Methane Recovery from Hydrate-bearing Sediments

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Hydrate formation permits very high concentration of methane in a given volume. This explains current estimates of carbon resources stored in methane hydrates which exceed the storage of carbon in coal and petroleum combined. Thus, the recovery of methane from hydrate bearing sediments gains great importance in the context of the ongoing unprecedented growth in energy demands worldwide. This is also one of the most challenging issues related to methane hydrates. The state-of-knowledge is summarized next. An annotated bibliography accompanies this review.

CURRENT STATE OF KNOWLEDGE

The review of the current state of knowledge is organized into two parts. First, we explore the different research tools and approaches that have been used to learn about potential production strategies. Then, we organize the existing information into the different production strategies that have been conceived and investigated.

Research Approach

- The study of methane production has been approached using mathematical analysis and models, numerical simulations, laboratory experiments and field experiments. Salient observations extracted from each approach follow.
- *Analytical*. Analytical studies have focused on kinetics and thermodynamic calculations (Jamaluddin et al., 1989; Ullerich et al., 1987). The majority of these studies have emphasized pure hydrate systems.
- *Numerical*. At the fundamental molecular scale, molecular simulations have been conducted to study properties of hydrates (Sean et al., 2005; Sun and Mohanty, 2006), however, there are no molecular-scale simulations for production purposes. At the field scale, most numerical simulations disregard geomechanical effects, yet phenomena such as hydraulic fracture can play a critical role in production, particularly in low-permeability sediments (McGuire, 1982). An annotated bibliography of numerical simulations/models and is presented in *Appendix A*.
- *Laboratory experiments*. Most production studies in the laboratory have been conducted in pure hydrate systems (Circone et al., 2003; Circone et al., 2005a, b; Circone et al., 2004; Stern et al., 2001, 2003). There are very few studies in controlled porous networks, and even fewer in sediments with synthetic hydrates (Handa and Stupin, 1992; Ogasawara et al., 2005; Sakamoto et al., 2005b; Sung et al., 2002; Uchida et al., 2004; Yousif et al., 1991).
- *Field experiments*. One production study has been conducted in the field in the Canadian permafrost region (Carcione and Gei, 2004; Chand and Minshull, 2004; Haberer et al., 2006; Henninges and Huenges, 2005; Kurihara et al., 2005; Moridis et al., 2004; Moridis et al., 2005; Riedel et al., 2006; Wright and Dallimore, 2005). The first production attempt used a heating approach, while the second attempt used a depressurization approach. The experiment had some, albeit limited success. Models (e.g., EOSHYDR2, TOUGH-Fx/HYDRATE) have been calibrated and tested against this test.

- *Experiments using undisturbed pressure cores*. Pressure cores extracted from the Indian ocean and kept within stable pressure and temperature conditions were monitored during controlled depressurization to assess the evolution of the sediment during production (Georgia Tech – JIP preliminary report - Santamarina et al., 2007).

Production Methods

The obvious production approaches involve depressurization, heating and their combinations. However, other production methods are under study. Brief comments follow. A comprehensive annotated bibliography for different production methods can be found in *Appendix B*.

