EXPERIMENTELLE SIMULATION VON METHANHYDRAT-EXTRAKTION UNTER HOCHDRUCKBEDINDUGEN

EXPERIMENTAL SIMULATION OF METHANE HYDRATE EXTRACTION UNDER HIGH PRESSURE CONDITIONS

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Abstract

Methane hydrate (MH) is a clathrate solid consisting of methane molecules enclosed in frozen water which is usually found in deep ocean floor at low temperature and high pressure. MH is currently considered as one of the most important future source of hydrocarbon fuel, being a more environmentally clean alternative to other fossil fuels. The low thermodynamic stability of MH, however, makes the exploitation of MH oceanic deposits a potential geohazard. Latest research reveals its possible implication for the formation of tsunamis and continental slope failures. Even though MH has been studied a lot over the last years, a lack of a rigorous study of transport phenomena involved on the physic-chemical and microbiological process taking place in natural ocean deposits is found. This is, however, of vital importance to ensure a safe and ecological extraction of MH.

To this end, we have installed at the FAU Busan campus (South Korea) a high pressure vessel which mimics the submarine conditions of MH on deep oceanic deposits. The vessel allows maximum pressures up to 150 bars, minimum temperatures of 3-4°C, and the seawater volumes of 475 liters. The design of this simulator includes 8 sapphire windows that ensure best optical accessibility and, thus, the use of non-invasive optical methods as Particle Image Velocimetry (PIV) or Digital Liquid Crystal Thermography among others.

We experimentally study how fluctuations in the environment, as for instance caused by changes in pressure, water temperature, flow velocity, sediment bed properties, salinity, or pH, affect the stability of MH inside the high pressure vessel. Besides, microbiological experiments with methanogenic microorganisms from waste water treatment plants have been carried out in order to check their adaptability to high pressure conditions. They demonstrated high level of survival under these special conditions.

Introduction

Methane hydrate (MH) is a clathrate solid consisting of methane molecules enclosed in frozen water which is usually found in deep ocean floor at low temperature and high pressure (Matsumoto *et al*., 2011). There is no bonding between frozen water and methane molecules: methane is free to rotate inside the frozen water cage and the stabilization resulting from methane molecule is supposed to be due to van der Waals forces (attraction forces between molecules) and hydrogen bonds (Khan, 2011). The deposits of this solid, similar to ice, is estimated to be more than 50% of all carbonaceous fuel reserves (Demirbas, 2010). Therefore, MH is currently considered as one of the most important future source of hydrocarbon fuel, being a more environmentally clean alternative to other fossil fuels.

The low thermodynamic stability of MH, however, makes the exploitation of MH oceanic deposits a potential geohazard (Bouriak *et al*., 2000, Paull *et al*., 2000). At normal temperature-pressure conditions (0°C and 1 atm), 1 m^3 of idealized MH dissociates to approximately 160 m^3 of methane (Ruppel, 2011). The release of large quantities of methane from deep oceans into the atmosphere has been suggested as a possible cause of global climate change (Kennett *et al*., 2000). Latest research also reveals its possible implication for the formation of tsunamis and continental slope failures (Kim *et al.*, 2013). Although MH has been studied a lot over the last years, a lack of a rigorous study of transport phenomena involved on the physic-chemical and microbiological process taking place in natural ocean deposits, is found in Literature. This is, however, of vital importance to ensure a safe and ecological extraction of MH.

South Korea has large MH deposits that can contribute decisively to reduce the available strong dependency from energy carrier import. Ulleung Basin Gas Hydrate expeditions in 2007 (UBGH 1) and 2011 (UBGH 2) corroborated the existence of MH deposits within a maximum saturation up to 90% (Lee *et al*., 2011). Therefore, South Korea has a strong national gas-hydrate program organized under the Korean Gas Hydrate Research and Development Organization (GHDO-K) and supported by the Ministry of Commerce, Industry and Energy in cooperation with industry partners as the Korean Gas Corporation (KOGAS) and the Korean National Oil Company (KNOC).

We have installed at the FAU Busan campus (South Korea) a high pressure vessel which mimics the submarine conditions of MH deep oceanic deposits. The vessel allows maximum pressures up to 150 bars, minimum temperatures of 3-4°C, and the seawater volumes of 475 liters. The design of this simulator includes 8 sapphire windows that ensure best optical accessibility and, thus, the use of non-invasive optical methods as Particle Image Velocimetry (PIV) or Digital Liquid Crystal Thermography among others.

