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National Centre for Sustainable Subsurface Utilization of the Norwegian Continental Shelf

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Geochemical challenges of hydrogen storage in Salt caverns

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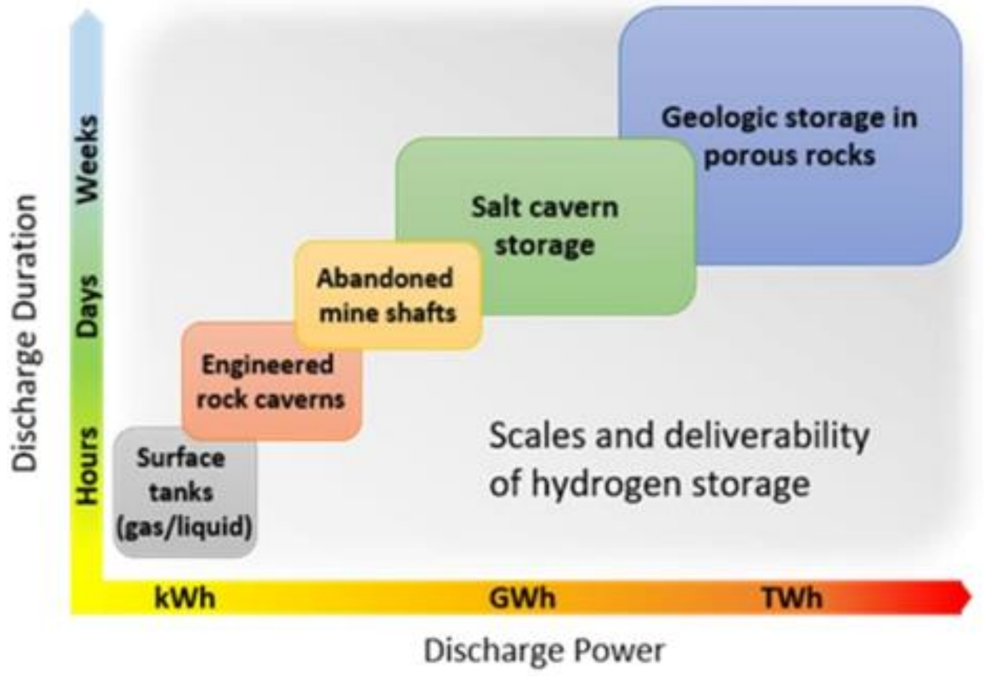
Importance of H2 Economy

- Efforts to achieve energy transition and climate neutrality in EU and the rest of the world
- **The European Hydrogen Backbone (EHB) initiative (2021):**
  - H2 Demand for transportation in 2050: 285 TWh ~ 12% of the total demand
    - 68 TWh for the **Aviation sector**
    - 217 TWh for **heavy-load transport**
  - H2 Demand for electricity generation: 626 TWh in 2050 ~ 7% of the EU electricity demand
- **The International Energy Agency (IEA,2022):** 520 MT of clean hydrogen needed annually by 2050 to reach net zero

H2 Storage importance

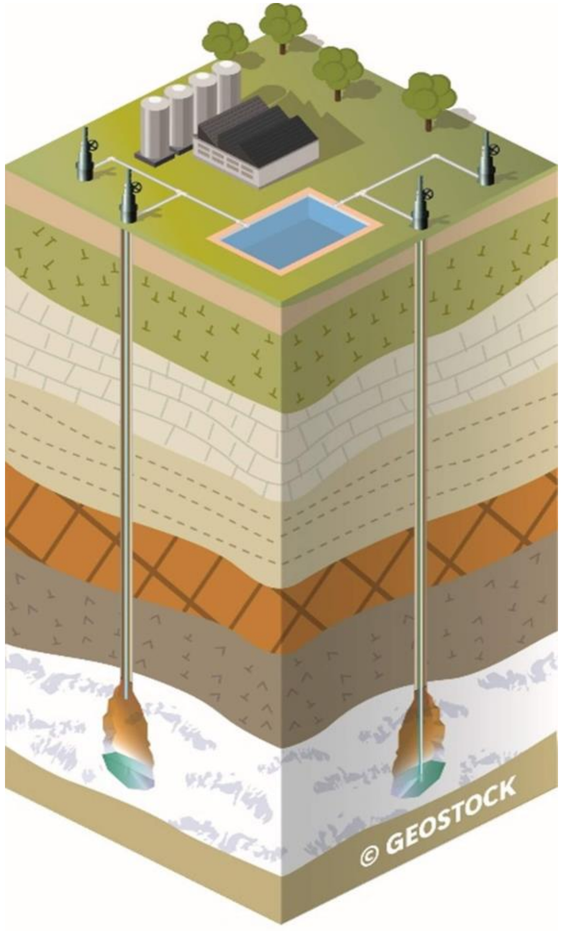
- TWh storage of H2: Only underground storage can provide enough capacity
- Other options have limited capacity



