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METHANHYDRAT-EXTRAKTION UNTER HOCHDRUCKBEDINDUGEN (PIV MESSUNGEN)

METHANE HYDRATE EXTRACTION UNDER HIGH PRESSURE CONDITIONS (PIV MEASUREMENTS)

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Abstract

Methane Hydrate (MH) is currently considered as one of the most important potential source for hydrocarbon fuel. This ice-like crystalline solid represents more than 50% of estimated carbonaceous fuel reserves, being a clean alternative to other fossil fuels. The low thermodynamic stability of MH, however, makes the exploitation of MH deposits a potential geohazard. The study of transport phenomena involved on the physical-chemical and microbiological processes taking place in natural ocean deposits is thus of vital importance to ensure a safe and ecological extraction of MH.
We have installed at the university campus of FAU Busan (Korea) a high pressure vessel (Deep Sea Simulator), which mimics the submarine conditions of MH deep oceanic deposits. The simulator includes 8 sapphire windows for using non-invasive optical methods. We experimentally study how fluctuations of water temperature, pressure conditions or flow velocity in the environment affect the thermodynamic MH stability. For this purpose, MH samples are illuminated with a 532 nm Nd: Yag laser and recorded by a 1600x1200 digital camera to characterize their structure response and stability under changes on the environment. First, PIV measurements are carried out to characterize the flow velocity profile inside the simulator during the pressurization and depressurization phases.
Besides, we studied the impact of geometrical properties of the porous sediment bed in MH nucleation. MH is synthesized in a 100 cm^3 batch vessel using regular substrates made of spherical beads with different diameters. The study of MH nucleation is complemented using a pore-size high pressure vessel specially designed for microscopic observation.

Introduction

Methane hydrates (MH) are crystalline solids in which methane molecules are confined in water at low temperatures and high pressures (Demirbas 2010). Water and methane molecules are not bonded inside the frozen cage in which methane is free to rotate. Methane gas is thermodynamically stabilized within the hydrate by interactions with the crystalline lattice

of water molecules due to van der Waals forces (attraction forces between molecules) and hydrogen bonds (Khan, 2011).
Huge reserves of hydrates can be found in deep ocean floors and on land under permafrost; the quantity of organic carbon in gas hydrates is estimated to be twice than that in all other fossil fuel sources combined (Hacisalihoglu *et al.* 2008). Furthermore, methane hydrates contain highly concentrated methane; 1 m³ of methane hydrate dissociates to approximately 160 – 170 m³ of methane at normal conditions (Kvenvolden 1993, Ruppel, 2011). Direct combustion of methane provides high energy density per weight, but also contributes to minimum emission of CO_2 as by-product, e.g. 30 times less than gasoline and 60 times less than coal (Sloan 1997). For all these reasons, MH is currently considered as one of the most important future source of hydrocarbon fuel (Max *et al.* 2006). Besides, the high energy density of MH and its stability at higher temperature as compared to Liquefied Natural Gas (LNG) makes MH as a potential greener method for energy transportation.
On the other hand, MH is very sensitive to its environment. Fluctuations in pressure, temperature, salinity, degree of gas saturation or sediment bed properties may cause methane gas release from the water lattice. As methane is a very strong greenhouse gas, exploitation of MH oceanic deposits are considered a potential geo-hazard (Bouriak *et al*., 2000, Paull *et al*., 2000, Reagan and Moridis 2008). Release of large quantities of methane from deep oceans into the atmosphere is supposed to be a possible cause of global climate change in past eras (Kennett *et al*., 2000). Latest research also reveals its possible implication for the formation of tsunamis and continental slope failures (Kim *et al.*, 2013).
During the last decades, several extraction methods have been suggested for the recovery of natural gas from the hydrate (see for instance Max *et al.* 2006). An exhaustive study of MH stability response to both natural and anthropogenic dynamic process is still needed to ensure a safe and ecological extraction of MH. For this purpose, we have designed a high pressure vessel (Deep Sea Simulator), which mimics the submarine conditions of MH deep oceanic deposits. The vessel is able to achieve the maximum pressure of 150 bars, keeping the temperature of about 475 L of seawater constant at 3-4°C. The design of this simulator includes 8 sapphire windows, which ensure optical accessibility. Thus, non-invasive optical methods such as Particle Image Velocimetry (PIV) or Digital Liquid Crystal Thermography can be used among others.
The main aim of the present research project is to 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, we studied the impact of geometrical properties of the porous sediment bed in MH nucleation. The formation and disassociation of MH within the porous sediment bed is of vital importance to approach the real phenomena occurring in Mother Nature (Kono et al. 2002, Walsh *et al.* 2009, Jung and Santamarina 2010). However, the study of hydrate formation in regular structures has been not considered until now. MH is synthesized in a batch vessel made of stainless steel with a total volume of 100 cm^3. The vessel is filled with water and with a known amount of sediments regularly arranged sediments in triangular and quadratic configurations. Optimal conditions for MH nucleation around the bed of sediments are achieved inside the vessel. We measure the MH formation indirectly via pressure decrease inside the vessel. Furthermore, MH nucleation inside sediment pores is studied using another high pressure vessel, specially designed for microscopic observation through two sapphire glass windows which permit the use of non-invasive methods. This high pressure vessel is made of steel and designed for pressures up to 3000 bar.

