

GAS HYDRATE DISSOCIATION STRUCTURES IN SUBMARINE SLOPES

lain Gidley

Civil Engineering - University of Calgary, Calgary, Alberta, Canada, idcgidle@ucalgary.ca Jocelyn Grozic

Civil Engineering - University of Calgary, Calgary, Alberta, Canada, jgrozic@ucalgary.ca

RÉSUMÉ

Perpétrations à l'équilibre thermodynamique de sédiments chargés d'hydrates peuvent induire la dissociation des hydrates gazeux et libérer de larges quantités d'eau et de méthane gazeux. Cette eau et ce gaz ainsi produits provoqueront, en fonction des sédiments environnants, une augmentation de pression des pores, une expansion volumétrique, et/ou un fluide permettant aux gaz de s'échapper, ce qui a pour effet de diminuer la stabilité du sol. Ce papier analyse les résultats des tests en laboratoire, tests utilisant un modèle physique à petite échelle de sols sous-marins avec inclusions d'hydrate. Les sols sont modélisés par la Laponite, une argile synthétique qui enfle dans l'eau et produit alors un gel thixotropic incolore et clair. Les inclusions d'hydrate disposées en strates et en nodules sont créées à partir d'un réfrigérant synthétique (R-11) d'hydrates. Il a été démontré que les hydrates R-11 ont des propriétés structurelles similaires à celles qui se produisent naturellement pour les hydrates de méthane. L'objectif de cette expérimentation est d'observer le chemin suivi par le fluide permettant aux gaz de s'échapper et le plan de glissement qui s'ensuit dû a la dissociation des hydrates R-11. Ces glissements sont observés par une caméra à haute vitesse et haute résolution.

ABSTRACT

Perpetrations to the thermodynamic equilibrium of hydrate-laden sediments can induce gas hydrate dissociation and result in the release of large quantities water and methane gas. Depending on the surrounding sediments, the produced gas and water will cause increased pore pressures, volumetric expansion, and/or fluid escape structures all of which have the effect of reducing the soil stability. This paper examines the results from laboratory tests performed using a physical, small-scale model of submarine soils with hydrate inclusions. The soils are modeled using Laponite, a synthetic clay which swells to produce a clear, colorless thixotropic gel when dispersed in water. Hydrate inclusions in the form of layers and nodules are created from R-11 refrigerant. R-11 hydrates, which form at low temperatures and atmospheric pressures, have been shown to have similar structural properties to naturally occurring methane hydrates. The objective of the experimental program is to observe the path of the fluid escape structures and the subsequent slip plane that develops due to dissociation of the R-11 hydrate. The slopes are examined using high speed, high resolution imaging.

BACKGROUND

Gas hydrates are ice-like compounds stable under the specific thermodynamic conditions of high pressure and low temperature. Perpetrations to this delicate system can induce hydrate dissociation resulting in increased pore pressures, volumetric expansion, generation of gas bubbles and/or fluid escape structures; all of which have the effect of reducing soil stability.

In marine environments gas hydrates are found in the sediments beneath the outer continental slopes and margins where dissociation can have the effect of reducing the seafloor stability and increasing the potential for gas blowouts. Gas hydrates have been linked to several submarine slope failures. Perhaps the most extensively studied of these is the Norwegian continental margin where Mienert et al. (2005), Jung and Vogt (2004), Vogt and Jung (2002), and Sultan et al. (2004a; 2004b) have suggested that gas hydrate dissociation may have triggered one or more large submarine slides in this area. They theorize that thermal warming and increased deposition resulted in destabilization of the hydrates, which can be seen intersecting the slide scar areas. Field and Barber (1993) postulated that hydrate dissociation weakened the

sediments of the Humbolt Slide Zone (Northern California continental margin), which resulted in a large retrogressive failure ultimately triggered by a seismic event. Extensive erosion is cited as the hydrate destabilizing mechanism leading to considerable local slumping on the New Jersey Margin (Haq, 1998). The well studied Blake Ridge hydrates are thought to be the cause of a large seafloor depression as documented by Dillon et al. (1998) and Booth et al. (1994). Although circumstantial evidence indicates that gas hydrates may play a role in submarine slope failures. our understanding of mechanics of the failures is still limited. To this end, a program has been developed using physical small-scale models of submarine soils containing hydrate inclusions with the objective of observing, mapping, and modeling the fluid escape structures and slip planes resulting from hydrate dissociation.

