

Panel Discussion : Impacts of microbiological activity in underground storages

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Acknowledgment



Clean Hydrogen Partnership

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Outline

Anne-Catherine Ahn - Wageningen University



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Technical Challenges



Microbial H₂ conversions: Background and HyUSPRe experimental results

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 Shell Global Solutions International B.V., The Netherlands







Acknowledgment



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H₂ team at WUR





HyUSPre: H₂ underground storage in porous reservoirs





Microbial life in the subsurface



- Subsurface environment harbors extreme conditions:
 - High temperature, pressure and salinity
 - Limited nutrients and energy source
 - Limited pore sizes
- Deep biosphere composes 2-19% of the Earth's total biomass
- Microbial cell number & diversity
 - Cell numbers between 8.65×10⁴ 1.01×10⁶/g rock
 - Decreases over the depth
 - Depends on environmental conditions
- Life is possible until at least a depth of 5000 m
- Most microorganisms are in dormant state



Microbial impact on subsurface H₂ storage

- H₂ is an important, easy & high energy source in subsurface where e- donors are scarce
- Potential impact of microbes in H₂ storage:
 - Loss of the stored H₂ through metabolic processes
 - Formation of contaminating products, such as H₂S and CH₄
 - Microbial-influenced corrosion (MIC)
 - Loss of H₂ injectivity due to bio-based solids (biomass, FeS, etc.)

Knowledge gaps:

- Microbial taxa which are relevant for potential UHS sites
- Microbial kinetics at high partial H₂ pressures and its dependency on T, P, salinity and pH





Aim of the WP3 in HyUSPre



Microbial community analysis of target UHS sites

https://www.hyuspre.eu/index.php/downloads/

• Determination of window of viability:



Aim of the WP3 in HyUSPre



• Microbial community analysis of target UHS sites



Case studies: Incubations at specific site's condition of formation water

Sampling & relevance of environmental samples

- Partners provided environmental brine samples:
- -29 porous reservoir samples from 4 partners
- -2 salt cavern samples from 2 partners
- \rightarrow Including potential UHS target sites and actual UHS pilots
- \rightarrow Ability to use environmental microbial communities for experiments









After 6 months H₂ storage test phase, liquid and filter samples, and cores were retrieved

Plan:

-Incubations at different temperatures at low pressure and at the site's conditions at high pressure

-Microbial community analysis of filter and core samples





Current state of knowledge for microbial survivability limits under subsurface H₂ storage conditions:

Parameters	Microbial optimum & limit	Methanogens	Sulfate reducers	Acetogens	- Q	 ▲ Methanogens ■ Homoaceteogens ○ SSRM
Tomporaturo	Ontimum	15,0890	10 10690	20, 20%	4 -	~
remperature	Optimum	15-98°C	10-100°C	20-30°C		
(H_2 storage: 22.5-100°C)	Limits	122°C	113°C	72°C	Ω	° 🗳
Pressure (H ₂ storage: 1-50 MPa)	Optimum		0-30/50 MPa		Critcal NaCl (2 3	o o o o o o o o o o o o o o o o o o o
Salinity	Optimum	0-0.77 M NaCl	0-0.4 M NaCl	0-0.4 M NaCl	U	¢¤°°°° ° م∧° ∧ .
(H ₂ storage: 0-5 M NaCl)	Limits	3.4 M NaCl	4.2 M NaCl	4.4 M NaCl		
рН	Optimum Limits	4-10	9.5	NA 3.6-10.7		
		. 10	1 10	0.0 10.7	0	20 40 60 80 100 120 Critical temperature (° C)

(Thaysen et al., 2021, doi: 0.1016/j.rser.2021.111481)

- Temperature and salinity are the most constraining factors
 - Temperature alone: upper life limit is 122°C
 - Combination of temperature and salinity: >55°C, and >1.7 M NaCl

Window of viability: Incubations



• Environmental samples with 80%H₂/20%CO₂ at 1.7 bar, different temperatures and media

