

# Modelling (Bio-)Geochemical reactivity in Underground Hydrogen Storage

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HYSTORIES FINAL CONFERENCE

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## Acknowledgment



# Why looking at Hydrogen reactivity ?

Main risks associated to H<sub>2</sub> reactivity:

Reaction induced by H <sub>2</sub>	Risk for UHS	Ranking of risk potential
Production of CH <sub>4</sub>	• Loss of stored H <sub>2</sub>	☆☆☆
Production of H <sub>2</sub> S	• Gas pollution	☆☆☆
	• Corrosion of installations	☆☆☆
	• Degradation of well integrity	☆☆☆
Dissolution/precipitation of minerals	• Changes of reservoir injectivity	☆☆☆
	• Alteration of mechanical properties of the reservoir	☆☆☆
	• Formation of gas leakage pathways in the caprock	☆☆☆

**Models to quantify H<sub>2</sub> reactivity, depending on conditions proper to a storage**

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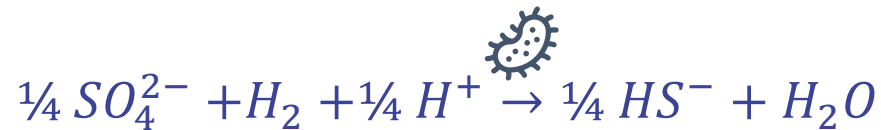
# Hydrogen reactivity in a storage

# Expected reactivity of H<sub>2</sub> in an underground storage

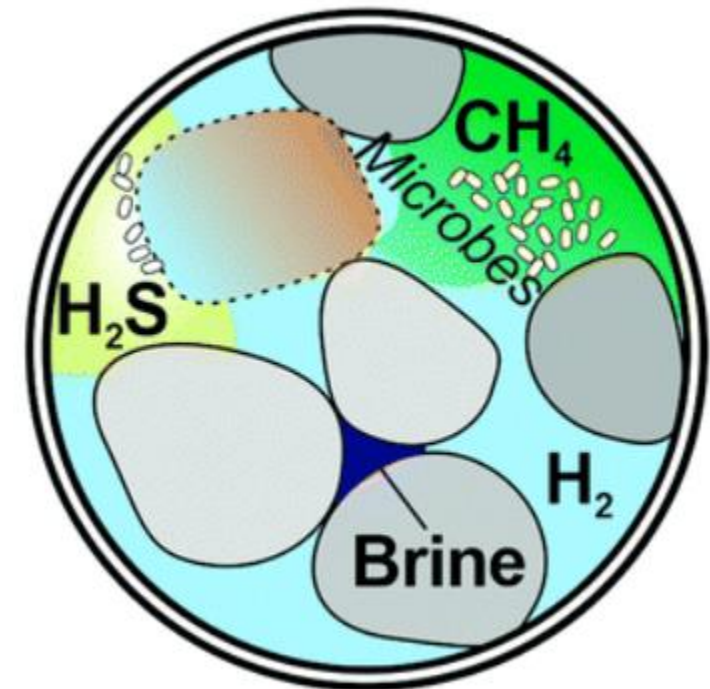
- H<sub>2</sub> is an electron donor that can induce chemical reactions
- Main reactions under storage conditions:
  - Methanogenesis: formation of methane (CH<sub>4</sub>) from carbonates (CO<sub>2</sub>(g), HCO<sub>3</sub><sup>-</sup>)



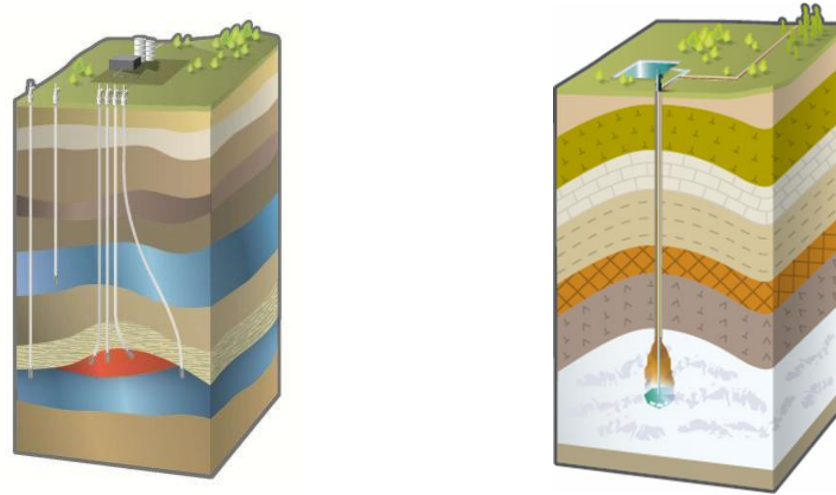
- Sulfate-reduction: formation of hydrogen sulfide (H<sub>2</sub>S) from sulfates (SO<sub>4</sub><sup>-2</sup>)



- These reactions occur only when catalyzed by microbial activity
  - Importance of methanogenic and sulfate-reducing bacteria
- Precipitation/dissolution of minerals (calcite, dolomite, anhydrite, pyrite...)



# Role of bacteria and environmental factors favorable for their activity



Depleted reservoirs and deep aquifers	Salt caverns
$\sim 20^{\circ}\text{C} < T < 120^{\circ}\text{C}$	$\sim 20^{\circ}\text{C} < T < 50^{\circ}\text{C}$
0.1 g/L < Salinity < 150 g/L (sometimes more)	Up to saturation in the sump (360 g/kgw)
Methanogens and SRB	Halophile SRB
<i>Low knowledge on microbial activity during H<sub>2</sub> storage</i>	

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**Modelling approach to  
simulate H<sub>2</sub> reactivity**

# Different ways to consider the aqueous redox reactions induced by H<sub>2</sub>

## Aqueous Thermodynamic equilibrium

- Most stable species according to thermodynamics is predominant
- Complete reduction of HCO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>-2</sup> by H<sub>2</sub>

