

From micro to macro: Experimental investigations of the CO₂/N₂-CH₄ exchange process in gas hydrates under conditions similar to the Ignik Sikumi Field Trial in different scales

Judith M. Schicks^{1,*}, B. Beeskow-Strauch¹, E. Spangenberg¹, K. Heeschen¹, M. Luzi-Helbing¹

¹GFZ German Research Centre for Geosciences, Telegrafenberg, 14473 Potsdam, Germany

*Corresponding author: schick@gfz-potsdam.de

Abstract

Since vast amounts of CH₄ are assumed to be bound in hydrate-bearing sediments worldwide, natural gas hydrates are considered as a potential future energy resource. For the production of CH₄ from hydrate reservoirs different approaches such as depressurization, thermal and chemical stimulation have been tested in laboratory studies and field trials. Using the injection of CO₂ into the hydrate-bearing sediments as a chemical stimulation method appears to be particularly favorable because it combines the release of CH₄ from the hydrate phase with the storage of CO₂ as a solid hydrate. Therefore, several experimental and modelling studies in the last decade focused on this approach showing that the injection of pure CO₂ into the hydrate bearing-sediments under conditions within the hydrate stability field may lead to an undesired formation of simple CO₂ hydrate with free pore water causing a permeability decrease. To preserve the injectivity by avoiding the formation of CO₂ hydrate with pore water in the near-well region a mixture containing 77 mol% N₂ and 23 mol% CO₂ was chosen for the Ignik Sikumi Field Trial in Alaska, U.S.A., in 2012. The field observations were interpreted to show the formation of secondary mixed hydrates and concurrent CH₄ release from primary gas hydrates.

Within the German gas hydrate project SUGAR we tested the production of CH₄ from hydrate bearing sediments using the same gas mixture (N₂:77 mol%, CO₂: 23 mol%) and conditions close to the Ignik Sikumi Field Trial in different scales. The volumes of the sample cells varied from 393 µl for the *in situ* Raman spectroscopic measurements to 210 l of the Large Scale Reservoir Simulator LARS. Pressure and temperature conditions were chosen following the observed conditions during the Ignik Sikumi Field Trial in Alaska. Here, the injection pressure was about 9.8 MPa while the reservoir pressure was 6.9 MPa. It is very likely that the pressure within the reservoir during the injection period and the time needed for the changeover from injection to production varied between 6.9 MPa and 9.8 MPa depending on the distance from the injection hole and the permeability of the reservoir. This assumption is supported by the observation that the bottom-hole pressure dropped from 9.8 MPa to 8.27 MPa during the four days needed for the changeover from injection to production. Therefore, we conducted a series of measurements at different pressures between 6.9 MPa and 9.8 MPa at 278 K (reservoir temperature).

In situ Raman spectroscopic measurements:

Within the *in situ* Raman spectroscopic measurements we formed CH₄ hydrate from 150 µl deionized water placed into the pressure cell and pure CH₄. The experimental set-up for the *in situ* Raman spectroscopic measurements facilitates a continuous gas flow of 1 ml/min. The gas flow assures that the gas phase will be exchanged continuously during the experiment. Although a continuous gas flow was used throughout the whole experiment, the chosen pressure was kept constant. Care was taken that the incoming gas was cooled down before entering the sample cell in order to enable an isothermal experiment. The CH₄ hydrate formation took place over several days until Raman spectra indicated that the water phase was completely converted into CH₄ hydrate. At that point the gas phase was changed to the CO₂-N₂ gas mixture. Changes regarding the composition of the gas and the hydrate phase were continuously detected by Raman spectroscopy. At 6.9 MPa and 278 K we observed the dissociation of the CH₄ hydrate phase within 26 hours. The composition of the (CH₄) hydrate phase remained without any changes until it was dissociated. No formation of any other hydrate phase was observed. When the chosen pressure was ≥8.1 MPa we observed the formation of new hydrate crystals containing CO₂, N₂ and CH₄ besides the CH₄ hydrate phase. After three days the primary CH₄ hydrate still coexisted besides CO₂-N₂-CH₄ mixed hydrates. However, microscopic observations indicate that the amount of CH₄ hydrate decreased in favor of the growing mixed hydrate phase.

Ex situ Raman spectroscopic and X-ray diffraction measurements

For the *ex situ* Raman spectroscopic and X-ray diffraction measurements we prepared ice from deionized water sprayed in liquid nitrogen. 100-130 ml ice or a mixture of 100 ml sand and 30 ml ice were placed in a pressure vessel and pressurized with CH₄ (9.0 – 11.0 MPa). The pressure vessels were placed in a freezer at 268K. A pressure drop indicated the formation of CH₄ hydrate. After several weeks the gas phase was exchanged by releasing CH₄ and pressurizing the vessel with the CO₂-N₂ gas mixture (8.08-8.27 MPa). The vessels were placed into a cooler at 278 K for 48 h. Upon opening the pressure vessels we observed that no hydrate remained in those vessels which were loaded at the beginning with pure ice. The sample containing sediments was quenched in liquid nitrogen and analyzed. There was also no indication for the existence of hydrate in the sediment matrix.

Experiments in LARS

LARS is equipped with several temperature and pressure sensors and an electrical resistivity tomography (ERT), which allows for the determination of the hydrate saturation in the sandy sediment. CH₄ hydrate was formed from CH₄ saturated water before the CO₂-N₂ gas mixture was injected. The produced gas was analyzed by gas chromatography. The results indicate that CH₄ was released from the hydrate phase: similar to the Ignik Sikumi Field Trial the first flush of the “unassisted” produced gas contained about 35 mol% CH₄, 50 mol% N₂ and 12 mol% CO₂. No significant secondary hydrate formation could be detected.

Conclusions

The results of our experiments indicate that the interactions between the CO₂-N₂ gas mixture and CH₄ hydrate phase strongly depend on the pressure condition at given temperature. At lower pressures (about 6.9 MPa) the interaction of the CH₄ hydrate phase with a gas mixture containing 23 mol% CO₂ and 77 mol% N₂ results in the dissociation of the CH₄ hydrate phase. At higher pressures (≥ 8.1 MPa) the changes of the gas phase induces a slow dissociation of the CH₄ hydrate and the formation of a secondary mixed hydrate phase containing CO₂ and N₂ besides CH₄. During the Ignik Sikumi Field Trial the injection of the CO₂-N₂ mixture probably induced manifold processes: the dissociation of CH₄ hydrate as well as the formation of a mixed hydrate from free pore water and/or water released due to the CH₄ hydrate dissociation.