[PS]Nuclear Magnetic Resonance Compatible Cell Design for Thermally Controlled Hydrate-Bearing Sediments Formation and CO_2 Exchange*

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Abstract

Natural gas hydrates (NGH) have been studied for decades as a vast potential hydrocarbon resource, which also encompass several economic and technological challenges. NGHs contain methane molecules that are trapped by water cages in the pore space of sediments, typically under high-pressure and low temperature regimes. Although the estimate of the amount of energy remain uncertain, several models indicate that it could be twice the amount of conventional fossil fuels in the world. In order to recover the hydrocarbon content within NGHs, the injection of CO_2 has been regarded as a thermodynamically favourable method of enhancing the recovery of the natural gas whilst sequestering the CO_2. This exchange process, and the associated heat and mass transfer phenomena in the context of porous media, is however, poorly understood.

With the aim of enhancing our understanding of the CO_2-CH_4 exchange process in complex porous media, various non-invasive Nuclear Magnetic Resonance (NMR) and Magnetic Resonance Imaging (MRI) measurements will be exploited to essentially visualize the process. This initially has required the design and construction of a hydrate core holder that is able to accommodate the temperature and pressure conditions relevant to NGH systems, whilst being compatible with NMR/MRI equipment. The final apparatus was designed and assessed with 3-D finite element methods (FEM) simulations, and includes cooling from the centre of the core holder such that and isothermal porous medium can be sustained and pressure controlled without affecting the NMR/MRI magnet temperature.

The functionality of the core holder has been based on using a combined configuration of thermoplastic materials, such as PEEK and PEEK with 30% of carbon fibre, which form the hard structure of the core holder, with silica aerogel as an external thermal insulator. Once manufactured, the core holder was subjected to pressure and temperature testing protocols in order to validate the development of favourable conditions for hydrate formation and dissociation. These tests consisted of combining progressive high-pressure injections of inert fluids (water and nitrogen), and subsequently circulating an ethylene-glycol-water mixture through the core holder at various temperatures down to -20 °C. The results indicated that the core holder was able to sustain pressure differentials up to 80 bar, while maintaining isothermal conditions down to -10 °C.

By implementing this NMR compatible cell, MRI and NMR relaxometry will be used to non-invasively quantify the pore-scale interactions between hydrates and their host sediments when conducting CO_2- CH_4 exchange processes. This will be spatially resolved within the hydrate sediment and the role of unconverted water and methane diffusion will be systematically studied.

NMR Compatible Cell Design for Thermally Controlled Hydrate-Bearing Sediments Formation and CO_2 Exchange

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FLUID SCIENCE & RESOURCES

Abstract

Natural gas hydrates (NGH), located principally in the sediments of oceanic and artic regions, have been studied as a prospective hydrocarbon resource. The energy trapped within these ice-like compounds can be an order of magnitude greater that known fossil fuels reserves[1,2]. Exploitation however also encompass several significant economic and technological challenges.

In order to harness such energy, CO2 injection has been considered as a promising production method, which essentially can extract the CH4 molecules within the NGH whilst sequestering CO2 without, in principle, compromising the hydrate-sediment stability.3 However, the heat and mass transfer phenomena associated with this exchange process are poorly understood.

Nuclear magnetic resonance (NMR) and magnetic resonance imaging (MRI) techniques will be used to directly measure this CO_2-CH_4 exchange process in a spatially resolved manner. To this end, a novel NMR/MRI hardware compatible hydrate core holder was designed, built and tested to allow for non-invasive observation of the CO_2-CH_4 exchange process in host sediments at Temperature and Pressure conditions approaching those of the reservoir.

Background

The possibility of CO_2-CH_4 exchange in hydrates arises from the difference between phase equilibria for CH_4 hydrates and CO_2 hydrates.