## Inert H<sub>2</sub> under abiotic conditions

- Without microbial catalysis, reduction of HCO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>-2</sup> is negligible over UGS timescale

## Microbial activity governing kinetics of redox reactions

- Monod equation describing reduction rate of HCO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>-2</sup> by microbial activity

$$-\frac{dS}{dt} = K_{max} \frac{S}{(K_S + S)} X$$

- Gibbs energy threshold constraint also considered
- Uncertainties on rates of microbial activity

- Kinetic control of dissolution and precipitation of minerals
- Minerals reactive to H<sub>2</sub>:
  - Calcite, dolomite, siderite
  - Hematite, goethite
  - Pyrite → Pyrrhotite
  - Anhydrite, gypsum
  - Fe(3) bearing clays and micas



- PHREEQC: geochemical calculation code for gas/water/rock equilibrium and kinetic interactions in 0D and simple 1D geometry
- CMG STARS: 3 phases (water/gas/oil) compositional reservoir model in 3D geometry dedicated to fluid recuperation (thermal and EOR processes). Includes the option of geochemical reactions and user-defined additional reactions

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**Model of H<sub>2</sub> reactivity in 0D**

**Case-study of Lobodice gas storage**

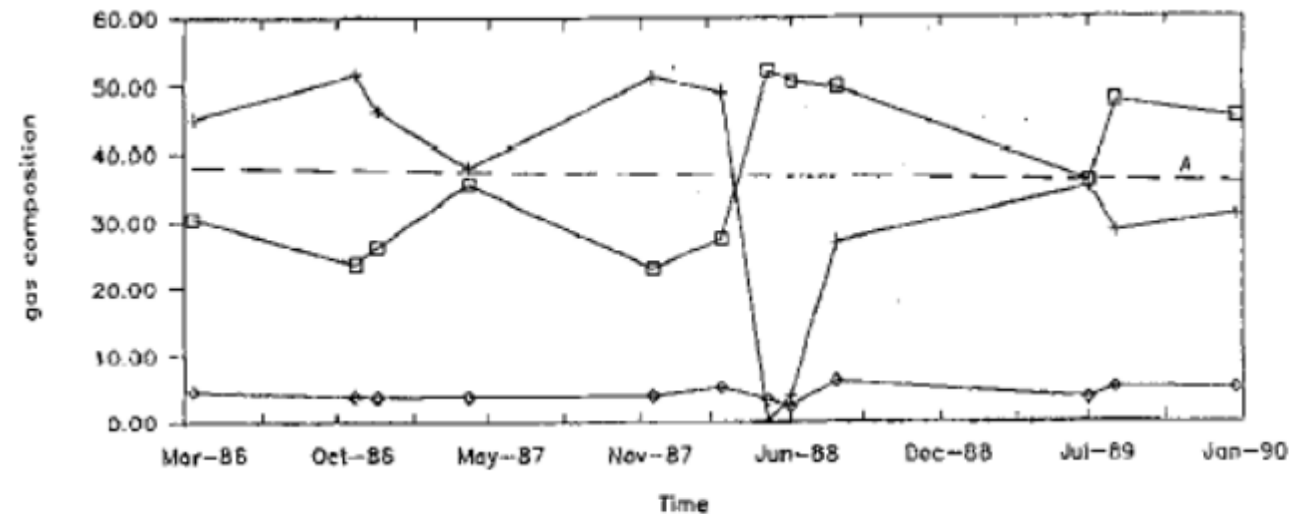
# Town gas storage of Lobodice (Czech Republic)

- Town gas storage until its conversion to natural gas storage (1991-92)
- Consumption of H<sub>2</sub> and CO<sub>2</sub> and formation of CH<sub>4</sub>

Chemical composition \* of town gas before (Input) and after storage (Output) for 7 months in the underground reservoir

Component	Input (vol %)	Output (vol %)
CH <sub>4</sub>	21.90	40.00
C <sub>2</sub> H <sub>4</sub>	0.05	0.01
C <sub>2</sub> H <sub>6</sub>	0.36	0.52
C <sub>3</sub> -hydrocarbons	0.08	0.16
C <sub>4</sub> -hydrocarbons	0.01	0.02
CO	9.00	3.30
CO <sub>2</sub>	11.67	8.78
N <sub>2</sub>	2.50	8.60
H <sub>2</sub>	54.00	37.00

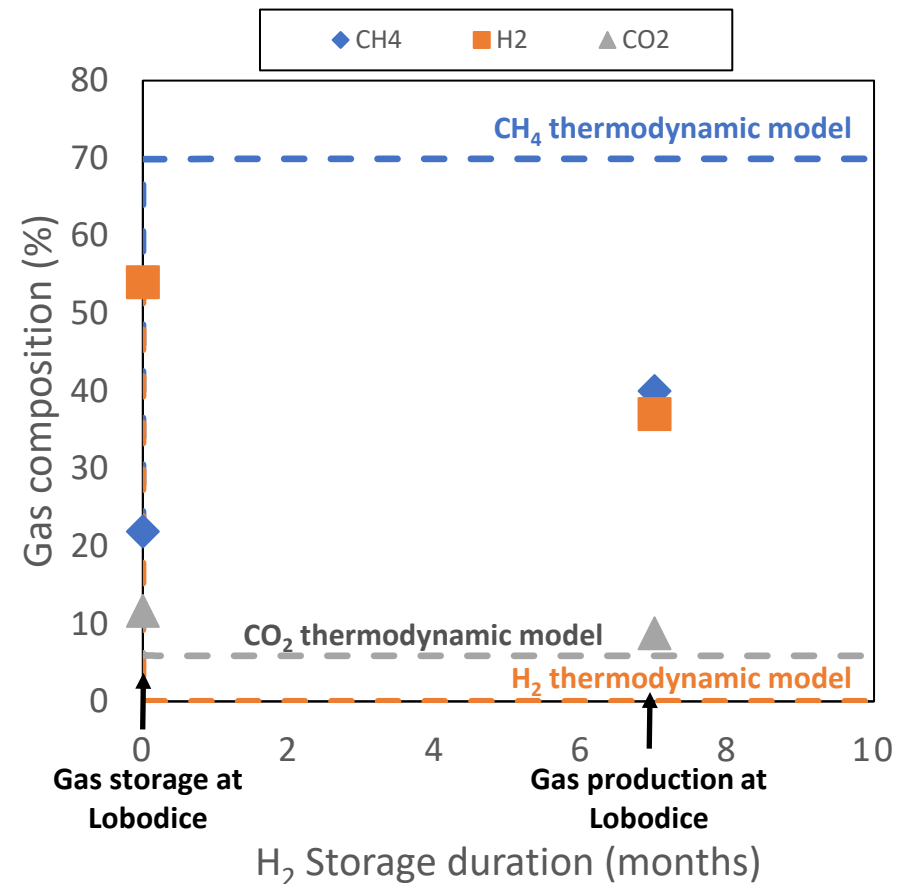
\* The data were kindly provided by the analytical laboratory of the Reservoir Gasworks at Lobodice.



