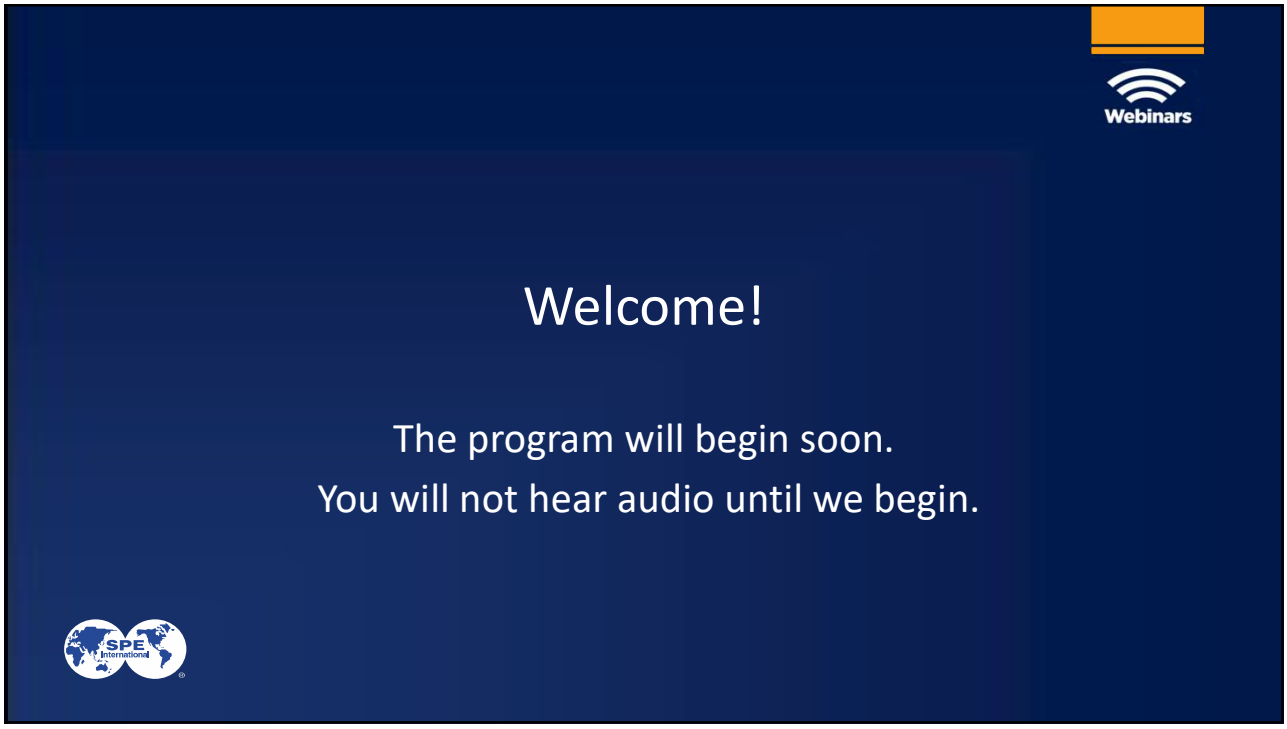
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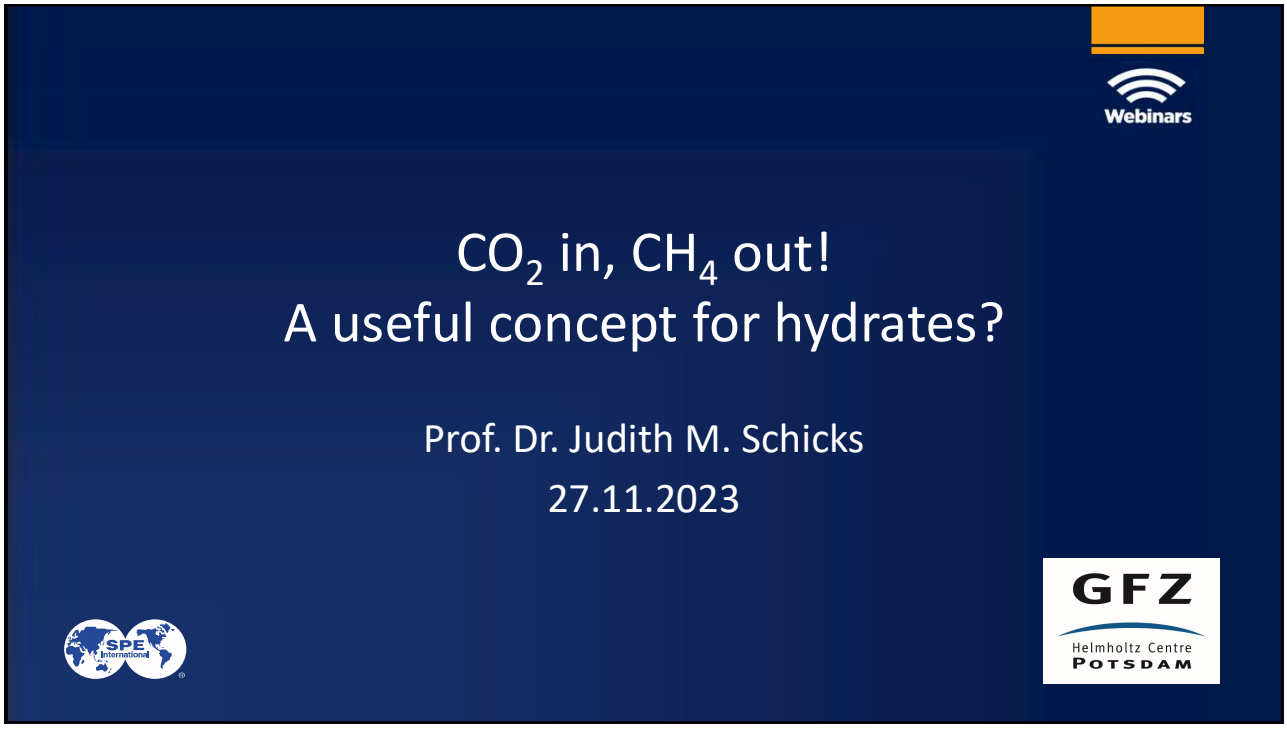
Webinars
CO_2 in, CH_4 out!
A useful concept for hydrates?
Prof. Dr. Judith M. Schicks
27.11.2023
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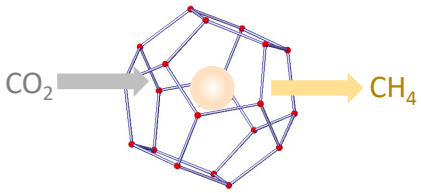
Background