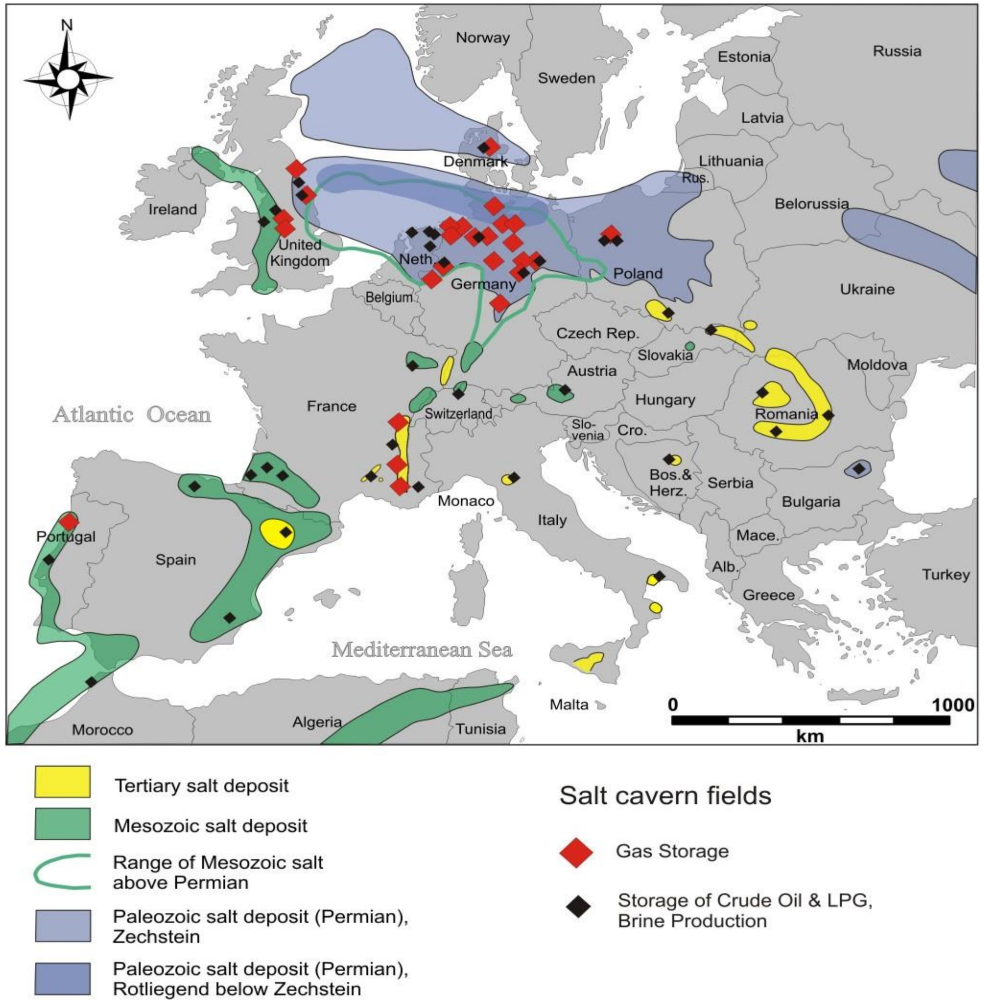
Fangxuan Chen et al., 2022

Background

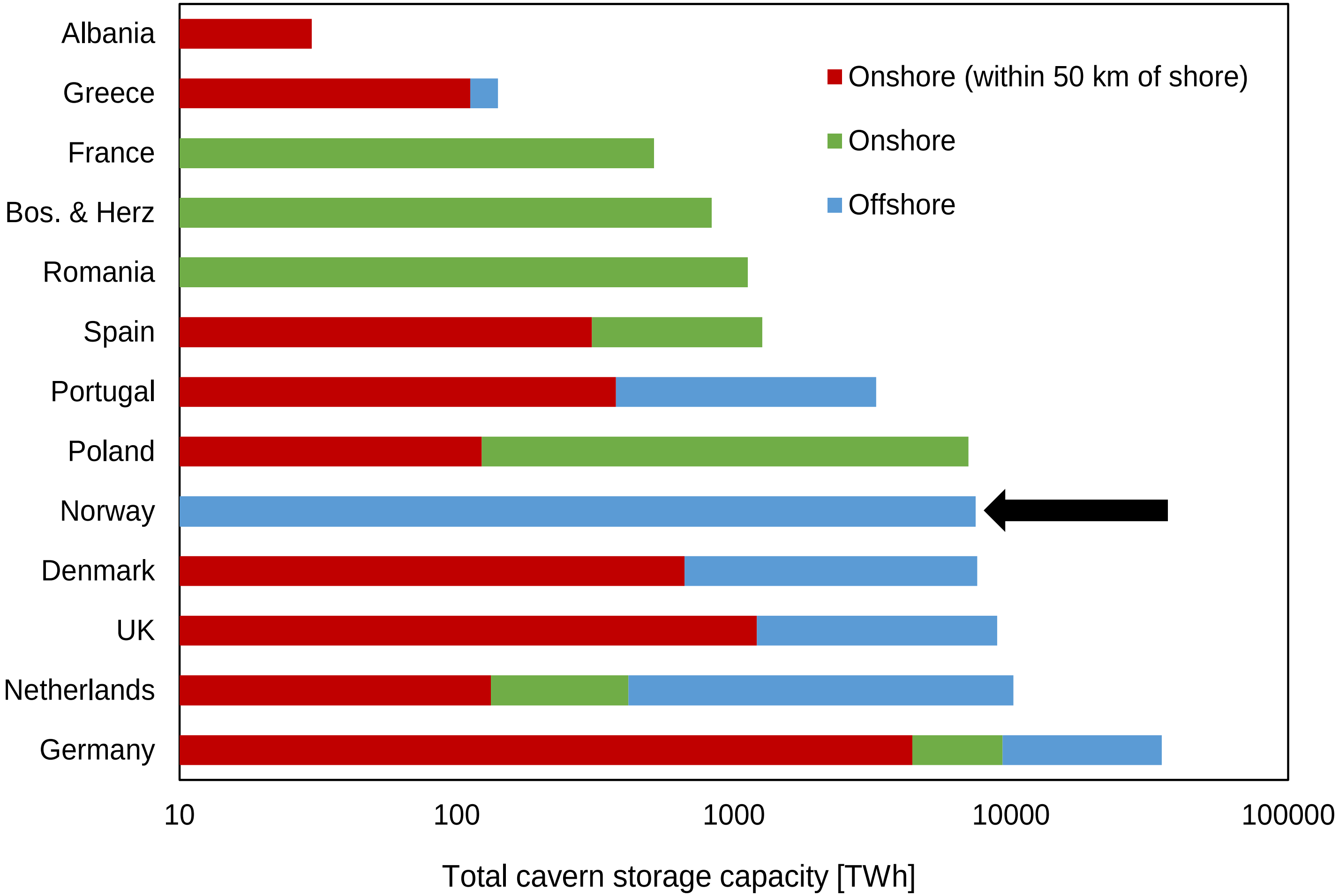
- Advantages of salt caverns vs porous rocks for H2 storage
  - Ductility of salt rock
  - Impermeable: less prone to H2 leakage
  - Less surface contact with rock minerals
  - Less cushion gas requirement
  - Less storage costs



Salt Formations and H2 Storage Capacity in Europe

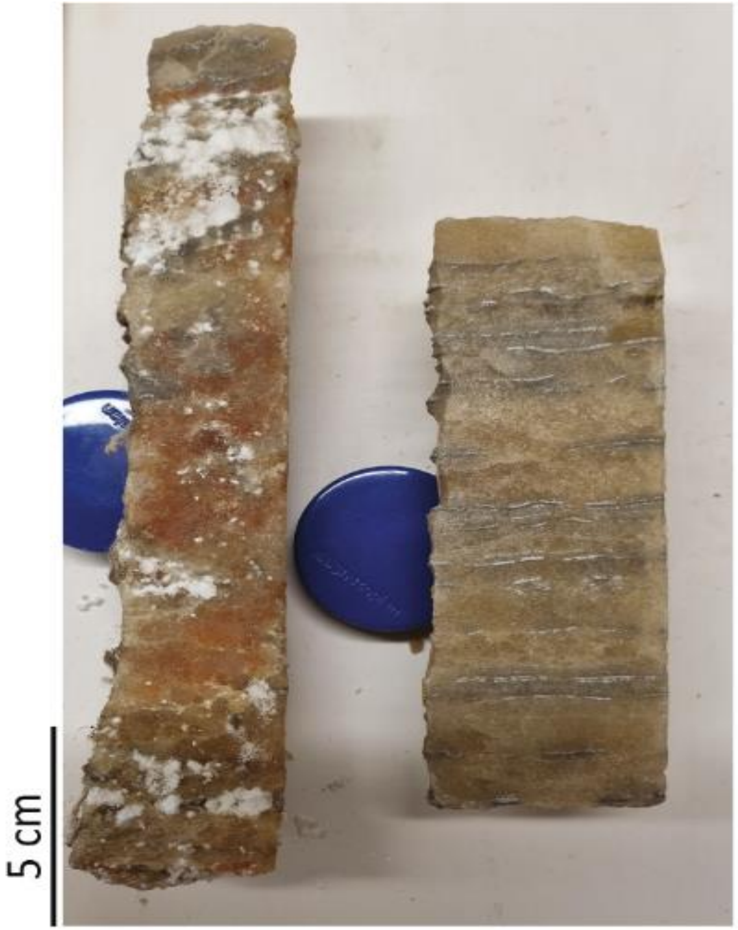


Salt deposits, their distribution, and the cavern storage sites across Europe (Gillhaus et al., 2006)



