

A clean solution? - The potential and limitations of the CH₄-CO₂ exchange in gas hydrates

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Natural gas hydrates occur at all active and passive continental margins and are supposed to contain tremendous amounts of methane (CH₄), which makes them attractive as a potential source of energy. During the last two decades several methods have been developed and tested to produce CH₄ from gas hydrates in lab experiments and field trials. In principle, three different approaches, namely thermal stimulation, depressurization, and chemical stimulation have been tested (Dallimore and Collett, 2005; Yamamoto et al., 2014; Boswell et al., 2017). The chemical stimulation via injection of carbon dioxide (CO₂) into hydrate-bearing sediments appears to be particularly favorable because it combines the production of CH₄ from the hydrate reservoir with the simultaneous encasement of CO₂ in the clathrate phase and, thus, the safe storage of CO₂ as a solid phase. The expected exchange of CH₄ with CO₂ molecules in the hydrate phase seemed to permit a more or less carbon neutral usage of hydrate bonded CH₄. During the last decades several experimental and modeling studies focused on this approach, but depending on the chosen scale and experimental conditions the results differ substantially (e.g. Zhao et al., 2012, and literature within). It is generally accepted that the driving force for the transformation of pure CH₄-hydrate into CO₂-CH₄ mixed hydrate when exposed to a CO₂ phase is the chemical disequilibrium between hydrate phase and the environment; however, some other issues related to the process are still under discussion:

- Recrystallization versus diffusion: how does the exchange process of the CH₄ molecules with CO₂ molecules proceed on a molecular level?
- Kinetics versus thermodynamics: what are the relevant factors affecting the efficiency of the process?
- Clean versus contaminated: what effects do additional components and impurities have on the transformation process?
- Permeability versus clogging: how can the undesired formation of CO₂ hydrate with free pore water at the injection well be avoided?
- Safe storage versus throughput: how safe is the storage of CO₂ as CO₂ hydrate in natural environment?

During the last decade we performed experiments on different scales, varying from micro (250 µl) to pilot plant scale (425 L) to investigate the above mentioned issues.

Microscale experiments:

For the investigation of the replacement process of hydrate-bonded CH₄ with CO₂ on a molecular level, we performed time-resolved *in situ* Raman spectroscopic measurements combined with microscopic observations exposing a CH₄ hydrate to a CO₂ gas phase at 3.2 MPa and 274 K. The measurements were performed continuously at defined depth from the surface into the core of several hydrate crystals. The results clearly indicate the incorporation of CO₂ into the hydrate phase with a concentration gradient from the surface to the core of the hydrate particle (Figure 1).