**Figure 3** Chemical and isotopic composition measured at well 44: +, H<sub>2</sub> (vol.%); □, CH<sub>4</sub> (vol.%); ◇, CH<sub>4</sub>/N<sub>2</sub> ratio; △, δ<sup>13</sup>C<sub>CH<sub>4</sub></sub>; ×, δ<sup>13</sup>C<sub>CO<sub>2</sub></sub>; ▽, δ<sup>13</sup>C<sub>CO</sub>

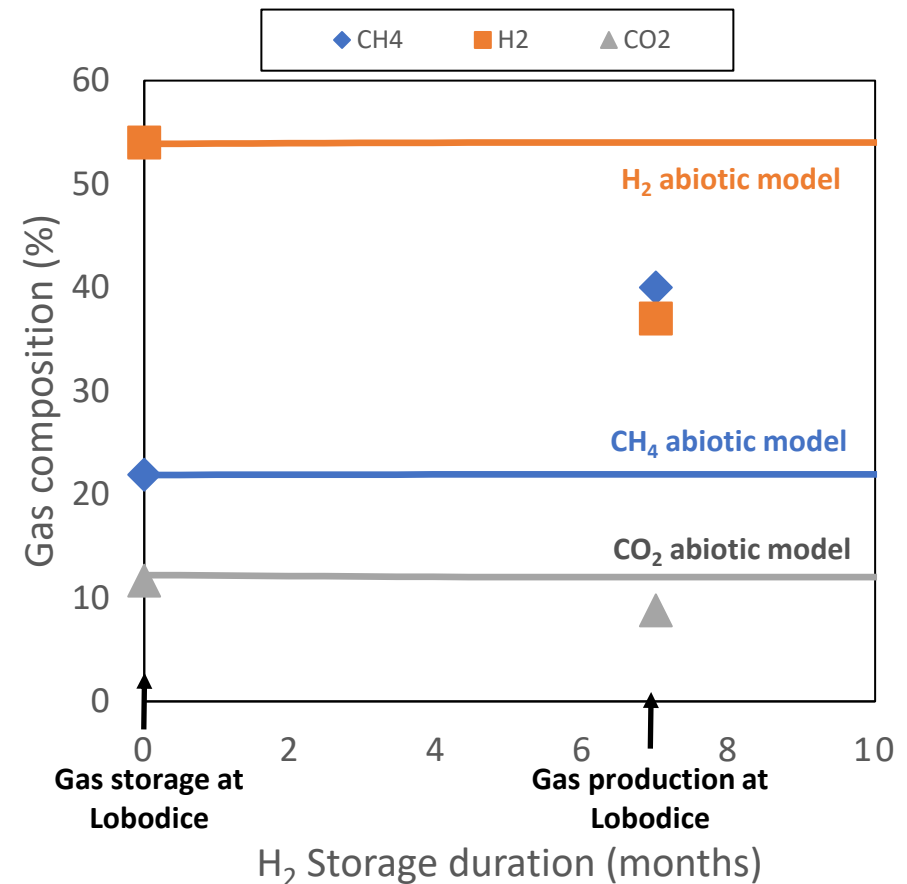
# Model: thermodynamic equilibrium in solution

- Exaggerated reactivity
- All H<sub>2</sub> is consumed during the first time step
- H<sub>2</sub>S ≈ 1.5 % after 7 months



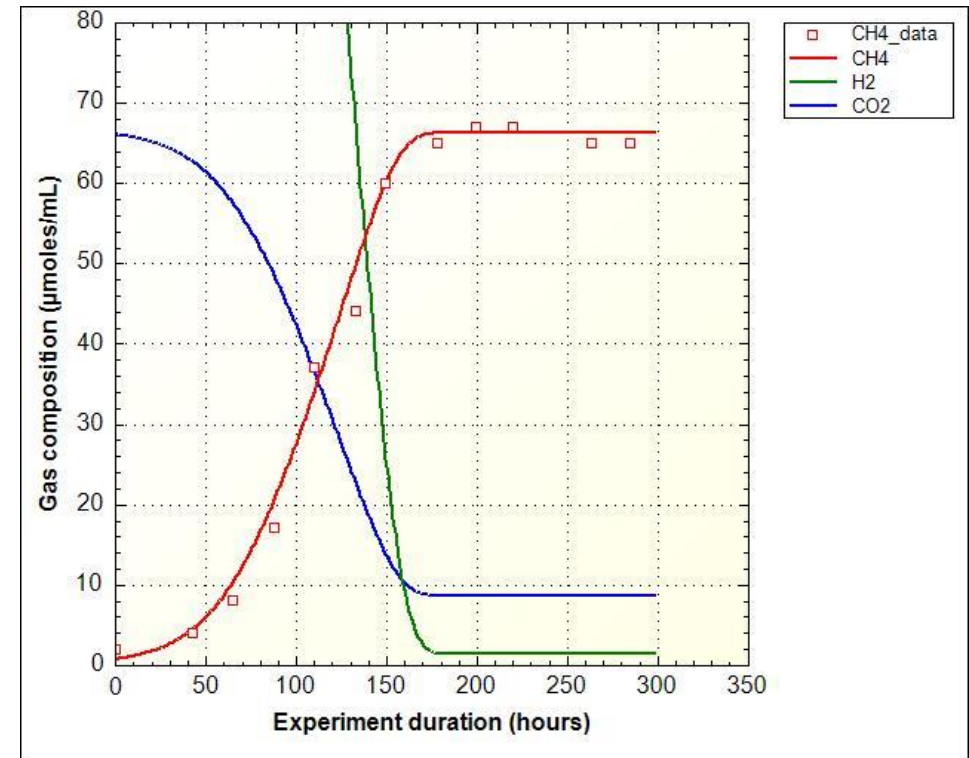
# Model: abiotic conditions with H<sub>2</sub> considered as inert