Estimated hydrogen storage capacity across Europe (Caglayan et al., 2020))

Geochemical Challenges

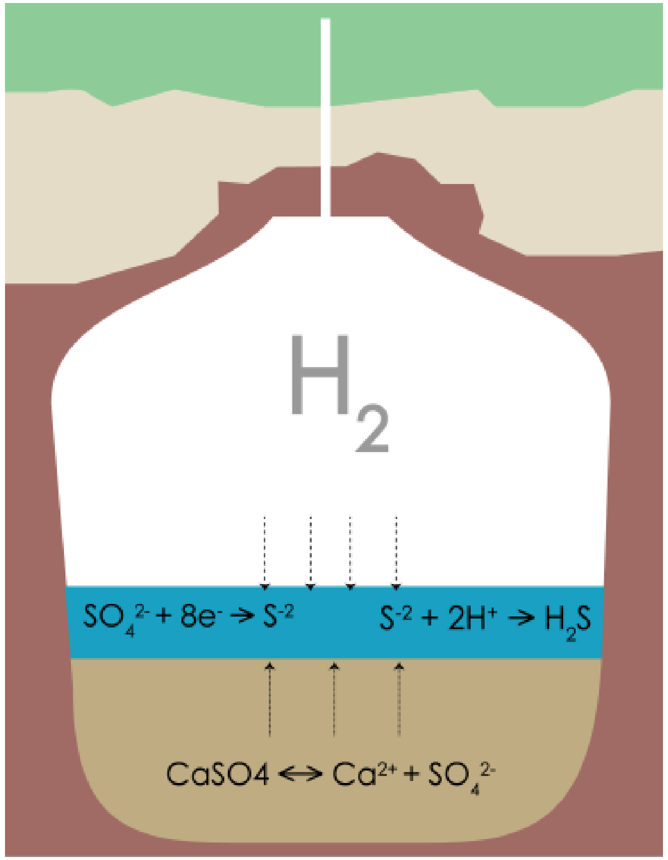


Halite with sylvite (left core, NPD, 2022) and halite with discontinuous stringers of anhydrite and claystone (right core).

- Salt formations are usually associated with high amounts of impurities
- Impurities such as anhydrite, clays, carbonates, and iron that could react with hydrogen and generate unwanted gases
- The presence of Halophilic bacteria in the cavern could lead to the formation of hydrogen sulfide in the presence of dissolved sulfate resulting from the leaching.

Challenges

- Hydrogen is an electron donor for certain types of bacteria
- The presence of sulfate-reducing bacteria in salt caverns has been proven (Laura Schwab et al, 2022)
- Anhydrite and gypsum dissociation during the leaching can release sulfate, which could react with H2 at the interface
- The catalytic reactions result in H2S production
- The presence of H2S in the gas phase is detrimental to the safety of the storage operation



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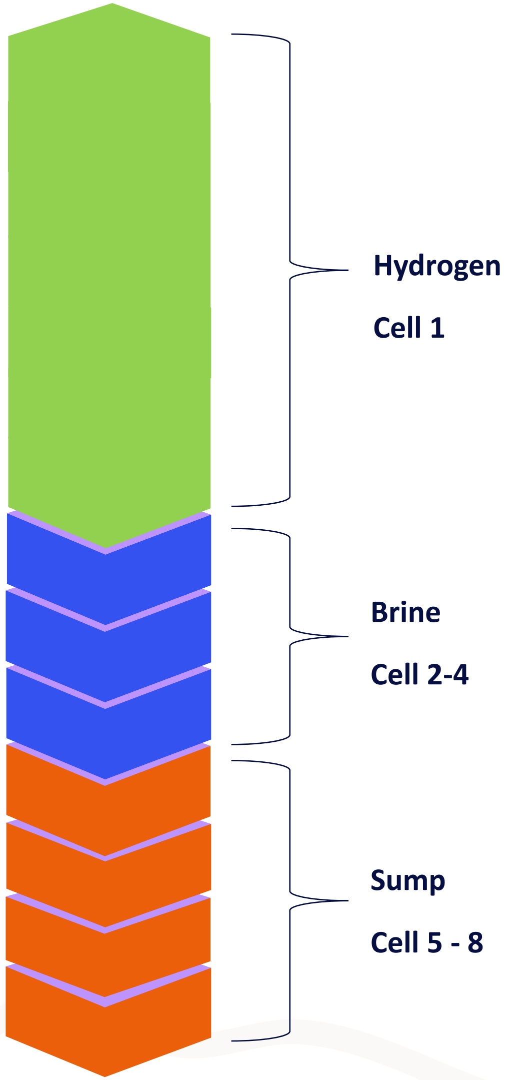
Chemical model in PHREEQC



Reaction: SO4-2 + 9H+ + 8e- = HS- + 4H2O

- H_2 is stored in the cavern at 180 bar
- H_2 is diffused from the gas cap to the brine phase
- Sulfate is allowed to diffuse from the sump to the brine
- The reaction kinetics is determined by microbial activity
- The kinetic rate depends on the environment
- In this model, k = 9e-8 mol/kgw/s (Herrera, L. et al. 1997)
- The Monod Equation for bacterial sulfate reduction:

$$H2S\ rate = k * \frac{[SO_4^{2-}]}{1E-04+[SO_4^{2-}]} * \frac{[H_2]}{1E-04+[H2]}$$

(Laban, 2020)

Cavern data (brine and sump)

Data are taken from C. Hemme, W. van Berk, 2017

- Pressure: 180 bar
- Temperature: 50 C
- pH of the brine: 5.7

Brine

Al	3.706e-07
Ba	9.097e-07
C	7.077e-03
Ca	6.333e-02
Cl	6.310e+00
Fe	1.415e-03
K	1.010e-04
Mg	1.315e-03
Mn	9.100e-07
N	3.008e-04
Na	6.310e+00
P	4.840e-07
S	6.262e-02
Si	3.368e-05

