Conversion of Methane Hydrate Using Injection of Carbon Dioxide / Nitrogen Injection

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Conversion of in situ methane hydrate over to carbon dioxide dominated hydrate through injection of carbon dioxide has proven feasible even up to pilot scale in Alaska. The use of carbon dioxide mixed with nitrogen increases permeability and reduces risk for blocking pores with new hydrate. As a consequence of the first and second laws of thermodynamics the most stable hydrate will form first in a dynamic situation, which involves that carbon dioxide will dominate the first hydrates formed from water and carbon dioxide / nitrogen mixtures. This selective formation process is further enhanced by favorable selective adsorption of carbon dioxide onto mineral surfaces as well as onto liquid water surfaces, which facilitates efficient heterogeneous hydrate nucleation. Given this favoritism of carbon dioxide in the new hydrate formation the question is whether the carbon dioxide will be stored safely or affected in thermodynamic stability by a contacting gas phase with reduced content of carbon dioxide. In this work we apply residual thermodynamics (ideal gas phase as reference) for all components in all phases as basis for a free energy analysis of hydrate stability. It is found that if the flux of gas through the reservoir is high enough to prevent the gas from being depleted for carbon dioxide prior to subsequent supply of new gas, then combined carbon dioxide storage and natural gas production is still feasible. Otherwise gas dominated by nitrogen will still dissociate the methane hydrate if the released in situ methane from hydrate do not mix in with the nitrogen dominated gas. The ratio of nitrogen to carbon dioxide in such mixtures is therefore a sensitive balance between flow rates and rates for formation of new carbon dioxide dominated hydrate.