

Fiery Ice from the Seas

Final Report Final Report

**8th International Workshop
on Methane Hydrate Research & Development
Sapporo 2012**

**28th May – 1st June 2012
ROYTON, Sapporo, Hokkaido, Japan
<http://www.2012fieryice.jp/>**



Fiery Ice International Steering Committee

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SUMMARY

The 8th International Workshop on Methane Hydrate Research and Development (2012 Fiery Ice) was held in Hokkaido, Japan, on 29th ~ 31st May 2012 at the Royton Sapporo Hotel. The workshop was preceded by a tour of Toya Caldera and Usu Volcano Global Geopark on 28th May and followed by a laboratory tour on 1st June of the Methane Hydrate Research Center, National Institute of Advanced Industrial Science and Technology (AIST). A total of 101 registrants from 16 countries (about a half of them from overseas) took part in the workshop.

The workshop comprised three overview lectures (two keynote speeches and the banquet talk), 13 national reports, six breakout sessions and 50 individual research presentations consisting of 15 oral and 35 poster presentations.

Two keynote speeches summarized the state of the art of the gas hydrate researches and future challenges. Professor Yasuhiko H. Mori provided an overview of fundamental and industrial application issues, and Dr. Scott R. Dallimore reviewed critical areas in hydrate geoscience and exploitation. In his banquet talk, Professor Yoshihiro Masuda reviewed the history and the background of the national program on gas hydrate development in Japan.

The national reports described the present status of gas hydrate research in each country (Japan, USA, Russia, Australia, Norway, Korea, Canada, Chile, New Zealand, Germany, Taiwan, India and China) and provided essential information for planning future collaborations.

The six breakout sessions offered opportunities for participants to confer and learn more about the state of the art of the selected topics through detailed discussions with their peers in an informal setting. The titles of the breakout sessions, the names of the chairs and rapporteurs, the number of participants and key highlights are provided below:

1. Evaluation of Methane Hydrate Resource Potential (Chair: Dr. Tatsuya Fujii, Rapporteur: Dr. Miko Fohrmann; 25 participants)
 - * State of the art: methane hydrate, especially around Japan, and current methods to evaluate methane hydrate resource potential.
 - * Discussions: supplementary methods for evaluating methane hydrate resource potential; trap and seal effect of methane hydrate, and resource assessment and production methods.
2. Environment Impact (Chair: Prof. Bjorn Kvamme; Rapporteur: Dr. Harald Nesse; 22 participants)
 - * State of the art & Discussions: will CO₂ storage underground assist in sealing the reservoir?; storing CO₂ in Hydrate Reservoirs; methane hydrate in relation to global warming; and geo

hazard and bio system health assessment.

3. Industrial Utilization of Gas Hydrate (Chair: Dr. Ken-ich Sano; Rapporteur: Dr. Yutaek Seo; 21 participants)

* State of the art & Discussions: gas transportation by means of hydrate pellets; economic evaluation of gas transportation via hydrate (what should we know for feasibility study?).
Recommendation: more publication about this topic are needed in international journals.

4. Methane Gas Hydrate Exploitation and Development (Chair: Dr. Koji Yamamoto; Rapporteur: Dr. Scott R. Dallimore; 23 participants)

* Define questions: discussions focused on production rather than exploration considerations.
* Find possible solutions and discuss research strategy for reservoir characterization; reservoir simulation modeling and field test; and commercial-scale production.

5. Mechanisms of Hydrate Accumulations in Nature (Chair: Dr. Hideyoshi Yoshioka; Rapporteur: Dr. Richard B. Coffin; 17 participants)

* State of the art: CH₄ origin, CH₄ accumulation processes and analysis, geochemistry — case studies for various regions.
* Discussions: depth of CH₄ sources and vertical flux; importance of cap rock.

6. Fundamental Hydrate Science Challenges (Chair: Prof. Yasuhiko H. Mori; Rapporteur: Prof. Stephen M. Masutani; 20 participants)

* State of the art: self-preservation effect and hydrate guest molecule exchange.
* Discussions: what is the mechanism?; can these properties be reliably applied for engineering applications?

Two poster sessions were held in the afternoon of 29th ~30th May and all oral presentations were given on 31st May. The posters and talks provided detailed information on a wide range of technical topics. Based on the associated discussions, several common problems were identified for future collaborations.

The 14 workshop sponsors included private companies, government agencies and institutes, and universities. Four of the gold-level sponsors had booths in the poster session room and provided information about their activities and products associated with gas hydrate research. Schlumberger hosted a casual cocktail party on the evening of 29th May. This party offered a relaxed and informal environment for the participants to unwind and to socialize after the first day of technical sessions.

The pre-workshop tour of Toya Caldera and Usu Volcano Global Geopark on 28th May was attended by 18 participants. They learned about the volcanic activities around the lake Toya area and observed the relationship between the volcanic activities and human.

The post-workshop laboratory tour of the Methane Hydrate Research Center (MHRC) at the National Institute of Advanced Industrial Science and Technology (AIST) on 1st June was attended by about 50 participants. Following an introductory address about the MHRC by Dr. Hideo Narita, the Director of MHRC and Chair of 2012 Fiery Ice, the members of MHRC showed the visitors several experimental facilities including a newly-installed large-scale experimental apparatus to simulate gas production processes from methane hydrate sandy sediment.



Group photo of 2012 Fiery Ice

SCHEDULE

	28, May Mon	29, May Tue			30, May Wed			31, May Thu	1, Jun Fri			
9:00	Field Trip (Geo-Park)	Opening Remarks Narita (AIST), Coffin (NRL), METI			Report of Breakout Sessions			Report of Breakout Sessions	Lab Tour (AIST)	9:00		
10:00		Keynote (R&D, Fundamental) Prof. Mori, Keio Univ., Japan			Keynote (Resource & Geosci.) Dr. Dallimore, GSC, Canada			Individual Research-Fundamental (Yu, Univ. Coll. London, UK)				
		National Report -Japan (Saeki, JOGMEC, Japan)			National Report-Canada (Wright, GSC, Canada)			Individual Research-Fundamental (Liang, Kyoto Univ., Japan)				
		National Report -USA (Seol, DOE, USA)			National Report-Norway (Hafidason, NRC, Norway)			Individual Research-Fundamental (Falenty, August Univ., Germany)				
11:00					National Report-New Zealand (Fohrmann, GNS Sci., New Zealand)			Individual Research-Fundamental (Cheng, Dalian Univ., China)				
								Individual Research-Fundamental (Xue, Dalian Univ., China)				
12:00			Lunch			Lunch				Lunch	Adourn	12:00
13:00		National Report-Russia (Chuvilin, Moscow State Univ., Russia)			National Report-Germany (Kossel, GEOMAR, Germany)			Individual Research-Geology (Yoshioka, AIST, Japan)				
		National Report-Australia (Seo, KAIST, Korea)			National Report-Taiwan (Yang, Nat'l. Taiwan Univ., Taiwan)			Individual Research-Geology (Katayama, AIST, Japan)				
14:00		National Report-China (Li, Nat'l. Offshore Oil, China)			National Report-India (Sain, CSIR, India)			Individual Research-Geology (Neber, Schlumberger, Malaysia)				
	National Report-Korea (Seo, KAIST, Korea)			National Report-Chili (Coffin, NRL, USA)			Individual Research-Geo Tech. (Yamamoto, JOGMEC, Japan)					
15:00	Break			Break			Break					
							Individual Research-Geo Tech. (Kimoto, Kyoto Univ., Japan)					
16:00	Poster Session1			Poster Session2			Individual Research-Ind. Tech. (Li, Chinese Nat'l. Offshore Oil, China)					
							Individual Research-Others (Brumby, Univ. Tokyo, Japan)					
17:00	Registration	Breakout Session No. 1 Evaluation of Methane Hydrate Resource Potential	Breakout Session No. 2 Environmental Impact	Breakout Session No. 3 Industrial Utilization of Gas Hydrate	Breakout Session No. 4 Methane Gas Hydrate Exploitation and Development	Breakout Session No. 5 Mechanisms of Hydrate Accumulations in Nature	Breakout Session No. 6 Fundamental Hydrate Science Challenges	Summary	Closing Remarks	17:00		
18:00					Banquet					18:00		
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KEYNOTES

Recent advances in hydrate-based energy technologies - an overview

Yasuhiko H. Mori

Keio University

This keynote lecture aims to present recent advances in technologies, particularly those related to the utilization, storage and transport of energy depending on the formation, preservation and/or dissociation of clathrate hydrates (abbreviated hydrates hereafter). The formation and dissociation of hydrates are free from any chemical reaction, and thereby provide no byproduct that may impose a burden on the environment. If brought into contact with water under appropriate thermodynamic conditions, any hydrate-forming species such as methane, carbon dioxide, natural gas, etc. is fixed into the crystalline structure of a hydrate as it is (i.e., with no change in its quantity as well as its chemical state). In this respect, hydrates have high potential as the media for storing or transporting various materials or energy for industrial or commercial use. This lecture will provide an overview of such hydrate-based technologies now under development or yet-to-be developed, particularly focusing on several specific subjects in which the speaker has taken part -- i.e., the hydrate formation from natural gas for its storage, a refrigeration system utilizing a "hydrate-guest + water" mixture as the working medium, the large-capacity underground storage of hydrogen hydrate, and the storage of ozone in the form of a mixed hydrate. The state-of-the-art of each technology, the scientific/technical tasks for developing the technology, and its future prospects will be briefed and discussed.



Review of gas hydrate resource and production studies in the Mackenzie Delta, NWT, Canada

Scott R. Dallimore, Fred Wright

Geological Survey of Canada

The Mallik site in the Mackenzie Delta has a long history of gas hydrate investigation which has contributed to assessment of in place gas hydrate resources and culminated in the establishment of proof of concept of a simple and effective method for gas hydrate production. The first discovery at the site was made by Imperial Oil Ltd. in the course of drilling of the Mallik L-38 exploration well during the winter of 1972. Interest in the site was renewed in 1998, when the Japan National Oil Corporation (JNOC) and the Geological Survey of Canada (GSC) established a collaboration to advance gas hydrate drilling, coring and geophysics. This program included the collection of the first core samples and modern well logs from a permafrost gas hydrate deposit. The Mallik 2002 Gas Hydrate Production Research Well Program was undertaken with a primary goal to conduct the first modern production testing of gas hydrates. In addition to JNOC and GSC, 5 agencies from Canada, USA, India and Germany also participated. A unique aspect overall was the integration of science and engineering realized with the completion of two 1188 m science observation wells and a 1166 m production research well. Full-scale field experiments in the production well were monitored in the observation wells and small-scale formation tests were also undertaken. The most recent Mallik program was conducted in the winters of 2007 and 2008 with a smaller participant group that included the Japan National Oil Corporation (JOGMEC) and Natural Resources Canada (NRCan). Aurora College acted as the operator for field activities. This program completed the first successful production testing using depressurization. This talk will review the geology and reservoir setting of the Mallik gas hydrate field and summarize the implications of the production research and development studies that have been advanced at this site.



BANQUET TALK

Challenge to a big dream of commercial gas production from offshore methane hydrates

Yoshihiro Masuda

University of Tokyo

Japan's current account balance deteriorates after the March 11 disasters as we recorded a trade deficit of 2.56 trillion yen in 2011. The strong yen is a cause of this deficit, but the biggest factor is the increase in the import of mineral fuels. Import of mineral fuels jumped up to 21.82 trillion yen in value (25% increase over the previous year), accounting for 32% of the total value of imports to Japan. This is a bad economic situation, but is the result that we relied on nuclear sources for about 30 percent of its electricity before March 11. Now Japan's commercial nuclear reactors were shut down and mineral fuels are helping us to compensate for lost power generation capacity. Under these circumstances we started to review the Basic Energy Plan to secure Japan's energy future including the early implementation of renewable energy sources such as offshore wind power, geothermal energy, and photovoltaic power generation. Recently many people ask me when commercial gas supply will be possible from offshore Japan methane hydrates. What is the right answer?

The Japanese Ministry of International Trade and Industry (MITI, currently the Ministry of Economy Trade and Industry) started an 18-year plan called "Japan's Methane Hydrate R&D Program" in 2001. The final goal of this program is to establish a technology platform for commercial gas production from offshore-Japan methane hydrates by 2018. The MH21 Research Consortium (The Research Consortium for Methane Hydrate Resources in Japan) has been continuing research in accordance with a three-phase approach toward the final goal: Phase 1 (year 2001 to 2008), Phase 2 (year 2009 to 2015), and Phase 3 (year 2016 to 2018). In our research so far, we made remarkable achievements: In the Japanese-Canadian collaborative onshore methane-hydrate gas production test carried out in 2007 and 2008 at the Canada Mallik site, we succeeded in six-day continuous gas production of up to about 13,000 m³ by depressurization. We established the methodology to delineate methane hydrate concentrated zones and reported the original methane hydrate gas-in-place within the Eastern Nankai Trough area was 40 trillion standard cubic feet (tscf) in total, including 20 tscf in the highly concentrated zones. However, we have no evidence of producing gas from offshore methane hydrates. So, the current definition of offshore methane hydrates is still a prospective resource. The important step toward commercial gas production from these hydrates is to understand gas productivity of a methane hydrate well through implementation of offshore production tests. Laboratory experiments and numerical simulations show that the depressurization is a promising method to produce gas from methane hydrates, but we have to confirm the quality of methane hydrate reservoir and the verification of gas production technology to show the economic feasibility of future offshore methane hydrate development. To study safety and environmental issues related to methane hydrate development is also important. In the first quarter of 2013, we will implement an offshore production test. If we succeed in this gas production test, we will move on to the second production test (a longer

flow test to evaluate reservoir performance).

Commercial production from offshore hydrates is our big dream. A big dream is often a wish away, but our research efforts are now opening the heavy door of our dream. The offshore production tests will reveal how close we are to the realization of our dream. This banquet talk gives you a review on the recent findings in the area of hydrate development research and a perspective to commercial gas production from offshore methane hydrates.



SUMMARY OF NATIONAL REPORTS



Recent Progress of Research for Methane Hydrate Resources in Japan

Tatsuo Saeki

Japan Oil, Gas and Metals National Corporation

Since FY2009, the second phase of Japanese Methane Hydrate R&D Program has been conducted. The main missions in the second phase are the trials for methane hydrate production offshore Japan. The Daini-Atsumi knoll field, one of the methane hydrate concentrated zones delineated in the eastern Nankai trough area in the first phase of the Project (FY2001-2008), has been selected as a test site. Depressurization method, which is proved as a major dissociation method when it was applied to onshore methane hydrate bearing layer under the collaborative research project between Japan and Canada at the Mallik site in Mackenzie Delta in the Northwest Territories of Canada in FY2007, will be applied again in the deep sea with the water depth of about 1000 meters at the test site. MH21, Research Consortium for Methane Hydrate Resources in Japan, has already drilled a production well and monitoring wells at the trial site and has been going forward with the preparation works for the flow test scheduled in the first quarter of 2013.



Progress in Gas Hydrate Research and Development in the United States

Yongkoo Seol, Ray Boswell

US DOE National Energy Technology Laboratory

Gas hydrate R&D in the United States is conducted by private industry, government agencies, academia, largely with the support of federally-sponsored research programs. The bulk of private R&D in gas hydrate continues to remain focused on issues directly impacting oil and gas production operations: flow assurance and shallow hazard assessment and mitigation. In contrast, government R&D spending focuses on assessing gas hydrate as a future energy resource and as a dynamic constituent of the global environment. In the U.S., federally-sponsored field programs enabled by the U.S. Department of Energy/Office of Fossil Energy, and conducted in coordination with the six other federal agencies, have found success both in Alaska and in the Gulf of Mexico in recent years, where drilling programs have demonstrated safe operations, validated a new approach to gas hydrate exploration based on integration of direct geophysical detection with assessment of components of gas hydrate petroleum system, and furthered the understanding of gas hydrate reservoir response to both depressurization and chemical exchange.

In the Gulf of Mexico, a 2008 assessment by the Bureau of Ocean Energy Management (BOEM) indicated ~21,000 tcf gas-in-place in gas hydrates, with more than 6,700 tcf occurring at high saturations in sand reservoirs. Similar assessments for the other regions of the US Outer Continental Shelf are expected shortly. In 2009, DOE, in partnership with U.S. Geological Survey (USGS), BOEM, and an international industrial consortium (the "JIP") led by Chevron, conducted LWD operations at three deepwater sites that confirmed a range of gas hydrate occurrences, including highly-saturated, deeply-buried, gas-hydrate-bearing sands. Numerical modelling studies indicate that significant productivity could be expected from such reservoirs using existing production techniques. The JIP is currently finalizing the development of tailor pressure core acquisition and analyses equipment that will be necessary to further investigate the nature of these deposits. In Alaska, geological studies by the USGS, combined with the findings of the 2007 "Mount Elbert" gas hydrate test well (in partnership with BP), enabled the USGS to assess Alaska North Slope gas hydrate resources at 85 tcf of technically recoverable gas. The U.S. continues to pursue a series of in situ testing programs designed to investigate gas hydrate reservoir behavior. In 2008, DOE partnered with ConocoPhillips to evaluate the potential of CO₂-CH₄ exchange and in 2011, a fully-instrumented test well was installed in the western Prudhoe Bay Unit. In 2012, the partners, which had expanded to include the Japan Oil, Gas, and Metals National Corporation (JOGMEC), re-entered the well to conduct controlled gas injection and depressurization experiments. Going forward, the program will continue to pursue opportunities for extended duration depressurization testing on the North Slope via discussions with industry partners and interested international R&D programs.