Sump

Al	3.706e-07
Ba	8.136e-07
C	2.901e-05
Ca	5.488e-02
Cl	6.306e+00
Fe	2.257e-03
K	1.010e-04
Mg	1.464e-02
Mn	9.100e-07
N	1.152e-03
Na	6.306e+00
P	4.840e-07
S	7.108e-02
Si	5.242e-05

Equilibrium reactions reactions

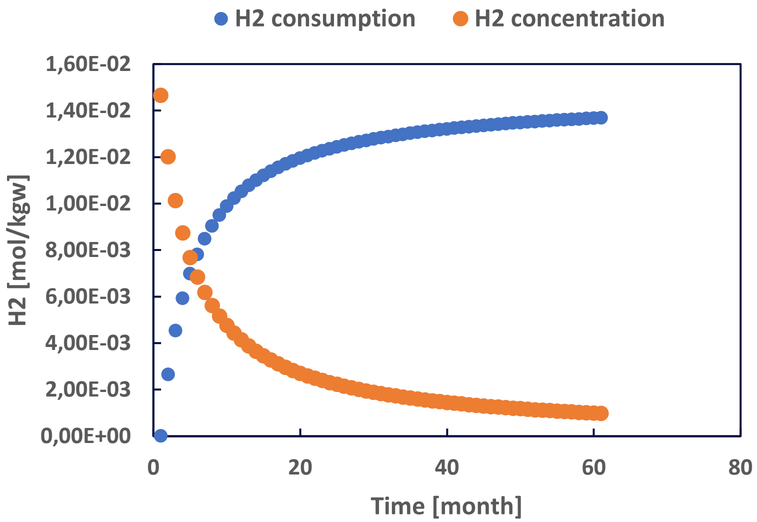
Equilibrium phase	Equilibrium reactions	logK
Halite	$NaCl = Cl^- + Na^+$	1.570
Anhydrite	$CaSO_4 = Ca^{2+} + SO_4^{2-}$	-4.39
Siderite	$FeCO_3 = Fe^{2+} + CO_3^{2-}$	-10.89
Quartz	$SiO_2 + 2H_2O = H_4SiO_4$	-3.98
Barite	$BaSO_4 = Ba^{2+} + SO_4^{2-}$	-9.97
Pyrite	$FeS_2 + 2H^+ 2e^- = Fe^{2+} + 2HS^-$	-18.479
Dolomite	$CaMg(CO_3)_2 = Ca^{2+} + Mg^{2+} + 2CO_3^{2-}$	-17.09
Mackinawite	$FeS + H^+ = Fe^{2+} + HS^-$	-4.648
Sulfur	$S + 2H^+ + 2e^- = H_2S$	4.882
Calcite	$CaCO_3 = CO_3^{2-} + Ca^{2+}$	-8.48

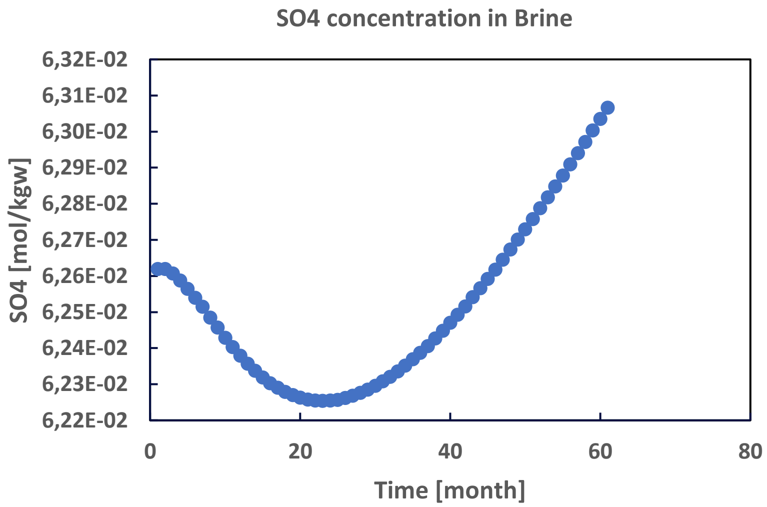
C. Hemme, W. van Berk, 2017

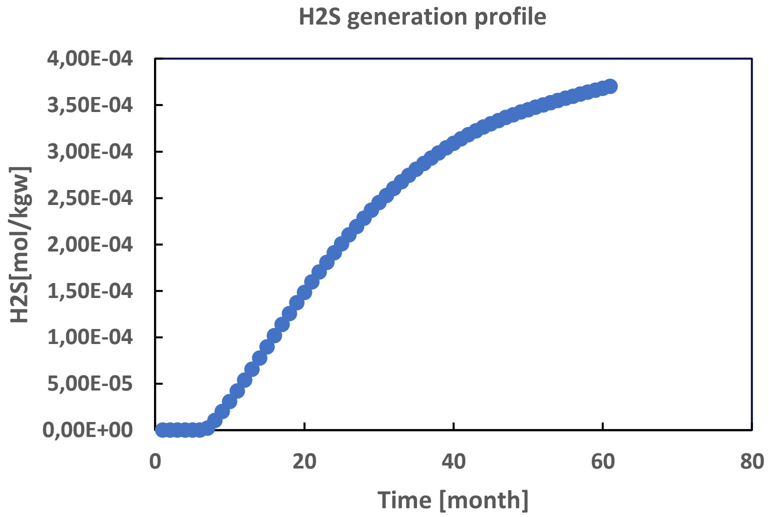
Hydrogen Diffusion: Fickian diffusion

- Hydrogen solubility calculated in Phreeqc at 50 C, 180 bar.
- Initial amount of hydrogen in the brine = 1.465e-02 mol/kgw
- Hydrogen diffusion in the brine and sump over time and space is defined using Fick's 2nd law of diffusion
- Fick's equation $\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 C}{\partial x^2}\right)$
- Solution for constant surface concentration: $C(x,t) = C_{sat}\,\mathrm{erfc}\left(\frac{x}{2\sqrt{Dt}}\right)$
- Diffusion coefficient : 5.13e-9 m2/s (Hemme et al., 2018)

