Recovery of Methane Hydrates by CO\textsubscript{2} Injection:
Experimental Investigation

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Natural gas hydrates are found in large amounts in the permafrost and subsea regions. To reduce the carbon dioxide footprint, the production of natural gas hydrates is intended to be combined with CO\textsubscript{2} sequestration. In this study, a feasibility analysis based on experiments has been carried out. Thereby, the actual exchange of methane by carbon dioxide in the hydrate cages was studied. Methane hydrates were firstly formed, then the gas phase was flushed with carbon dioxide at a slightly higher pressure to remove the methane. Subsequently, the system was kept at this temperature and pressure and the actual exchange process was monitored by analyzing the composition of the gas phase with the help of a micro-gas chromatograph. After no obvious change in the gas phase composition, the hydrate dissociation experiment was started. The pressure was released step-wise at isothermal conditions. At each pressure step the composition of the decomposed gas hydrate was analyzed.

It was found that in general the replacement of methane by carbon dioxide in gas hydrates is possible even though the experiments were carried out at a pressure clearly in the methane hydrate stability zone. However, the exchange is not very efficient and only takes place in the layers close to the hydrate-vapor interface. After the replacement of the gas in the hydrates in these layers, the process slows down and hardly any changes could be observed. This is due to the fact that the mass transfer of carbon dioxide into the methane hydrates layers below the formed CO\textsubscript{2} hydrates is by diffusion and therefore limited. In the subsequent dissociation experiment, it was seen that methane hydrate dissociation did not immediately start when the pressure was below the HLV equilibrium pressure of the water + methane system. This indicates that the methane hydrates are stabilized by the presence of CO\textsubscript{2} hydrates.

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