# 26th World Gas Conference

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***TS WOC 2-2***

## COMPATIBILITY OF NATURAL GAS SUBSTITUTES FROM RENEWABLE ENERGY SOURCES WITH UNDERGROUND GAS STORAGES

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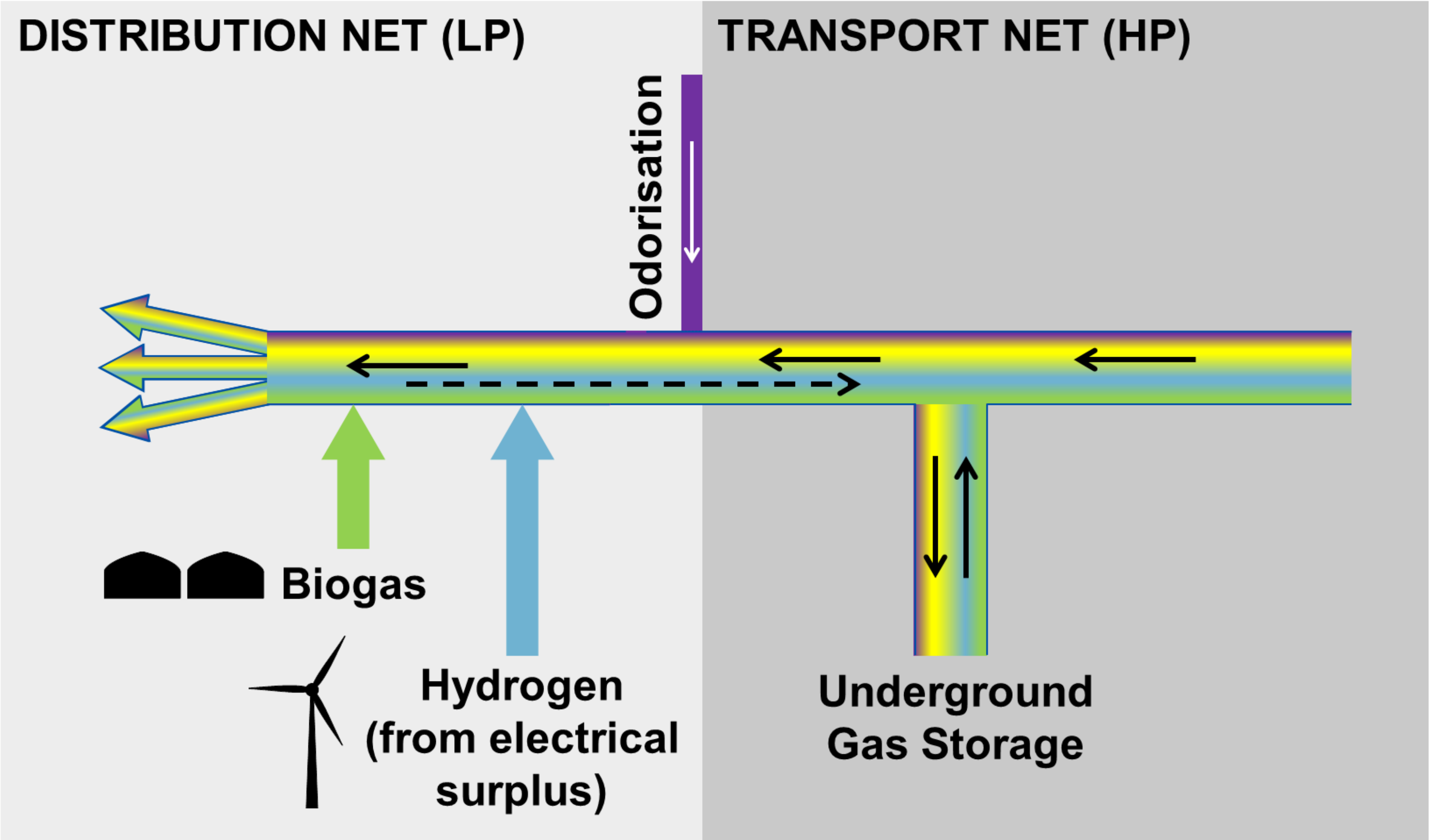
IGU