Base case simulation results – 5 years scenario

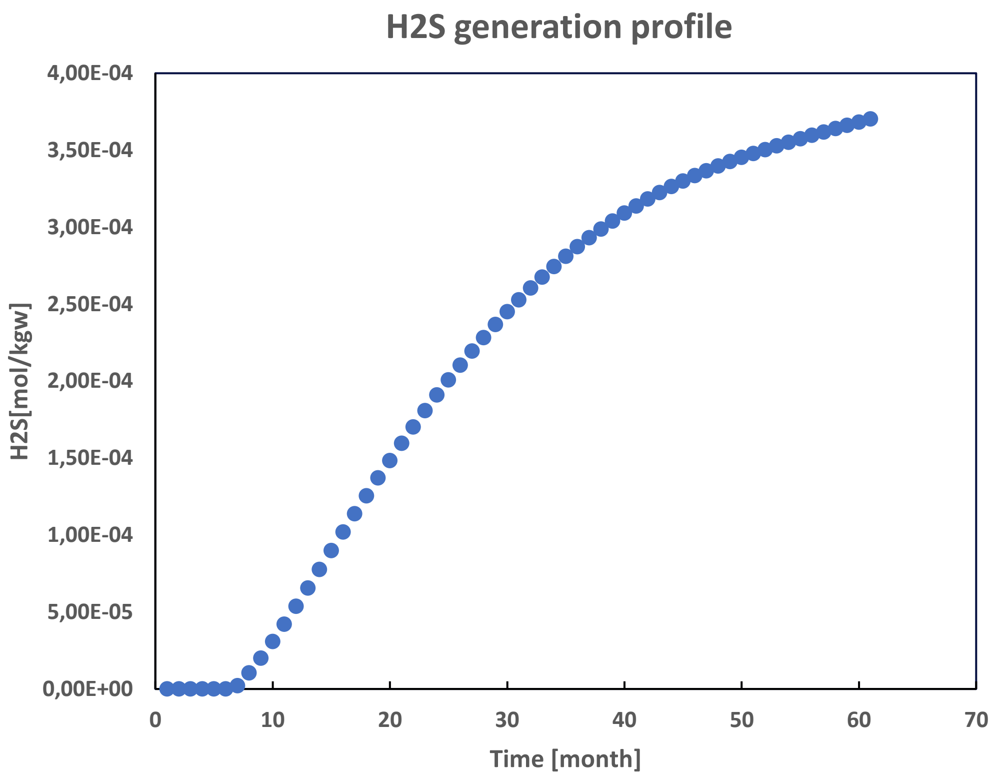


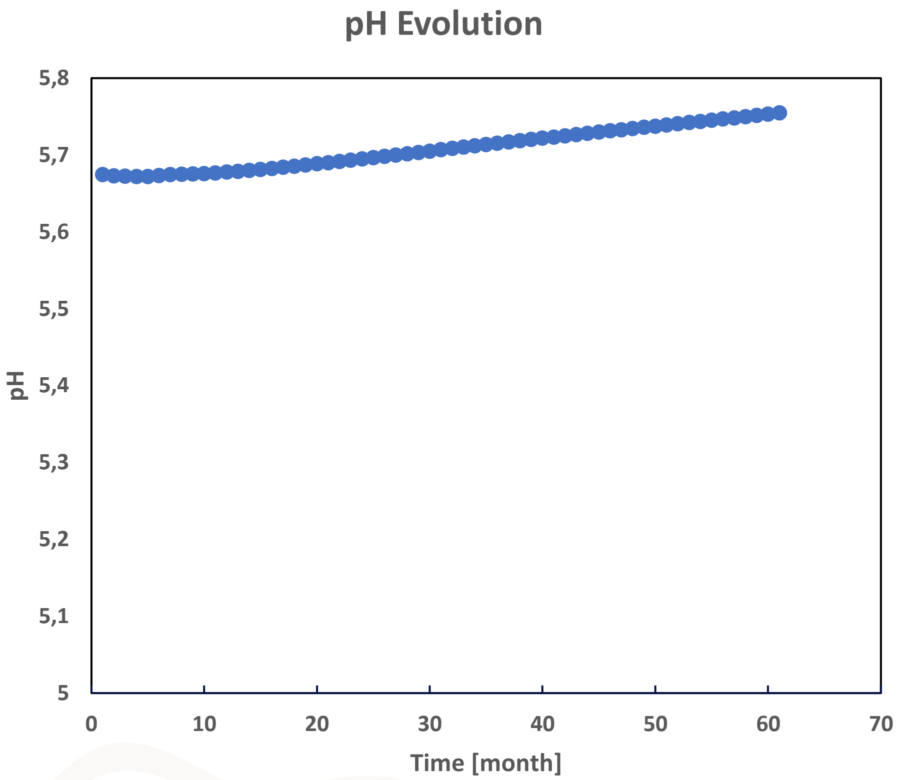




- H2 concentration is constantly declining meaning that consumption gradually increases
- Sulfate concentration steadily declines during the first 25 months
- H2S generation is maintained thanks to sulfate diffusion to the brine from the 25th months
- Sulfate diffusion from the sump is therefore the main driver of H2S generation in the brine

Effect on pH evolution





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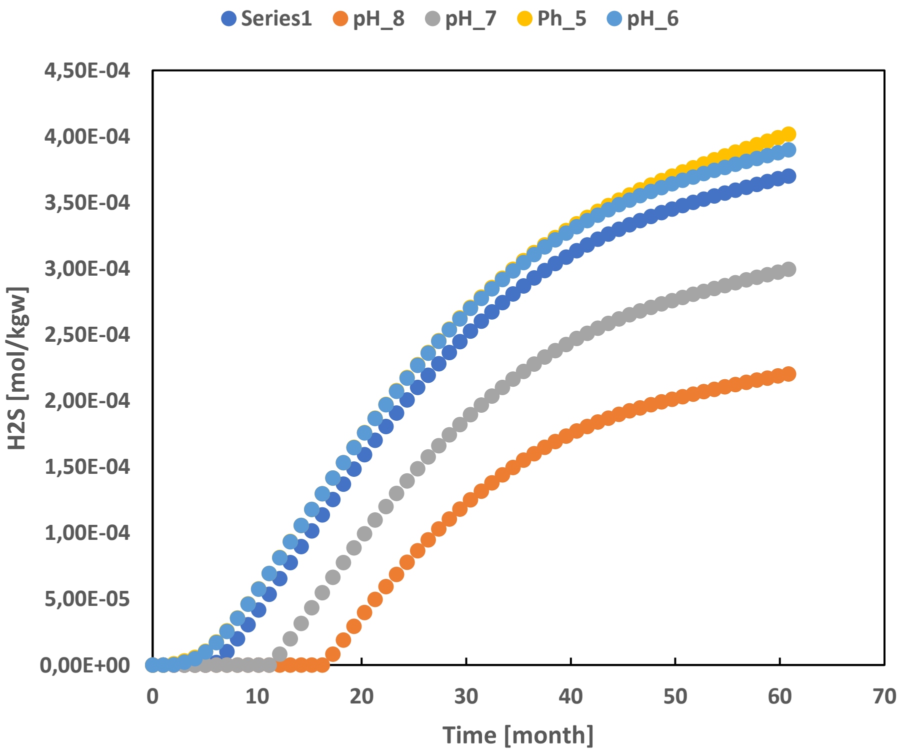
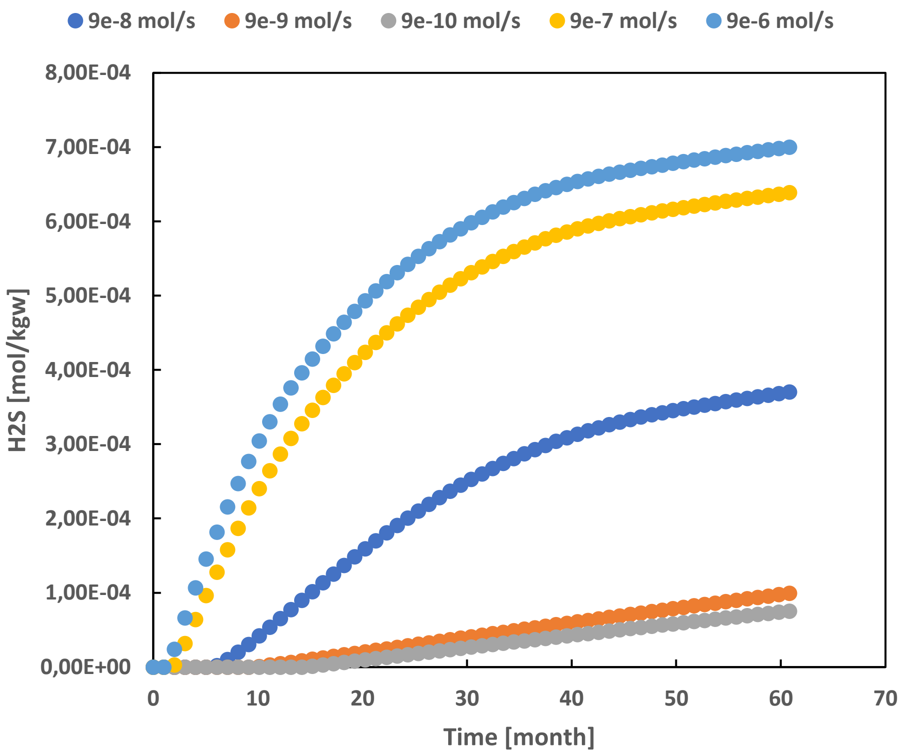
Sensitivity



