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## Numerical Simulation of Methane Hydrate Production from Geologic Formations via Carbon Dioxide Injection

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### Abstract

Scientific and technological innovations are needed to realize effective production of natural gas hydrates. Whereas global estimates of natural gas hydrate reservoirs are vast, accumulations vary greatly in nature and form. Suboceanic deposits vary from disperse concentrations residing at low saturations in the pore space of unconsolidated sediments with sand-sized particles to higher concentrations residing in the fractures of sediments with clay-sized particles. Conventional methods for gas hydrate production include depressurization, thermal stimulation, and inhibitor injection. For suboceanic accumulations in sandy sediments, depressurization has been shown, through numerical simulation, to be the most feasible production technology. However, recovery efficiencies are too low to justify pursuing these energy reservoirs. Under high pressure, low temperature suboceanic conditions the hydrate structure can accommodate small molecules other than methane ( $\text{CH}_4$ ), such as carbon dioxide ( $\text{CO}_2$ ) and nitrogen ( $\text{N}_2$ ) in both the small and large cages. Although  $\text{CO}_2$  and  $\text{N}_2$  clathrates generally are not naturally as abundant as those of  $\text{CH}_4$ , their occurrence forms the foundation of an unconventional approach for producing natural gas hydrates that involves the exchange of  $\text{CO}_2$  with  $\text{CH}_4$  in the hydrate structure. This unconventional concept has several distinct benefits over the conventional methods: 1) the heat of formation of  $\text{CO}_2$  hydrate is greater than the heat of dissociation of  $\text{CH}_4$  hydrate, providing a low-grade heat source to support additional methane hydrate dissociation, 2) exchanging  $\text{CO}_2$  with  $\text{CH}_4$  will maintain the mechanical stability of the geologic formation, and 3) the process is environmentally friendly, providing a sequestration mechanism for the injected  $\text{CO}_2$ . An operational mode of the STOMP simulator has been developed at the Pacific Northwest National Laboratory that solves the coupled flow and transport equations for the mixed  $\text{CH}_4$ - $\text{CO}_2$  hydrate system under nonisothermal conditions, with the option for considering NaCl as an inhibitor in the pore water. This paper describes the numerical simulator, its formulation, assumptions, and solution approach and demonstrates, via numerical simulation, the production of gas hydrates from permafrost accumulations in sandstone formations with high gas hydrate saturations and suboceanic accumulations in sandy sediments with low hydrate saturations using the  $\text{CO}_2$ - $\text{CH}_4$  exchange technology.

### Introduction

Gas hydrates are clathrate compounds in which water molecules encapsulate a guest molecule within a lattice structure. The lattice structure of gas hydrates form under low temperature, high pressure conditions via hydrogen bonding between water molecules. Gas hydrates with methane ( $\text{CH}_4$ ) guest molecules are abundant as geologic accumulations in offshore and permafrost environments where sufficiently low temperature and high pressure conditions exist. From an energy resource perspective, these geologic accumulations of natural gas hydrates represent a significant component of the world's organic carbon sources. Recent surveys by the United States Geological Survey (USGS) have estimated that reserves of methane in hydrate form exceed the all other fossil fuel forms of organic carbon (Booth et al., 1996). Under geologic environmental conditions, the lattice structure of a gas hydrate depends primarily on the guest molecule (Englezos, 1993; and Sloan, 1998). Interestingly, the two most prevalent emitted greenhouse gases (U.S. EPA, 2006) carbon dioxide ( $\text{CO}_2$ ) and methane ( $\text{CH}_4$ ) both form sl hydrate structures under geologic temperature and pressure conditions. Whereas their clathrate structures are similar,  $\text{CO}_2$  hydrates form at higher temperatures and have a higher enthalpy of formation compared with  $\text{CH}_4$  hydrates (Sloan, 1998).

Natural gas can be produced from geologic accumulations of natural gas hydrates either by dissociating the clathrate structure, yielding liquid water and gaseous methane, or by replacing the  $\text{CH}_4$  molecule with another guest. Conventional