Experimental set-up

Deep sea simulator

The deep sea simulator consists of a high pressure vessel with a total volume of 475 L, connected to a 560 L tank, which is filled with salt water, coupled to a cooling system. Dimensions of the deep sea simulator are described in Fig. 1b. Fig. 1d depicts the complete set-up. The salt water is cooled up to 2 °C in the tank and injected into the high pressure vessel using a double diaphragm pump from Lutz Pumpen GmbH (P1 in Fig. 1d). The pressure vessel is covered with a 32 mm thickness insulation material from Armaflex®. An extra coil system, connected to a thermostat, is coupled to the external housing of the vessel to ensure a constant temperature in the vessel (see Figure 1c). 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 for monitoring the temperature in different localizations. A piston pump from Maximator GmbH permits to achieve the maximum pressure of 150 bar (P2 in Fig. 1d). Pressure is kept constant with the help of a precision piston pump provided from the same company (P3 in Fig. 1d).

PIV measurements are performed to characterize the flow velocity profile inside the vessel during pressurization and depressurization phases. For this purpose, a 532 nm double pulse Nd: Yag laser from EverGreen® is used to illuminate silver coated hollow glass tracers of 10 µm diameter. The light scattered by the tracers is recorded with a 2MP CCD camera coupled to a 50 mm lens. Camera and laser pulse are synchronized by a programmable master timing control unit from TSI®. Data acquisition and post processing are performed with the software Insight 4G™. Given the low flow velocity inside the vessel, the time delay between illumination pulses was selected to be 60 ms. Two different experimental arrangements are set up to characterize the instantaneous velocity field in the horizontal and vertical plane, respectively. Fig. 2 illustrates both PIV arrangements. In both configurations, a cylindrical lens placed inside the vessel is used to generate the laser sheet with the appropriate thickness. A tilted mirror is used for the vertical plane PIV measurements (see Fig. 2b). The observation area inside the vessel is a circular area of 60 mm diameter for measurements taken from the top view, and a rectangular area of about 50 x 40 mm for measurements taken from the side. The area of interest corresponds to the sediment bed emplacement in which MH is expected to be placed.

Methane-Hydrate nucleation on regular substrates

MH is synthesized in a small batch vessel made of stainless steel with a total volume of 93.4 cm^3. The vessel is filled with distilled water and with a known amount of regularly arranged sediments and fixed according to triangular and quadratic configurations. The regular sediment beds are built from spherical soda-lime glass beads of 2, 5 and 7 mm diameter, respectively. An AC 200 Thermostat from Thermoscientific® is used to control the temperature which is set to 0.5, 1.5 and 3°C, respectively. The temperature is continuously monitored using a Type J thermocouple placed in the center of the vessel. We add high purity methane gas (99.90%) to achieve an initial pressure of 100 bar. The kinetics of methane hydrate generation is indirectly measured by pressure decrease inside the vessel. Fig. 3 describes the set-up for the MH generation.

