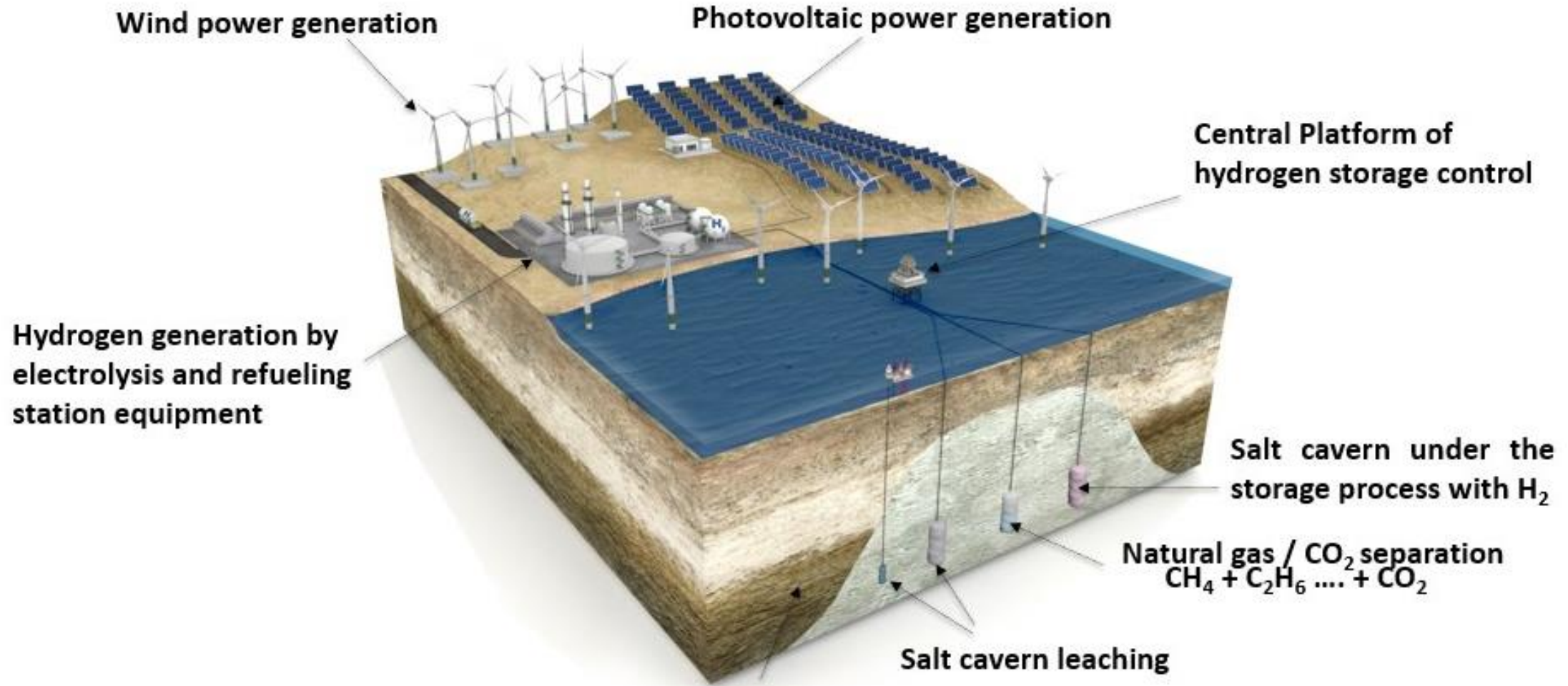


ONSHORE

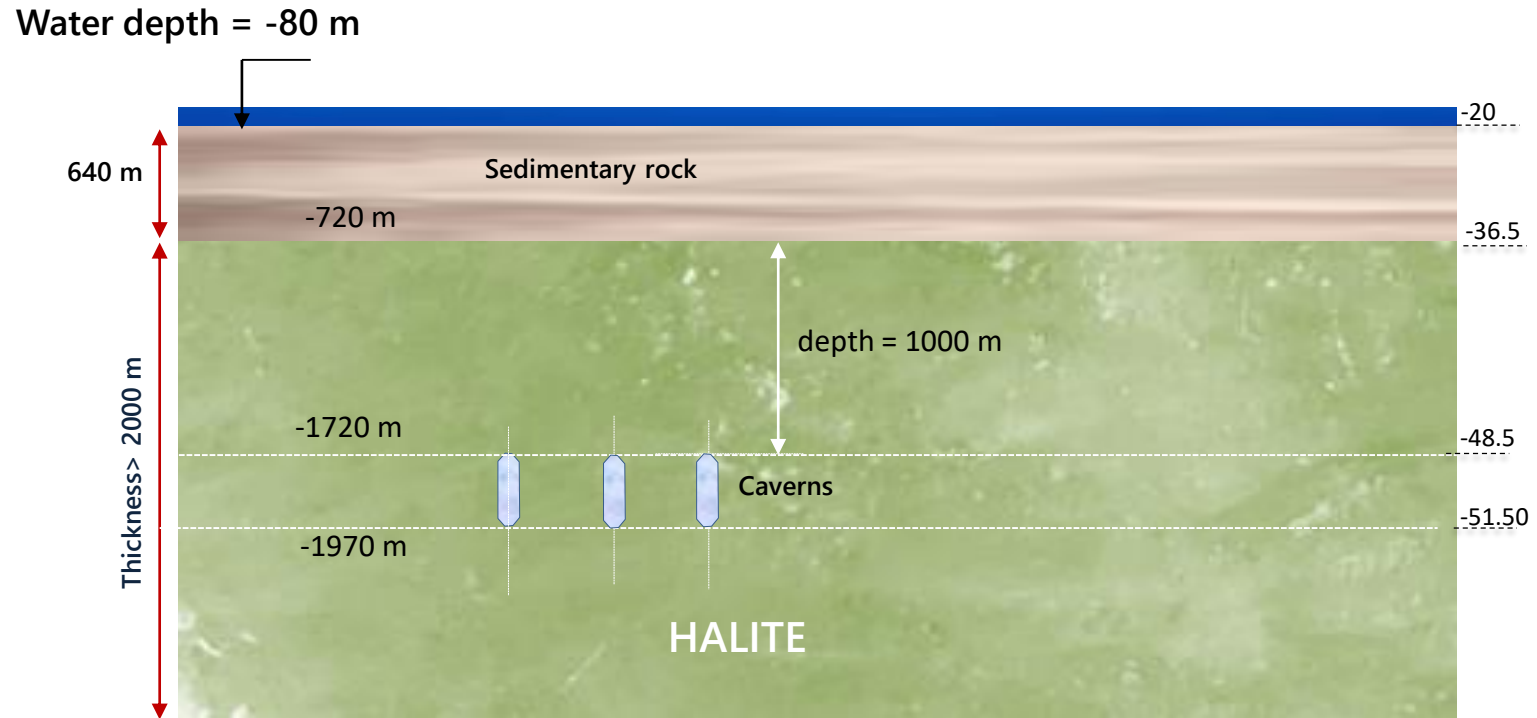


OFFSHORE

3D CONCEPTUAL VIEW OFFSHORE



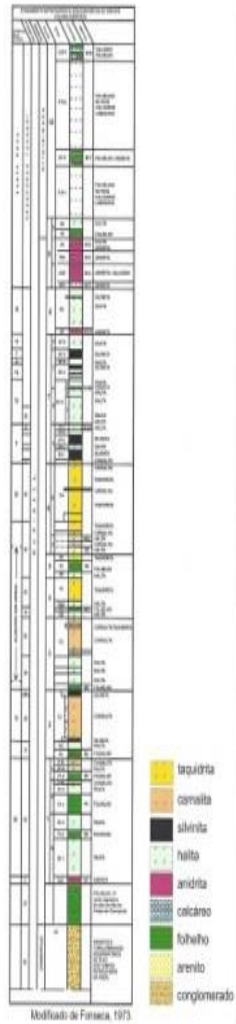
EXPECULATIVE GEOLOGICAL SECTION*



*Webster Ueipass Mohriak & Sylvie Leroy: Architecture of rifted continental margins and break-up Evolution:insights from the South Atlantic, North Atlantic and Red Sea-Gulf of Aden conjugate margins, Geological Society, London, Special Publications published online August 22, 2012 as doi:10.1144/SP369.17

**Agulles, M.; Jordà, G.; Jones, B.; Agusti, S.; Duarte, C. M. : Temporal Evolution of temperatures in the Red Sea and the Gulf of Aden based on in situ observations (1958-2017), Ocean Sci., 16, 149-166, <https://doi.org/10.5194/os-16-149-2020>,2020.

