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Energy Procedia 1 (2009) 3099–3106

**Energy
Procedia**www.elsevier.com/locate/procedia

GHGT-9

Designing a Pilot-Scale Experiment for the Production of Natural Gas Hydrates and Sequestration of CO₂ in Class 1 Hydrate Accumulations

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Abstract

Vast accumulations of methane hydrates have been found in suboceanic deposits and beneath the arctic permafrost. Because of the large volumetric storage densities, clathrate hydrates on the deep ocean floor have been suggested as a sequestration option for CO₂. Alternatively, CO₂ hydrates can be formed in the geologic settings of naturally occurring accumulations of methane hydrates. This paper describes the design (via numerical simulation) of a pilot-scale demonstration test of the CO₂ exchange production and sequestration technology for a geologic setting beneath the arctic permafrost, involving a gas-hydrate interval overlying a free-gas interval (i.e., Class 1 Hydrate Accumulation).

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Keywords: natural gas hydrate; numerical simulation; CO₂ exchange; gas hydrate dissociation; mixed gas hydrate

1. Introduction

Gas hydrates are clathrate compounds in which water molecules encapsulate a guest molecule within a lattice structure. The lattice structure of gas hydrates forms under low temperature, high pressure conditions via hydrogen bonding between water molecules. Gas hydrates with methane (CH₄) 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 [1]. Under geologic environmental conditions, the lattice structure of a gas hydrate depends primarily on the guest molecule [2,3]. Interestingly, the two most prevalent emitted greenhouse gases [4] carbon dioxide (CO₂) and methane (CH₄) both form sl hydrate structures under geologic temperature and pressure

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conditions. Whereas their clathrate structures are similar, CO₂ hydrates form at higher temperatures and have a higher enthalpy of formation compared with CH₄ hydrates [3].

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 CH₄ molecule with another guest. Conventional approaches to producing natural gas hydrate are through clathrate dissociation via: 1) thermal stimulation, 2) depressurization, and 3) inhibitor injection. The thermal stimulation approach involves raising the hydrate temperature above the stability point, causing the hydrate to dissociate. Thermal stimulation requires a continuous energy source to overcome the endothermic heat of dissociation. Depressurization involves lowering the hydrate pressure below the stability point, causing the hydrate to dissociate. Depressurization results in rapid hydrate dissociation, but with an associated drop in the hydrate temperature. Without an external heat source, depressurization lowers the hydrate temperature to a new equilibrium condition, halting the depressurization process. Inhibitor injection involves the injection of an organic or inorganic compound that shifts the hydrate equilibrium point to lower temperatures for isobaric conditions. As with depressurization, inhibitor injection could require additional inhibitor or a heat source to compensate for the decrease in hydrate temperature with dissociation.

Global assessments of natural gas resources have shown that gas hydrate resources exceed those of conventional resources, which is indicative of the potential for clathrate hydrate sequestration of CO₂. Recovery of natural gas from hydrate-bearing geologic deposits has the potential for being economically viable, but there remain significant technical challenges in converting these natural accumulations into a useable resource. Although CO₂ clathrates generally are not naturally as abundant as those of CH₄, their occurrence forms the foundation of an unconventional approach for producing natural gas hydrates that involves the exchange of CO₂ with CH₄ in the hydrate structure. This unconventional concept has several potential benefits over the conventional methods: 1) reducing production costs, 2) maintaining mechanical stability of the geologic formation, and 3) sequestering CO₂. Whereas the exchange production technology would not be feasible without the favorable thermodynamics of CO₂ hydrates over CH₄ hydrates, this situation yields technical challenges for the technology in avoiding secondary hydrate formation and clogging of the geologic repository. Laboratory-scale experiments have demonstrated the feasibility of producing natural gas and sequestering CO₂ using the direct exchange technology in geologic media. These results have been reproduced numerically using the STOMP-HYD simulator, which solves the nonisothermal multifluid flow and transport equations for mixed hydrate systems in geologic media.