- No reactivity
- Mineral reactions alone are minor
- Is also not able to reproduce gas composition evolution



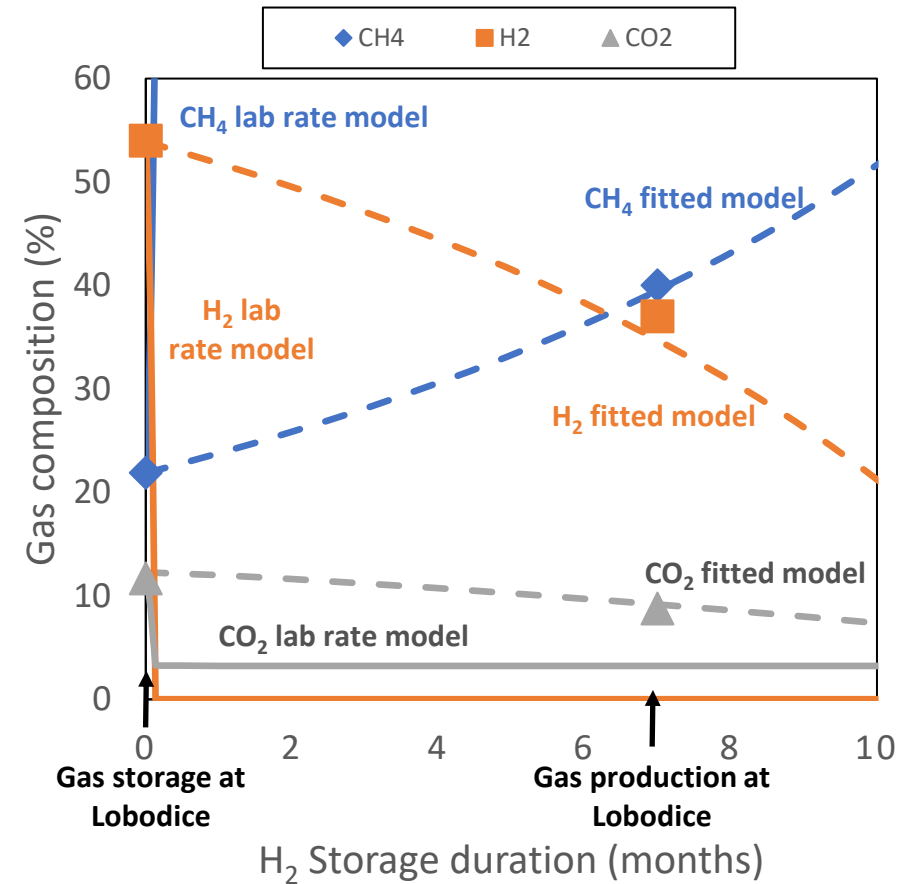
# Model: microbial kinetics of aqueous redox reactions

- Calibration of kinetic parameters on an experiment of H<sub>2</sub> consumption by the microbial consortium sample in Lobodice reservoir (*Smigan et al., 1990*)



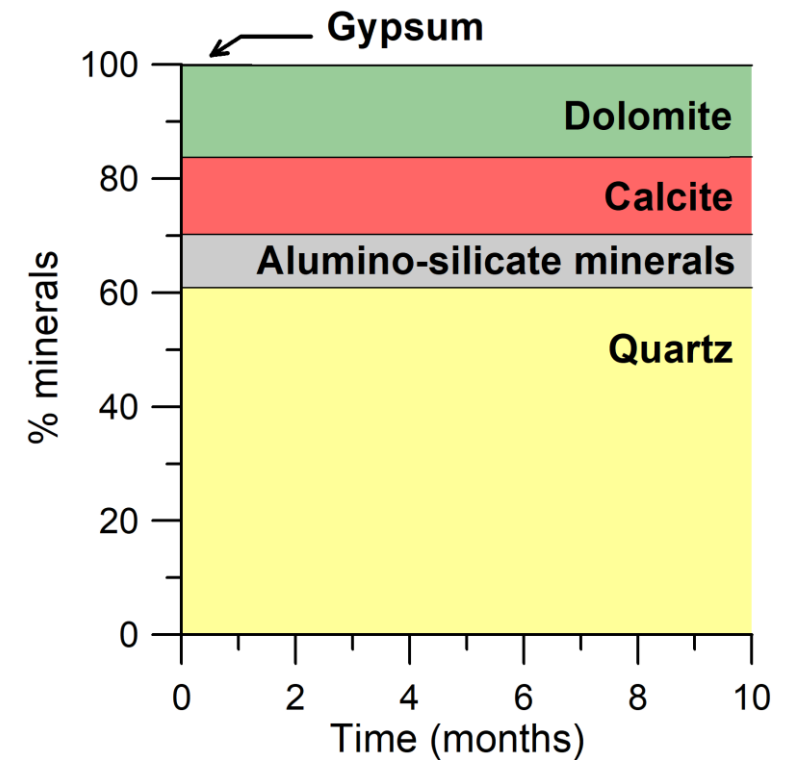
# Model: microbial kinetics of aqueous redox reactions

