TECHNICAL ASPECTS OF GAS HYDRATE CONVERSION AND SECONDARY GAS HYDRATE FORMATION DURING INJECTION OF SUPERCRITICAL CO_2 INTO CH_4-HYDRATE-BEARING SEDIMENTS

Christian DEUSNER[*], Nikolaus BIGALKE, Elke KOSSEL, Matthias HAECKEL
GEOMAR Helmholtz-Zentrum für Ozeanforschung Kiel, Wischhofstr.1-3, 24148 Kiel, GERMANY

ABSTRACT

The injection of CO_2 into CH_4-hydrate-bearing sediments has the potential to drive natural gas production and simultaneously sequester CO_2 by hydrate conversion. Currently, process conditions under which this goal can be achieved efficiently are largely unknown. While the recent *Ignik Sikumi* field test suggests that a combination of N_2/CO_2 injection with depressurization yields effective CH_4 production, in a previous study (Deusner et al., 2012) we showed that a combination of CO_2 injection and thermal stimulation eliminates mass transfer limitations observed at cold reservoir temperatures. These high-pressure flow-through studies revealed that the injection of supercritical CO_2 at 95 °C triggers dissociation of CH_4-hydrates and counters rapid CO_2-hydrate formation in the near-injection region. We also observed a strong effect of reservoir temperature on CH_4 production and CO_2 retention. The efficiency and yield of CH_4 production was highest at a sediment temperature of 8 °C compared to 2 °C and 10 °C. At 2 °C CO_2 hydrate formation was rapid and clogged the sediment at the injection spot. Outside the CO_2-hydrate stability region, at 10 °C, we observed fast CO_2 breakthrough and a comparably low CH_4 production. Experiments comparing discontinuous and continuous CO_2 injection showed that alternating periods of equilibration and CO_2 injection improved the overall CH_4 production. We hypothesize that slow formation of secondary CO_2-rich hydrate improves the accessibility of the CH_4-hydrate distributed in the sediment by locally changing permeability and fluid flow patterns. In situ measurements showed dynamic changes of local p-/T-gradients due to gas hydrate dissociation or dissolution and secondary gas hydrate formation. In addition, continued reconfiguration of guest molecules in transiently formed mixed hydrates maintain elevated gas exchange kinetics. Online effluent fluid analysis under in-situ pressure conditions indicated that CH_4 released from CH_4-hydrates is largely dissolved in liquid CO_2.. It is a current objective of our studies to further elucidate rheological properties and gas exchange efficiencies of CO_2-CH_4 mixed fluids that approach equilibrium with gas hydrates and to study the effect of in situ CH_4-CO_2-hydrate conversion and secondary gas hydrate formation on sediment geomechanical parameters.

Keywords: CO_2 injection, hydrate conversion, chemical activation, supercritical CO_2, gas hydrate reservoir, CH_4 production

[*] Corresponding author: Phone: +49 431 600 1415 Fax +49 431 600 1400 E-mail: cdeusner@geomar.de

INTRODUCTION

The combination of CH_4 production from submarine gas hydrate reservoirs with CO_2 injection attracted considerable research interest in recent years because of the vision of emission neutral energy production via a gas hydrate conversion process substituting CH_4 with CO_2 within the gas hydrate structure. With the current state of technology, the strategy to use in situ CH_4-CO_2-hydrate conversion as the driving force for CH_4 production is only one method amongst others and needs to be tested and validated against other strategies based on depressurization or thermal stimulation.

Currently, reservoir depressurization appears to be the method of choice for future CH_4 production from gas hydrate reservoirs, and depressurization was chosen as the basis for the first marine gas hydrate production field test in the Nankai Trough offshore Japan in 2013 [1]. However, gas production through depressurization comes with a number of unsolved problems. Among these problems are reservoir cooling as a consequence of gas hydrate dissociation, as well as water and sand production due to permeability changes resulting from a decrease in initial gas hydrate saturation, substantial pressure gradients and fluid flow induced drag forces. Currently, it is questionable if natural gas production from marine hydrates can be achieved through depressurization on longer time scales relevant for industrial production without combination with other technical measures such as thermal stimulation or chemical activation.