Carbon neutral production of CH_4 from natural gas hydrate reservoirs:
Injection of CO_2 → CH_4 production?



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Questions

1. Driving force: “higher stability” of CO_2 hydrate versus chemical disequilibrium?
2. Process on a molecular scale: exchange versus decomposition and reformation?
3. Efficiency: How much CH_4 will be recovered?
4. Long term stability: How long does the CO_2 hydrate remain stable in the natural environment?

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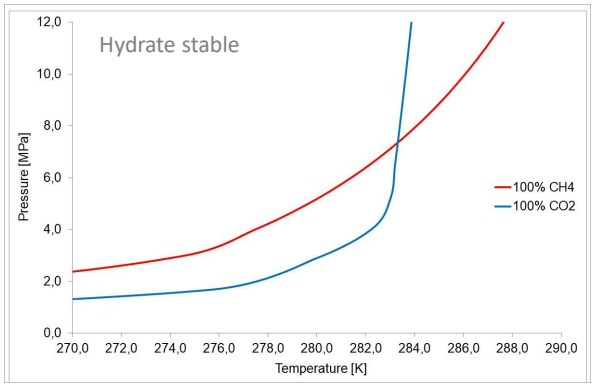
1. Driving force: "higher stability" of CO_2 hydrate versus chemical disequilibrium?