- Reactivity is too fast using the kinetic parameters determined from the laboratory experiment
- Gas composition evolution can be reproduced using the microbial kinetic model
- It is necessary to adjust the kinetic parameters (methanogenesis rate divided by 50)
- $H_2S \approx 100 - 1000$  ppm after 7 months



# Simulated mineralogical evolution

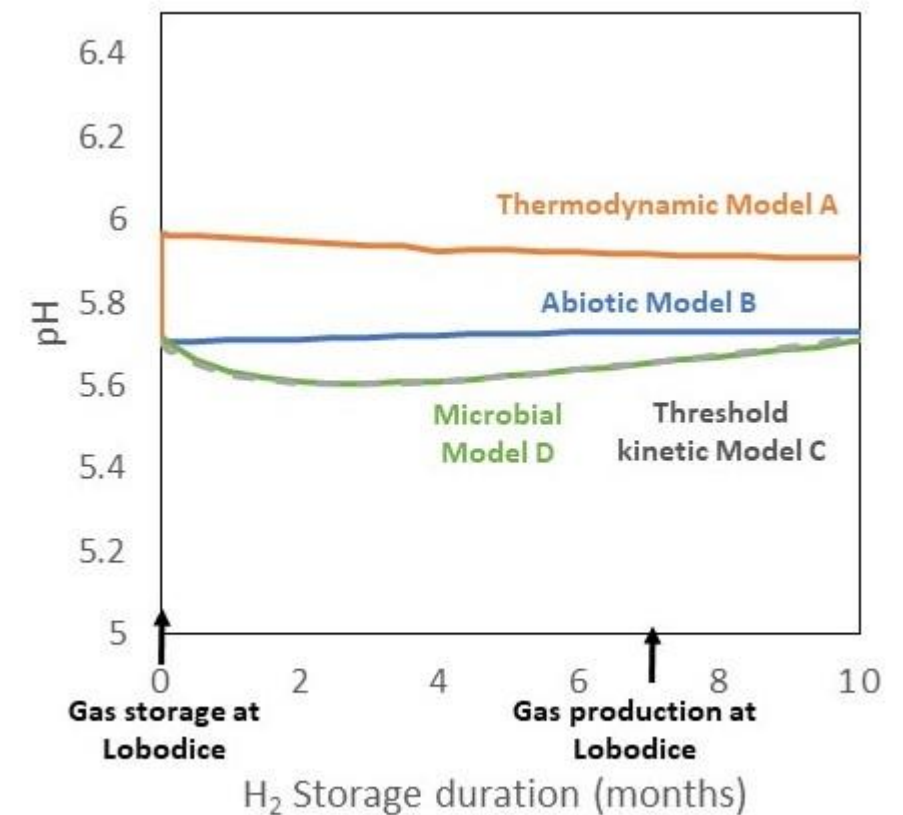
- Similar evolution when using the different models
- Main simulated reaction is a progressive dissolution of gypsum (0.1% in 7 months)
- Carbonate minerals participate in pH buffering





# pH evolution

- Efficient buffering by carbonate minerals
- pH tends to increase with dissociation of  $H_2$  in water
- pH tends to decrease with  $H_2S$  production



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3D reservoir model including  
H<sub>2</sub> reactivity

# 4. Modelling a high pressure experiment

- Monod Kinetic rates obtained by reproducing a high pressure H<sub>2</sub> consumption experiment on an UGS formation water
- Experiments by MicroPro (D3.2 and D3.4)
- For methanogenesis

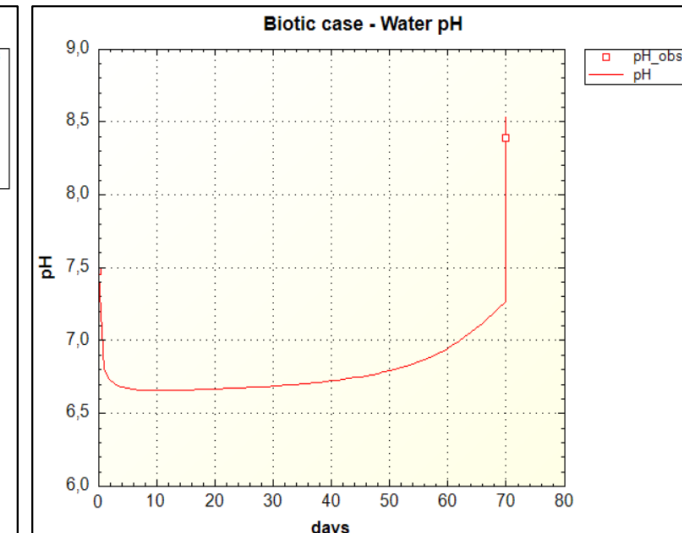
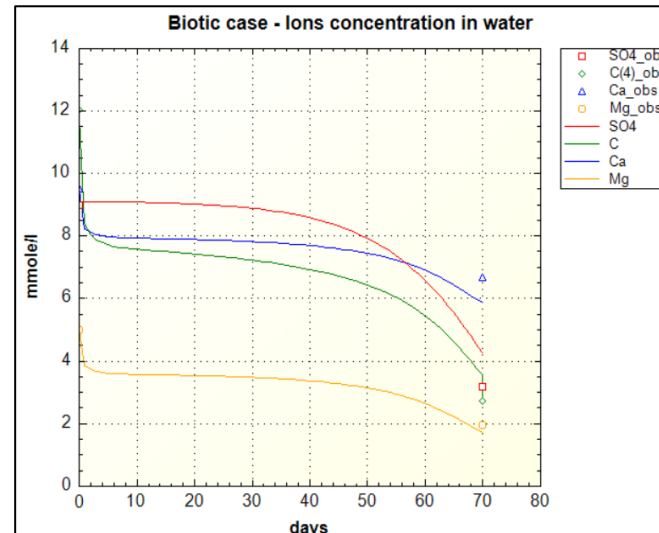
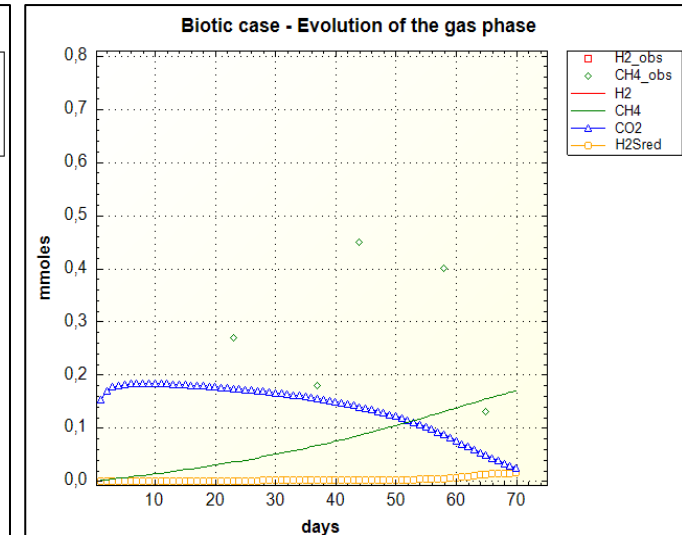
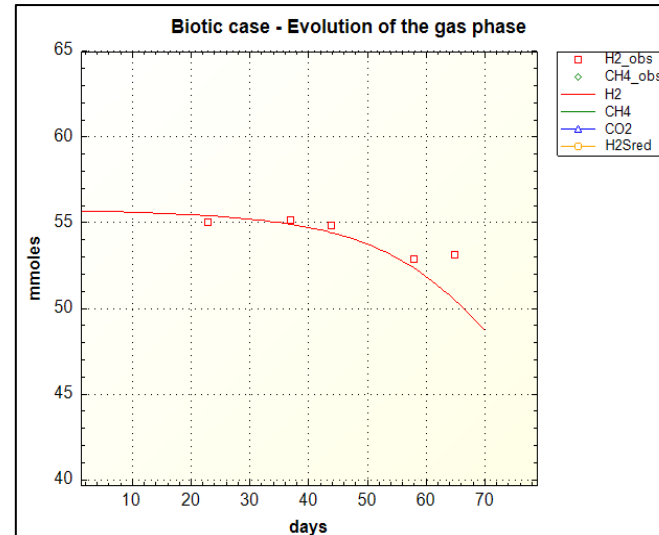
$$\frac{d HCO_3^-}{d t} = K_{max} [X] \left( \frac{[HCO_3^-]}{K_{S HCO_3^-} + [HCO_3^-]} \right) \left( \frac{[H_2]}{K_{S H_2} + [H_2]} \right)$$