We experimentally study how fluctuations in the environment, as for instance caused by changes in pressure, water temperature, flow velocity, sediment bed properties, salinity, or pH, affect the stability of MH inside the high pressure vessel. Besides, microbiological experiments with methanogenic microorganism from wastewater treatment plants have been carried out in order to check their adaptability to high pressure conditions. They demonstrated high level of survival under these special conditions.

Experimental set-up

The experiments are carried out using a high pressure vessel with a total volume of 475 L, which dimensions are described in Fig. 1a, connected to a 560 L tank coupled to a cooling system which is filled with salt water. The salt water is cooled up to 2 °C on the tank and injected into the high pressure vessel using a double diaphragm pump from Lutz Pumpen GmbH (P1 in Fig. 1b). The pressure vessel is covered with a 32 mm thickness insulation material from Armaflex$^{(R)}$. An extra coil system is coupled to the external housing of the vessel to ensure a constant temperature on the reactor. The design of the vessel offers 14 inlets/outlets for external currents and instrumentation. Three Type T thermocouples are connected to a National Instrument DAQ card. This permits us to monitorize the temperature in different localizations. We deposit glass beads with different diameters to characterize the sediment bed (Fig. 1d). Varying the particle size and the height of bed, we can control sediment bed properties such as the porosity.

First, MH is synthetized on a second small batch vessel made of stainless steel with a total volume of 93.4 cm^3. The vessel is filled with water and with a known amount of sediments with the same characteristics of the reactor. An AC 200 Thermostat from Thermoscientific(R) is used to control the temperature which is set to 1.5 °C. This is continuosly monitorized using a Type J thermocouple placed at the center of the vessel. We add high purity methange gas (99.90%) to achieve an initial pressure of 100 bar. Optimal conditions for MH nucleation around the bed of sedimets are therefore achieved inside the reactor. We indirectly measure the MH formation via Pressure drop on the vessel. A MH sample is then transferred to the high pressure reactor through one of the inlets situated on the top of the reactor after thermal equilibrium. The pressure is then increased on the reactor up to the corresponding value to achieve MH stability conditions on the reactor. For this purpose, we use a piston pump from the company Maximator GmbH (P2 in Fig. 1b). Pressure is kept constant with the help of a presicion piston pump provided for the same company (P3 in Fig. 1b).

The MH sample is illuminated and recorded by a 1600x1200 digital camera with a frame rate of 32 fps through one of the saphire glass (see.Fig 1c). A 532 nm Nd: Yag laser is used as a light source. We decrease the pressure to reach non-stability MH conditions and we study how therefore the MH structure vary with the help of an image processing algorithm (see Fig.2).

Besides, we study the adaptability of methanogenic microorganisms to a high pressure condition of 200 bar at different temperatures of 10 - 35 °C. First, mixed culture of methanogenic archae were taken from a methanogenic fixed bed reactor, the second stage of an anaerobic digestion process, and fed with artificial waste water. The culture were then incubated for 2 weeks in a mini reactor, flushed with nitrogen gas to maintain anaerobic conditions and filled with a methanogenic enrichment media to guarantee the survival of a methanogenic archae. A pressure of 200 bar was applied inside the high pressure vessel for 30 minutes for every experiment for different temperatures and pressure ramps of 50 and 100 bar/min. After applying the pressure, the methanogenic microorganisms were cultivated in a petri dish, wrapped to maintain anaerobic conditions. We developed an imaging processing algorithm to count the number of colonies formed after 3 days of incubation.