# The old times are gone



# Limit values for regenerative gases vs. natural gas

| | Biogas | Hydrogen ($H_2$) | German limit UGS | EASEE-Gas |
|---|---|---|---|---|
| $O_2$ [mol%] | ≤ 3 (30,000 ppm) | - | 0.001 (10 ppm) | 0.001 (10 ppm) |
| $CO_2$ [mol%] | ≤ 5 | - | - | 2.5 |
| $H_2$ [mol%] | - | ≤ 100 | - | - |
| Sulphur [mg/sm³] | ≤ 6 non odorised | ≤ 6 non odorised | 6 | 30 |
| Odorisation | odorised | odorised | not odorised | not odorised |
| Microbiology | - | - | - | - |

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# Effect renewables on underground gas storages

- Underground gas storages vital for secure energy supply in EU
- What is effect of renewable gases on
  - Reservoir rock ?
  - Subsurface installations?
  - Gas treatment ?
- ➔ **5 literature studies to evaluate risks:**
  - Hydrogen ($H_2$) (DGMK project 752)
  - Oxygen ($O_2$) (DGMK project 753)
  - Carbon dioxide ($CO_2$) (DGMK project 754)
  - Sulphur and Odorant (DGMK project 755)
  - Microbiology (DGMK project 756)

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# Influence of carbon dioxide ($CO_2$)

- No significant influence on geology of UGS
- No negative impact on tightness of geological seal of UGS
- Potential $H_2S$ liberation in reservoir by increased $CO_2$ content in injection gas
- No significant corrosion of cement expected
- Increases in steel corrosion with $CO_2$ content (next slide)
- ➔ **Keeping existing EASEE-Gas limit for $CO_2$ of 2.5 mol%**

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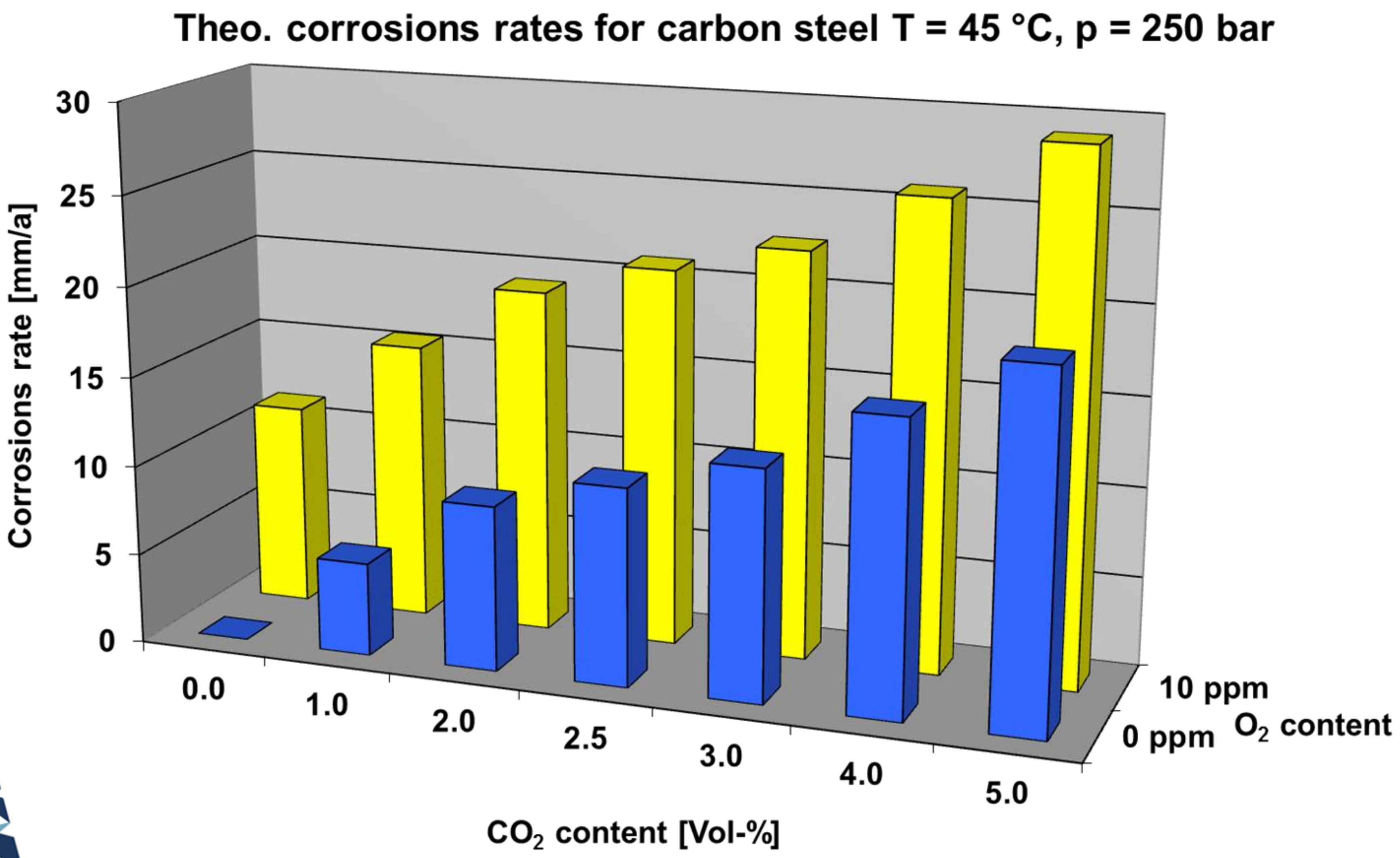
# Carbon dioxide and corrosion



