ISSN 2004-2965 Energy Proceedings, Vol. 17, 2021

Paper ID APEN-MIT-2021_215
Applied Energy Symposium: MIT A+B
August 11-13, 2021 • Cambridge, USA

Electricity Generation from Flowing Gas Hydrates

Boyun Guo
Department of Petroleum Engineering
University of Louisiana at Lafayette
Lafayette, USA
boyun.guo@louisiana.edu

Ning Liu
Department of Petroleum Engineering
University of Louisiana at Lafayette
Lafayette, USA
ning.liu@louisiana.edu

Jim Lee
Department of Mechanical Engineering
University of Louisiana at Lafayette
Lafayette, USA
jim.lee@louisiana.edu

Abstract— Gas hydrates are snow-like materials made of water molecules trapping gas molecules under high-pressure and low-temperature conditions such as that at chokes and valves installed on natural gas wellheads and pipelines. Electricity was found generated from flowing methane-, ethane-, propane-, and CO_2-hydrates along PVC tubes in laboratories. The rate of building electric charges and the level of the built voltage were found to depend on pressure drop/volume expansion when the hydrate was released to the PVC tube. Sparks/light were emitted when the static voltage reached a level of about 300 mV in the system investigated. An explanation of the observed sparks/light is the generation of static electricity when gas-hydrate passed through the PVC tube at a high velocity (flow electrification), or triboelectricity. The charge level is higher for poorly conductive gas-hydrate flowing through the PVC tube. In addition, the large amounts of gas bubbles flowing through the tube should amplify the static electricity. However, in this investigation, it was noticed that no spark/light was observed and no voltage pulse was detected during the active flow of hydrates. Instead, sparks/light were observed and voltage pulses were detected after the choking valve was switched on. The positive voltage probe was connected to the choking valve and the negative voltage probe was connected to the PVC tube. The voltage meter measured positive pulses of voltage difference between the two probes when the choking valve was off. This indicates current flow from the choking valve to the PVC tube, or electron charge flow from the PVC tube to the choking valve. Our hypothesis to explain these phenomena is that the flowing hydrates captured electrons from the low-conductive PVC tube and transported them in the flow stream, resulting in a "positive charged" PVC tube in the entry portion. When the flow was terminated by valve closing, the electrons in the down-stream of the PVC tube flew back to the entry portion to minimize the charge unbalance, causing sparks/light and current flow from the choking valve to the PVC tube. This hypothesis needs to be proven in future investigations. Further studies are recommended in this area and more investigations are required for flowing methane-, ethane-, propane-hydrates. Potential applications of the hydrate-triboelectricity include harvesting electricity in the downstream of surface chokes installed on the natural gas wellheads where there exist flowing gas hydrates.

Keywords— CO_2, gas, hydrate, triboelectricity, experiment.

I. Introduction

Gas hydrates are snow-like materials made of water molecules trapping gas molecules under high-pressure and low-temperature conditions. Hydrate-forming gases include methane, ethane, propane, iso-butane, carbon dioxide, and their mixtures (natural gas). Gas hydrate trapping methane molecules has a composition formula of $(CH_4)_4(H_2O)_{23}$, corresponding to about 13.4% gas by mass. One volume of methane-hydrate contains about 160 volumes of methane under standard condition (Sloan, 2003).

U.S. Geological Survey reported that natural gas hydrates hold twice as much carbon as Earth's other fossil fuels combined (USGS, 2009). The amount of gas hydrates accounts for at least 10 times the supply of conventional natural gas deposits. If the natural gas stored in the gas hydrates can be safely, efficiently, and economically released, it can displace coal and oil as the major sources of the world's energy supply (Ruppel, 2014).

Many researchers investigated the kinetics of gas hydrates last century (Kim et al. 1987). A great number of hydrate-related publications were made in the past decade. Sloan et al. (2007) collate this vast amount of information into the book *Clathrate Hydrates of Natural Gases*. Recent research work has a tendency to shift to efficient recovery of natural gas from gas hydrates deposits. Four methods have been proposed/tested for gas production from nature gas hydrate deposit: 1) depressurization (Ahmadi et al., 2007; Li et al., 2010; Janicki et al., 2017) – this method decreases the gas hydrate reservoir pressure below the hydrate dissociation pressure; 2) thermal stimulation (Kawamura et al., 2007; Li et al., 2006; Li et al., 2008; Zhao et al., 2012) – this approach uses external heat to the gas hydrate reservoir temperature above hydrate dissociation temperature with hot water/brine/steam; 3) thermodynamic inhibitor injection (Kawamura et al., 2005; Najibi et al., 2009; Li et al., 2011) – this technique uses chemicals, such as salts and alcohols, to change the hydrate pressure-temperature equilibrium conditions; 4) a combination of these methods (Moridis et al., 2009). Max and Johnson (2016) reviewed the current practices in the exploration and production of oceanic natural gas hydrate.