Background of rock salt geomechanics of MODECOM (Conventional underground potash mine)



Saline aquifer → Pressure 45 bar

Interval with limestone rocks with strong heterogeneity, faults, micro-cracks and fractures

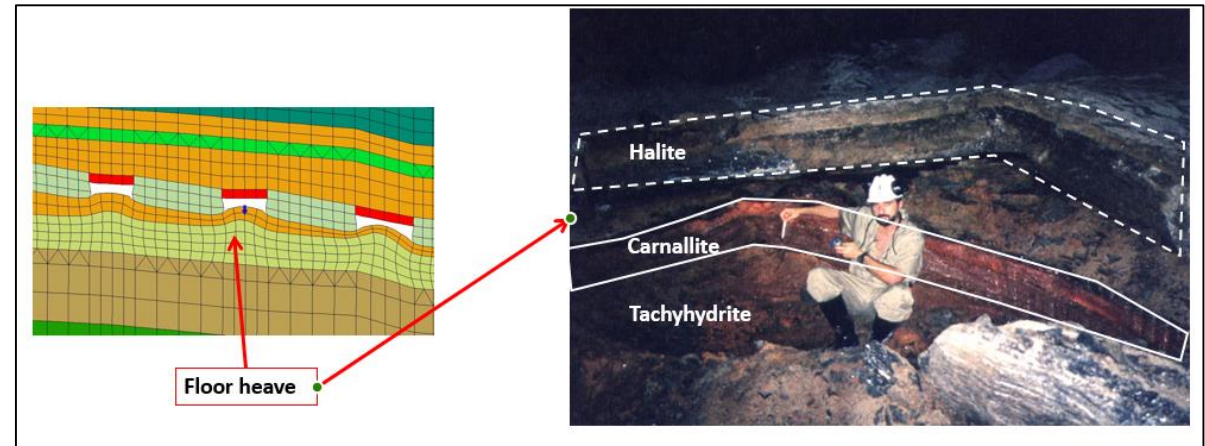
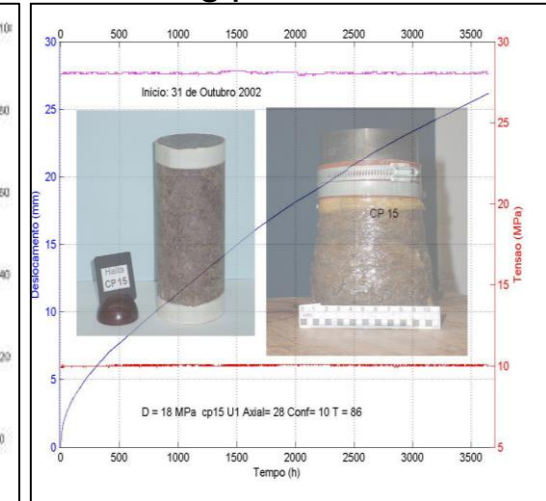
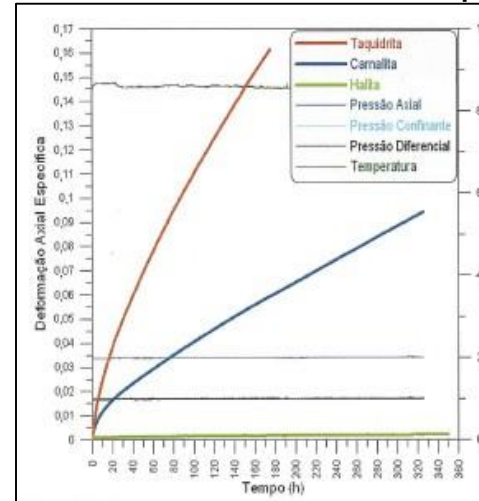
Presence of water from the saline aquifer above

Safety slab of salt rock as a protection against water migration from the aquifers into the mine (~20 m)

Tachyhydrite Rock with creep strain rate two orders of magnitude higher than the Halite and Sylvinitite and compression resistance about 15 times smaller