$$\frac{d X}{d t} = -Y \frac{d HCO_3^-}{d t} - D[X]$$

- For sulphate reduction

$$\frac{d SO_4^{2-}}{d t} = K_{max} [X_{sr}] \left( \frac{[SO_4^{2-}]}{K_{S SO_4^{2-}} + [SO_4^{2-}]} \right) \left( \frac{[H_2]}{K_{S H_2} + [H_2]} \right)$$

$$\frac{d X_{sr}}{d t} = -Y_{sr} \frac{d SO_4^-}{d t} - D_{sr} [X_{sr}]$$



# 4. Modelling approximation

It is currently not possible to model double-Monod-type reactions with CMG-STARs. The reaction rates need to be approximated to follow CMG-STARs modeling framework.

## Monod

## CMG-STARs

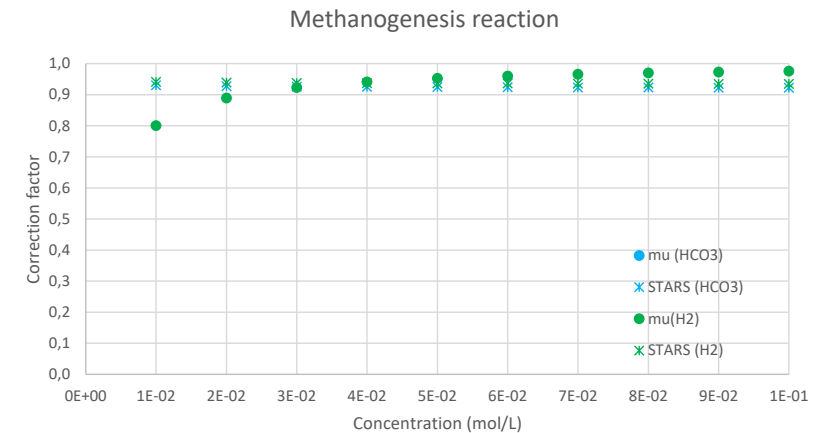
$$K = K_{max} \frac{[Substrate][bacteria]}{[bacteria] + [Substrate]}$$

$$K = K_{max} \frac{1}{(1+a[H_2])^b} [bacteria][Substrate]$$

Where (a, b) parameters are tuned to the laboratory experiment modeling with PHREEQC

## Methanogenesis

$$\frac{d HCO_3^-}{d t} = K_{max} [X] \underbrace{\left( \frac{[HCO_3^-]}{K_{SHCO_3^-} + [HCO_3^-]} \right)}_{\mu_{HCO_3^-}} \underbrace{\left( \frac{[H_2]}{K_{SH_2} + [H_2]} \right)}_{\mu_{H_2}}$$



CMG-STARs formalism tends to predict faster reaction than Monod kinetics at low concentrations but converges toward Monod rate as concentration increases