Both Japan and China announced mining of marine gas hydrates to extract natural gas (Li et al., 2011; Hiroko, 2013; Macfarlane, 2017). As the technologies for producing natural gas from gas hydrate reservoirs are becoming mature, the flow behavior of gas hydrates has recently attracted significant research interest in multi-phase flow mechanics

(Li et al., 2017; Guo et al., 2018). It is highly desirable to know the electric behavior of gas hydrates for safe harvesting natural gas from gas hydrate deposits.

A state-of-art experimental setup was developed for the rapid formation of gas hydrates in this study. Electricity generation from flowing methane-, ethane-, propane-, and CO_2-hydrates was experimentally studied using the setup. Electricity was observed for hydrate flow in PVC tubes. Because CO_2 is an inflammable gas, more lab tests were performed on this gas than on other gases for safety considerations. Distribution of electric potential along a transparent tube through which gas hydrates flowed was measured. Electric sparks and light were observed and recorded. It was found that the magnitude of the intensity of the sparks/light depends on several factors including pressure and temperature.

II. EXPERIMENTAL SETUP AND PROCEDURE

The experimental setup for testing the electric behavior of flowing gas hydrates is depicted in **Figure 1**. The gas bottle and water pump feed hydrate-forming gas and water to the system. The hydrate-forming cell cooled by the water bath provides a high-pressure and low-temperature condition for hydrate formation. The thermal control unit makes the water bath temperature adjustable. The operating valve creates a pressure reduction and thus local cooling of gas by the Joule-Thomson effect. The clear PVC tube (EZ-FLO 0.170-in ID PVC Clear Vinyl Tubing) offers an in-situ condition for observing electric spark/light generated by the gas hydrate flowing through it. The camera video-records the spark/light in the PVC tube. The Voltage meter measures and records electric potential along the PVC tube. All measurements are saved in the data acquisition computer. A close look at the PVC tube is shown in **Figure 2**.

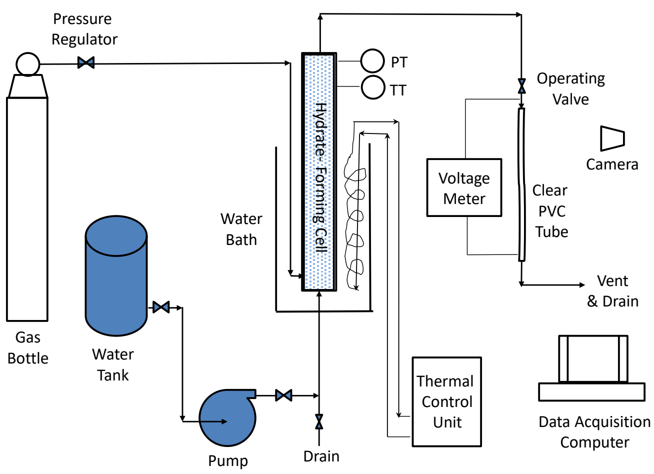

Figure 1: Experimental setup for testing the electric behavior of flowing gas hydrates

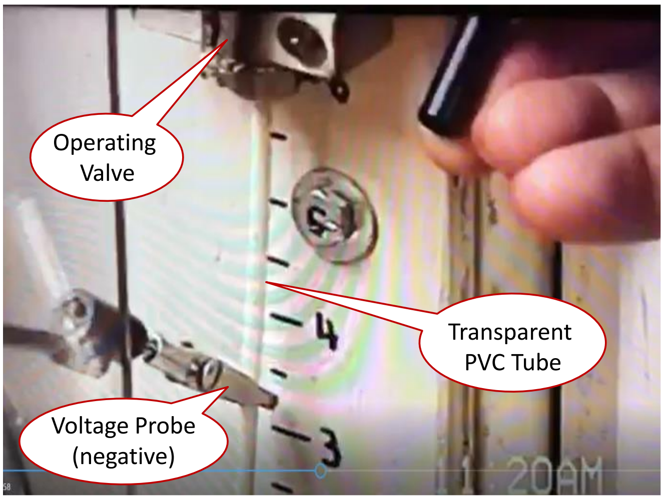

Figure 2: Clear PVC tube installed in the downstream of the operating valve.