Salt rocks in the salt deposit of Sergipe and Santos basin



Geological composed profile of well GTP – 24 – pilot well of the service shaft of the potash mine in Sergipe

MECHANICAL PROPERTIES OF HALITE

The mechanical properties of halite were obtained in experiments carried out at the underground dry mining located at the state of Sergipe in Brazil *

Constitutive creep equation:

$$\dot{\epsilon} = \dot{\epsilon}_0 \cdot \left(\frac{\sigma_{ef}}{\sigma_0} \right)^n \cdot e^{\left(\frac{Q}{R \cdot T_0} - \frac{Q}{R \cdot T} \right)} \quad n = \begin{cases} n_1 \rightarrow \sigma_{ef} \leq \sigma_0 \\ n_2 \rightarrow \sigma_{ef} > \sigma_0 \end{cases}$$

Where:

$\dot{\epsilon}$ – Scalar magnitude corresponding to creep strain rate at Temperature T (Kelvin) and effective stress at the finite element integration point;

$\dot{\epsilon}_0$ – Creep strain rate at the creep test temperature of reference;

σ_0 – Differential stress of the creep test temperature of reference;

Q – Activation Energy (kcal/mol), Q = 12 kcal/mol;

R – Universal constant of the perfect gas (kcal/mol.K), R=1.98x10⁻³

n_i – Exponent of differential stress or second invariant of stresses;

T- Temperature of the geomechanical model;

T_0 - Reference temperature of the test where the pair ($\dot{\epsilon}_0, \sigma_0$) is obtained

The pair ($\dot{\epsilon}_0, \sigma_0$) is obtained by intersecting the variation curves of the creep strain rate as a function of the differential stress for a given Temperature T_0 on the scale (Log x Log)

Elastic Properties:

Young Modulus : 20.4 Gpa

Poisson coefficient: 0.36

Creep parameters:

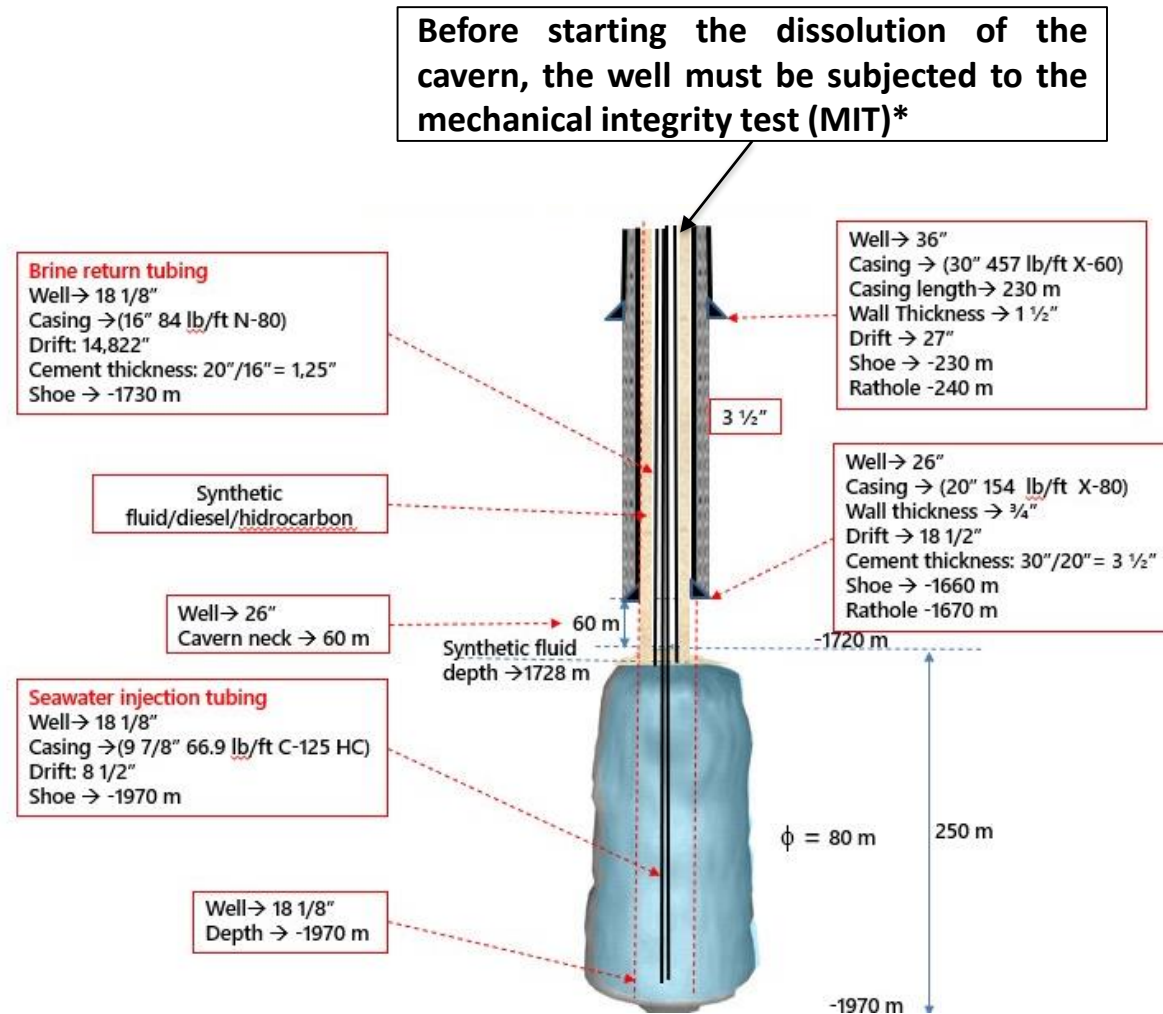
$\dot{\epsilon}_0 = 1.827 \text{ E-07 (T= 316.5 K) Temperature of the mine}$

$\sigma_0 = 10000 \text{ kPa}$

$n_1 = 3.0$

$n_2 = 5.80$

CASINGS SPECIFICATION



*Abreu, J. F.; Costa, A. M.; Costa, P. V.; Miranda, A. C.O.;Zheng, Z.;Wang, P.;Ebecken, N.F.F.; Carvalho, R.S.;Santos, P.L.P.;Lins, N.;Melo, P.R.C.;Goulart, M.B.R.;Bergsten, A.;Bittencourt, C.H.;Assi, A.;Meneghini, J.R.;Nishimoto, K.: Carbon net zero transition: *A case study of hydrogen storage in offshore salt cavern, Journal of Energy Storage, 62 (2023)106818;