# Sulphur compounds and odorants

- Solution of sulphur components & odorants in formation water
  - Problems in water treatment and disposal
  - Entry in gas treatment units
  - Glycol degeneration
- Odour trouble
  - Risk of need gas additional purification steps
- Potential $H_2S$ liberation by well work overs
- ➔ **No odorised gas in UGS**
- ➔ **Keeping up existing limits for sulphur compounds**

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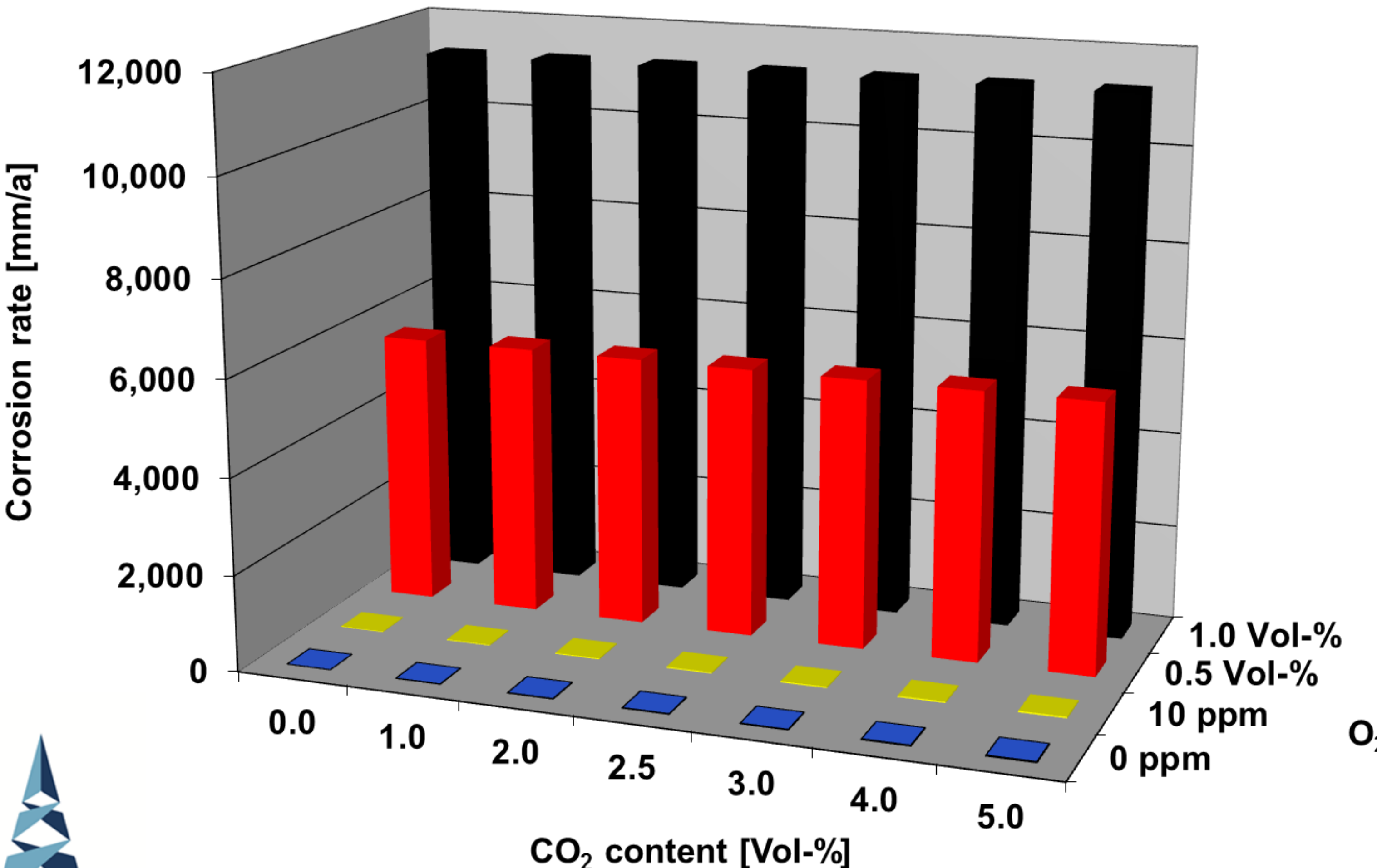
# Oxygen ($O_2$) and corrosion