The experimental procedure is outlined as follows:

1. Prepare water in the water tank and water bath.
2. Turn on the thermal control unit to cool the water bath to a desired hydrate forming temperature level.
3. With the operating valve open, pump water into the hydrate-forming cell up to 60% of its volume.
4. With the operating valve closed, adjust the pressure regulator to feed gas into the hydrate-forming cell up to the desired hydrate forming pressure level.
5. Turn off the pressure regulator and observe pressure decline in the hydrate-forming cell. The pressure decline indicates the formation of gas hydrate clathrates in the cell (the time required to form hydrate is long for the first time, depending on pressure, temperature, water purity, and agitation).
6. Adjust pressure regulator to feed gas into the hydrate-forming cell up to desired hydrate forming pressure level.
7. Switch on and off the operating valve quickly and observe sparks/light in the PVC tube and transmits voltage data and video into the data acquisition computer.

III. EXPERIMENTAL RESULT

Carbon dioxide forms hydrate at pressures above 18 bars at temperature 275K in distilled water. Three experiments were conducted under different pressures with distilled water. The upstream pressure (above the operating valve) varied from 35 bar to 140 bar. The downstream (in the PVC tube) fluctuated between 4 bars and 14 bars. Measured temperatures in the PVC tube were between 200 K and 283 K. During one experiment, the upstream pressure dropped from 105 bars to 70 bars within 3 minutes, the downstream pressure fluctuated between 7 bars and 10 bars, the measured downstream temperature was 268 K, and the flow velocity in the transparent tube was estimated to be about 40 m /s.

The first experiment was conducted with a hydrate-forming cell condition of 70 bar and 275K. Two sparks are shown in **Figures 3** and **4**. Voltage signals measured at 6.35 cm from the tube entry are presented in **Figure 5.** Sparks were observed after the static voltage built to greater than about 300 mV.

The second experiment was carried out with a hydrate-forming cell condition of 105 bar and 285K. Two sparks/light signals are shown in **Figures 6** and **7.** Voltage signals measured at 6.35 cm from the tube entry are presented in **Figure 8.** Sparks/light were observed after the static voltage built to greater than about 300 mV.

The third experiment was performed with a hydrate-forming cell condition of 140 bar and 295K. Two sparks/light signals are shown in **Figures 9** and **10**. Voltage signals measured at 6.35 cm from the tube entry are presented in **Figure 11.** Sparks/light were observed after the static voltage built to greater than about 300 mV.

Figure 3: A short spark observed at the entry point of PVC tube with a hydrate-forming cell condition of 70 bar and 275K.

Figure 4: A long spark observed at the entry point of PVC tube with a hydrate-forming cell condition of 70 bar and 275K.

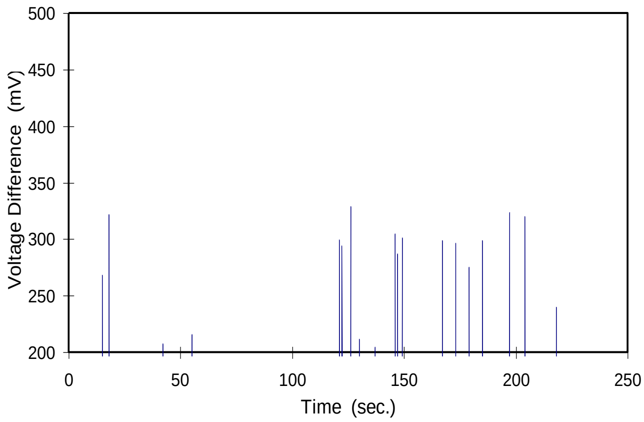

Figure 5: Voltage signal measured at a point 6.35 cm from the tube entry with a hydrate-forming cell condition of 70 bar and 275K.

Figure 6: A short light beam observed near the entry point of PVC tube with a hydrate-forming cell condition of 105 bar and 285K.