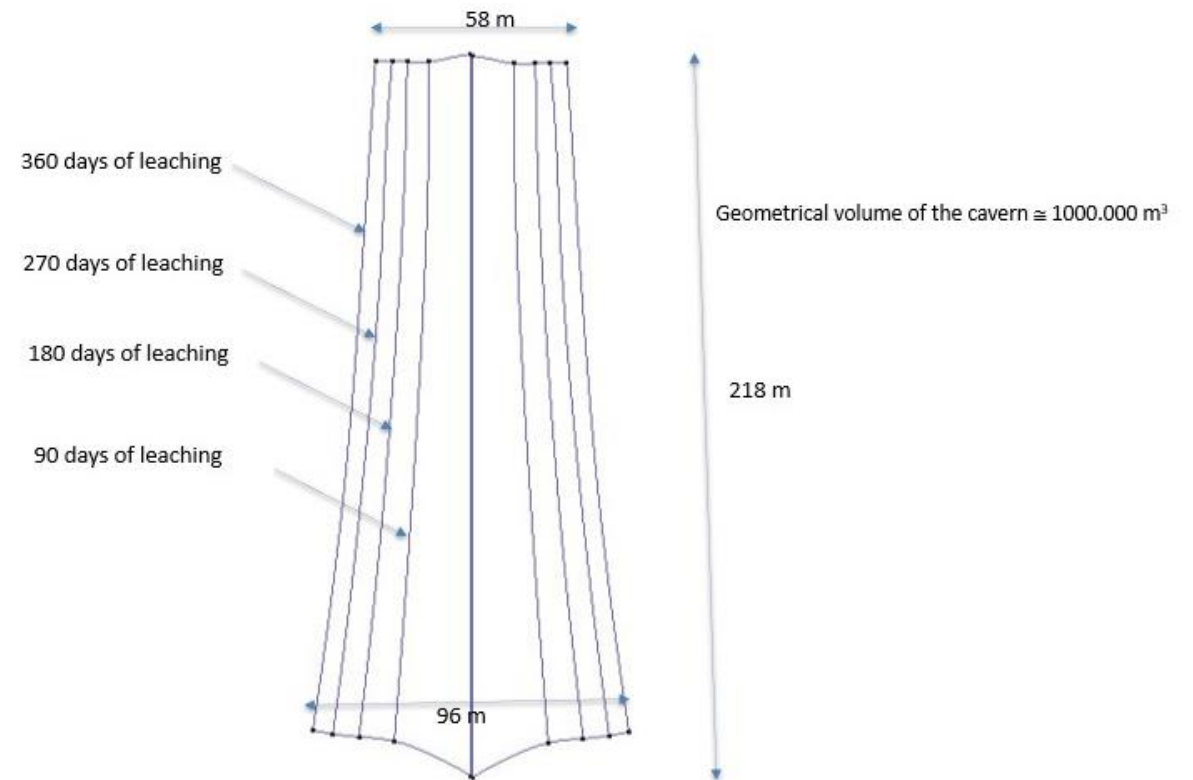
*Costa, P. V. M., Potencial de Estocagem Subterrânea de Gás Natural em Cavernas de Sal Abertas por Dissolução em Domo Salino Offshore no Brasil, Doctor of Science Thesis, COPPE/UFRJ, 2018.
<http://hdl.handle.net/11422/12307>

EVOLUTION OVER TIME OF THE CAVERN LEACHING

Data adopted for the simulation of the cavern dissolution

Description	Value
Depth to the top of the salt caverns (m)	1720.0
Depth to the injection level (m)	1970.0
Depth to the production level (m)	1730.0
Initial height salt exposed to dissolution (m)	250.0
Depth to blanket level (m)	1728.0
Depth to top of insoluble (m)	10.0
The bulking factor for insoluble [24]	1.1
The outside diameter of hanging casing (mm)	406.40
The outside diameter of tubing (mm)	250.82
The specific gravity of salt rock [24]	2.16
Constant production rate (m ³ /hr)	960.0
The temperature at the seafloor (°C)	5°C
The geothermal gradient in the sediments (°C/m)	2.56/100
The geothermal gradient in the salt rock (°C/km)	12
Temperature at the top of the salt dome (°C)	36.5
Temperature at the roof of the caverns (°C)	48.50
Temperature at bottom of the caverns (°C)	51.5
Leaching flow rate (m ³ /hour)	960

During the dissolution of the cavern, it must have its shape and geometric volume monitored by the application of scan sonar (3D)*



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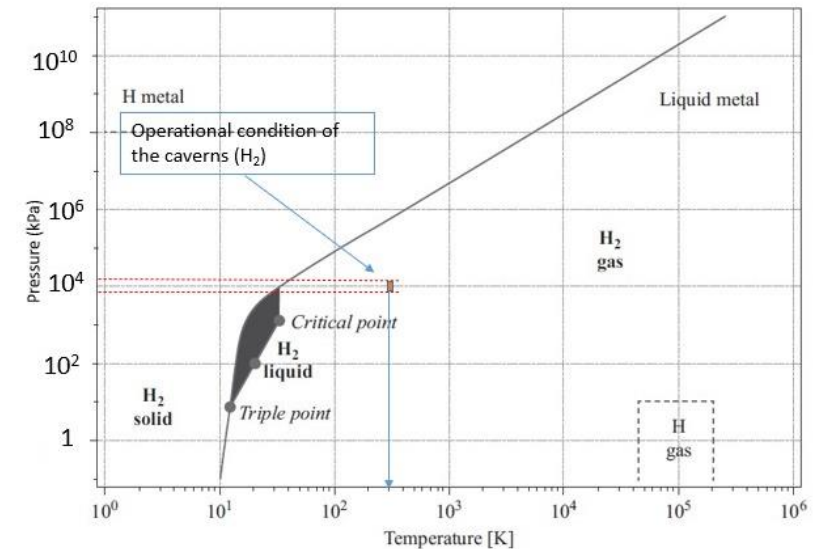
DEFINITION OF MAXIMUM AND MINIMUM OPERATING PRESSURES OF THE CAVERNS