	Sample	T (°C)	P (bar)	рΗ	Conductivity (mS/cm)	Medium	35°C	50°C	65°C	80°C		
\$			45	7.72	49.24	Sample amended with nutrients/trace	Acetogen	Methanogen	Methanogen			
	А	51				Mineral medium (MM)	Methanogen	Methanogen	Methanogen			
						MM with 0.5 M Na ⁺ + 3mM SO_4^{2-}	SO ₄ ²⁻ reducer	SO ₄ ²⁻ reducer				
					79.74	Sample amended with nutrients/trace	Methanogen					
oir	В	51	87	5.95		Mineral medium (MM)	Methanogen	Acetoaen				
SLV(MM with 0.5 M Na+ + 3mM SO ₄ 2-	Methanogen + SO ₄ ²⁻ reducer	SO ₄ ²⁻ reducer			4	
averns Porous rese	C	72 107	97-206	ND	ND	Sample amended with nutrients/trace	Acetogen	Methanogen	Methanogen		СН	
	C	72-107				MM with 0.5 M Na+ + 3mM SO ₄ 2-	SO ₄ ²⁻ reducer + Acetogen	Methanogen	Methanogen			
	D	20.41	56	ND	ND	Sample amended with nutrients/trace	Methanogen	Methanogen				
	D	59-41				MM with 0.5 M Na ⁺ + 3mM SO_4^{2-}	Methanogen	SO ₄ ²⁻ reducer	SO ₄ ²⁻ reducer			
	Б	E 109	50 150	150 5.2	217	Sample amended with nutrients/trace		SO ₄ ²⁻ reducer			N	
		109	00-100	5.2	217	MM with 0.5 M Na+		SO ₄ ²⁻ reducer	SO ₄ ²⁻ reducer			
	- F 103 5	103	50-150	5.2	211	Sample amended with nutrients/trace						
		105 50-150 5.5	5.5	211	MM with 0.5 M Na+		SO ₄ ²⁻ reducer	SO ₄ ²⁻ reducer	SO ₄ ²⁻ reducer			
						Sample amended with nutrients/trace	SO ₄ ²⁻ reducer	SO ₄ ²- reducer + Acetogen				
	G	45	80-200	6.3	240	MM with 0.5 M Na ⁺			SO ₄ ²⁻ reducer		/	
						MM with 2 M Na+						
ö						Sample amended with nutrients/trace						
alt	Н	20-80	40-275	6.9	219	MM with 0.5 M Na+						
Ň						MM with 2 M Na⁺						



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Window of viability: Incubations



• Environmental samples with 100% H₂ at 1.7 bar and different temperatures:

ervoirs	Sample	T (°C)	P (bar)	рΗ	Conductivity (mS/cm)	35°C	50°C	65°C	80°C
res	А	51	45	7.72	49.24	Methanogen	Methanogen	Methanogen	
SUC	В	51	87	5.95	79.74				
Porc	С	72-107	97-206	ND	ND	Methanogen	Methanogen	Methanogen	Methanogen
s _	D	39-41	56	ND	ND		SO ₄ ²⁻ reducer	SO ₄ ²⁻ reducer	
ern	G	45	80-200	6.3	240		SO ₄ ²⁻ reducer		
Cav	Н	20-80	40-275	6.9	219				
Salt				N		00			





Window of viability: Incubations



• "Master mix" incubation

Medium	35°C	50°C	65°C	80°C
MM with 0.5 M Na+ + 3mM SO ₄ ²⁻	Methanogen + SO₄ ²⁻ reducer	Methanogen + SO ₄ ²⁻ reducer	Methanogen	
MM with 2 M Na+ + 3mM SO ₄ ²⁻	Methanogen + SO ₄ ²⁻ reducer	Methanogen + SO ₄ ²⁻ reducer	SO ₄ ²⁻ reducer	





 \rightarrow 16S rRNA: Peptococcaceae (amongst others)

Redefines the currently known window of viability to the combination of at least >65°C, and >2 M NaCl

Determination of microbial kinetics



- High pressure & temperature reactors:
- In-house systems:
- 3 reactors
- 0.6 L
- 70 Bar (56 Bar op)
- pH/P/°T monitor
- °T (max 350 °C)
- SS 316
- Lining



- Newly arrived systems:
- 4 reactors
- 0.5 L
- 250 Bar (200 Bar op)
- P/°T monitor
- °T (max 350 °C)
- SS 316
- Lining and coating



Conclusions and outlook



- Window of viability
- Limits in incubations so far:

Acetogenesis: 50 °C Sulfate reduction: 80 °C Methanogenesis: 80 °C

- Sulfate reduction could take place when sulfate was added/present
- Window of viability shifted to at least the combination of 65° C and 2 M NaCl
- Determination of kinetic data
- Design and installation of HP/HT reactors
- Determine kinetics of microbial growth & activity
 Implement results into DuMuX model (TU Clausthal)
 Predict overall performance of H₂ storage in porous reservoirs







WUR:

- H₂ team: Adrian Hidalgo-Ulloa, Yehor Pererva, Ton van Gelder, Bart Lomans, Diana Sousa
- Microbial Physiology and Molecular Ecology groups at Microbiology

Industrial and project partners:



/Stock



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oreReact



Thank you for your attention!

Questions?

Hydrogen H2

zero emission









Injection of new gases (H_2 and O_2) in UGS in deep aquifers

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Injection of H_2 (Power-to-gas) and O_2 (biomethane) in the natural gas network

Expected arrival of these gases in the UGS

Is there a risk to the storage facilities ?



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3

How do indigenous microbial communities respond ?