Hypothesis:

- The stability area of CO_2-hydrate is larger compared to the stability field of CH_4-hydrate
  → this induces the transformation of CH_4-hydrate into CO_2-hydrate
- The formation enthalpy of CO_2- hydrate is larger than the dissociation enthalpy of CH_4-hydrate
  → continuation of the process



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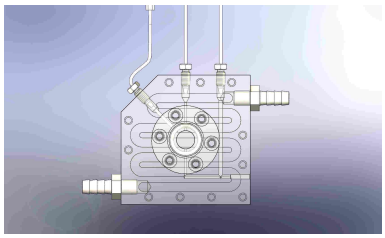
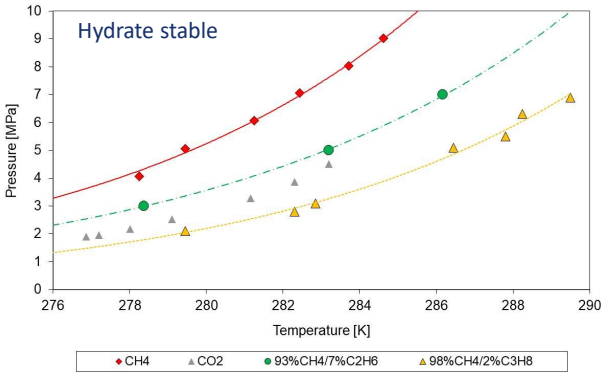
in situ Raman spectroscopy and X-ray diffraction at our laboratory



- cell volume: ~400 µl
- pressure: 10 MPa
- temperature: 267 K and 274 K
- gas flow rate: ~1 ml/min

Investigations on C_1-C_3 exchange with CO_2 in sII hydrates



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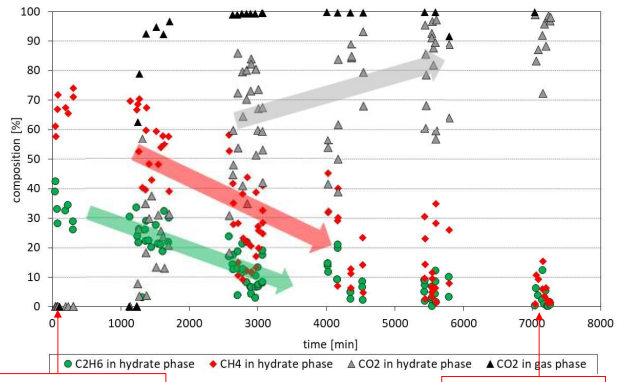
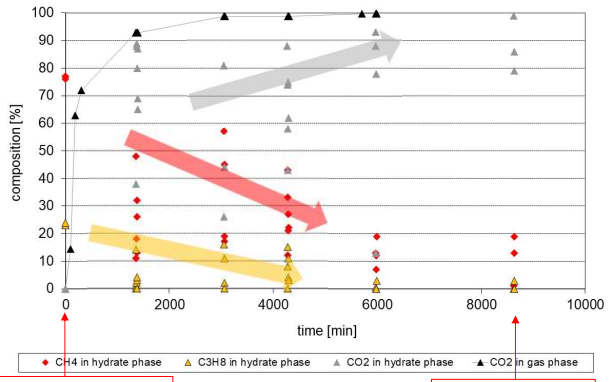
in situ Raman spectroscopy: change of composition in the hydrate phase





Start: sII mixed CH_4-C_2H_6- hydrate

End: CO_2-CH_4-C_2H_6- hydrate

Start: sII mixed CH_4-C_3H_8- hydrate

End: CO_2-CH_4-(C_3H_8)- hydrate

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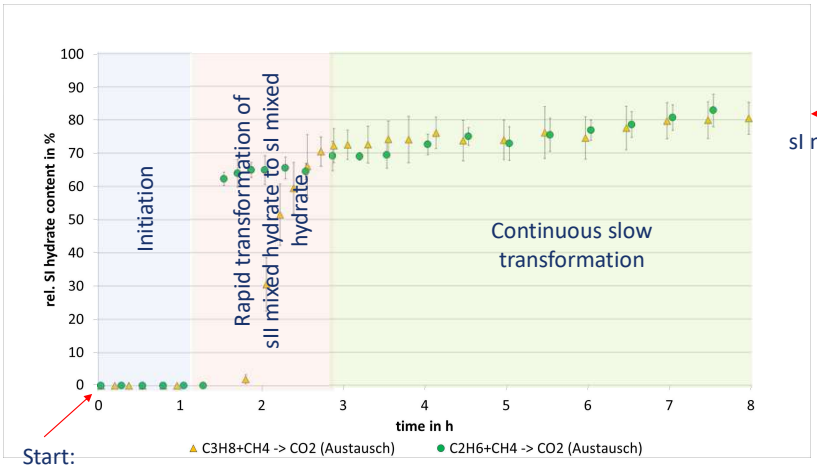
in situ X-ray diffraction: structural changes of the hydrate phase