- Maximum pressure of H_2 :
 - Between 80 % and 90 % of the initial lithostatic stress at the top of the cavern (P_{max}). $P_{max} = 80 \% \sigma_0$;
- A minimum pressure of H_2 :
 - Between 30 % and 40 % of the initial lithostatic stress at the top of the cavern (P_{min}). $P_{min} = 30\% \sigma_0$;
- Initial lithostatic stress (σ_0) at the top of the salt caverns:
 - The specific weight of seawater: 10 kN/m^3 ;
 - The specific weight of sedimentary rock [Total Stress]: 22.56 kN/m^3 ;
 - The specific weight of salt rock: $\sim 21 \text{ kN/m}^3$
- $\sigma_0 = 80 \times 10 + 22.56 \times 640 + 1000 \times 21 = 800 + 14438.40 + 21000 = 36238.40 \text{ kPa}$
- **Pressure range:** $[30 \% \sigma_0 = 10900 \text{ kPa}] \leq P_{H_2} \leq [80 \% \sigma_0 = 29000 \text{ kPa}]$:
 - $109 \text{ Bar} \leq P \leq 290 \text{ Bar}$;

H₂ VOLUME AT MAXIMUM AND MINIMUM PRESSURES → "WORKING H₂" (website: <https://webbook.nist.gov/chemistry/>).

- Density of H₂ at normal conditions of temperature and pressure at surface (25 °C {298 K}, 1 atm (1 bar) → $\rho = 0.082351 \text{ kg/m}^3$
- Temperature range inside the cavern: $48.5 \text{ °C} \leq T \leq 51.5 \text{ °C} \rightarrow T_{\text{average}} = 50 \text{ °C} = 323.15 \text{ K}$
- Density of H₂ at the state conditions of [minimum pressure = 109 bar, T= 323.15 K] in the cavern → $\rho = 7.7011 \text{ kg/m}^3$
 - Compression factor $\cong 7.7011 / 0.082351 \cong 93.51$
- Density of H₂ at the state conditions of [maximum pressure = 290 bar, T= 323.15 K] in the cavern → $\rho = 18.551 \text{ kg/m}^3$
 - Compression factor $\cong 18.551 / 0.082351 \cong 225.27$
- Useful geometrical cavern volume obtained by leaching simulation $\cong 1,000,000 \text{ m}^3$
 - H₂ volume at the minimum pressure = $93.51 * 1,000,000 = 93.510.000 \text{ Sm}^3$
 - H₂ volume at the maximum pressure = $225.27 * 1,000,000 = 225.270.000 \text{ Sm}^3$
- Volume of useful or maneuverable H₂ ("working H₂") = $225.270.000 - 93.510.000 = 131.760.000 \text{ Sm}^3 = \mathbf{10850 \text{ tons}}$
- Lord et al* presents an interesting study on the demand of hydrogen for vehicular use, required under normal operating conditions of 4 major cities in the United States. It was concluded that the daily demand would be ~40 tons of hydrogen per day, assuming a market penetration of 25% of the total energy demand of the city. The total working hydrogen volume available in each cavern is $131.760.000 \text{ Sm}^3 = 10.850 \text{ tons}$, which corresponds to one complete cycle between the maximum and minimum pressures in **250 days**.

Operational conditions of the hydrogen inside the caverns



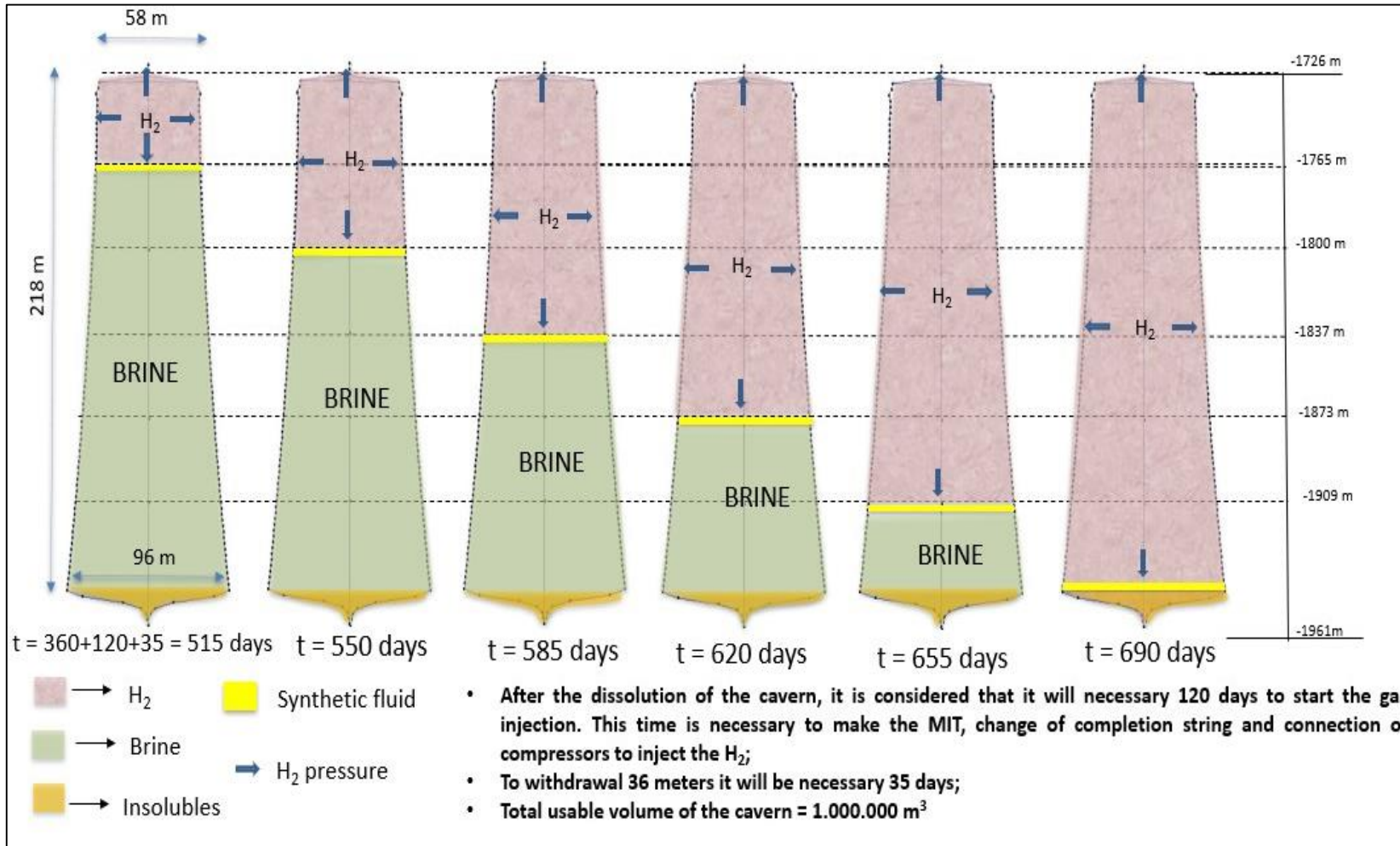
Average Temperature inside the cavern = 50 °C = 323.15 K

