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# Bio-UGS – Biological conversion of carbon dioxide and hydrogen to methane

# Potential Analysis of underground Bio-Methanation

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DBI Gas- und Umwelttechnik GmbH

1st Status Conference $CO_2$-WIN

Online, 2021-06-09

# Agenda

# Background and allocation in $CO_2$-WIN

DBI

$CO_2$WIN CONNECT

Use Carbon Sustainably

**Chemical and bio-technological $CO_2$-conversion**

**Electro- und Photocatalysis**

**$CO_2$-Mineralisation**

**Bio-UGS**
Targeted biological conversion of carbon dioxide and hydrogen to methane in porous underground gas storage facilities

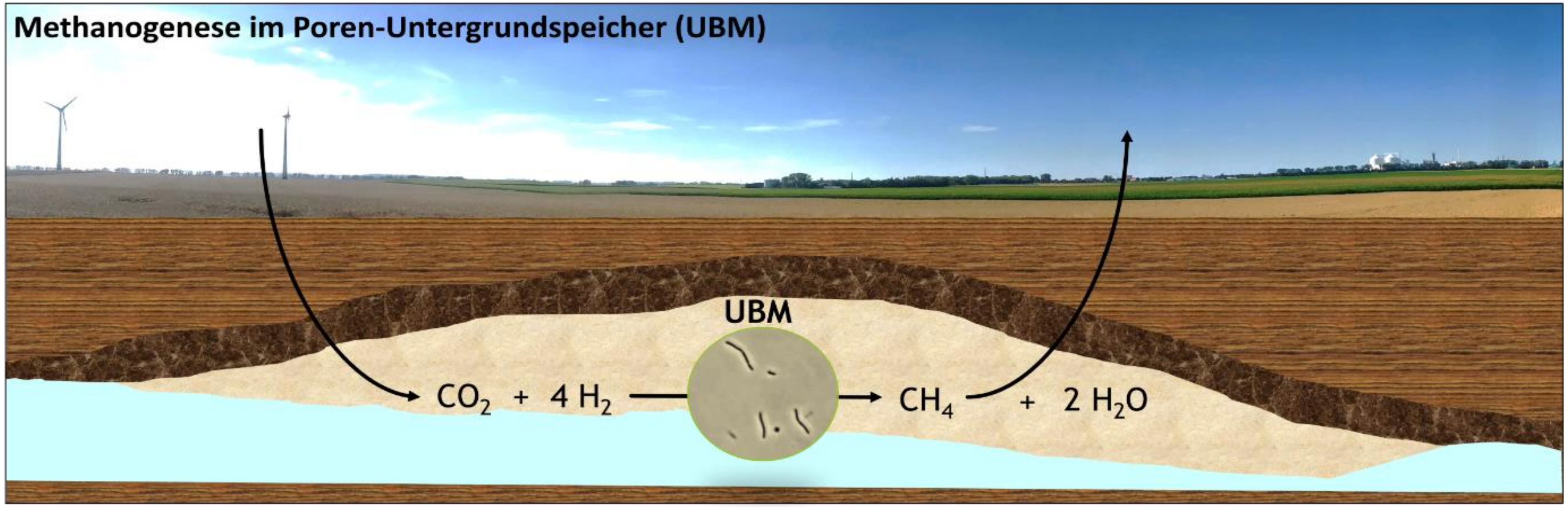
- Reduction of carbon footprint trough re-cycling of $CO_2$
- Reduction of imported fossil fuels
- Large-scale storage of energy from renewable sources

# Background

**$CO_2$: Recycling**

**Green $H_2$: Storability**

→ Combination of both Topics?
→ Underground Bio-Methanation




- Generation of biogeneous methane, utilization in analogy to Natural Gas
- Provide storage possibilities for green Hydrogen

Underground Bio-Methanation scheme © MicroPro GmbH

# Project Overview

- Partners from Industry and Science: proximity to application and in-depth basic knowledge

***Research and Analysis on geological and lithological Reservoir-Properties***

***Lab investigations on real reservoir rocks, -fluids, micro organisms under real p, T, S -conditions***

***Reservoir simulation incl. implementation of micro-biological processes***

***Analysis of reaction kinetics and potential side effects, enhancing of positive, and imhibiton of negative processes***

***Facility concept, operation scenarious, risk assessment, monitoring***

# Associated Partners

- Huge interest from operators
- National and international support trough
  - Providing sample material
  - Information about geology, UGS properties, hydrochemistry
  - Thermodynamical-geo-chemical Modelling
  - Results verification

Bio-UGS

# Agenda

# Bio-Methanation process and effects in the reservoir

- Methanogenesis

$$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O$$

- Acetogenesis

$$2CO_2 + 4H_2 \longrightarrow CH_3COOH + 2H_2O$$

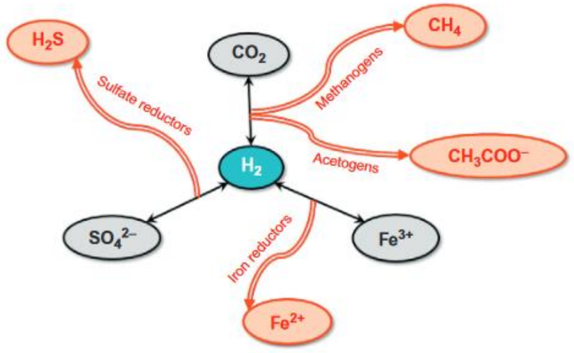
- Sulfate-Reduction

$$SO_4^{2-} + 5H_2 \longrightarrow H_2S + 4H_2O$$

- Iron(III)-Reduction

$$3Fe_2^{III}O_3 + H_2 \longrightarrow 2Fe_3^{II}O_4 + H_2O$$

- Microbial Kinetics

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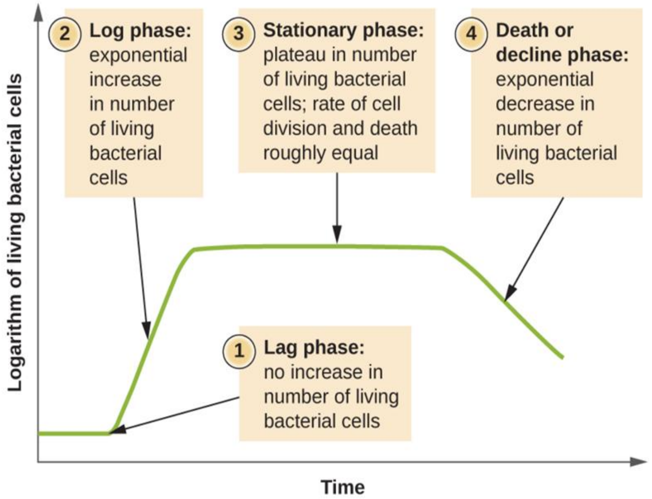