Is there an effect on the quality of the stored gas ?



Recreating the UGS in situ conditions in a laboratory reactor

Recreating the UGS in situ conditions in a laboratory reactor





 \rightarrow RINGS reactor can work up to 150°C and 150 bars

 \rightarrow Downhole water (containing microorganisms) and rock phases are sampled in the real UGS

 \rightarrow The initial gas phase is composed of CH₄ (99%), CO₂ (1%) and traces of monoaromatic hydrocarbons (benzene and toluene).

 \rightarrow Deformable reactor (Piston to compensate for the pressure drop)



Formation water sampling

Formation water sampling





- \rightarrow Sampling of the formation water (- 580m to 1200m)
- $\rightarrow\,$ Guarantee the non contamination of the microbial community
- \rightarrow Control the pressure / depressurization



TYPE Original Research PUBLISHED 04 January 2023 DOI 10.3389/fmicb.2022.1012400



A deep continental aquifer downhole sampler for microbiological studies

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Three aquifers tested for the injection of H_2

B

Three aquifers tested



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Microbial communities monitoring

Microbial communities monitoring





 \rightarrow A community initially dominated by fermenters and sulfate-reducers

 \rightarrow The Ammonificaceae family includes sulfate-reducers

 \rightarrow Formate production (assumed by (homo)-acetogens)

 \rightarrow Methanogenesis does not necessarily take place

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+ Comparative study of three H₂ geological storages in deep aquifers simulated in high pressure reactor (in process)



An aquifer tested for O₂ injection (1% & 100 ppm)

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An aquifer tested for 1% O₂ injection (=10 000 ppm) → changes observed on the water





Sulfate evolution



- \rightarrow sulfate was consumed by sulfate-reducers
- \rightarrow O₂ injection stopped the sulfate consumption (death or inhibition of sulfate-reducers)
- \rightarrow Acetate is produced from micro-organisms at the beginning of the experiment

An aquifer tested for 1% O₂ injection (=10 000 ppm) → changes observed on the water





- \rightarrow Decrease of toluene before O₂ injection
- \rightarrow 1% O₂ injection stopped the toluene disappearance



An aquifer tested for 1% O₂ injection (=10 000 ppm) → changes observed on the microbial community



→ Negative effect of the 1% O_2 injection on the microbial community = hyperoxic conditions = toxicity

storengy Terega

Science of The Total Environment Volume 806, Part 3, 1 February 2022, 150690



Biological, geological and chemical effects of oxygen injection in underground gas storage aquifers in the setting of biomethane deployment

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An aquifer tested for 100 ppm O₂ injection → changes observed on the microbial community

storengy 💮 terēga

hystories Hydrogen Storage in European Subsurface

Physicochemical and microbiological effects of geological biomethane storage in deep aquifers: introduction of O_2 as a cocontaminant (submitted)

Thank you !





Reactive transport modelling for underground gas storage

Irina SIN

Mines Paris - PSL, France



Acknowledgment



Clean Hydrogen Partnership

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Outline

Reactive transport

Phase equilibria

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Gas storage: oxygen reactivity

Extension to other gases



Reactive transport



HYTEC

Flow

(Un)saturated, multiphase Non-isothermal Double porosity Anisotropy

Transport

Aqueous and gaseous Advection, diffusion, dispersion Particle transport

Thermodynamics

Phase equilibria, EOS Non-ideal gas, solution Multicomponent mixtures Thermodynamic properties

Biogeochemistry

Acid/base, redox Precipitation, dissolution Microbiological reactions Isotopic fractionation

Mechanics

- **HYTEC=T**hermo+**H**ydro+**C**hemistry
- **CHESS** geochemical core of HYTEC
- (Un)structured mesh
- History matching
- Coupling with mechanics
- Water balance
- Variable porosity
- Chemical and mechanical clogging

References

- van der Lee et al., Comp & Geos, 2003
- Sin, Lagneau and Corvisier, Adv. in Water Res, 2017
- Seigneur et al., Adv. in Water Res, 2018

Reactive transport code HYTEC since 1996







Phase equilibria

Phase equilibria



Assymetric approach

$$f_i^g = Py_i \varphi_i = K_i^H \gamma_i x_i = f_i^l$$

▶ φ is the fugacity coefficient calculated by EOS models: e.g. cubic EOS – Peng-Robinson (1978)

$$P = \frac{RT}{v - b^{\mathrm{PR}}} - \frac{a^{\mathrm{PR}}(T)}{v(v + b^{\mathrm{PR}}) + b^{\mathrm{PR}}(v - b^{\mathrm{PR}})}$$

▶ K^H is the corrected Henry's constant

$$K_{i}^{H}\left(T,P\right) = K_{g}^{H,0}\left(T,P^{sat}\right)\exp\left[\frac{\left(P-P^{sat}\right)V_{i}^{\infty}}{RT}\right]$$