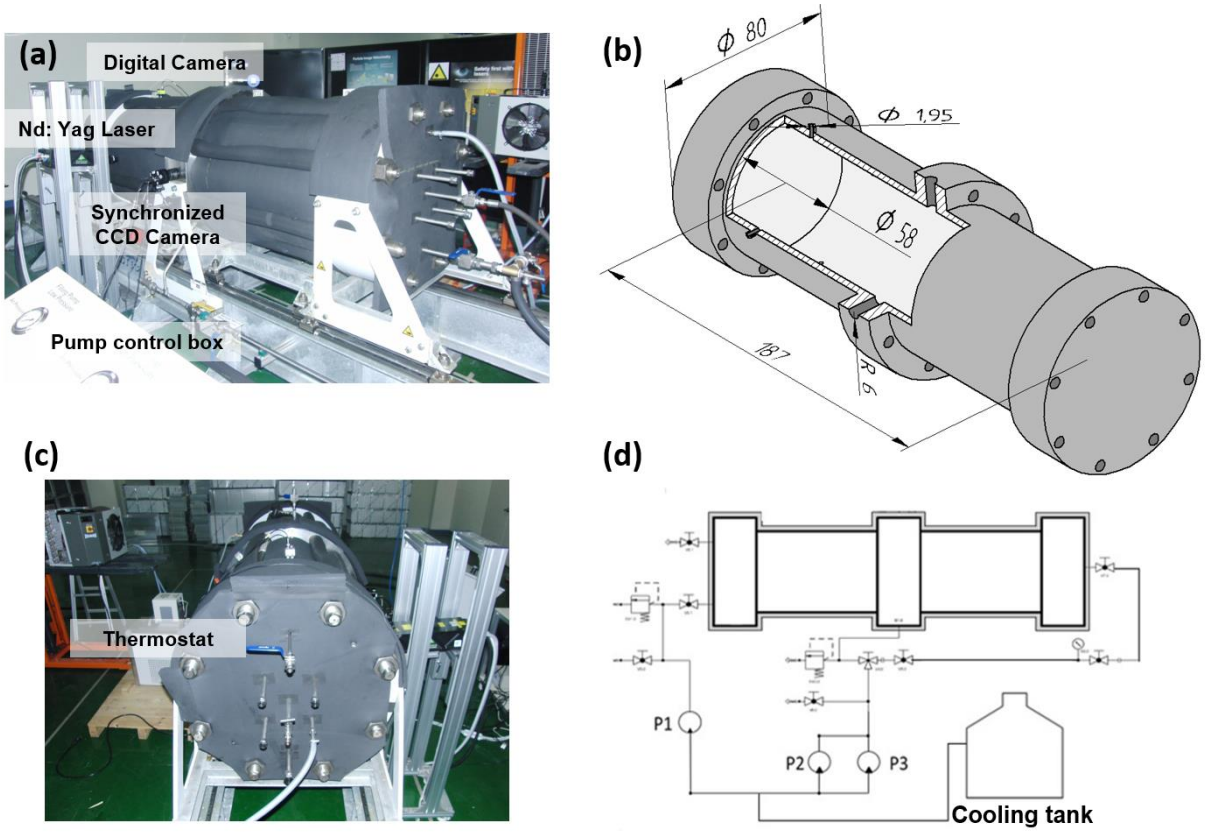

Fig. 1: Deep sea simulator together with the PIV system (a)-(c). High pressure vessel dimensions in cm (b). System diagram of the high pressure vessel and the cooling tank (d).

