

From lab to field, from micro to macro – test of technologies for the production of hydrate bonded CH₄ via CO₂ sequestration in hydrates

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Abstract

Since huge amounts of CH₄ are bound in natural gas hydrates occurring at all active and passive continental margins as well as permafrost regions, these hydrate reservoirs are supposed to be a promising resource for natural gas. The injection of CO₂ into hydrate-bearing sediments as a chemical stimulation method for the exploitation of gas hydrate reservoirs appears to be particularly favorable because it combines the release of CH₄ from the hydrate phase with the storage of CO₂ as a solid clathrate. Therefore, several experimental and modelling studies worldwide and also in the framework of the German national project SUGAR (Submarine Gas Hydrate Reservoirs) focused on this approach during the last decades.

Laboratory data from micro-scale experiments using analytical methods such as Raman spectroscopy, X-ray and neutron diffraction, nuclear magnetic resonance and others provide information about the structural changes of the hydrate phase and the gas exchange processes on a molecular scale. The results indicate that the processes related to the exchange of the guest molecules are quite complex. It is now generally accepted that the driving force for this process is the chemical potential gradient between the CH₄ hydrate phase and the injected CO₂ phase inducing the release of CH₄ from the hydrate lattice and the incorporation of CO₂ into the hydrate structure. Raman spectroscopic and X-ray diffraction measurements indicate that this process correlates with a (partial) decomposition or opening of the hydrate cavities. In case of mixed hydrates containing larger hydrocarbons such as C₂H₆ and C₃H₈ besides CH₄ in the hydrate phase the exchange of the guest molecules with CO₂ comes along with a change of the hydrate structure (sII to sI and vice versa). The exchange of the guest molecules generally results in the formation of a secondary mixed hydrate phase containing CO₂ besides CH₄ and other hydrocarbons depending on the gas mixture content of the environmental phase.

Laboratory data from large-scale experiments provide information about the CH₄ recovery and fluid migration, hydrate dissociation and formation of a secondary hydrate phase, heat and mass transfer. The experimental results show a wide variation indicating that the recovery rate of CH₄ strongly depends on the experimental conditions such as the volume of the sample, hydrate saturation and thus permeability of the hydrate bearing sediment, hydrate morphology as well as pressure and temperature of the injected CO₂ phase. Also, the use of gas mixtures containing N₂ besides CO₂ has an impact on the recovery rate of CH₄ and the potential formation of a secondary CO₂-rich hydrate phase. In any case, the use of CO₂ injection as a production method for CH₄ from hydrate bearing sediments will result in the production of a gas mixture rather than the extraction of pure CH₄. Since the injected CO₂ forms a mixed hydrate a certain amount of CH₄ remains in the hydrate phase. In addition, the long-term stability of the secondary formed CO₂-rich hydrate phase also depends on the potential changes of the chemical environment which may result in the release of CO₂ due to a re-exchange of the hydrate bonded gas molecules or dissociation of the hydrate phase. These results make the approach of CH₄ production via CO₂ injection maybe less attractive than original expected in particular if compared to other production technologies such as depressurization and/or thermal stimulation.