In addition to resource characterization and production evaluation activities, the U.S. devotes considerable resources to the evaluation of gas hydrate's role in the natural environment. Current programs are focused on 1) tracing the sources, mobility, and fate of methane in gas-hydrate bearing environments that are most prone to perturbation through natural environmental change, and 2) developing numerical models that can indicate the potential implications of gas hydrate destabilization on ocean ecology and global climate.



Gas hydrate researches in Russia: current state

E.M. Chuvilin (1), V.A. Istomin (2)

(1) Faculty of Geology, Moscow State University, (2) Gazprom VNIIGAZ

Russia has significant experience in gas hydrate research since 1960th. As it is known, the results of these researches are discovery and proof of natural gas hydrates existence, the self-preservation effect below 0°C, discovery and exploration of gas hydrate reservoirs and accumulations in seas and waters of Russia, development of several models of gas hydrates accumulation mechanisms in sediments. Moreover, a research of a number of physico-chemical parameters and properties of gas hydrates has been performed. At present, gas hydrate researches are carried out in several institutes of the Russian Academy of Sciences, the universities, as well as in scientific and industrial organizations. Unfortunately up to now there is no coordinating national gas hydrate program for hydrate research, which can be explained by the considerable reserves of conventional natural gas in Russia.

Marine gas hydrates in Russia, are studied in the Sea of Okhotsk (Pacific Oceanic Institute, Vladivostok), in the Black and the Arctic seas (VNIIOkeangeologia St. Petersburg). A number of organizations together with the Institute of Limnology (Irkutsk) participate in the study of gas hydrates in Lake Baikal. Gas hydrate existence and formation conditions in the areas of distribution of permafrost are studied in the Geological Faculty of Moscow State University. Fundamental studies of gas hydrates, including the study of gas hydrate structures, phase equilibria and thermodynamic properties of gas hydrates are held at the Institute of Inorganic Chemistry (Novosibirsk), Institute of Cryosphere (Tyumen), etc. A special attention is given to the experimental study of metastable states of gas hydrates. A new concept of non-clathrated water is introduced and analyzed by analogy with unfrozen water in soil systems. Studies of mechano-chemistry of gas hydrates are started.

Applied research related to the formation of technogenic gas hydrates during production and transportation of natural gas are engaged in Gazprom VNIIGAZ (Gazprom VNIIGAZ JSC.), University of Petroleum and Gas (Moscow), Institute of Oil and Gas (Yakutsk), etc. In addition to traditional research activity, the new aspects are studied for reservoir conditions (gas hydrate formation at bottom-hole of new low temperature gas fields). The study of gas hydrates now focuses on environmental problems, in particular a gas emission from the permafrost during drilling and operating of wells in the North West Siberia, methane emissions in the Arctic seas with degradation of permafrost and gas hydrate decomposition.



The CSIRO's research activities to investigate gas hydrates from fundamentals to industrial practices

Yutaek Seo*, Karen Kozielski

CSIRO Earth Science and Resources Engineering (*current affiliation: KAIST)

Rich oil and gas resources in offshore Western Australia drives research on gas hydrate in Australia to mitigate flow assurance risk. CSIRO has been leading the hydrate research project composed of three major areas. First, the development of reliable statistical methods for quantifying nucleation probability is underway and new apparatus was designed for the statistical study of hydrate nucleation and growth which is named HP-ALTA. Hydrate inhibitors developed in CSIRO's lab will be tested and screened using the statistical method. The second area is to study hydrate growth and dissociation using in-situ neutron powder diffraction. Anomalous hydrate preservation was observed during the dissociation process due to heat flow from melting hydrate. The third area is to simulate hydrate formation process in the offshore flowlines transporting hydrocarbon fluids. CSIRO has built a test facility to investigate gas hydrate behavior in offshore flowlines which consists of a 40 meters long pilot size flow loop and lab scale autoclave. Two types of tests have been performed in the flow loop, continuous flow test and restart test. Both of them are to study hydrate dynamics under continuous or transient flow conditions. An autoclave system is installed to investigate the formation kinetics of gas hydrates under various conditions and its application to qualify CSIRO-developed or company-provided hydrate inhibitors. Recent results from the autoclave suggest that methane hydrate re-formation is highly desirable during the production of seabed methane hydrate due to remaining hydrate crystals in aqueous phase. The knowledge on production system and the understanding of hydrate kinetics would be highly related to the design of methane hydrate production system as the amount of melting water may induce serious flow assurance risks.



The Primary achievement and Challenge of Chinese Natural Gas Hydrate Research Projects

Qingping Li

CNOOC Research Institute

This paper briefly introduces the typical research records during Chinese natural gas hydrate research history, from 1990 to now. It was in 1990, the artificial synthesis gas hydrate was made in Lanzhou, from then on, more and more researchers with various majors turned their eyes to the research areas of natural gas hydrate as one of the biggest potential resources in the 21st century. The natural gas hydrate samples were obtained in southern Chinese sea in 2007 and permafrost regions in 2009. Meanwhile, a series of experimental facilities were built, such as acoustic parameter measurements, phase equilibrium equipment and the 3D development simulation facility. And the mathematic simulation program was developed. However, how to avoid the environmental risk and utilize natural gas hydrate in a safe and cost-effective way is the biggest challenge in the future.

Keywords: Chinese natural gas hydrate, hydrate sample, experimental facilities

Korean R&D projects to develop methane hydrate in East Sea of Korea

Yutaek Seo

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Korean researchers have been studying various topics of methane hydrate deposited in East Sea of Korea. 2nd Ulleung Basin Gas Hydrate Expedition (UBGH2) was performed from early July 2010 to September 2010 to explore gas hydrate in the Ulleung Basin, East Sea, offshore Korea, onboard the D/V Fugro Synergy. Based on geological and geophysical data, including 2-D and 3-D seismic survey, from 25 prospect sites, 10 were selected and ranked by priority. These 10 sites were then divided into four groups according to seismic characteristics that indicated gas hydrate presence. UBGH2 consisted of two phases. Phase one included Logging-While-Drilling (LWD) operations at 13 sites and lasted about one month. Phase two included coring and Wireline Logging (WL) operations at nine sites. The shipboard analysis results collectively indicate that recovered gas hydrates mainly occur either as "pore-filling" bounded by discrete sand or ash layers, or as "fracture-filling" veins and nodules in mud. Hydrate veins and 10 to 30 cm-thick hydrate layers were found and could be visually observed. In a few sites, relatively thick hydrate-bearing sandy layers interbedded with muddy layers were found, suggesting the possibility of test production. This study aims to suggest the recent status of Korean methane hydrate R&D projects for the future test production.



Gas Hydrate Research in Canada

Fred Wright

Geological Survey of Canada

Canada has a proud tradition of gas hydrate research spanning more than 50 years, with many substantial contributions in the field of molecular chemistry, petroleum engineering, resource assessment, and production research and development. During the past several years, field initiatives led by academia, industry and government institutions have been undertaken in the Canadian north and in deep water marine settings offshore of all three of Canada's coasts. New laboratory and modeling studies have also been undertaken, which investigate dissociation kinetics and related physical processes at the nano-to-pore-to-field scales. In this Country Report we will provide an overview of recent advances in gas hydrate R&D in Canada, including geologic studies in the Beaufort Sea, a gas hydrate observatory established offshore of Vancouver island, assessments of the sensitivity of gas hydrates to climate change, and new insights regarding reservoir responses to production stimulation based on gas and water flow patterns observed during the 2008 gas hydrate production test at Mallik. We will also provide an update on the current status of the Canadian program of gas hydrate R&D, and a prospectus of new R&D activities to be undertaken over the next decade.



The presenter of this report was Dr. Dallimore.

Gas Hydrates on the Mid-Norwegian margin; an overview

Haflidi Haflidason (1), Jurgen Mienert (2)

(1) University of Bergen, Norway, (2) University of Tromsø, Norway

The Mid-Norwegian margin has been a target area for broad multidisciplinary geophysical, geological and geochemical studies on gas hydrates the last decade. The main objective has been to quantify gas accumulations in the form of hydrates in sediments and assess their dynamics and impacts on the seabed, geophysical characterization and their geological and geochemical setting. An overview of the results achieved within this multidisciplinary project will be presented.



The presenter of this report was Professor Kvamme.

Towards assessing New Zealand's gas hydrate endowment

Miko Fohrmann (1), Ingo Pecher (1,2,3), Andrew Gorman (4), Philip Barnes (5), Andreia Plaza-Faverola (1), Karsten Kroeger (1),
Rosalind Archer (2), Douglas Fraser (4), the GHR team

(1) GNS Science, Lower Hutt, New Zealand, (2) University of Auckland, New Zealand, (3) Heriot-Watt University, Edinburgh,
UK, (4) University of Otago, Dunedin, New Zealand, (5) National Institute of Water and Atmospheric Research (NIWA),
Wellington, New Zealand

We will present the latest results and advances in New Zealand's effort towards gas hydrate exploration and outline our plans leading towards exploration drilling envisioned around 2015.

New Zealand's Exclusive Economic Zone (EEZ) is predicted to contain significant gas hydrate deposits that may be economically produced as a new source of a natural gas. Our programme targets two key objectives, [1] to constrain the regional distribution of gas hydrates deposits around New Zealand and [2] to characterise individual reservoirs on the Hikurangi Margin east of the North Island, New Zealand's most prospective gas hydrate province.

By screening various under-explored basins such as the deep-water Taranaki Basin and the Great South Basin for signs of gas hydrate occurrences we expect to discover new gas hydrate provinces in addition to the already known Hikurangi Margin and Fiordland-Puysegur provinces.

In terms of reservoir characterisation on the Hikurangi Margin, we adapted a petroleum-system approach largely based on seismic data to identify potential gas hydrate reservoirs. This approach includes the identification of high-quality reservoir rocks, i.e. high-permeability sands combined with seismic rock-physics inversion, a tool that has been successfully applied to constrain gas hydrate saturation in sandy intervals in the Gulf of Mexico. First results indicate the presence of ~0.3 tcf of gas in individual potential reservoirs on the Hikurangi Margin.



The German Gas Hydrate Initiative SUGAR: From Exploration to Exploitation of marine gas hydrates

Elke Kossel, Matthias Haeckel, Joerg Bialas, Klaus Wallmann, SUGAR partners
GEOMAR, Helmholtz Centre for Ocean Research Kiel

SUGAR (SUBmarine GAs hydrate Reservoirs) is a collaborative R&D project with 20 partners from SMEs, industry and research institutions. It was launched in 2008 and is now successfully continuing in its second phase, running until summer 2014.

The portfolio of technologies developed in SUGAR includes state-of-the-art hydro-acoustic, 3-D seismic and electromagnetic devices for the exploration of marine gas hydrate deposits as well as the monitoring of hydrate exploitation operations. The novel joint inversion technique combines the interpretation of seismic and electromagnetic data and was successfully applied to hydrate accumulations off New Zealand and in the Black Sea. New autoclave systems for drilling and recovering marine hydrates under in situ pressure have been designed that are suitable for deployments from both drilling vessels and small research vessels. A further outcome of the project is a unique 3-D basin modeling software for the prediction of the formation of gas hydrate deposits in marine and permafrost settings.

Exploitation strategies for marine hydrate deposits are being developed in laboratory experiments as well as in numerical reservoir simulations. Their primary focus is on the production of methane by injection of CO₂, combining natural gas recovery with the safe sequestration of carbon dioxide in CO₂ hydrates below the seafloor. While the reservoir simulations test field-scale strategies and assess these in terms of gas production rates and economics, the laboratory experiments focus on the optimization of the hydrate conversion reaction by application of supercritical CO₂, heat supply via in situ combustion and addition of polymers. In the 2nd SUGAR phase, a new subproject started developing novel drilling technologies specialized for marine hydrate deposits which are significantly shallower below the seafloor than standard oil and gas reservoirs.



Introduction of present status of the Gas Hydrate Master Project of Energy National Science and Technology Program of Taiwan

Tsanyao Frank Yang (1), Gas hydrate research team of Taiwan (2)

(1) Department of Geosciences, National Taiwan University, (2) Central Geological Survey, MOEA, Taiwan

Bottom Simulating Reflectors (BSRs), which have been considered as one of major indicators of the gas hydrate in sub-seafloor, have been detected and widely distributed in offshore SW Taiwan. The Central Geological Survey of Taiwan launched two 4-year multidisciplinary gas hydrate investigation programs in 2004 to explore the potential of gas hydrate resources in the area. In addition to the field investigations, phase equilibrium of gas hydrate via experiment, theoretical modeling, and molecular simulations has also been studied. The results can provide insights into gas hydrate production technology. The results indicate that enormous amounts of gas hydrate should occur beneath the seafloor, although none of solid gas hydrate samples have been found. Therefore, another 4-year program started in 2012 to extend the studies/investigation. In the ongoing projects, some specific areas will be studied in detail to assess the components of gas hydrate petroleum system and provide a better assessment of the energy resource potential of gas hydrate in the target area. Considering the high potential energy resources, the committee of the energy national science and technology program initiated a national master program to plan the strategy and timeline for the gas hydrate exploration, exploitation and production in Taiwan. The program includes six components: resource assessment, production and exploitation, exploration safety and sea-floor stability, carbon cycle, deep sea bio-diversity, energy transportation and industrial application. The present status and details of the program will be introduced in this presentation.



Potential and Development of Gas-hydrates in India

Kalachand Sain

CSIR-National Geophysical Research Institute

Study of gas hydrates has attracted due to their wide-spread natural occurrences and huge energy potential. Several parameters like bathymetry, seafloor temperature, total organic carbon (TOC) content, sediment thickness, rate of sedimentation, geothermal gradient indicate that shallow sediments along the Indian margin are good hosts for gas hydrates. The methane in gas hydrates within Indian exclusive economic zone has been prognosticated to be more than 1500 times of country's present natural gas reserve. Production of even 10% from this treasure is sufficient to meet India's overwhelming energy requirement for about 100 years. Hence, it was felt necessary to map the prospective zones and evaluate the resource potential of gas hydrates. Recently, we have updated the gas hydrate stability thickness map that provides the spatial and depth domains of gas hydrates occurrences. We have identified the BSRs, main marker for gas hydrates, in the Krishna-Godavari (KG), Mahanadi, Andaman, Kerala-Konkan, and Saurashtra regions respectively. The Cauvery and Kerala-Laccadive basins are also found to be prospective for gas hydrates. The study indicates free-gas below the gas hydrate-bearing sediments. Various seismic attributes like the reflection strength, blanking, attenuation (Q-1) and instantaneous frequency have been used to characterize the hydrate- and gas-bearing sediments. We have developed several approaches based on seismic travel time tomography, full-waveform inversion, AVO modeling, each coupled with rock-physics, and utilized them for the quantification of gas hydrates. Recently, a large volume of multi-channel seismic data has been acquired in water depths between 500 to 2500 m in KG and Mahanadi basins. The new data exhibits wide-spread occurrences of BSRs and reveal prospective zones, and are being modeled for the delineation of sediments containing gas hydrates, and evaluation of resource potential using the indigenous techniques.



National Report of Chile

Juan Diaz-Naveas

Escuela de Ciencias del Mar, P. Universidad Catolica de Valparaiso

Chile lacks massive hydrocarbon reserves from conventional deposits and depends on prices of these resources and is being affected by international market fluctuations. However, it is proven that the Chilean continental margin, from Valparaiso to Cape Horn (33°-56°S), contains large quantities of non-conventional hydrocarbon reservoirs in the form of gas hydrates.

Several techniques were used for carrying out the exploration: geophysics (2D seismics and multibeam bathymetry), geology (coring, ODP Legs 141 and 202 data and geological interpretation) and geochemistry (compiled sediment data plus water column measurements). Also an environmental study was accomplished, including oceanography (temperature, salinity, winds, waves and currents) and benthos (overlain water above the seafloor, sediments and benthonic organisms). Besides the study area was divided into subzones according to various geotechnical criteria. As a result, within the study zone several subzones (“leads”) were defined, where gas hydrates and underlying free gas effectively exists (BSR). The total area of the zones was determined, as well as the thickness of the gas hydrates and free gas layers, their porosities and saturations. It was possible to compute the natural gas contained at standard temperature and pressure in these zones. The geotechnical zones gave variable geotechnical conditions from low to high geotechnical instability. However, a model of the seafloor stability gave fairly good stability conditions. Also, conceptual engineering studies of drilling, production and transport allowed to obtain information on the technical means to exploit gas hydrates and underlying free gas and their inherent costs.

All these efforts have been driven by Chilean academia with cooperation of Chilean industry and very significant cooperation of foreign research centers. Therefore the Chilean program on gas hydrates cannot be regarded as real national program as compared with other countries. At present, an evaluation of the Chilean hydrates program is being conducted in order to refocus future research.



The presenter of this report was Dr. Coffin.

SUMMARY OF BREAKOUT SESSIONS

1. Evaluation of Methane Hydrate Resource Potential

Session chair: Tetsuya Fujii, JOGMEC

Rapporteur: Miko Fohrmann, GNS Science

25 participants

Key words: Methane Hydrate Resource Potential, 2D-3D Seismic Data, Well Logging, Geochemical Assessment, New Developments (CSEM, seismic)

Tetsuya Fujii initiated the discussion by presenting the Japanese Methane Hydrate (MH) exploration programme.

MH occurrences

MH occurrences along the Nankai Trough and the Japan Sea can be divided into 3 main categories:

- 1) Massive hydrate mounds & shallow accumulations close to the seafloor
- 2) Hydrates within mud layers and fractures
- 3) Hydrates within turbidite sand layers

MHs stored within sandy layers are currently the primary target in exploration as they provide sufficient permeability to guarantee a steady flow of gas.