# 4. Upscaling from lab to storage conditions

Experiment



Volume =  $1.5 \cdot 10^{-3} \text{ m}^3$

Rock / Fluid ratio = 11 / 89

**Optimal growth conditions**

grid block scale

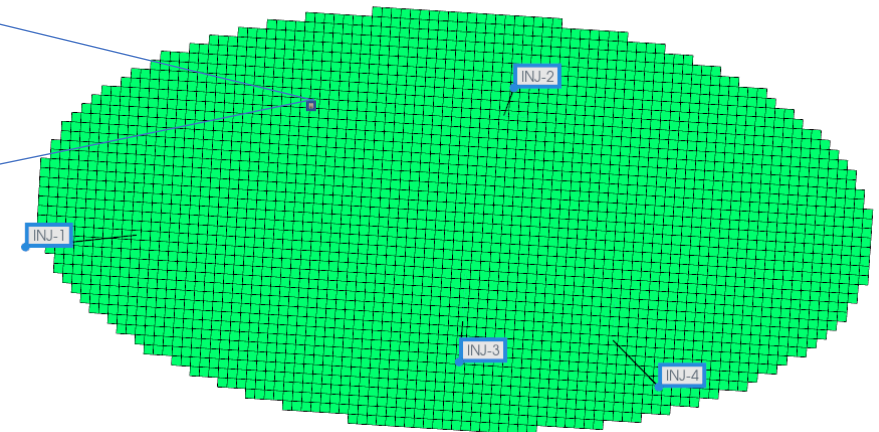


$50 \cdot 50 \cdot 10 = 25 \cdot 10^3 \text{ m}^3$

80 / 20 if porosity = 20%

**Starving conditions**

Storage scale



$\sim 370 \cdot 10^6 \text{ m}^3$

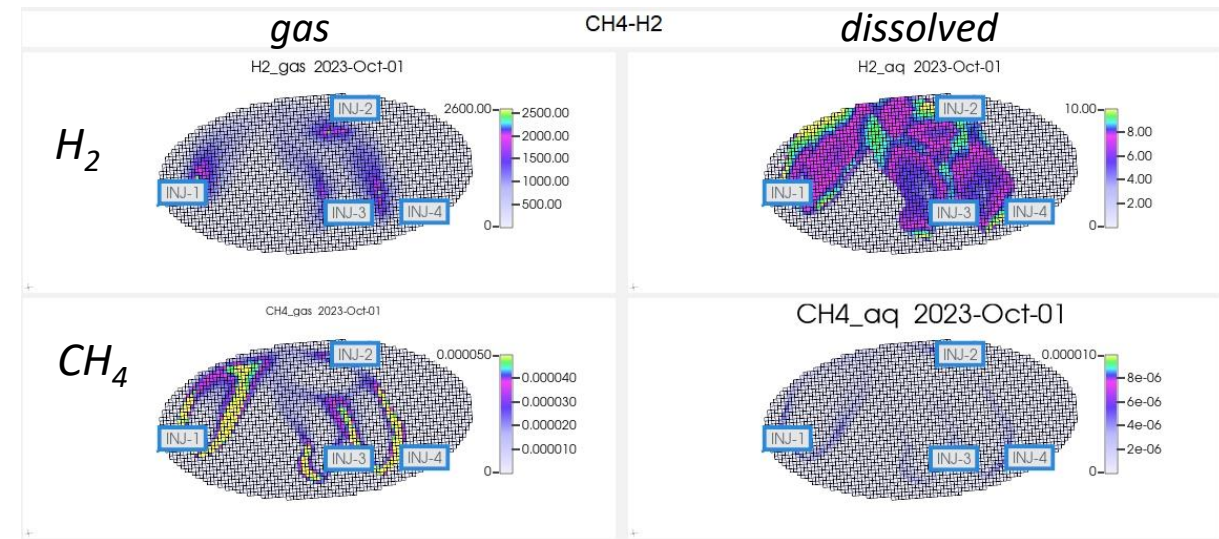
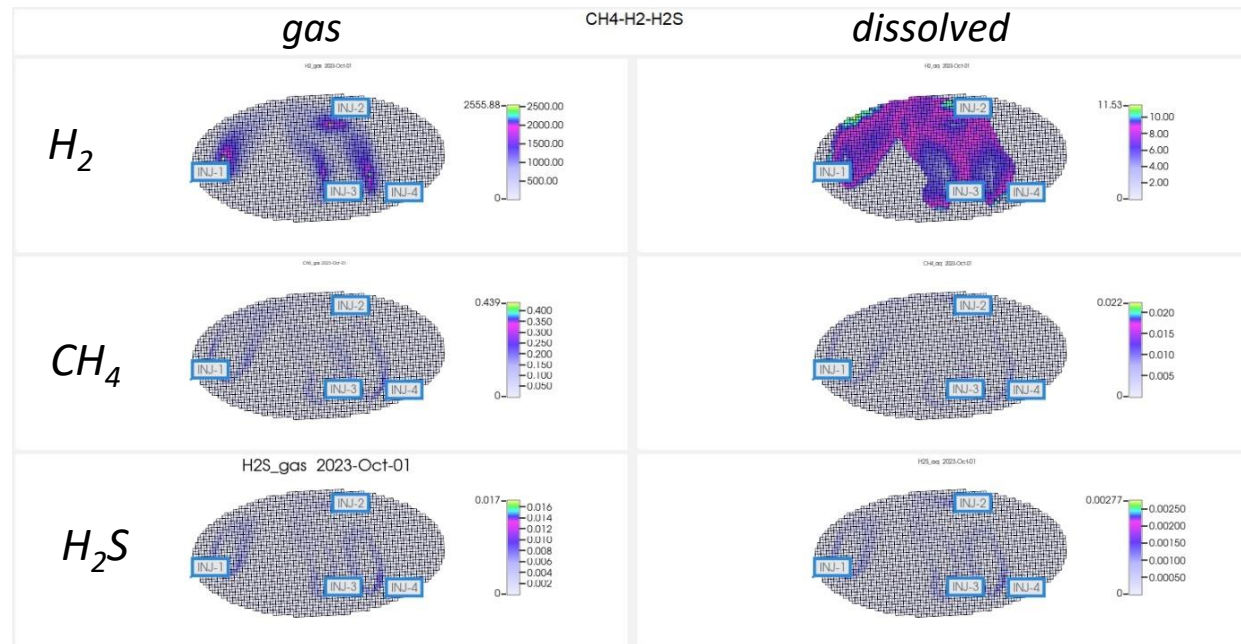
Upscaling factor to damp the reactivity between laboratory and storage conditions

