CO2 Injection for Methane Production from Hydrate Reservoirs

by

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GAS HYDRATES

- Solid state of gas and water where the water molecules form a cavity that encapsulates the guest molecule.
Why are hydrates of interest?

- Initial interest as a curiosity
- Plugging of production and transportation pipelines
Renewed interest

– Significant amount of energy
  • Permafrost regions
  • Marine environments (high water column)
Hydrate as Energy Resource

Ref.: Fire in the Ice, U.S. Department of Energy • Office of Fossil Energy • National Energy Technology Laboratory

Gas Hydrates Resource Pyramid (left). To the right is an example gas resources pyramid for all non-gas-hydrate resources.
Gas Hydrate Production Methods

Depressurization

- Gas Out

Hydrate
Dissociated
Free-Gas

Cap
Reservoir

Thermal Injection

- Gas Out

Imperm.
Hydrate
Dissociated Hydrate

Rock
Impermeable Rock

Inhibitor Injection

- Gas Out

Methanol

Imperm.
Hydrate
Dissociated Hydrate

Rock
Impermeable Rock

CO₂ Flood

Modified from "GAS HYDRATES OF NORTHERN ALASKA", January 2005
Bob Fisk, USBLM, Anchorage, Alaska, Tim Collett, USGS, Denver, Colorado & Jim Clough, DGGS, Fairbanks, Alaska
CH$_4$ PRODUCTION INDUCED BY CO$_2$ INJECTION

- Provides thermodynamically more stable gas hydrate than CH$_4$

Husebø, 2008
GAS HYDRATE PRODUCTION METHODS

- Move the gas hydrate outside its stability region
  - Depressurization
  - Thermal stimulation
  - Hydrate inhibitors

- CO2 exchange
CO2 Exchange: Project Motivation

- The amount of energy bound in hydrates may be more than twice the world’s total energy resources in conventional hydrocarbon reservoirs; i.e. oil-, gas- and coal reserves

- Simultaneous CO$_2$ Sequestration

- Win-win situation for gas production

- Need no hydrate melting or heat stimulation

- Spontaneous process

- No associated water production

- Formation integrity
CO2 storage in hydrates with associated methane gas production

**Challenge:**
Determine exchange mechanisms during potential sequestration of CO₂ to produce methane from hydrates
Three component Phase Field Theory

\[
F = \int dr \left\{ \frac{\epsilon^2 T}{2} (\nabla \phi)^2 + \sum_{i,j=1}^{3} \frac{\epsilon_{ij}^2 T}{4} \left( c_i \nabla c_j - c_j \nabla c_i \right)^2 + f_{bulk}(\phi, c_1, c_2, c_3, T) \right\}
\]

\[
f_{bulk} = wTg(\phi) + [1 - p(\phi)] f_S(c_1, c_2, c_3, T) + p(\phi) f_L(c_1, c_2, c_3, T)
\]

\[
\dot{\phi} = -M_\phi \frac{\delta F}{\delta c} + \zeta_\phi
\]

\[
\sum_{i=1}^{3} c_i = 1
\]

\[
\dot{c}_i = \nabla M_{ci}(c_1, c_2, c_3) \nabla \left( \frac{\delta F}{\delta c_i} - \zeta_i \right)
\]

Parameters \( \epsilon \) and \( w \) can be fixed from the interface thickness and interface free energy. \( \epsilon \) \( ij \) set equal to \( \epsilon \)
Objectives:

Experimentally and theoretically determine spontaneous methane production when hydrate is exposed to CO2; with the purpose of CO2 sequestration.