The concept of exchanging CO₂ with CH₄ as guest molecules in geologic accumulations of natural gas hydrates as a production technology was first advanced by Ohgaki et al. [5]. This concept was then extended to ethane hydrates by Nakano et al. [6]. Their original concept involved injecting CO₂ gas into an aqueous-gas-hydrate system and allowing the CO₂ and CH₄ to equilibrate. The greater chemical affinity for CO₂ over CH₄ in the hydrate structure, as evidenced by the higher heat of formation and equilibrium temperature, yields a mixed CO₂-CH₄ hydrate. Resulting equilibrium concentrations of CO₂ are greater than CH₄ in the hydrate phase and less than CH₄ in the gas phase. If this molecular exchange technology can be realized for field production of geologic accumulations of natural gas hydrates, it could offer two secondary benefits; mechanical stability and mitigating global warming. If the exchange process is conducted without significant hydrate dissociation the mechanical stability of the hydrate-bearing formation could be maintained. The exchange technology would additionally represent a nearly neutral carbon process, sequestering one molecule of CO₂ for each produced molecule of CH₄, which could then be burned to produce energy and CO₂.

Accumulations of natural gas hydrates were originally divided into three main classes by Moridis and Collett [7]. Class 1 accumulations comprise two permeable layers; a hydrate-bearing interval overlying a mobile-gas interval. For these accumulations the boundary between the hydrate-bearing and mobile-gas intervals coincides with the lower limit of the hydrate stability zone. Class 2 accumulations, also comprise two permeable layers, but with a hydrate-bearing interval overlying a mobile-aqueous interval. Class 3 accumulations comprise a single permeable layer of hydrate-bearing geologic media. In Class 2 and 3 accumulations, the hydrate bearing interval will occur within the hydrate stability zone. The mobile-aqueous interval of the Class 2 accumulation can occur within or outside the hydrate stability zone. More recently, Moridis and Sloan [8] proposed a fourth accumulation type

(Class 4), characterized by disperse, low-saturation gas hydrate deposits, lacking a confining geologic strata. Suboceanic gas hydrate accumulations generally are characterized as being Class 4.

This paper investigates, using numerical simulation, the production of natural gas hydrates from geologic deposits via the combined processes of depressurization, thermal stimulation and direct molecular exchange of CO₂ and CH₄. Numerical simulations are conducted using a five-spot well configuration with the center well being an extraction or injection well and perimeter wells being strictly extraction wells. During the injection stages CO₂ is injected as either liquid, sub-critical gas, or supercritical gas. Liquid-CO₂ is assumed to form a separate phase from the aqueous and gas phases, having an intermediate wettability between the aqueous and gas phases. Two implementations of the numerical simulator have been developed: 1) equilibrium and 2) kinetic. In the equilibrium implementation the CO₂ and CH₄ components (i.e., hydrate forming components) in the mobile phases (i.e., aqueous, liquid-CO₂, and gas) are assumed to be in equilibrium with their counterparts in the immobile phase (i.e., hydrate). In the kinetic implementation the CO₂ and CH₄ components in the mobile and immobile phases are tracked separately, with a kinetic rate controlling the exchange of hydrate forming components between the mobile and immobile phases. In both implementations the water component is assumed to be in equilibrium between the mobile and immobile phases. During this study only the equilibrium model is applied. The objective of these numerical investigations is to demonstrate the feasibility of directly injecting CO₂ into a natural gas hydrate bearing reservoir to produce CH₄, where the principal concerns are production rates and energy costs.