- *Depressurization & heating (Appendix B.1 and B.2)*. Laboratory studies have been conducted on pure hydrate specimens (Circone et al., 2003; Circone et al., 2005a, b; Circone et al., 2004; Stern et al., 2001, 2003). and in sediments with synthetic hydrate (Handa and Stupin, 1992; Ogasawara et al., 2005; Sakamoto et al., 2005b; Sung et al., 2002; Uchida et al., 2004; Yousif et al., 1991). Heating has been implemented by either injecting hot water or heating the chamber (Kamata et al., 2005; Kamath and Holder, 1987; Ogasawara et al., 2005; Sakamoto et al., 2004; Sakamoto et al., 2005b; Ullerich et al., 1987). In all cases, depressurization has involved the pore fluid, therefore, destabilization effects associated with changes in effective stress remain unknown. Multiple studies have explored the beneficial effects of combining heating and depressurization.
- *Chemical methods (Appendix B.3)*. There are two approaches based on chemical concepts
  1. Chemical substitution: A very promising approach is the substitution of CH_4 for CO_2, thus recovering methane while sequestering carbon dioxide at the same time. The CO_2 can be brought into contact with the methane hydrate in gas phase, liquid phase, or potentially dissolved in the circulating pore water (Ota et al., 2005a; Park et al., 2006). Raman spectroscopy, NMR, and MRI data provide insightful information about the evolution of the substitution (Graue et al., 2006; Gupta et al., 2005; Ota et al., 2005a; Ota et al., 2005b; Sakamoto et al., 2005b; Yoon et al., 2004). Optimal P-T operating conditions and underlying phenomena are reviewed in.
  2. Chemical injection - Change in stability conditions. Methanol, ethylene glycol, nitrogen and salt brines are inhibitors that depress equilibrium conditions, so that their injection prompts hydrate dissolution and CH4 production; their effect is intimately coupled with the imposed temperature difference (Chatterji and Griffith, 1998; Graue et al., 2006; Haneda et al., 2005; Kamath et al., 1991; Kawamura et al., 2005; Ostergaard et al., 2005; Ota et al., 2005b; Sira et al., 1990; Sung et al., 2003; Sung et al., 2002; Yoon et al., 2004). Two solutions can be injected so that their exothermic reaction destabilizes the methane hydrate, liberating CH_4, while hindering its reformation by altering the fluid chemistry and lowering the phase transformation boundary (Chatterji and Griffith, 1998).

There is some evidence that nitrogen gas combined with heating is more effective than heating alone (Sakamoto et al., 2005b).

- *Other energy forms (Appendix B.4)*. Early studies of the role of other forms of energy have been found, including high frequency mechanical vibration(Miura et al., 2006), and microwaves (Li et al., 2006).

LIMITATIONS IN THE CURRENT STATE-OF-THE-ART - NEEDS

The approaches and production methodologies that have been investigated cover a wide range of alternatives. However, there are some salient limitations in the state of knowledge, in particular, lack of knowledge on production-related *phenomena in hydrate bearing sediments* and limited exploration of *other forms of energy* including possibly energy coupling effects.

The following variables and processes require further attention given the potential important role they may play on gas production from hydrate bearing sediments:

- *Molecular-level understanding of substitution*. The molecular evolution of CH_4 hydrate during diffusion/substitution would be revealing with respect to the enhanced understanding of this potential production method. There is no data on the evolution of mechanical properties.
- *Mixed fluid flow*. Gas may be removed dissolved in water (very low solubility), in gas phase in the form of bubbles (get trapped at pore throats, reduce hydraulic conductivity and alter the pore pressure field), or as a percolating phase (a fractal network that converges towards the production well).
- *Hydrate distribution*. The literature on hydrate formation at the pore scale is still controversial, and their impact on gas production is unknown. It is anticipated that percolation effects will depend on and vary with hydrate concentration in pore space, and its spatial distribution including the presence of lenses.
- *Underlying mechanism in CH_4 production in sediments - Fluid-sediment interaction*. There is no study -known to the PIs- that has properly taken into consideration the formation of hydrates in sediments, their dissociation, and related production strategies.
- *Innovative production methods that benefit from sediment-hydrates-fluid interaction*. Such initiatives could contemplate/benefit from phenomena such as the self prompted formation of hydraulic fractures and the contrasting properties between hydrates and pore fluid (e.g., complex permittivity).
- *Production methods based on other forms of energy*. Mechanical energy applied through the sediment, electromagnetic energy, other chemical substitutions, combinations.
- *Reservoir geometry – Spatial variability*. The geometric characteristics of the reservoir can have a major impact on production. Studies must take into consideration hydrates on water, hydrates on trapped gas, inclined pinching layer.