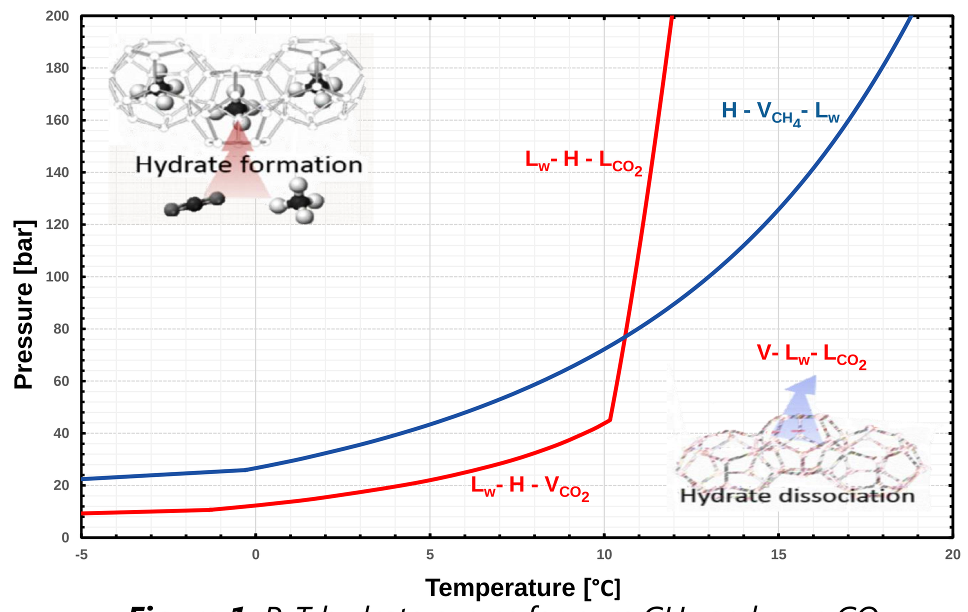

Figure 1. *P-T hydrate curves for pure CH_4 and pure CO_2 hydrates [4].*

According to figure 1, it can be seen that CO_2, as a guest molecule, is thermodynamically more favorable for forming hydrates than CH_4.

Methods

Design and Materials

The core holder design included cooling from the centre, via a coolant circulation, such that an isothermal annular porous medium can be achieved, as well as thermally and pressure controlled without affecting the surrounding magnet temperature. Figure 2 illustrates the geometric design, and the experimental apparatus containing the core holder.

The functionality of this design relies on the combined use of various thermoplastic materials, such as PEEK and PEEK with 30% of carbon fibre. Additionally as external thermal insulator, silica aerogel is used, which can provided a thermal conductivity below 0.05 (W/m/K). Figure 3 shows pictures of the core holder, and the thermal insulation.