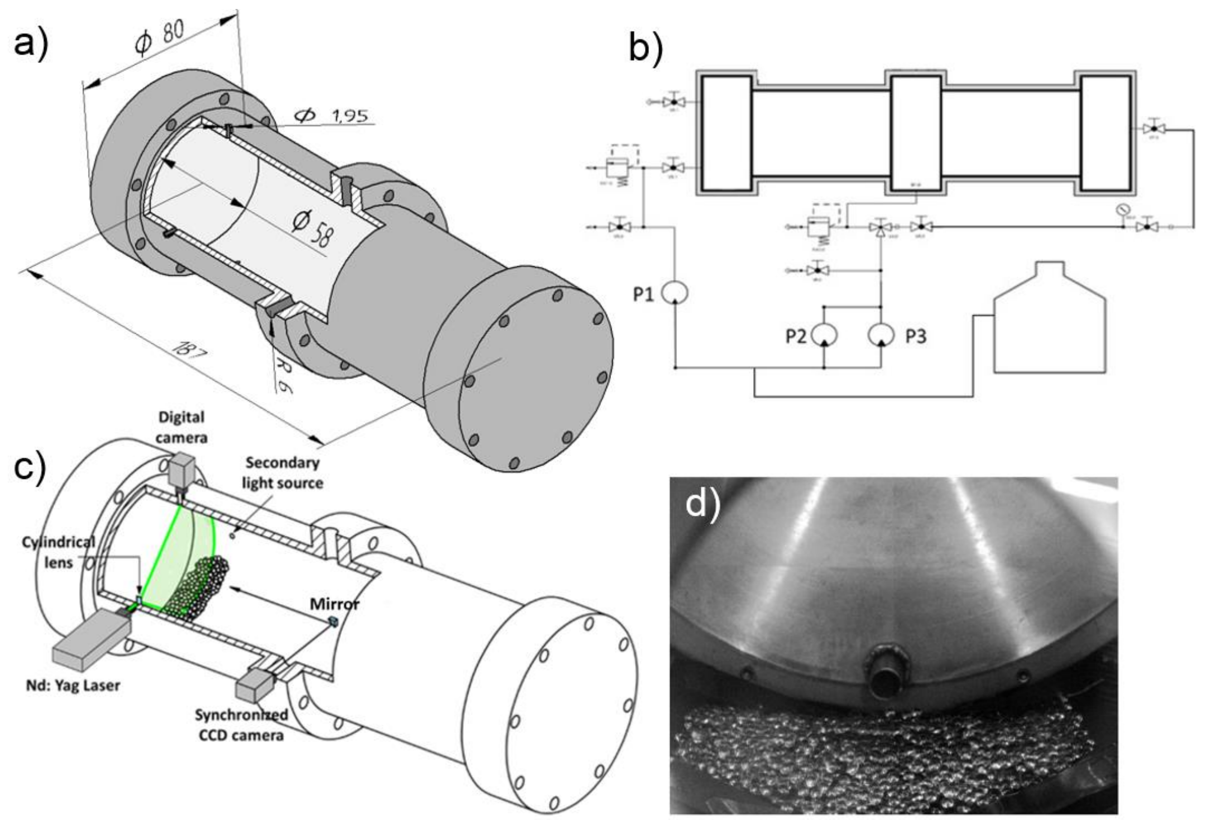

Fig. 1: High pressure reactor dimensions in cm (a). System diagram of the high pressure vessel and the cooling tank (b). Sketch of the optical system (c). Picture of the sediment bed taken from inside the reactor (d).

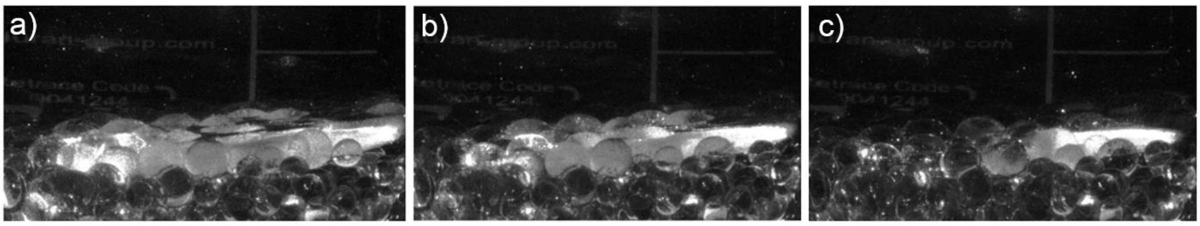

Fig. 2: From left to right, evolution of the ice-like solid structure exposed to non-stability conditions. The structure is illuminated and tracked according to the experimental set-up described in Fig. 1c.

Experimental results and discussion

We synthesized methane hydrate in the small high pressure vessel with cooling system. Figure 3a shows methane pressure and consumption with the time. Initial pressure and temperature were kept constant at 1.5 °C and 100 bar, respectively, until 54 h.
After 54 h, the decrease in pressure and the sudden increase in temperature were observed (Fig.3). This corresponds to a nucleation of methane hydrate since it is an exothermic reaction. The sudden increase in temperature was again observed at 57 h. However, at 70 h, the pressure became constant. We observed a total MH consumption of about 0.025 moles. This corresponds to a 9.05% of methane gas converted to hydrate (Fig. 4).