CHALLENGES AND BARRIERS TO OVERCOME

In view of the state of the art, it is anticipated that the main challenges to be faced during the conduction of this research project can be grouped into:

- *Hydrate formation in sediments*. This challenge has been critical to the development of this field. It can be argued that proper simulation approaches are still lacking. Furthermore, while synthetic hydrates (such as THF - Yun et al., 2006) have proven most useful for the study of the physical properties of hydrate bearing sediments, they are inadequate for production studies.
- *Monitoring tools* to gain adequate information about the ongoing processes taking place during gas production of hydrate bearing sediments.
- *Numerical simulation of the great complexity of underlying physical processes.* Combining particle level processes to address reservoir scale production, properly taking into consideration of chemical, mechanical (flow and deformation), thermal and even electrical effects, become a challenge of overwhelming complexity very soon. Thus, we have to identify the governing processes and variables at each scale, without disregarding important phenomena that can play a critical role in the development of viable production strategies.

The evolution of the project, from 1D to 2D and 3D systems, is particularly advantageous from the point of view of these challenges. On the one hand it provides time for the development of the field and gives us the opportunity to incrementally address these challenges.

In the meantime, we can identify alternatives to fall back to. For example, it may be argued that disseminated hydrates formed by techniques such as the ice-seeding method may be adequate to gain relevant information related to chemical, thermal and mechanical (flow and sediment) phenomena during production. We will continuously re-assess the state of knowledge as part of this investigation (Task #3).

Appendices:

Annotated Bibliographies

Appendix A. Annotated Bibliography on numerical models and simulators

References	Features
Ullerich et al. (1987)	1-D planar semi-infinite system - Moving boundary condition with constant heat flux (heating method) as dissociation begins - Implemented with the experimentation (fine-grained snow + methane gas under 4.1MPa and 274K) - Limitation: thermal conduction in sediment
Jamaluddin et al. (1989)	1-D planar semi-infinite hydrate - Constant heat flux at the boundary surface - Couple the intrinsic kinetics with heat transfer rate - Highlight the heat transfer controlled regime (lower system pressure) and both heat transfer and kinetics controlled regime (higher system pressure)
Yousif et al. (1991)	1-D (3 phase) model by isothermal depressurization for Berea sandstone - Implemented with the kinetics of hydrate dissociation in porous media
CSMHyd (Sloan, 1998)	- Prediction of hydrate temperature and pressure with or without methanol, salts (3~4 phase) - Calculation of water content of hydrocarbon vapor or liquid
Ji et al. (2001)	1-D linearized model for isothermal depressurizing well - Variables: well pressure, reservoir temperature, zone permeability - Well pressure $\uparrow$ = decomposition front movement and gas production $\downarrow$ - Decomposition front $\propto$ time$^{1/2}$ - Reservoir porosity and permeability $\uparrow$ = decomposition front movement $\downarrow$, gas output $\uparrow$
Sung et al. (2002)	3-D, multiphase field scale gas hydrate reservoir simulator - Simulate the effect of methanol injection with depressurizing well - Limited effect of methanol on the dissociation due to the low permeability of hydrate reservoir - Methanol content $\uparrow$ = Hydrate decomposition rate $\uparrow$
Wilder and Smith (2002)	- Hertz-Knudsen-Langmuir equation for maximum rate of an endothermic dissociation - Hydrate particle size $\uparrow$ = required max. heat transfer rate $\uparrow$
Ahmadi et al. (2004)	1-D model by depressurizing well - Well pressure $\downarrow$ = Gas production rate $\uparrow$ - Less effect by reservoir temperature
CSMgem (Ballard and Sloan, 2004)	- Gibbs energy minimization based on hydrate, aqueous, hydrocarbon and pure hydrate fugacity models - User-friendly window version
Moridis et al. (2004)	- EOSHYDR2 simulation for Class 1 hydrate accumulation - Modeling site: Mallik, Alaska - Depressurization: promising, but low operating pressure results in hydrate cooling and lower gas release rate due to endothermic. - Coupling depressurization with thermal stimulation (for the case of thin hydrate and free gas zone): modest gas production - Hydrate deposits with very thin gas zone underlain by aquifer: standard dissociation approach is not enough. Horizontal well would be better than vertical one.
Sun et al. (2005)	- Non-isothermal 1-D model by depressuriztion - Highlight dissociation controlled regime (laboratory-scale) and flow controlled regime (field scale) - Minute effect of different temperature boundary condition
Kurihara et al. (2005)	- Thermal stimulation – field scale model (Mallik 2002 5L-38 well) - Variables: 3 phase equilibrium pressure and temperature, gas saturation, permeability

