A New Method for Enhanced Production of Gas Hydrates with CO₂

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Presently, depressurization, thermal stimulation, inhibitor injection, or a combination of these methods have been considered as possible means of gas hydrate production. Depressurization is the most often considered method for commercial production of hydrates (Sloan, 1998), but combined depressurization and thermal stimulation have been used recently to produce a small amount of gas from the Mallik 5L-38 research well located on the Mackenzie delta, Northwest Territories, Canada. Additional studies are needed to ascertain the economic viability of any of these methods for commercial production of gas hydrates.

Another method that has been discussed for gas hydrate production involves the injection of CO₂. The idea of swapping CO₂ for CH₄ in gas hydrates was first advanced by Ohgaki et al. (1996) and then for ethane hydrate by Nakano et al. (1998). Their concept involves injecting CO₂ gas, which is then allowed to equilibrate with methane hydrate along the three-phase equilibrium boundary (Smith et al., 2001). Because of the difference in chemical affinity for CO₂ versus methane in the sI hydrate structure, the mole fraction of methane would be reduced to approximately 0.48 in the hydrate and rise to a value of 0.7 in the gas phase at equilibrium. However, neither Ohgaki et al. (1996) or Nakano et al. (1998) addressed the important issue of the kinetics of the reaction. The first attempt to do so was performed by Uchida et al. (2001). Using a Raman spectroscopic method, they confirmed the guest-molecule swapping reaction at the solid-gas interface. Although the authors did not directly address the issue, their results suggested that the exchange mechanism was slow with induction times requiring several days.

Because the prior work did not address the more difficult question of the rate of CO₂ gas penetration beyond the first few micrometers at the solid-gas interface, we conducted a series of experiments to directly measure the rate of penetration of CO₂ into bulk methane hydrate. Methane hydrate was formed overnight by equilibrating a measured amount of deionized water in the pressure cell with 1400 psia methane at -1°C while a magnetic stir bar vigorously agitated the water. The next morning, the cell was placed into a refrigerated chamber and the cell temperature was kept within a range of ±0.2°C of the desired test temperature. The headspace CH₄ gas was then swapped for CO₂. During the headspace swap, cell pressure was maintained between 500 and 600 psia, varying slowly so as not to cause disruption to the upper layer of the methane hydrate. Gaseous CO₂ was passed through the cell until compositional analysis of the exit gas exceeded 95% CO₂. The pressure of the cell was then maintained at 500 psi during the subsequent penetration analysis. A scanning laser Raman spectrometer system was used to track the penetration depth of CO₂ into the methane hydrate layer as a function of time and temperature. The signature symmetric stretching mode vibration at 1384 cm⁻¹ (Sum et al., 1997) in the Raman spectra was used to track the position of the CO₂ in the hydrate phase.
Results from the penetration experiments are presented in Figure 1. The data again validate the thermodynamic favorability of swapping CO2 for methane but the exchange rates deeper into the gas hydrate are slow. The calculated rate of CO2 penetration into the methane hydrate is only about 0.25, 0.55, and 1.3 mm/hr at 0, 2.5, and 4.5°C, respectively. As most gas hydrate reservoirs of interest are in porous media, the additional tortuosity imposed by the sediment would reduce our measured exchange rates by ½ to ¼ of the rates measured for bulk gas hydrate. In addition, recovered methane would be contaminated with significant amounts CO2 that would have to be removed by cryogenic distillation or some other energy intensive separations method. It appears highly unlikely that practical gas hydrate production can be accomplished using the method proposed by Ohgaki et al. (1996).

Our new concept for enhanced gas hydrate recovery (EGHR) discussed in this paper takes advantage of the physical and thermodynamic properties of mixtures in the H2O-CO2 system combined with controlled multiphase flow, heat, and mass transport processes in hydrate-bearing porous media. Because of intellectual property concerns, details cannot be provided here but the process involves forming a microemulsion with CO2 and water using a proprietary method. The two-phase microemulsion is injected into the hydrate bearing strata at a temperature higher than the stability point of methane hydrate, which upon contacting the methane hydrate decomposes its crystalline lattice and releases the enclathrated gas. The freed gas is recovered at an extraction well. Sensible heat of the emulsion and heat of formation of the CO2 hydrate provide a low grade heat source for further dissociation of methane hydrate away from the injectate plume. Conversion of the microemulsion to CO2 hydrate occurs over time as controlled by heat transfer, diffusion, and the intrinsic kinetics of CO2 hydrate formation. Process control is afforded by variation in the temperature of the emulsion, ratio of CO2 and water, and droplet size of the discrete CO2 phase.

Experiments have been conducted that verify introduction of stoichiometric ratios of CO2 and water in unconsolidated sand at the laboratory bench-top scale using our proprietary method. Subsequently, injection experiments were performed to evaluate use of the microemulsion to produce free gas from methane hydrate. Methane hydrate was formed in columns packed with 20/30 mesh Accusand. A gas flow-through method was used to produce the methane hydrates with hydration numbers between 6 and 7 at volumetric water contents between 70 and 80% of saturation. After forming the methane hydrate, the columns are allowed to equilibrate in a controlled-temperature water bath at 1°C for 48 hours at 1000 psig. A known volume of the microemulsion is then injected into the column containing methane hydrate. Temperature recovery to 1°C differed significantly following injection of the microemulsion versus identical experiments with water only, indirectly indicating that CO2 hydrate formation was occurring. Sand samples extracted from the column after quenching in liquid N2 were examined with Raman spectroscopy, x-ray diffraction, and environmental scanning electron microscopy and confirmed the

![Figure 1. Apparatus developed to measure the kinetics of clathrate guest molecule swapping](image-url)
presence of CO$_2$ hydrate. Gas samples were also obtained from the outlet port of the column and analyzed by gas chromatography. Peak area analysis revealed no CO$_2$ in the extracted gas phase, only methane.

In addition to the laboratory experiments, reservoir modeling is being conducted to determine optimal injection methods for gas hydrate production in a real reservoir. Because of the highly specialized needs for handling microemulsion injection and multicomponent gas hydrate formation and dissociation, a custom model is being developed around the STOMP-CO2 (WHITE and McGRAIL, 2003) multiphase flow simulator developed at PNNL for simulating geologic storage of carbon dioxide. An equation of state module was added to STOMP-CO2 for calculating equilibrium stability, physical, and thermodynamic properties of gas hydrates in the H$_2$O-NaCl-CO$_2$-CH$_4$ system. A full kinetic model for gas hydrate formation and decomposition is used to compute mass balance at each grid node. Early results confirm that heat transfer from the emulsion combined with depressurization destabilizes gas hydrate over more than three times the injected emulsion volume.

In summary, a new method for production of gas hydrate reservoirs has been developed and the key steps in the process have been validated in laboratory-scale experiments. The method is attractive from a climate change perspective in that injected CO$_2$ is permanently sequestered as a solid gas hydrate as part of the production process. Additionally, refilling pore space with CO$_2$ hydrate is expected to maintain the mechanical stability of gas producing sediments, thus enhancing safety during gas production from both terrestrial and marine environments. Considerable additional experimental and theoretical work is needed to assess the overall economics of the process. In particular, the economic value of future carbon credits expected to be obtained with EGHR needs to be assessed to determine whether marginal resources may be developed as economic reserves.

References