Methane hydrate reservoirs

In-Situ imaging (MRI) of hydrate formation

Methane production by CO2 injection in field test in Alaska 2012
Summary of Field Test (Injection Test)

Schedule:

Apr. 2011: Drilling test well (Complete)
Nov. 2011: Finalizing parameters for the field test
Jan.-Apr. 2012: Field test

Location: Prudhoe Bay operating unit in Alaska, USA
Operator: ConocoPhillips Company (COP), through its wholly owned subsidiary, ConocoPhillips Alaska, Inc.
Investors: The United States Department of Energy (DOE)
           JOGMEC; Japan Oil, Gas and Metals National Corp.
Gas Production from the Field Test

Iğnik Sikumi #1 Flowback/Drawdown: Gas composition
STATUS

Alaska Field Injection Test 2011-2012

- ConocoPhillips and JOGMEC
- US$ 11.6 mill funding from US DOE, total cost ca. US$30mill
- CO2 injection
Core properties

- Bentheim sandstone cores
  - Porosity ~22%
  - Permeability ~1.1 Darcy
  - Grain density ~2.65 g/cm³
  - Mineralogy ~95% quartz
Experimental design

Hossainpour (2013)
Hydrate formation

- Pressure: 83 bar
- Temperature: 4.0 °C
- Initial brine salinity: 3.5 wt% (NaCl)
- Initial brine saturation: 0.69 [frac.]
- Final brine saturation: 0.31 [frac.]
- Final gas saturation: 0.20 [frac.]
- Final hydrate saturation: 0.49 [frac.]
CH$_4$-CO$_2$ exchange

![Graph showing the exchange of methane (CH$_4$) and carbon dioxide (CO$_2$). The graph plots methane recovery and cumulative methane produced against PV injected fraction.](image)
Conclusion

- A binary mixture of 60% N₂ and 40% CO₂ [mole percent] was successfully injected into a hydrate-filled whole core containing excess water. The initial rate of methane recovery from hydrates was high but had a rapid decline.
How will the unconventional gas boom affect prices in other markets?

Average natural gas prices by region, May 2012

Unconventional gas boom will spur a degree of convergence in global prices by putting pressure on oil-price indexation of gas contracts in Europe & Asia.
Thank you!
CONDITIONS OF A HYDRATE RESERVOIR

- Hydrate reservoirs are often found in porous media
  - Sedimentary rock

Mineralogy: mainly quartz
Porosity: 22-23%
Permeability: 1.1 D
Pore diameter: 125 microns
Experimental Setup

- CO$_2$ & CH$_4$ Pumps
- Insulated Lines & Heat Exchanger
- Temperature & Confining Pressure Controls
- High Pressure Cell Inside Bore of Magnet
Core Sample Design

Bentheim Sandstone

20-25% porosity, ~1.1 D Perm

• Whole Core
• Longitudinal Cut With Machined Spacer to Simulate Open Fracture.
0.0 hrs
Methane in Spacer
0.0 hrs
Sw=0.5 + Methane
5.0 hrs
Cooling Starts
7.2 hrs
9.4 hrs
12.0 hrs
14.0 hrs
16.3 hrs
18.6 hrs

![Graph showing volume over time](image)
20.9 hrs

![Graph showing volume changes over time.](image)
23.2 hrs
25.5 hrs
27.7 hrs
Core Halves Saturated with hydrate
0.0 hrs
9.1 hrs
20.6 hrs
32.0 hrs
43.4 hrs
54.9 hrs
66.3 hrs
77.8 hrs
89.2 hrs
112.1 hrs
123.5 hrs
135.0 hrs

Inset graph:
- X-axis: Time (Hours)
- Y-axis: Intensity
- Data points: (0, 0.004), (100, 0.008), (200, 0.012), (300, 0.016), (400, 0.020), (500, 0.024), (600, 0.028)
146.4 hrs
157.8 hrs
169.3 hrs
237.9 hrs
295.1 hrs
352.3 hrs
501.0 hrs
523.8 hrs
Methane Production

- Total Methane Production (50-85%)

Molar methane concentration in fracture

Time (Hours)

after 1st CO₂ flush - duplicate experiments, $S_{wi}=50\%$

1st flush, $S_{wi}=45\%$

2nd flush, $S_{wi}=45\%$

Free gas diffusion level at $S_{wi}=50\%$

after 2nd CO₂ flush - duplicate experiments, $S_{wi}=50\%$
Thank you!