1.1 Gas Hydrate Properties

Gas hydrates are solid crystalline compounds comprised of hydrogen-bonded water molecules forming a rigid ice-like crystal lattice that encapsulates free gas molecules at a denser state, also known scientifically as a clathrate Methane is the predominant gas that forms natural hydrates but there are a variety of other gases with the same ability such as light alkanes of higher density like ethane, propane, isobutene and some non-hydrocarbons (Kvenvolden, 2000)

Gas hydrates form under high pressures and low temperatures in the presence of excess methane. The thermodynamic conditions required for formation are found in two specific regions of the shallow geosphere. Polar regions are known to contain hydrates located below the permafrost with some extension into the offshore sediment of the polar continental shelves (Max and Dillon 2000). The second and most prominent region of gas hydrate significance is located within shallow sediments under the deep water of oceanic outer continental margins, restricted to continental slopes and outer continental margin rises (Kvenvolden 1995). The distribution of naturally occurring hydrates is spread worldwide as illustrated in Figure 1. The Gas Hydrate Stability Zone (GHSZ) defines areas where conditions are favourable to gas hydrate formation. The GHSZ for oceanic hydrates is shown in Figure 2.



Figure 1: Worldwide locations of gas hydrates (U.S. Geological Survey, March 2001)

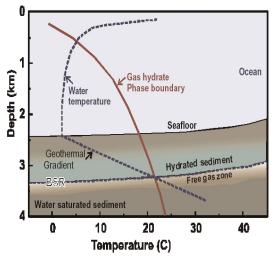


Figure 2: Stability zone for oceanic gas hydrates (Hyndman & Dallimore, 2000)

The majority of gas hydrates are biogenic where the methane originates from the anaerobic decay of organic matter through methanogenesis. The resulting hydrate usually contains 99% methane (Hovland & Judd, 1992). Thermogenic hydrates contain methane, which has been formed at greater depths and temperatures and subsequently migrated upwards from vents and seeps. Although methane is predominant, these hydrates may also contain larger molecules such as ethane and propane (Coffin, Grabowski, & Chanton, 2003).

Gas hydrates contain an immense amount of gas. For example one cubic meter of hydrate will yield 0.8 cubic meters of water and 164 cubic meters of methane at standard pressure and temperatures (Carstens, 2004). The global amount of carbon contained within methane clathrates is estimated at 5 to 25 x 10¹⁴ kg (Milkov, 2004). For ease of comparison, the quantity of natural gas held in hydrate form globally is in excess of twice all the known conventional reserves (oil, gas, and coal deposits) with over 98% located in marine sediments (Kvenvolden, 1988).

1.2 Formation and Dissociation of Gas Hydrates

When gas hydrates are formed, water and gas are extracted from the surrounding pore space causing an increase in the shear strength as well as a decrease in the porosity, permeability and pore volume of the surrounding soil mass. The resulting soil structure will exhibit properties similar to ice, creating a more stable environment (Paull, Ussler III, & Dillon, 2000).

If the formation of gas hydrates causes a more stable environment it stands to reason that the dissociation of gas hydrates creates a less stable environment. Perpetrations to the thermodynamic equilibrium can cause the once stable gas hydrate to dissociate. The result is an increase in porosity and permeability along with the development of gas bubbles and excess pore pressures, all of which decrease the shear strength of the surround soil mass (Paull *et al.*, 2000, Judd, 1995).