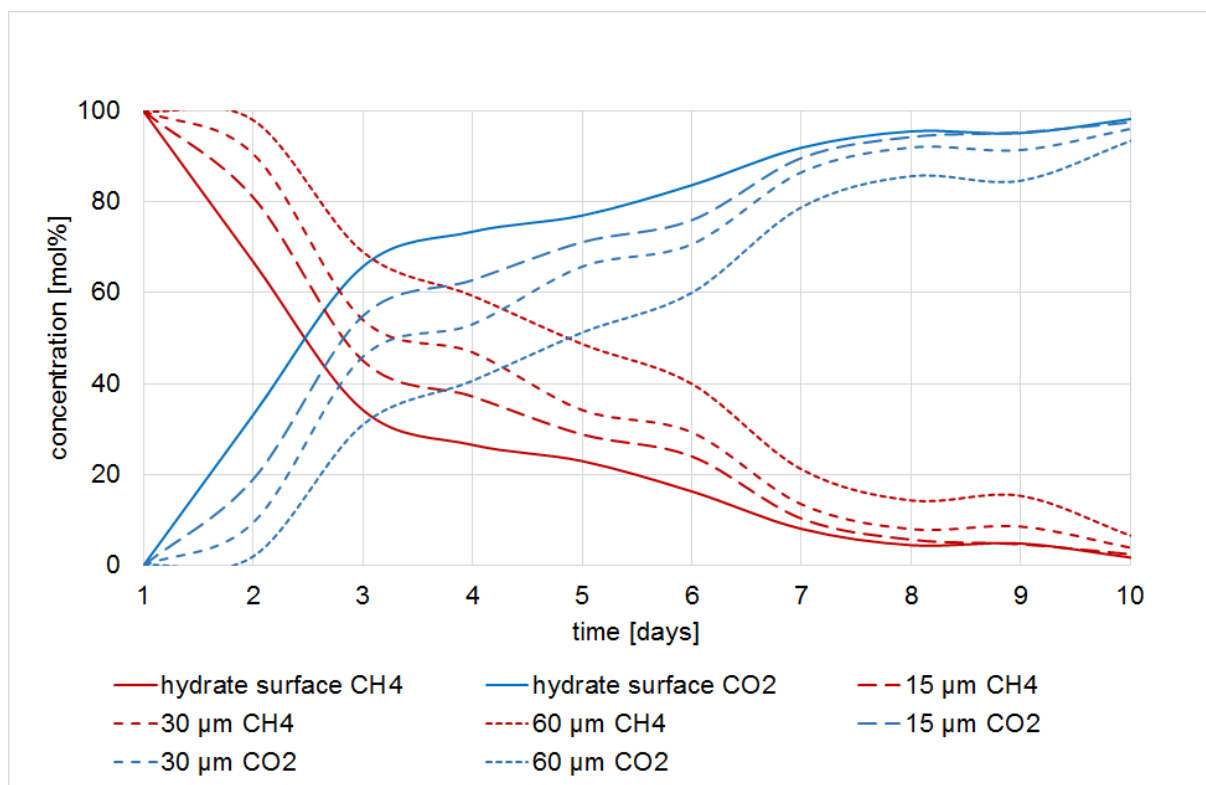


Figure 1: Changes of the average composition in mol% of the hydrate phase at defined depth (from surface to 60 m depth) over time after the initial CH₄ hydrate was exposed to a CO₂ gas phase.

Therefore, our experimental results generally support the hypothesis of the shrinking-core model discussed by e.g. Lee et al. (2014) and Falenty et al. (2016). However, it is still under discussion if the incorporation of CO₂ into the hydrate layer comes along with the dissociation of CH₄ hydrate (e.g. Ota et al., 2005), the re-arrangement of the water molecules (Schicks et al., 2011) or the diffusion of the molecules in the hydrate phase through “holes-in-the-cages” (Falenty et al., 2016). Microscopic observations during the measurements give no indication for the formation of a CO₂ hydrate layer on the surface of the hydrate particle. The slow reaction rate indicates a diffusion controlled process. The observation of growing hydrate crystals with distinct crystal surfaces and a mixed composition containing CO₂ and CH₄ indicate the ongoing formation of hydrate rather than the exchange of molecules in already existing cavities.

We also performed time resolved Raman spectroscopic and X-ray diffraction measurements for structure II CH₄-C₂H₆ and CH₄-C₃H₈ mixed hydrates which were exposed to a CO₂ gas phase. The results clearly show the transformation of the initial structure II mixed hydrates to a CO₂-rich structure I hydrate, containing CH₄ besides CO₂ in the hydrate phase. For this transformation of a structure II hydrate into a structure I hydrate the re-arrangement of the water molecules is indispensable because the type of cavities as well as the ratio of small-to-large cavities is different in both structures (Schicks et al., 2011). Interestingly, the structural change results in a faster CO₂ incorporation compared to the exchange or transformation process observed when a pure CH₄ hydrate was exposed to a CO₂ gas phase (Figure 2, Beeskow-Strauch and Schicks, 2012). The results also indicate that the presence of impurities in the CO₂ gas phase, such as SO₂, enhance the conversion rate. However, when discussing the safe storage of CO₂ as gas hydrates it should be noted that our experiments also show that the exchanges of hydrate-bonded hydrocarbons with CO₂ are a reversible process. This is an expected outcome because the system always wants to achieve an equilibrium state between the hydrate phase and the environment and, thus, the composition of hydrate phase adapt to the chemical environment.

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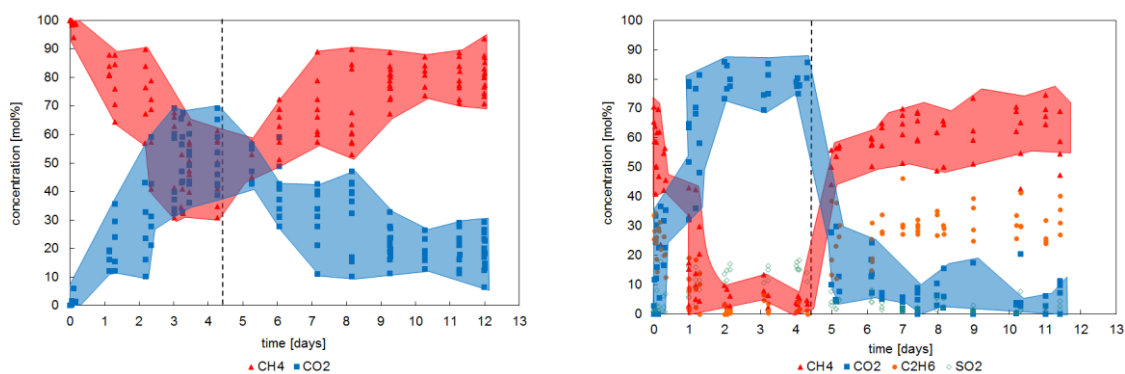


Figure 2, left: Changes in composition of the hydrate phase after the initial CH₄ hydrate was exposed to a CO₂ gas phase for about 4.5 days (black dotted line) and subsequent exposure of the mixed hydrate to CH₄ again. Figure 2, right: Changes in composition of the hydrate phase after the initial CH₄-C₂H₆ hydrate was exposed to a CO₂-SO₂ gas phase for about 4.5 days (black dotted line) and subsequent exposure of the mixed hydrate to the CH₄-C₂H₆ gas mixture again.