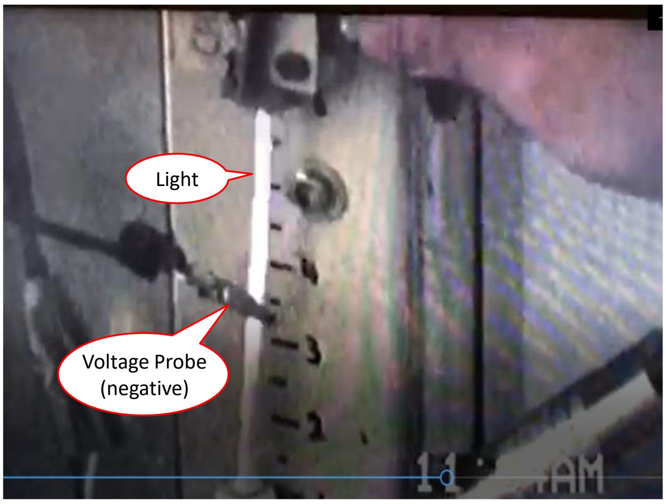

Figure 7: A long light beam observed near the entry point of PVC tube with a hydrate-forming cell condition of 105 bar and 285K.

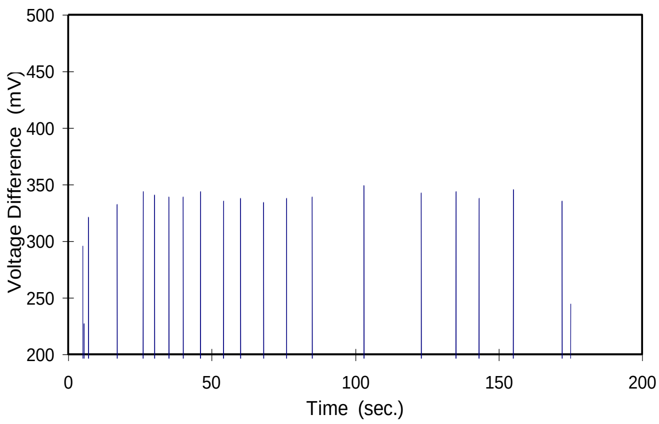

Figure 8: Voltage signal measured at a point 6.35 cm from the tube entry with a hydrate-forming cell condition of 105 bar and 285K.

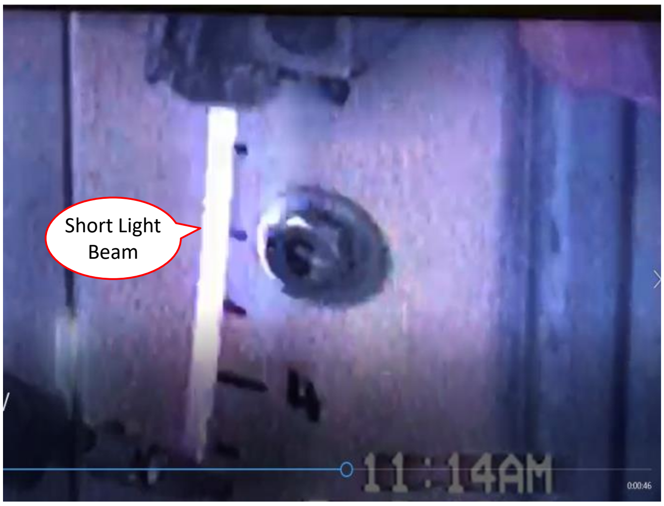

Figure 9: A short light beam observed near the entry point of PVC tube with a hydrate-forming cell condition of 140 bar and 295K.

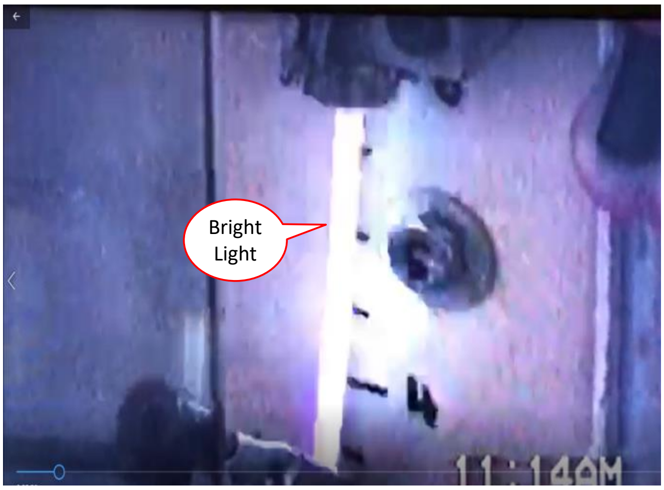

Figure 10: Bright light observed in the PVC tube with a hydrate-forming cell condition of 140 bar and 295K.