2. Numerical Approach and Assumptions

Numerical simulations executed for this paper were conducted with the STOMP-HYD simulator [9]. STOMP-HYD solves conservation equations for water mass, CH₄ mass, CO₂ mass, water-soluble inhibitor (salts or alcohols) mass, and thermal energy. The conservation equations for CO₂ and inhibitor mass are optional. The simulator considers mass and energy transport over three mobile phases (i.e., aqueous, gas, and liquid CO₂) and four immobile phases (i.e., hydrate, ice, precipitated salt, and geologic media). Hydrate properties, including cage occupancies and equilibrium conditions are functions of the guest molecule concentrations (i.e., CH₄ and CO₂). Hydrate dissociation/formation are assumed to be equilibrium processes, as is the exchange mechanism for gas hydrate guest molecules. The STOMP-HYD simulator solves the governing conservation equations using integral volume differencing on structured orthogonal grids for spatial discretization and a fully implicit formulation for temporal discretization. Nonlinearities in the discretized governing equations are resolved using Newton-Raphson iteration with continuous property updating. Phase transitions (i.e., appearances and disappearances) are handled using a primary variable switching scheme.

3. Conceptual Model

The production of Class 1 through 4 hydrates using depressurization and thermal stimulation have been numerically investigated by Moridis and Collett [7], Moridis et al. [10], Moridis [11], and Moridis and Sloan [8]. The Class 1 gas hydrate reservoir considered for this paper is identical to the Class 1W, Reference Case, defined by Moridis et al. [10], which is representative of a permafrost accumulation. This reservoir comprises three 30-m-thick strata; an impermeable shale layer, overlying a permeable sandstone, overlying an impermeable shale layer. The upper half of the permeable sandstone layer is gas hydrate bearing without free gas, whereas the lower half is a variably saturated gas-aqueous system. Initially the gas and gas-hydrate comprise only CH₄. To maintain stable initial conditions, preventing the downward migration of aqueous phase and upward migration of gas phase across the gas-hydrate lower boundary, gas hydrate saturation dependent entry pressure model was implemented, following Moridis et al. [10]. The Moridis model for capillary-pressure function used a variant of the Brooks-Corey function [12] which included an effective-aqueous saturation dependent smoothing function, based on the *error function*, and a gas-hydrate saturation dependent entry pressure function, based on the *regularized incomplete beta function*:

$$\bar{s}_l = \frac{s_l - s_{lr}}{1 - s_{lr}} = \left(\frac{\psi}{h_{gl} H(s_h) F(\bar{s}_l)} \right)^\lambda; F(\bar{s}_l) = \text{erf} [60(1 - \bar{s}_l)]; H(s_h) = 1 + 9.28 \left(\frac{B(s_h; 2.1, 2.2)}{B(2.1, 2.2)} \right) \quad (1)$$

where, \bar{s}_l is the effective aqueous saturation, s_l is the actual aqueous saturation, s_{lr} is the residual aqueous saturation, h_{gl} is the gas-aqueous capillary head (m), ψ is the entry-pressure head (m), λ is the Brooks-Corey function exponent, and s_h is the hydrate saturation. The capillary-pressure function used for this paper altered the Moridis model by eliminating the smoothing function and replacing the *regularized incomplete beta function* with a *sinusoid function*:

$$\bar{s}_l = \frac{s_l - s_{lr}}{1 - s_{lr}} = \left(\frac{\psi}{h_{gl} \beta_{gl} H(s_h)} \right)^\lambda ; H(s_h) = 1 + 9.28 \left(5.6075 + 4.6567 \sin [3.1275 s_h - 1.5166] \right) \quad (2)$$

where, β_{gl} is the gas-aqueous interfacial tension scaling factor. Formation properties for the permeable (sandstone) and impermeable (shale) strata are provided in Table 1.

