

KINETICS OF HYDRATE FORMATION AND DECOMPOSITION OF METHANE IN SILICA SAND

Sung Chan Nam¹, Praveen Linga², Cef Haligva², John A. Ripmeester³ and Peter Englezos^{2*}

**¹ Energy Conversion Research Department,
Korea Institute of Energy Research,
Yuseong-gu, Daejeon, 305-343, Korea**

**² Department of Chemical and Biological Engineering,
University of British Columbia,
Vancouver, BC, V6T 1Z3, Canada**

**³ Steacie Institute for Molecular Sciences,
National Research Council Canada,
Ottawa, ON, K1A 0R6, Canada**

ABSTRACT

Kinetics of hydrate formation and decomposition of methane hydrate formed in silica sand particles were studied in detail at three temperatures of 7.0, 4.0 and 1.0°C, respectively. A new apparatus was setup to study the decomposition behavior of the methane hydrate formed in the bed of silica sand particles. Six thermocouples are placed in different locations to study the temperature profiles during hydrate formation and decomposition experiments. Gas uptake measurement curves for the formation experiments and the gas release measurement curves for the decomposition experiment were determined from the experimental data. Percent conversion of water to hydrates was significantly higher for the experiments conducted at 4.0 and 1.0°C compared to 7.0°C. Recovery of methane occurred in two stages during the decomposition experiments carried out with a thermal stimulation approach at constant pressure. Methane recovery in the range of 95 to 98% was achieved.

Keywords: Methane, gas hydrates, silica sand, decomposition, formation

INTRODUCTION:

Natural gas hydrates are non-stoichiometric, crystalline, inclusion compounds [1, 2]. They are known to plug hydrocarbon pipelines [3] and to occur naturally in the earth [4]. The first indication of natural gas hydrates outside of the Soviet Union was the report by Stoll et al. [5] observing that the formation of natural gas hydrates can result in significant increases in the acoustic wave velocity in ocean sediments. Based on wireline logs from two exploratory wells in the Mackenzie Delta, Canada, Bily and Dick [6] concluded that gas hydrates were contained in shallow sand reservoirs. As soon as the significance of the natural gas potential of gas hydrates stored in the earth was realized, efforts to develop extraction methods started [7-12]. Potential reserves of natural gas hydrates are over 1.5×10^{16} m³ and are distributed all over the earth on the land and

offshore [13-16].

In order to reliably predict the feasibility of producing natural gas from hydrates several key information are needed namely [17]: (1) Abundance of hydrates in the selected reservoir, (2) Lithology and geologic structure of the reservoir, (3) Presence or absence of a free zone, (4) Arrangement of hydrate within the porous medium, (5) Permeability, relative permeability-saturation relationships, capillary pressure-saturation relationships, and thermal conductivity of the hydrate-bearing and hydrate-free medium, (6) Energy required to dissociate the hydrate, (7) Kinetics of dissociation.

Several of these needs are reservoir specific but others such as dissociation kinetics have components of general applicability that can be

evaluated in the laboratory [17]. Two reports from the Los Alamos National laboratory presented the first state of the art and pointed out the difficulties associated with these gas recovery techniques [10, 18, 19]. Holder et al. [20] concluded that reservoir porosity and the thermal properties of the hydrates and the reservoir are determining factors that would enable a gas hydrate reservoir to produce gas in an energy efficient manner. It was also realized during these early studies that knowledge of the rate of hydrate decomposition is required although the term rate of decomposition is not precisely defined and more importantly it does not distinguish between intrinsic kinetic effects and those attributed to transport factors. Selim and Sloan [21] used thermal stimulation to decompose hydrates formed in porous media in the laboratory. The dissociation rate was found to depend on the thermal properties and the porosity of the reservoir. Further work reported from Sloan's laboratory found that the endothermic hydrate decomposition process could cause such a temperature drop that would allow hydrates to re-form or ice to freeze [22, 23].