pH effect



Kinetic Rate effect

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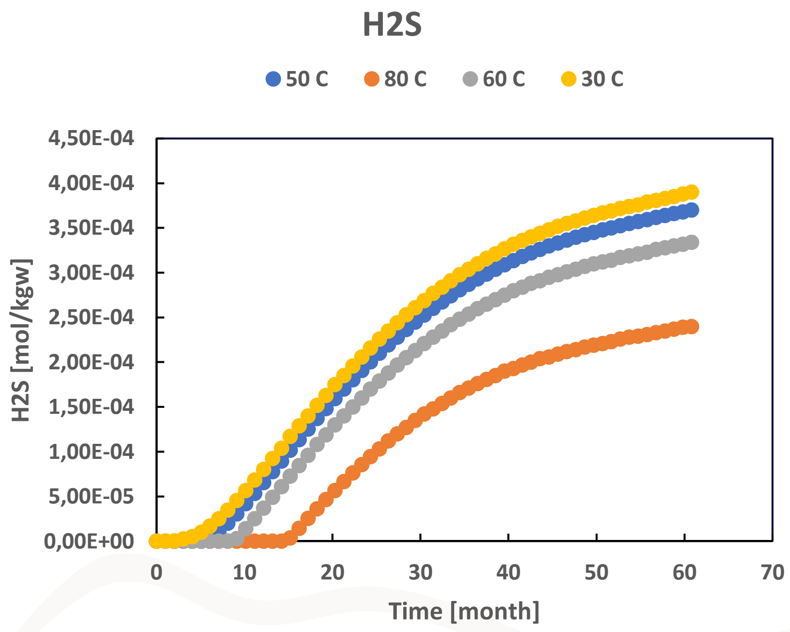
FeS precipitation at high temperature

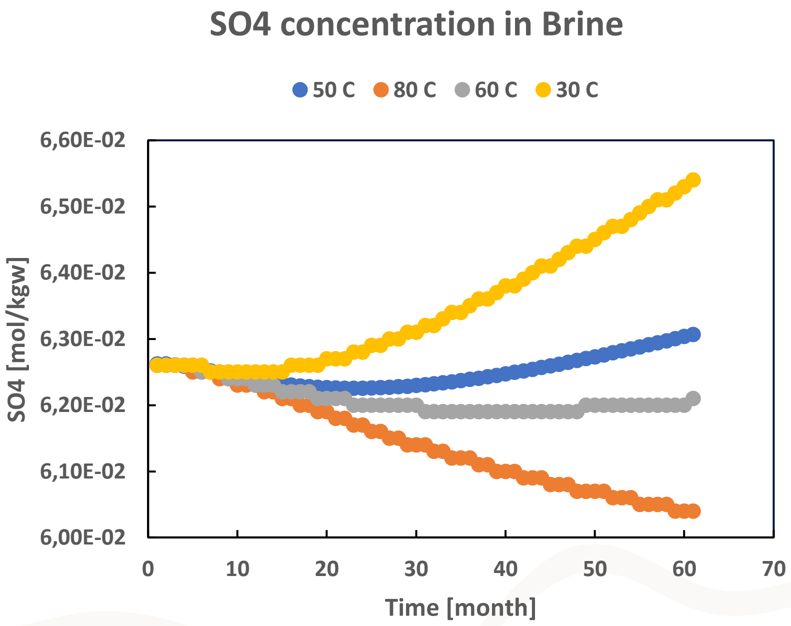
Sulfate reduction

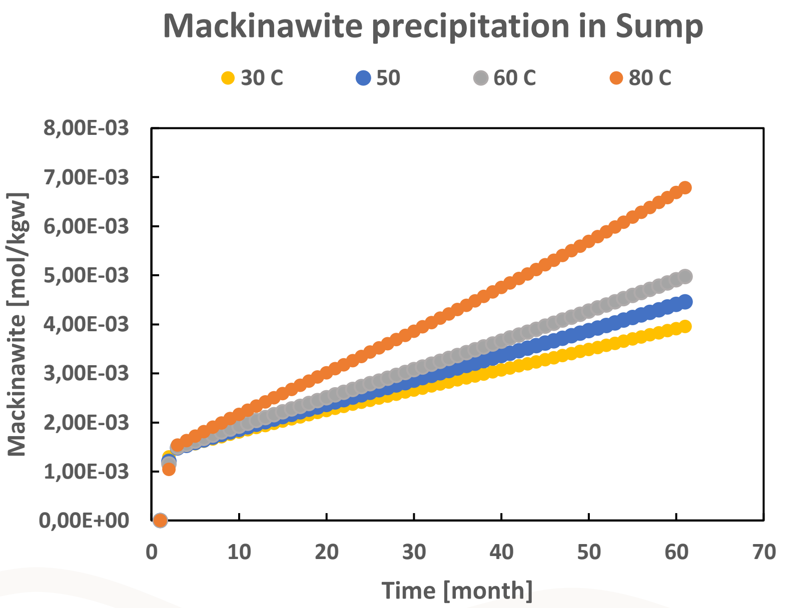
4H2 + SO2−4 → H2S + 4H2O
ΔG_r^o = −20 kJ mol−1
(Tori M. Hoehler et al., 2001)