Table 1. Formation Properties

Parameter	Value	Parameter	Value
Initial Pressure @ Hydrate Interface	10.67 MPa	Porosity (sandstone)	0.3
Initial Temperature @ Hydrate Interface	13.5 C	Porosity (shale)	0.1
Intrinsic Permeability k_a and k_v (sandstone)	1 Darcy	Dry Thermal Cond. (shale and sandstone)	0.5 W/m K
Intrinsic Permeability k_a and k_v (shale)	0 Darcy	Wet Thermal Cond. (shale and sandstone)	3.1 W/m K
Gas Effective Saturation	$\bar{s}_g = \frac{s_g - s_{gr}}{1 - s_{lr}}$	Aqueous Relative Permeability Model (sandstone and shale)	$k_{rl} = \left(\frac{\bar{s}_l}{s_l}\right)^3$
Aqueous Effective Saturation	$\bar{s}_l = \frac{s_l - s_{lr}}{1 - s_{lr}}$	Gas Relative Permeability Model (sandstone and shale)	$k_{rg} = \left(\frac{\bar{s}_g}{s_g}\right)^3$
Liquid CO ₂ Effective Saturation	$\bar{s}_n = \frac{s_n}{1 - s_{lr}}$	Liquid CO ₂ Relative Permeability Model (sandstone and shale)	$k_{rn} = \left(\frac{\bar{s}_n}{s_n}\right)^3$
Brooks-Corey λ (sandstone and shale)	1.538	Brooks-Corey ψ (sandstone and shale)	1.5827 m
s_{lr} (sandstone and shale)	0.25	S_{gr} (sandstone and shale)	0.02
β_{gl} (sandstone and shale)	0.9804	Geothermal Gradient	0.029 C/m
β_{gn} (sandstone and shale)	1.485	β_{nl} (sandstone and shale)	2.885

A five-spot well pattern produced CH₄ and sequestered CO₂, using the single center well for fluid injection and the four perimeter wells for gas extraction. A 500-m spacing between the injection and production wells (i.e., 25 ha/well) is envisioned for commercial production. For the purposes of designing a pilot-scale production experiment a 50-m spacing (i.e., 2.5 ha/well) was investigated numerically. The reservoir depth of 1150 m and pressure of 10.67 MPa creates a condition where the equilibrium temperature for pure CO₂ hydrate is lower than that for pure CH₄ hydrate, according to Figure 1. The production/sequestration system was simulated with a 3-dimensional Cartesian grid that modeled ¼ of the five-spot well system, assuming homogeneous conditions in the horizontal direction. The domain was discretized into 21 x 21 x 38 = 16,758 grid blocks, all of which were active. The top and bottom of the domain (adjacent to the impermeable rock) were treated as constant temperature, no fluid-flow boundaries. The sides of the domain were treated as adiabatic, no fluid-flow boundaries.

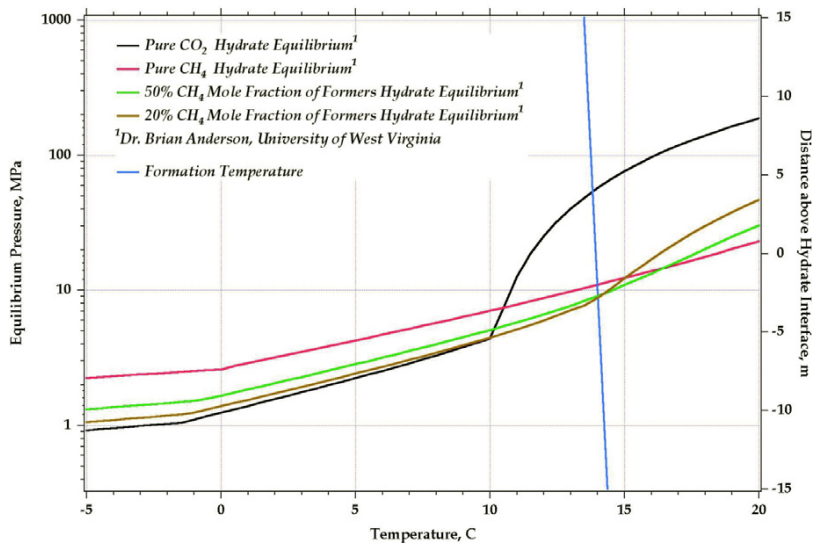


Figure 1. Equilibrium temperature as a function of pressure for pure and mixed CH_4 and CO_2 hydrates and formation temperature as a function of depth.