Although significant progress has been made regarding modeling and numerical simulation of natural gas hydrate reservoirs [24-30], very few papers are available in the literature on experimental data on hydrate kinetics investigated in porous medium [17, 31-33]. Handa and Stupin [31] reported thermodynamic properties and dissociation characteristics of methane and propane in silica gel pores. Stern et al [32] observed the peculiarities of methane clathrate hydrate formation and solid state deformation. However, the conditions at which the observations [31, 32] were made are $< 105\text{ K}$ and 10^{-3} Pa , whereas the natural environment for the samples is moderate pressures (approximately 3 to 10 MPa) and above-freezing temperatures [17].

Kneafsey et al. [17] studied hydrate formation of methane-water system in the presence of silica sand (Foundry 110, U. S. Silica, Berkeley Springs WV) with particle size primarily between 100 to 200 μm . They studied methane hydrate formation/dissociation in a large X-ray transparent pressure vessel monitoring pressure and temperature. In addition, they monitored the local density changes using X-ray computed topography during the experiment. They observed that the rate of hydrate formation is not always proportional to

the driving force in the porous medium. They also conclude the need for multiple means of measurement as critical for understanding hydrate behaviour during hydrate formation and decomposition. Tang et al. [33] studied the production behaviour of gas hydrate under thermal stimulation in unconsolidated segment. They reported that the gas production rate increased with time until it reaches a maximum, then it begins to decrease. However, hydrate content for all the experiments that were reported was less than 18.0 volume%.

The objective of this work is to study the kinetics of hydrate formation and decomposition of methane hydrates in the presence of silica sand. Key information like the gas uptake and gas recovery curves along with the percent conversion of water to hydrates and methane recovery rates are presented.

EXPERIMENTAL SECTION:

Methane used for the present study was supplied by Praxair (UHP grade). The silica sand was supplied by Sigma Aldrich. Water used for the experiments was distilled and deionised. The silica sand has an average diameter of 329 μm (diameter ranges from 150 to 630 μm). BET surface area analysis of the sand showed that the silica sand used in this work is micro porous with a pore volume of $0.000152\text{ cm}^3/\text{g}$ and a pore diameter of 0.90 nm.

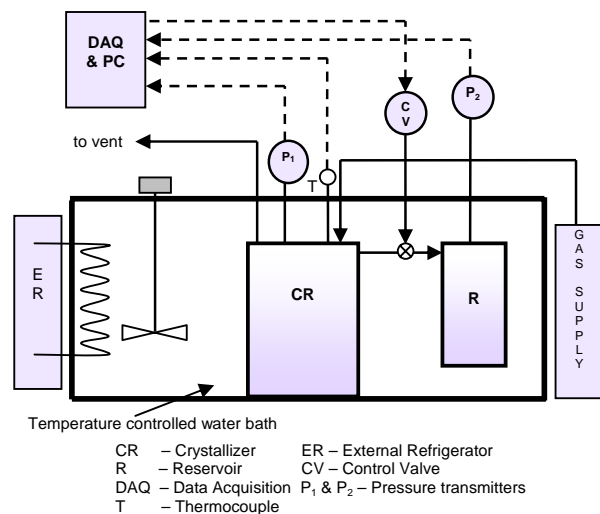


Figure 1. Schematic of the apparatus

A schematic of the apparatus is given in Figure 1. It consists of a crystallizer (CR) with a volume of 1236.05 cm³. The experimental set up also consists of a reservoir (R), which is used to collect the decomposed gas during hydrate decomposition. Both CR and R are immersed in a water bath. The temperature of the water bath is controlled by an external refrigerator. The apparatus is instrumented with two pressure transmitters and several thermocouples connected to a data acquisition system to record the pressure and temperature data. The apparatus also consists of a control valve coupled with a PID controller in order to decompose the hydrates at constant pressure. Six thermocouples are located inside the silica sand bed.

Hydrate formation procedure:

The amount of silica sand placed in the crystallizer for each experiment is 914.1g (Height of silica bed = 7 cm). 198.5 ml of water is added into the sand. Once the crystallizer bed is setup the thermocouples are positioned and then the crystallizer is closed. The pressure in the crystallizer is then set to the desired experimental pressure (8.0 MPa) and the temperature is allowed to reach the experimental temperature. This is time zero for the formation experiment. Data is then logged in the computer for every 20 seconds. All hydrate formation experiments are carried out with a fixed amount of water and gas (closed system). The temperature in the crystallizer is maintained constant by an external refrigerator. When hydrate formation occurs, gas will be consumed and hence the pressure in the closed system drops. The experiment is allowed to continue until there is no significant change in the crystallizer pressure.