2. GAS HYDRATES AND SLOPE STABILITY

Dissociation of gas hydrates can cause destabilization of sediments and ultimately induce failure in very gentle slopes (less than 6 degrees slope angle). These slopes would not generally be considered at risk according to classical slope failure analysis. Booth, Winters, and Dillon, (1994) suggest investigating these gentle slopes after failure to determine if: 1) hydrates are present in large quantities; 2) the slide scar intersects hydrate boundaries; and 3) low permeability soil or hydrate cap exists to facilitate the build-up of pore pressures. The presence of these indicators does not guarantee that hydrates are responsible for the failure but lends strong indications that they played a role.

The main triggers for hydrate dissociation relate to a pressure or a temperature change. The following are common processes that will cause a change in the gas hydrate stability zone (W. P. Dillon & Max, 2003; Grozic,

2003; J. Mienert, Posewang, & Baumann, 1998; Paull *et al.*, 2000).

- Pressure changes
 - Sediment deposition/erosion
 - Sea level rise/drop
 - Falling objects
 - Localized slumping, excavations
- Temperature changes
 - Global warming/cooling
 - Sea current temperature change
 - Anthropogenic activities such as heat from production wells
- Earthquakes
- Sediment salinity changes

3. TESTING PROGRAM

3.1 Methodology

A small-scale physical model of a marine slope was built to examine the effect of hydrate placement and slope angle on gas escape structures and the slopes stability. Slopes were constructed from a synthetic clay containing hydrate inclusions; dissociation was induced and the resulting structural changes observed.

3.2 Materials

Materials were chosen to best represent in-situ conditions while creating a flexible testing environment.

3.2.1 Laponite clay

Laponite is synthetic clay that, when introduced to distilled water, swells to create a clear, colourless, thrixotropic gel that behaves similarly to marine clays found in hydrate environments (Figure 3). The Laponite is prepared by slowly adding Laponite RD powder (up to 4.65% weight by volume) to distilled water while continuously mixing. The mixture is allowed to cure for 16 to 24 hours at a temperature of 15 degrees Celsius. Wet burlap is used as a cover to prohibit a dried crust from forming on the top of the Laponite. The remolded shear strength was found to be 280 Pa at the conclusion of testing. The viscosity drops 10-15% due to temperature increases during a test. This was determined by converting viscometer readings from MacNeill (2007), to remolded shear strength using the method outlined in Locat and Demers (1988). The remolded friction angle was found to be 7.5 degrees from the angle of repose of the failed soil. The major advantage to using Laponite is it is completely clear and colourless. This allows the bubble production and resulting gas escape structure from the hydrate to be observed in real time. It also facilitates the ability to monitor the test using high speed photography and video.

3.2.2 R-11 (Trichlorofluoromethane) Hydrate

Methane hydrate is the most commonly occurring natural hydrate. However using methane hydrates would require high pressure and low temperatures, thus making

experimental setup, control, and repeatability extremely difficult. Hydrates formed with R-11 refrigerant are of the same structural type as those formed with methane and thus exhibit similar behaviour. To form the hydrates a mixture of 30% R-11 and 70% distilled water is prepared in a sealable container (Wittstruck, Brey Jr., Buswell, & Rodebush, 1961). The container is placed in a freezer with a temperature of -18 degrees Celsius. The mixture requires frequent agitation. The formed hydrate is white in colour as seen in Figure 4 and when exposed to room temperatures audibly crackles and pops as it returns to R-11 and water.

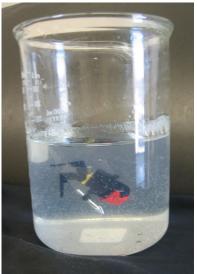


Figure 3: Clear Laponite clay



Figure 4: Formed R-11 hydrate

When the R-11 hydrate is warmed above 4 degrees Celsius, dissociation is initiated and the refrigerant begins to vapourize, forming gas bubbles as seen in Figure 5. As the hydrate warms closer to the boiling point for R-11 (24 degrees Celsius) the gas production increases. One cubic meter of R-11 hydrate will produce 0.6 cubic meters of water and 45.4 cubic meters of gas, this compares to 0.8 and 164 cubic meters of water and gas respectively for methane hydrate.



