Swapping guests: Laboratory large-scale experiments on CH_4 production by CO_2-CH_4 exchange in a CH_4 hydrate reservoir

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Abstract

Methane hydrates are considered as a player in the field of energy supply, which has initiated a series of laboratory and field tests for the exploitation of gas hydrate resources. Besides the more conventional production methods depressurization and thermal stimulation, the exchange of methane (CH_4) by carbon dioxide (CO_2) as a guest molecule in hydrates has attracted a great deal of attention. The method is based on the chemical potential gradient between the CH_4 hydrate phase and the injected CO_2 phase as well as the assumption that conversion rates are sufficient for an energy and cost effective production of CH_4 with a concurrent sequestration of CO_2. For this purpose, pure CO_2 or N_2/CO_2 mixtures are injected into the CH_4 hydrate reservoir, e.g. in the Ignik Sikumi Field Trial in Alaska, USA.

Laboratory data from small-volume flow-through experiments often indicate an incomplete conversion of CH_4 hydrate that is owed to the early formation of a CO_2-rich hydrate shell preventing the direct contact of free CO_2 and CH_4 hydrate and, thus, slow down the guest exchange. In the presence of free/pore water the conversion rates considerably decrease in comparison to rates measured in water-free lab experiments where less secondary hydrate formation occurs. The injection of N_2/CO_2 mixtures and a combination of CO_2 injection and thermal heating have been put forward to counteract issues of reduced conversion rates as well as plugging.

Earlier small-scale experiments at GEOMAR by Chr. Deusner and colleagues (Energies, 5: 2112-2140, **2012**) used heated (95 °C) supercritical CO_2 in a pressurized sample of 2 L consisting of gas hydrate, water and sand. The highest conversion rates with a CH_4 yield of ~ 40% were observed at reservoir conditions of 13 MPa and 8 °C, which is within the stability conditions of both, pure CO_2 and CH_4 hydrates. A change in temperature conditions led to a considerable decrease in conversion rates due to clogging (colder) or a locally enhanced increase in permeability and channel formation (warmer) within the flow through system. In a co-operation of GFZ and GEOMAR within the German SUGAR project we used LARS (Large Scale Reservoir Simulator) to upscale the experiment by 100 times. LARS accommodates a sample of 210 L volume and allows for the simulation of in situ conditions typically found in gas hydrate reservoirs. Data from the spatially distributed temperature sensors within LARS, pressure sensors at the outlet and inlet, high resolution electrical resistivity tomography (ERT), gas chromatography, and flow measurements serve to interpret gas flow patterns, calculate mass balances and interpret the complex physico-chemical processes in LARS.

We injected a total of 50 kg heated CO_2 into a CH_4 hydrate-bearing sand with the pore space occupied by gas hydrate and CH_4 saturated pore water in equal shares. Experiment 1 (E1) was carried out in a “huff’n puff” manner with distinct injection and equilibration intervals, whereas CO_2 was continuously injected in experiment 2 (E2). The experiments were carried out at 13 MPa and 8 °C. In the “huff’n puff” experiment ~23 kg of heated CO_2 had been injected and ~21 kg (20 L) of water produced by the time the CO_2 content in the effluent fluid reached 95%. The total fluid production up to this point exceeded the water production by only 12% suggesting that the prevailing

majority of produced CH_4 had originally been dissolved in the pore water. After the CO_2 breakthrough the water production nearly ceased and CH_4 volume fractions quickly decreased to below 1% with an expected but short increase to 8% in the early production period after the first overnight equilibration interval. In this first production period after the breakthrough more CO_2 was produced than injected and clogging due to secondary hydrate formation became less of a problem than before. In the experiment with continuous CO_2 injection (E2), the increase in the CO_2 fraction of the effluent was very sudden and occurred after the injection of ~15 L CO_2 and the production of a similar amount of water. In comparison to E1, the CO_2 breakthrough was immediate but the CH_4 volume fractions in the effluent gas were twice as high and only dropped below 1% after ~ 40 kg of CO_2 injection. However, the total CH_4 production was half as much compared to E1 and the CO_2 retention was 30% compared to 55% in E1. The ERT data supported the gas and flow measurements. In E1 the ERT plots showed a broad front of high resistivity, which is induced by gas hydrate and CO_2/CH_4 fluids, rising up to the middle of the sample before the CO_2 breakthrough occurred. Afterwards, a broad central conduit of higher resistivity appeared in the upper half of the specimen. For E2 the areas of high resistivity were somewhat smaller as was the conduit. At the top of the conduit a patch of high resistivity likely pointed to locally and quickly rising CO_2 concentrating below the lid. Most of the original CH_4 hydrate had been located in the lower half of the LARS sample.

In line with small-scale experiments, up-scaled experiments in LARS suggest that focused non-homogeneous fluid migration in the gas hydrate-bearing sediments limits the accessibility to gas hydrates and, thus, potential gas production yields. Both, CH_4 production and CO_2 retention benefit from equilibration periods within the “huff’n puff” production scenario compared to the continuous flow strategy. Whereas in the huff’n puff production, slightly higher temperatures of CO_2 might have been advantageous, slightly lower temperatures might have enhanced CH_4 production during continuous CO_2 injection. In conclusion, the overall CH_4-CO_2-conversion was little and both, production and retention are strongly correlated to the displacement of pore water.