Thus, provided that reservoir p-/T-conditions are suitable for formation of CO_2-hydrate, a combination of CO_2 injection with CH_4 production might be beneficial, since the injection of CO_2 is an additional driving force for hydrate exchange, and the exothermic CO_2-CH_4-hydrate exchange reaction and secondary gas hydrate formation could counteract reservoir cooling.

In the *Ignik Sikumi* field test in the Alaska permafrost CO_2 was injected Huff'n Puff style [2]. To avoid CO_2-hydrate formation near the borehole, resulting in clogging of formation pore space and potential failure of the field test, 77 mol-% N_2 was added to the injected CO_2. As an alternative strategy to the injection of mixed N_2:CO_2 we recently successfully tested the injection of heated supercritical CO_2 to avoid CO_2-hydrate formation near the injection point [3].

This study has further shown that the overall production of CH_4 from gas hydrates can be improved and accelerated. Since the injection of heated supercritical CO_2 can be regarded as a combination of chemical activation and thermal stimulation, CH_4 is released both from hydrate dissociation and CH_4-CO_2-hydrate conversion. The effluent showed high initial CH_4 concentrations, which expectedly decreased relative to CO_2 concentration over time. However, it was not possible to analyze fluid composition prior to depressurization. Whether CH_4 is transported as a free gas phase or as solute in CO_2 is currently not known. Knowledge about the in situ fluid composition is important to constraining the composition and thermodynamic characteristics of the remaining hydrates and to predicting process efficiency on larger scales.

Here we continue our earlier studies and apply various high-pressure flow-through experimental systems together with online and in situ monitoring techniques to better understand multiphase fluid flow characteristics and dynamics of CH_4-hydrate dissociation, CH_4-CO_2-hydrate conversion and secondary CO_2- or mixed hydrate formation. We focus on results from (1) investigation of various CO_2 injection strategies, (2) online analysis of high-pressure multiphase fluid composition and (3) analysis of hydrate conversion kinetics on different scales.

MATERIALS AND METHODS

High-pressure flow-through experiments

Continuous flow-through experiments were carried out in a custom-made high pressure apparatus (NESSI, **N**atural **E**nvironment **S**imulator for **S**ub-seafloor **I**nteractions, Fig. 1, [3]. All wetted parts of the set-up are made of stainless steel, titanium or PEEK. Experiments were carried out in upflow mode with continuous injection of CO_2 at flow rates between 0.5 and 5 ml/min at the bottom of the sample vessel. CO_2 was supplied with a piston pump (Teledyne ISCO, Lincoln NE, USA) and heated to 95 °C inside a temperature controlled conditioning chamber prior to injection into the sample vessel. Flow was controlled by the high-pressure pumps that supplied the fluids. Pressure was adjusted with a back-pressure regulator valve (TESCOM Europe, Selmsdorf, Germany). Pressure was monitored in the influent and the effluent fluid streams and at 3 different positions inside the pressure vessel (Fig. 1). In situ

pressure measurements were carried out with autonomous pressure-temperature sensors (DST-centi TD data loggers, Star-Oddi, Iceland). Experiments were carried out at constant temperature conditions. Temperature control was achieved with a thermostat system (Huber, Offenburg, Germany). The sediment samples were prepared at −20 °C from a homogeneous mixture of quartz sand (grain size 0.1–0.6 mm, G20TEAS, Schlingmeier, Schwülper, Germany) and fine grained ice particles (grain size fraction 0.3–1.0 mm, deionized water) as described previously [3]. The sample mixture consisting of approximately 1400 g of quartz sand and 275 g of ice was filled into a sample bag made of PTFE cloth and was placed inside a stainless steel pressure vessel which was cooled to −7 °C. The pressure vessel was then pressurized with CH_4 gas to 13 MPa. To accelerate hydrate formation, water availability was increased by freezing-thawing cycles from −7 °C to +2 °C in a procedure similar to [4]. After completion of CH_4-hydrate formation and prior to CO_2-injection the remaining CH_4 gas was replaced by seawater medium via rapid depressurization and water flushing. Water saturation was confirmed by monitoring pressure evolution for at least 24 h after water flushing. The absence of pressure changes during this period indicated that no free CH_4 gas was available for further CH_4-hydrate formation.