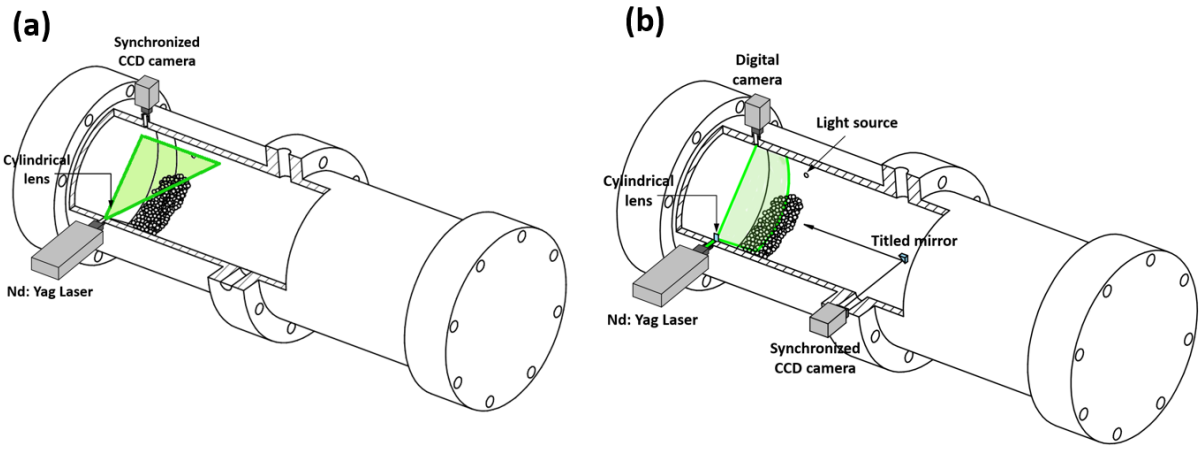

Fig. 2: Experimental arrangement for particle image velocimetry in the deep sea simulator for measuring the flow velocity from the top (a) and from the side view (b), respectively.

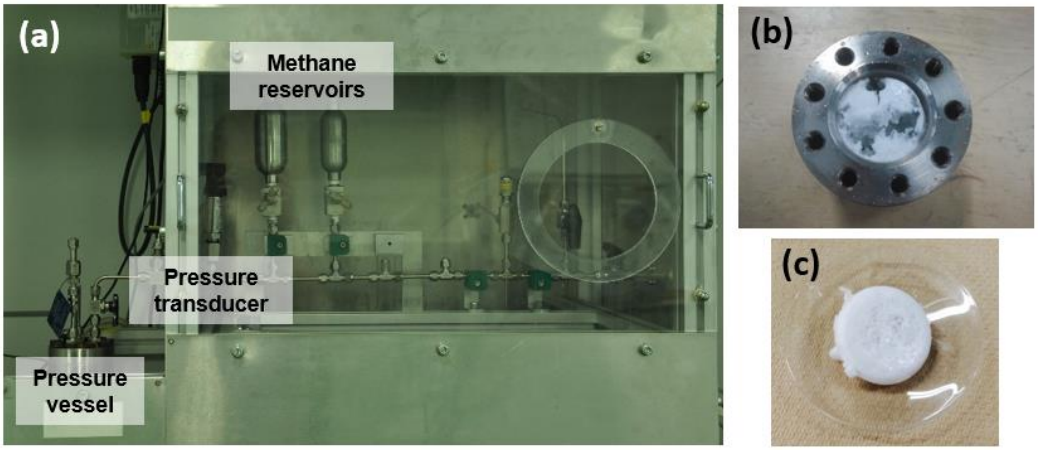

Fig. 3: Experimental equipment for synthesis and disassociation of MH (a). MH samples synthesized at FAU Busan (b)-(c).

Experimental results and discussion

We characterize the flow velocity profile in the region of interest, i.e. where the MH is located inside the high pressure vessel during pressurization and depressurization phases. Note that the main purpose of the present work is to study how fluctuations on a single variable, e.g. pressure or temperature, affect the stability of MH. Quantifying the flow velocity is thus important to ensure that stability of MH samples is not affected by non-desired currents arising from increasing or decreasing the pressure inside the vessel. Similarly, convection currents are expected inside the vessel during internal cooling process since the temperature close to the wall remains slightly lower than in the bulk of water (i.e. in the center of the vessel). PIV measurements taken from the top, and from the side of the vessel according to configurations a) and b) in Fig. 2, respectively, show how the flow velocity is barely affected by convection currents in our region of interest.