Current standard for evaluating the MH resource potential

- 1) Seismic data

Seismic data (2D/3D) and well data are the main tools to evaluate the potential MH reservoirs along the Nankai Trough.

Seismic mapping of BSRs (2D) was conducted to determine the extent of MH along the margin. Key parameters that distinguish hydrate deposits on seismic data along the Nankai Trough are:

- High velocity anomaly in MH zone compared to the background trend
- Strong (high amplitude) reflectors indicate (highly concentrated) MHs

- 2) Well data

In well data, MHs are characterized as high resistivity and high velocity intervals.

- 3) Geochemical analysis

Biogenic vs. thermogenic gas

Geochemical analysis can identify the source of methane (thermogenic (dry or wet gas) vs. biogenic (dry gas)). In Nankai Trough, geochemical analyses indicate that the source of methane is mainly biogenic, i.e. methane contains isotopically lighter carbon.

Sulfate profiles

Sulfate profiles are measured from sediment porewater profiles to assess the migration rate (i.e. vertical flux) of methane. These data provide an indirect estimate of sediment anaerobic oxidation of methane which occurs at the sulfate methane transition (SMT)

4) Facies analysis

The tectonic setting and the sedimentary environment control the formation of MH. To assess the resource potential, structural modeling has been carried out to identify the depositional system and facies distribution by following a sequence stratigraphic approach. This is best done using 3D seismic data.

Discussion

Supplementary methods for evaluating the MH resource potential

How can we more confidently relate measurements along the seafloor (geochemistry, temperature profiles, multibeam data) with what we observe on a seismic scale in the deeper section?

- CSEM can be used to reliably delineate MH hydrate distribution when combined with seismic data (e.g. Schwalenberg et al, 2010).
- Pressure cores. India developed an autonomous system to recover pressure cores from as deep as 100 m below seafloor. Pressure cores can be used to reliably assess in-situ conditions, especially since well logs do not always accurately measure properties in unconsolidated sediments.
- Pressure cores may also be used to assess permeability directly from CT scans.
- Seismic attributes such as attenuation of frequencies may support interpretations beyond velocity anomalies.
- Can laboratory simulation of seismic wave propagation through hydrate filled sediment samples be utilized to aid our interpretations?
- 4D seismic, however, only useful once production has started.

Trap and Seal

MH may be self-sealing since the precipitation of MH can lead to reduced permeability. However, many questions were raised and remain unsolved:

- How can we confidently map the top of gas hydrates? Velocities? AVO?
- What controls the top of (highly) concentrated hydrates? Sediment distribution (sand vs. shale)? Migration pathways? Authigenic carbonates?

Resource assessment and production methods

Well data is required to assess the resource potential (e.g. to constrain net/gross ratio and cage occupancy).

Japan plans to produce MH like a conventional reservoir. During production tests, constant monitoring of

the site will be carried out (e.g. temperature, strain meters). Problems that arise are two-fold:

- 1) Technical issues (e.g. production of water).
- 2) Geomechanical behavior during production phase (e.g. subsidence and/or slope instabilities).
Sediments within the hydrate deposit dip ~15-20 deg, seafloor ~2-3 deg. Strain meter will constantly record any instabilities.

Alternative MH reservoirs

- The primary indicator for identifying potential MH reservoirs is still the BSR. Many questions were raised with regards to the nature of BSRs in MH systems.
- What about potential reservoirs where we do not observe BSRs, e.g. GoM?
- What controls the formation of a BSR? In the GoM, 50% of MH occurrences are not underlain by a BSR!
- How can we identify them? Is attenuation of frequency an effective tool?
- Geochemical analyses are not sufficient to explain distribution of BSRs, e.g. in the Beaufort Sea.
- What parameters are we still missing?
- How can we produce hydrates within fractures and/or muds.

Reference:

K. Schwalenberg, M. Haeckel, J. Poort, M. Jegen, 2010, Evaluation of gas hydrate deposits in an active seep area using marine controlled source electromagnetics: Results from Opouawe Bank, Hikurangi Margin, New Zealand. *Marine Geology* 272 (2010) 79–88.



2. Environment Impact

Chaired by Professor Bjørn Kvamme, University of Bergen

reported by Mr. Harald S. Nesse, Statoil

Keywords: Storage of CO₂ Hydrate underground (CO₂ Capture and Storage), Global Warming, Geo-Hazard, Ecosystem Health Assessment

CO₂ storage underground; will it assist in sealing the reservoir?

- Snøhvit CO₂ storage have a hydrate cap – should we look for this type of systems and can CO₂ cap be relied on as a seal?
 - EU Country program for CO₂ storage; exclusively on the environmental aspect; monitoring, but no plans for testing
 - There is a small test program in Norway for releasing CO₂ into an unsealed reservoir
 - Japan; pursuing CO₂ storage, but not in connection with hydrate reservoirs
 - Russia; programs for capturing CO₂ underneath permafrost – results not published
 - Future programs on CO₂ storage in depleted reservoirs
 - Canada; has looked & found reservoirs for depositing CO₂ underneath the Great Lakes; issue on potential storage areas not available near CO₂ sources

Storing CO₂ in Hydrate Reservoirs:

- German program SUGAR includes method of injecting CO₂ in Methane Hydrate reservoirs
- Japan: researching production method to enhance recovery factor from methane hydrate; future programs include injection

Methane Hydrate in relation to Global Warming: Natural methane flux/ sealing/....

- Canada: Launching program jointly with Korea and US to investigate the release of methane and geo-hazard resulting from global temperature increase
- Deep water marine settings: Important to separate natural seepage from any release of methane through industrial action. Low efforts in this area.
- GoM studies has shown that methane plumes disappear rapidly – inconclusive but possibly being consumed by microorganisms
- Funding of marine type research programs are very problematic.
- Norway do not have a specific program for the marine environmental side of hydrate; easier to get funding for the reservoir side
- Germany – SUGAR Program; oriented towards the technical aspect. Additional work has to be covered by the additional funding/separate sources.
- Japan: funding sources are government ministries focusing on the energy aspect. Educational ministry is also interested from the HSE aspect; collaboration has been initiated between the two “sides”.

Geo Hazard

- Geo-mechanical challenges on the MH21 program is evaluated through a collaboration between several academic institutions associated with the consortium
- Russia: Some investigation into the subsidence around Messoyakha has been performed in the past – nothing recent.
- Numerical tools for subsidence modeling are available, but room for improvements. How to couple the reservoir simulation with the geo-mechanical simulation is an area that could be improved.

Bio system health assessment

- Difficult to monitor and assess
- Bio systems surrounding methane seeps varies greatly; difficult to get any consistent comparative data



3. Industrial Utilization of Gas Hydrate

Chaired by Dr. Ken-ichi Sano, Mitsui Engineering & Shipbuilding Co., Ltd.

reported by Dr. Yutaek Seo, Korea Advanced Institute of Science and Technology

Keywords: Gas Transportation/ Storage, Engineering Production Technology, Hydrate Slurry, Other Application by Hydrate Technology

- For breakout session for “Gas hydrate utilization and transportation, there were 15 participants who had interests in transportation of gas in the form of hydrates and utilization methods of gas produced from methane hydrate deposits
- Dr. Egami from Mitsui Engineering & Shipbuilding presented the project status of methane transportation via making hydrate pellets.
- During the discussion, there was a suggestion that we may need to consider the full picture of producing methane from hydrate deposits. Unfortunately, due to time constraint, participants agreed to focus on transportation of gas hydrates after discussing issues involved with hydrate developments
- Professor Mori suggested many ideas to encourage discussion between participants to accommodate more ideas for engineering production technology.
- People from SUGAR projects suggested the concept of transporting methane in the form of hydrate might not be feasible based on their assessment on economic and technology constraints.
- Participants in the breakout session agreed that we need more publication from industry discussing issues for transportation of gas in the form of hydrate. Dr. Falenty would publish their results on assessing the idea of transporting natural gas in the form of hydrates. MES was encouraged to publish their results in an international journal to boost further discussion.



4. Methane Gas Hydrate Exploitation and Development

Chaired by Koji Yamamoto, JOGMEC

Recorder Scott Dallimore, GSC

-23 attendees

Keywords:

Exploration

- Applicable geophysical techniques and their process
 - Seismic (conventional, 3D (combination with geological features), 4C)
 - Electromagnetic
 - Gas flare detection etc.
- Exploration drilling
 - Geophysical logging
 - Core sampling and tests on them
 - Characterization
- Quantification
 - Resource scale -> commercialization
- Projects
 - R&D
 - Field program
- Permafrost?

Reservoir characterization and modeling

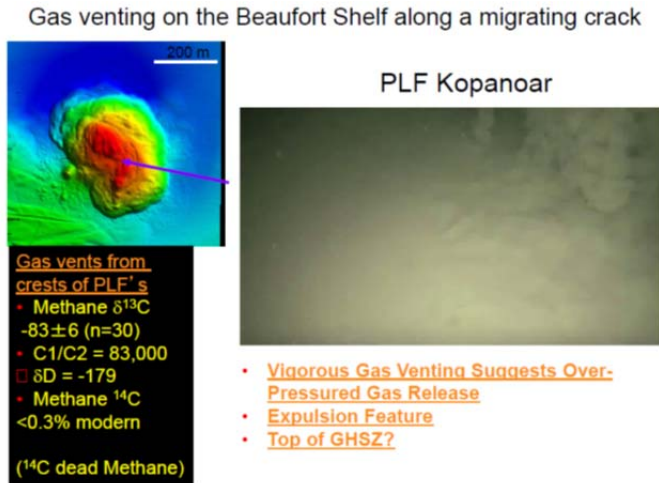
- Data and samples
- Application of conventional (reservoir rock orientated) techniques
- New R&D
- Benchmark test
 - e.g. DOE model comparison program
 - Test data

Production Break out session:

- introduction by Koji to goals and objectives of session
- discussions focussed on production rather than exploration considerations

Reservoir characterization

Bjorn- It may be important to consider the stability of natural reservoirs and flux occurring naturally. Learning's can be tabled in terms of ongoing processes, it may be possible to extend application of reservoir simulators to quantify natural system response and understanding systematic controls on seepage may be a factor deciding how to develop and where to develop a reservoir.



Reservoir simulation modeling

Kurihara- described challenge of assigning reservoir properties...

- lateral heterogeneity very challenging issue as geophysical data generally is not sufficient to understand system.

Dallimore -heterogeneity also a risk in some cases to operations.

For instance if water-bearing sands are in contact with hydrate reservoir sands. If you interest the water bearing sand this could be a show stopper for production from pressure draw down.

- heterogeneity has to be appraised with a sound geologic/facies model. Geostatistics not always best approach.

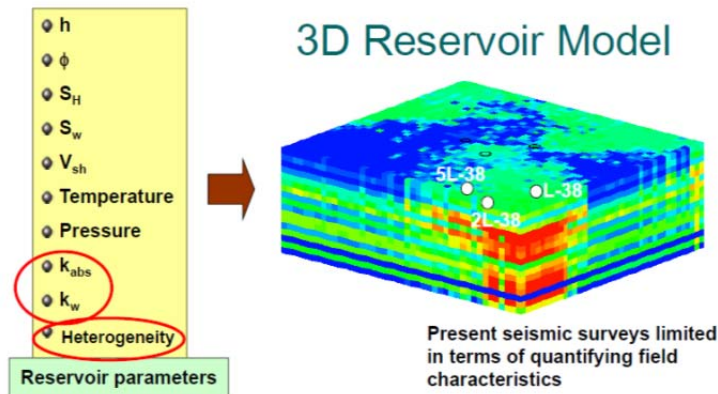
Bjorn- perhaps consider evaluating the short comings of the present suite of reservoir simulators... are there common flaws that are common to each?

- fundamental flaw in present approach is that we are trying to model a non-equilibrium phenomena but models presently don't consider this. More work needed to improve fundamentals

Masuda-san- Important to understand permeability esp. effective permeability

All- heterogeneity also dictates well spacing

The challenge of getting our input parameters right



c/o Kurihara-san

Field test and commercial scale production

- Data from field projects useful for code comparison studies
 - Mallik 2002
 - Mt. Elbert 2007
 - Mallik 2007-2008
 - North Slope 2012
- Major barriers and possible solution
 - Production techniques
 - Well stimulation and improved recovery
 - Cost
 - Infrastructure



5. Mechanisms of Hydrate Accumulations in Nature

Chair: Hideyoshi Yoshioka, AIST

Rapporteur: Rick Coffin, NRL

Keywords: CH₄ origin, CH₄ accumulation processes and analysis, geochemistry

→ Methane origin, Microbial, Thermogenic

Methanogenesis, Gas source, Reservoir

Fault, Diffusion gas

Gas/Fluid Migration

Seal rock

Gas hydrate petroleum system

Fields: Eastern Nankai Trough, Gulf of Mexico, Alaska North Slope, Arctic permafrost
Mallik, Ullung Basin, Baikal Lake, East Siberian Arctic Shelf, Mid-Norwegian margin
Hikurangi Margin, Chilean continental margin, Krishna-Godavari (KG) basin
Off shore SW Taiwan

Questions: Occurrence of hydrate – pore space type, fracture/vein, or shallow accumulation?

Origin of methane - microbial or thermogenic?

Lithology of reservoir

Where is gas source (rock)?

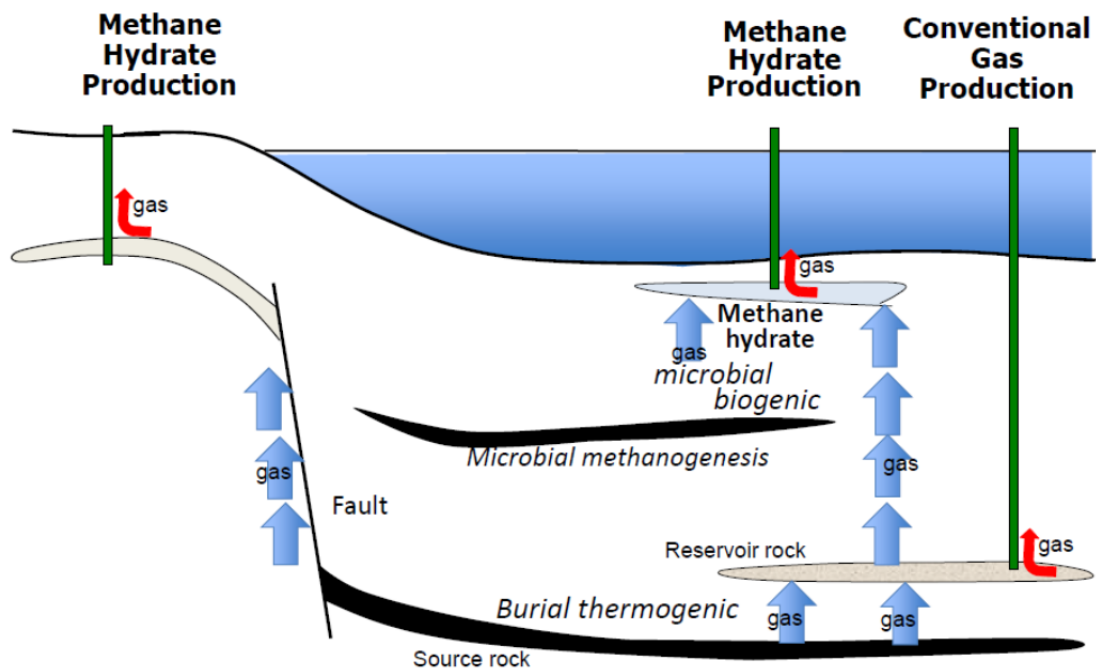
Where is microbial methanogenesis region?

Is there seal rock?

Is there fault? Or fluid migration?

How to simulate accumulation of hydrate numerically?

(Any recommendation of simulator?)



Discussions:

Eastern Nankai Trough

- Kumano Basin, biogenic dominated at some locations however, there is thermogenic. Mud Rich, mud seal Basin. Mud volcanoes are present. There is an observation of many faults. Shallow sediment methanogenesis below the SMT. SMT is located at 23 meter below sea level at a major focus region.
- Need to determine amount of methane that is shallow production, to assess the vertical methane flux.
- Cannot model methane accumulation in a 2-D model, can be horizontal flux also. Methane migration is important for hydrate formation. Migration is directed sandy sediments. Nankai Trough gas trapping is a clay layer.

INDIA

- ***Krishna-Godavari (KG) basin***
 - Fracture gas hydrates in clay sediments, origin is microbial. No gas below the BSR. Massive gas hydrates in fractures. Signature faults on high resolution data is clear, faults are observed.
- ***Mahanadi Basin***
 - Sand layer distribution, biogenic also, faults are observed in one area, the other area no faults.

Offshore SW Taiwan

- Methane is microbial, coring samples are clay, faults drives vertical methane flux in advection, SMI is 2-3 meter. Biogenic dominated. Some thermogenic migration input when moving toward the deep faults.

Gulf of Mexico

- Shallow SMI profiles indicative of high vertical methane flux in more near shore regions, rapid spatial transition between thermogenic and biogenic gas source regions. Shallow sediment clay layers. Deep sediment salt diapirs can create mound formations and advection with deep seismic observation of a upward bowed BSR. This is noted with high chlorinity in porewaters.

Alaska North Slope

- Moderate SMIs, biogenic methane, modern formation as a function of physical sediment transport and deposition.

Chilean continental margin

- High vertical methane fluxes up to ~50 cm bsf observed over seismic blanking. Biogenic methane advection on mound that supports high biological activity. Observed bubble fluxes show high advection at other locations.

Hikurangi Margin

- Focus vertical migration, biogenic methane, moderate flux.