Minimum pressure = 109 bar (10.900,00 kPa)

Maximum pressure = 290 bar (29.000,00 kPa)

*Lord, A. S.; Kobos, P. H.; Borns, D. J.: Geologic storage of Hydrogen: Scaling up to meet city transportation demands, International Journal of Hydrogen Energy 39 (2014).

WITHDRAWING OF THE BRINE BY H₂ INJECTION



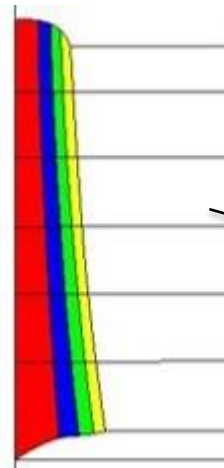
Observation: Before starting injection of H₂, the cavern must be subjected to the mechanical integrity test (MIT)*

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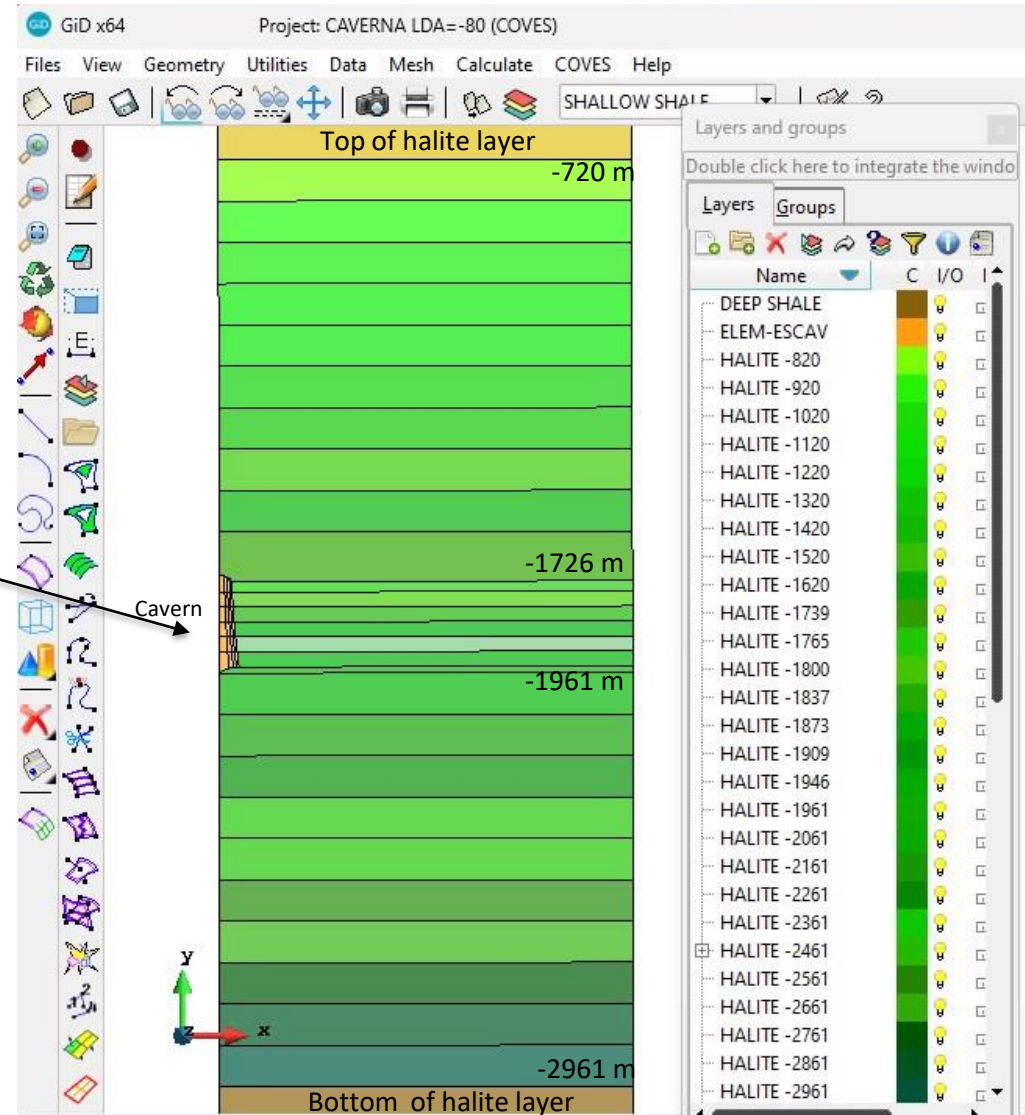
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GEOMECHANICAL STRUCTURAL MODEL USED IN THE SIMULATIONS*

Excavation Steps in the geomechanical simulation



- Excavation at $t = 90$ days
- Excavation at $t = 180$ days
- Excavation at $t = 270$ days
- Excavation at $t = 360$ days