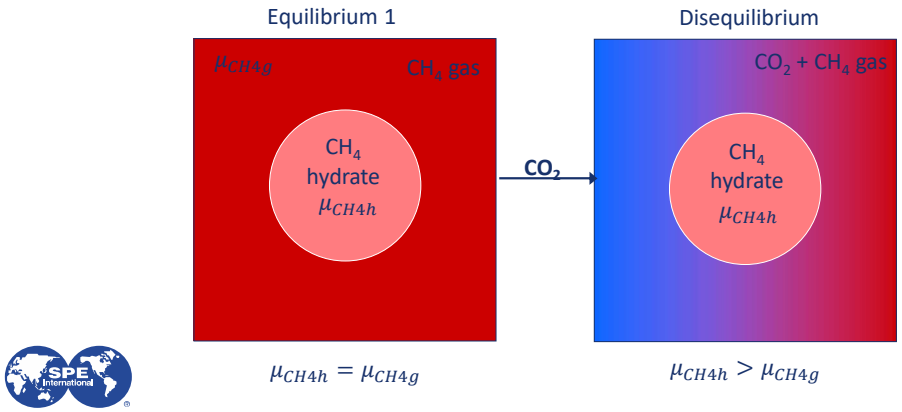


Start: sII mixed hydrate

End: sI mixed hydrate

Observations and conclusions from in situ Raman spectroscopic and X-ray diffraction measurements:

- driving force: chemical disequilibrium between hydrate phase and surrounding phase



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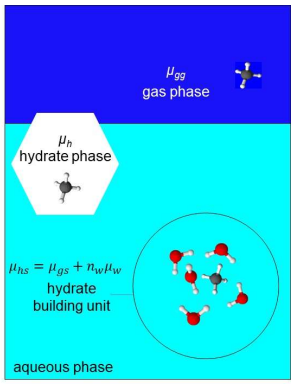
1. Long term stability: How long does the CO_2 hydrate remain stable in the natural environment?

According to Kashchiev and Firoozabadi (2002) the coexisting aqueous and gaseous phase has to be saturated with the hydrate forming gas at equilibrium state.

When the coexisting aqueous phase is undersaturated with a hydrate forming gas, the hydrate phase dissociate:



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2. Process on a molecular scale: exchange versus decomposition and reformation?

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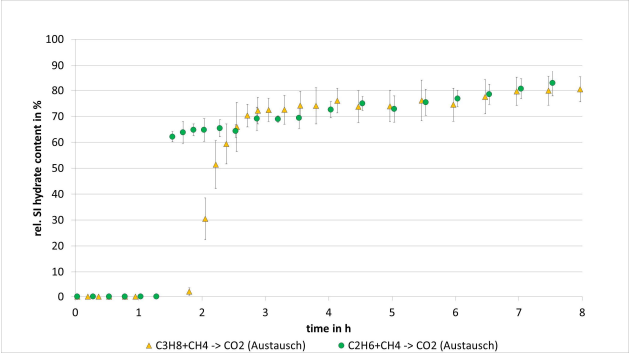
Observations and conclusions from *in situ* X-ray diffraction measurements:

- fast transformation of sII mixed gas hydrate into sI mixed gas hydrate
- initiation time depends on thermodynamic properties of initial hydrate phase
- structural change requires rearrangement of H_2O molecules: indication for decomposition and reformation process