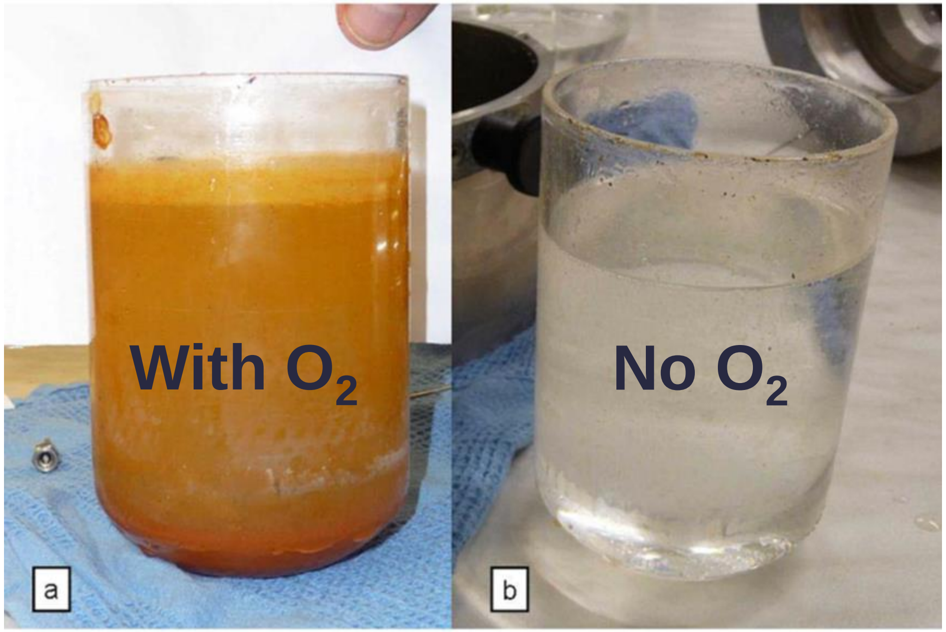
Theo. corrosions rates for carbon steel T = 45 °C, p = 250 bar




# $O_2$ and formation damage

- Mineral transformation and precipitation, e.g. $Fe^{2+} \rightarrow Fe^{3+}$

**$Fe^{2+}$ containing solution**




- For 1 m³ Biogas ($O_2$: 2 %) blending with min. 2,000 m³ natural gas for reaching 10 ppm $O_2$ limit

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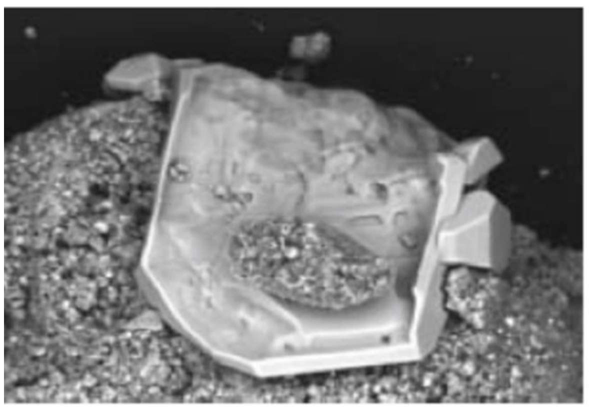
# $O_2$ and sulphur compounds