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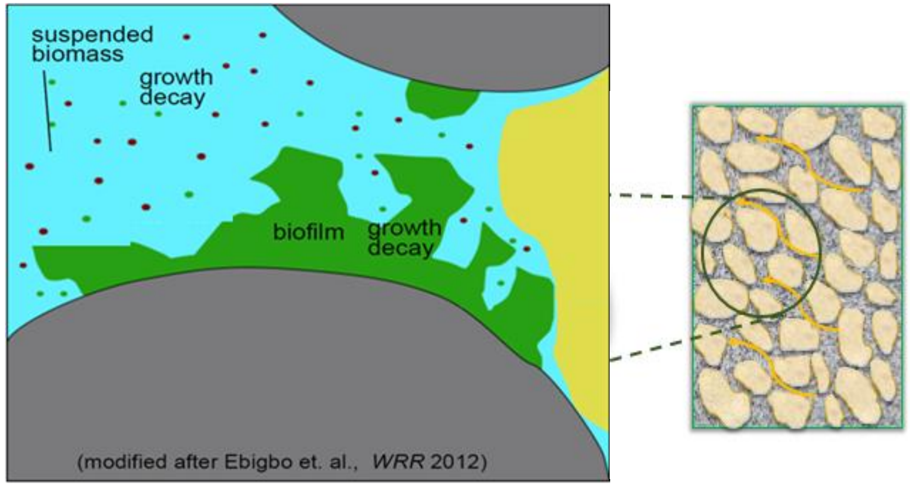
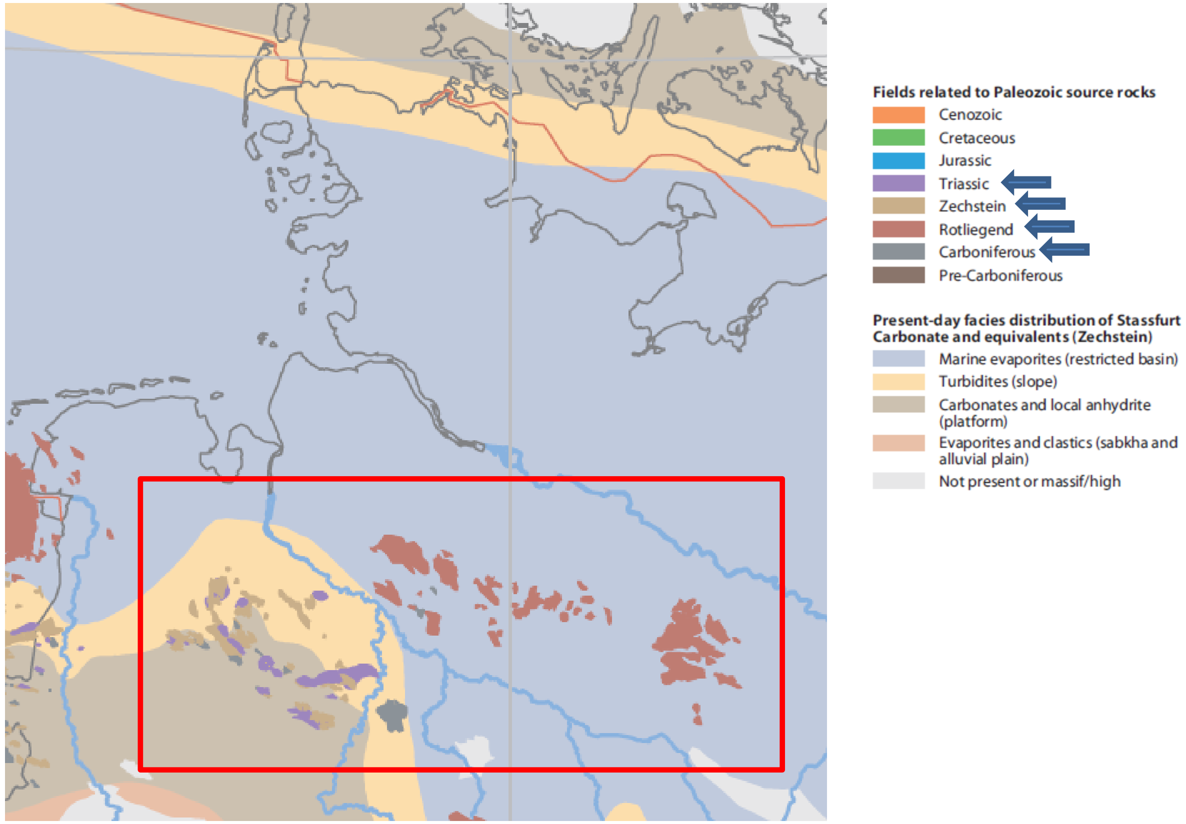


# Bio-Methanation process and effects in the reservoir

- Classification of Geological Conditions, Candidate Reservoirs
  - North German Basin
  - Thuringian and Sub-Hercynian basins
  - Brandenburg
  - Lower Saxony Basin and Dogger Troughs
  - Bavarian Molasse region

- Pre-Screening-Criteria according to:
  - Porosity
  - Permeability
  - Salinity
  - Depth
  - Temperature
  - Water Saturation



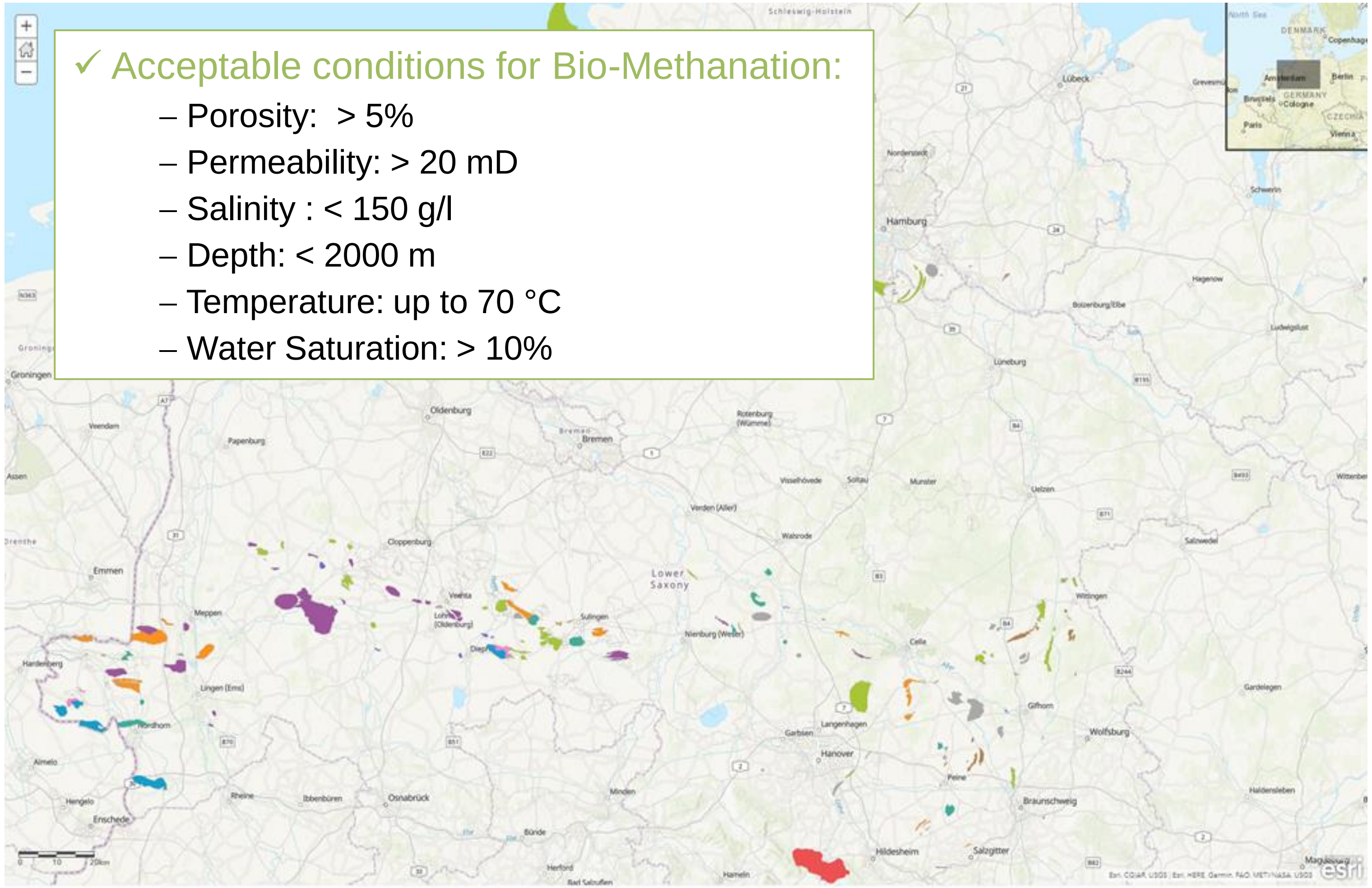

North German Basin petroleum province related to Paleozoic source rock

# Bio-Methanation process and effects in the reservoir

- Classification of Geological Conditions, Candidate Reservoirs, Clustering

  - Oil and gas fields classification
    - Cluster 1: depth < 1000 m
      - Type 1: Sandstone formation
      - Type 2: Carbonate
    - Cluster 2: 1000 < depth < 2000 m
      - Type 1: Sandstone formation
      - Type 2: Carbonate