Figure 3. Core holder assembly and thermal insulation

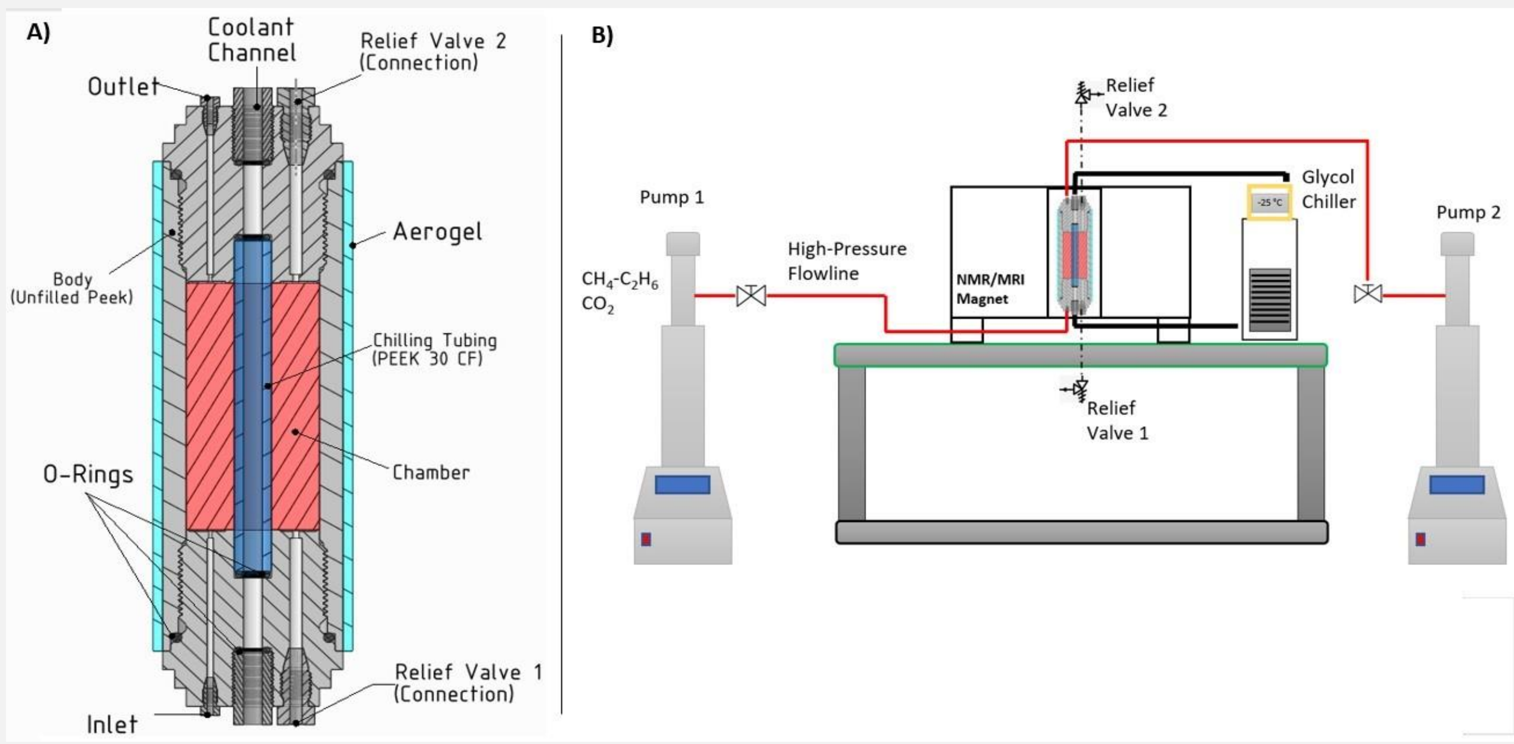

Figure 2. *A) Schematic cross-sectional illustration of the core holder assembly. B) Full experimental apparatus for CO_2-CH_4 exchange production tests*

Functional Assessment

By using 3D finite element methods (FEM), the collective mechanical and thermal properties of the core holder were assessed in order to ensure that the pressure regimes and thermal behaviour, as required for hydrate formation and dissociation, could be routinely created and contained. In figure 4, the maximum equivalent stresses generated are shown for the core holder when a pressure load of 80 bar is applied on all inner channels, with a coolant temperature of -10 °C.

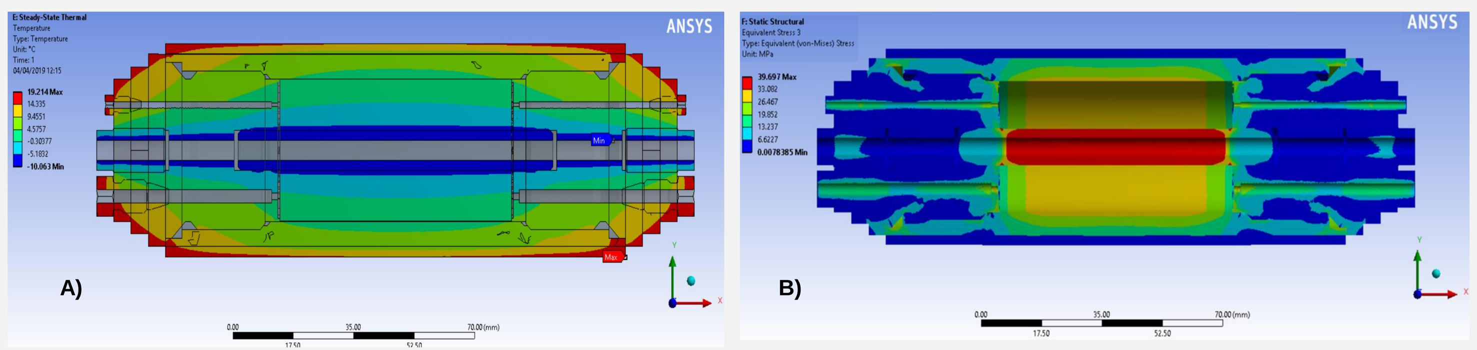

Figure 4. A) *Steady-state thermal simulation.* ***B)*** *Thermal-stress 3-D FEM simulation , with coolant temperature at -10 °C.*