- Sulphur deposits by caused by $O_2$
    - Formation damage
    - Damage of installations
    - Localized corrosion



Suphur crystal in pipeline generated by $O_2$

Sulphur deposits in subsurface valve

Pipeline corrosion by sulphur deposits

➔ **Limitation of $O_2$ content to 10 ppm in injection gas**

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# Microorganisms in biogas

- So far no pathological germs observed in biogas
- If sufficiently treated no other microorganisms (MO) expected in biogas than in natural gas
- Installation of micro filter as additional safety measure possible
    - Current practice in the Netherlands
- ➔ **Microbiology of biogas no concern if treated sufficiently**

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# Hydrogen ($H_2$) – the big unknown

- Hydrogen ($H_2$) – different properties than methane
- No experiences with effect of $H_2$ on natural gas storages
- Currently no limit value for $H_2$ content in natural gas
- → **Many open questions**
  - → **Demand for research**
    - Geological integrity and amount of storable energy
    - Technical integrity
    - Effect on microbiology in UGS

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# $H_2$ – Integrity of storages & storable amount of energy

- $H_2$ content in gas up - amount of storable energy down
- Diffusion of $H_2$ through cap rock no risk
  - But losses by initial $H_2$ saturation of formation water
- Hydraulic integrity of the cap rock?
  - Modification surface tensions of stored gas and capillary bound water?
- Geochemical stability of reservoirs?
  - Reaction von $H_2$ with reservoir rock?
- ➔ Porous rock storages more at risk than cavern storages

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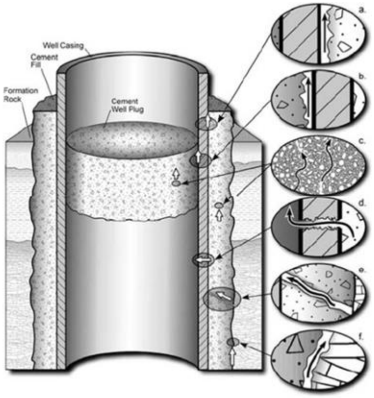
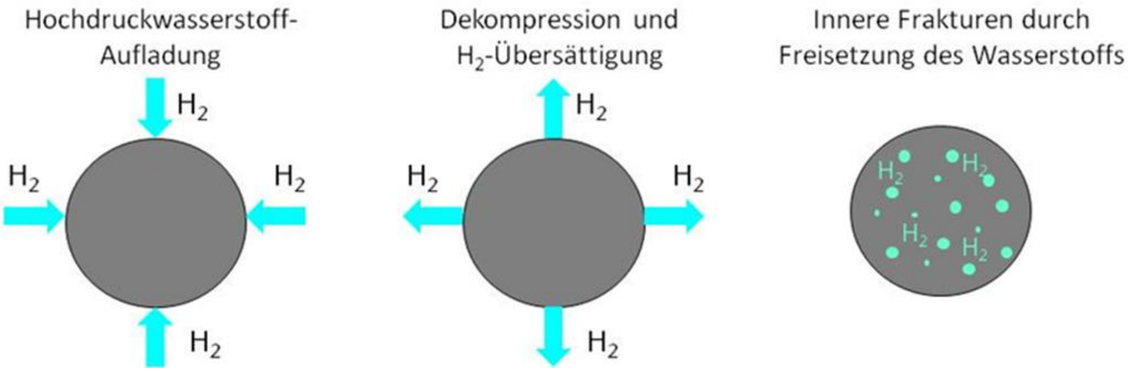
# $H_2$ - Integrity of subsurface installations

- Influence on cementation
  - Modification recipes & additives necessary to prevent $H_2$ diffusion
- Influence on steel installations (e.g. tubings)
  - Critical: steels with strength ≥ 800 MPa
- Influence on elastomer based seals (e.g. packers)
  - Problematic: rapid pressure release







# $H_2$ - Integrity of surface installations

- $H_2$ has other safety properties than natural gas
  - Lower ignition energy
  - Faster speed of flame
- $H_2 \leq 10$Vol.-% so far no indications for critical safety issues
- Current $H_2$ tolerance of turbine compressors: 1 - 5% $H_2$
- Work of compression increases with increasing $H_2$ content