  - UGS classification
    - Cluster 1: depth < 1000 m
      - Type 1: Aquifer
      - Type 2: Depleted Field
    - Cluster 2: 1000 < depth < 2000 m
      - Type: Depleted Field

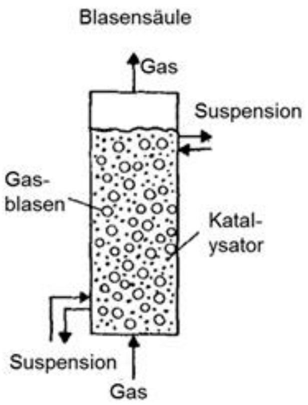


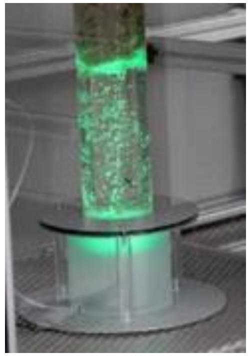
✓ Acceptable conditions for Bio-Methanation:
- Porosity:  > 5%
- Permeability: > 20 mD
- Salinity : < 150 g/l
- Depth: < 2000 m
- Temperature: up to 70 °C
- Water Saturation: > 10%

# Agenda

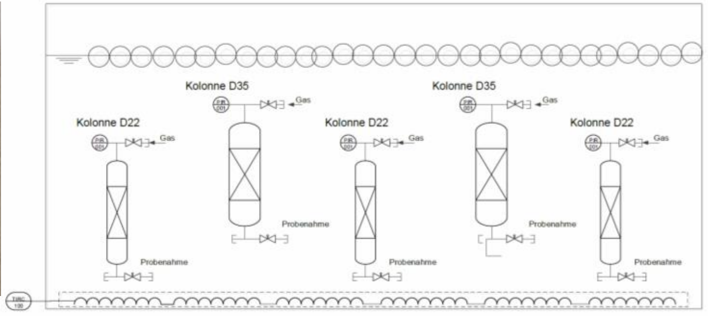
# Laboratory Investigations

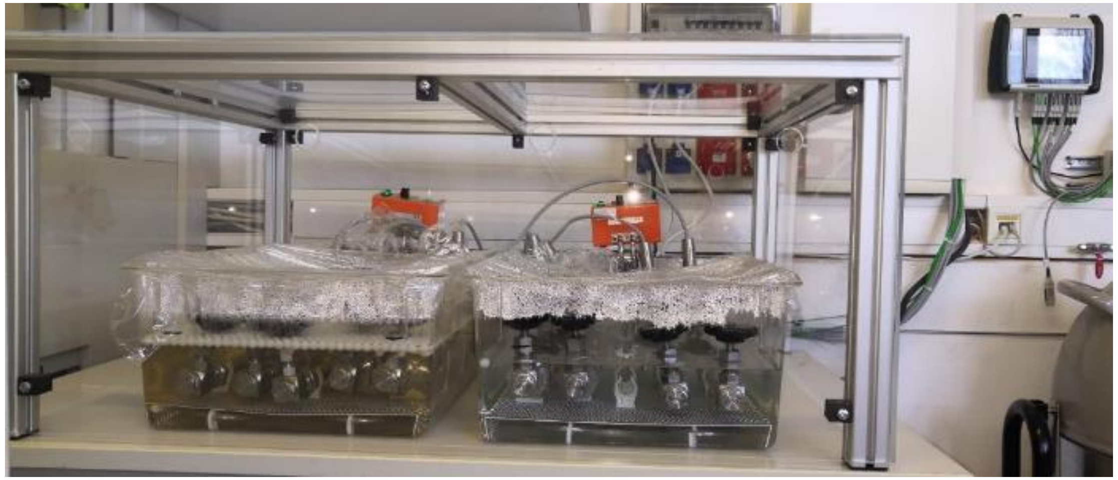
- Investigation of biological methanation on rocks via inoculation waters
  - Adaption of results from bubble column experiments to reservoir conditions
  - Investigation of reaction kinetics on formation water



**Development Bio-UGS**



**Batch reactors: up to 100 bar, up to 100 °C**

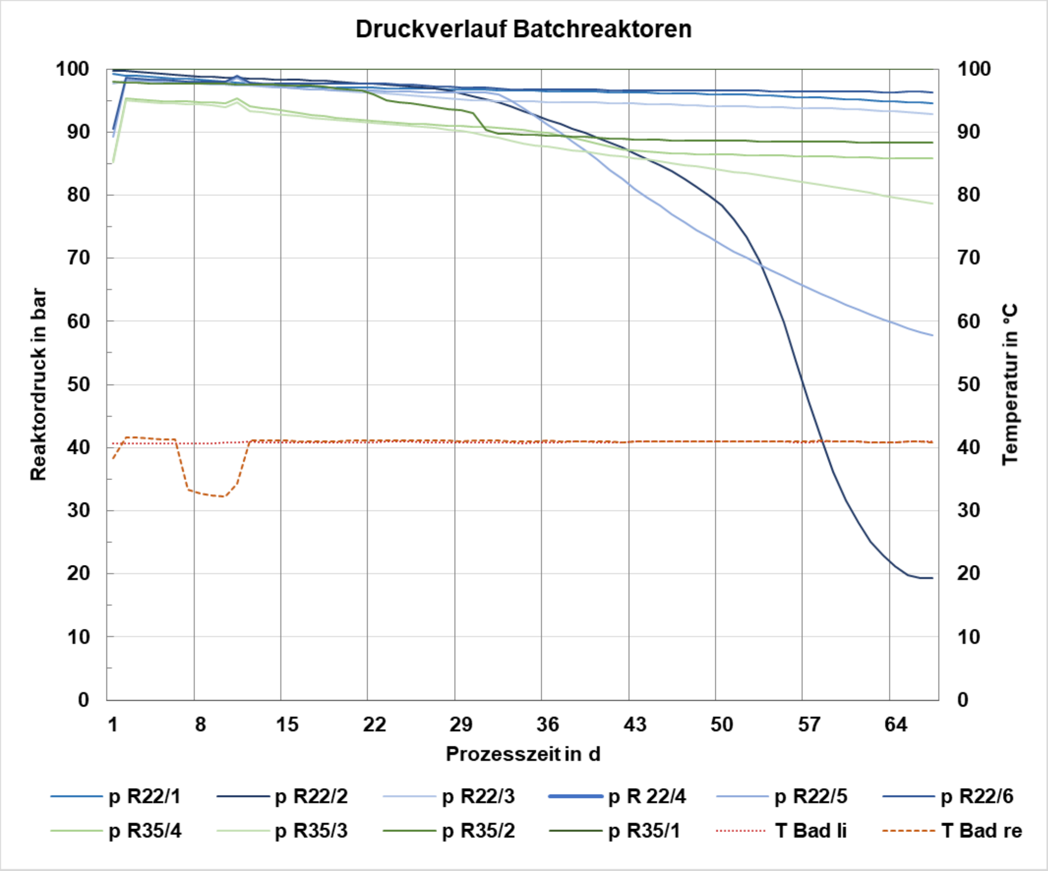
Laboratory equipment: bubble column and batch reactors © DBI-Gruppe

# Laboratory Investigations

- Test procedure in batch reactors
  - Standard inoculum: digested sludge (DS)
    - 22er reactors with 40 ml DS, 80 ml total
    - 35er reactors with 100 ml DS, 200 ml total
    - Gas mix: 80 Vol.-% $H_2$ : 20 Vol.-% $CO_2$
    - 100 bar initial pressure
  - Assumption: pressure decrease to ca. 20 bar at the end of the conversion process
  - General idea about kinetics of different cultures