On-line continuous analysis of the fluid composition was done with Raman spectroscopy using custom made high-pressure flow-through cells (Fig. 3) attached to a Horiba Jobin Yvon iHR320 Imaging Spectrometer. The sample fluid was excited in intervals of 120 s using a 125 mW 532 nm Nd:YAG Laser. Raman intensities were derived by fitting Pseudo-Voigt profiles to the $2\nu_2$ and ν_1 bands of the symmetric stretching vibrations of the CO_2 and CH_4 molecules, respectively. Due to unchanging p-/T-conditions in the cells throughout the experiment, phase-specific peak areas were assumed to be proportional to the concentration of the respective component. The flow-through cells were coupled in pairs and mounted in opposite direction with respect to gravity (Fig. 2). The fluid composition was additionally analyzed by gas chromatography from the bulk effluent after expansion into gas-tight Tedlar™ bags.
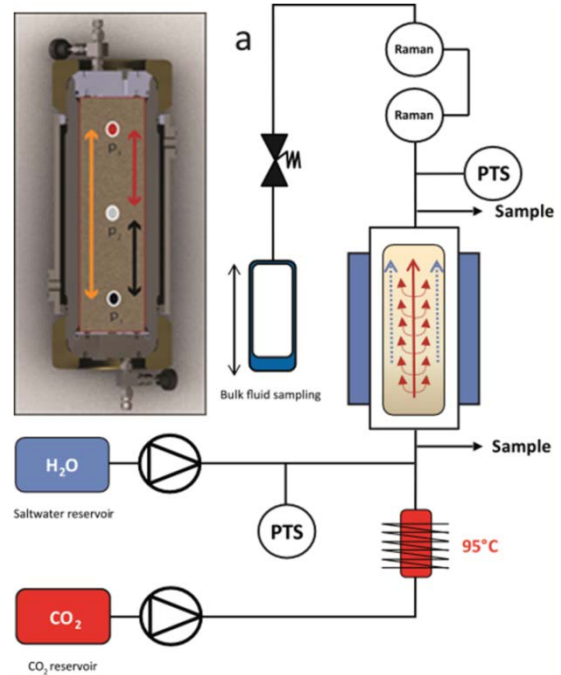

Figure 1.
Scheme of the experimental setup for flow-through experiments with the high-pressure apparatus NESSI [3] and cross section of the pressure vessel filled with a sediment sample. Locations of in-situ P-loggers within the sediment as indicated by $P_1 – P_3$.
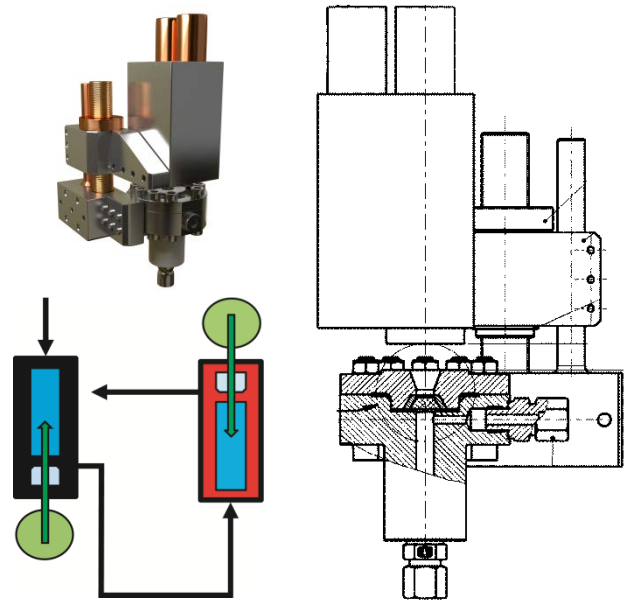

Figure 2.
The stainless steel flow-through cells have an approximate volume of 2.3 mL. The fluid composition was analyzed by focusing the Raman laser through a sapphire glass window into the sample fluid.