	▪ Suggestion of hot fluid invasion into the production zone
Moridis et al. (2005)	▪ Thermal stimulation – TOUGH-Fx/HYDRATE (Mallik 2002 5L-38 well) ▪ Suggestion of microfractures generated by gas hydrate dissociation process
Hamaguchi et al. (2005) Norway	▪ Analytical, numerical and experimental study ▪ Material: HCFC141B hydrate (no sediment) ▪ Decomposition phenomena simulated by LGA (lattice gas automation) using Nusselt number and Reynold number ▪ Proposing gas-lift system for recovery system from ocean using 1D unsteady compressible 3 fluid model and adopted CFD $\rightarrow$ utilizing recovered CH_4 gas for the production system to reduce the power consumption
Masuda et al. (2005) Norway	▪ Numerical simulator (lab scale) ▪ 4 mass balance (CH_4, H_2O, methanol, salt) and 1 energy balance ▪ Depressurization on the production end is immediately conveyed to another end inducing the entire core dissociation ▪ Dissociated gas tends to be trapped inside the pore with ice
Bondarev and Popov (2005) Norway	▪ Numerical simulation for heating ▪ Heating affects narrow zone near the well ▪ Speculation of the effect of cyclic thermal recovery
Pawar et al. (2005) Norway	▪ FEHM numerical simulator (LANL) for hot water injection and depressurization ▪ Hot water injection (30^oC injection, 2MPa pumping well) >> depressurization ▪ Injection water temperature $\uparrow$, injection rate $\uparrow$, production well pressure $\downarrow$, porous media permeability $\uparrow$ = gas production $\uparrow$ ▪ Residual water saturation and hydrate re-formation does not affect production
Sean et al. (2005) Norway	▪ Non-equilibrium numerical analysis in micro-scale (single CH_4 hydrate particle) for the estimation of CH_4 hydrate dissociation rate ▪ Dissociation rate = function (temperature), not pressure and flowing water rate
Hong et al. (2006) Norway	▪ Numerical and approximate analytical model for hydrate plug dissociation in pipeline ▪ Positive effect of ice formation during dissociation (higher thermal conductivity) until 262K below which self-preservation effect exists
Larsen and Schwartz (2006) Norway	▪ SINTEF 1D hydrate plug dissociation model incorporating porosity and permeability ▪ Depressurization and mono-ethylene glycol (MEG) simulation
TOUGH-Fx / HYDRATE (LBNL)	▪ Equilibrium and kinetic models for hydrate formation and dissociation (up to 4 phases)
PVTsim (Calsep A/S)	▪ Prediction of hydrate formation conditions of gas and oil mixtures ▪ Variables: percent water cut, composition by weight water, salts, inhibitors
Multiflash (Infochem Computer Services Ltd.)	▪ Calculation of thermodynamic gas hydrate stability curves for produced hydrocarbon ▪ Variables: inhibitors, temperature, pressure
DBRHydrate (DBRobinson Software Inc.)	▪ Prediction of minimum operation conditions to prevent hydrate formation in plant facility ▪ Variables: hydrate former, inhibitors, mol percent