Other regions

- Other regions mentioned but not address : Arctic permafrost, Mallik, Ullung Basin, Baikal Lake

Consistent and Key Points

- SMI 23 m below sea floor, is a primary drill site, but this is a low vertical methane migration
- Big conversation about the depth of sourced biogenic, thermogenic, mixtures and the vertical flux. Does it matter?
- There is a discussion on the cap rock importance, it is important from the production perspective, with hydrates forming there is no cap rock need. Porous cap gets thorough diffusion, no porous gets fractures in the cap.
- Many dimensions/parameters in the formation



6. Fundamental Hydrate Science Challenges

Chair: Professor Y.H. Mori

Rapporteur: Professor S.M. Masutani

(~20 participants)

Keywords: self-preservation effect; cage occupancy; guest diffusion in hydrate lattice; nucleation; memory effect; hydrate in micropores; sintering; kinetics of gas-gas guest exchange (e.g., $\text{CH}_4 \rightarrow \text{CO}_2$, etc.)

- Since the number of potential topics of discussion of this breakout session was very large, the participants were polled to determine their specific interests.
- Topics mentioned: hydrate decomposition/dissociation; self-preservation; nucleation; rheology of hydrates; guest molecule exchange; hydrate thermochemistry & kinetics; hydrates in porous media/heterogeneous nucleation; cage occupancy; gas-water interface phenomena; hydrates & microbiology.

SESSION SUMMARY

- Many more questions than answers
- Food for thought

1. SELF-PRESERVATION

The self-preservation phenomenon is relevant to a host of important hydrate science & engineering issues. A brief overview of the state of the art was presented by Dr. Takeya:

- Persistence of the hydrate phase under slow heating or rapid depressurization—decomposition is inhibited, possibly by ice.
 - Exploit this phenomenon for practical applications such as hydrate storage?
 - Explains unexpected hydrate occurrences in nature (e.g., certain cases in permafrost)?
- PROBLEM: questionable reproducibility of phenomena; hard to definitively determine under what conditions the phenomena will occur.
- What is the mechanism; is it deterministic/stochastic/truly random? What are the critical parameters?
- Does self-preservation represent quasi-equilibrium? Is it a kinetic phenomenon?
- Why does self-preservation seem to depend on the guest molecule? Or does it? Evidence is inconclusive.
- Based on current level of understanding, can self-preservation be reliably applied for certain engineering applications?

COMMENTS

- Ice structure considerations play a role in self-preservation; is ice crystal mapping consistent with self-preservation/hydrate stability?

- In the context of natural occurrence of hydrates (e.g., permafrost), self-preservation has been observed and may explain certain unusual observations.
- In pelletized storage, certain anecdotal indicators may be sufficient—such as the color of hydrates, etc.—to reliably characterize (or predict) macroscopic behavior to the extent that practical application may be possible.
- We need to be able to compare results from studies which utilize different methods, conditions, and protocols before beginning to posit the underlying mechanism(s) of self-preservation.

2. GAS EXCHANGE (hydrate guest molecule exchange)

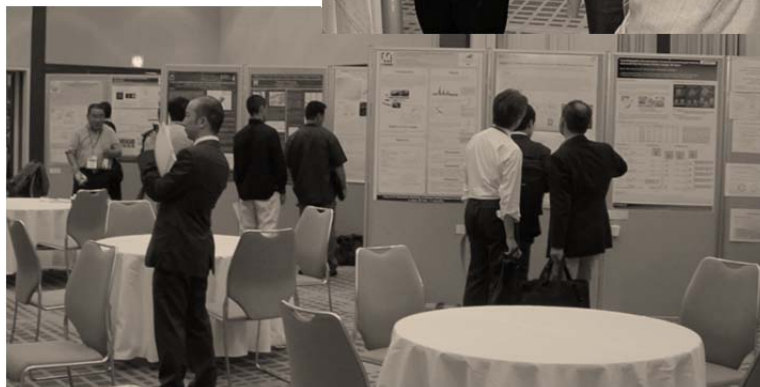
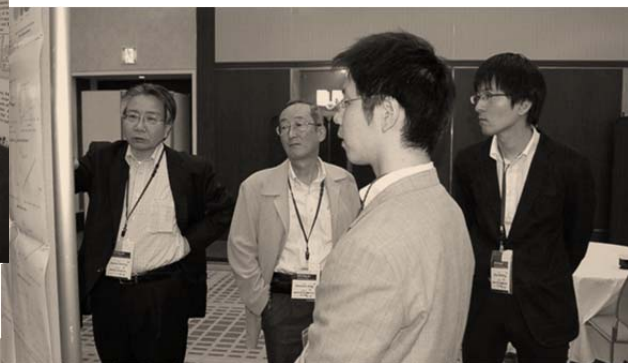
Relevance: CH₄ to CO₂ hydrate transformation

QUESTIONS & COMMENTS:

- Can gas exchange occur without breaking down the crystal; i.e., via solid state diffusion?
 - Probably not: exchange likely involves the destruction of the lattice and subsequent reformation.
 - While microscopic mechanisms of this process can be posited, confirmation is very difficult with the techniques currently available since the length and time scales are very small.
 - “Bucket-brigade” type transfer of guest molecules between adjacent cavities appears difficult since there is no “space” to diffuse (due to the level of cage occupancy).
 - It may be useful to apply an ice analog to try to explain the gas exchange process; perhaps crystal defect pathways?
-
- How can we increase the diffusion of CO₂ into the methane hydrate crystal?
 - Perhaps by exploiting grain boundary/dislocation transfer phenomena.
 - Consider changing the approach (i.e., process) to try to exploit liquid phase pathways.
-
- From a fundamental perspective, how should we express (predict) *in situ* rate of exchange? Are laboratory results relevant to field applications?
 - Perhaps it is possible to extend results from studies of hydrate formation in ice to the CO₂-CH₄ gas exchange problem.
 - If the gas exchange is conceptualized as comprising consecutive dissociation/reformation steps, then perhaps the process could be modeled accordingly using existing corresponding (crystal dissociation & formation) results.
 - Assuming that exchange is driven by differences in chemical potential, how can we determine the coefficient linking chemical potentials and kinetic rates?



ABSTRACTS OF INDIVIDUAL RESEARCHES (ORAL AND POSTER)



ID No.
42

Presentation Style
Oral

Category of Presentation
Fundamental Physical Properties

Micromechanical investigation of methane hydrate soil sediments using Discrete Element Method: cementation model

Yanxin Yu (1), Yi Pik (Helen) Cheng (1), Kenichi Soga (2)

(1) Civil, Environmental and Geomatic Engineering, University College London, (2) Geotechnical Research Group, Department of Engineering, University of Cambridge

Gas hydrate was recovered in the Andaman Sea along the eastern coast of the Andaman Islands during the NGHP Expedition-01. Available 2D multi-channel seismic data were analyzed and BSR was imaged along several seismic profiles. The depth of the BSR is more than 600 m along the seismic line crossing Site NGHP-01-17. To understand the unusual depth of the BSR, we mapped its depth and estimated heat flow from the BSR depth using a simple conductive model. BSR-derived heat flow values range from ~11.9 to ~41.5 mW/m² from the study area and follow the bathymetry trend. We also modeled the base of gas hydrate stability zone to analyze the linkage between gas hydrate occurrences in the Andaman Sea and its relation to the tectonic activity. Our analysis suggests an extensively variable gas hydrate stability zone in the Andaman Sea controlled mainly by low geothermal gradients. Consistent local variations were observed with low heat flow values over prominent topographic highs. This variation may be due to general focusing and defocusing effects of topography.

Pore water chemistry, electrical resistivity and P-wave velocity logs are used to estimate gas hydrate saturations at Site NGHP-01-17. Gas hydrate saturation estimated from chloride concentrations shows values up to ~90% of pore space for distinct ash layers from ~400 meter below seafloor to the BSR. Gas hydrate saturations estimated from the electrical resistivity and acoustic velocity logs using standard empirical relations and rock physics modeling approach are comparable to each other, but saturations are only ~20% of the pore spaces on average. This much lower gas hydrate saturation estimate is a result of overall reduced resolution of the logging tools with typically 20-30 cm thick hydrate-bearing ash layers.

ID No.
40

Presentation Style
Oral

Category of Presentation
Fundamental Physical Properties

Phase Equilibrium, Cage Occupancy and Optical Spectra of CO₂-hydrate

Yunfeng Liang, Yohei Mikami, Toshifumi Matsuoka
Kyoto University

We have performed molecular dynamics simulations in order to investigate the stabilities of CH₄- and CO₂-hydrate. It was found that the cage occupancy of hydrates influences the stability of the hydrates. More importantly, the actual three phase coexistence line of CO₂ hydrate may be higher than the value ever observed. Our simulations suggested that the "lowered" three phase coexistence line stemmed from the partial occupancy occurred during the lab measurements.

First principles calculations of the excited state properties of CO₂ hydrate of various cage occupancies have then been performed in the framework of many-body Green's function formalism. The quasi-particle band structure is evaluated using the GW approximation. Optical spectra are obtained by solving the Bethe-Salpeter equation, which included excitonic effects. This study is still undergoing in the hope to obtain some spectrum insights for CO₂ at different environment, e.g. small cage vs. large cage, and to develop a comprehensive method to measure the CO₂ occupancy formed at different thermodynamic conditions.

ID No.
25

Presentation Style
Oral

Category of Presentation
Fundamental Physical Properties

Gas replacement in sl and sll clathrate hydrates: experimental study and phenomenological model

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With growing concerns about the climate warming due to anthropogenic emission of CO₂ and pressing demand of energy worldwide, there is an increasing need of carbon-neutral energy sources. In this context, deposits of natural gas hydrates (NGH) create a particularly interesting solution to both issues. As the carbon content of this natural reservoir, dominated by CH₄, has been estimated as large as the total inventory of carbon in all known coal, oil, and gas deposits, NGH may become an alternative future source of energy. Concomitantly, the clathrate structure might strand combustion products in a solid crystalline lattice by replacing hydrocarbons with anthropogenic CO₂ thus providing a quasi carbon-neutral balance. This idea became an important part of the German research effort "SUGAR II" aiming at the development of new technologies for a recovery of methane gas from NGH deposits.

Here we present the progress in the development of a μm to mm scale model to describe the gas exchange reaction of sl CH₄- and sll CH₄-C₂H₆ clathrates with liq. CO₂. The model is based on a "shrinking core" principle in which the replacement progresses from the particle surface to the center with adjustable parameters like the permeation rate constants of the participating gases as well as the reaction rate constant for the initial part of the reaction. Other parameters like the nominal averaged grain radius, the sample porosity and the statistical thermodynamic description of the system (Langmuir constants and dissociation fugacities) are usually fixed, based on experimental observations constrained by a combination of diffraction, Raman scattering and cryoSEM observations. The model is used to fit kinetic curves from replacement experiments followed with in-situ neutron diffraction. The results will be eventually linked to large scale reservoir simulations, from which strategies for a later field application will be derived.

ID No.
39

Presentation Style
Oral

Category of Presentation
Fundamental Physical Properties

Experimental investigation of heat transfer of methane hydrate dissociation in porous media with different production method

Xiao C. Cheng (1), Yongchen Song (1), Jiafei Zhao (1), Qingping Li (2), Weiguo Liu (1), Yu Liu (1), Dayong Wang (1)

(1) Dalian University of Technology, (2) China Ocean Oil Company

The heat transfer is one of the most important mechanisms which govern the hydrate decomposition. The understanding of heat transfer analysis of hydrate-bearing sediments involved phase change is critical to requirements of gas hydrate exploitation techniques. In this paper, the experiments were conducted to examine the heat transfer performance during hydrate formation and dissociation using a 5L volume reactor with different production methods. A thermistor based method for measurement of effective thermal conductivity of hydrate sediments was also invested. This study simulated porous media by using glass beads of uniform size. 16 platinum resistance thermometers were placed in different position in the reactor to monitor the temperature difference in the sediment. The purpose of this research was to investigate the effect of thermal conductivity, thermal convection on the heat transfer during hydrate dissociation which is involved phase change by using a thermistor based method with different production methods. Thermistor probes were constructed in house and calibrated in three materials of known thermal conductivity. The depressurization technique and thermal method were studied separately. The experimental results indicated that phase change has an effect on the thermal properties of hydrate sediments and a significant temperature difference along with the radial direction of the reactor was obtained when the hydrate dissociates and this phenomenon could be enhanced by raising the production temperature. In addition, the hydrate dissociates homogeneously and the temperature difference is much smaller than the other condition when the production temperature is around the 10°C. With the increase of the production temperature, the maximum of ΔT_{oi} grows except the temperature comes to 40°C. The period of ΔT_{oi} have an accordance with influence on the whole time of hydrate dissociation. Especially, the effective thermal conduction of hydrate sediments was also obtained.

ID No.
13

Presentation Style
Oral

Category of Presentation
Fundamental Physical Properties

In-situ Monitoring hydrate growth in porous media with magnetic resonance imaging

Kaihua Xue, Di Liiu, Jiafei Zhao, Yongchen Song, Chuanxiao Cheng, Yiming Zhu

Dalian University of Technology

The microstructure and growth habit of hydrate in pore space significantly affects the physical and chemical properties of hydrate. It is generally acknowledged that there are three pore-scale hydrate distributions. They are (a) free floating in the sediment matrix (b) contacting, but do not cement, (c) actually cementing and stiffening the sediment. In this paper, to investigate the growth law and microstructure of hydrates in the sediment and the differences between gas hydrate and liquid hydrate, the growth of Tetrahydrofuran (THF) hydrate, carbon dioxide hydrate and methane hydrate was in-situ observed by Magnetic resonance imaging (MRI). MRI has been shown to be a very effective tool for monitoring the formation and dissociation of hydrates because of the large intensity contrast between the images of the liquid components and the solid hydrate. A set of experimental system was designed and constructed for the three-dimensional visual experimental study of the hydrate growth. The hydrate forms in quartz glass beads of uniform size (3.962~4.699mm, average 4.5mm) at 1°C after precooling at -3°C for 10 minutes. The pressure is specified, liquid hydrate is at atmospheric pressure and gas hydrate is at 5 MPa. Through the images acquired from the MRI, the result suggested that THF hydrate formed preferentially at grain contacts, and then occupies the pore of the porous media gradually, but with the decrease of the THF concentration of the solution, the growth model changed to free floating in the porous media. However, the growth of the gas hydrate was influenced by the dissolved quantity and dissolution rate of the gas in the water. If the gas supply is abundantly provided, the hydrate will grow as the cementing model. By contrary, it will grow as free floating model.

ID No.
64

Presentation Style
Oral

Category of Presentation
Fundamental Physical Properties

Dissociation and Preservation of Clathrate Hydrates below 273 K

Satoshi Takeya

National Institute of Advanced Industrial Science and Technology (AIST)

Storage of gas in hydrate crystal is attracting attention for its storage and transportation because hydrate is dissociation composed of only natural gas and water, which might be one of the most favorable and environmentally friendly candidates for natural gas storage. In this respect, understandings of dissociation process of gas hydrates are important.

Existence of enhanced preservation phenomena of structure I CH₄ hydrate in the temperature region from 240 K to 273 K is one remaining puzzle, a phenomenon which has been termed "anomalous preservation". This has been observed only for CH₄ hydrate upon dissociation by rapid pressure-release from high pressures, at which CH₄ hydrate is stable, to an ambient pressure of CH₄ gas in this temperature region. [1]. Recent non-distractive observations by means of phase-contrast X-ray imaging revealed that a thin ice layer keep CH₄ hydrate without dissociation for several weeks at 253 K [2]. On the other hand, dissociation of gas hydrates by temperature-ramping depends on neither the thermodynamic stability nor the crystal structure, but the type of the guest molecules [3]. Additionally, preservation phenomena of gas hydrates far outside their stability zone below 273 K, is shown to depend on the type of guest molecule and the morphology of the hexagonal ice grown during hydrate dissociation by rapid pressure-release [4].

Here, the dissociation mechanism of clathrate hydrates below 273 K will be discussed on the basis of the experimental results reported.

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ID No.
34

Presentation Style
Oral

Category of Presentation
Geology-Geochemistry

Microbial methanogenesis in methane hydrate-bearing regions

Hideyoshi Yoshioka, Susumu Sakata

National Institute of Advanced Industrial Science and Technology (AIST)

Methane forming methane hydrates along continental margins is produced mostly by microbial methanogenesis. Geochemical studies of gas compounds and stable isotopic compositions of methane indicate that methane is produced through carbonate reduction pathway. It is further proposed from the isotopic relationship between methane and CO₂ dissolved in pore waters that most methane should be produced in the shallow sediments below SMI. As the concentration of methane in sediment pore water increases and the sediment is buried to depth, methane becomes trapped in clathrates. However, the geochemical interpretation is not supported by microbiological studies. Methanogens were found in the hydrate-bearing sediments (Mikucki et al. 2003) and reboseome RNA of methanogens and their functional gene, *mcrA* were detected in the deep sediments. Results of tracer experiments showed relatively high activity of methanogenesis in the hydrate-bearing regions, or the sediments deeper than BSRs (Wellsbury et al., 2002; Yoshioka et al., 2009; 2010) comparing with shallow sediments. Another idea is proposed that methane forming hydrate is produced in the deeper region and transferred upward to the sediments above BSR.

In this study we will present our microbiological data of marine sediments from the eastern Nankai Trough and the Cascadia Margin. We will also review other studies, and introduce three models of methane hydrate formation assuming the following regions of methane production: (1) near surface sediments below the sulfate-methane interface (SMI), (2) sediments within the hydrate-bearing region and just below the BSR, and (3) deep region far below the BSR. So far, it is not obvious which model is true. Multidisciplinary studies are necessary to clarify where methane contributing to the formation of methane hydrate was produced.