4. Initial Conditions

The initial conditions, developed by Moridis et al. [10], involved an aqueous-hydrate region overlying an aqueous-gas region, with a system pressure of 10.67 MPa and temperature of 13.5 C at the interface between the aqueous-hydrate and aqueous-gas regions (interface), with a geothermal temperature gradient of 0.029 C/m. To establish hydraulic, thermal, and thermodynamic equilibrium conditions, which would be used as initial conditions for the production simulations, initial simulations were conducted from near-equilibrium conditions through a false transient to an equilibrium state. For these simulations the domain boundaries were closed to fluid flow. The upper and lower boundaries were assigned temperatures of 11.65 and 15.42 C, respectively, establishing a temperature gradient of 0.029 C/m with a temperature of 13.5 C at the interface. Aqueous pressure for the near-equilibrium conditions was specified via the interface pressure of 10.67 MPa and an estimate of the hydrostatic gradient (-9.85 kPa/m). Hydrate saturation for the near-equilibrium conditions was specified as being 0.7 above the interface within the permeable rock and zero elsewhere. The gas pressure for the near-equilibrium conditions was assigned a constant value within the aqueous-gas region of permeable rock at the maximum value (10.60 MPa) that would not allow gas to enter the overlying aqueous-hydrate region. Without the capillary pressure barrier to drainage modification, described by Equation (2), liquid-unsaturated conditions could not be maintained under equilibrium conditions. The impermeable rock was specified to be aqueous saturated, without hydrate or gas. The aqueous phase was specified to be saturated with dissolved CH_4 throughout the entire domain, including both the permeable and impermeable rocks. The resulting equilibrium conditions included a hydrostatic pressure gradient in gas pressure within the aqueous-gas region of the permeable rock; a sharply decreasing gas saturation (i.e., from a maximum of 0.873 immediately below interface, with depth within the aqueous-gas region of the permeable rock; and a slightly increasing hydrate saturation and dissolved aqueous mass fraction of CH_4 with depth within the aqueous-hydrate region of the permeable rock.

5. Production Simulations

The theoretical advantages of producing natural gas hydrate accumulations via CO_2 injection versus depressurization are reduced pumped water, shorter production periods, mechanical stability of the formation, and

sequestration of injected CO₂. Potential disadvantage of the CO₂ production/sequestration technology are incomplete production of CH₄, from hydrate bypass or mixed hydrate formation; and pore clogging, from secondary hydrate formation. To investigate the application of the CO₂ injection production/sequestration technology to Class 1 hydrate accumulations at series of numerical simulations were conducted. A number of options exist for injecting CO₂ into a hydrate bearing formation: 1) pure CO₂ (i.e., sub-critical gas, sub-critical liquid, supercritical gas), 2) saturated aqueous solution, or 3) micro-emulsion. The underlying free gas layer of a Class 1 hydrate accumulation makes natural gas production via CO₂ injection challenging, because of the potential for hydrate bypass and appearance of CO₂ in the effluent stream (i.e., production wells). To avoid hydrate bypass of the injected CO₂ all injection and production wells were screened only over the initial hydrate interval. Fracing pressure for the hydrate bearing formation was estimated as 18.21 MPa using a pressure gradient of 15.83 kPa/m (0.7 psi/ft) for an injection depth of 1150 m. To maintain injection pressures below the fracing pressure level an injection pressure of 15 MPa was assigned. To maintain production pressures above the critical pressure of CO₂ an extraction pressure of 8 MPa was assigned.

5.1. Pure-CO₂ Injection

Pure CO₂ injection involves the injection of only CO₂ into the formation through the screened interval. The advantage of injecting pure CO₂ is that water pumping costs are reduced. Two production simulations were conducted that involved injecting pure CO₂, using injectant temperatures of 15 and 45 C. At an injection pressure of 15 MPa at either temperature, CO₂ enters the formation as a supercritical gas. The applied implementation of STOMP-HYD simulator assumes thermodynamic equilibrium conditions, which ignores the kinetic effects of hydrate dissociation and hydrate guest molecular exchange. Simulation results indicate that injecting pure CO₂ produces secondary hydrate around the well, greatly reducing the permeability of the formation for injectant. At either injectant temperature the region around the injection well becomes clogged with secondary mixed CH₄-CO₂ hydrate, which halts the further injection of CO₂. A 50:50 mass ratio of hydrate formers for mixed CH₄-CO₂ hydrates would be within the stability range for conditions of 15 MPa and 15 C, but would be outside the stability range for conditions of 15 MPa and 45 C, as shown in Figure 1. Secondary hydrate formation was anticipated for the 15 C injectant. For the 45 C injectant, secondary hydrate and formation clogging occurred, because insufficient CO₂ fluid enters the formation prior to clogging to elevate the formation temperature above the stability point.