- First Results
  - Differing kinetics
  - Reactor 22/2 reaching 20 bar after 65 days, after initial 29 days lag-phase
  - Additional results to be obtained via GC-analysis of gas and liquid phase

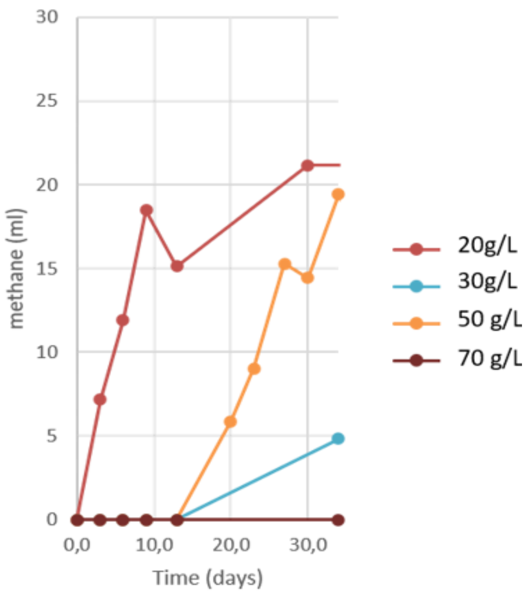
- Next Step: Experiments with samples from UGS

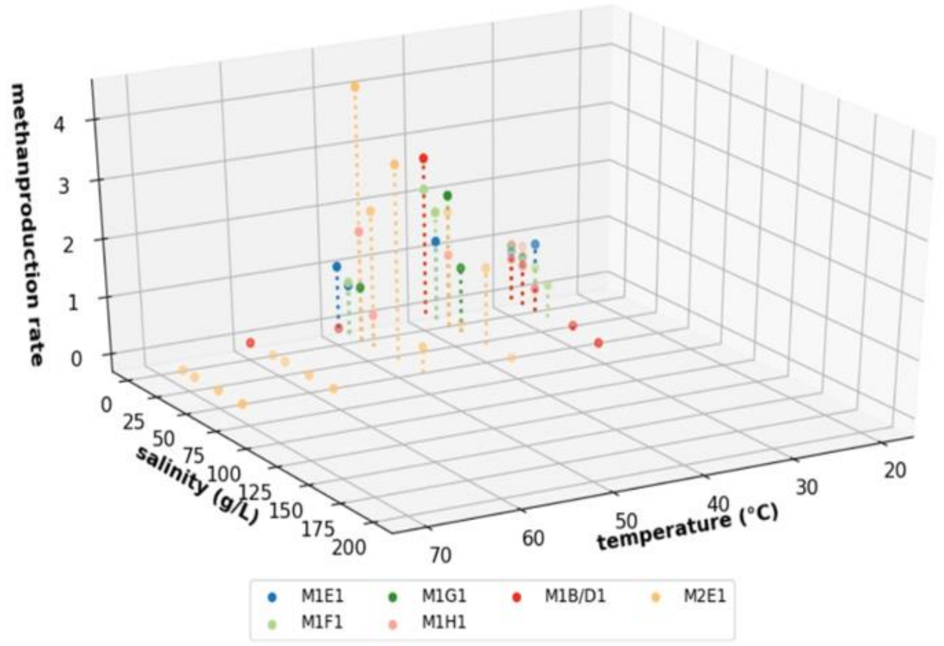


# Laboratory Investigations

- Microbial Stimulation potential:
  - UGS formation water samples → cultivation on selective media:
    - Hydrogenotrophic Microorganisms ($CO_2$ / $H_2$)
      - SRB
      - Methanogens
      - Acetogens
    - Other Microorganisms
      - SRB / lactate or acetate
      - Anaerobic heterotrophic
      - Acid producers
      - Alkane reducers
      - Methane degraders
  - Methane production depending on salinity and temperature:
    - < 50 g/l seems to be a characteristic boundary
    - 20 °C < T < 55 °C seems to be the appropriate range

Example of enriched cultures © MicroPro GmbH

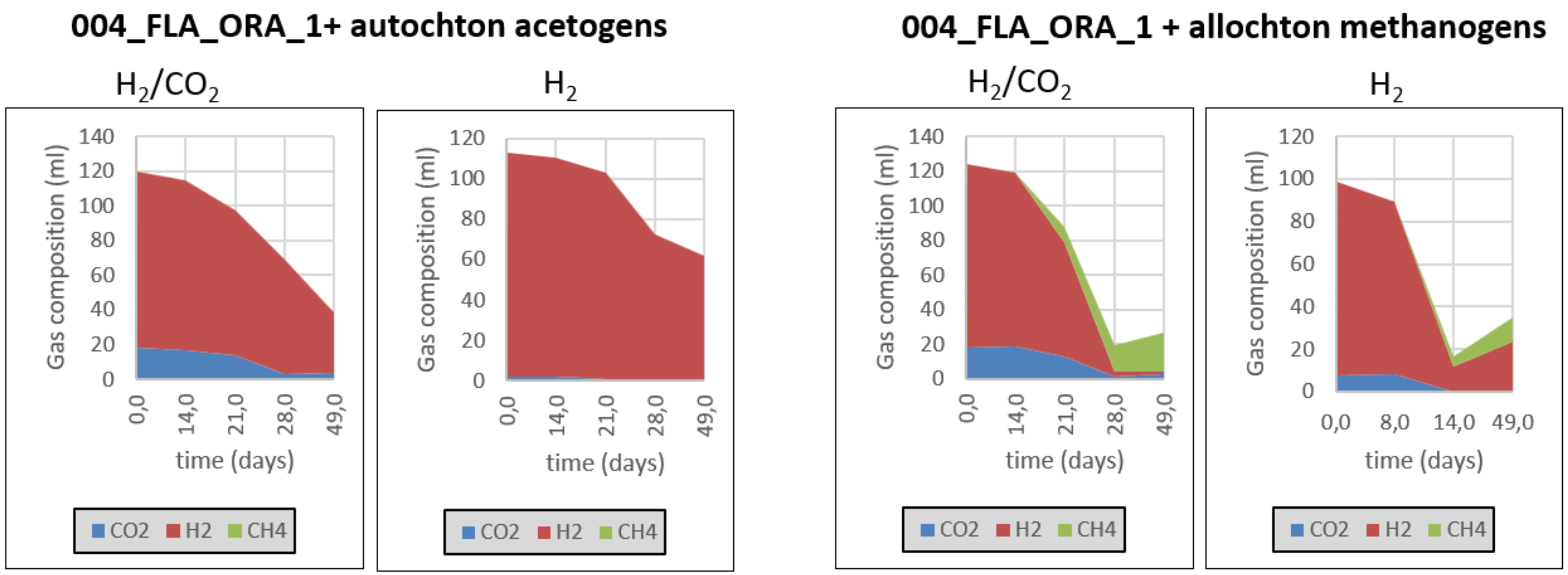



Methane production dependent on salinity and temperature, left: 40 °C, M2E1 © MicroPro GmbH

# Laboratory Investigations

- Microbial Stimulation potential:
  - fluids: 004_FLA_ORA_1 and 004_FLA_ORA_3; 30°C, 2000mbar
  - variants: $H_2$ (100%) vs. $H_2/CO_2$ (80/20%); inoculation with autochton SRB, acetogens/methanogens or allochton methanogens
  - Analysis of: gas composition, cell content, pH, anions, acids (isotops, kationen, bicarbonates by isodetect and FSU)

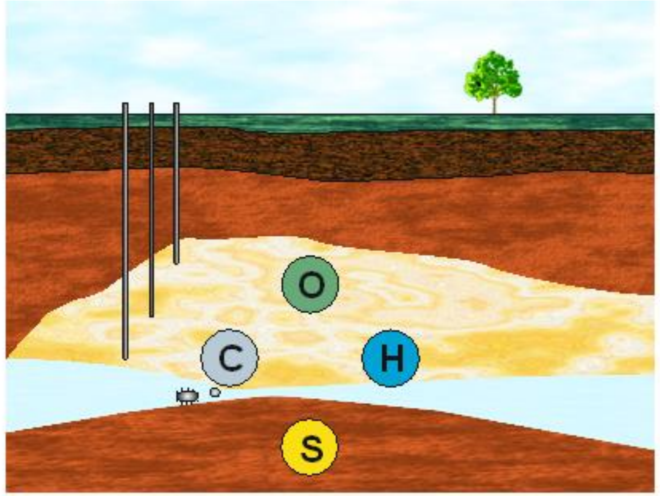



→ Conversion of $CO_2$ and $H_2$ to methane within 28 days, only with extern methanogens