RESULTS AND DISCUSSION

CO$_2$-injection strategy

It was previously shown that the discontinuous injection of heated supercritical CO$_2$ with alternating injection flow periods and no-flow equilibration periods accelerates CH$_4$ release from CH$_4$-hydrates and results in CH$_4$ proportions peaking at 65.2% of the released gas mixture [3]. The comparison with continuous injection at comparable injection mass and volume flow rates now revealed that discontinuous injection yields substantially higher CH$_4$ production efficiencies than continuous injection (Fig. 3).
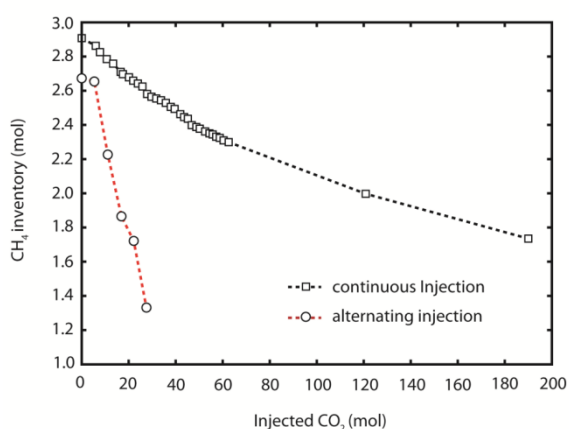

Figure 3.
Total CH$_4$ inventory in pressure vessel during continuous and discontinuous injection of supercritical CO$_2$ at 13 MPa and 8 °C.

Equilibration periods as part of a discontinuous injection strategy lead to higher hydraulic retention times of CO$_2$ and ongoing enrichment of CH$_4$ in the production bulk fluid. As revealed by comparison of production efficiencies at different reservoir temperatures of 2 °C, 8 °C and 10 °C, the formation of secondary CO$_2$ or CO$_2$-CH$_4$-mixed hydrates contributes to the increase in CH$_4$ production efficiency [3]. At reservoir temperatures of 2 °C and 8 °C the formation of both pure CO$_2$-hydrate and mixed CO$_2$-CH$_4$-hydrates is thermodynamically feasible. At 2 °C, CO$_2$-hydrate formation appeared to be fast under the experimental conditions and resulted in a reduction of permeability and irreversible clogging of fluid pathways. However, at 8 °C clogging of fluid pathways was not observed and CH$_4$ production efficiency was substantially higher than at 10 °C outside the stability region of pure CO$_2$-

hydrate. Also, at 10 °C, the effluent CO$_2$ concentration was higher than at lower temperatures and CO$_2$ breakthrough occurred earlier.

Our results suggest that the flow-controlled injection of heated supercritical CO$_2$ is advantageous over the injection of cold CO$_2$ and clogging of fluid pathways can be avoided. This shows that the injection of supercritical CO$_2$ is a suitable strategy to avoid problems from rapid CO$_2$-hydrate formation in the near-borehole region and thus offers a technical alternative to injection of N$_2$-CO$_2$ gas mixtures such as applied in the *Ignik Sikumi* field test [2]. A further advantage of pure CO$_2$ injection is that CO$_2$ can be delivered at a higher density, and that CH$_4$-CO$_2$-hydrate conversion and secondary hydrate formation dynamics might be better constrained in the absence of an additional compound N$_2$, which also participates in gas hydrate formation under relevant pressure-temperature conditions.

Local and temporal permeability changes

In situ pressure measurements during continuous injection of heated supercritical CO$_2$ further resolved the pressure gradient over the sample length with highest absolute pressure in the region of CO$_2$ injection and lowest absolute pressure downstream, near the effluent port in the upper part of the sample vessel (Figs. 1, 4).
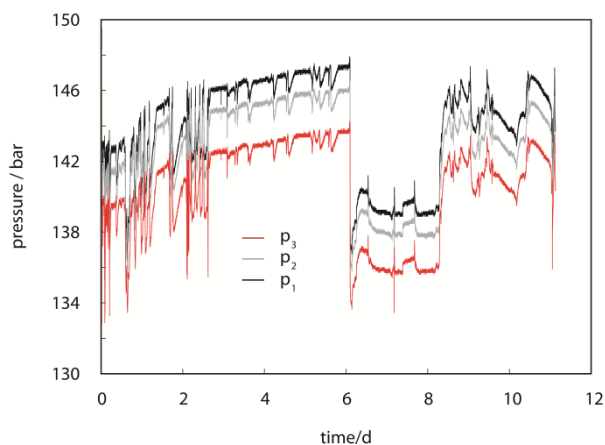