Testing Protocols

Once manufactured, the core holder was subjected to high-pressure injections of inert fluids (water and nitrogen), which probed the overall mechanical integrity of the cell. Subsequently, a model porous medium (glass beads) was placed in the annular sample chamber; coolant was circulated at temperatures down to -20 °C and the thermal behavior was successfully monitored. (Figure 5)

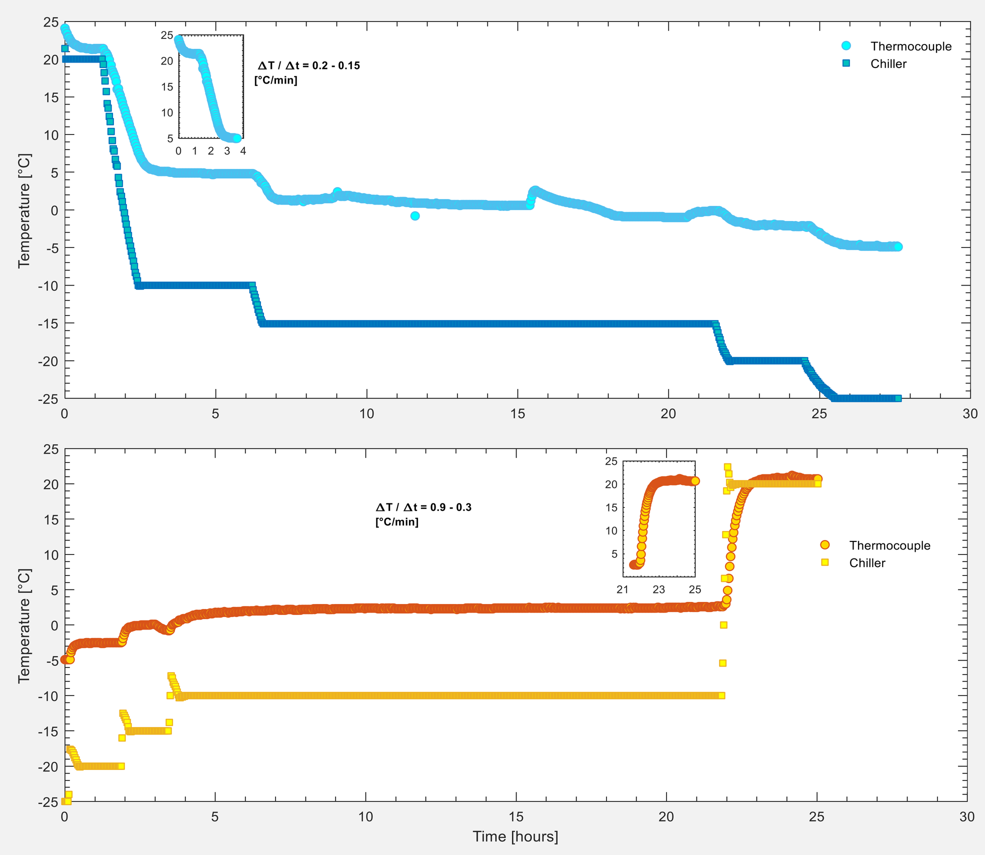

Figure 5. *Core holder thermal behavior (testing period).*

Results

The mechanical integrity of the core holder was shown to be able to reliably accommodate pressure differentials up to 100 bar, whilst maintaining overall temperatures in the chamber ranging from 4.9 °C to -5°C as required.

