

# SCA2003-55: MONITORING THE FORMATION AND DISSOCIATION OF GAS HYDRATE IN RESERVOIR ROCK USING MAGNETIC RESONANCE IMAGING

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## ABSTRACT

Formation and dissociation of gas hydrate have been monitored in a sandstone core plug using Magnetic Resonance Imaging (MRI). This paper describes the experimental procedures developed to form carbon dioxide (CO<sub>2</sub>) and methane (CH<sub>4</sub>) hydrate in sandstone rock while monitoring the process with MRI. MRI was found to provide excellent resolution between the hydrate and its liquid/gas precursors and allowed the dynamic, spatial imaging of the formation and dissociation of hydrate under various injection conditions.

## INTRODUCTION

Gas hydrate in porous media may play an important role within reservoir engineering by:

- *representing an enormous energy potential:* The total energy corresponding to natural gas entrapped in hydrate reservoirs might be more than twice the energy of all known sources of coal and other hydrocarbons.
- *exhibiting potential hazardous production scenarios:* Hitting formations rich in methane in the form of gas hydrate may result in sudden and dramatic increase in gas production and a gas blow out situation may occur.
- *providing safe long-term storage of CO<sub>2</sub>:* a) The thermodynamic stability of carbon dioxide hydrate is significantly higher than the corresponding stability of natural gas hydrate at typical reservoir conditions of temperature and pressure. Injection of carbon dioxide into hydrate reservoirs will therefore lead to conversion from natural gas hydrate to carbon dioxide hydrate. Transformation of natural gas hydrate to carbon dioxide hydrate will therefore represent a safe, stable, long term, storage option for carbon dioxide, while at the same time releasing natural gas. Replacement of natural hydrate by CO<sub>2</sub> hydrate will reduce the net cost of the CO<sub>2</sub> storage due to the value of the released natural gas. b) Another situation is the potential role of hydrate in different scenarios related to storage of carbon dioxide in aquifers. In cold regions such as the Barents sea and the North Atlantic the thermodynamic conditions around the injection zones may be well within the region of thermodynamic stability of carbon dioxide hydrate
- *causing harm to ocean bottom construction/installations:* Conditions of stability for hydrate depends on temperature and pressure as well as the surrounding phases (natural gas, CO<sub>2</sub>, water). If a surrounding gas phase is under saturated with respect to water then the hydrate will dissociate in a fashion similar to sublimation of ice in to air. Similarly, if the hydrate is exposed to ground water containing little or no dissolved hydrate formers, the hydrate will dissociate due to low chemical potential of hydrate former in the aqueous solution. This may result in geological deformations and reservoir compression. This is likely to be the reason for the creation of the Storegga slide and is a concern related to the development of Ormen Lange.

- *causing injection problems for deep reservoirs*: Carbon dioxide can cause problems when it is re-injected into oil reservoirs. Direct contact between pure carbon dioxide and water may result in hydrate formation. Hydrate can also be formed at the contact between the hydrocarbon mixture containing dissolved carbon dioxide, and water. The vigorous mixing between water and carbon dioxide close to the injection zone might lead to the formation of hydrate that partially can plug the pores in the reservoir structure, resulting in lower distribution efficiency or even complete blockage. If the temperatures and pressures in the reservoir cap regions are within the hydrate stability zone the carbon dioxide that reaches the reservoir cap may contribute to a more efficient closing of this cap through hydrate formation. This applies of course only if the reservoir cap zone is above the depths where CO<sub>2</sub> is heavier than water (~2800 m).
- *hydrate slurry as a transport medium for CO<sub>2</sub> injection*: For reservoirs in which the thermodynamic conditions around the injection zone is outside the stability region for CO<sub>2</sub> hydrate it might be a cost efficient option to pump the CO<sub>2</sub> into the reservoir as a hydrate/water slurry rather than the expense to compress the CO<sub>2</sub> fluid to the required injection pressure.