▶ γ_i is the activity coefficient (B-dot, SIT)

$$\ln \gamma_i = -\frac{AZ_i^2 \sqrt{I}}{1 + 1.5\sqrt{I}} + \sum_j [C_j]\epsilon_{ij}$$

Advantages

- ▶ Activity models adapted for aqueous geochemistry.
- K^H , BIP and EOS parameters adapted to non-ideal gases regarding P and T.
- ▶ Analytical solution for the PR-type EOS models.
- ► Group contribution structure, easy application for mixtures. Required data
 - φ : critical temperatures and pressures T_c, P_c, Z_c, Ω , mixing rule, binary interaction parameters
 - ► K^H: Henry's constants at saturated vapor pressure, molar volumes for pressure correction
 - ► γ_i : Debye-Hückel and B-dot general parameters, binary interaction parameters for solutes (SIT)
 - ▶ Experimental lab of CTP&Geosciences, Mines Paris PSL
 - ► ANR GAZ ANNEXES, SIGARRR, FLUIDSTORY

Phase equilibria



Solubility of H2 in water and NaCl-brine

Solubility/reactivity of CO₂ in water and NaCl-brine



FluidSTORY project, Chabab et al., 2019, Sin and Corvisier 2019



Gas storage: oxygen reactivity

B

Air injection into a sandstone reservoir (the Paris Basin) **Construction**



- 1) Caprock
- 2) Reservoir
- 3) Surface facilities
- 4) Injection and withdrawal wells
- 5) Monitoring wells
- 6) Monitoring wells of the upper aquifer
- 7) Upper aquifer
- 8) Cushion gas with O2-depleted air





Air injection into a sandstone reservoir (the Paris Basin) **Construction**



▶ What are the key mechanisms? What impact on the aquifer?

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Gas-water-rock interactions



PSL 🗶

Ine société de ENGIE MINES PARIS





• What are the key mechanisms? What impact on the aquifer? storengy

Gas-water-rock interactions: batch modelling





- + Available data (borehole water sampling and gas composition before and after injection) are used to establish the model.
- + Representation of major mechanisms vs site data.
- Closed system \rightarrow production of CO₂ is overestimated.
- Reactive transport model is needed.



Radial 1D reactive transport model



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- Dissolution of pyrite/calcite \rightarrow goethite/gypsum
- ! 22% of pyrite is dissolved. Rapid O₂ consumption (same profiles at 30 d and 0.5 yr)
- ! CO_2 accumulation grows with time, > 4 mol%
- > A slower kinetics is needed

Radial 1D reactive transport model





- Slower kinetics $\rightarrow \sim 2\%$ of pyrite is dissolved.
- Slower O_2 consumption $\rightarrow O_2$ can be transported further \rightarrow pyrite oxydation not only at near-wellbore zone.
- Damköhler number is analysed, confirms the results.
- CO_2 accumulation still grows with time, ~ 3 mol%
- Radial 2D reactive transport model is needed...



Reactive transport model at reservoir scale

O₂(g)

-0

 $O_2(aq)$

-(2)

Pyrite

SO42.





- Pyrite kinetics is a key factor: Damköhler number derived for O2 reactivity and pyrite kinetics explains gas changes. +
- The multiphase reactive transport model was built based on the field data. From batch to reservoir scales. +
- Importance of reactive transport -> geometry/scale changing is game changing
- This workflow can be applied for gas storage facilities (compressed air, biomethane, H_2) +





Extension to other gases

Extension to other gases



PSL 😿 53

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• Biomethane and natural gas



• Hydrogen

- Additional complexity: microbial activity, parametrization of models.
- Modelling experiments (Haddad et al 2022 etc) with Monod like laws
- Upscaling, integrating to the storage model

HYTEC and consortium PGT





Since 2000, \mathbf{PGT}

- ► shared funding
- ► shared scientific research

► shared expertise

PGT V 2020 - 2023

Thank you !





Technical Challenges

Acknowledgment





06/06/2023



Representativeness of laboratory tests, compared to field observation



Upscaling factor to damp the reactivity between laboratory and storage conditions

Technical Challenges



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Bacteria Reactivity Assessment Risk depending on storage type / Definition of the most favorable environment for hydrogen storage

Simplified chart for the assessment of microbial risks





Mitigations solutions for environment that are less favorable

- Biocides in porous reservoirs:
- are diluted in porous storages with increasing distance from the injection well
- become ineffective if the concentration falls below the effective concentration due to dilution
- can be degraded or even serve as nutrients themselves
- do not distribute ideally in the pore space, as the liquids do not migrate evenly in the layer



Hystories project consortium















Mineral and Energy Economy Research Institute Polish Academy of Sciences

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> Clean Hydrogen Partnership



Thank for your attention !