→ Turnover of $CO_2$ and $H_2$ with intern enrichments within 28 days, but no methane production

# Laboratory Investigations

- Isotopic Analysis for differentiation between biological and abiotic reactions: Isodetect




| | | |
|---|---|---|
| Kohlenstoff | $^{12}C$ (98,9 %) | $^{13}C$ (1,1 %) |
| Wasserstoff | $^{1}H$ (99,99 %) | $^{2}H$ (0,01 %) |
| Sauerstoff | $^{16}O$ (99,8 %) | $^{18}O$ (0,2 %) |
| Schwefel | $^{32}S$ (95,0 %) | $^{34}S$ (4,2 %) |

$$\delta^{13}C\,[‰] = \left(\frac{\text{Probe}}{\text{Standard}} - 1\right)$$

Standard: Vienna Pee Dee Belemnite - VPDB

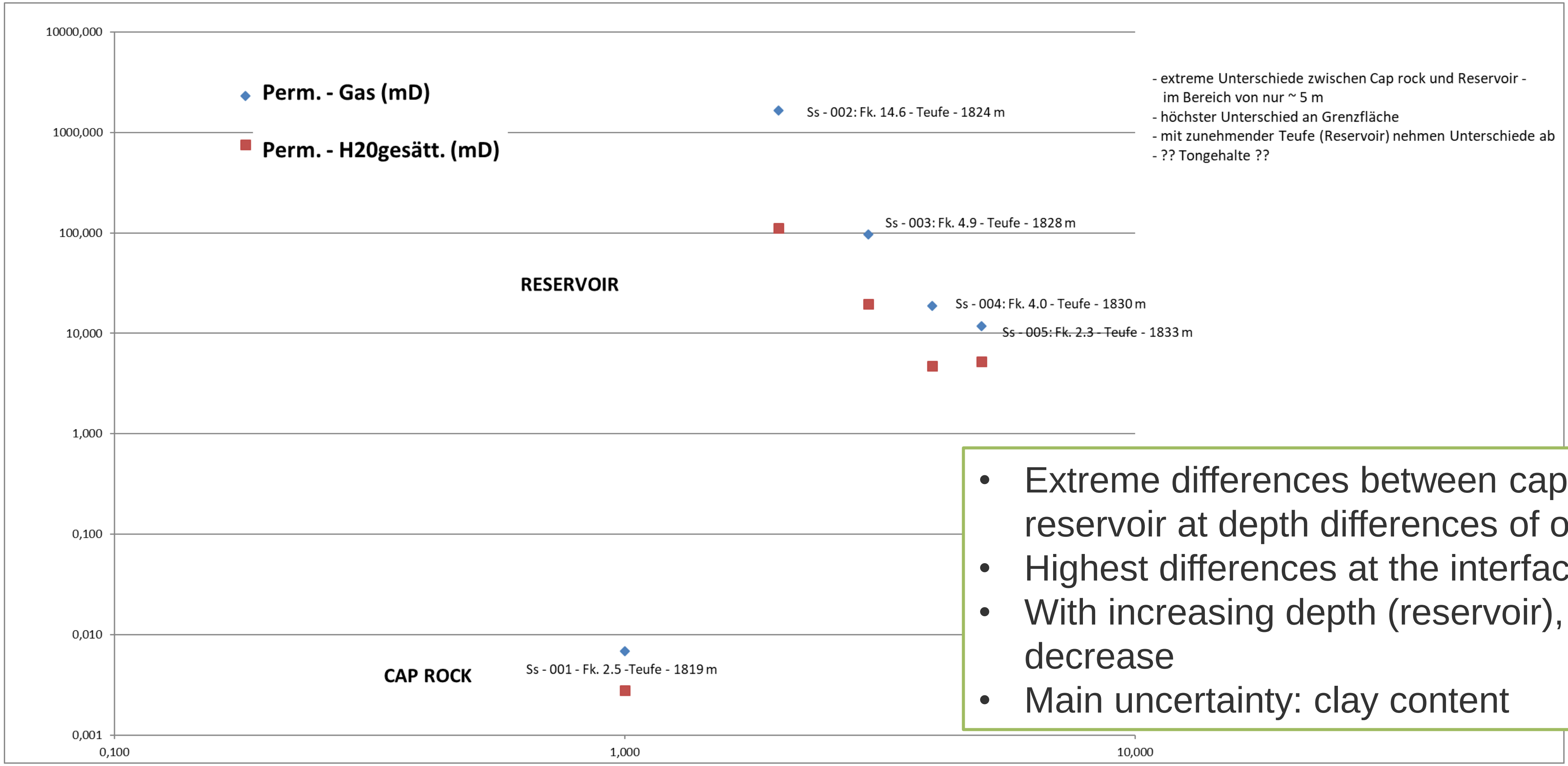

© Isodetect GmbH


Microorganism cultures © Isodetect GmbH

<u>Cultures,</u>
004-FLA-ORA_1
Methanogene/Acetogene
80% $H_2$, 20% $CO_2$

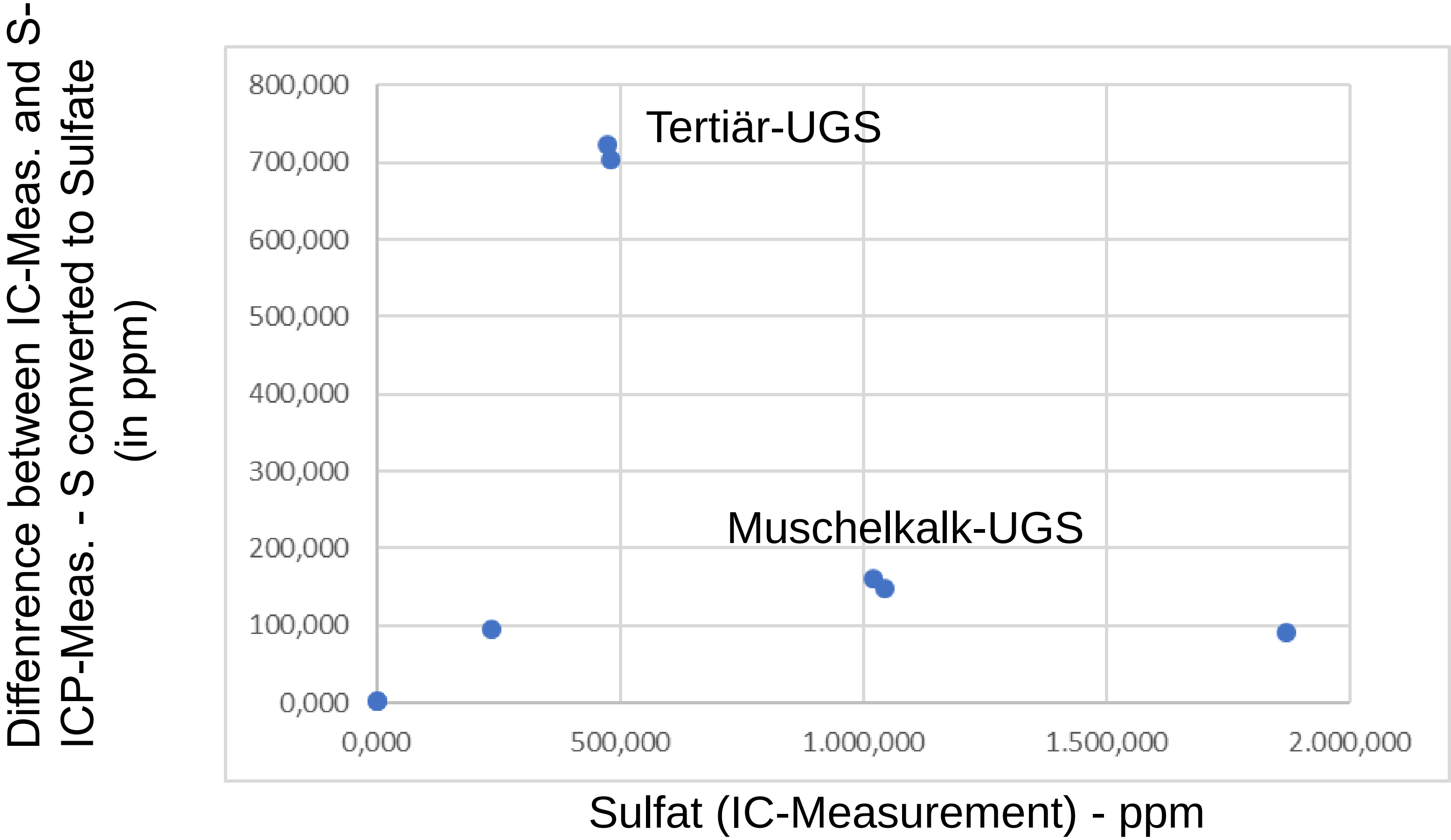
# Laboratory Investigations

- Petrophysical Analysis of rock material:




- Extreme differences between cap rock and reservoir at depth differences of only 5 m
- Highest differences at the interface
- With increasing depth (reservoir), differences decrease
- Main uncertainty: clay content

- Petrophysical Analysis of rock material:





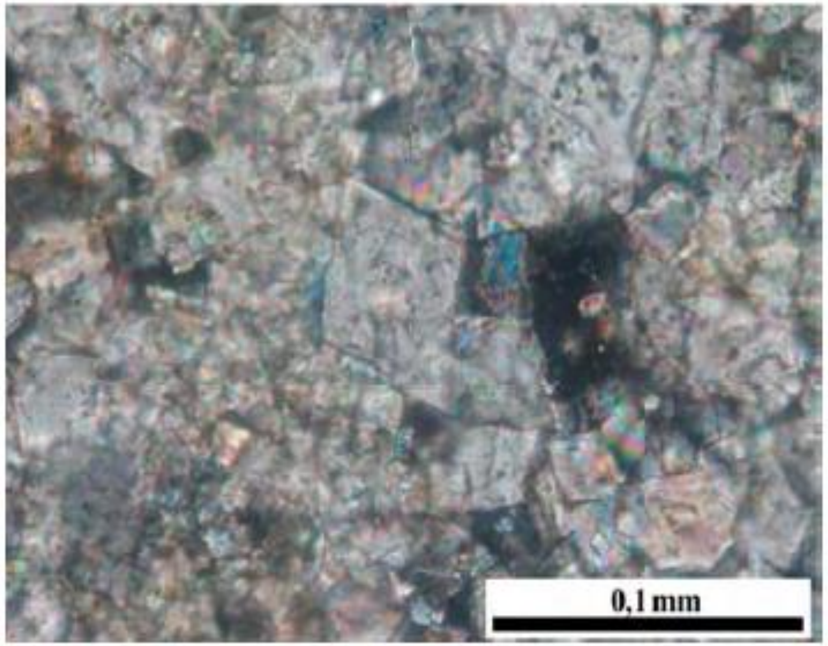
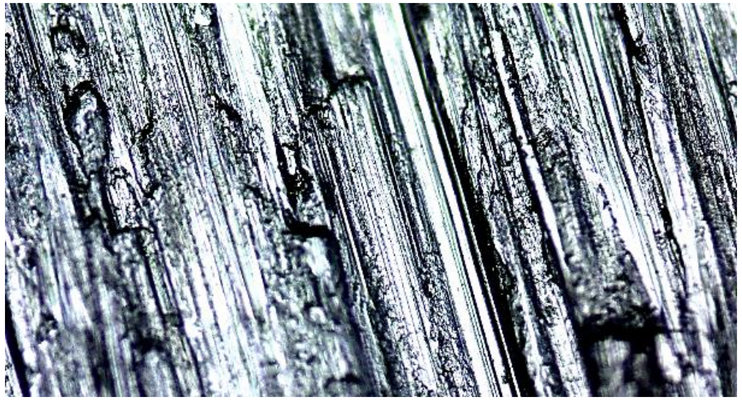