5.2. Saturated-Aqueous-Solution Injection

At an injection pressure of 15 MPa, a saturated aqueous solution has mass fractions of CO₂ of 8.44% (15 C) and 5.98% (45 C), which are significantly lower than the mass fraction of CO₂ in sI hydrates of 28.45% (15 C). The concept for using a dilute solution of CO₂ is that the injectant water would be recycled. Water produced at the extraction well would be separated from the produced CH₄ and then saturated with CO₂ before being reinjected into the hydrate-bearing formation. As the injectant moves through the formation dissolved CO₂ is exchanged with clathrated CH₄, because the exchange is thermodynamically favored. Injecting a CO₂-saturated aqueous solution at 15 C into the hydrate-bearing reservoir also resulted in secondary hydrate formation and formation clogging as seen with the injection of the pure CO₂ at 15 C, shown in Figures 2 and 3. Simulation results for the injection of a saturated aqueous solution at 45 C were not available for this submission of the paper, but will be available on the poster and the published version of this paper.

5.3. Micro-Emulsion Injection

Injecting CO₂ into a natural-gas-hydrate-bearing formation as an aqueous micro-emulsion is a production concept first proposed by McGrail et al. (13). The original concept involved forming a microemulsion of liquid CO₂ within the well casing, using a proprietary method, yielding a ratio of CO₂ to water that matched the hydration number of sI hydrates formed with CO₂. The microemulsion is then injected into the formation at a temperature above the stability point of the formation CH₄ hydrate, causing dissociation of the clathrate structure and gaseous release of the CH₄. Released gas is then displaced ahead of the emulsion injection front toward the extraction well.

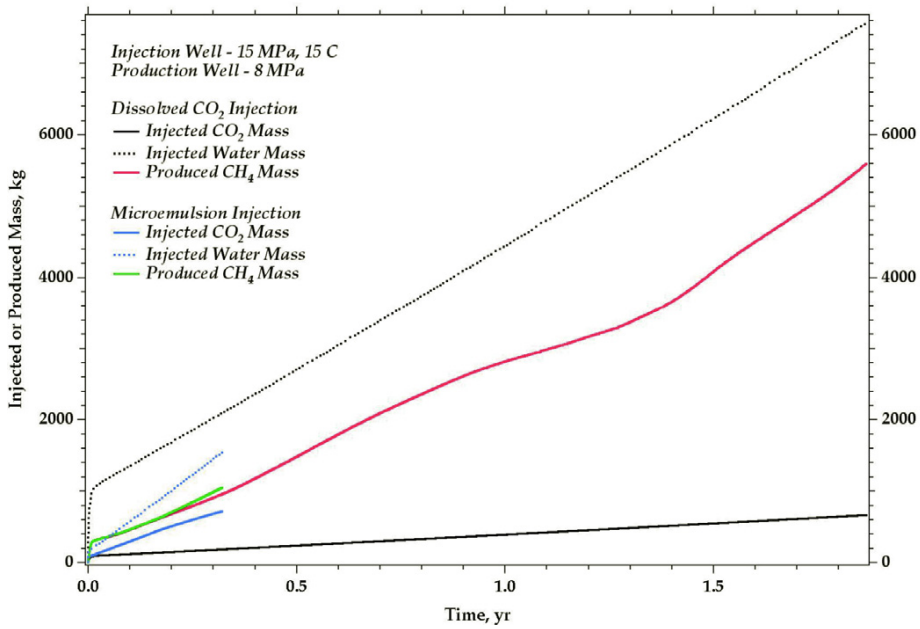


Figure 2. Injected CO₂ and water mass and produced CH₄ mass as a function of time for the dissolved CO₂ and micro-emulsion injection simulations at 15 C injectant.