Figure 5: Initial bubble production from R-11 hydrate

3.3 Apparatus

The tests are performed in a 3660 cubic centimeter plexiglass box shown in Figure 6. The box is mounted on a frame that rotates to angles between 0 and 45 degrees from the horizontal.



Figure 6: Test box

The bottom of the box is equipped with 3 rows of fittings that enable access to the pressure, temperature and slope monitoring equipment (Figure 6). One end of the box can be removed to induce catastrophic failure by allowing material to exit the test box.

3.4 Monitoring Equipment

Each test is monitored for pressure, temperature and slope changes as well as structural changes captured by high-speed camera.

3.4.1 Pressure Measurement

The pressure is measured using standpipes (Figure 7) closed with a fine wire mesh to prevent the clay from entering the system. The water levels are monitored during the test both at the hydrate inclusion location and at the same elevation within the Laponite. Changes in pressure head are recorded with the objective of capturing any pressure changes.



Figure 7: Thermocouple and standpipe placement

3.4.2 Temperature Measurement

The temperature is measured using type T thermocouples (Figure 7) with an accuracy of +/- 0.2 degrees Celsius. The temperature is acquired every second during testing. Temperature measurements are taken at six locations with two at the hydrate inclusion, two within the Laoponite clay, and two on the outside of the box for control purposes.

3.4.3 Slope Monitoring

Soil rotation and inclination is monitored using a "homemade" slope inclinometer. Brown yarn was chosen as the inclinometer since it is highly visible on camera and it moves with the slope, instead of cutting through it, as finer thread would (Figure 8). The inclinometer is attached to one of the fittings on the bottom of the box and held tight and level by a bar across the top of the test box during test preparation. Once the test begins the yarn is cut away from the bar allowing it to move with the slope. Two slope inclinometers have been used at locations within the Laponite on either side of the hydrate inclusion. The inclination is determined from analysis of the high-speed camera images.



Figure 8: Two slope inclinometers within test apparatus

3.4.4 Video Monitoring

Two high speed, black and white cameras are used to continuously monitor the experiment. The cameras can take images from 3 to 30 frames per second. One is set to monitor the front side of the box the other is set to monitor a side of the box (Figure 9). The video is used to watch the development of the gas escape structures as well as monitor changes in the slope inclinometers.

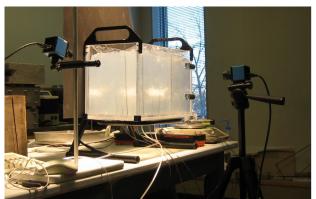


Figure 9: Video monitoring equipment

3.5 Testing Procedure

The clay and hydrate mixtures are made at least 16 hours and no more than 24 hours before a test to ensure they have properly set up. Before placing the clay in the test apparatus, the test box is mounted on the frame and the standpipes are filled with water. The thermocouples, standpipe tubing and inclinometer are placed in their final position. The buckets containing the clay are then unwrapped and the hydrate is freed from its mould. Data acquisition is also started before the clay is placed. The clay is then layered into the test box horizontally and the hydrate nodules are placed. While layering the clay into the box care is taken to minimize void creation, any large voids from the layering process are sucked out of the clay using a pasteur pipette. Once all of the clay has been layered into the box the frame is tilted to the desired slope angle. Video capturing commences once the box is titled to the desired slope angle.

4. RESULTS AND DISCUSSION

4.1 Sequence of Events

As the hydrate temperature warms dissociation is initiated causing some of the refrigerant to turn to gas. As the dissociation process continues, the initial space occupied by the hydrate inclusion turns into a cavity filled with hydrate, water, refrigerant and gas (Figure 10). As more of the refrigerant becomes gas, the gas bubbles begin to coalesce on the upslope side of the hydrate cavity (Figure 5); this marks the beginning of the formation of the escape structure. The hydrate continues to warm and more and

more gas is produced leading to the formation of a narrower, tubular escape structure (Figure 11). Finally this culminates into a full escape structure that vents to the atmosphere (Figure 12). Once the escape structure has fully formed the gas production increases dramatically. This indicates that the pressure build up necessary to overcome the overburden stress of the clay is enough to suppress dissociation of the hydrate.