Pressure and temperature data are used to calculate the moles of methane consumed in the crystallizer (gas uptake) for hydrate formation. At any given time, the total number of moles ($n_{T,t}$) in the system (crystallizer and the connecting tubing) remains constant and equal to that at time zero ($n_{T,0}$). The total number of moles at any given time is the sum of the number of moles (n_G) in gas phase (G) of the crystallizer and the number of moles (n_H) in the hydrate phase. Thus, the number of moles of the gas that has been consumed for hydrate formation at time $t = t$ is given by the following equation.

$$n_{H,t} - n_{H,0} = n_{G,0} - n_{G,t} \quad (1)$$

or

$$\Delta n_{H,\downarrow} = n_{H,t} - n_{H,0} = \left(\frac{PV}{zRT} \right)_{G,0} - \left(\frac{PV}{zRT} \right)_{G,t} \quad (2)$$

where $\Delta n_{H,\downarrow}$ is the number of moles consumed at any given time for hydrate formation, z is the compressibility factor calculated by Pitzer's correlation [34] and G denotes the gas phase of the crystallizer.

Hydrate decomposition procedure:

After the completion of hydrate formation experiment, the hydrates are decomposed at a constant pressure as follows. The pressure in the crystallizer is decreased to the desired pressure (20% above the equilibrium hydrate formation pressure). The temperature in the crystallizer is then allowed to become stable. This takes less than about 10 min. The temperature of the crystallizer is then increased to the desired value by heating the water bath with an external refrigerator/heater. This is time zero for the decomposition experiment. During the experiment, when the temperature of the crystallizer crosses the equilibrium phase boundary, hydrate starts to decompose and since the pressure in the crystallizer is maintained constant by the PID controller, the excess gas is released from the crystallizer and collected in the reservoir (R). The experiment proceeds until there is no further release of methane gas from the silica sand.

At any given time, the total number of moles ($n_{T,t}$) in the system remains constant and equal to that at time zero ($n_{T,0}$). The system in this case includes the crystallizer (CR), the reservoir (R) and the connecting tubing. The total number of moles at any given time is the sum of the number of moles (n_G) in gas phase (G) of the crystallizer, the number of moles (n_R) collected in the reservoir and the number of moles (n_H) in the hydrate phase.

The number of moles of gas released from the hydrate at any time during hydrate decomposition can then be calculated as follows,

$$n_{H,0} - n_{H,t} = n_{G,t} - n_{G,0} + n_{R,t} - n_{R,0} \quad (3)$$

or

$$\Delta n_{H,\uparrow} = \left(\frac{PV}{zRT} \right)_{G,t} - \left(\frac{PV}{zRT} \right)_{G,0} + \left(\frac{PV}{zRT} \right)_{R,t} - \left(\frac{PV}{zRT} \right)_{R,0} \quad (4)$$

The percent methane recovery is calculated for the decomposition experiment based on information obtained from its formation experiment and is calculated by the following equation.

$$\% \text{ methane recovery} = \frac{(\Delta n_{H,\uparrow})}{(\Delta n_{H,\downarrow})} \times 100 \quad (5)$$

Where $(\Delta n_{H,\downarrow})$ is the number of moles of methane consumed for hydrate formation at the end of a typical formation experiment and $(\Delta n_{H,\uparrow})$ is the number of moles of methane released from hydrate during hydrate decomposition.

Results and discussion:

Formation experiments were carried out at three different temperatures of 7.0, 4.0 and 1.0°C, respectively. The initial experimental pressure for all the experiments was 8.0 MPa. The experiment was allowed to continue until there was no further gas consumption for hydrate formation. This is indicated by a near-zero rate of pressure drop as seen in Figure 2 for a typical formation experiment.