# 4. 3D MODELLING

Results with laboratory scale reactivity

Results with upscaled reactivity

After the fifth cycle

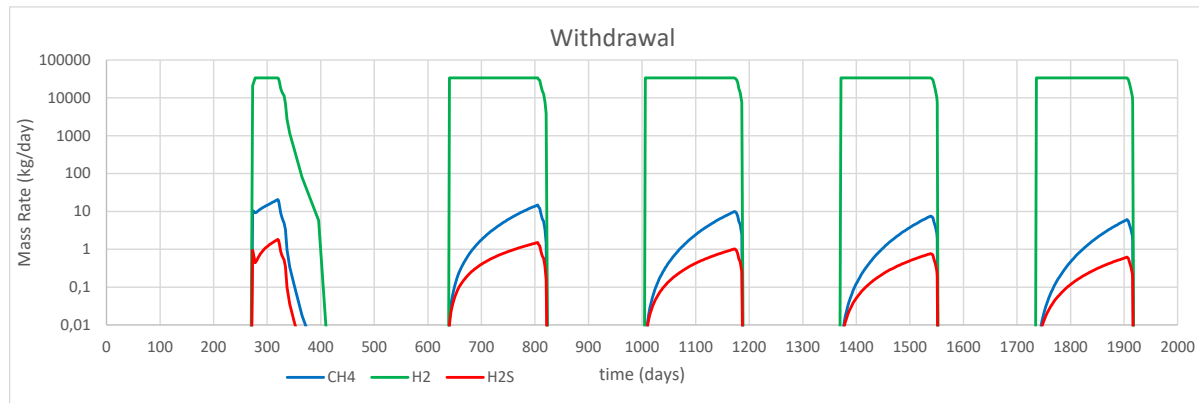


$CH_4$  or  $H_2S$  generation occurs at the edge of  $H_2$  front where  $H_2$  meets fresh brine

# 4. 3D MODELLING

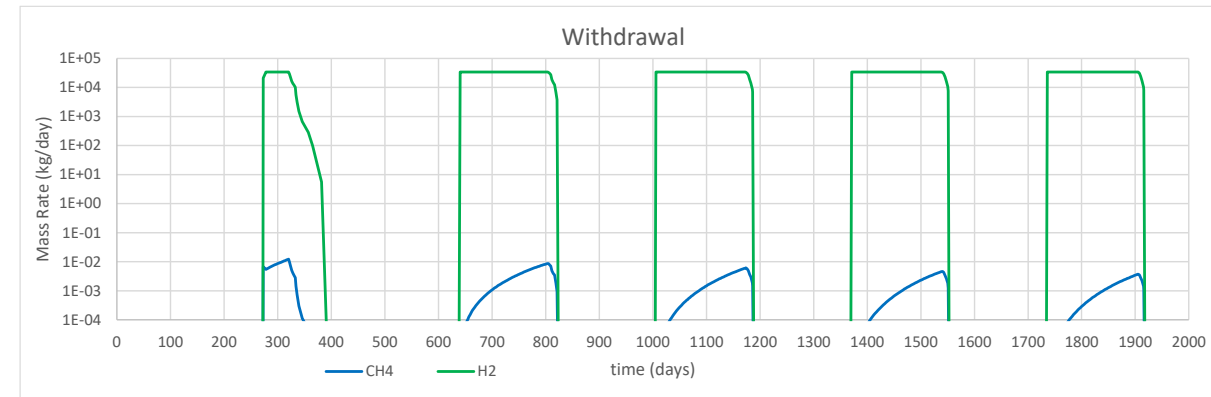
Results obtained for salinity 15 g/l and only 5 mg/l of  $\text{SO}_4^{2-}$

### Results with laboratory scale reactivity



Apparition of methane and  $\text{H}_2\text{S}$  in the withdrawn gas  
Methane max : 0.06 %  
 $\text{H}_2\text{S}$  max : 54 ppm

### Results with upscaled reactivity



Apparition of methane but no detection of  $\text{H}_2\text{S}$  in the withdrawn gas  
Methane max : 0.4 ppm  
 $\text{H}_2\text{S}$  max : 0 ppm

Reactivity is the highest during the first cycle, then it decreases

**Results highly dependant on upscaling factor...**

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# Conclusions



# Synthesis

- Reactive model in 0D to simulate laboratory experiments and for a first evaluation of the H<sub>2</sub> reactivity in a storage
- 3D reactive transport model to consider the storage/withdrawal cycles and to predict the reactivity at the reservoir scale
- Helpful in the evaluation of the risks due to reactivity in a H<sub>2</sub> storage and the associated costs (gas treatment, loss of H<sub>2</sub>...)

## Perspectives

- Models need to be calibrated on reservoir data
- Uncertainties on microbial kinetics and on the lab-to-field scaling factor
- Needs to better constrain the influence of environmental factors on microbial activity

# Find more details

Tremosa J, Jakobsen R and Le Gallo Y (2023),  
Assessing and modeling hydrogen reactivity in  
underground hydrogen storage: A review and  
models simulating the Lobodice town gas storage.  
*Frontiers in Energy Research* 11:1145978. doi:  
[10.3389/fenrg.2023.1145978](https://doi.org/10.3389/fenrg.2023.1145978)

Hystories public deliverables:

- D 2.4 on hydrogen reactivity
- D 3.3 on microbial modelling



#### OPEN ACCESS

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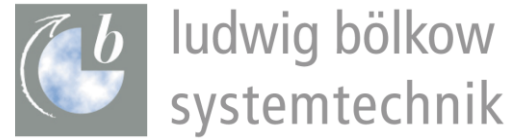
## Assessing and modeling hydrogen reactivity in underground hydrogen storage: A review and models simulating the Lobodice town gas storage

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Underground Hydrogen storage (UHS) is a promising technology for safe storage of large quantities of hydrogen, in daily to seasonal cycles depending on the consumption requirements. The development of UHS requires anticipating hydrogen behavior to prevent any unexpected economic or environmental

# Hystories project consortium



Mineral and Energy  
Economy Research  
Institute  
Polish Academy of Sciences

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**Thank you !**

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