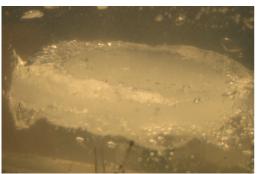


Figure 10: Initial gas formation



Figure 11: Early gas escape structure formation



Figure 12: Fully formed gas escape structure

4.2 Gas Escape Structures

After the initial gas formation, the gas begins to collect on the upslope side of the hydrate, likely showing a preference to buoyancy, as the cavity is now full of liquid. Interestingly, the observed escape structures are near vertical but not entirely; in close proximity to the hydrate the gas moves slope parallel as well as upward (Figure 13).



Figure 13: Gas escape structure trending away from vertical line (upslope direction left of picture)

This could indicate that the escape structure is influenced by the stress distribution within the clay as well as buoyancy. When the escape structures reach the clay surface, a cone like structure is formed from sediment that is ejected from the hydrate or the formed gas vent. These cones appear similar to those found in undersea gas vents and volcanoes (Figure 14).



Figure 14: Large cone in foreground with smaller cone in rear on top of gas escape structures

4.3 Temperature Data

All tests are conducted at room temperature (or slightly above), which provides the driving force for dissociation. The initial clay temperature (T3) is approximately 11 degrees Celsius, while the initial hydrate temperature is 7.5 degrees (T2). Because the initial hydrate temperature is lower than that of the clay, it would be expected that the hydrate would warm faster. However, hydrate dissociation is an endothermic reaction, which cools the surrounding soil thus the warming rate for the hydrate should be suppressed. This is confirmed in the early stages of dissociation as illustrated in Figure 15. Once the dissociation process is completed, the temperature increases rapidly until it is similar to the temperature of the surrounding clay.

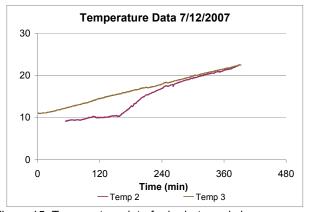


Figure 15: Temperature data for hydrate and clay

4.4 Slope Failures

As the gas begins to form an escape structure, this observed structure is not entirely vertical, which would be expected if buoyancy were the only controlling factor. Figures 16-19 show the development of a circular slip plane formed during a test conducted on a 10 degree slope.

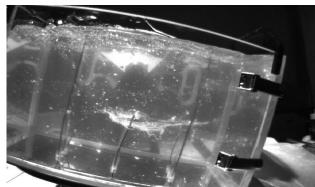


Figure 16: Slope at time zero

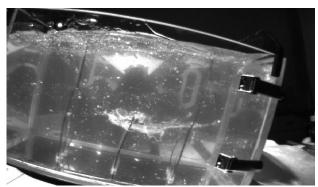


Figure 17: Slope at 10 minutes

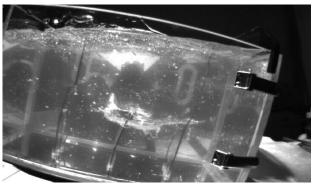


Figure 18: Slope at 20 minutes 15 seconds

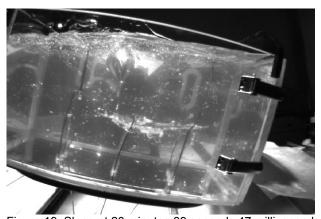


Figure 19: Slope at 20 minutes 39 seconds 47 milliseconds

Although it is more difficult to see from limited still frames, it is possible to observe a circular slip plane forming, particularly if close attention is paid to the inclinometers. The bottom of the slip plane coincides to the location of the hydrate inclusion and as the early escape structure begins to form it takes a dish shape cupping the bottom of the slip plane. These photos, along with the other observed escape structures, seem to indicate that the escape structures are influenced by the stress distribution in the slope. Then as the gas pressure builds, buoyancy becomes the controlling mechanism for further formation of the vent and an upward escape structure is observed.