Pyrite formation

Fe+2 + 2 HS- = FeS2 + 2H2
ΔG_r^o = −41 kJ mol−1
(Joana Thiel, 2019)







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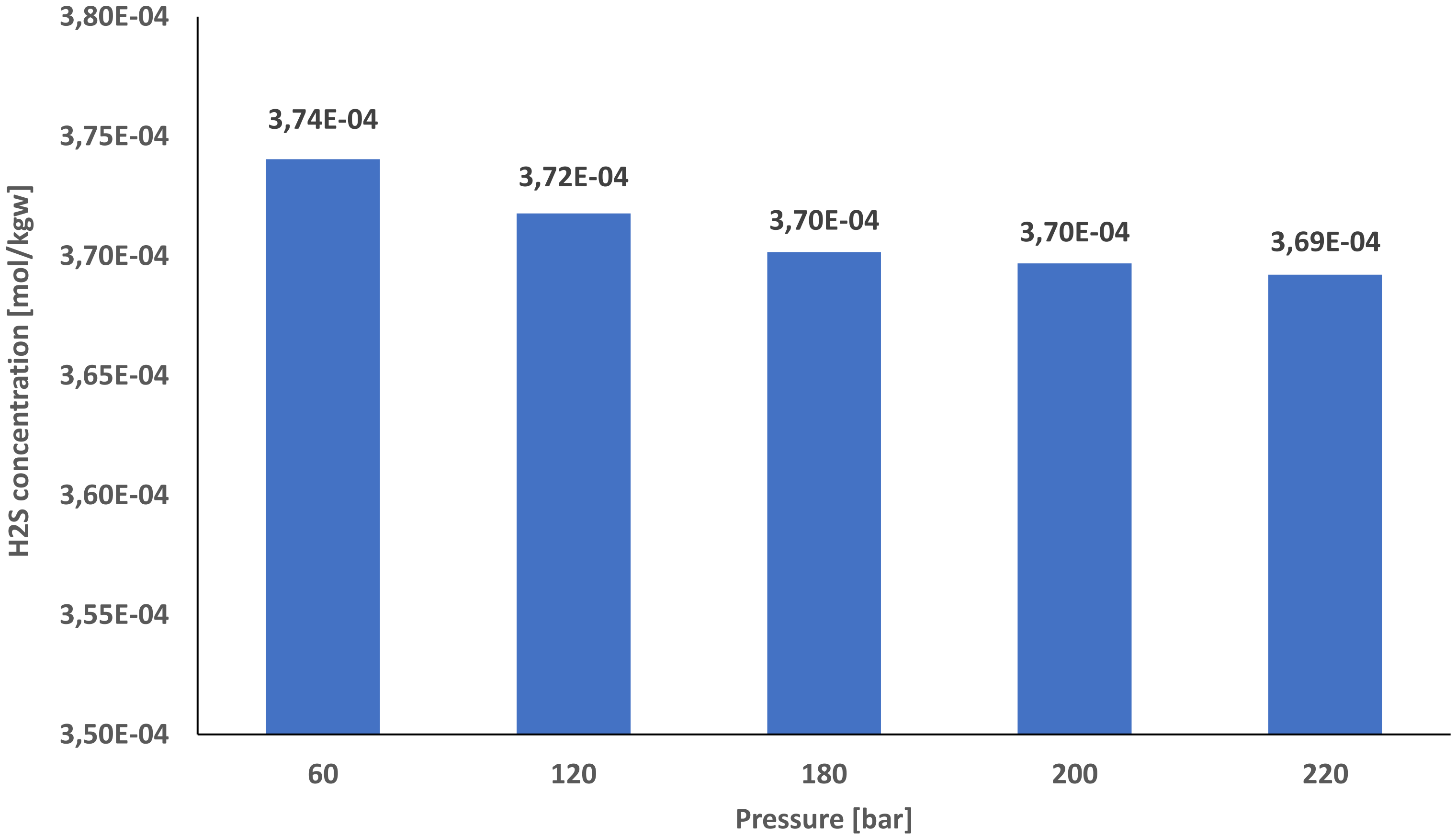
Pressure effect