Figure 4.
Pressure trends during continuous injection of supercritical CO$_2$ at reservoir temperature 8 °C and reservoir pressure 13MPa.

Apparent pressure oscillations throughout the experimental period coincide for all sensors and either result from temporal changes of effluent fluid composition and corresponding variations in the response of the back pressure regulator, or from events outside the measurement length very near the influent or effluent ports. In the early phase of the injection (until day 3) effluent fluid is largely characterized by changing contents of replaced pore water and produced gas, whereas after day 3 the amount of pore water in the effluent is reduced and is below detection limit of bulk fluid sampling and analysis near the end of the experiment (data not shown).

The comparison of differential pressures between single sensors (Fig. 5) indicates slow and steady changes in local permeability profiles. In the early phase of the experiment the differential pressure between the bottom and the middle sensor (sensors p1 and p2, Fig.2) decreased, while the differential pressure between the middle and the upper sensor (sensor p2 and p3) increased. The changes in differential pressure indicate time dependent changes in local permeability due to gas hydrate dissociation in the inflow region and secondary CO_2- or mixed CO_2-CH_4-hydrate formation with pore water after cooling of the injection fluid. Overall, in the early injection period (day 1) bulk sediment permeability decreased as can be seen from the slight increase in differential pressure between the bottom and the upper pressure sensor (sensor 1 and 3).
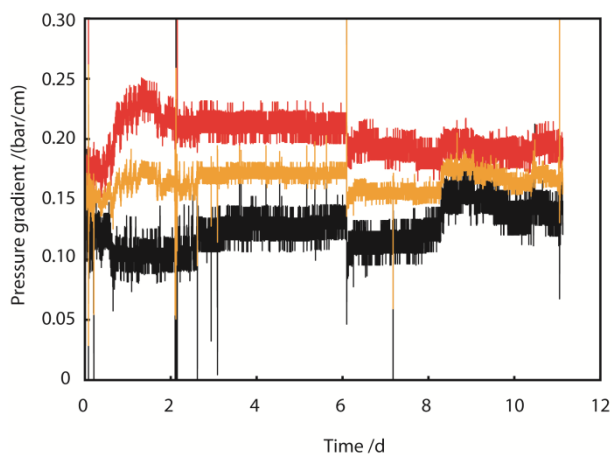

Figure 5.
Pressure gradients between sensors P_1-P_2 (black), P_2-P_3 (red) and P_1-P_3 (orange) during continuous injection of supercritical CO_2 (see also Fig. 1).

Throughout the experiment overall sediment permeability slightly decreased. This indicates that secondary CO_2- or CO_2-CH_4-hydrate formation either compensates CH_4-hydrate dissociation with regard to gas hydrate saturation, or free gas is retained in the pore space due to capillary forces. This aspect needs further evaluation and will be constrained from analysis of volume balances of influent and effluent fluids, as well as gas hydrate composition analysis with Raman microscopy.

Markedly, in the late period of the experiment the differential pressure between the middle and the upper sensor and the increase in differential pressure between the bottom and the upper pressure sensor indicate permeability increase in the upper part of the sample and permeability decrease in the lower part of the sample which indicates ongoing alterations of gas hydrate saturation.