[Acknowledgements] This study was performed as a part of MH21 Research Consortium Japan

ID No.
30

Presentation Style
Oral

Category of Presentation
Geology-Geochemistry

Archaeal diversity and methanogenic activity in methane hydrate-bearing sediment in Nankai Trough

Taiki Katayama (1), Hideyoshi Yoshioka (1), Daisuke Mayumi (1), Susumu Sakata (1), Miki Amo(2)

(1) AIST, (2) JOGMEC

Recent geomicrobial studies have shown that microbiological processes related to methane production and oxidation become evident in subseafloor sediments and may contribute to global carbon cycle, despite the potentially low levels of metabolic activity therein. However, geochemical features that affect microbial community and activity are not well understood, mainly due to the limited availability of subseafloor samples. In February 2010, by the operation of scientific drilling vessel CHIKYU, drilling site survey was conducted at two sites in eastern Nankai Trough, where methane hydrates are widely distributed in offshore sediments. During the expedition, a total of 38 core samples were collected from approximately 1 to 270 meters below the seafloor and 24 samples selected were subjected to microbial analysis. Here, we report the distributions of microorganisms including methanogens and methanogenic activity along with the depth. Chemical compounds dissolved in sediment pore waters were measured. We also measured potential methane production rates by radiotracer experiments, and analyzed the microbial community structure and population by molecular techniques including deep ribosomal RNA gene sequencing. We will discuss the relationship among the geochemical features, distribution and activity of methanogens.

ID No.
84

Presentation Style
Oral

Category of Presentation
Geology-Geochemistry

Assessment of Methane Hydrate Resources along the Alaska North Slope- advances in Numerical 2D and 3D Modeling

Kadir, Z. , Rottke, W., Hantschel, T., Derks, J., Wygrale, B., Neber, A.

Schlumberger

Petroleum resource assessments are used to quantify discovered and undiscovered petroleum that is technically and economically recoverable within a certain time frame (e.g. 30 years). It is understood that what is technically recoverable can change significantly due for example to new technical developments, and what is economically recoverable can also change significantly due for example to oil/gas prices. Rapid changes are also possible, due e.g., to the development of new resource types such as shale gas (and oil), coal-bed methane and gas hydrates. The exploitation of these unconventional hydrocarbons was so far uneconomical, mostly due to technological limitations. However, an increasing awareness of the resource potential of natural gas and recent technological developments allow an economical exploitation of these resources.

Dynamic 2D/3D basin models can be used to simulate the biogenic generation of methane and formation of gas hydrate using petroleum systems based approaches. The simulation of gas hydrate accumulations in marine and permafrost environments are done with algorithms describing (1) the physical, thermodynamic, and kinetic properties of gas hydrates; (2) a kinetic continuum model for the microbially mediated, low temperature degradation of particulate organic carbon in sediments; and (3) the transport of dissolved constituents in the pore fluid. In contrast to conventional resource assessments, the temporal and spatial resolution has been increased up to several tens of years and within decimeters of spatial extension.

The gas hydrate simulation was tested on the petroleum systems model of the Alaska North Slope, where gas hydrates have been drilled in fine-grained sand layers in marine and permafrost environment. Hydrate saturations and the methane source rock are well known. Several simulations were run to predict the thickness of the gas hydrate stability field, the generation and migration of biogenic and thermogenic methane gas, and finally its accumulation as gas hydrate in the Alaska North Slope area under marine and permafrost conditions, as well as the evolution of these properties over the geological past.

ID No.
28

Presentation Style
Oral

Category of Presentation
Geo-technical Engineering

Integrated geomechanical and geotechnical site characterization for the first offshore methane hydrate production test

Koji Yamamoto, Yu Nagano, Satoshi Noguchi, Ryosuke Sato, Machiko Tamaki (1), Norio Tenma, Kiyofumi Suzuki, Jun Yoneda (2), Shinya Nishio (3), Kaibin Qiu, Richard Birchwood, Than Tin Aung (4), Kenichi Soga, Shun Uchida (5), Assaf Klar (6), Masayuki Hyodo (7), Hiroyuki Tanaka (8), Sayuri Kimoto (9), Ryoko Yamazaki (10), Tore Jan Kvalstad (11)

(1) Japan Oil, Gas and Metals National Corporation, (2) National Institute of Advanced Industrial Science and Technology, (3) Shimizu Corporation, (4) Schlumberger, (5) University of Cambridge, (6) Technion, (7) Yamaguchi University, (8) Hokkaido University, (9) Kyoto University, (10) Kochi University, (11) Norwegian Geotechnical Institute

Geomechanical and geotechnical site characterization is a main component and the first step of geohazard analyses for deepwater drilling. Modelling efforts for engineering purposes should follow for specific engineering purposes such as drilling hazard and wellbore instability prediction, completion design, prediction and mitigation of formation damage and production troubles such as solid production, compaction and fines migration, seafloor stability, and reservoir scale character changes caused by mechanical reasons. In the case of gas hydrate-bearing sediments, involved formations consists of unconsolidated sediments, and mechanical behavior is far different from usual reservoir rocks.

For the purpose of design for production test systems of the methane hydrate first offshore production test that is planned in early 2013 in the Eastern Nankai Trough, an integrated study is underway. This geomechanical site characterization efforts includes site surveys including micro bathymetry, shallow seismic and drilling campaign for in-situ testing and core sampling, laboratory testing, stress evaluation, development of appropriate constitutive models considering gas hydrates in pore spaces, log-based one-dimensional and seismic based three-dimensional geomechanical model buildings, fault modelling, seafloor stability study, and developments of numerical models for specific purposes such as sand production.

In this presentation, overview of the study scheme and role of each research team will be introduced with some preliminary results of studies. New logging data and cores will be used to improve the model and results, and finally verified by data to be obtained during production test. This research was entrusted by the Ministry of Economy, Trade, and Industry (METI), Japan and the MH21 Research Consortium, as a part of the research group for production method of methane hydrate.

ID No.
41

Presentation Style
Oral

Category of Presentation
Geo-technical Engineering

Dissociation induced γ – transmissivity and electrical resistivity changes of hydrate bearing soil

Simon Falser, Matilda Loh, Andrew Palmer, Thiam Soon Tan

National University of Singapore, Department of Civil and Environmental Engineering

The presence of gas hydrates has been confirmed by bottom simulating reflectors (BSR) during conventional seismic surveys in numerous locations, and hydrate containing sediment-cores have been recovered in places of particular interest. The local pore space saturation can be assessed by a seismic wave form inversion, by down-hole logging or by dissociating and measuring the amount of gas in recovered cores. Little is however known about the dissociation behavior of naturally occurring gas hydrates, the vital process of every gas production scheme from hydrates. While the total required energy for the endothermic dissociation process can easily be derived from the hydrate's latent heat and its saturation, the hydrate's dissociation rate is unknown. The vast majority of studies still link it back to Kim-Bishnoi's (1987) dissociation model, but a range of studies have shown that the rate depends rather on the heat transfer mechanisms than on the dissociation kinetics.

This study presents a concept of experimentally determining the hydrate dissociation rate in-situ by means of a controlled heat dissociation. For that, uniformly saturated hydrate samples are dissociated by a constant heat flux from a miniature wellbore, while the radial dissociation front is localised by γ -ray transmissivity measurements. Combining the energy input and the progression of the dissociation front yields the dissociation rate. These measurements are enhanced by monitoring changes in electrical resistivity in the radial direction, which in turn give independent evidence of the degree of dissociation.

At the National University of Singapore we have developed the first hydrate-testing setup which enables line dissociation around a wellbore by a combination of depressurisation and heating. With a vertical effective stress of 5.5 MPa, the setup allows for efficient hydrate testing at near in-situ conditions.

ID No.
49

Presentation Style
Oral

Category of Presentation
Geo-technical Engineering

A Chemo-Thermo-Mechanically Coupled Simulation of the Subsurface Ground Induced by Gas Hydrate Dissociation by Depressurizing Method

Sayuri Kimoto, Fusao Oka, Hiromasa Iwai, Takashi Kitano, Toshifumi Akaki

Kyoto University

Numerical simulation examples of the gas production process by depressurizing method in the seabed ground are shown in the present study. The simulations has been conducted by a chemo-thermo-mechanically coupled analysis method in which the phase changes from solids to fluids, the flow of water and gas, heat transfer, and the ground deformation are taken into account.

From the site investigation at the eastern Nankai Trough area, hydrate bearing zone have been discovered in turbidite sand and mud alternation layers. From the view point of geomechanics, the ground deformation may be induced during hydrate dissociation by the change of the pore pressures, and the soil skeleton stress, and the loss of hydrate bonding. In the proposed simulation method, an elasto-viscoplastic constitutive model is used for soil, in which, Cam-clay type static yield function and potential function are adopted to the viscoplastic flow rule in order to describe both the viscous nature and the plastic nature of soil. In addition, the soil is treated as an unsaturated soil by using the concept of skeleton stress and the suction effect in the constitutive model.

For the governing equations, weak forms of conservation of the mass for water and gas, conservation of momentum, conservation of energy are discretized in space by the finite element method. As for the finite element method, an updated Lagrangian method with the objective Jaumann rate of Cauchy stress is used based on the finite deformation theory. Numerical simulation of the production process by depressurizing in the seabed ground at the water depth of around 1,010 m will be shown. The ground is assumed to consist of silty soil and hydrate-bearing sediment exists at a ground depth of 288-332 m.

ID No.
33

Presentation Style
Oral

Category of Presentation
Industrial Technology

The Status of the Concept Development Method of Natural Gas Hydrate

Qingping Li (1), Hengyi Zeng (1), Chenwei (2)

(1) CNOOC, (2) CNOOC.RI

Based on the brief review of the progresses on the natural gas hydrate exploration, a three dimensional experimental facility and the three dimensional mathematic simulation program to simulate general natural gas hydrate development methods were built. The experimental simulations of the general development methods, mainly including depressurization, thermal simulation, chemical injection used for produce natural gases from hydrates have been carried out. The hydrate dissociation kinetics, gas and water production rate have been analyzed, which are meaningful for the pilot scale and real industry scale production of natural gas hydrate. On these base, this paper presents a concept development method for offshore natural gas hydrate, considering the current deepwater engineering practice.

Keywords: natural gas hydrate, deepwater engineering; depressurization production; thermal simulation, chemical injection

ID No.
54

Presentation Style
Oral

Category of Presentation
Others on the fields related to methane hydrate R & D

A study on the erosion of cohesive marine clay particles due to shear flows using coupled LBM-DEM simulations

Paul E.Brumby (1), Toru Sato (1), Jiro Nagao (2), Norio Temma (2), Hideo Narita (2), Takao Ebinuma (2)

(1) University of Tokyo, (2) Methane Hydrate Research Center, National Institute of Advanced Industrial Science and Technology

The issue of sediment erosion is an important consideration during methane extraction from offshore, hydrate bearing, sediments. This problem stems from the fast fluid flow towards the extraction well during the depressurisation process. The rate of erosion of cohesive clay particles subjected to shearing flows is investigated for a range of surface shear stresses. The motivation for this work is to model, at a micro-metre scale, the erosion rate of clay particles at locations, within sedimentary layers, exposed to shear flow conditions. Fluid-particle interactions are solved using the lattice Boltzmann method (LBM), while the particle-particle interactions are treated by coupling with the Distinct Element method (DEM). This research was entrusted by the Ministry of Economy, Trade, and Industry (METI), Japan and the MH21 Research Consortium, as a part of the research group for production method of methane hydrate.

ID No.
65

Presentation Style
Oral

Category of Presentation
Exploration Geophysics & Well Logging

Estimated heat flow and gas hydrate saturation from resistivity and P-wave velocity logs in the Andaman Sea, India

Uma Shankar (1), Michael Riedel (1), Kalachand Sain (2)

(1) CSIR-National Geophysical Research Institute, (2) Geological Survey of Canada

Gas hydrate was recovered in the Andaman Sea along the eastern coast of the Andaman Islands during the NGHP Expedition-01. Available 2D multi-channel seismic data were analyzed and BSR was imaged along several seismic profiles. The depth of the BSR is more than 600 m along the seismic line crossing Site NGHP-01-17. To understand the unusual depth of the BSR, we mapped its depth and estimated heat flow from the BSR depth using a simple conductive model. BSR-derived heat flow values range from ~11.9 to ~41.5 mW/m² from the study area and follow the bathymetry trend. We also modeled the base of gas hydrate stability zone to analyze the linkage between gas hydrate occurrences in the Andaman Sea and its relation to the tectonic activity. Our analysis suggests an extensively variable gas hydrate stability zone in the Andaman Sea controlled mainly by low geothermal gradients. Consistent local variations were observed with low heat flow values over prominent topographic highs. This variation may be due to general focusing and defocusing effects of topography.

Pore water chemistry, electrical resistivity and P-wave velocity logs are used to estimate gas hydrate saturations at Site NGHP-01-17. Gas hydrate saturation estimated from chloride concentrations shows values up to ~90% of pore space for distinct ash layers from ~400 meter below seafloor to the BSR. Gas hydrate saturations estimated from the electrical resistivity and acoustic velocity logs using standard empirical relations and rock physics modeling approach are comparable to each other, but saturations are only ~20% of the pore spaces on average. This much lower gas hydrate saturation estimate is a result of overall reduced resolution of the logging tools with typically 20-30 cm thick hydrate-bearing ash layers.

ID No.
72

Presentation Style
Poster

Category of Presentation
Exploration Geophysics & Well Logging

Drilling mud invasion into gas hydrate-bearing sediments: numerical simulations

Fulong Ning (1), Keni Zhang (2), George Moridis (2), Nengyou Wu (3)

(1) China University of Geoscience, (2) LBNL, (3) Guangzhou Institute of Energy Conversion

Except washouts, the invasions of drilling fluid probably also seriously distort the results of well logging. In this work, we performed numerical simulations to study the dynamic behavior and general rules of mud invasion into oceanic gas hydrate bearing sediments (GHBS). Compared with the conventional oil/gas-bearing sediments, hydrate dissociation and reformation are the main characteristics of mud invasion in GHBS when the invasion condition is in the unstable region of gas hydrates phase diagram. The simulation results show that the density (i.e., corresponding pressure), temperature, and salt content of drilling fluids have great effects on the process of drilling fluid invasion. When the temperature and salt content of drilling fluids are constants, the higher the density of the drilling fluid is, the greater degree of invasion and hydrate dissociation are. The increased pore pressure caused by the mud invasion, endothermic cooling with hydrate dissociation compounded by the Joule-Thompson effect and lagged effect of heat transfer in sediments, together make water and gas forming secondary hydrates. The secondary hydrate together with existing hydrate probably made the hydrate saturation higher than original hydrate saturation. This high saturation hydrate ring could be attributed to the displacement effect of mud invasion and the permeability reduction because of secondary hydrates forming. Under the same temperature and pressure of drilling fluids, the higher the salt concentration of the drilling fluid, the faster rate and greater degree of hydrate dissociation due to the stronger thermodynamic inhibition effect and heat transfer efficiency. The dissociated free gas, the dilution of water salinity associated with hydrate dissociation and the occurrence of high saturation hydrate ring probably cause the calculated hydrate saturation based on well logging is higher than that of actual hydrate-bearing sediments.

ID No.
29

Presentation Style
Poster

Category of Presentation
Exploration Geophysics & Well Logging

Characterization of hydraulic permeability of methane-hydrate-bearing sediment estimated by T2-distribution of proton NMR.

Hideki Minagawa, Kosuke Egawa, Yasuhide Sakamoto, Takeshi Komai, Norio Tenma, Hideo Narita

National Institute of Advanced Industrial Science and Technology (AIST)

Natural gas hydrate is a crystalline compound consisting of water molecules and gas molecules and is expected to become a new energy resource. These gas hydrates consist mainly of methane and are called methane hydrates. Several methods of extracting gas hydrate from reservoirs have been proposed, including depressurization, thermal stimulation, and inhibitor injection. These are all based on the in-situ dissociation process of gas hydrate that is transformed into methane gas and water. In any method, gas permeability and water permeability in methane-hydrate-bearing sediments are important factors for estimating the efficiency of methane gas production. Therefore, it is very important to clarify the permeability of gas and/or water flow in MH-bearing sediment and the properties of formation and dissociation of gas hydrates. The permeability of MH-bearing sediment is considerably affected by several properties of sediment, i.e., pore-size distribution, porosity, cementing, MH production methods, and MH saturation.

In petrophysical applications, NMR is used in bore holes as a wire-line logging tool (the Schlumberger Combinable Magnetic Resonance Tool (CMR)) in order to measure the pore-size distribution for oil reservoir rock and/or sandy sediment layers containing methane hydrate. Pore-size distributions are calculated by relaxation time, and permeability can be estimated by the SDR model and /or Timur-Coates model.

In this paper, we investigate the methane-hydrate bearing sediment concerning the relation between the pore-size distribution measured by NMR and the permeability measured by water flow and calculated by NMR-T2 distributions. NMR-T2 distributions which had been measured at Nankai Trough area have been compared with the NMR-T2 distribution measured by laboratory NMR system.

This work was financially supported by the Research Consortium for Methane Hydrate Resources in Japan (MH21 Research Consortium), part of Japan's Methane Hydrate R&D program planned by the Ministry of Economy, Trade and Industry (METI).