Appendix B. Annotated Bibliography on different production methodology

B.1. Depressurization

References	Features
Kim et al. (1987)	▪ Isothermal depressurization: using a semibatch stirring-tank reactor ▪ Mixture: pure water + methane gas ▪ Decomposition rate $\propto$ surface area, pressure gradient ▪ Stirring speed $\uparrow$ = decomposition rate $\uparrow$ ▪ Decomposition pressure $\downarrow$ = Decomposed gas $\uparrow$ ▪ Intrinsic kinetics depend on pressure, temperature and particle surface area.
Yousif et al. (1991)	▪ Isothermal depressurization (2.8MPa) in porous media ▪ Three phase 1D model implemented by experimental results ▪ Material: hydrate bearing Berea sandstone (1.5wt% NaCl solution at ~8MPa, 273.7K) ▪ Key: consideration of water flow in porous media during dissociation ▪ Prediction of volume of gas and dissociation front location ▪ Resistance $\uparrow$ during production (evolution shape= smooth spike) ▪ Complemented with a numerical model (dissociation reaction rate)
Gudmundsson et al. (1994)	▪ Depressurization under different temperature (-5°C to -18°C) ▪ Pure water + pressurized gas (2-6MPa), magnetic stirrer ▪ When T <0°C, long term exposure to atmospheric pressure has minute effect (self-preservation) if the heat energy is properly hindered for the dissociation. ▪ Ice forms a protective coating for the hydrate.
Ji et al. (2001)	▪ 1D linearized model by Makogon ▪ Limitation: neglecting heat conduction in reservoir and energy balance at dissociation front
Sung et al. (2002)	▪ Hydrate formation in porous rock (sediment) ▪ Constant gas production rate with time controlled ▪ Pressure $\uparrow$ sharply whenever dissociated gas reaches to the critical limit ▪ Resistance decreases due to the water after dissociation, then increases again due to water migration to outlet and gas fills pore
Moridis (2002, 2003)	▪ TOUGH2 -> EOSHYDR2 (mass and heat coupled) ▪ 9 components (hydrate, wter, native CH4, dissociated CH4, native and dissociated hydrocarbon, salt, water-soluble inhibitors, heat pseudo-comp) and 4 phases (gas, liquid, ice, hydrate) in 3D ▪ Prediction of the formation and dissociation and hydrocarbon composition ▪ Combined method > thermal simulation > depressurization
Ji et al. (2003)	▪ 1D linearized model ▪ Key variable: reservoir temperature and hydrate zone permeability for constant rate gas production ▪ Axisymmetric reservoir by depressurization well ▪ Pressure reduction with time is needed for constant rate production
Ahmadi et al. (2004)	▪ 1D model in a confined reservoir by depressurization well ▪ Heat conduction and convection in hydrate zone (sandwiched hydrate+free gas zone between impermeable rock) ▪ Simulating about different well pressures, reservoir temperatures, the gas flow, the pressure and temperatures conditions ▪ Well pressure $\downarrow$ = Gas production rate $\uparrow$ ▪ Less effect by reservoir temperature

Moridis et al. (2004)	▪ Depressurization and hot fluid injection through multiple well ▪ Depressurization for free gas underlying hydrate deposit (zone 1) = production ↑ ▪ Depressurization of hydrate underlain by aquifer (zone 2) produce large amount of water ▪ Thermal simulation for hydrate with no gas, no water ▪ S_{hyd} ↑, hydrate initial temperature ↑, circulating water temperature ↑, thermal conductivity of system ↑ at constant pressure = production ↑ ▪ Gas production less sensitive to rock and gas hydrate specific heat and permeability
Circone et al. (2005a)	▪ Hydrate formation: 290K, 30MPa by ice seeding method ▪ At pressure below quadruple points, dissociation follows a thermal boundary just below ice/water boundary.
Circone et al. (2005b)	▪ Isothermal depressurization ▪ Pure, porous synthetic methane hydrate with granular ice ▪ Pressure ↓ = dissociation rate ↑ ▪ Thermal self-regulation increases during dissociation

Sun et al. (2005)	▪ Non-isothermal, 1D simulation
	▪ Defining "dissociation-flow time scale ratio" to identify 'dissociation controlled (lab scale)' with 'flow controlled (field scale)"
	▪ Lab scale
	  - First stage: fast fluid flow rate after the beginning of depressurization -> quick drop of sample inside pressure
	  - Second stage: uniform pressure distribution, temperature decrease
	▪ Field scale
	  - Dissociated zone (15% length near production well) // dissociating zone (~ 30%) // untouched zone
	  - Dissociation occurs only in a narrow region (after 3days, only 20% length lies below equilibrium P.)
	▪ Minor effect of Temp. boundary condition for both cases