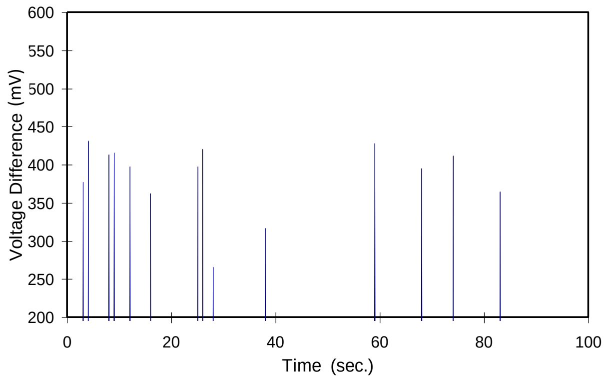

Figure 11: Voltage signal measured at a point 6.35 cm from the tube entry with a hydrate-forming cell condition of 140 bar and 295K.

IV. DISCUSSION

An explanation of the observed sparks/light is the generation of static electricity when CO_2-hydrate was passed through the PVC tube at a high velocity (flow electrification), or triboelectricity. The charge level is higher for poorly conductive gas-hydrate flowing through the PVC tube. In addition, the large amounts of CO_2 bubbles flowing through the tube should amplify the static electricity. However, in this investigation, it was noticed that no spark/light was observed and no voltage pulse was detected during the active flow of hydrates. Instead, sparks/light were observed and voltage pulses were detected after the operating valve was switched on. The positive voltage probe was connected to the operating valve and the negative voltage probe was connected to the PVC tube. The voltage meter measured positive pulses of voltage difference between the two probes when the operating valve was off. This indicates current flow from the operating valve to the PVC tube, or electron charge flow from the PVC tube to the operating valve. Our hypothesis to explain these phenomena is that the flowing hydrates captured electrons from the low-conductive PVC tube and transported them in the flow stream, resulting in a "positive charged" PVC tube in the entry portion. When the flow was terminated by valve closing, the electrons in the down-stream of the PVC tube flew back to the entry portion to minimize the charge unbalance, causing sparks/light and current flow from the operating valve to the PVC tube. This hypothesis needs to be proven in future investigations. Triboelectricity was also observed by the investigator in methane-, ethane-, and propane-hydrates flow in PVC tubes. Further studies are recommended. More investigations are required in this area. Potential applications of the hydrate-triboelectricity include harvesting electricity in the downstream of surface chokes installed on the natural gas wellheads where there exist flowing gas hydrates.

V. CONCLUSIONS

1. Electricity can be generated when carbon dioxide (CO_2) hydrate is passed through a PVC tube at high velocity. The rate of building electric charges and the level of built voltage depend on pressure drop/volume expansion when the hydrate is released to the PVC tube.
2. Sparks/light were emitted when the static voltage reached a level of about 300 mV in the system investigated. The emission of sparks/light balanced electric charges through the flow of electrons in the direction that is opposite to the fluid flow, i.e., the electric current is in the direction of fluid flow.
3. It is hypothesized that the electricity generated by the flowing gas hydrates is triboelectricity. The flow hydrates captures electrons from the low-conductive PVC tube and transports them in the flow stream, resulting in a "positive charged" PVC tube in the entry portion. When the fluid flow was terminated, the electrons in the down-stream of the PVC tube flew back to the entry portion, causing sparks/light, to minimize the charge unbalance.
4. Future investigations are recommended to investigate methane-, ethane-, and propane-hydrates flow systems. Potential applications of the hydrate-triboelectricity include harvesting electricity in the downstream of surface chokes installed on the natural gas wellheads where there exist flowing gas hydrates.

ACKNOWLEDGMENT

This research was supported by the U.S. - Israel Center of Excellence in Energy, Engineering and Water Technology through the project "Safe, sustainable, and resilient development of offshore reservoirs and natural gas upgrading through innovative science and technology: Gulf of Mexico – Mediterranean."

REFERENCES

Ahmadi, G., Ji, C.A., Smith, D.H. 2007. Production of natural gas from methane hydrate by a constant downhole pressure well. Energy Convers. Manage. 48 (7), 2053–2068.

Guo, B. and Shan, L. Heat Transfer in Counter-Current Two Phase Flow Applied to Feasibility Study of Harvesting Natural Gas from Seabed Hydrates, *International Journal of Heat and Mass Transfer*, 126 (2018) 603-612.