ID No.
78

Presentation Style
Poster

Category of Presentation
Exploration Geophysics & Well Logging

Basic logging interpretation for gas hydrate

Tadahiro Nagano

Schlumberger

Gas hydrate (GH) bearing formation is usually represented as higher resistivity and velocity (e.g. Sager et al., 2000). But conventional logs are also useful to find GH. For example, GH makes the neutron porosity be overestimated than the one of formation filled with water. On the other hand, nuclear magnetic resonance porosity cannot distinguish GH from matrix. Therefore the separation of two porosity curves may indicate GH distribution. Although it is not difficult to find typical GH intervals in the ideal condition like above, the other conventional logs like gamma-ray measurements are also essential to clarify the formation properties like porosity, resistivity and saturation affected by clay minerals for example.

To use the logging results for research, it is necessary to understand the uncertainties of data. Logging data are affected by the movement of acquisition device, tool inclination and borehole deviation, borehole size, drilling mud and its invasion, lithology, relative dips, formation fluid type and salinity, temperature, pressure and so on. Loggings are based on various acquisition principles, and are affected by the environmental factors derived from them. In the other word, the environmental factors caused by acquisition principles enable to measure the arbitrary information. Therefore the lack of environmental corrections and principle specific processing will be the critical issues of data quality. If there are still some gaps between the measurements of laboratory and the ones of processed logging data, we should consider about the quality of logging and cores, the limitation of acquisition principles and processing and the resolution of measurements.

Reference:

Sager, W. W., Kennicutt II, M. C. and Gas Hydrate Science Team (2000). "Proposal to the Ocean Drilling Program for Drilling Gas Hydrate in the Gulf of Mexico" Proceedings of the 2000 Offshore Technology Conference, Houston, 1-4 May 2000, paper 12111.

ID No.
15

Presentation Style
Poster

Category of Presentation
Fundamental Physical Properties

Entropic effect of guest encapsulation

Kirill Glavatskiy (1), Thijs J.H. Vlugt (1), Signe Kjelstrup (2)

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Studying the thermodynamic properties of hydrates is important for understanding the fundamental aspects of hydrate formation. One of such properties is the entropy change due to the encapsulation of a guest molecule into the clathrate. It is related to the energy associated with the hydrate formation since a new ordered structure is being created. The encapsulation of the guest molecules in clathrate cages reduces their degrees of freedom which affects the entropy. We perform Monte Carlo simulations to find the entropy of encapsulation for different guest gases. Preliminary results show that this quantity does not depend on the hydrate occupancy. Is this explained by the little interaction between the guest molecules in different cages or there are more fundamental reasons for this?

ID No.
14

Presentation Style
Poster

Category of Presentation
Fundamental Physical Properties

Memory Effect between Different Structure (I, II and H) Hydrates

Jiafei Zhao, Kun Xu, Jiafei Zhao, Yongchen Song, Weiguo Liu, Yu Liu, Yi Zhang, Dayong Wang
Dalian University of Technology

The induction time plays an important role during the process of hydrate formation. It affects the hydrate formation rate to a large extent. The induction time has close relationship with the structure of water, and experiments show that the induction time is shorter for hydrate formation with recently decomposed water than that with fresh distilled water. This phenomenon is known as memory effect. The present study on the memory effect focuses on the induction time's variation in the formation and re-formation processes of the same gas hydrate, however the study on memory effect between different structure hydrates hasn't been reported. In this paper, we study the memory effect between different structure hydrates with the experimental method. In our experiment, the processes of gas hydrate formation with decomposed and fresh water in porous media are observed and investigated in a constant-volume system. The hydrates include methane hydrate (structure I), propane hydrate (structure II) and methyl cyclohexane hydrate (structure H), the decomposed water used for reformation of different hydrates is from methane hydrate and propane hydrate. The induction time of different groups of experiments is recorded and compared as an important parameter of the memory effect. The result shows that the induction time of hydrate formation with decomposed water, either from the same hydrate or from other structure hydrates, is shorter than that with fresh water. It is proved that the memory effect between different structure hydrates exists.

ID No.
43

Presentation Style
Poster

Category of Presentation
Fundamental Physical Properties

What is the hydrate stiffness? - Pore-filling model and Cementation model using Discrete Element Method

Yanxin Yu (1), Yi Pik (Helen) Cheng (1), Kenichi Soga (2)

(1) Civil, Environmental and Geomatic Engineering, University College London, (2) Geotechnical Research Group, Department of Engineering, University of Cambridge

Methane hydrate bearing soil is usually found under deep seabed and permafrost regions. It attracts research interest as a possible energy resource, but its potential impacts on climate change and geotechnical issues during extraction have also raised concern. Due to the limitations in laboratory and field testing data in natural or synthetic samples of hydrate-bearing soils, there are not enough data regarding the stiffness of hydrate particles. In this research, Discrete Element Method (DEM) simulation is used to provide unique insights into the mechanical response of hydrate-bearing sediments with pore-filling hydrate distribution model and cementation model. The hydrate-soil stiffness ratio has an important effect on the stress-strain relationship and on the volumetric response of hydrate-bearing soils. A series of drained triaxial shearing tests are simulated systematically varying the hydrate-soil stiffness ratio from 0.001 to 1 at different hydrate saturations. It is shown in the simulations that when the hydrate-soil contact stiffness ratio reaches a value of 0.1, the peak shear strength increases and dilation is enhanced at the same hydrate saturation as hydrate stiffness increases, but the critical state shear strength at the large axial strain reduces slightly as hydrate-soil stiffness ratio reaches 0.1. After the slight reduction of shear strength, the strengths of different hydrate contact stiffness keep constant. Further data of micromechanical investigations would be presented during the conference.

ID No.
56

Presentation Style
Poster

Category of Presentation
Fundamental Physical Properties

Function of CO₂/water emulsion for enhanced recovery of methane hydrate.

Yojiro Ikegawa, Kimio Miyakawa, Koichi Suzuki, Shiro Tanaka, Kenji Kubota

CRIEPI: Central Research Institute of Electric Power Industry

Methane hydrate is expected as natural gas resources in the future. On the other hand, there would be a subject for commercial production, and some research are carried out for enhanced recovery. Our institute had proposed an exothermic heating by CO₂ hydrate formation. A CO₂ injection technique for the heating is experimentally testing. We had also proposed a new injection technique using CO₂/water emulsion in order to control phase change from liquid to solid. We had obtained data with high reproducibility that show a heating at the top of emulsion flow, the hating position is moved with the seepage of the emulsion though saturated super cooled Toyoura sand in a pressure cell. And the emulsion would flow through sedimentary layers that are warmed to the phase equilibrium by the exothermic heat. CO₂ could not be conventionally injected to the saturated layers that temperature is less than or equal to 10 degree Celsius, because the formed solid CO₂ hydrate blocks the pore of the sediments. The emulsion could improve the blocking, then CO₂ hydrate can be formed a few ten percent of the pore, and the remained pore can be used for emulsion flow. If this warming flow of CO₂ emulsion works in the field stratum, CO₂ could be injected for long term.

ID No.
36

Presentation Style
Poster

Category of Presentation
Fundamental Physical Properties

Effects of cations and anions on methane hydrate phase equilibrium conditions

Mingjun Yang (1), Yongchen Song (1), Weiguo Liu (1), Jiafei Zhao (1), Qingping Li (2)

(1) Dalian University of Technology, (2) CNOOC Research Center

The influences of the cations (Na⁺、Mg²⁺、K⁺、Ca²⁺) and anions (CO₃²⁻、SO₄²⁻、Cl⁻), and their concentrations on the phase equilibrium conditions of methane hydrate in a porous media were investigated experimentally using an orthogonal test method at a pressure of 56 bar. The results of the experiments indicate the present of ions decreases the equilibrium temperature of methane hydrate with the same pressure because both ion clustering and salting out combine to require substantially more sub-cooling to overcome the structural changes and cause hydrates to form. The experimental data were processed in orthogonal table by variance analysis. The variance analysis results indicated that Mg²⁺ level variation impacts remarkably to the final result, and Ca²⁺、Na⁺、K⁺ level variance hardly influence the result. The influences of actors are compared each other as follow order Mg²⁺、Ca²⁺、Na⁺、K⁺. The equilibrium temperature decreases with the increase of concentration of anions. The main factors affecting phase equilibrium are in order of importance SO₄²⁻、CO₃²⁻、Cl⁻. Range analysis showed all three anions have a great impact on the experimental result. The experimental measurements were also in close agreement with the Song et al.'s (2010) thermodynamic model, in which mechanical equilibrium of force between the interfaces in hydrate-liquid-vapor system was considered. Induction time is irregular and rarely affected by the kinds and concentrations of ion. Prediction results show good agreement with the experimental values. This study also showed that the induction time is irregular and rarely affected by ion and concentration and the proper usage of the orthogonal test can reduce experimental time and period.

ID No.
45

Presentation Style
Poster

Category of Presentation
Fundamental Physical Properties

Nucleation phenomena in the sl structure of methane hydrate

Grigory S.Smirnov, Vladimir Stegailov

Joint Institute for High Temperatures of RAS

We investigated methane hydrate nucleation phenomena during formation and decomposition of crystal from molecular dynamic simulation.

Stability of superheated crystal depends on different parameters: temperature and pressure, cage occupancy, lattice defects, existence of free surface, etc. A concept of the spinodal is introduced to denote the stability limit of homogeneous phase. However the thermodynamic spinodal cannot be usually reached because of the kinetic instability caused by nucleation. The kinetic stability boundary due to the homogeneous nucleation; the universal dependence of the kinetic stability boundary on the heating rate and the system volume; the effect of defects was determined for the sl structure of methane hydrate.

Nucleation phenomena during formation of methane hydrate from aqueous phase was studied in the very large systems (more than 100000 atoms) where the effect of periodic boundary conditions is very small.

This work was financially supported by the Russian Foundation for Basic Research grant 11-01-12131-ofi-m.

ID No.
48

Presentation Style
Poster

Category of Presentation
Fundamental Physical Properties

Study on mechanical property for the mixed gas-hydrate under the normal temperature

Tomoaki Egami (1), Wataru Iwabuchi (1), Kiyofumi Suzuki (2), Jiro Nagao (2)

(1) Mitsui Engineering & Shipbuilding Co., Ltd., (2) National Institute of Advanced Industrial Science and Technology

Clathrate hydrates draw attention as a transport method of natural gas and a storage one of it. Mitsui Engineering & Shipbuilding Co., Ltd., (MES) has planned to construct the total system of transportation, storage of natural gas by means of natural gas hydrate (NGH). We have to solve some problems to handle the natural gas hydrate in the generation and transportation system for hydrates industry. Investigating mechanical and physical properties in these systems is very important. In order to clarify the mechanical and physical properties of gas hydrate crystal assemblage, we carried out the triaxial compression test with high dense mixed gas-hydrate containing methane, ethane, and propane and tried to measure the internal friction angle of the hydrates. Apparatus of our test was installed in temperature controlled room. We set up it into the pressure vessel at 279 K (+6 °C). The condition of our test was consolidated and drained under four effective confining pressures; 0.5, 1.0, 1.5, and 3.0 MPa. Our axial strain rate for the compaction is 10, 1.0, 0.1 and 0.01 %/min. As the result of the tests, we found the dependencies of strain rate and confining pressure. The stress curves with low strain rate have no peaks to reach 30 % strain and share strength increased with increasing the axial strain.

ID No.
50

Presentation Style
Poster

Category of Presentation
Fundamental Physical Properties

Dissociation behavior of methane-ethane-propane mixed gas hydrate by powder X-ray diffractometer

Masato Ito (1), Masahiro Takahashi (1), Hiroko Mimachi (1), Ken-ichi Sano (1), Masato Kida (2), Yusuke Jin (2), Jiro Nagao (2)
 (1) Mitsui Engineering & Shipbuilding Co., Ltd., (2) Methane Hydrate Reserch Center, National Institute of Advanced Industrial Science and Technology (AIST)

Mitsui Engineering & Shipbuilding Co., Ltd. has been developing a chain of natural gas transportation using hydrates. This chain is composed of production process, hydrate storage and transportation process, hydrate decomposition process. To understanding formation and dissociation behavior of hydrate is important from the viewpoint of basic data for construction of process. In this study, dissociation characteristic of methane-ethane-propane mixed gas hydrate verified by powder X-ray diffractometer at constant temperatures. We investigated effect on dissociation rate of the difference of crystal structure and of percentage of ice in sample.

ID No.
63

Presentation Style
Poster

Category of Presentation
Fundamental Physical Properties

Structure of methane clathrate hydrate formed within different size of pore spaces

Satoshi Takeya (1), Akihiro Hachikubo (2), Evgeny Chuvilin (3), Vladimir Istomin (4)
 (1) National Institute of Advanced Industrial Science and Technology (AIST), (2) Kitami Institute of Technology, (3) Moscow State University, (4) Gazprom VNIIGAZ

Although understanding of methane hydrate within natural settings is important, not so many studies have been performed on crystal structure of methane hydrate within pore spaces from microscopic point of view. Recently, it was revealed that methane hydrate formed with hydrophilic glass beads less than a few microns in size show very high stability up to just below the melting point of ice, even though this temperature is well outside the zone of thermodynamic stability of the hydrate.[1] In contrast, methane hydrate formed with hydrophilic coarse glass beads (> 10 μm) dissociate quickly at 150–200 K; in this temperature range methane hydrate dissociates at the atmospheric pressure. In this respect, the effects of interfacial forces and capillary forces such as surface or interfacial tension due to beads is of important to understand from both thermo dynamical stability and kinetic stability of CH₄ hydrate.

Herein we report crystal structure of CH₄ hydrate within pores composed of hydrophobic and hydrophilic beads. Powder X-ray diffraction (PXRD) method was employed to identify crystal structure of methane gas hydrate formed within pores of several types of beads.

Reference

[1] Hachikubo et al., Phys. Chem. Chem. Phys., 13 (2011) 17449.

ID No.
68

Presentation Style
Poster

Category of Presentation
Fundamental Physical Properties

Crystallographic characterization of naturally occurring gas hydrates recovered from the eastern Nankai Trough, off Japan

Masato Kida (1), Hiroyuki Suzuki (2), Kiyofumi Suzuki (1), Hideo Narita (1), Jiro Nagao (1)

(1) National Institute of Advanced Industrial Science and Technology, (2) Nihon University

Natural gas hydrates are crystalline clathrate compounds, which encage a large amount of natural gas. The crystallographic structure of natural gas hydrates depends on the encaged natural gas components. The hydrate cages can contain C1 - C7 hydrocarbons. Massive and pore-space natural gas hydrates were obtained from the eastern Nankai Trough area during Japan's Methane Hydrate R&D Program conducted by the Ministry of Economy, Trade and Industry (METI) of Japan. In this study, hydrate-bound gas, crystal structure, and hydration number of the natural gas hydrates were characterized.

The PXRD profiles of the massive and pore-space natural gas hydrates revealed that the crystallographic structures of the all natural gas hydrates studied were structure I.

All samples contained CH₄ as a main hydrocarbon component, indicating that the natural gas in marine sediment at the study areas is mainly CH₄. In addition, almost all samples contained small amounts of hydrocarbons C₂ - C₄. In some cases, remarkably higher concentrations of heavier hydrocarbons such as C₃H₈ or i-C₄H₁₀ were found.

¹³C NMR and Raman spectroscopic techniques were used to obtain molecular information on the encaged hydrocarbon molecules. The ¹³C NMR chemical shifts and Raman shifts of guest molecules showed that the primary component of guest molecule is CH₄ and their crystallographic structure is structure I, supporting the PXRD data. The hydration number estimated from the obtained cage occupancies was 6.1–6.2. The obtained hydration numbers are important parameters for estimation of amount of hydrocarbons in hydrate-bound natural gases in the eastern Nankai Trough area.

This work was supported by funding from the Research Consortium for Methane Hydrate Resources in Japan (MH21 Research Consortium) planned by METI.

ID No.
74

Presentation Style
Poster

Category of Presentation
Fundamental Physical Properties

Ice-Shielding Models for Self-Preservation Effect of Gas Hydrates

Tsutomu Uchida, Toshimitsu Sakurai, Takeo Hondoh

Hokkaido University

The self-preservation of methane hydrate is a key process in its engineering applications because the hydrate can survive for a significant period under atmospheric pressure and moderate temperature. We propose ice-shielding models of gas hydrates to investigate the dissociation rates quantitatively, including the self-preservation process, at temperatures below the ice-melting point and at atmospheric pressure. Three general models are constructed for two temperature ranges. The rate-determining process for the lower temperature range is hydrate dissociation, and those for the higher range are gas diffusion through ice or hydrate layers, which depend on the thickness of the shielding-ice layer. Our models suggest that the extent of self-preservation depends on temperature, original hydrate size, and guest substances, which can explain the previously reported experimental results.

ID No.
32

Presentation Style
Poster

Category of Presentation
Fundamental Physical Properties

Characterization of CO₂ clathrate hydrate formation and dissociation using high pressure differential scanning calorimetry

Pierre Le Parlouer, Rémi André

Setaram Instrumentation

In addition with the research for alternative energies to reduce hydrocarbons use, every realistic scenario confirms a slowly decreasing but continuous use of fossil fuel and thus the release of carbon dioxide. Therefore carbon capture and sequestration (CCS) technologies are an important option to reduce the atmospheric carbon dioxide content. CO₂ sequestration may involve the injection of the gas into geologic formations such as depleted oil or gas reservoirs, or deep unminable coal seams. Other possibilities include the injection of CO₂ in large amounts of natural methane hydrate in ocean sediments. In that case, formation of carbon dioxide hydrates is expected, together with a dissociation of methane hydrates. Several national research programs such as the French SECOHYA (SEparation of CO₂ by HYdrate Absorption) or the German SUGAR project (Submarine Gas Hydrate Reservoirs) have placed efforts in such fields. Calorimetry has proved to be a very interesting technique in the investigation of gas hydrates formation and dissociation. It allows determining compositions, dissociation enthalpies and heat capacities. As high pressure is needed for gas hydrate investigations, a methodology has been developed based on High Pressure Micro Differential Scanning Calorimeter. Tests can be conducted under isothermal, isobaric, temperature scanning or pressure scanning conditions. Different application examples will be given, especially dealing with the enhancing / inhibiting effects of additives on CO₂ hydrate formation for sequestration.

