

Magnetic Resonance Imaging of Gas Hydrate Formation and Conversion at Sub-Sea-floor Conditions

Elke Kossel, Christian Deusner, Nikolaus Bigalke, Matthias Haeckel

GEOMAR Helmholtz Centre for Ocean Research Kiel, Germany

Corresponding author: Elke Kossel, GEOMAR Helmholtz Centre for Ocean Research Kiel, Wischhofstr. 1-3, 24148 Kiel, Germany, E-Mail: ekossel@geomar.de

Abstract

The production of natural gas from sub-sea-floor gas hydrates is one possible strategy to meet the world's growing demand for energy. On the other hand, climate warming scenarios call for the substitution of fossil energy resources by sustainable energy concepts. Burning natural gas from gas hydrates could be emission neutral if it was combined with a safe storage of the emitted CO₂. Laboratory experiments, that address corresponding strategies, need to be performed under high pressures and low temperatures to meet the thermodynamic conditions of the sub-sea-floor environment. In this paper, we present a high-pressure flow-through sample cell that is suitable for nuclear magnetic resonance (NMR) experiments at realistic marine environmental conditions, i.e. pressures up to 15 MPa and temperatures from 5 to 20 °C, and we demonstrate its suitability in applied gas hydrate research.

Keywords

NMR, MRI, gas hydrates, high pressure, instrumentation

1. Introduction

Gas hydrates are ice-like crystalline compounds that form at high pressures and low temperatures. Natural gas hydrates in sub-sea-floor sediments and in permafrost soil contain vast amounts of natural gas, which is predominantly composed of methane. Estimates of the amount of natural gas, that is stored in marine gas hydrates, range from 500 to 74,400 gigatonnes of carbon [1-5]. Even the more conservative numbers are significantly higher than the total estimated economically exploitable resources for coal, oil and conventional natural gas. Consequently, world-wide research efforts are on the way to develop gas hydrates as an energy resource, e.g. in Japan [6], the US [7], South Korea [8], India [9].

A promising concept for an environmentally sustainable production technology is the injection of carbon dioxide into methane hydrate bearing sediment layers. The CO₂ activates the release of natural gas by replacing it as guest molecule in the hydrate structure [10-12]. Consequently, it is retained in the reservoir as immobile CO₂-hydrate. In this way, natural gas

production can be combined with carbon capture and storage to an emission-neutral energy production strategy.

2. Methods and Materials

2.1. The High-Pressure Flow-Through Reactor System NESSI

The development and characterization of gas hydrate production strategies requires conducting laboratory experiments at thermodynamic conditions that match those of the sub-seafloor gas hydrate deposits. Within the German national gas hydrate initiative SUGAR [13], we have constructed the high pressure flow-through reactor system NESSI (Natural Environment Simulator for Sub-seafloor Interactions). With pressures up to 40 MPa and temperatures ranging from 0-60 °C, it is capable of simulating sub-marine environments. The core elements of NESSI are various pressure- and temperature-controlled sample cells: a 2000 ml pressure vessel made of stainless steel for pressures up to 35 MPa and temperatures from 0-60 °C, a 2000 ml pressure vessel made of fiberglass for pressures up to 15 MPa and temperatures from 0-60 °C and a 15 ml pressure vessel made of sapphire for pressures up to 15 MPa and temperatures from 5-20 °C. The vessels can be operated in flow-through mode. Feed fluids include water with controlled amounts of dissolved gases and salts as well as CO₂ in gaseous, liquid or supercritical state and CH₄ gas. The inflow and outflow of the sample cell is equipped with sensors for monitoring of temperature, pressure, salinity and concentrations of dissolved CO₂ and CH₄. Additional Raman sensors can be used for a more detailed surveillance of the effluent fluid composition and subsamples of the fluids can be taken for further analyses. Fig. 1 shows a flow chart of the basic experimental set-up with NESSI.