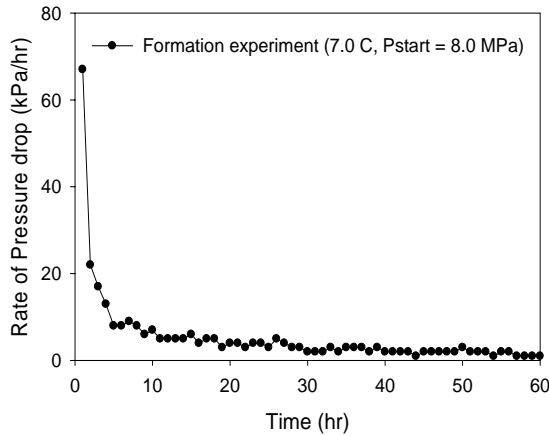


Figure 2. Rate of pressure drop due to hydrate growth during hydrate formation

The number of moles consumed for hydrate formation is determined using equation 2 for the formation experiments. Figure 3 shows the gas uptake measurement curve for a formation experiment carried out at 7.0°C along with the temperature profiles of the thermocouples located

inside the bed. Hydrate formation is an exothermic crystallization process. Hence during hydrate formation, heat is released which can be seen in the figure at 207 min. This point during hydrate formation is called the nucleation point or turbidity point. The temperature of the system is gradually restored to its set point due to the constant temperature bath controlled by an external refrigerator. The nucleation point is shown as an expanded graph in Figure 3.

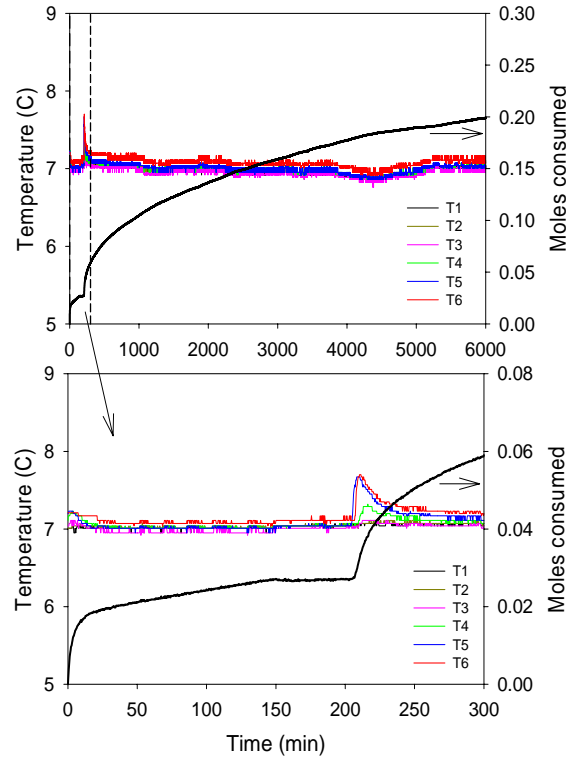


Figure 3. Gas uptake measurement curve at 7.0°C.

Figure 4 shows the gas uptake measurement curve for the formation experiment carried out at 1.0°C. It can be seen that the temperature profiles show several nucleation regions occurring during the formation experiment. The first temperature increase at the nucleation point can be seen in section A in the figure. In section B, the temperature increase is not localized and there is a larger consumption of gas for hydrate formation during that region. Overall, as can be seen in figure 4, hydrate formation does not proceed at a constant rate. Similar observation was made by Kneafsey et al.,[17] when hydrates were formed at 6.2 MPa and 1.1°C in the presence of silica sand with a particle size of 100 to 200 μm . It can also

be seen from figure 3 and 4 that the moles consumed for hydrate formation is higher for the experiment carried out at 1.0°C compared to the one conducted at 7.0°C. A similar trend was observed for the experiment carried out at 4.0°C. This is because multiple nucleation points were observed for formation experiments carried out at 4.0 and 1.0°C resulting in a significantly higher methane uptake.