ID No.
66

Presentation Style
Poster

Category of Presentation
Fundamental Physical Properties

Methane Hydrate Accumulation Habits in Porous Media: X-ray CT Scans and Core Scale Modeling

Yongkoo Seol, Eilis Rosenbaum, Ray Boswell

US DOE National Energy Technology Laboratory

Physical properties of hydrate bearing sediments largely depend of the nature of pore-scale interactions between gas hydrates and sediment particles. We formed methane hydrate in artificial sand packs and observed water migration patterns with a medical X-ray CT scanner. Core-scale numerical modeling was performed using a numerical grid that was converted from X-ray CT images. The impacts of pore space hydrate accumulation habits (e.g., pore body filling or grain coating) on fluid migration were examined by comparing numerical predictions with experimentally measured water saturation distribution and breakthrough curves. CT images show discrete flow pathways in a sand pack sample with varied hydrate distribution. A model case with 3D heterogeneous initial conditions (hydrate saturation, porosity, and water saturation) and pore body preferred hydrate accumulation best captured the water migration behavior captured through the hydrate-bearing sample. Due to the restrictions of image resolutions (250 μm) and computational capacity, however, the study was limited to indirect conjecture of hydrate accumulation habits in pore space. In order to explicitly capture the accumulation habits, we are currently developing imaging and quantification techniques of hydrate bearing sediments with a micro X-ray CT scanner, segmenting out laboratory-synthesized hydrate and hydrate analogues from mixed sediments.

ID No.
85

Presentation Style
Poster

Category of Presentation
Geology-Geochemistry

Experimental study of the thermal conductivity of frozen hydrate saturated sediments in equilibrium and nonequilibrium conditions

E.M. Chuvilin, B.A. Bukhanov

Faculty of Geology, Moscow State University

In this report we present the results of laboratory measurements of the thermal conductivity of artificial hydrate-bearing sediments in equilibrium and nonequilibrium conditions. In the first case our researches of thermal properties were carried out on a specially created experimental cell. This device allows us to investigate thermal conductivity of gas saturated sediments in pressures chamber under gas pressure during hydrate accumulation in porous media, and also during freezing of hydrate saturated sediment. In the second case thermal conductivity measurements were carried out frozen gas hydrate contained sediment samples under atmospheric pressure. For estimation of heat conductivity of frozen hydrate contained samples under non-equilibrium conditions the analyzer KD2 by company Decagon Devices, Inc (USA) was used. The results of laboratory measurements of the thermal conductivity of hydrate-bearing sediment samples in equilibrium and nonequilibrium conditions were compared properties of similar frozen sediment samples without gas hydrate. Experimental data showed that the thermal conductivity is very different for hydrate-bearing sediment samples, than for similar ice-bearing sediment samples. This difference depends on the type of sediments and hydrate saturation. Experimental results show that thermal conductivity of self-preserved hydrate-bearing sediments at atmospheric pressure increases with time because of the pore gas hydrate dissociation at non-equilibrium conditions. Our results show the possibility of using thermal conductivity to single out frozen hydrate containing layers both in stable and metastable states.

ID No.
73

Presentation Style
Poster

Category of Presentation
Geology-Geochemistry

Mineralogical and geochemical composition of Pleistocene fine-grained marine sediments in the Northeast Nankai Trough area

Kosuke Egawa (1), Okio Nishimura (1), Kiyofumi Suzuki (1,2), Takuma Ito (1), Hideo Narita (1)

(1) MHRC/AIST, (2) JOGMEC

We conducted sediment core analysis in understanding mineralogical and geochemical composition of silty and clayey sediments in oceanic gas-hydrate fields along the Northeast Nankai Trough, off central Japan. The core samples were collected from the interval where Pleistocene forearc marine sediments of alternating sand and mud were thickly deposited. It is known from a 3D seismic survey that stratigraphic unit of the studied coring site is subdivided into submarine slope failure and downslope-thickening turbidite sequences in the upper and lower intervals, respectively. X-ray diffraction analysis demonstrated predominance of calcite and pyrite in the upper interval, together with a clear negative correlation between quartz and calcite. These patterns are supported by the result of X-ray fluorescence analysis that in this interval calcium carbonate and loss on ignition are high in ratio and are inversely correlated with detrital composition such as silicon dioxide and potassium oxide. From scanning electron microscope images showing abundant calcareous nannoplankton fossils such as coccolith and foraminifera in the upper interval, it is likely that such a negative correlation between organic and detrital contents suggests temporal variation of detrital influx into the study area probably in response to climatic and/or tectonic events. Pyrite in the upper interval mostly occurs in primary framboidal form, and commonly fills intergranular pore space and calcareous fossil shell. Presence of such a pyrite strongly indicates anoxic conditions with syngenetic or early-diagenetic microbial activity. This study is financially supported by METI and the MH21 Research Consortium.

ID No.
23

Presentation Style
Poster

Category of Presentation
Geology-Geochemistry

Petrographic and stable isotope characterization of authigenic carbonates from the northern South China Sea

Hong Shu Wang (1), Wen Yan (1), Vitor Hugo Magalhães (2), Zhong Chen (1), Fernando Rocha (2), Luis Menezes Pinheiro (2)

(1) South China Sea Institute of Oceanology, Chinese Academy of Sciences, (2) University of Aveiro

This study focus on two cold seep areas in the northern South China Sea, in order to investigate the authigenic carbonates formation mechanisms and their possible relation with gas hydrates. The results of SEM, XRD and stable isotopes reveal that the authigenic carbonate samples are mainly composed of dolomite, calcite and aragonite, with small amounts of high-Mg calcite and siderite. Their formation is related with the migration and seafloor seepage of hydrocarbon-rich fluids and gas hydrate dissociation. The aragonite-dominated carbonates are formed near or at the sediment surface while the formation of the dolomite-dominated cements occurs probably in deeper parts of the sedimentary column. Stable isotope results reveal that the $\delta^{13}\text{C}$ values of the samples for the southwestern Dongsha area ($-49.21\text{‰} \sim -16.86\text{‰}$ VPDB) show a clear contribution of methane oxidation to the carbon pool from the authigenic carbonates where precipitated from, and most probably this carbon source corresponds to thermogenic or a mixed source of thermogenic and biogenic methane. Assuming the formation under a present-day seafloor temperature, modeling was carried out to determine the initial composition of the fluids from which the carbonates precipitated, based on oxygen isotopic compositions. The $\delta^{18}\text{O}$ values ($2.97\text{‰} \sim 3.72\text{‰}$ VPDB) indicate enrichment in ^{18}O that is most probably related to destabilization of gas hydrates. In contrast, the Baiyun Sag sample exhibits normal seawater carbon (2.36‰ VPDB) and oxygen (0.44‰ VPDB) isotopic values, indicating that this sample is not related to methane seepage but instead to precipitation from normal seawater. These results confirm previous studies and show that the southwestern Dongsha area samples are related to methane seepage and the dissociation of gas hydrates, while the Baiyun Sag sample is apparently a normal marine carbonate.

Keywords: Authigenic carbonate; Cold seeps; South China Sea; gas hydrates

ID No.
27

Presentation Style
Poster

Category of Presentation
Geology-Geochemistry

Sulfur speciation of marine sediments related to gas hydrates in north part of South China Sea

Guodong Zheng (1), Nengyou Wu (2), Yidong Zhao (3), Rui Yang (2)

(1) Key Lab Petrol. Resource Research IGG CAS, (2) Key Lab Renew Energ Gas Hydrate, GIEC, CAS, (3) BSRF, IHEP, CAS

The releasing of hydrocarbons from marine bottom may induce various mineralogical and geochemical anomalies in marine sediments such as sedimentary elements, hydrocarbon gases, core water, microbes, authigenic minerals and secondary carbonates. However, there is limited information about redox change related to the occurrence of gas hydrate using chemical speciation of some redox sensitive elements. In this study, we applied XANES to measure sulfur species of cored samples from Shenhu area in north part of South China Sea. Samples of core site4B showed a specific profile of sulfur speciation with sharp and frequent variations in relative contents of sulfate and sulfide in compression to normal marine sediments, the core site5B and site6A collected from different area of the same part of South China Sea. The core site4B can be divided into two parts; the upper part in depth of 0-95 cm is soft and rich in pore water, containing mainly coarse silt sand. The lower part deeper than 95 cm is relatively dry and in darker color, and dominated by silts and clay, being very similar to mud volcanic sediments. For sulfur speciation, sulfate takes almost 100 percent of all sulfur in the samples of the upper core, revealed a strong oxidative condition. There are much more sulfide in the lower core with high relative contents of sulfide, even near 100% S^{2-} , and the relative contents of sulfide and sulfate changed rapidly and frequently. Such a specific pattern of sulfur speciation may indicate the occurrence of methane hydrate underneath in this area with fluids and gas emission to the sea floor even some eruption of marine mud volcanoes from time to time. The vertical profiles of sulfur species for the cores site5B and site6A are relatively consistent with lower content of sulfide, showing stable and weaker reducing conditions.

ID No.
71

Presentation Style
Poster

Category of Presentation
Geology-Geochemistry

Analysis of equilibrium conditions for determination of hydrate forming gasses offshore Uruguay

Pablo Gristo, Juan Tomasini, Pablo Gristo, Pablo Rodriguez, Hector de Santa Ana

ANCAP Exploracion y Produccion

At the Uruguayan continental margin, seismic evidence for the occurrence of gas hydrate has been identified based on the presence of bottom simulating reflections (BSRs) in densely spaced 2D seismic from different surveys. Mapping of BSRs by interpretation of new seismic data suggests the presence of gas hydrates in areas that were not previously identified; hence hydrate occurrence offshore Uruguay is more widespread than previously thought. Interpretation results in a mean value of 25,890 km² for the area of occurrence, thus showing a great potential for this unconventional resource, and encouraging further research in a country with non commercial hydrocarbon discoveries up to now, and therefore a net oil and gas importer.

In this work we calculate the temperature and pressure at the base of gas hydrate stability zone (GHSZ) for specific sites offshore Uruguay, by using the geothermal gradient from 2 exploratory wells and the BSR depth. Then we compare calculated values with the temperature and pressure equilibrium values which correspond with different hydrate forming gases. Sites were selected based on available seafloor temperature data, while the BSR depth was obtained from interpretation of the closest seismic sections.

Due to the uncertainty of some of the input parameters (mainly geothermal gradient), we used a probabilistic approach, assigning each parameter a range of values and probability distribution, hence obtaining distributions for temperature and pressure at the base of the GHSZ.

As a result, at the studied locations, the thermodynamic analysis of the equilibrium conditions suggests that the hydrate forming gas would be methane. In particular for one of the sites, located at deeper waters, hydrates may contain other heavier hydrocarbons like ethane. In addition, for the studied sites, the P-T conditions calculated at the base of GHSZ are far away from the stability conditions of carbon dioxide hydrates.

ID No.
22

Presentation Style
Poster

Category of Presentation
Geology-Geochemistry

Influence of water flow associated with gas venting on hydrate accumulation: A case study at the southern summit of Hydrate Ridge, Cascadia Margin off Oregon

Duofu Chen, Yuncheng Cao

CAS Key Laboratory of Marginal Sea Geology, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences

Massive gas hydrate were recovered at many cold vent sites, e.g. Hydrate Ridge, Bush Hill, Okhotsk Sea. At these cold vent sites, water and gas transmit from deep depth at high temperature to seafloor at relative low temperature. During this process, deep source fluid warms shallower sediments to affect hydrate accumulation. To know how the water flow affect hydrate crystallization, we use a kinetic model for gas hydrate crystallized to simulate gas hydrate accumulation at gas venting sites. The parameters used in our calculation are determined from the measurements at the southern summit of Hydrate Ridge, where three distinct active fluid regimes were identified. The first province is represented by discrete sites of methane gas ebullition, where the bulk of the flow occurs through channels. The other two provinces are characterized by the presence of extensive bacterial mats and calm sites, respectively. Our calculation shows that calm sites have much higher chloride concentration than bacterial mats sites, but much lower temperature. And calm sites have much deeper base of hydrate stable zone and much larger amount of gas hydrate. And in the province of methane gas ebullition, the fluid flux is so high that temperature in the channel increase to the value of source area, which results no gas hydrate accumulation.

Therefore, upward fluid can significantly increase temperature, which inhibits the crystallization of gas hydrate. However, it can also inhibit the chloride concentration increase. The influence of temperature increase on hydrate system is more effective than that of chloride concentration decrease. With an increase of water flux, the thickness of hydrate stable zone and the rate of hydrate precipitation would decrease, resulted in less hydrate accumulation and even no gas hydrate precipitated at extremely high water flux area.

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ID No.
31

Presentation Style
Poster

Category of Presentation
Geology-Geochemistry

Archaeal and bacterial biomarkers in gas hydrate bearing sediments from the eastern Nankai Trough

Miki Amo, Ryuko Izawa, Emiko Shinbo, Keiko Hatano, Tadaaki Shimada

Japan Oil, Gas and Metals National Corporation

In order to clarify the microbial activities related to methane generation in the eastern Nankai Trough, we performed analyses of biomarkers in the sediment samples obtained from the METI Exploratory Test Wells "Tokai-oki to Kumano-nada" by using the comprehensive two-dimensional gas chromatography (GC x GC). Previous geochemical study has shown that the biogenic methane forms methane hydrate (MH) in the eastern Nankai Trough. However, at which depth methane is generated in sediments is an unresolved issue. In this study, we attempted to identify and quantify the biomarkers of methanogenic archaea in the sediment cores by GC x GC equipped with qMS and FID.

Samples for the analyses were collected from two holes (α -1 and β -1) of the METI Exploratory Test Wells "Tokai-oki to Kumano-nada" by JOIDES Resolution in the eastern Nankai Trough. The extracted lipids were analyzed using a ZOEX KT2006 comprehensive GC x GC.

The neutral lipids fractions of the both core samples mainly consisted of n-alkanes, acyclic isoprenoids, n-alcohols, sterols and hopanols. Several hopanols, which indicates bacterial activity, such as 17,21-homohopanol, 17,21-bishomohopanol, trishomohopane-32,33-diol and anhydrobacteriohopanetetrol were detected in all sediment samples. The hopanols concentrations showed significant higher values in clay layers than in sand layers. TOC showed also higher values in clay layers than in sand layers. 2,6,10,15,19-Pentamethylcosane (PMI), which is the biomarker indicating methanogen, was detected in all samples from both sites. The $\delta^{13}C$ values of PMI suggest that PMI could be derived from methanogen. The PMI concentrations increase at the MH bearing zone and below the MH bearing zone in α -1 and β -1, suggesting an increase of methanogen biomass. This might be due to fluid flow simulating microbial activities around and below the MH bearing zone.

ID No.
80

Presentation Style
Poster

Category of Presentation
Geo-technical Engineering

Development of Multi-Sensor-Tap Core Holder for Relative Permeability Measurement in Methane-Hydrate-Bearing Sediments

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Depressurization is thought to be a promising method for gas recovery from gas hydrates deposits; however, considerable water production is expected when this method is applied for oceanic gas hydrate deposits. The gas-water relative permeability of gas-hydrate-bearing sediments is a key parameter to predict gas-water-ratio (GWR) during gas production. However, the experimental measurement of gas-water relative permeability for gas-hydrate-bearing sediments is a challenging problem due to a phase change (gas hydrate formation/dissociation) during gas-water flooding test.

We developed a novel core holder to measure gas-water relative permeability for gas-hydrate-bearing sediments. X-ray CT was used to image a displacement front and quantify density changes during water flooding test in methane-hydrate-bearing cores. We obtained CT images every two minutes during a water flooding test for a gas-saturated methane-hydrate-bearing core. The movement of displacement front was captured from these CT images. Quantitative analysis of density change was also done to analyze the change of gas/water saturations. We developed a multi-sensor-tap core holder to minimize capillary end effect on the pressure measurements. To obtain CT images by X-ray, the core holder was made of aluminum alloy. We successfully measured pressure differences of the intermediate section of the core during water flooding test. The change of pressure differences during water flooding test showed strong correlation with the movement of displacement front. By combining the date of density changes and pressure differences, we can estimate the water/gas effective permeability in gas-hydrate-bearing sediments.

ID No.
52

Presentation Style
Poster

Category of Presentation
Geo-technical Engineering

Prediction of stresses and deformation of production well and seabed ground for methane hydrate production using multi phase coupled simulator COTHMA

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In the Methane hydrate extraction project, a well is drilled into the sea floor from a marine platform. Then, fluids in the well are depressurized to induce hydrate dissociation and the dissolution of methane gas is collected in-situ. During the production, there are concerns about the deformation of the seabed and the possibility that negative friction will occur along production well due to change in effective stress induced by water movement due to depressurization, dissociation of hydrate, methane gas generation and thermal change, which are all inter-connected. A multi phase coupled simulator named "COTHMA" had developed and used for predicting stresses and deformation of production well and the deep seabed which simulating Eastern NANKAI trough where is planned as Japan's first offshore production test area (conducted by MH21 Research Consortium). According to analytical results, depressurization area was extended rapidly in first 10 days, and the tip of depressurized area attained 20m from production well. Then, a lower layer heaved vertically by effect of consolidation centered on depressurization source. On the other hand, an upper layer had deformed downward in perpendicular. The maximum principal stresses are distributed like arch structure over the upper and lower layer. Moreover it has supported overburden. However, high tensile stresses appear on cement about 50m range above the depressurization area, and compression stress appear on the borehole which is depressurization part. But finally, it was found that the arch structure disappears after long-term production by depressurization area spreads uniformly and deformation reached sea bottom gradually.