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# $H_2$ and microorganisms

- There are fully functioning $H_2$ – UGS, but
  - They have no carbon source needed for biological growth
    - Natural gas - hydrogen mixtures in contrast have a carbon source

- Experiences with underground storage of town gas
  - Town gas: mixture predominantly of CO, $H_2$ und $CH_4$
  - of CO, $H_2$ und $CH_4$
    - Significant microbiological activity observed

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# Change of gas quality by $H_2$ consumption

Tabelle 10: Gasqualitätsänderung im Horizontalmodell

1. Einlagerung: 7. 12. 84 - 8. 2. 85 63 Tage

Gasvolumenänderung: eingesetztes Stadtgasvolumen 400 ml
Gasverbrauch: 195 ml = 48,75 %
Restgas 205 ml

| Komponenten | Einspeisegas | | Ausspeisegas | | Gasvolumen-änderung | |
|---|---|---|---|---|---|---|
| | % | ml | % | ml | ml | % |
| $CH_4$ | 29,5 | 118 | 34,2 | 70,11 | -47,85 | -40,55 |
| $C_2H_6$ | 0,37 | 1,48 | 0,36 | 0,738 | - 0,742 | -50,01 |
| $C_3H_8$ | 0,044 | 0,176 | 0,026 | 0,053 | - 0,123 | -69,89 |
| i $C_4H_{10}$ | 0,0041 | 0,016 | 0,0021 | 0,004 | - 0,012 | -75,0 |
| n $C_4H_{10}$ | 0,0055 | 0,022 | 0,0016 | 0,0033 | - 0,019 | -86,36 |
| 22 PM Pr | 0,001 | 0,004 | 0,0005 | 0,001 | - 0,003 | -75 |
| i $C_5H_{12}$ | 0,0012 | 0,005 | 0,0001 | 0,0002 | - 0,0048 | -96 |
| n $C_5H_{12}$ | 0,001 | 0,004 | $10^{-4}$ | 0 | - 0,004 | -100 |
| i $C_6H_{14}$ | 0,0006 | 0,002 | n.w. | 0 | - 0,002 | -100 |
| n $C_6H_{14}$ | 0,0002 | 0,001 | n.w. | 0 | - 0,001 | -100 |
| i $N_2$ | 32,5 | 130 | 56,2 | 115,21 | -14,79 | -11,38 |
| $O_2$ | 0,31 | 1,24 | 0,2 | 0,41 | - 0,83 | -66,93 |
| $CO_2$ | n.w. | 0 | 8,4 | 17,22 | +17,22 | + |
| $H_2$ | 24,2 | 96,8 | 0,05 | 0,102 | -96,7 | -99,9 |
| He | 0,12 | 0,48 | n.w. | 0 | - 0,48 | - |
| Ar | 0,26 | 1,04 | 0,53 | 1,08 | + 0,04 | - 3,85 |
| CO | 12,9 | 51,6 | n.w. | 0 | -51,6 | -100 |