Abb. 1: Die kompakten Dolomitkristalle erscheinen gräulich-bunt mit einer rautenförmigen Kornform. *Dünnschliff in polarisiertem Licht mit gekreuzten Polarisatoren.*

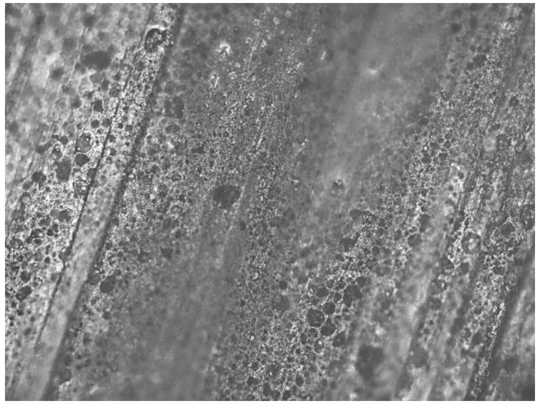
# Laboratory Investigations

- Investigation of corrosion
  - Material:
    - X56 (FE203)
    - L80
  - Methodology
    - Samples are exposed to bio-gas stream
    - Investigations on $H_2S$-corrosion and / or Bio-fouling
    - Investigation of samples after 1, 3, 6 and 12 months
    - Eye-optical and miscroscopical investigation of material alteration
  - First Results, L80:
    - After 1 month:
    - Circular material removal & discoloration recognized

Corrosion test rig © DBI-Gruppe



L80, before exposure © DBI-Gruppe

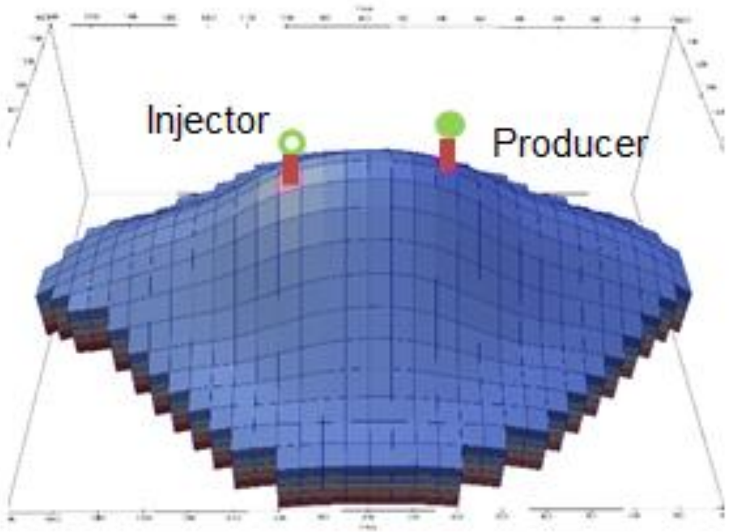


L80, 1 month exposure to bio-gas © DBI-Gruppe

# Agenda

# Reservoir simulation:
# challenges and workflow for field-scale simulation

- Generation of conceptual field-scale models
  - Homogeneous
  - Heterogeneous




Model grid with dimensions and wells positions

$$\frac{\partial n}{\partial t} = S_w \psi^{growth}(c_w^S, c_w^A) \cdot n - \psi^{decay} \cdot n + \nabla \cdot (D_m \nabla n)$$

$$q^k = \phi S_w \gamma^k \frac{\psi^{growth}}{Y} n$$

$$\psi_m^{growth} = \psi_{m,max}^{growth} \left( \frac{c_w^{k,1}}{\alpha_{m,1} + c_w^{k,1}} \right) \left( \frac{c_w^{k,2}}{\alpha_{m,2} + c_w^{Ck,2}} \right)$$