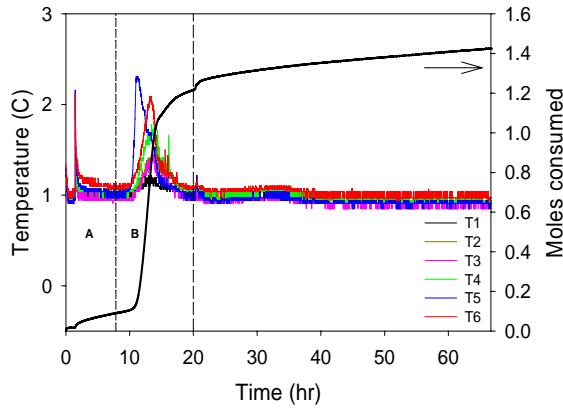


Figure 4. Gas uptake measurement curve at 1.0°C

The conversion of water to hydrate during the formation experiment was determined using the gas uptake information. The hydration number for methane/water system was assumed as 6.1 for our calculations [35]. The conversion of water to hydrate was 11.0, 78.5 and 79.8 mol% for the experiments carried out at 7.0, 4.0 and 1.0°C, respectively. Experiments at 4.0°C and 1.0°C achieve the same level of water to hydrate conversion. However, there is a distinct difference in water to hydrate conversion percentages between 7.0°C and 4.0°C (i.e. 11.0% vs. 78.5%).

After the end of each formation experiment, the hydrates are decomposed using thermal stimulation at a constant pressure. Decomposition experiments were carried out at constant pressure of 6.2, 4.6 and 3.5 MPa for the formation experiments carried out at 7.0, 4.0 and 1.0°C, respectively. The number of moles of methane released from hydrates is calculated using equation 4. Figure 5 shows the typical gas recovery curve obtained from the decomposition experiment with temperature as the driving force ($\Delta T = 4.0^\circ\text{C}$) at a constant pressure of 3.5 MPa. As it can be seen in the figure, there is no gas release till the

temperature crosses the phase boundary. For this experiment, when the temperature crosses 3.0°C , hydrate starts to decompose and since the pressure in the crystallizer is maintained constant, the gas released is collected in the reservoir (R).

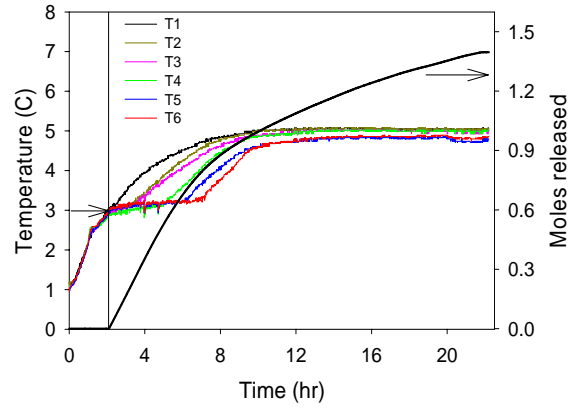


Figure 5. Typical gas release measurement curve carried out at 3.5 MPa and a temperature driving force (ΔT) of 4.0°C

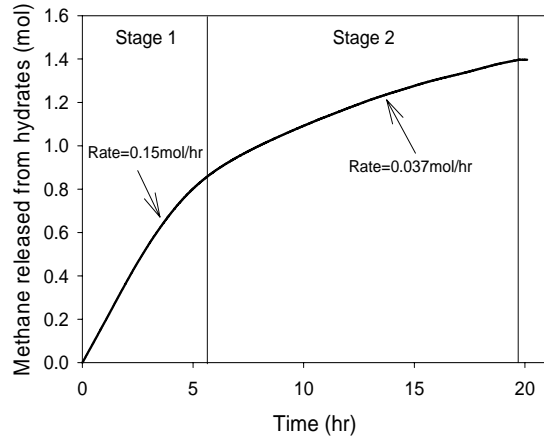


Figure 6. Methane recovery from hydrate ($P_{\text{exp}} = 3.5 \text{ MPa}$, $\Delta T = 4.0^\circ\text{C}$)

Figure 6 shows the methane gas recovery as a function of time. Time zero in this figure is the time when methane is released from the hydrate during the decomposition experiment. As it can be seen in the figure, methane recovery occurs in two stages (Stage 1 & Stage 2). The recovery rates were calculated for the stages and are given in the figure. As expected the recovery rates are higher in stage 1 compared to stage 2 because the hydrate zone is being depleted of methane gas during the decomposition experiment. It is noted that the

amount of methane is fixed (closed system). The percentage recovery of methane from hydrates for the decomposition experiments was determined using equation 5 and found to be 96.0, 97.6 and 98.1 for the experiments carried out at 8.2, 4.6 and 3.5 MPa, respectively.