Gerami and Pooladi-Darvish (2005)	▪ Highlight the invalidity of 'sharp-interface' that divide the reservoir into hydrate zone and dissociated zone → pressure reduction propagates from interface into hydrate zone, leading to decomposition of hydrate throughout hydrate zone ▪ During non-equilibrium stage, heat transfer from cap- and base rocks has small effect on gas production. ▪ Heat of decomposition is mainly by the sensible heat of hydrate and its dissociated rock.
Okui et al. (2005) Mallik	▪ Depressurization ▪ Uniform and quick dissociation for lower S_{hyd} (14%) ▪ Gradual dissociation from the surface to the core, self-blocking by hydrates and confining pressure ▪ Heating: Gas entrapped in the pore space (should be followed by depressurization)
Sun and Mohanty (2006)	▪ 3D kinetic simulator ▪ Mass, two phase flow, molecular diffusion and heat transfer fully coupled. ▪ 4 component (hydrate, CH_4, water, salt) and 5 phases (hydrate, gas, water, ice, salt precipitation) ▪ Kim-Bishnoi model for kinetics of hydrate + phase equilibrium for water freezing and ice melting ▪ Initial temperature ↑ (at constant pressure), salt introduction, pressure ↑, boundary temperature ↑ = hydrate dissociation ↑
Sun and Chen (2006)	▪ Depressurization ▪ Hydrate dissociation controlled by gas diffusion through ice when T <0^oC (moving boundary condition)

B.2. Heating

References	Features
McGuire (1982)	- Frontal sweep model (upper bound – higher permeability reservoir) - Fracture-flow model (lower model – lower permeability reservoir) - Variables: porosity, bed thickness, injection temperature, facture length - Front-sweep model: hot water injected into a central -> dissociated gas flow to surrounding production well (using Marx-Langenheim heavy oil recovery equation = heat transfer model, not a porous flow model) - gas production rate: $G_p = \dfrac{IB_{hyd}\phi F_{hyd}}{M\Delta T} e^{z^2} erfc(z)$ - B=produced gas, M=heat capacity, F=S_{hyd}, ϕ: reservoir porosity - Injection temperature $\uparrow$ = production $\downarrow$ (150-250ºF) - Reservoir thickness, porosity $\uparrow$ = production $\uparrow$ (scale >25ft, porosity > 15%) - Fracture-flow model: hydraulic fracture from injection well to production well (using Graetz laminar-flow conduction problem) - gas production rate: $G_p = B_{hyd}q(L1, L2)\tau\phi / M\Delta T$ - Fracture length $\uparrow$ = production $\uparrow$
Kamath and Holder (1987)	- Warm water flow over the top surface of the hydrate (constant temperature) - Hydrate formation: 274K, 7.6MPa - Constant CH_4 recovery rate with time - Formation of thin-film of water on the surface of remaining hydrate $\rightarrow$ induce the heat transfer resistance $\rightarrow$ generated gas bubble makes convective heat path (role of water) - Hydrate recovery rate = power function (ΔT) - Granular ice + pressurized gas - Determination of dissociation heat transfer characteristics - Water film on hydrate that is being dissociated
Ullerich et al. (1987)	- Heating laboratory chamber - Planar, 1D smiinfinite system - Hydrate formation: snow + CH_4 $\rightarrow$ heating chamber radially – no sediment - Water formed during dissociation is blown away by the gas produced
Jamaluddin et al. (1989)	1D semi-infinite body: intrinsic kinetic + heat transfer rate - Activation energy in kinetic $\uparrow$ = decomposition rate $\downarrow$ - Hydrate slab surface roughness $\uparrow$ = decomposition rate $\uparrow$ due to increasing intrinsic kinetic rate with surface area)
Handa and Stupin (1992)	- Hydrate in 70Å-radius silica gel pores (sediment) - After dissociation, hydrate becomes entrapped within pores, ice caps forms at the pore opening making the hydrate stable until pore ice melting point reaches (self-healing effect) - Higher P condition of hydrate is defined in porous material (more unstable at same condition) $\leftrightarrow$ competing effect when dissociated below ice-melting T due to the ice formation).
Wilder and Smith (2002)	- Calculation of required heat to keep system temperature constant during endothermic dissociation event by Hertz-Knudsen-Langmuir equation - Suggest the maximum dissociation rate for hydrate and required heat
Circone et al. (2004)	- Temperature buffering: slower increase of sample temperature when most gas produced - Depending on the boundary temperature, it matters whether ice forms during dissociation (role of water).
Uchida et al. (2004)	- Step Heating (0.06K/hr) - Soils: sand, sandstone, clay (kaolinite and bentonite) and glass bead - Saturation: soil-water mixture, soil+granular ice, vapor pressure controlled.