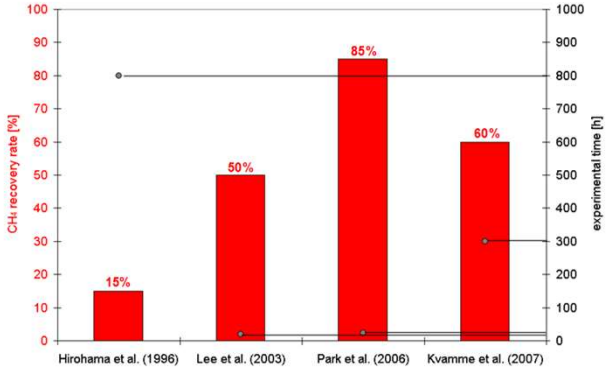


3. Efficiency: How much CH_4 will be recovered?

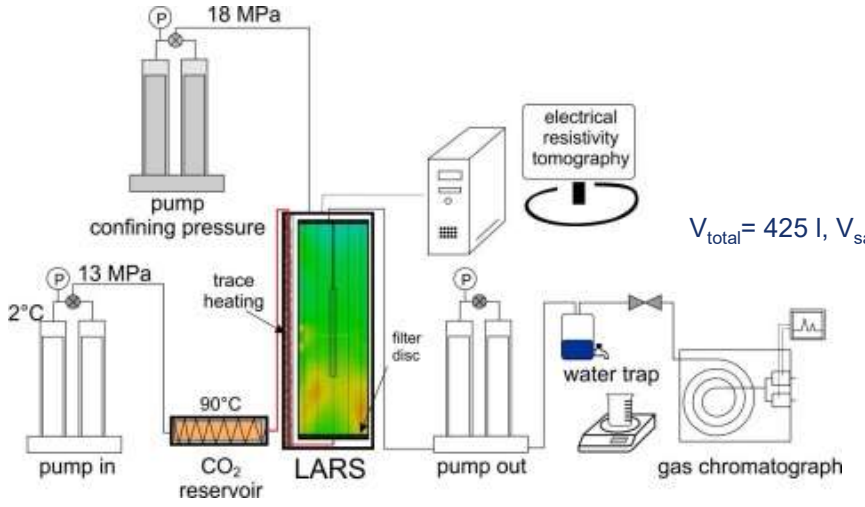
CH_4-CO_2 exchange in hydrates: four examples from literature

CH_4 recovery rate depends on:

- surface/volume ratio
- composition of the injected fluid (CO_2/N_2 versus CO_2)
- p-T-conditions (→ gaseous, liquid, or supercritical CO_2)
- Permeability of the hydrate bearing (sediment) system



3. Efficiency: How much CH_4 will be recovered?
CH_4-CO_2 exchange in hydrate bearing sediments:
Experiments in LARS – LArge scale Reservoir Simulator

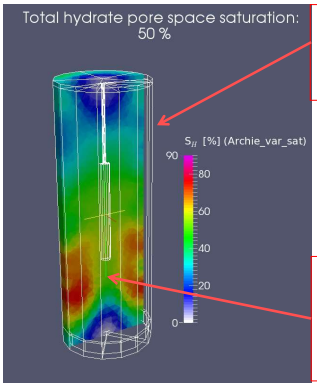


V_{total}= 425 l, V_{sample} = 210l

3. Efficiency: How much CH_4 will be recovered?
CH_4-CO_2 exchange in hydrate bearing sediments:
Experiments in LARS – LArge scale Reservoir Simulator

Starting conditions:
- ~ 50% hydrate saturation (average for both samples)
- p = 130 bar, T = 8°C

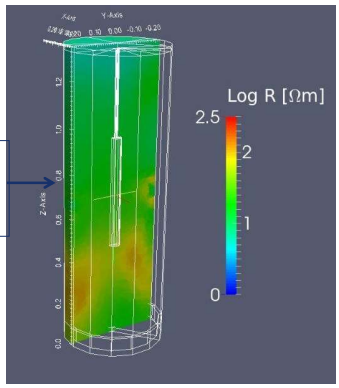
Experiment 1:



very heterogeneous hydrate distribution

„channel“ with higher permeability/less hydrate

Experiment 2:



less heterogeneous hydrate distribution, no „channel“

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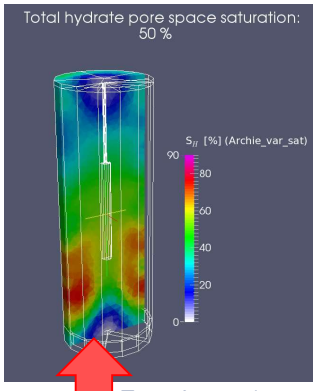
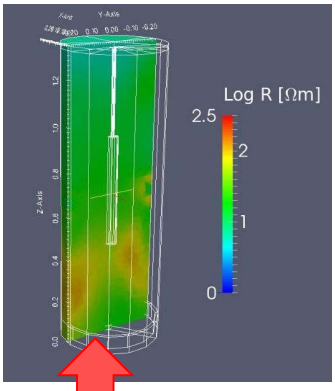
3. Efficiency: How much CH_4 will be recovered?
CH_4-CO_2 exchange in hydrate bearing sediments:
Experiments in LARS – LArge scale Reservoir Simulator



CO_2 injection

Experiment 1:
- discontinuous CO_2 injection:
- 100 g/min
- 10 kg per injection period
- 24 hours rest period between injection



CO_2 injection

Experiment 2:
- continuous CO_2 injection:
- 100 g/min
- no rest period

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Observations and conclusions from experiments in LARS

- use of $scCO_2$ avoid clogging at injection site; melting effect due to $scCO_2$ limited to vicinity of injection site
- preferred reaction of injected CO_2 with free water
- alternating CO_2 injection: formation of injected CO_2 with free pore water → clogging as a result of CO_2-hydrate formation
- continuous CO_2 injection: CO_2 follows the path of highest permeability (and thus lowest hydrate saturation): limited interaction with CH_4 hydrate → hydrate saturation and distribution and thus permeability for fluid migration crucial for efficiency of the process

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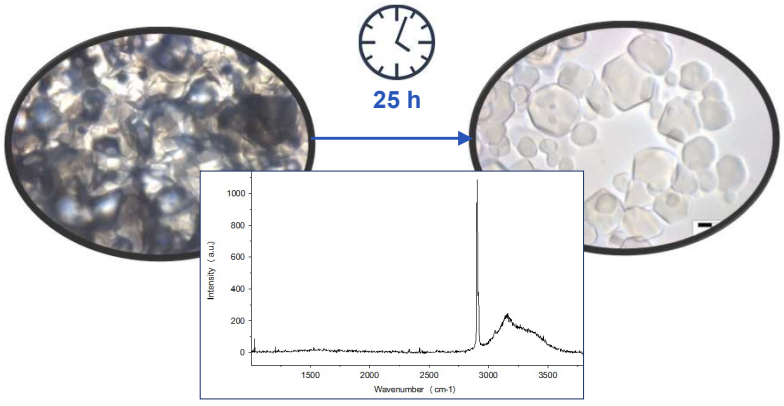
3. Efficiency: How much CH_4 will be recovered? Increasing the efficiency using CO_2-N_2 gas mixture?

Results from *in situ* Raman spectroscopic measurements

Gas composition: 23 mol% CO_2 + 77 mol% N_2
P = 6.9 MPa, T = 278 K:

- slow dissociation of CH_4 hydrate
- no formation of a mixed hydrate phase

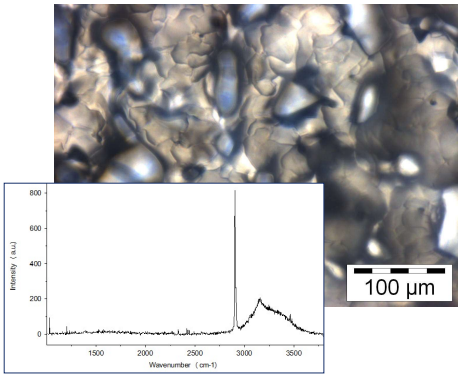


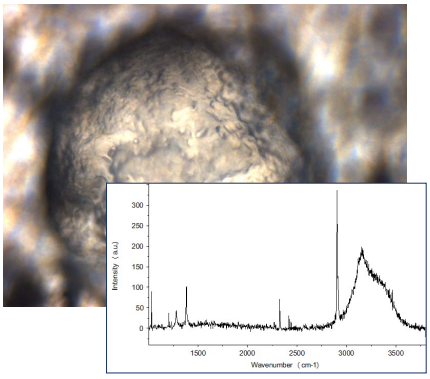
3. Efficiency: How much CH_4 will be recovered? Increasing the efficiency using CO_2-N_2 gas mixture?