CONCLUSIONS:

A new apparatus was set up to study methane hydrate formation and decomposition behavior in silica sand. Hydrate formation experiments were studied at three different temperatures of 7.0, 4.0 & 1.0°C, respectively. Multiple nucleation points were observed for formation experiments carried out at 4.0 and 1.0°C resulting in a significantly higher methane uptake. This resulted in achieving a higher percent conversion of water to hydrates in the range of 78 to 80%. Decomposition experimental procedure adopting thermal stimulation approach was carried out for recovering methane from hydrates. Methane recovery occurred in two stages during the decomposition experiments. Methane recovery in the range of 95 to 98% was achieved.

ACKNOWLEDGEMENT:

The financial support from the *Natural Sciences and Engineering Research Council of Canada* (NSERC) and *Natural Resources Canada* (NRCan) is greatly appreciated.

REFERENCES:

- [1] Davidson DW. *Gas Hydrates. In Water: A Comprehensive Treatise*. New York: Plenum Press; 1973. 115 - 234 p.
- [2] Sloan ED, Jr. *Clathrate Hydrates of Natural Gases, Second Edition, Revised and Expanded*. NY: Marcel Dekker; 1998. 754 pp. p.
- [3] Hammerschmidt EG. *Formation of Gas Hydrates in Natural Gas Transmission Lines*. Industrial and Engineering Chemistry 1934; 26, No. 8:851-855.
- [4] Makogon YF, Trebin FA, Trofimuk AA *et al*. *Detection of A Pool of Natural Gas in a Solid (Hydrated Gas) State*. Doklady Akademii Nauk SSSR 1971; 196:203-206.
- [5] Stoll RD, Ewing J, Bryan GM. *Anomalous Wave Velocities in Sediments Containing Gas Hydrates*. Journ. of Geophysical Research 1971; 76, No. 8:2090-2094.
- [6] Bily C, Dick JWL. *Naturally Occurring Gas Hydrates in the Mackenzie Delta, N.W.T.* Bulletin of Canadian Petroleum Geology 1974; 22, No. 3:340-352.
- [7] Davidson DW, El-Defrawy MK, Fuglem MO, Judge AS. *Natural Gas Hydrates in Northern Canada*. Int. Conf. Permafrost Proc. 1978; 3(1):937-943.
- [8] Bowsher AL. *Proceedings of a Workshop on Clathrates in NPRA held in Menlo Park 7/16-17/79*. USGS Open File Report 1981; 81-1298:0-164.
- [9] Stoll RD, Bryan GM. *Physical Properties of Sediments Containing Gas Hydrates*. Jour. Geophys Research 1979; 84:B4:1629.
- [10] Barraclough BL. *Methane Hydrate Resource Assessment Program. April-June 1980*. Los Alamos Sci Lab Progr Rep No. LA-8569-PR 1980:27 pp.
- [11] Makogon YF. *Perspectives for the Development of Gas-Hydrate Deposits*. 4th Can. Permafrost Conf. Proc. R.J.E. Brown Memor. Volume 1982:299-304.
- [12] Judge A. *Natural Gas Hydrates in Canada*. 4th Can Permafrost Conf.Proc. R.J.E. Brown Memor Volume 1982:320-328.
- [13] Kvenvolden K. *Potential effects of gas hydrate on human welfare*. Proc. Natl. Acad. Sci. US 1999; 96:3420.
- [14] Milkov AV, Dickens GR, Claypool GE *et al*. *Co-existence of gas hydrate, free gas, and brine within the regional gas hydrate stability zone at Hydrate Ridge (Oregon margin): evidence from prolonged degassing of a pressurized core*. Earth and Planetary Science Letters 2004; 222:829-843.
- [15] Kvenvolden KA. *Gas Hydrates - Geological Perspective and Global Change*. Reviews of Geophysics 1993; 31(2):173-187.
- [16] Makogon YF, Holditch SA, Makogon TY. *Natural gas-hydrates - A potential energy source for the 21st Century*. Journal of Petroleum Science and Engineering 2007; 56:14-31.
- [17] Kneafsey TJ, Tomutsa L, Moridis GJ *et al*. *Methane hydrate formation and dissociation in a partially saturated core-scale sand sample*. Journal of Petroleum Science and Engineering 2007; 56:108-126.
- [18] McGuire PL. *Methane Hydrate Gas Production: An Assessment of Conventional Production Technology as Applied to Hydrate Recovery*. LASL Report LA-9102-MS, Order No. DE82006746 from NTIS 1981:20.
- [19] McGuire PL. *Methane Hydrate Gas Production by Thermal Stimulation*. 4th Can.