Effluent fluid composition
The on-line Raman analysis of the effluent revealed dynamic changes in fluid composition (Fig. 6). In the early phase of the experiment, effluent pore water reached near saturation levels with respect to CH_4-hydrates. Similar CH_4 Raman intensities in both sensors indicate single fluid effluent composition and the absence of free CH_4 gas. This confirms that CH_4-hydrate preparation followed by seawater flushing is suitable to achieve initial water saturation prior to CO_2 injection. The initial one-phase fluid regime was followed by multiphase fluid flow starting at the end of the first day and lasting throughout the experiment. Multiphase fluid production was characterized by large oscillations of intensity signals of CO_2 and CH_4. Towards the end of day 1 marked concentrations of CO_2 were detected, which indicate breakthrough of the CO_2 liquid phase. With breakthrough of CO_2 the CH_4 concentration also increased, indicating that CH_4 was either transported as free gas or dissolved in CO_2.

Changing fluid compositions, low concentrations of CO_2 and CH_4 as well as the dampening of the oscillatory behavior of CO_2 and CH_4 Raman intensities between day 6 and 8 are in excellent agreement to the marked change in pressure inside the pressure vessel (Fig. 4) and indicate an event of substantial water production. Assuming that liquid CO_2 forms a continuous phase inside the pressure vessel, water production after the initial CO_2 breakthrough at the end of day 1 suggests that

secondary CO_2- or mixed CO_2-CH_4-hydrate formation with pore water force reactive fluids to access previously untouched regions of the reservoir. Thus CO_2-hydrate formation itself is a means to improve CH_4 production efficiency.
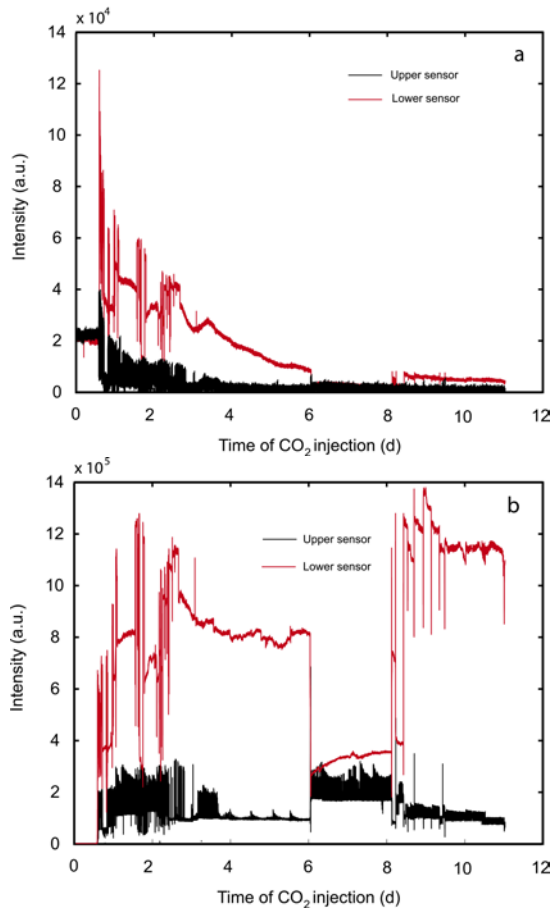

Figure 6.
Raman intensities of the CH_4 (a) and CO_2 (b) components in the effluent phases of the hydrate reservoir during continuous CO_2 injection. A gravitational phase separation allowed preferential analysis of different phases in multiphase fluids: Upper cells were oriented to analyze the components in the denser, usually aqueous, phase while lower sensors were oriented to analyze less dense gaseous phases or CO_2-rich liquid

After day 8 no marked change in effluent CH_4 concentration was observed. It is presumed that the remaining CH_4 hydrate is located beyond reach for CO_2 hot enough to trigger dissociation. Instead, CH_4 accumulation occurs via slow CH_4-CO_2 hydrate conversion. This again indicates the suitability of heated supercritical CO_2 injection to overcome mass transfer limitations and suggests