Hagenmann, 2014; Megee et al., 1972

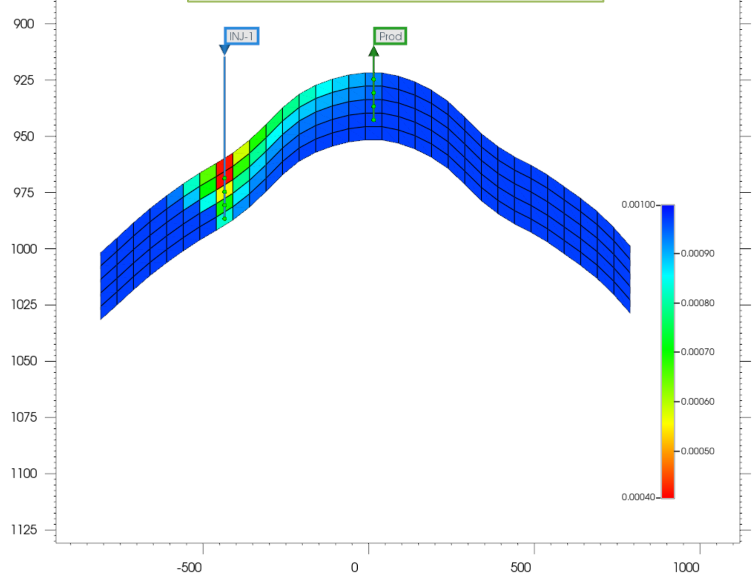
| Microbial Kinetic Parameters from Lab Experiment Results | |
|---|---|
| Maximum specific growth rate | $\psi_{m,max}^{growth}$ |
| $H_2$ half-velocity constant | $\alpha_{m,1}$ |
| $CO_2$ half-velocity constant | $\alpha_{m,2}$ |
| Decay coefficient | bM |
| Yield coefficient | YM,e |

# Reservoir simulation:
# challenges and workflow for field-scale simulation

- Bio- Reactive Transport
- Concept of Dispersed Components
- Bacterial Life Cycle
- Chemical Reaction & Reaction Kinetics

**Microbial Kinetic Parameters: growth, decay, transport**

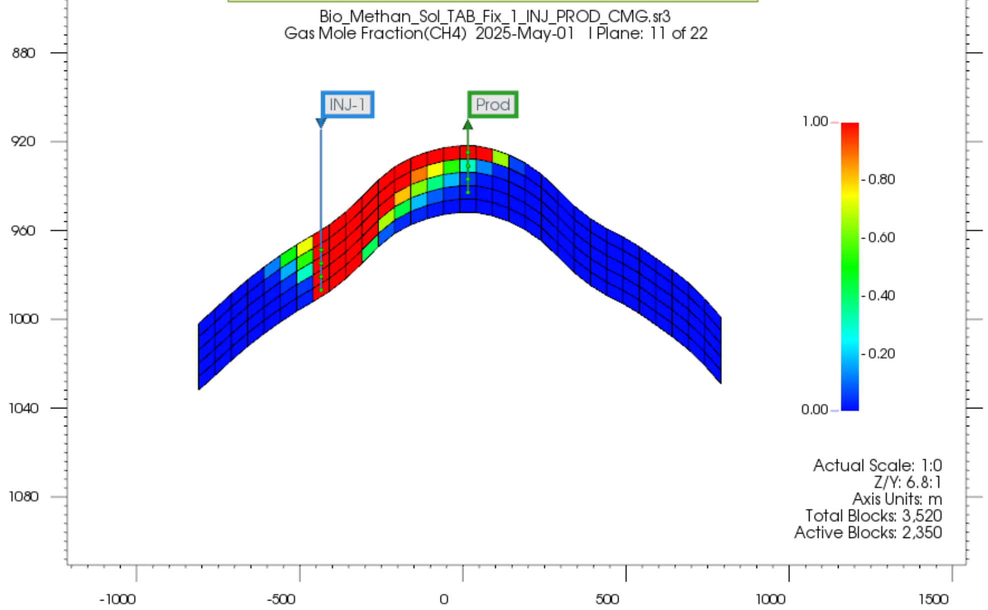
## Bacterial Growth




$$a\ Bacteria + b\ Nutrients \rightarrow c\ Bacteria + d\ Products$$

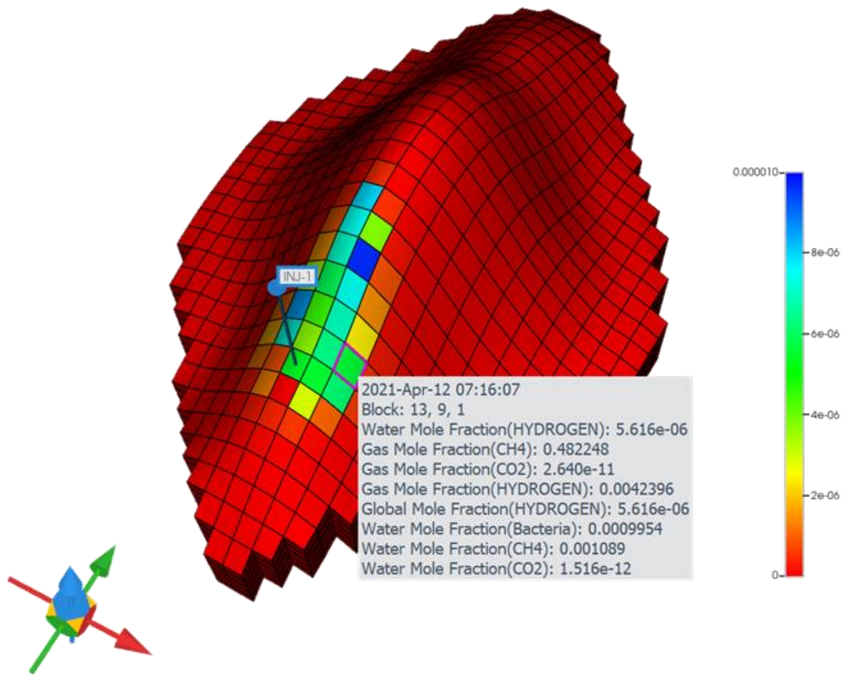
$$r = F_{Freq} \cdot e^{\left(\frac{-E_a}{R.T}\right)} \cdot \prod c_i$$

## Methanogenesis Effect



# Reservoir simulation:
# challenges and workflow for field-scale simulation

**Hydrogen Solubility**




Henry‘s Law

Gas-Liquid K-Values

$$K_i(p,T = kv1_i / p + kv2_i \bullet p + kv3_i) \bullet \mathrm{EXP}\ [\ kv4_i / (T - kv5_i)\ ]$$

# Reservoir simulation:
# challenges and workflow for field-scale simulation

**Diffusion / Dispersity Models**

Molecular Diffusion

$$J_{ijk} = -\left(\varphi S_j D^*_{ij} / F_{jk}\right) \nabla_k \left(\rho_j x_{i,j}\right)$$

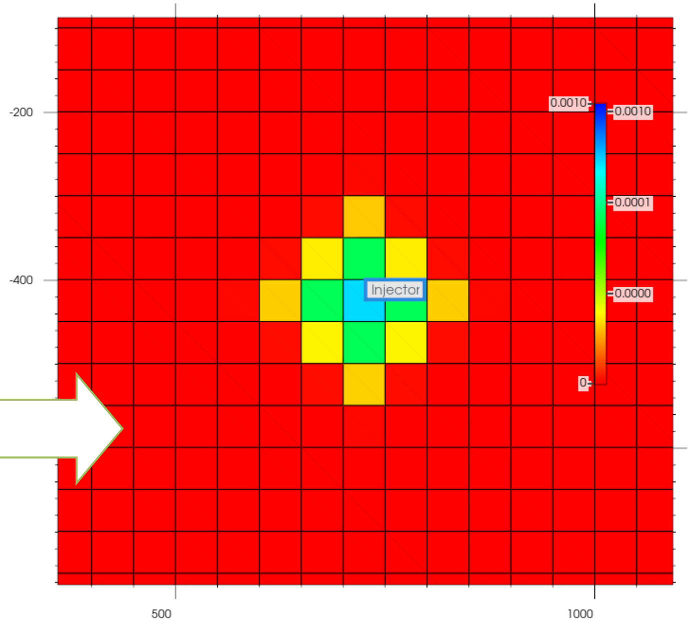
Mechanical Dispersion

$$J_{ijk} = -\varphi S_j a_{jk} \left[u_j\right] \nabla_k \left(\rho_j X_{i,j}\right)$$