4.5 Foam Production

As the temperature increases near the hydrate, melting results in the hydrate cavity filling with water and gas. As the gas escape structure forms, gas is seen traveling from the bottom of the cavity, along the edges of the cavity, until it finally coalesces with the main bubble. Gas bubbles are observed forming directly from the chalky white substance at the bottom of the cavity (Figure 20); however upon deconstruction of the sample it is evident that it is not part of the original hydrate. The structure is more similar to foam than ice. It appears that during the dissociation process some of the refrigerant forms a hydrate structure with the clay. These structures seem to produce the vast majority of the gas subsequent to the initial escape structure formation.

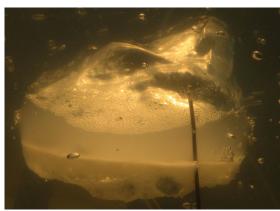


Figure 20: Initial gas escape structure with center void filled with water and lower layer of a foam like substance

5. CONCLUSIONS

Even though gas hydrates have been linked with slope failures from local slumps to massive slides there is still considerable debate as to their overall role in the events. The overall mechanics and effects of hydrate dissociation are still not well understood. In this paper temperature changes have been shown to destabilize hydrates, resulting in bubble production, which ultimately leads to the formation of gas escape structures. The production of gas has destabilized the slopes and precipitated slip planes forming through the hydrate layer. These preliminary results compare favourably to field observations where seafloor instability has been linked to gas hydrate dissociation. Future research will be carried out to establish the effect of slope angle, hydrate placement (horizontal and vertical) and hydrate distribution (size and shape) on the development of gas escape structures and slope stability.

6. ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support by Natural Science and Engineering Research Council of Canada that made this research possible. We also thank Dr. Ryan Phillips for the excellent review and commentary.

7. REFERENCES

- Booth, J. S., Winters, W. J., & Dillon, W. P. (1994). Circumstantial evidence of gas hydrate and slope failure associations on the united states atlantic continental margin. *Natural gas hydrates* (Annals of the New York Academy of Sciences ed., pp. 487-489)
- Carstens, H. (2004, September). Gas hydrates: A giant resource and possible environmental threat. *GEO ExPro*, (2) 14-23.
- Coffin, R. B., Grabowski, K. S., & Chanton, J. P. (2003). The role of methane hydrate in ocean carbon chemistry and biochemical cycling. In M. D. Max (Ed.), *Natural gas hydrate in oceanic and permafrost environments* (Volume 5 ed., pp. 77-90). Boston, Mass.: Kluwer Acedemic Publishers.
- Dillon, W. P., & Max, M. D. (2003). U.S. atlantic continental margin; the best-known gas hydrate locally. In M. D. Max (Ed.), Natural gas hydrate in oceanic and permafrost environments (Volume 5 ed., pp. 157-170). Boston, Mass.: Kluwer Acedemic Publishers.
- Dillon, W. P., Danforth, W. W., Hutchinson, D. R., Drury, R. M., Taylor, M. H., & Booth, J. S. (1998). Evidence for faulting related to dissociation of gas hydrate and release of methane off the southeastern united states. Geological Society Special Publications, 137, 293-302.
- Field, M. E., & Barber, J. H., Jr. (1993). A submarine landslide associated with shallow sea-floor gas and gas hydrates off northern california (07 Oceanography; 30 Engineering geology No. B 2002). United States (USA):
- Grozic, J. L. H. (2003).
 Gas hydrates and submarine slope instability.
 in Proceedings of 3rd Canadian Conference on Geotechnique and Natural Hazards, Edmonton, AB.
 143-150.
- Haq, B. U. (1998). Natural gas hydrates; searching for the long-term climatic and slope-stability records. Geological Society Special Publications, 137, 303-318.
- Hovland, M., & Judd, A. G. (1992). The global production of methane from shallow submarine sources. In A. M. Davis (Ed.), Methane in marine sediments, edinburgh, scotland, united kingdom, sept. 19-21, 1990 (pp. 1231-1238). Oxford, U.K.: Pergamon.
- Hyndman, R. D., & Dallimore, S. R. (2000). Natural gas hydrate studies in canada; offshore west coast and arctic mackenzie delta; GeoCanada 2000; the millennium geoscience summit. Abstract Volume (Geological Association of Canada), 25
- Judd, A. G. (1995). Gas and gas mobility in the offshore sediments of the fraser delta, british columbia. Sunderland, United Kingdom: Geological Survey of Canada
- Jung, W., & Vogt, P. R. (2004). Effects of bottom water warming and sea level rise on holocene hydrate dissociation and mass wasting along the norwegianbarents continental margin. *Journal of Geophysical Research*, 109(B6), 18.
- Kvenvolden, K. A. (1988). Methane hydrate A major reservoir of carbon in the shallow geosphere? Chemical Geology, 71(1-3), 41-51.