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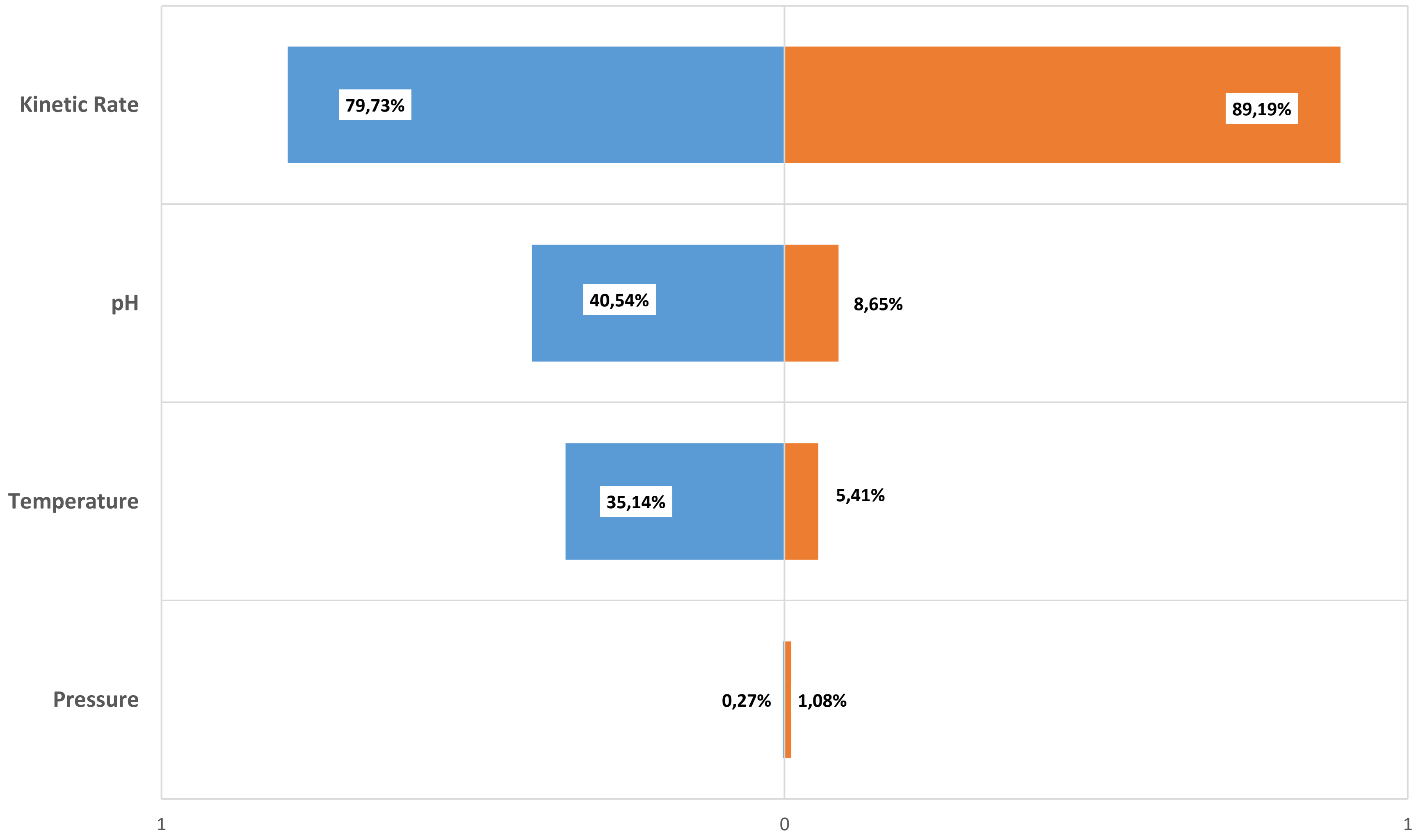
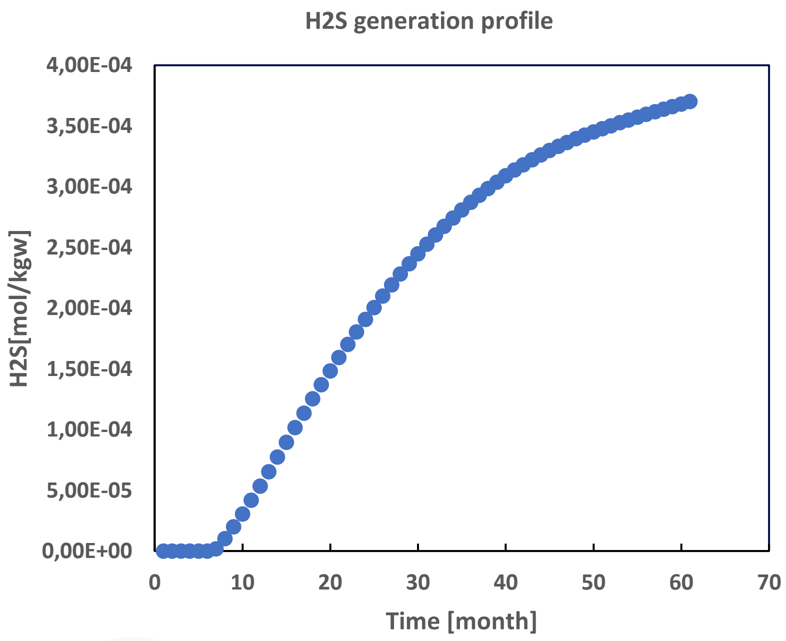
Parametric Variation of H2S formation

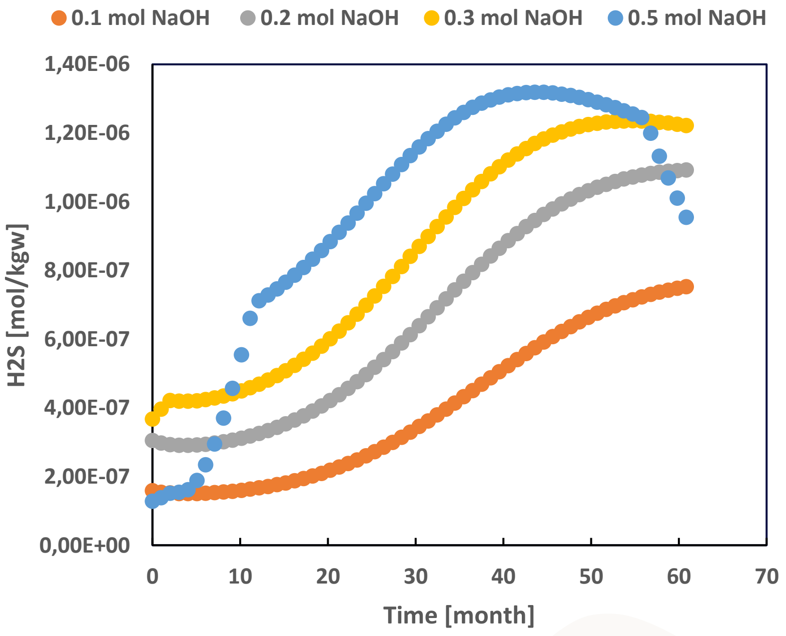


H2S mitigation methods

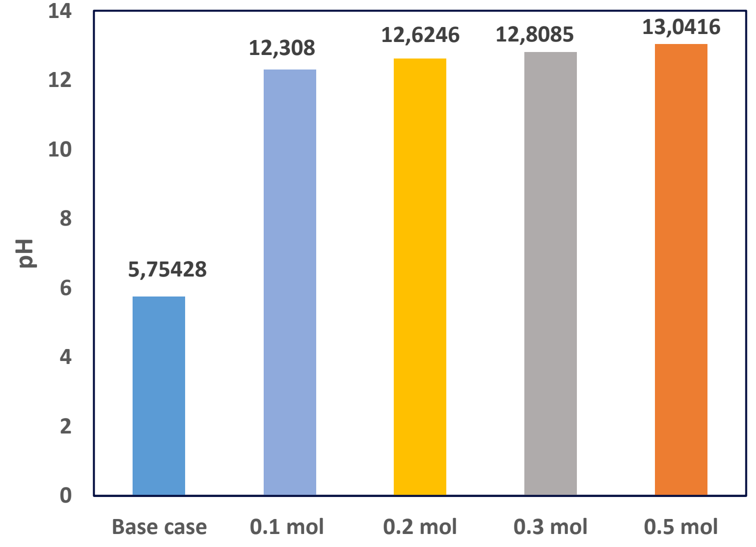
- Adding NaOH leads to pH increase, hence a reduction in H2S amount generated in comparison to the base case



Base case



Moles NaOH added and H2S amounts



pH Evolution

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Conclusion

- Under optimum conditions, the presence of sulfate in the brine can lead to sulfate reduction and H_2S production
- Main Parameters influencing H_2S generation: kinetic rate
- H_2S generation can be mitigated by increasing the pH through $NaOH$ addition

Future Work

- Model Calibration
- Application to the Salt deposition in Norway

THANKS FOR LISTENING

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