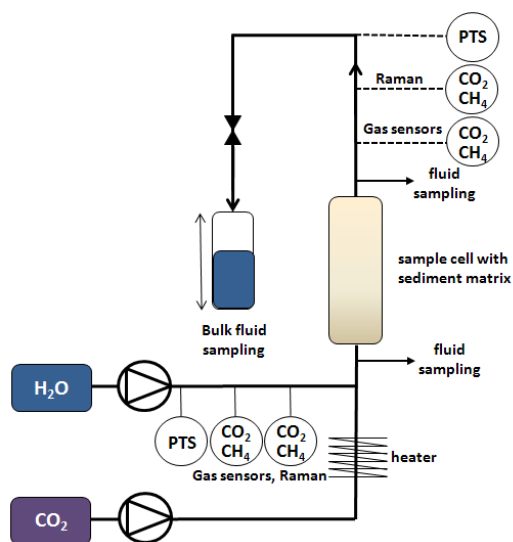


Fig. 1: NESSI flow chart: depicted are the feed lines for water and CO₂ and the positioning of the different sensor types. The CO₂ feed can be replaced by a CH₄ gas supply. Most sensors cannot be used with the 15 ml sample cell due to their comparatively large interior volume.

2.2. A Pressure and Temperature controlled Sample Cell for NMR Microimaging

The sapphire sample cell is specifically designed for NMR microimaging experiments. It consists of a pressure-resistant sapphire tube, polyether ether ketone (PEEK) end-caps and a PEEK cooling jacket (Fig. 2). The sapphire tube has an outer diameter of 19 mm, an inner diameter of 12 mm and a length of 165 mm. Temperature control of the sample is maintained by a counter current pressurized air cooling. Additional heating of the cap regions prevents gas hydrate formation in the inflow and outflow. Fluids are supplied to the sample cell via

1/16'' PEEK capillaries with a volume flow rate of 0.025-10 ml/min. All fluids are injected at room temperature.

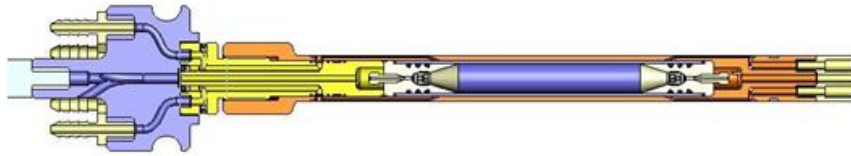


Fig. 2: Technical drawing of the NMR compatible high pressure sample cell: the sapphire tube (central violet cylinder) is surrounded by a cooling jacket (orange). Air for sample cooling is supplied through additional adapters (violet, yellow, beige). The cell is operated in vertical orientation with the light violet adapter (left hand side of the drawing) on top.

NMR experiments are performed with a 400 MHz Bruker Avance III vertical bore NMR Spectrometer that is equipped with a microimaging gradient unit. We use a custom-built imaging probe with a 30 mm resonator (Bruker Biospin, Rheinstetten, Germany). The probe has a minimum inner diameter of 25 mm, which corresponds to the outer diameter of the cooling jacket. A stepping motor is employed to move the sample cell in the vertical direction. The sample is imaged piece-wise and the different data sets are combined using an in-house MATLAB code (TheMathWorks, Natick, USA).

2.3. Sample Preparation

The sapphire tube was filled with quartz sand with a grain size of 0.09-0.5 mm (Schlingmeier, Schwülper, Germany). The sand was partly saturated with deionised water and exposed to a 13 MPa CH_4 atmosphere at a temperature of 8 °C. After CH_4 -hydrate formation had been completed, the remaining gas was flushed out of the sample by seawater injection. Subsequently, liquid CO_2 was pumped into the pressure vessel. Relaxation times of deionised water inside the sand matrix are $T_1 \approx 2$ s and $T_2 \approx 50$ ms. Exact relaxation times depend on the local compaction of the sand. We performed standard spin echo imaging sequences with an echo time of 2.9 ms to qualitatively visualize the distribution of the pore water over time.

3. Results and Discussion

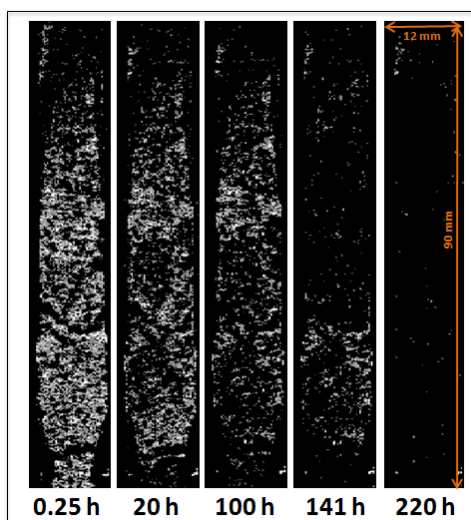


Fig. 3: Formation of CH_4 -hydrate: The NMR signal of water in a quartz sand sample is shown as grey scale images. Hydrate formation causes a disappearance of the water signal over time. Shown is the central slice of the sample.