Results *in situ* Raman spectroscopic measurements

Gas composition: 23 mol% CO_2 + 77 mol% N_2
P = 8.15 MPa, T = 278 K:

- slow dissociation of CH_4 hydrate (> 72 h no change in composition)
- formation of a mixed hydrate phase





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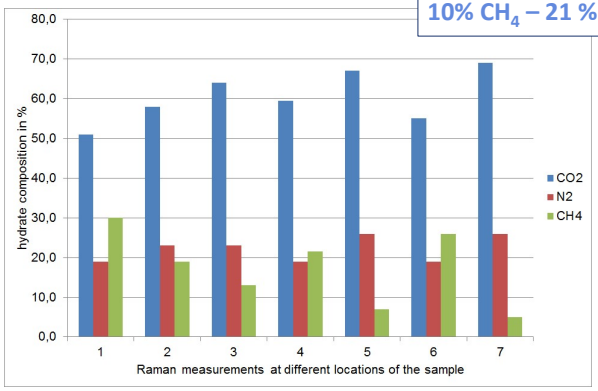
3. Efficiency: How much CH_4 will be recovered? Increasing the efficiency using CO_2-N_2 gas mixture?

Results *in situ* Raman spectroscopic measurements: composition of the secondary formed hydrate phase

Composition of gas phase: 10% CH_4 – 21 % CO_2 - 69% N_2



Observations and conclusions from *in situ* Raman spectroscopic

Depending on p-T- conditions injection of a CO_2-N_2 gas mixture results in:

- slow but continuous dissociation of the initial CH_4 hydrate phase
- the formation of a secondary mixed hydrate phase containing CH_4-CO_2-N_2
- the release of gas mixture containing mainly N_2, but also CO_2 and CH_4

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Results of selected recently published studies:

Li et al., Chemical Engineering Journal 420 (2021) 129936:

*Objective of the study: Experimental investigations of the decomposition and replacement of CH_4 with the injection of **CO_2-N_2** into hydrate bearing sediments at submarine conditions:*

- Several marine gas hydrate deposits exist under p-T conditions outside the CO_2-hydrate stability field
- Increasing hydrate saturation results in decreasing CH_4 recovery: the highest CH_4 recovery efficiency was achieved at hydrate saturation of 31.5-31.7 %

Kan et al., Energy 221 (2021) 119919:

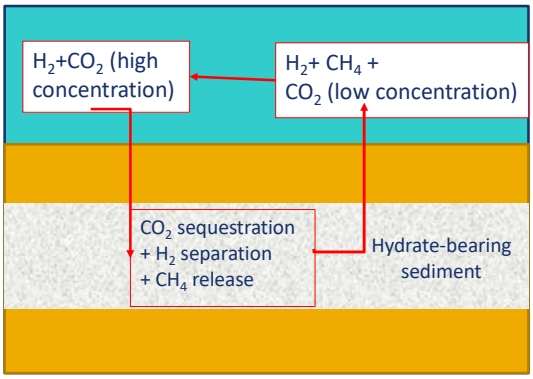
*Objective of the study: Numerical simulation of gas production applying CO_2/N_2 injection from permafrost hydrates applying **CO_2-N_2** injection* :

- Increasing N_2 mole fraction from 30% to 50% significantly enhanced the CH_4 production efficiency compared to the conventional methods, while its increase from 50% to 100% mainly resulted in higher N_2 production.
- Increasing the CO_2/N_2 ratio of the injection gas composition results in a larger CO_2 sequestration ratio
- Raising the injection pressure from 4.5 to 5 MPa improved CH_4 recovery by 1.5 times, while increase from 5 to 7 MPa reduced CH_4 recovery by 8.3%.
- Conclusion: A favorable CH_4 recovery with relatively low cost can be achieved by finding an appropriate balance between CH_4 release and CO_2 sequestration

Results of recently published investigations on CH_4 recovery from hydrate using CO_2-H_2 injection :

Sun et al. 2018 and Sun et al. 2019:
Objectives of the studies: Experimental investigations on the interactions between CH_4-hydrate and CO_2-H_2 gas mixture with respect to CH_4 release and CO_2 sequestration:

- CH_4 recovery rates 40-50%
- low mole fraction of CO_2 (22%) in the injection gas
  → higher CH_4 hydrate dissociation and CH_4 release
  → low CO_2 sequestration.
- H_2 recovery rates 70-90%
- fast breakthrough of the injected gas



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4. Long term stability: How long does the CO_2 hydrate remain stable in the natural environment?