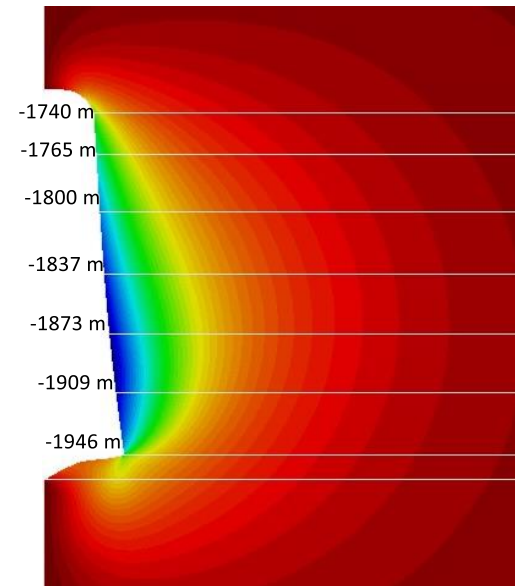
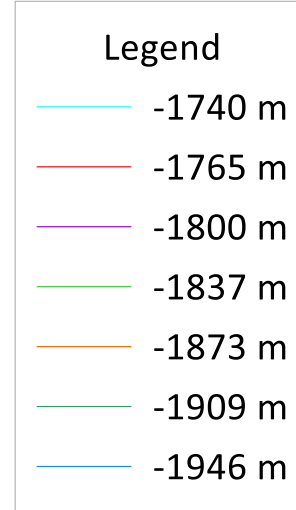
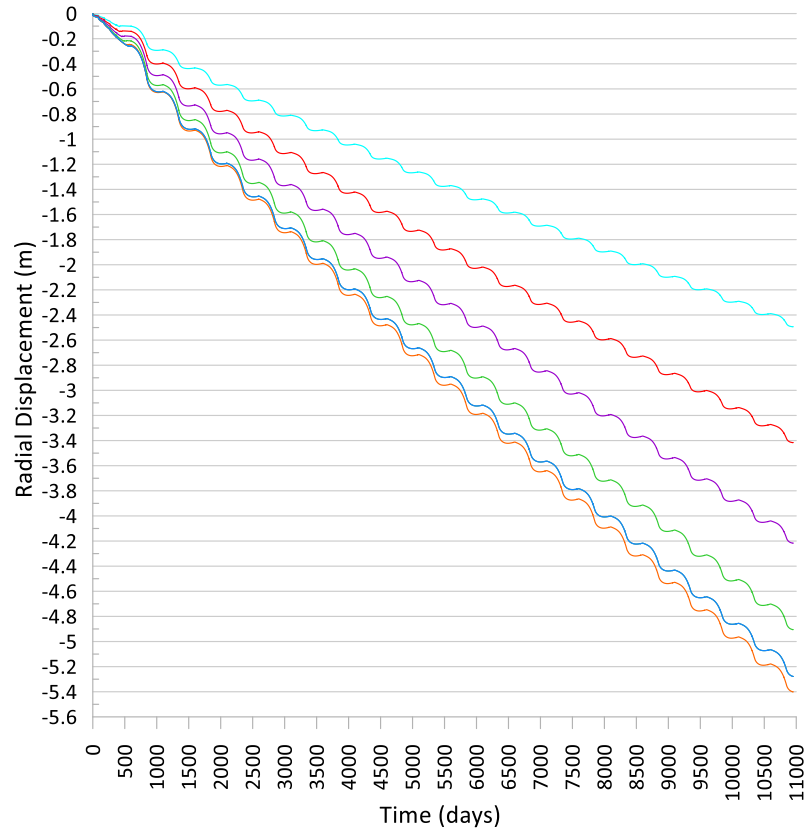


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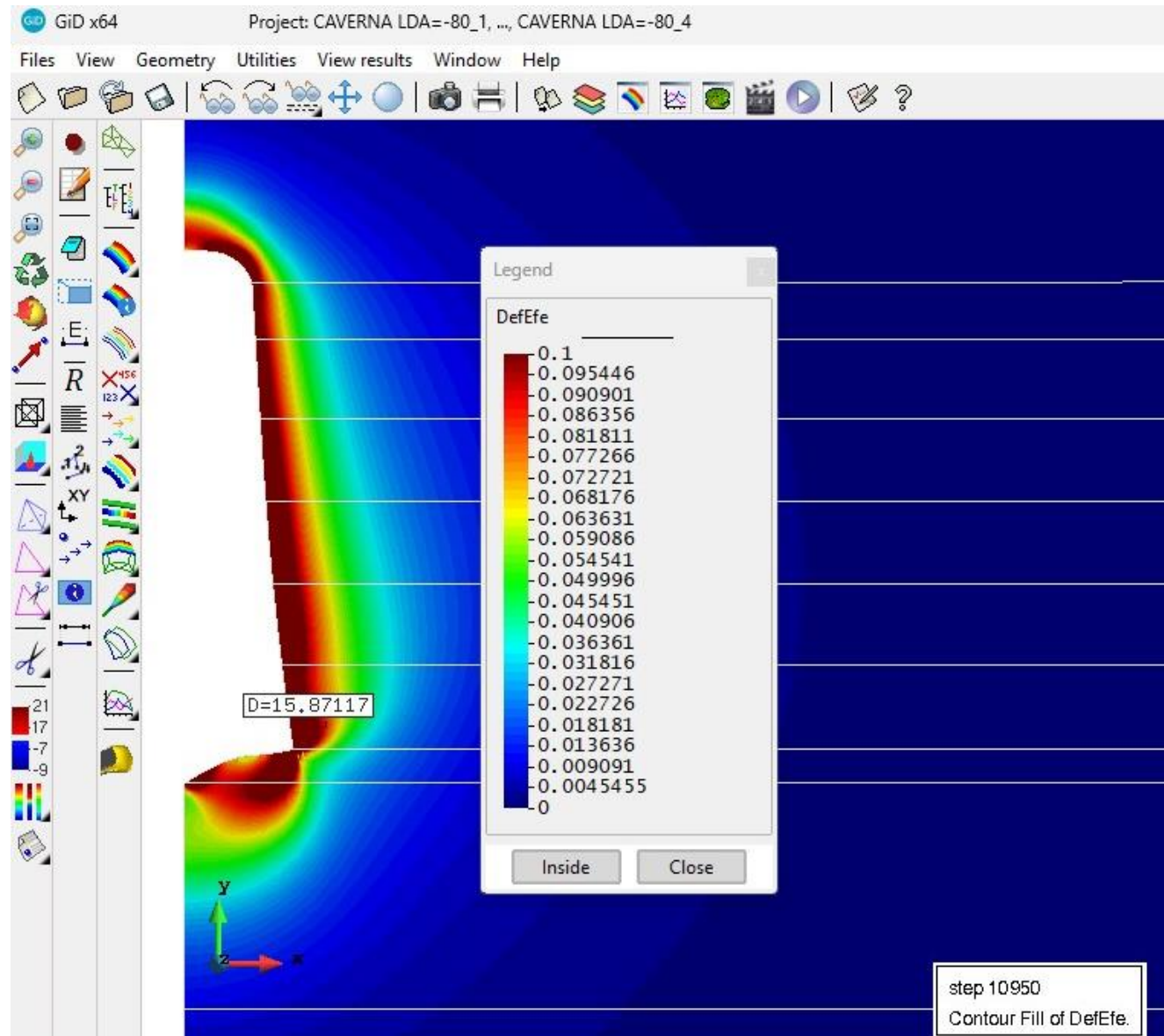
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EVOLUTION OVER TIME OF THE RADIAL DISPLACEMENT AT THE LATERAL WALL OF THE CAVERN