**Loss of almost 50% of volume**

**Complete loss of $H_2$**

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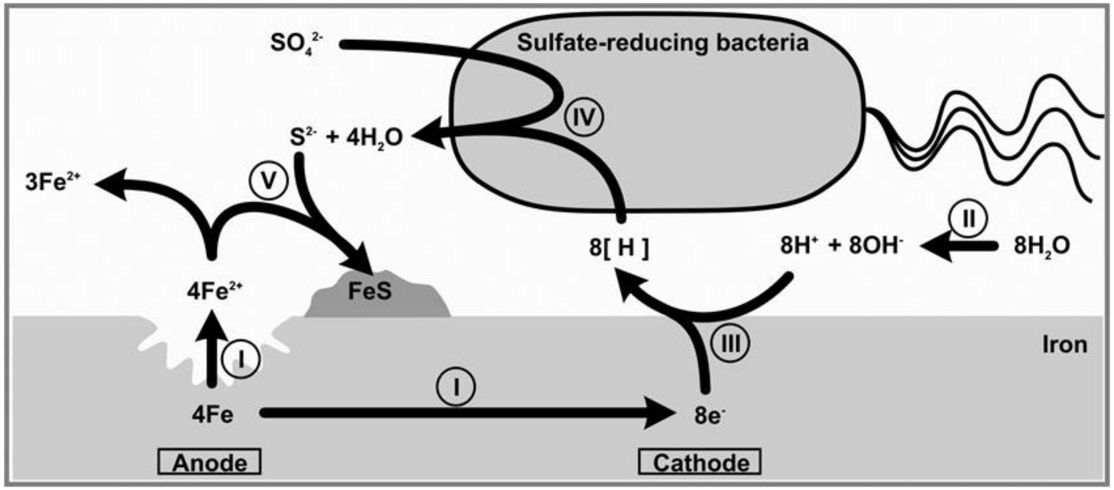
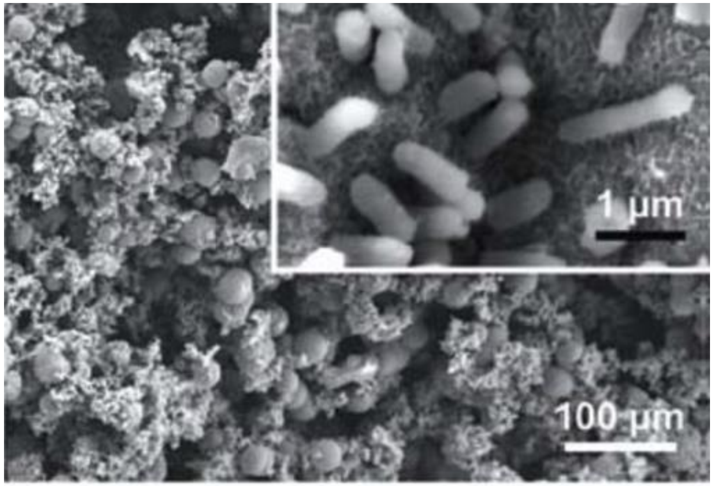
# $H_2$ – Food for microorganisms

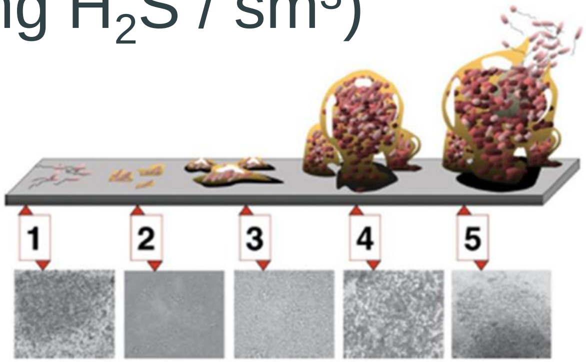
- $4H_2 + SO_4^{2-} + 2H^+ \rightarrow H_2S + 4H_2O$ - Sulfat Reducing Prokaryotes
- $2CO_2 + 4H_2 \rightarrow CH_3COOH + 2H_2O$ - Acetogenese
- $4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$ - Methanogenese



# $H_2$ – Effect of microbiological activity

- Corrosion
  - MIC (Microbiologically Influenced Corrosion)
  - Formation of $H_2S$ und organic acids
- Risk of limit exceeded for natural gas (5 mg $H_2S$ / $sm^3$)
- Loss of permeability
  - Porous rock reservoirs only
- $H_2$ conversion in UGS
  - Loss of energy and change of gas composition
  - Loss of storage capacity by temperature increase

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# $H_2$ – Factors influencing microbiological activity

- Pressure – no great influence
- Temperature – optimum 30-50°C, but also higher temperatures suitable
- Salinity – The higher the worse for microbiological activity
- Surface area – The more the better for microbiological activity
    - Surface good basis for growth, adsorption and reaction
- ➔ **Porous rock storages more at risk than cavern storages**

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# Conclusions

- Underground gas storages vital part of gas infrastructure
- Change in gas composition by gases from renewable energies
- Damage of underground gas storages (UGS) must be avoided
- Necessary measures:
- ➔ **Biogas**
  - **Keeping the existing limit values**
  - **Sufficient treatment of microbiology**
- ➔ **Hydrogen ($H_2$)**
  - **So far no limit values in place**
  - **Need for research to establish limit value**
    - **e.g. 'Underground Sun Storage' project**

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# Co-authors

- Special gratitude to the **co-authors**:

- **Joachim Wallbrecht**
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- **Thomas Höcher** VNG Gasspeicher GmbH