- Kvenvolden, K. (1995).
 Natural gas hydrate occurrence and issues. Sea Technology, 36(9), 232.
- Kvenvolden, K. A. (2000). Gas hydrate and humans. In G. D. Holder, & P. R. Bishnoi (Eds.), *Gas hydrates;* challenges for the future (pp. 17-22). United States: New York Academy of Sciences.
- Locat, J., & Demers, D. (1988). Viscosity, yield stress, remolded strength, and liquidity index relationships for sensitive clays. *Canadian Geotechnical Journal*, 25(4), 799-806.
- MacNeill, C. (2007). Sedimentary structure modeling through gas hydrate dissociation. Unpublished Undergraduate Thesis, University of Calgary.
- Max, M. and Dillon, W. (2000). Natural gas hydrate: A frozen asset? *Chemistry and Industry*, **10**: 16-18.
- Mienert, J., Posewang, J., & Baumann, M. (1998). Gas hydrates along the northeastern atlantic margin; possible hydrate-bound margin instabilities and possible release of methane. In J. P. Henriet, & J. Mienert (Eds.), Gas hydrates; relevance to world margin stability and climate change (pp. 275-291). London, U.K.: Geological Society of London.
- Mienert, J., Vanneste, M., Bunz, S., Andreassen, K., Haflidason, H., & Sejrup, H. P. (2005). Ocean warming and gas hydrate stability on the mid-norwegian margin at the storegga slide. *Marine and Petroleum Geology*, 22(1-2), 233-244.
- Milkov, A. V. (2004). Global estimates of hydrate-bound gas in marine sediments: How much is really out there? Earth-Science Reviews, 66(3-4), 183-197.
- Paull, C. K., Ussler III, W., & Dillon, W. P. (2000). Potential role of gas hydrate decomposition in generating submarine slope failures. In M. D. Max (Ed.), *Natural* gas hydrate in oceanic permafrost environments (pp. 149-156). Netherlands (NLD):
- Sultan, N., Cochonat, P., Foucher, J. P., & Mienert, J. (2004a). Effect of gas hydrates melting on seafloor slope instability. *Marine Geology*, 213(1-4), 379-401.
- Sultan, N., Cochonat, P., Canals, M., Cattaneo, A., Dennielou, B., Haflidason, H., et al. (2004b). Triggering mechanisms of slope instability processes and sediment failures on continental margins: A geotechnical approach. *Marine Geology*, 213(1-4), 291-321.
- U.S. Geological Survey. (March 2001). U.S. geological survey fact sheet 021-01: Natural gas Hydrates—Vast resource, uncertain future., January 2008, from http://pubs.usgs.gov/fs/fs021-01/fs021-01.pdf
- Vogt, P. R., & Jung, W. (2002). Holocene mass wasting on upper non-polar continental slopes, due to post-glacial ocean warming and hydrate dissociation? *Geophysical Research Letters*, 29(9), 4.
- Wittstruck, T. A., Brey Jr., W. S., Buswell, A. M., & Rodebush, W. H. (1961). Solid hydrates of some halomethanes. *Journal of Chemical and Engineering Data*, *6*(3), 343-346.