Fig. 4 depicts the vector map of instantaneous velocity field from the top view (configuration a) in Fig.2) during a sudden increase of pressure from 10 bar to 100 bar in around 60 seconds. The pressure is increased by pumping water through the middle inlet of the vessel. The initial flow velocity before starting the pressurization remains close to zero, showing a quasi-stationary flow regime slightly perturbed by convection currents (not shown in Figure). The instantaneous velocity in the horizontal plane barely changes during the interval of about 60 seconds of injection phase. Immediately after the desired pressure is achieved in the vessel and P2 is stopped injecting water to the system, a flow recirculation in the horizontal plane is observed. The maximum instantaneous velocity achieves a value of around 7 mm/s (see Fig. 4b) and decreases up to levels of around 2 mm/s after a few seconds (see Fig. 4c).

Figure 5 depicts the vector map of instantaneous velocity field from the side view (configuration b) in Fig. 2). In the vertical plane, we observed an upward flow with a constant velocity of around 0.5 mm/s during the water injection phase (see Figure 5a). After final pressure is achieved in the vessel, the flow recirculation is clearly identified from the side view. Fig. 5b shows for instance the flow velocity field after 2 min of achieving the final pressure in the vessel. Fig. 5c and d show the velocity profile after 5 and 20 min after achieving 100 bar in the vessel, respectively. After around 20 min, the flow velocity profile achieves a stationary regime, showing about the same velocity module as before starting pressurization on the system.

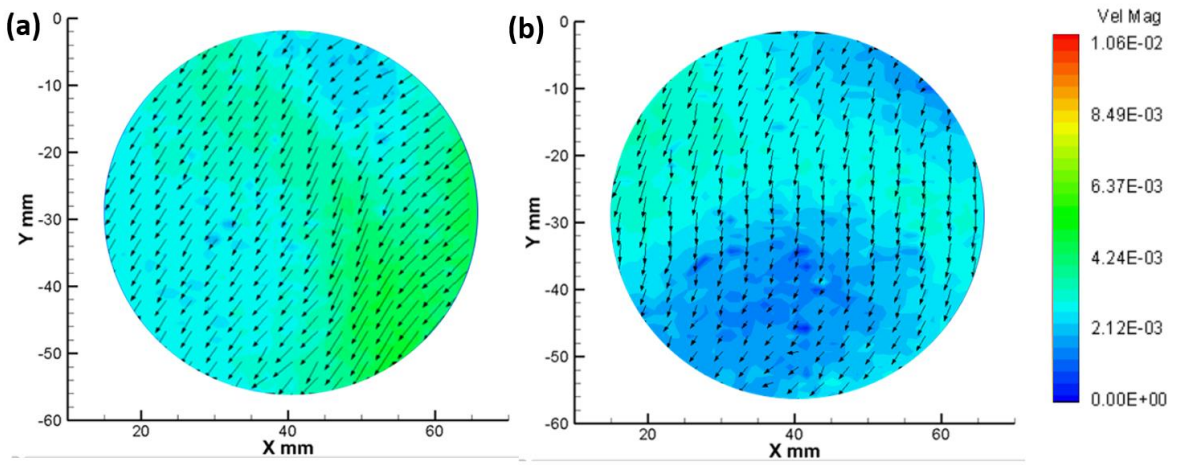

Fig. 4: Vector map of instantaneous velocity field on the horizontal plane after a sudden increase of pressure from 10 to 100 bar in about 60 s. Time resolved PIV measurements immediately after final pressure was achieved (a) and about 5 s after final pressure was achieved (b).