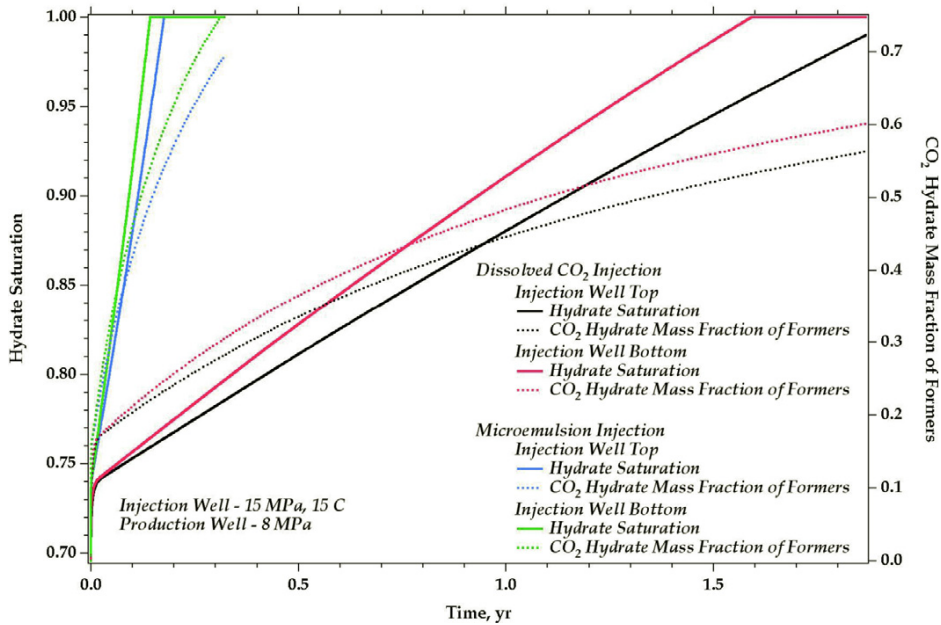


Figure 3. Hydrate saturation and CO₂ hydrate mass fraction of formers at the bottom and top of the injection well as a function of time for the dissolved CO₂ and micro-emulsion injection simulations at 15 C injectant.

After the formation had been produced, the injection would be stopped, and the formation would eventually cool via heat transfer to its ambient state, reforming CO₂ hydrate in the formation. Two simulations were conducted that injected a 50% volume ratio of water and supercritical CO₂, using an injection pressure of 15 MPa and injectant temperatures of 15 and 45 C. As with the other simulations the extraction well was maintained at 8 MPa. The micro-emulsion injection option allows for CO₂ to water injection ratios that span between a saturated aqueous solution and pure CO₂ injection. Using an injectant temperature of 15 C does not follow the protocol originally envisioned for the technology. As with the other injection schemes at 15 C, the micro-emulsion injection at a 50:50 volume ratio of water and supercritical CO₂ resulted in secondary hydrate growth and formation clogging around the injection well, as shown in Figures 2 and 3. Simulation results for the injection of a saturated aqueous solution at 45 C were not available for this submission of the paper, but will be available on the poster and the published version of this paper.

6. Conclusions

Producing Class 1 hydrate accumulations using CO₂ injection has the potential benefits of sequestering CO₂, shortening production time, and reducing the quantity of produced water, but also has the potential detrimental effect of injectant bypassing the hydrate-bearing region. This paper investigated using CO₂ and water injectants that ranged from pure CO₂ to saturated aqueous solutions. Simulations conducted using a 15 C injectant, resulted in formation of mixed secondary hydrates with formation clogging around the injectant well. To prevent the formation of secondary hydrate around the well a higher temperature injectant is required, which will necessitate heat addition to the injectant. Simulations conducted using a 45 C injectant will be available on the presented poster and published version of this paper.

7. References

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