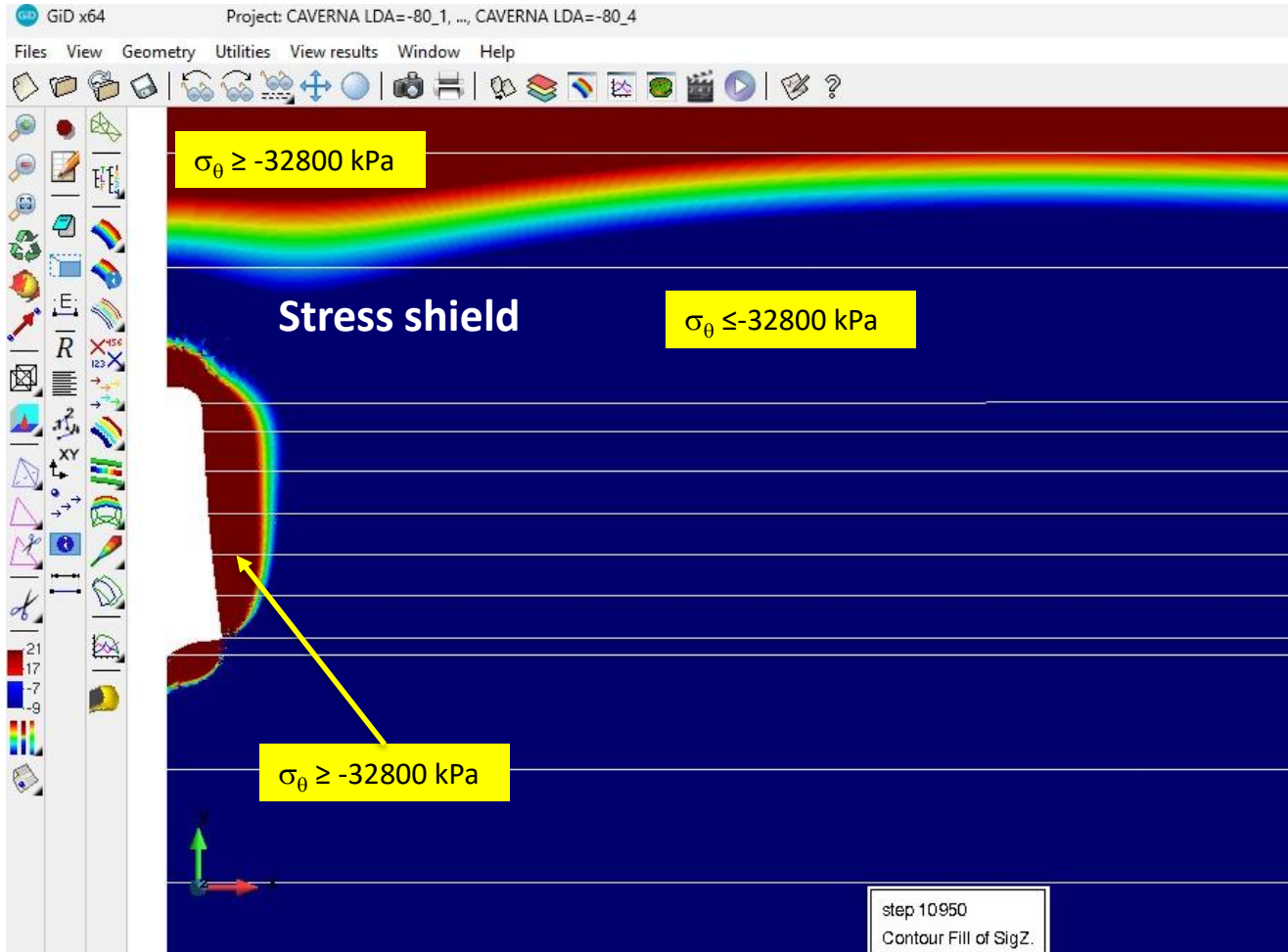
Evolution over time of the radial displacement at the wall face of the cavern



EFFECTIVE CREEP STRAIN ACCUMULATED IN 30 YEARS



STRESS SAFETY SHIELD OBTAINED BY SIMULATION - CREEP PARAMETERS FROM THE POTASH MINE IN BRAZIL



The leak of gases in a salt rock cavern open by leaching will occur through fractures normal to the tangential stress σ_{θ} in the axisymmetric structure model. The compressive tangential stress must be greater than the maximum pressure designed for the cavern, in this "Case study," equal to 290 bar or 29000 kPa multiplied by the safety factor:

$\sigma_{\theta} \leq (-29000 * 1.2) = -34800 \text{ kPa}$. The tension strength of the Halite is equal to 2000 kPa [26], which will be decreased from the tangential limit stress resulting in -32800 kPa. Figure shows the iso surfaces with the boundaries $[-34000 \text{ kPa} \leq \sigma_{\theta} \leq -32800 \text{ kPa}]$ at $t = 30$ years.

CONCLUSIONS

The simulation of the geomechanical structural behavior of the cavern demonstrated that Hydrogen could operate between a maximum pressure of 290 bar (29000 kPa) and a minimum pressure of 109 bar (10900 kPa), assuming a complete cycle of 250 days, and can dispatch to the market 40 tons per day of blue or green Hydrogen. The total working volume of working Hydrogen between the maximum and minimum operating pressures is 131.760.000 Sm³, which corresponds to **10.850tons** of Working Hydrogen;