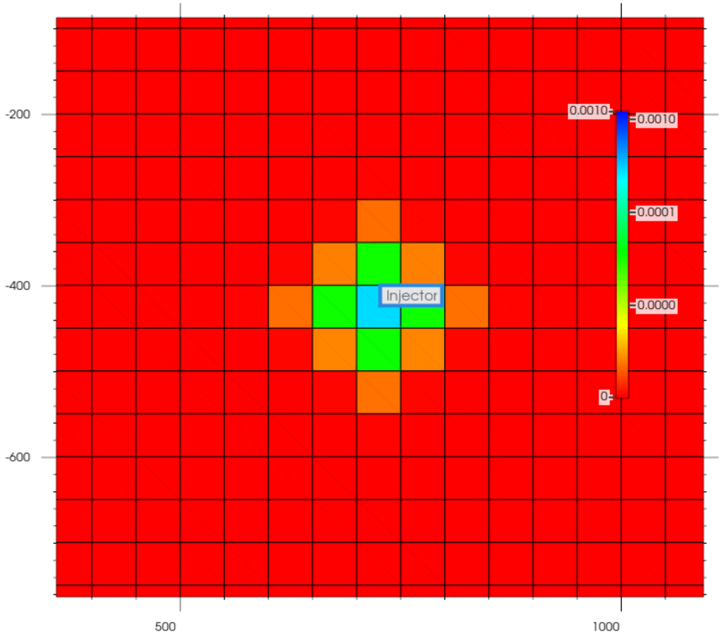
Total Dispersion

$$J_{ijk} = -D_{ijk} \nabla_k \left(\rho_j x_{i,j}\right)$$

Model with Total Dispersivity



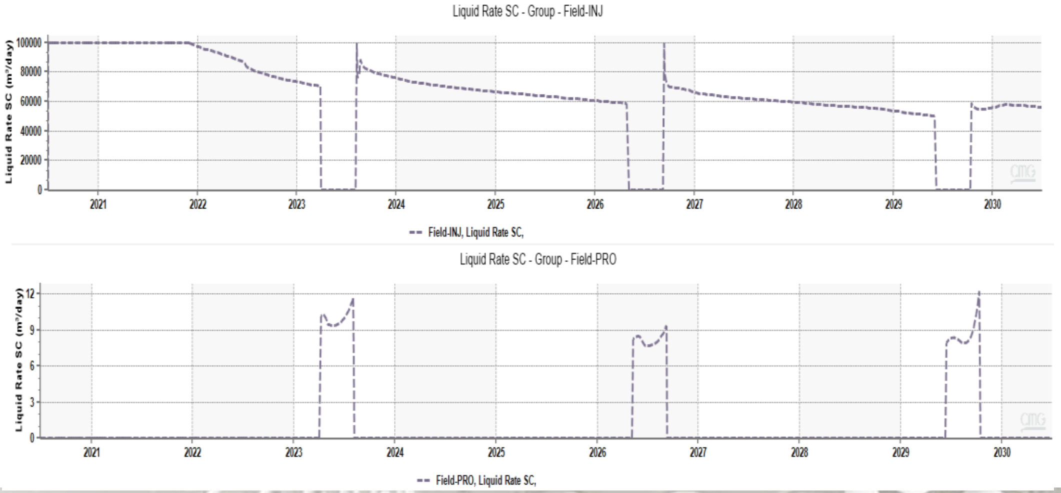

Model without Total Dispersivity

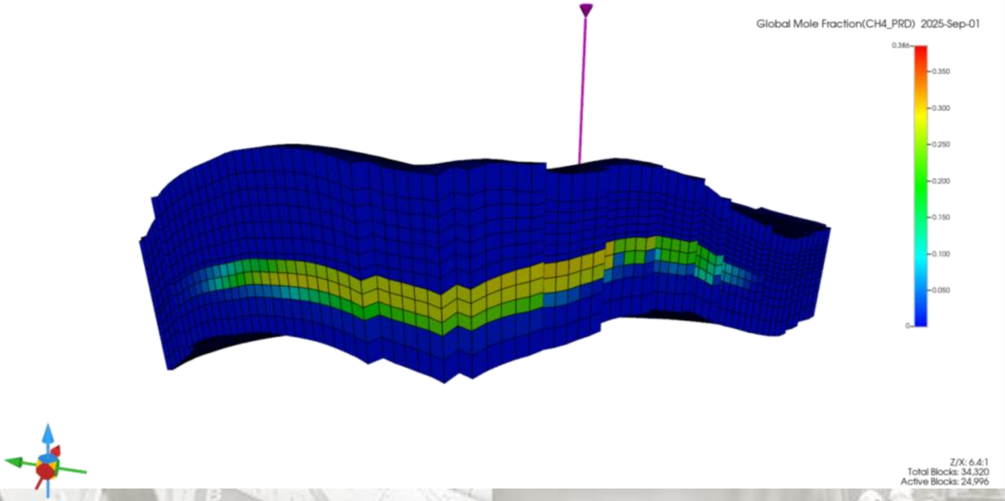


# Agenda

# Wrap-Up and Outlook

- Achievements
  - Characterization of UGS sites in Germany according to rock type and lithology / mineralogy
    - Pre-selection of favourable conditions for underground bio-methanation
  - Lots of support by UGS-operators and lots of representative sample material to cover the entire range (95 %)
  - Analysis of rock material, formation water samples, and various microbial cultures
  - Successful bio-methanation in laboratory microcosmos observed for some cultures
  - Conceptional reservoir models were generated, resembling different lithological and reservoir-mechanical conditions
  - Modelling bio-methanation in DuMuX
  - Resembeled workflow in STARS and integrated methanogenesis and bio-reactive transport, bacterial growth and decay dependent on nutrient supply

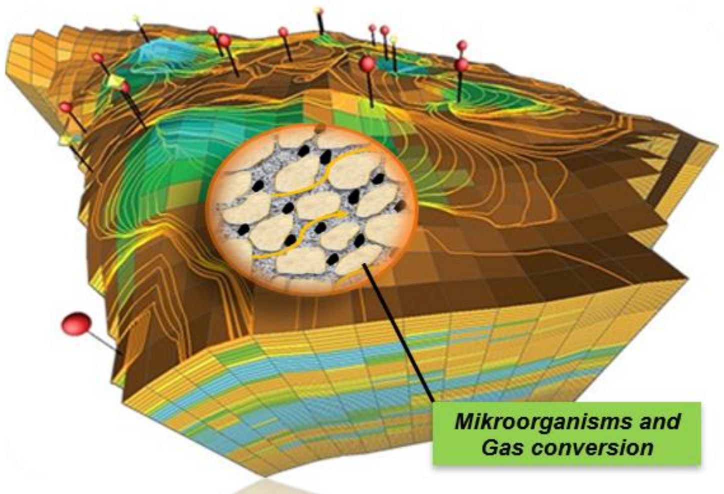


# Wrap-Up and Outlook

- Upcoming works
  - Model calibration with laboratory results
  - Include geo-chemistry modelling and pore-plugging effects in simulation
  - Sensitivity Analysis to assess the most influential parameters
  - Process optimization, determine
    - Feasible operation scenarious
    - Effects on wellbore, material selection

*„From Lab to Field“*




Methanation reactor, reservoir model © DBI-Gruppe

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# Thank you very much for your attention!


## Your contact person

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