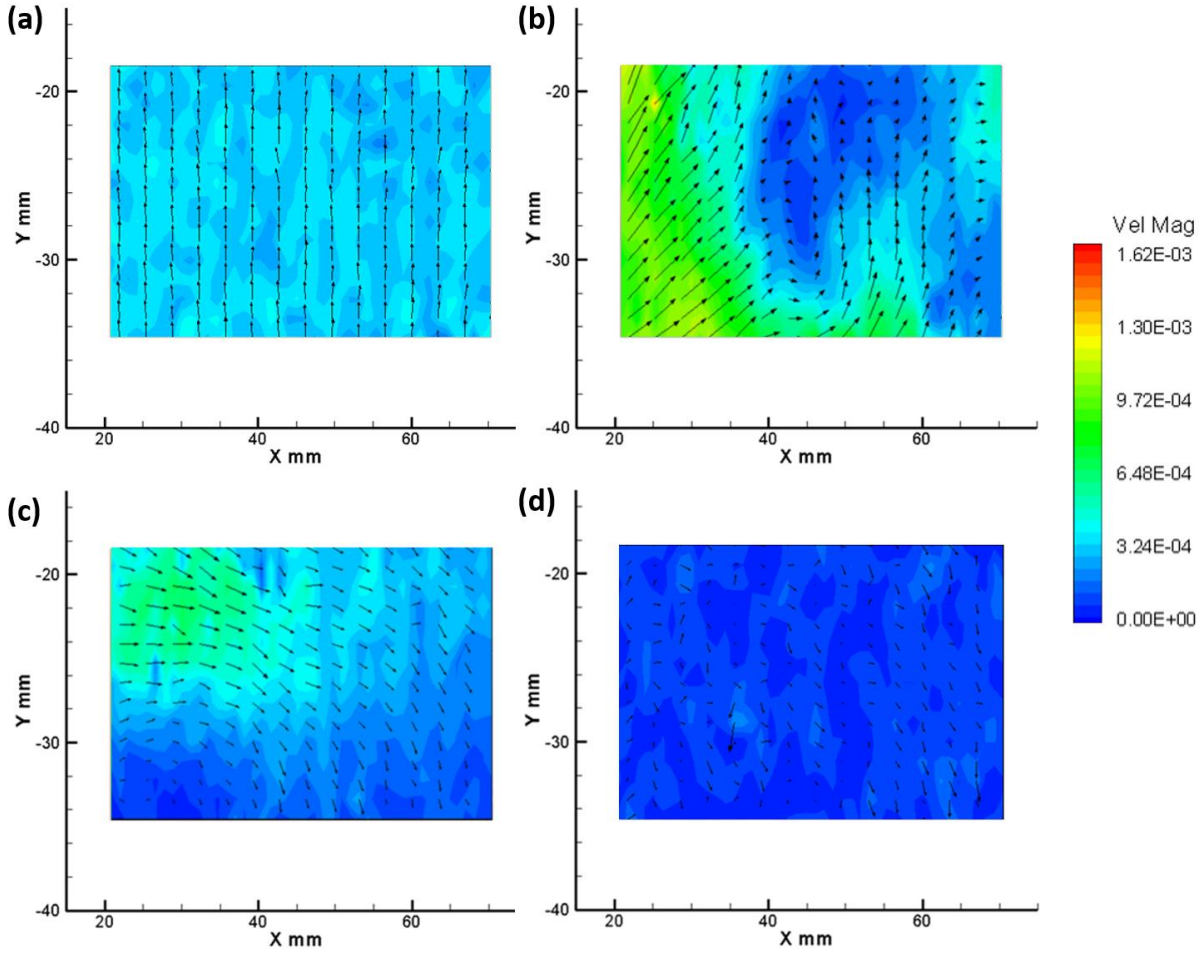

Fig. 5: Vector map of instantaneous velocity field on the vertical plane after a sudden increase of pressure from 10 to 100 bar in about 60 s. Time resolved PIV measurements during water injection phase (a), after 2 min of final pressure was achieved (b), after 5 min of final pressure was achieved (c), and after 20 min of final pressure was achieved (d).

Finally, Fig. 6 shows the vector map of instantaneous velocity field in the horizontal plane (configuration a) in Fig. 2) during a sudden depressurization in the vessel from 100 bar to 10 bar in about 30 s. The decrease in pressure is achieved by opening a valve placed exactly in the middle of the vessel. A right to left flow through the open valve is observed. The maximum velocity module of around 6 mm/s is measured at about 0.18 s after opening the valve (see Fig. 6a). The stationary velocity profile in the horizontal plane is achieved immediately after closing the valve (see Fig. 6b).

Fig. 7 depicts the results obtained in the vertical plane for PIV measurements taken from the side for a depressurization at similar conditions. The flow velocity field is in good agreement with the previously measured ones on the horizontal plane. At about 0.18 s after opening the valve, an inward flow through the open valve is identified with maximum the velocity of around 0.7 mm/s (see Fig. 7a). Immediately after closing the valve, we reached a stationary regime inside the vessel (see Fig. 7b).