that fast discontinuous injection of CO_2 with optimized heat transport is superior to continuous injection. However, in contrast to findings identifying a diffusion limited transport to effectively impede cold hydrate conversion beyond surface near layers of hydrate grains (e.g. [5]), additional Raman experiments carried out for this study demonstrate that significant accumulation of exchanged CH_4 in the mobile phase is feasible for long periods of time and at cold reservoir conditions. The Raman experiments were carried out by exposing pure CH_4 hydrate to a cold CO_2 gas phase at -1 °C and 3.34 MPa. At this *p*-/*T*-condition both hydrate species are within their respective stability fields. 2D-mapping of a hydrate grain revealed a monotonic overall increase in the CO_2 component and a concomitant decrease of the CH_4 component in the hydrate throughout the entire 288 h the grain composition was monitored (Fig. 7). Moreover, the slopes of guest molecule concentrations at the end of this experimental period indicate an ongoing exchange thereafter (Fig. 8). The monotonic change of the bulk hydrate composition with time is in contrast with local changes. The high lateral resolution of the Raman analysis reveals highly fluctuating hydrate compositions with transiently decreasing CO_2 and simultaneously increasing CH_4 levels in the hydrate. Although the reason is not fully understood at present we hypothesize that the immediate exchange of guest molecules results in formation of defect-rich hydrates, exhibiting transient CH_4/CO_2 mixing ratios. The inferred high defect density in these transitional hydrates maintains an efficient pathway of gas exchange even within deeper parts of the hydrate grain. This implies that prolonged contact times of CH_4 hydrates with CO_2-rich fluids will result in significant accumulation of CH_4 in the mobile phase.

For the prediction of production efficiency, gas hydrate dissociation, conversion and formation dynamics knowledge of the actual fluid composition is of particular interest. To date it was not possible to distinguish between the presence of a two-phase fluid with liquid CO_2 and free CH_4 gas, or the presence of a one-phase fluid with CH_4 being dissolved in CO_2. The local fluid composition inside the sample determines the gas hydrate composition with either pure CO_2-hydrate or mixed CO_2-CH_4-hydrates being formed in situ. Comparing CO_2/CH_4 Raman intensity ratios measured in both Raman cells suggest that the

production fluid can be described as a two-phase fluid being composed of pore water and a CH_4-enriched, liquid CO_2 phase (Fig. 9). Although the individual sensor response is different, CO_2/CH_4 Raman intensity ratios are very similar. In the presence of free CH_4 gas a deviation between sensor responses would be expected due to fluid density differences and different phase separation characteristics as a consequence from the orientation of the sensors with respect to gravity. Further data analysis and signal filtering is necessary, and kinetics and characteristics of phase separation as well as storage and retention effects need to be evaluated based on multiphase fluid flow modeling and history matching with bulk fluid composition data.
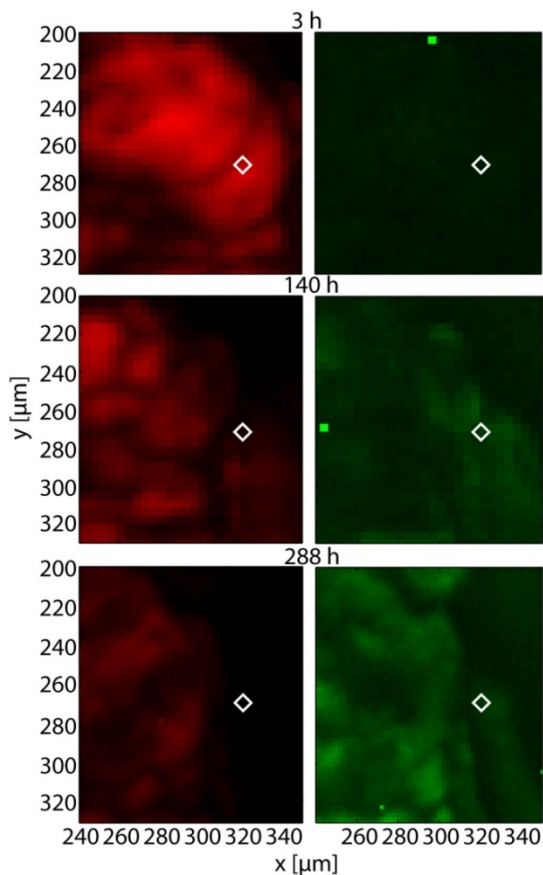

Figure 8.
Evolution of CH_4 (red) and CO_2 (green) guest molecules in the hydrate grain of Fig. 7. Solid lines and triangles denote Raman intensity changes in the bulk grain, while dashed lines and diamonds indicate compositions at x=321 µm, y=269 µm.