	▪ Pore size determines the decomposition condition: decomposition temperature decreases as pore size decreases while the swelling clay (bentonite) indicates the higher decomposition temperature. ▪ Surface texture and mineral composition: no affect on decomposition temperature ▪ Continuous heating method indicates the similar results as step heating method

Sakamoto et al. (2004)	▪ Hot water injection
	▪ Hydrate formation: saturated sand (200μm) → CH_4 injection → cooling → formation → CH_4 injection → hot water (21°C) from the top
	▪ 3 zones within sample: dissociated zone at top - dissociating zone (narrow) - untouched zone
	▪ 4 stages during dissociation
	  1) gas displacement by hot water (no dissociation)-pressure building
	  2) T lower than equilibrium T, dissociation starts, pressure peaks
	  3) Temperature $\cong$ equilibrium T during dissociation
	  4) dissociation completed.
	▪ $S_{hyd} \downarrow$ = faster dissociation (lower energy needed)

Sakamoto et al. (2005b)	▪ Hot water injection ▪ Physical model: porosity and permeability varies while hydrate dissociated, migration of gas and water, temperature / enthalpy changes due to the heat generation and mass flow ▪ Mass and energy conservation + regressed expressions for water and gas saturation + regressed gas and water permeability ▪ 100m x 100m site, 45m distance between injection well and production well assuming that pure hydrate layer is sandwiched by impermeable layer

Sakamoto et al. (2005)	▪ Hydrate formation: sand saturated with water → CH_4 flown through cell → cooling
	▪ Formation sequence
	  - Crystallization begins at the water-sand interface
	  - Growth toward inside of pore water (investigated by Raman spectroscopic)
	▪ Dissociation sequence (heating bath)
	  - Start from sand-hydrate interface and grows to pore space.
	▪ Modification of Kim (1987) model which considers the driving force as a change of fugacity between methane in three phase equilibrium and in free gas assuming the hydrate coating sand grain.
	▪ Heat transfer controlled at first stage → mass transfer controlled at second stage

Sakamoto et al. (2005a) Norway	▪ Nitrogen and hot water injection ▪ Material: sands with CH_4 hydrate ▪ Production: Nitrogen+hot water > nitrogen > hot water
Liang et al. (2005)	▪ Decomposition kinetic behavior below ice melting point to see ice-shielding mechanism ▪ Hydrate formation in 5cm^3 porous wet activated carbon (sediment)
Kamata et al. (2005) Norway	▪ Hot brine water injection (30°C) ▪ Material: wet Toyoura sand with brine water with CH_4 hydrate ▪ Temperature and pressure fluctuated between stability region and decomposition region
Ogasawara et al. (2005) Norway	▪ Warming water injection ▪ Material: sand and glass bead with CH_4 hydrate ▪ Estimation of CH4 flow rate
Gupta et al. (2005) Norway	▪ Heating with NMR and Raman spectroscopic study ▪ No difference in decomposition kinetic rate between large and small cages in hydrate