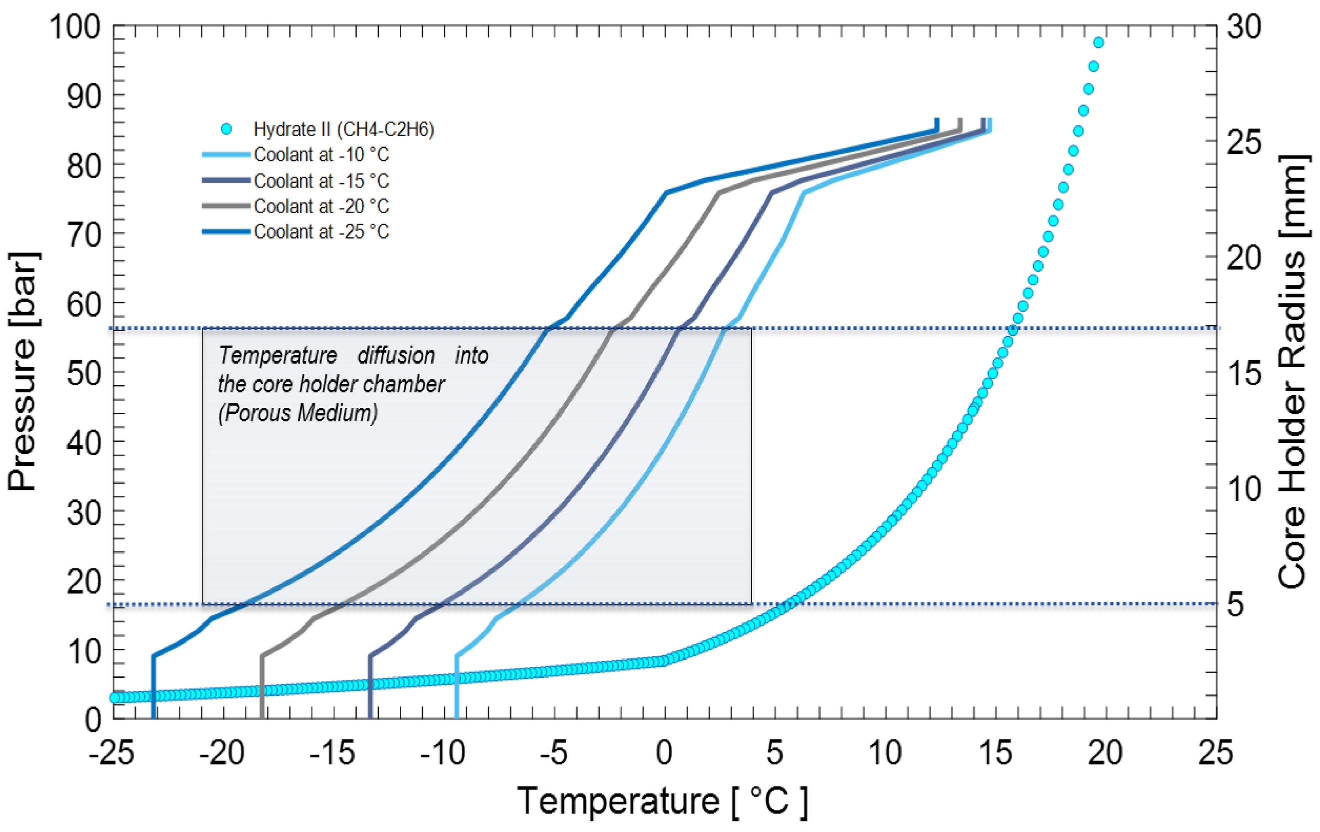

Figure 5. *Temperature profiles through the core holder and hydrate zone, from 3D-FEM*

Data obtained from the temperature test were also utilized to calibrate the 3D FEM model, which ultimately is used to calculate the temperature distribution through the core holder as a function of core sample radius. These are comfortably within the relevant hydrate formation P-T curve (for a mixture of methane (CH_4) and ethane (C_2H_6). (Figure 5)

Conclusions

- Via 3D FEM we were able to optimize the design and validate the functionality of an NMR-compatible hydrate core holder that is capable of providing a pressure and temperature controlled environment for promoting hydrate formation, without affecting NMR/MRI magnet conditions.
- By implementing this cell, MRI and NMR relaxometry can be used to study the hydrate sediment and the role of unconverted water and methane diffusion during CO_2-CH_4 exchange experiments.

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