Figure 7.
Color-coded Raman intensities of CH_4 (red) and CO_2 (green) guest molecules in a hydrate grain during a 288 h conversion experiment in a 1 mL pressure cell. The exchange was triggered by exposing a CH_4 hydrate grain to CO_2 gas at -1 °C and 33.4 bar. The system was closed after exchange of the cell atmosphere. Diamonds mark coordinates resolved in Fig. 8.
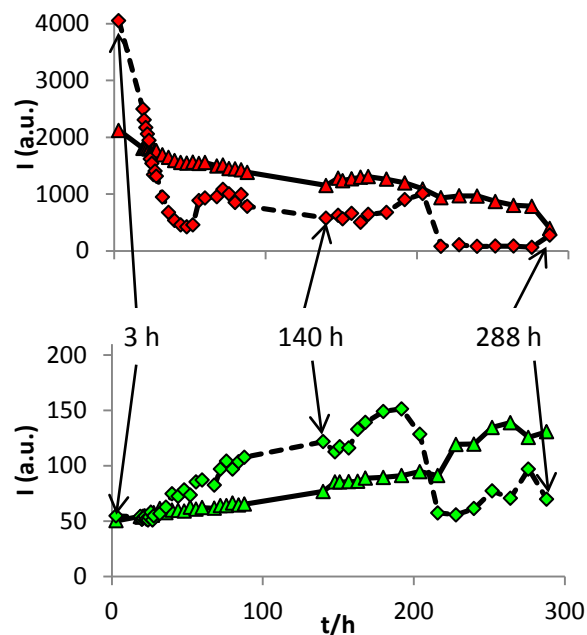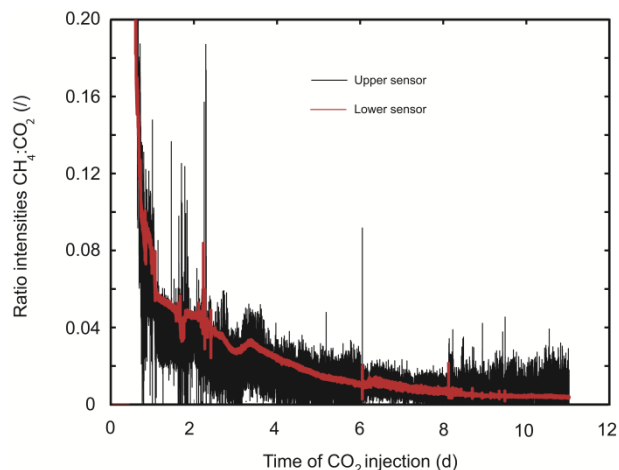

Figure 9.
CH_4/CO_2 intensity ratios of Raman peaks

While our results cannot be extrapolated to ongoing CH_4 enrichment of liquid CO_2 on the reservoir scale, and phase separation and presence of free CH_4 gas at higher CH_4 loads and longer contact times could well be possible on the

reservoir scale, our results provide valuable evidence that numerical modeling can treat fluid flow as a two-phase fluid in the surrounding of the injection well and, thus, computational models can be simplified tremendously.

SUMMARY AND OUTLOOK

Recent experimental results have provided further evidence that the injection of CO_2 is a suitable strategy for production of CH_4 from natural gas hydrates. Injecting heated CO_2 as a pure supercritical fluid provides a measure to avoid rapid CO_2-hydrate formation and pore space clogging in the near injection region. Thus, supercritical CO_2 injection appears to be a suitable alternative to mixed N_2:CO_2 injection which was chosen in the recent onshore field test in the Alaska permafrost. Our results suggest that during and after injection of supercritical CO_2 different processes occur on different timescales and result in heterogeneous phase distributions and gas hydrate structures. Ongoing and future work focus on the understanding of fluid flow characteristics and gas hydrate conversion kinetics in particular in the presence of CH_4-enriched CO_2 or two-phase CO_2:CH_4 fluids and on constraining geomechanical consequences for the reservoir formation during and after production.

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