## Quantifying CH<sub>4</sub>-CO<sub>2</sub> Hydrate Exchange in Microscopic and Macroscopic Systems using Raman Spectroscopy

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Recovering CH<sub>4</sub> from a hydrate via the injection and exchange of CO<sub>2</sub> in a hydrate-bearing reservoir has been acknowledged as a potential future resource, both in terms of energy production and CO<sub>2</sub> storage. Optimizing CH<sub>4</sub> recovery is particularly important for the resource to become economic, requiring knowledge of CH<sub>4</sub>-CO<sub>2</sub> exchange dynamics with respect to the thermodynamic equilibrium set by a combination of temperature, pressure, and chemical inhibition. Some progress has been made in understanding the fundamental aspects of this process: for example, molecular exchange of hydrate guests has been found to be a diffusion-limited process, influenced by particle sizes, temperature-pressure conditions, and nature of the guest molecules. However, the microscopic exchange mechanism is still a subject of debate, and there are large discrepancies in the literature regarding the fraction of recoverable CH<sub>4</sub> and the CO<sub>2</sub>-CH<sub>4</sub> exchange rate, even for measurements conducted at similar experimental conditions. In this work, we have applied Raman spectroscopy to quantify the extent and rate of exchange through macroscopic core-flooding experiments and microscopic imaging of exchange on individual crystals of differing morphology. Our results, combined with an analysis of literature data, support a shrinking-core model of hydrate exchange with a consistent diffusion-limited exchange-length of approximately 5 µm across a range of particle sizes, which can in turn be enhanced through thermal stimulation. Furthermore, crystal morphology has been shown to play a critical role in the rate of exchange. Defects in the crystal structure have been observed to act as initiation points for the exchange process, with imperfect crystals exchanging more rapidly and uniformly, reaching approximately 95 % after 120 hours. In contrast, near-perfect crystals showed extended stability, reaching only 6 % exchange in the same time period. Clearly, understanding the nature of the crystal morphology present in naturally occurring hydrate sediment will be crucial for the design of simultaneous CO<sub>2</sub> sequestration and CH<sub>4</sub> recovery processes.