Hiroko, T. (2013). An Energy Coup for Japan: "Flammable Ice. New York Times. Retrieved March 14, 2013.

Janicki, G., Schlüter, S., Hennig, T., Deerberg, G. 2017. Numerical simulation of gas hydrate exploitation from subsea reservoirs in the Black Sea, In Energy Procedia, Volume 125, 2017, Pages 467-476, ISSN 1876-6102.

Kawamura, T., Yamamoto, Y., Ohtake, M., Sakamoto, Y., Komai, T., Haneda, H., 2005. Experimental study on dissociation of hydrate core sample accelerated by thermodynamic inhibitors for gas recovery from natural gas hydrate. Paper 3023, Proceedings of the 5th International Conference on Gas Hydrates. Trondheim, Norway, 13–16 June 2005.

Kawamura, T., Ohtake, M., Sakamoto, Y., Yamamoto, Y., Haneda, H., Komai, T., Higuchi, S., 2007. Experimental study on steam injection method using methane hydrate core samples. Proceedings of the Seventh (2007) ISOPE Ocean Mining Symposium. Lisbon, PORTUGAL, 1–6 July, pp. 83–86.

Kim, H.C. et al. 1987. "Kinetics of Methane Hydrate Decomposition," Chemical Engineering Science, vol. 42, No. 7, pp. 1645-1653.

Li, G., Tang, L.G., Huang, C., Feng, Z.P., Fan, S.S., 2006. Thermodynamic evaluation of hot brine stimulation for natural gas hydrate dissociation. J. Chem. Ind. Eng. China 57 (9), 2033–2038.

Li, G., Li, X.S., Tang, L.G., Li, Q.P., 2008. Control mechanisms for methane hydrate production by thermal stimulation. Paper 5783, Proceedings of the 6th International Conference on Gas Hydrates. Vancouver, British Columbia, Canada, 6–10 July 2008.

Li, G, Moridis GJ, Zhang K, Li XS., 2011. The use of huff and puff method in a single horizontal well in gas production from marine gas hydrate deposits in the Shenhu Area of South China Sea. J Petrol Sci Eng 2011;77:49–68.

Li, G, Moridis GJ, Zhang KN, Li XS., 2010. Evaluation of gas production potential from marine gas hydrate deposits in Shenhu Area of South China Sea. Energy Fuels 2010;24:6018–33.

Li, B., Li, H., Guo, B., Cai, X., and Konggidinata, M.I. 2017. A New Numerical Solution to Predict the Temperature Profile of Gas-Hydrate-Well Drilling. *SPE Journal* (February 2017). SPE-185177-PA http://dx.doi.org/10.2118/185177-PA.

Macfarlane, A. 2017. China makes 'flammable ice' breakthrough in South China Sea. CNN Money. Retrieved 11 June 2017.

Max, M.D., Johnson, A.H. 2016. Exploration and Production of Oceanic Natural Gas Hydrate. Springer International Publishing. pp. 39–73.

Moridis, G.J., Reagan, M.T., Boyle, K.L., Zhang, K., 2009. Evaluation of the gas production potential of challenging hydrate deposits. TOUGH Symposium 2009. Lawrence Berkeley National Laboratory, Berkeley, California.

Najibi, H., Chapoy, A., Haghighi, H., Tohidi, B., 2009. Experimental determination and prediction of methane hydrate stability in alcohols and electrolyte solutions. Fluid Phase Equilib. 275 (2), 127–131.

Ruppel, C. 2014. Gas Hydrates and the Future of Natural Gas (PDF), Gas Hydrates Project, Woods Hole, MA: U.S. Geological Survey, archived from the original (PDF) on 6 November 2015, retrieved 28 December 2014.

Sloan, E.D. Fundamental principles and applications of natural gas hydrates. *Nature* 426, 353–359 (2003). https://doi.org/10.1038/nature02135.

Sloan, Jr., E.D., Koh, C.A., and Koh, C. Clathrate Hydrates of Natural Gases, 3rd Edition, CRC Press, 2007.

USGS. 2009. Gas Hydrate: What is it?, U.S. Geological Survey, 31 August 2009, archived from the original on June 14, 2012, retrieved 28 December 2014.

Zhao, J., Cheng, C., Song, Y., Liu, W., Liu, Y., Xue, K., et al. 2012. Heat transfer analysis of methane hydrate sediment dissociation in a closed reactor by a thermal method. Energies 2012;5:1292–308.