



Simulating CO₂ injection into submarine, CH₄-hydrate bearing sediments in high-pressure experiments

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Meeting the increasing demand for energy and simultaneously keeping cumulative CO₂ emissions below a potentially dangerous threshold value is one of the most challenging tasks of present times. The production of natural gas via injection of fossil-fuel derived CO₂ into submarine gas hydrate reservoirs could potentially be realized on industrial scales in order to exploit these hydrocarbon energy sources in a CO₂-neutral manner. However, the mechanisms of hydrate dissociation and conversion under CO₂-injection conditions are not fully understood and various engineering aspects make a future industrial application challenging. Within the German gas hydrate initiative SUGAR a combination of high-pressure laboratory experiments and transport-reaction modelling is used to elucidate the process mechanisms and technical parameters on different scales.

The high-pressure systems presented here were developed and built to simulate conditions in natural hydrate reservoirs (P, T, Q , fluid composition, sedimentary settings) in both batch and continuous operation and for different sample volumes (1mL to 2000mL). For carrying out disturbance-free experiments, IR- and Raman-spectroscopy as well as NMR-imaging are used for online monitoring and process visualization.

We used flow-through experiments with artificial sediment (CH₄ hydrate and quartz sand) to determine methane yields from CH₄-hydrate decomposition using CO₂-rich brines, pure liquefied, supercritical as well as gaseous CO₂. CH₄ yields in flow-through experiments were low when injecting either CO₂-rich brines or CO₂-seawater mixtures. Sample permeability became severely impaired due to spontaneous formation of CO₂-hydrate from over-saturated solutions and large pressure spikes were followed by apparent sediment fracturing. However, the injection of pure CO₂ did not reduce permeability to that extent because water availability was limited. Expectedly, CH₄ yields were highest with additional heat injection with supercritical CO₂. To this end, high yields are interpreted as a consequence of accelerated hydrate dissociation and subsequent replacement of CH₄ gas by supercritical and liquid CO₂. The hypothetical two-step mechanism of initial hydrate dissociation prior to reformation of CO₂-hydrate was also confirmed with Raman microscopy. It was shown that upon introduction of CO₂ gas the prevalent CH₄-hydrate decomposes very quickly with respect to simultaneous CO₂-hydrate formation. Moreover, the spectroscopic analysis revealed that there is no preferential release of methane from either of the two cages in the hydrate structure.

Ongoing experiments focus on optimizing yields and efficiencies for CH₄ recovery and CO₂ sequestration, especially trying to elucidate the effect of bulk sediment permeability on the conversion dynamics.