Image resolution: $0.176 \times 0.25 \times 0.5 \text{ mm}^3$

The results of first gas hydrate formation and conversion experiments confirm the capability of high-pressure NMR imaging to provide valuable data on kinetic processes that are important for applied gas hydrate research. Examples are given in figures 3 and 4: Fig. 3 shows the disappearance of the pore water signal during gas hydrate formation. Information on gas hydrate formation kinetics as well as on spatial heterogeneity can be extracted from corresponding experiments. The invasion of liquid CO₂ into the CH₄-hydrate containing sediment sample is depicted in Fig. 4. Again, the knowledge of the spatial heterogeneity is of major importance: Gas exchange can only take place in areas that are permeable to CO₂.

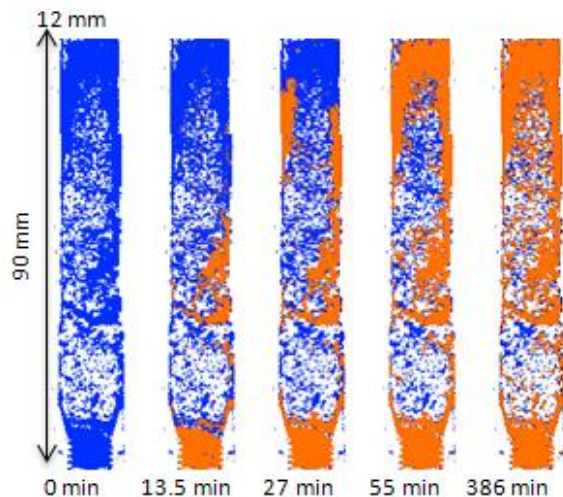


Fig. 4: Invasion of liquid CO₂ into a sediment sample that contains CH₄-hydrate.
 Colour coding: Orange: CO₂, Blue: seawater; White: gas hydrate and quartz sand.
 The CO₂ distribution is obtained from image subtraction.
 Image resolution: 0.176 x 0.25 x 2.5 mm³

In conclusion, temperature-controlled high-pressure sample cells are needed for creating experimental conditions that match the natural environment of gas hydrates. We could demonstrate that our experimental set-up NESSI is capable of providing these conditions and that it is compatible with NMR imaging equipment.

4. Acknowledgements

This work was funded within the scope of the SUGAR project by the German Ministry of Economy (BMWI, grant no. 03SX250 & 03SX320A) and by RWE-Dea AG, E.ON Ruhrgas AG and Stadtwerke Kiel AG. NESSI has been designed and constructed in cooperation with the University of Applied Sciences, Kiel, Germany.

References

- [1] D. Archer, B. Buffett, V. Brovkin, Proc. Nat. Acad. Sci. USA 106 (2009), 20596–20601
- [2] K. Wallmann et al., Energies 5 (2012), 2449-2498
- [3] V. Gornitz, I. Fung, Global Biogeochem. Cycles 8 (1994), 335–347
- [4] K.A. Kvenvolden, Rev. Geophys. 31 (1993), 173–187
- [5] J.B. Klauda, S.I. Sandler, Energy & Fuels 19 (2005), 459-470
- [6] <http://www.mh21japan.gr.jp/english/>
- [7] <http://www.netl.doe.gov/technologies/oil-gas/FutureSupply/MethaneHydrates/maincontent.htm>
- [8] <http://www.gashydrate.or.kr/>
- [9] <http://www.dghindia.org/NonConventionalEnergy.aspx?tab=0>
- [10] Y. Park et al., Proc. Nat. Acad. Sci. USA 103 (2006), 12690–12694
- [11] B. Kvamme et al., Int. J. Greenhouse Gas Control 1 (2007), 236–246
- [12] C. Deusner, N. Bigalke, E. Kossel, M. Haeckel, Energies 5 (2012), 2112-2140
- [13] <http://www.sugar-projekt.de>