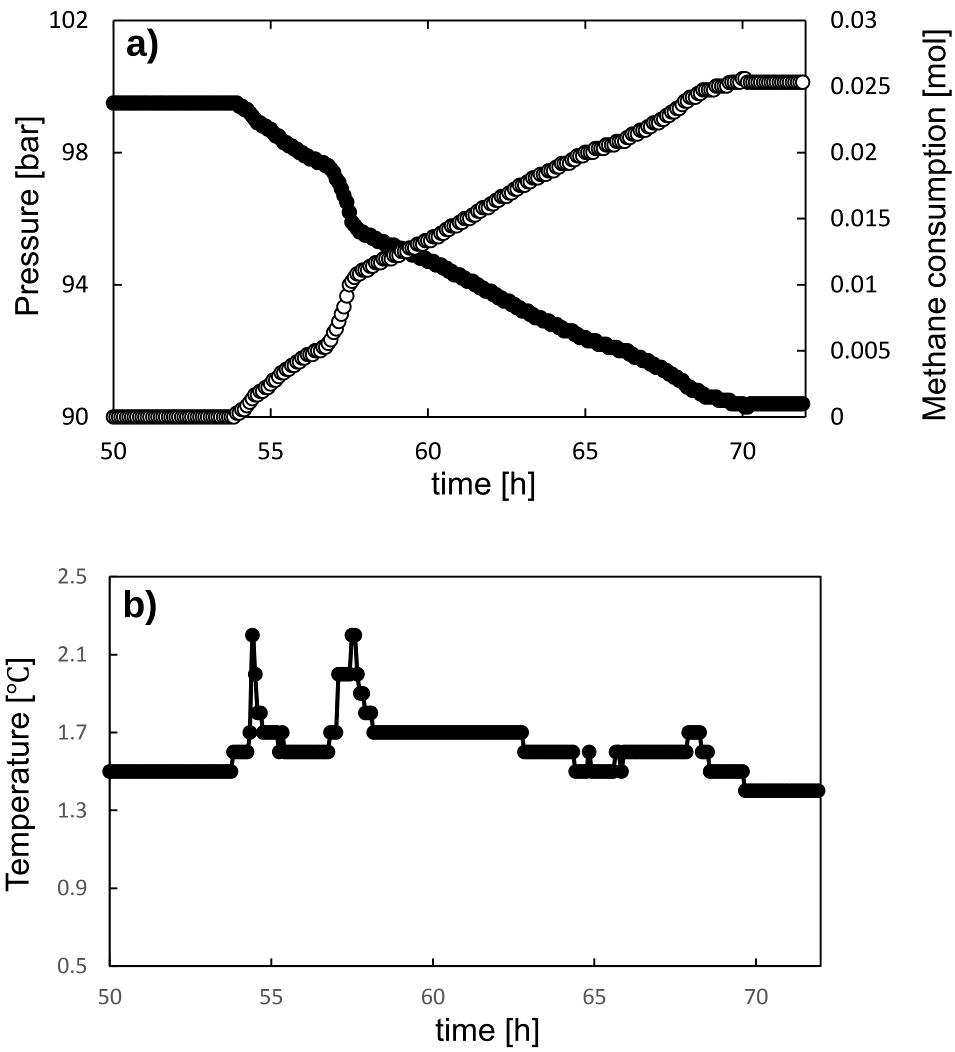

Fig. 3: Pressure drop and the corresponding Methane molar consumption (a) and Temperature (b) as a function of time on the pressure vessel. Solid and open symbols in (a): Pressure and Methane molar consumption, respectively. Solid symbols in (b): Temperature. The sediment bed consisted of glass beads with diameters of 7 and 10 mm, respectively.

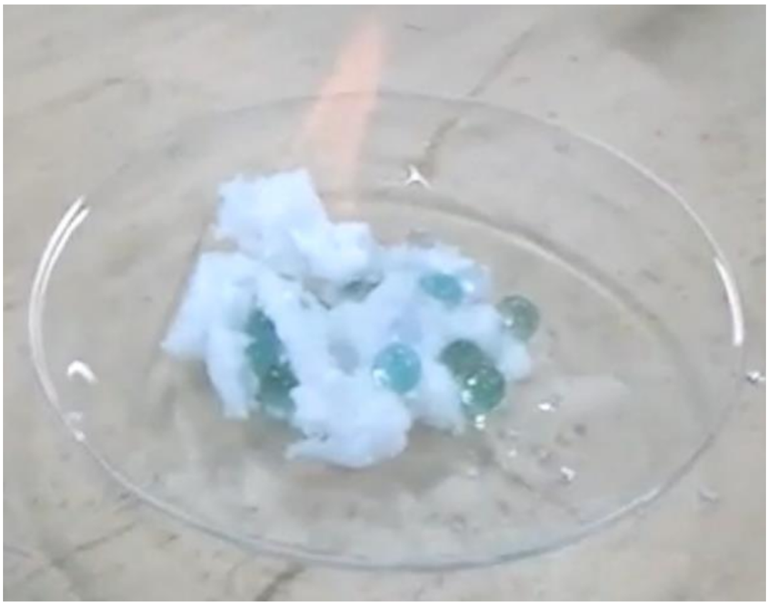

Fig. 4: A burning sample of synthesized methane hydrate.