Macroscale experiments:

When CO₂ is injected into a host sediment containing natural gas hydrates the free pore brine tends to form CO₂ hydrate inducing clogging at the injection well. This could be shown in our experiments performed in our Large Scale Reservoir Simulator LARS with a total volume of 425 l. LARS is equipped with several pressure and temperature sensors as well as an electrical resistivity tomography (ERT) and the released and produced gas phase can be analyzed via gas chromatography. A detailed description of LARS can be found elsewhere (Spangenberg et al., 2015). The ERT enables us to calculate the amount of gas hydrate and visualize its distribution since gas hydrates have a high electrical resistivity compared to brine. Our experiments with LARS clearly indicate the formation of a CO₂ hydrate phase with residual brine in the sediment pores resulting in a local blockage of the CO₂ flow when the pressure and temperature conditions are within the CO₂ hydrate stability field. To avoid this, a gas mixture containing N₂ besides CO₂ (e.g. 23 mol% CO₂ and 77 mol % N₂) was used in the Ignik Sikumi Field Trial (Boswell et al. 2017). Our experiments in LARS and also at smaller scales show that depending on the p-T conditions the usage of this mixture primarily results in the decomposition of the initial natural gas hydrate and not in a transformation to a CO₂-rich hydrate phase (Schicks et al., 2018).

In summary, the results of our experiments at different scales show that the efficiency of the complex interaction of CO₂ with a natural gas hydrate phase appears to be questionable with respect to reaction kinetics and conversion rate as well as safe storage on a long term perspective.

Beeskow-Strauch, B., Schicks, J., 2012. The driving forces of guest substitution in gas hydrates - A laser Raman study on CH₄-CO₂ exchange in the presence of impurities. *Energies*, 5, 420-437.

Boswell, R., Schoderbek, D., Collett, T. S., Ohtsuki, S., White, M., & Anderson, B. J., 2017. The Ignik Sikumi Field Experiment, Alaska North Slope: Design, operations, and implications for CO₂-CH₄ exchange in gas hydrate reservoirs. *Energy & Fuels*, 31, 140–153.

Dallimore, S. R., & Collett, T. S. (2005). Summary and implications of the Mallik 2002 gas hydrate production research well program. *Scientific results from Mallik 2002 gas hydrate production research well program, Mackenzie Delta Northwest Territories, Canada; Geological Survey of Canada, Natural Resources Canada: Ottawa, Ontario, Canada.*

Falenty, A., Qin, J., Salamatin, A.N., Yang, L., Kuhs, W. F., 2016. Fluid Composition and Kinetics of the in situ Replacement in CH₄-CO₂ Hydrate System. *J. Phys. Chem. C*, 120, 27159–27172.

- Lee, B.R., Koh, C. A., Sum, A. K., 2014. Quantitative measurement and mechanisms for CH₄ production from hydrates with the injection of liquid CO₂. *Phys.Chem.Chem.Phys.*, 16, 14922-14927.
- Ota, M., Abe, Y., Watanabe, M., Smith Jr., R. L., Inomata, H., 2005, Methane recovery from methane hydrate using pressurized CO₂, *Fluid Phase Equilibria*, 228–229, 553–559.
- Schicks, J., Luzi, M., Beeskow-Strauch, B., 2011. The Conversion Process of Hydrocarbon Hydrates into CO₂ Hydrates and Vice Versa: Thermodynamic Considerations. *J. Phys. Chem. A*, 115, 13324-13331.
- Schicks, J., Strauch, B., Heeschen, K., Spangenberg, E., Luzi-Helbing, M., 2018. From Microscale (400 µl) to Macroscale (425 L): Experimental Investigations of the CO₂/N₂-CH₄ Exchange in Gas Hydrates Simulating the Iġnik Sikumi Field Trial. *J. Geophys. R.*, 123, 3608-3620.
- Spangenberg, E., Priegnitz, M., Heeschen, K., Schicks, J., 2015. Are Laboratory-Formed Hydrate-Bearing Systems Analogous to Those in Nature? *J. Chem. Eng. Data*, 60, 258-268.
- Yamamoto, K., Terao, Y., Fujii, T., Ikawa, T., Seki, M., Matsuzawa, M., Kanno, T., 2014. Operational overview of the first offshore production test of methane hydrates in the Eastern Nankai Trough. *Proceedings of the Offshore Technology Conference; Houston, TX, May 5–8, 2014.*
- Zhao, J., Xu, K., Song, Y., Liu, W., Lam, Y., Liu, K., et al., 2012. A review on research on replacement of CH₄ in natural gas hydrates by use of CO₂. *Energies*, 5(2), 399–419.

Presenter CV:

Judith M. Schicks studied chemistry at the Gerhard-Mercator University Duisburg, Germany, and completed her PhD in physical chemistry in 1999. After she received a scholarship of the Max Planck Society for 15 month she joint GFZ in 2001 and participated at the first gas hydrate production field trial in Mallik, Canada, in winter 2001/2002. Since 2007 she is the head of the gas hydrate research group at GFZ and since 2014 Privatdozentin at the University of Potsdam.

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