- Permafrost Conf, Calgary 3/2-6/81, R.E. Brown Mem Volume 1982:356-362.
- [20] Holder GD, Angert PF, John VT, Yen S. A *Thermodynamic Evaluation of Thermal Recovery of Gas From Hydrates in the Earth*. J. Petrol Tech. 1982; 34(5):1127-1132.
- [21] Selim MS, Sloan ED. *Hydrate Dissociation in Sediment*. Soc. Petr. Eng. Reservoir Eng. 1990:245.
- [22] Yousif MH, Abass HH, Selim MS, Sloan ED. *Experimental and Theoretical Investigation of Methane Gas Hydrate Dissociation in Porous Media*. SPE Reservoir Engineering 1991; 6:69-76.
- [23] Yousif MH, Sloan ED. *Experimental investigation of hydrate formation and dissociation in consolidated porous media*. SPE Reservoir Engineering 1991; 6:452-458.
- [24] Moridis G, Collett TS, Dallimore SR *et al*. *Numerical Simulation Studies of Gas Production Scenarios From Hydrate Accumulations at the Mallik Site, Mackenzie Delta, Canada*. Proc. 4th International Conference on Gas Hydrates, Yokohama May 19-23, 2002 2002:239-244.
- [25] Moridis GJ. *Numerical studies of gas production from methane hydrates*. Spe Journal 2003; 8:359-370.
- [26] Moridis GJ. *Numerical studies of gas production from Class 2 and Class 3 hydrate accumulations at the Mallik site, Mackenzie Delta, Canada*. Spe Reservoir Evaluation & Engineering 2004; 7:175-183.
- [27] Moridis GJ, Collett TS, Dallimore SR *et al*. *Numerical studies of gas production from several CH₄ hydrate zones at the Mallik site, Mackenzie Delta, Canada*. Journal of Petroleum Science and Engineering 2004; 43:219-238.
- [28] Moridis GJ, Kowalsky MB. *Response of oceanic hydrate-bearing sediments to thermal stresses*. Spe Journal 2007; 12:253-268.
- [29] Kowalsky MB, Moridis GJ. *Comparison of kinetic and equilibrium reaction models in simulating gas hydrate behavior in porous media*. Energy Conversion and Management 2007; 48:1850-1863.
- [30] Gerami S, Pooladi-Darvish M. *Predicting gas generation by depressurization of gas hydrates where the sharp-interface assumption is not valid*. Journal of Petroleum Science and Engineering 2007; 56:146-164.
- [31] Handa YP, Stupin D. *Thermodynamic Properties and Dissociation Characteristics of Methane and Propane Hydrates in 70Å Radius Silica Gel Pores*. J. Physical Chemistry 1992; 96:8599.
- [32] Stern LA, Kirby SH, Curham WB. *Peculiarities of Methane Clathrate Hydrate Formation and Solid-State Deformation, Including Possible Superheating of Water Ice*. Science 1996; 273:1843-1848.
- [33] Tang LG, Xiao R, Huang C *et al*. *Experimental investigation of production behavior of gas hydrate under thermal stimulation in unconsolidated sediment*. Energy & Fuels 2005; 19:2402-2407.
- [34] Smith JM, Van Ness HC, Abbott MM. *Introduction to Chemical Engineering Thermodynamics*. New York: McGraw-Hill, Inc.; 2001.
- [35] Ripmeester JA, Ratcliffe CI. *Low-Temperature Cross-Polarization Magic Angle Spinning C-13 Nmr of Solid Methane Hydrates - Structure, Cage Occupancy, and Hydration Number*. Journal of Physical Chemistry 1988; 92:337-339.