Note that the valve is placed in the same horizontal plane as our region of interest and the flow velocity magnitude is therefore expected to be maximum. If we decrease the pressure by opening the valve placed on the top of the vessel, the maximum module of velocity strongly reduces down to values of about 0.5 mm/s. We remark that no significant changes in temperature are observed during pressurization and depressurization phases.

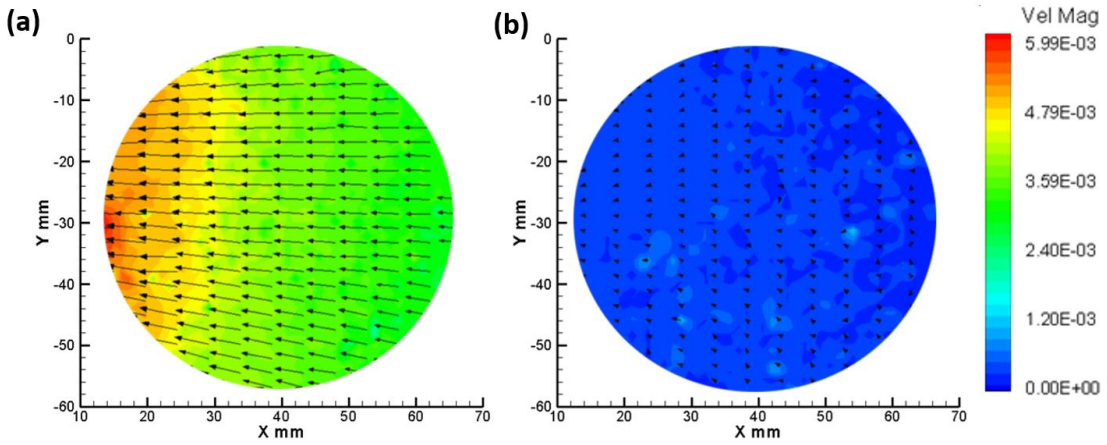

Fig. 6: Vector map of instantaneous velocity field on the horizontal plane after a sudden decrease of pressure from 100 to 10 bar in about 30 s. Time resolved PIV measurements at 0.18 s after opening the valve (a) and about 1.4 s after final pressure was achieved (b).

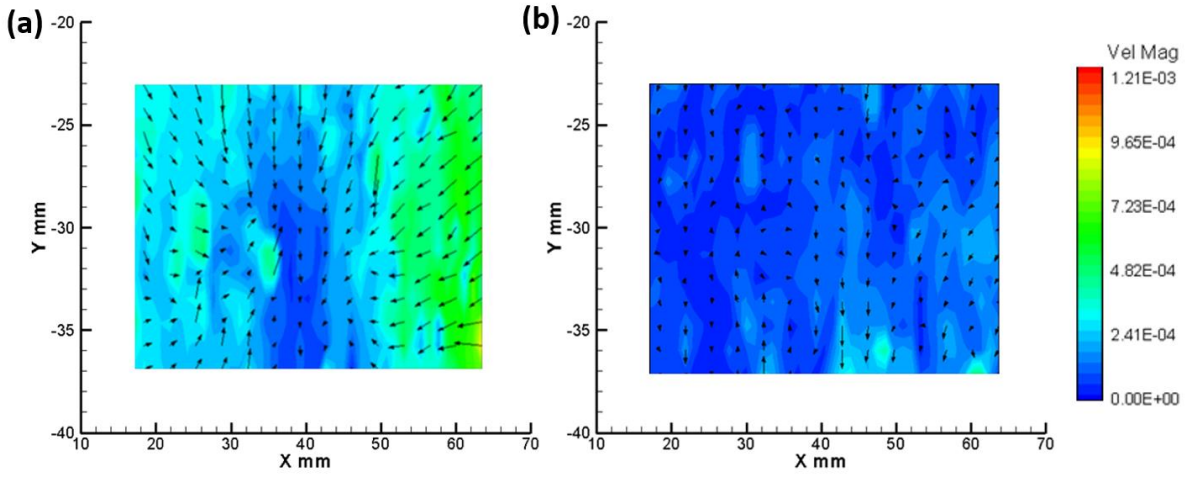

Fig. 7: Vector map of instantaneous velocity field on the vertical plane after a sudden decrease of pressure from 100 to 10 bar in about 30 s. Time resolved PIV measurements at 0.18 s after opening the valve (a) and about 1.4 s after final pressure was achieved (b).