B.3. Chemical Injection

References	Features
Sira et al. (1990)	▪ Methanol and Glycol injection ▪ Hydrate formation: 274K, 8.3MPa ▪ By given concentration and injection rate, the inhibitor contacts the top of hydrate surface (same as Kamath 1989) while pressure keeps constant. ▪ Injection rate, inhibitor concentration ↑ = gas production ↑ ▪ Hydrate dissociation rate = power function (ΔT) representing α, β (No control of inhibitor temperature. Injection rate ↑ = keep warm)
Kamath et al. (1991)	▪ Brine injection and depressurization ▪ ΔT ↑ = gas production ↑ at given salinity ▪ Salinity ↑ = hydrate dissociation rate ↑ by factor of 4. ▪ Brine injection rate effect << temperature driving force ΔT ▪ Brine injection rate ↑ = dissociation rate ↑ (salinity effect > brine injection rate) ▪ Porous hydrate formed under 8.3 MPa and 274K
Sung et al. (2002)	▪ Methanol injection (with depressurization) ▪ Kim-Bishinoi kinetic theory + thermodynamic equilibrium ▪ Limited effect of methanol injection near the well (due to low permeability) ▪ Possible impact of sharp increase of pressure by methanol injection ▪ Sensitive factor = methanol content
Sung et al. (2003)	▪ Methanol injection (30 wt% with 0.5ml/min for 22min – 6.3% of pore volume) ▪ Methanol injection increases equilibrium pressure to 21MPa against 5.5MPa system pressure → immediate dissociation → sudden pressure drop → increased gas production
Yoon et al. (2004)	▪ CO_2 injection ▪ Reduced replacement rate of CO2 with time due to the surface shielding of CO_2 hydrate formed in outer layer (retardation phenomena) ▪ Water produced during replacement → presumably improve production rate due to higher diffusion resistance
Ota et al. (2005a)	▪ CO_2 injection ▪ Temp: 271.2 – 275.2 K / pressure: 3.25MPa ▪ Raman spectroscopy through high pressure optical cell ▪ Amount of CH_4 hydrate decomposition $\cong$ CO_2 hydrate formation ▪ Replacement mechanism - When CO_2 contacts CH_4 hydrate, CH_4 hydrate undergoes surface replacement. - Surface reaction → diffusion limited process for CO_2 hydrate formation - CH_4 hydrate close to CO_2 hydrate becomes unstable / decomposed - CO_2 molecules diffuses / penetrate into remaining hydrogen bond structure - CH_4 gas $\leftrightarrow$ gaseous CO_2
Ota et al. (2005b)	▪ Liquid CO_2 injection ▪ Temp: 273.2K / within stable pressure ▪ Hydrate formation: magnetic agitator ▪ Raman spectroscopy through high pressure optical cell ▪ Kinetic model for replacement ▪ Higher decomposition rate of medium cage (M-cage) in CH_4 hydrate than that of small cage (S-cage)
Ostergaard et al. (2005)	▪ Injection method correlation ▪ 1:1 increase of temperature suppression with increasing inhibitor mole (%) fraction ▪ At low C, dT increases with C regardless of the types (methanol, ethylene glycol). ▪ Mole fraction of electrolyte ↑ = dT ↑ (CaCl2 > NaCl > methanol)

Graue et al. (2006)	CO_2 injection - Material: porous sandstone (sediment) / MRI - Hydrate formation: CH_4 introduce $\rightarrow H_2O \rightarrow$ cooling - Conversion of methane hydrate into CO2 hydrate in sandstone takes place without adding heat - No water phase during exchange
Chatterji and Griffith (1998)	- Chemical injection - Hindering its reformation by altering the fluid chemistry and lowering the phase transformation boundary
Haneda et al. (2005) Norway	- Nitrgjen injection (inhibitor) - Injecting air makes the phase equilibrium shifted to dissociate hydrate
Kawamura et al. (2006)	- Chemical injection with depressurization - Pressurized gas + ice (271.2K, 8.5-10MPa) - Ethylene glycol: become dilute solution near the reaction surface - Silicone oil: produce the thin water film on the reaction surface, lose the contact between MH and chemical.

B.4. Other Energy Forms

References	Features
Miura et al. (2006)	- Ultrasonic wave underwater (frequency = 28kHz) - Material: dry ice and CH4 hydrate - Ultrasonic wave makes the more gas production at given time, less elapse time and lower dissociation time - Heat may be transferred to methane hydrate by ultrasonic wave
Li et al. (2006) Norway	- Microwave heating and water bath heating - Microwave: up to 750 watt / frequency = 2.45GHz - Material: CH_4 hydrate - Rate of dissociation = power function (microwave power) - Microwave is more effective than water bath heating

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