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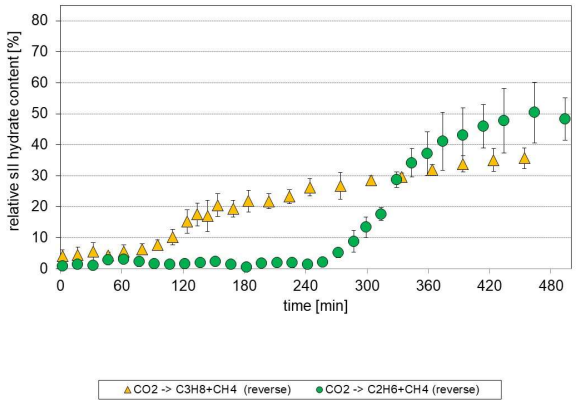
Observations and conclusions from *in situ* Raman spectroscopic and X-ray diffraction measurements:

Driving force: chemical disequilibrium
→ transformation process reversible depending on gas migration
Transformation kinetics depend on thermodynamic properties of resulting hydrate phase



CO_2 in, CH_4 out!
A useful concept for hydrates?
Summery and Conclusions

- Driving force: chemical disequilibrium between hydrate phase and environment
- Transformation kinetics depends on:
  - the thermodynamic properties of the hydrate phase
  - surface-to-volume ratio of the hydrate crystals
- Process is characterized by (partial) decomposition of the initial hydrate phase and re-formation of the (new) hydrate structure
- CH_4 recovery rate depends on:
  - surface/volume ratio
  - composition of the injected fluid
  - p-T-conditions
  - hydrate saturation and distribution (permeability) of the hydrate bearing sediment system
- Process is reversible

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Further reading:

- Heeschen, K., Deusner, C., Spangenberg, E., Priegnitz, M., Kossel, E., Strauch, B., Bigalke, N., Luzi-Helbing, M., Haeckel, M., Schicks, J. (2021): Production Method under Surveillance: Laboratory Pilot-Scale Simulation of CH_4–CO_2 Exchange in a Natural Gas Hydrate Reservoir. - Energy & Fuels, 35, 13, 10641-10658.
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- Kvamme B, Graue A, Buanes T, Kuznetsova T, Ersland. (2007) Storage of CO_2 in natural gas hydrate reservoirs and the effect of hydrate as an extra sealing in cold aquifers. Int. J. Greenhouse Gas Control 1:236–246.
- Lee H, Seo Y, Seo YT, Moudrakovski IL, Ripmeester JA (2003) Recovering Methane from Solid Methane Hydrate with Carbon Dioxide. Angew. Chemie Int. Ed., 42:5048–5051.
- Pan, M., Ismail, N. A., Luzi-Helbing, M., Koh, C. A., Schicks, J. (2020): New Insights on a µm-Scale into the Transformation Process of CH4 Hydrates to CO2-Rich Mixed Hydrates. - Energies, 13, 22, 5908.
- Park Y, Kim D-Y, Lee J-W, Huh D-G, Park K-P, Lee J, Lee H (2006) Sequestering carbon dioxide into complex structures of naturally occurring gas hydrates. Proc Natl Acad Sci U S A 103(34):12,690–12,694.
- Schicks, J., Strauch, B., Heeschen, K., Spangenberg, E., Luzi-Helbing, M. (2018): From Microscale (400 µl) to Macroscale (425 L): Experimental Investigations of the CO_2/N_2-CH_4 Exchange in Gas Hydrates Simulating the Iġnik Sikumi Field Trial. - Journal of Geophysical Research, 123, 5, 3608-3620.
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