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. To focus on a single variable, we have first quantified the flow velocity field inside the high pressure vessel (Deep Sea Simulator) during cooling process and under sudden changes in pressure. Even though convection current can be expected due to the gradient of temperature between the wall and the bulk of water, flow velocity approaching zero have been measured in our region of interest. During a sudden increase in pressure of about 90 bar in around 60 s, we have identified a flow recirculation with maximum velocity of about 7 mm/s, which is reduced to 2 mm/s after a few seconds of having achieved the maximum pressure. We have observed a stationary velocity profile after 20 min of the pressure increase. A right to left flow in direction to the open valve with maximum module of about 6 mm/s have been measured if we decrease the pressure from 100 to 10 bar in about 30 s. This is achieved by opening a valve situated in the same horizontal plane as our area of interest. A flow velocity approaching zero is observed, however, immediately after closing the valve. No significant changes in temperature are recorded during increasing and decreasing the pressure. The experiments here performed correspond to extreme fluctuations in pressure, i.e. most unfavourable cases to change from MH thermodynamic stability conditions to unstable conditions. Even though, we have identified that the velocity profile inside the vessel becomes stationary just a few seconds after the sudden decrease in the pressure. Similarly, the temperature in the system barely decreases. We can therefore conclude that pressure was the only variable affecting MH stability in our experiments. This fact is also important to quantify methane gas release through indirect measurement of velocity flow profile fluctuation in the vessel in future experiments. Note that in that case, since the velocity is almost stationary inside the vessel, any alteration in the velocity field is identified to be the release of methane gas from the solid hydrate. We remark that preliminary experiments introducing MH samples in the vessel indeed show satisfactory results to qualitatively measure if methane gas releases from the cage under pressure fluctuations.

References

Bouriak, S., Vanneste, M., Saoutkine, A., 2000: “Inferred gas hydrates and clay diapirs near the Storegga slide on the southern edge of the Vøring plateau, offshore Norway”, Mar. Geol., 163, 125-148

Demirbas, A., 2010; “Methane gas hydrate”, London: Springer.

Hacisalihoglu B, Demirbas AH, Hacisalihoglu S., 2008: Hydrogen from gas hydrate and hydrogen sulfide in the Black sea. Energy Educ. Sci. Technol., 21, pp. 109-115.

Kennett, J.P., Cannariato, K.G., Hendy, I.L., Behl, R.J. “Carbon isotopic evidence for methane hydrate instability during quaternary interstadials”, Science, 288, pp. 128-133

Khan, M.R., 2011: “Advances in clean hydrocarbon fuel processing: Science and technology”, Cambridge: Woodhead Publishing Limited

Kim, Y.G., Lee, S.M., Jin, Y.K., Branov, B., Obzhirov, A., Salomatin, A., Shoji, H., 2013: “The stability of gas hydrate field in the northeastern continental slope of Sakhalin Island, Sea of Okhotsk, as inferred from analysis of heat flow data and its implications for slope failures’, Mar. Petrol. Geol., 45, pp.198-207

Kvenvolden, K. A., 1993: Gas Hydrate- Geological perspective and flobal change. Reviews of Geophysics, 31, pp. 173-187.

Max, D. M., Johnson H. A., and Dillom V. P. 2006: “Economic Geology of Natura Gas Hydrate”, Dordrecht: Springer.

Paull, C.K., Ussler III, W., Dillon, W.P., 2000: “Potential role of gas hydrate decomposition in generating submarine slope failures”, In M.D. Max (Ed.), Natural gas hydrate in Oceanic and permafrost environments (pp. 146-156), Dordrecht: Kluwer Academic Publishers

Ruppel, C., 2011: “Methane hydrates and the future of natural gas”, MITEI Natural Gas Report, Supplementary Paper on Methane Hydrates No.4.