ID No.
70

Presentation Style
Poster

Category of Presentation
Geo-technical Engineering

Monitoring system for sea floor deformation in the methane hydrate production test

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We are now developing a monitoring system for seafloor deformations during Methane Hydrate production test. Seafloor deformations are evaluated by measuring subsidence and inclination of the seafloor. Subsidence is measured with change of water pressure on the seafloor. A pressure gauge we selected is applied a quartz crystal resonator. The range of the pressure gauge is 0 to 1,400m, the resolution is 0.014mm, and actual accuracy is around 10mm in conversion to water level. An inclinometer we selected is applied liquid electrolyte. The range of the inclinometer is ± 30 degree, resolution is 0.001degree, and actual accuracy is around 0.03-0.3degree depending on measuring condition. According to simulation of seafloor deformation around the production hole, the range of subsidence will be from 10cm to 30 cm. This system has been examined in the offshore of Suruga Bay which has water depth more than 1000m. All the features of this system were confirmed by examination of deep water area in Suruga Bay. We will do a final check during the production test of Methane Hydrate at East Nankai trough in 2013. This work was carried out by OYO corporation with the support of JOGMEC which is a member of MH21 consortium sponsored by Ministry of Economy, Trade and Industry in Japan.

ID No.
51

Presentation Style
Poster

Category of Presentation
Industrial Technology

Issues of the Drilling and Well Completion for the Offshore Methane Hydrates on the Commercial Phase

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Several exploration and survey drillings for offshore methane hydrate study have been conducted in many locations in the world. Except for some academic projects, Japan, US, Korea, India and China succeeded in drilling in offshore methane hydrate formations as the development researches. However, only Japan has conducted well construction experiments such as cementing and horizontal well drilling for future development of well completions in a methane hydrate concentrated zone which is recognized as a possible pay zone in future commercial phase.

For commercial MH resource development, production wells must be completed in unconsolidated sediments of shallow intervals below seafloor. Furthermore the more numbers of production well than conventional oil and gas production cases is required because of the lower gas production rate from a single well.

The Research Consortium for Methane Hydrate Resources in Japan (MH21) proposes that the depressurization method is an efficient methane production technique. The production method requires quite high draw-down (70-80%) that we have never experienced in conventional oil and gas production. Formation damages (ex. severe sanding, deformation of the sediments etc.) are expected by the high degree of draw-down.

The production wells will be constructed in unconsolidated and soft sediments, and should withstand in conditions of strong differential-pressure for a long period. Efficient and economical methods for drilling and well completion should be investigated for future commercial production.

This presentation will introduce the following items based on present knowledge and experience;

- (1) overview of the past drilling campaigns for offshore methane hydrates exploration
- (2) expected issues while drilling and productions of offshore methane hydrates
- (3) efficient and economical methods of the drilling and well completion for offshore methane hydrates we propose

This study has been conducting as a part of study of MH21.

ID No.
47

Presentation Style
Poster

Category of Presentation
Industrial Technology

Size effect on self-preservation phenomena of natural gas hydrates

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Natural gas hydrate is useful to keep gases under mild conditions. It is important to understand so-called self-preservation phenomenon so that gases in hydrates are preserved and handled effectually. To examine an effect of gas species on the decomposition phenomena, natural gas hydrate which was made from stimulant LNG and methane gas hydrate were formed artificially and stored at 253 K for two weeks. Additionally, to research an effect of hydrate sizes on self-preservation, hydrates were shaped some types of size before stored.

ID No.
26

Presentation Style
Poster

Category of Presentation
Industrial Technology

Development of a Large-Scale Laboratory Vessel for Methane Hydrate Production Tests

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Production Technology Team, Methane Hydrate Research Center, AIST

Natural gas hydrates, in which hydrocarbon molecules are encaged in water cage structural molecules, are valuable resources. To utilize these resources, the establishment of a gas production technology and investigation of suitable conditions for extraction of methane from methane hydrate reservoirs are important. On the one hand, core-scale dissociation experiments give us the reproducible results on quantitative parameters on the methane hydrate dissociation under various conditions. On the other hand, a production test at a real methane gas hydrate reservoir would provide information about the type of dissociation phenomena. The natural gas production behaviour is dependent upon the size and characteristics of reservoirs, such as temperature and permeability. In other words, while a core-scale dissociation experiment can demonstrate the heat transport process, dissociation in an actual geological reservoir is dominated by the material flow process. Thus, it is important to couple data obtained from core-scale tests with the results of field-scale tests by using a large-scale laboratory vessel which can provide dissociation experiments under the similar conditions of actual reservoir. On this presentation, the research objective and certification of a large-scale laboratory vessel for methane hydrate production tests at the Methane Hydrate Research Center of the National Institute of Advanced Industrial Science and Technology are presented. Comparison between the experimental result for depressurization and its numerical prediction are described.

ID No.
44

Presentation Style
Poster

Category of Presentation
Marine Environment

Methane Recovery from Gas Hydrates by Injection of Supercritical CO₂: Influence of Thermodynamic and Structural Properties

Elke Kossel, Christian Deusner, Nikolaus Bigalke, Matthias Haeckel

GEOMAR, Helmholtz Centre for Ocean Research Kiel

The recovery of natural gas from CH₄-hydrate deposits in sub-marine and sub-permafrost environments through injection of CO₂ is considered a suitable strategy towards CO₂-neutral energy production: CO₂ activates the release of CH₄ from the gas hydrate and is retained in the reservoir as immobile CO₂-hydrate. In our experiments we could show that the injection of hot, supercritical CO₂ is particularly promising. The addition of heat dissociates the CH₄ hydrate and leads to a fast and continuous release of the encaged methane. However, the total production yield depends strongly on the structural properties of the surrounding hydrate/sand matrix. Additional CH₄ can be liberated if percolating cooled, liquid CO₂ gets in contact with CH₄-hydrate triggering a direct exchange of the guest molecule. Furthermore, the transport of CH₄ to a production well requires sufficient permeability of the sediment matrix and is hindered by the reformation of gas hydrates during the process. We present experimental data from a high-pressure flow-through reactor at different sediment temperatures (2 °C, 8 °C, 10 °C) and hydrostatic pressures (8 MPa, 13 MPa). The efficiency of both CH₄ production and CO₂ retention was evaluated and best results were achieved at 8 °C, 13 MPa. This behavior can be explained by the different percolation properties of the mobile phases at the various sediment temperatures. To substantiate these findings, we performed magnetic resonance imaging experiments that provided spatially resolved information on the fate of liquid CO₂ in the sand/CH₄-hydrate matrix. The results confirm the good accessibility of the pore space for liquid CO₂ at 8 °C, 13 MPa.

ID No.
24

Presentation Style
Poster

Category of Presentation
Marine Environment

The Carbon Isotope Evidence of Gas Hydrate Dissociation in South China Sea

Wen Yan, Shuhong Wang

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The main purpose of this study is to discuss the relationship between climate change and gas hydrate decomposition from Late Quaternary and understand the response characteristics of gas hydrate decomposition in the South China Sea by high-resolution carbon and oxygen isotopes analysis. The carbon and oxygen isotopes analysis of Planktonic foraminifera were conducted for cores NS93-5 and NS97-37 from southern South China Sea and the rapid negative excursion of carbon isotope in the last deglaciation (about 18ka) and the penultimate deglaciation (about 130ka) were observed. In the same layers, the oxygen isotope also appeared similar phenomena and the Globigerinoides ruber (Pink) died out in midpoint of MIS 5/6 (about 129.84ka). The stable carbon and oxygen isotopes of benthic foraminifera were also analyzed for core O8CF7 from Baiyun Sag in northern South China Sea, near where the gas hydrate was collected in 2007, and a rapid negative excursion of carbon isotope was also found, and the oxygen isotope has the same trend in this core. The change of carbon and oxygen isotope is in consonance with atmospheric methane concentration from the Vostok ice core. The rapid negative excursions of carbon isotope recorded in South China Sea is likely related to gas hydrate dissociation or methane releasing, i.e. the changes of temperature and pressure induced gas hydrate dissociation and released methane in South China Sea and/or other areas, which made the climate warmer, ocean anoxic and further led the extinction of some marine organism and accelerated glacial termination.

Key Words: South China Sea, Gas hydrate, Carbon isotope

ID No.
77

Presentation Style
Poster

Category of Presentation
Others on the fields related to methane hydrate R & D

Formation process of methane clathrate hydrate in porous media.

Yusuke Jin, Yoshihiro Konno, Jiro Nagao

Pro-Tech, AIST

Natural gas-hydrates, whose guest gas are primarily of methane, are widely distributed in oceanic and permafrost sediments. These gasses in natural gas-hydrates are expected to become a new energy resource. Therefore, gas production methods for natural gas from hydrate-bearing sediments are currently being developed. In gas production process by dissociating natural gas hydrates from sediments, initial/absolute permeability of water/gas in sediments are very important. To understand how does hydrate grow in pore spaces of sediment is very important for mechanism of hydrate formation. We observed process of methane (CH₄) hydrate formation in unconsolidated sandy media by using an ATR infrared (ATR-IR) spectroscopy. IR absorption region of H₂O molecules is very useful to evaluate hydrogen-bonded (HBd) states of O-H group (OH). With increasing HBd OH species (namely, phase transition from liquid to solid), ATR-IR absorption band of OH shifts to lower-wavenumber region. On the other hands, the OH band shifts to higher-wavenumber region during decreasing HBd OH species (phase transition from solid to liquid phase). From ATR-IR spectra during CH₄ hydrate formation, two discrete hydrate growth was observed after pressurization. This two-step growth was not reported in bulk hydrate formation. At the first step, randomly hydrate double-exponentially increased after nucleation. The second discrete growing step randomly occurs. Moreover, the process of the two-step hydrate growth was also observed using an optical scanning microscopy. The two-step growth reflects the change in the nature of hydrates, from a film to a cement-like hydrate.

ID No.
79

Presentation Style
Poster

Category of Presentation
Others on the fields related to methane hydrate R & D

A submarine fan model based on the facies analysis of 2D and 3D seismic data for the exploration of Methane Hydrates in the Ulleung Basin, East Sea, offshore Korea

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Conventional hydrocarbon evaluations methods were applied for Methane Hydrates explorations in the Ulleung Basin, East Sea, offshore of Korea. Total 13,086 L-km 2D and 700 sq. km 3D seismic and 14 well data evaluation revealed several submarine fans within the hydrates stability zone in the Basin. According to the tectonic evolution and sedimentation of the Basin, it is expected that sediments has supplied from southwest toward northeast as a form of a point source submarine fan. Seismic facies and gamma ray logging patterns are analyzed for identification of submarine fans. Stacked several submarine fans are well recognized from 2D and 3D seismic data interpretation especially by isochrones. The average length of several submarine is around 50 km and few fans are longer than 200 km. A model of submarine fans has developed for Methane Hydrates explorations in the Basin.

ID No.
55

Presentation Style
Poster

Category of Presentation
Others on the fields related to methane hydrate R & D

Study on Morphology of the Methane Hydrate in Porous Media

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(1) University of Tokyo, (2) Methane Hydrate Research Center, National Institute of Advanced Industrial Science and Technology

Since reformation of hydrate may block gas-water two-phase flow in sub-seabed sand sediments during the methane production from gas hydrate, it is important to know how it forms in the sediment to design a safe and efficient process. In this study, we calculated the morphology of methane hydrate in porous media by using the phase-field model, tacking account of mass and heat transfer. Starting points of hydrate growth are determined by the fluctuation of methane in water, which is derived from the Brownian motion. The presence of foreign substances is considered by using the idea of the classical nucleation model of heterogeneous nucleation.

Acknowledgement: This research was entrusted by the Ministry of Economy, Trade, and Industry (METI), Japan and the MH21 Research Consortium, as a part of the research group for production method of methane hydrate.

ID No.
46

Presentation Style
Poster

Category of Presentation
Others on the fields related to methane hydrate R & D

An investigation of thermodynamic inhibitors used to decompose methane hydrates

Christopher Kinoshita, Stephen Masutani, Gerard Nihous, Traci Sylva

University of Hawaii

Hydrate inhibitors are used extensively by industry in flow assurance applications. An investigation was conducted to elucidate the mechanism by which ethylene glycol and different alcohols decompose methane hydrates. This study employed a novel experimental facility which couples calorimetry with Raman spectroscopy. Hydrate samples were formed within the calorimeter cell and were decomposed by injection of various reagents at constant temperature and pressure. A fiberoptic probe was used to bring laser radiation into the pressurized cell and to collect the Raman shifted light to detect hydrate at various points of the process. The effectiveness of the different inhibitors that were tested (in terms of moles of hydrate decomposed per mole of inhibitor) were inferred from the calorimetric data. Results indicate that, all other factors being the same, ethylene glycol decomposes the largest quantity of methane hydrate, followed in order by methanol, ethanol, and then 2-propanol.

Mobile Order Thermodynamics (MOT) was applied to explain the behavior of the chemical inhibitors. MOT considers the impact that the hydrogen-bonding ability of alcohols and the size of the alkyl group has on the chemical potential of water. This approach was extended to include glycols, which have twice the number of hydrogen bonding sites as alcohols. We posit that the application of alcohols or glycols induces hydrate decomposition by binding to water molecules in the quasi-liquid layer, effectively decreasing their chemical potential. This would explain why glycols are more effective than alcohols at dissociating hydrates, and why smaller alcohols are more effective than larger alcohols.

PRE WORKSHOP TOUR:

Toya-Caldera and Usu-Volcano Global Geopark

The workshop was preceded by a tour of the Toya-Caldera and Usu-Volcano Geopark on 28th May, 2012. The Toya-Caldera and Usu-Volcano Global Geopark was designated as one of the first Japanese Global Geoparks in 2009. There are many beautiful and educational sites there created by volcanic activities. In 2008, the G8 Hokkaido Toyako summit was held in this area.

The Toya caldera was formed by a gigantic eruption and collapse around 110000 B.C. Then, about 20,000 years ago, the Usu-volcano erupted and is still active. Between 1663 and 2000, Usu volcano has experienced cyclic eruptions every few decades. The Showa shinzan is one of the lava domes near the Usu volcano which grew to a height of 400 m between 1944-45, after only one-year. During the last eruption in 2000, roads near the volcano around the Toya caldera lake were destroyed by lava flows. Many disasters have been sustained in the area every few decades.



Showa-shinzan



Footpath of Nishiyama trail

18 participants visited the Showa-shinzan and Usu volcano trails to see the powerful volcanic activities. They also visited the hazard museum of volcanism in Toyako onsen town; "onsen" means hot spring. They learned that the local people coexist with the volcano since the volcano also provides them the blessings of hot spring spas, agricultural products and beautiful scenery and other things, along with the occasional disasters.



Group photo at Nishiyama crater

POST WORKSHOP LABORATORY TOUR:

Methane Hydrate Research Center, National Institute of Advanced Industrial Science and Technology (AIST), Hokkaido Center

The workshop was followed by a laboratory tour on 1st June of the Methane Hydrate Research Center (MHRC) of the National Institute of Advanced Industrial Science and Technology (AIST). MHRC was established in 2009 as a research laboratory for gas hydrate chemistry in AIST. MHRC has branches in Tsukuba and Sapporo, and consists of four research teams: “Production Technology Team,” “Reservoir Analyses Team,” “Reservoir Simulator Team,” and “Physical Property Analyses Team,” consisting of 18 research scientists and 33 technical staff. The goals of MHRC include securing a stable and long-term supply of natural gas, and boosting Japan’s energy self-sufficiency and the efficiency of natural gas utilization technologies. Toward these ends, MHRC conducts R&D on developing practicable natural gas production technologies from methane hydrate reservoirs, and establishing commercial infrastructure through the development of natural gas transportation and storage technologies which utilizes the specific physical properties of gas hydrates. MHRC is a member of the Research Consortium for Methane Hydrate Resources in Japan (MH21 Research Consortium), and plays a key organizational role in “Research Group for Production Method and Modeling.” This research group focuses on establishing economical and efficient production methods which MHRC supports through its ongoing research activities.

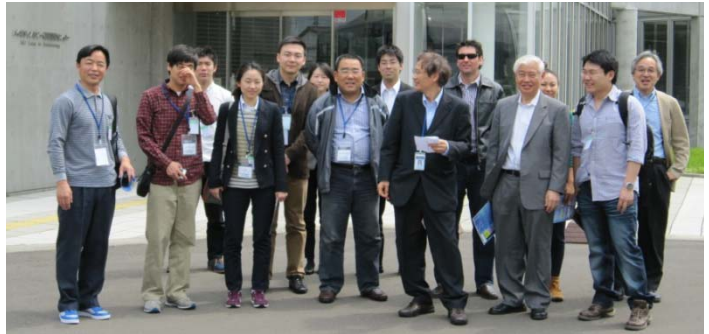
About 50 attendees visited the AIST Hokkaido Center on the morning of 1st June. Following the introduction of MHRC by its Director, Dr. Hideo Narita who was also the Chair of 2012 Fiery Ice, the members of MHRC showed the visitors the experimental facilities including a newly-installed large-scale experimental apparatus to simulate gas production processes from methane hydrate sandy sediment.



Introduction of MHRC by Dr. Narita



Snapshots during the laboratory tour



Group photos



A large-scale experimental apparatus to simulate gas production processes from methane hydrate sandy sediment

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