We find the adaptability of methanogenic microorganisms to the high pressure condition at different temperatures. At the initial trial, mixed culture of acetogenic bacteria and methanogenic archae showed better adaptation at higher temperature ranges (Fig. 5). However, after repeated trials with survived culture of acetogenic and methanogenic organisms, an improved adaptation was shown in the lower temperature ranges of 10 °C and 15 °C (Fig. 5). This opens up a possibility to synthesize methane hydrate biologically since in nature, the condition of the methane hydrate formation is below 18 °C at 200 bars.

In contrast, we find the single strain of *Methanosarcina mazei* did not survive the high pressure condition. This suggests a symbiotic interaction between the methanogenic archae and the acetogenic bacteria for better survival at high pressure conditions.

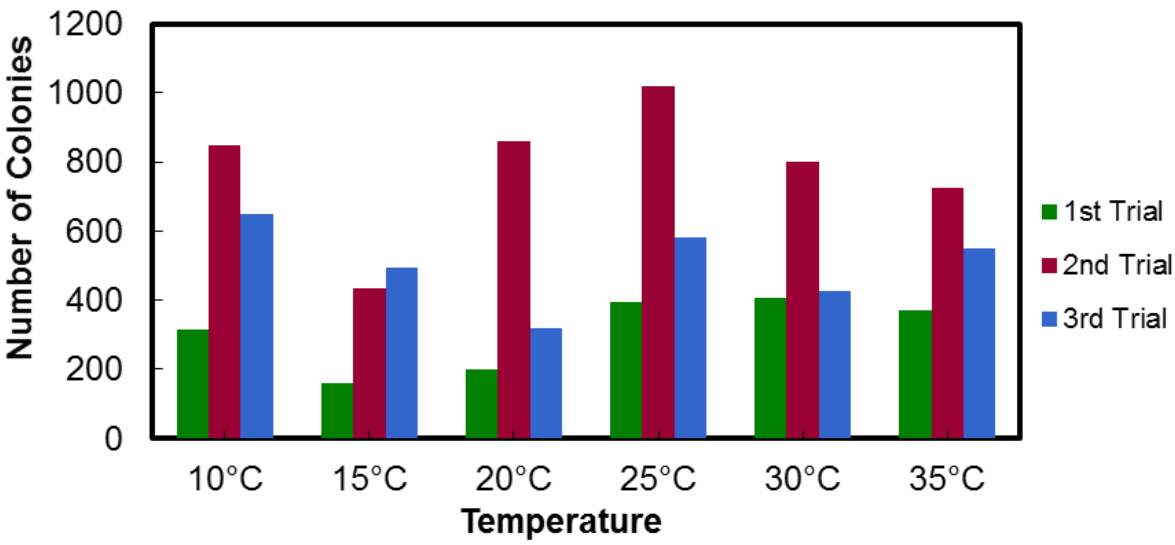

Fig. 5: Adaptation of methanogenic microorganisms to high pressure condition of 200 bar at different temperatures of 10-35 *°C* for the pressure ramp at 50 bar/min.

Summary

We study how fluctuations in the environment, such as pressure, water temperature, flow velocity or sediment bed properties, affect the stability of methane hydrate. For this purpose, we first synthesized methane hydrate in a 93.4 cm^3 pressure vessel. The MH samples are then introduced in a 475 L pressure reactor in which MH stability conditions are well controlled. We use non-invasive methods to experimentally study how changes on that stability conditions affect the MH structure.
Besides, we find the adaptability of methanogenic microorganisms to the high pressure condition at different temperatures. Mixed culture of acetogenic bacteria and methanogenic archae showed better adaptation at lower temperature ranges after repeated trials with survived culture of acetogenic and methanogenic organisms. This opens up a possibility to synthesize methane hydrate biologically. In contrast, we find the single strain of *Methanosarcina mazei* did not survive the high pressure condition. This suggests a symbiotic interaction between the methanogenic archae and the acetogenic bacteria for better survival at high pressure conditions.

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