Therefore characterizing gas hydrate in porous rock is very important for reservoir engineering and core analysis [1,2]. The work was undertaken both for measuring possible CO<sub>2</sub> sequestering procedures and the preparation of samples for methane production studies. This paper describes the experimental method that allowed us to image the formation and dissociation of gas hydrate in porous rock with dynamic 3D imaging on a sub millimeter scale.

## EXPERIMENTAL

Formation and disassociation of carbon dioxide (CO<sub>2</sub>) and methane (CH<sub>4</sub>) hydrate were first studied in the bulk phase to experimentally identify temperature and pressure conditions for the hydrate formation and disassociation processes. Gas hydrate formation and disassociation were then monitored in a sandstone core plug using MRI tomography. MRI tomography allowed dynamic in-situ imaging of the formation and dissociation of hydrate under various injectivity conditions. A cooling system capable of holding the core holder at a selected, stable temperature within the range of 0-20°C, with an accuracy of 0.1°C, for an extended period of time was constructed. The cooling fluid selected, Fluorinert (FC-84), needed to be invisible for MRI and was also used as the confining fluid for pressure maintenance in the core holder. To keep the volume of the confining fluid small and the cooling bath and pumps at a safe distance from the magnet the heat exchange system shown in Figure 1 was used. The tubing which circulated the high-pressure confining fluid was embedded in a larger plastic tubing filled with the temperature controlled circulating antifreeze fluid, which was not piped through the MRI. The core holder was made of a composite material to minimize influence on the imaging capabilities. Figure 1 shows the MRI with the cooling system. Figure 2 schematically describes the MRI cooling set up.

The core was initially characterized and saturated with brine, see Table 1 for core data and Table 2 for fluid data. The core was placed inside the core holder in the MRI and pressurized to approximately 80 bars. In an attempt to duplicate conditions that are, or would be, present in nature, i.e. gas with water present, a gas water displacement process was initiated. A liquid gas phase, CO<sub>2</sub> at 63 bars and 25 °C, was introduced at one end of the core sample. The liquid gas-water displacement was imaged and the final water saturation after 0.5PV of CO<sub>2</sub> had been injected is shown as the upper profile in Figure 3. The core holder was then cooled to 2.0 °C where hydrate began to form. Successive images of the hydrate formation were then collected over the next 24 hours and the profiles are shown in Figure 3 as decreasing intensity from liquid water.

After heating and cooling the system several times the formation and disassociation of hydrate were monitored as function of time. The experiments were also performed at two different temperatures, first at 2 °C, then again at 8 °C to be certain that no ice was formed in the aqueous phase. The formation of hydrate was observed both by a reduction in MRI free water signals and by a reduction in the fluid permeability.

Finally, methane was also used as the gas phase. Similar experimental procedures were performed as for the CO<sub>2</sub> injection.

## **RESULTS AND DISCUSSION**

Figure 3 shows the profile of the MRI intensity along the length of a partially water saturated sandstone core plug as a function of time. Liquid CO<sub>2</sub> was injected into the plug at the face represented by the left-hand side of this plot and the water saturation distribution after 0.5PV of liquid CO<sub>2</sub> displaced water is shown as the upper saturation profile in Figure 3. At static conditions the temperature was then lowered to 2° C. The downward arrows show the trend of intensity with time. Decreasing intensity indicated the formation of hydrate because the MRI parameters were adjusted to image only the liquid hydrate precursors. Hydrate formation was indicated by the measurable decrease in the amount of free water and the simultaneous decrease in permeability with time. The noticeable difference in the change of the MRI intensity along the length of the plug suggests that the hydrate formation was primarily limited by the amount of CO<sub>2</sub> available, i.e. the greatest change was near the CO<sub>2</sub> inlet face and the smallest of change was at the far end of the plug. Permeability decreased to zero as hydrate formed, implying that selected, but not readily detected, areas were completely filled with hydrate before all of the pore volume was filled.

Figure 4 shows a sequence of 2D longitudinal images of a 4mm thick slice through the center of the core plug during hydrate formation. These images indicate that hydrate primarily formed, indicated by areas of reduced intensity, near the CO<sub>2</sub> inlet end of the plug, the right-hand side of these images. The hydrate formation process continued over a relatively long period of time and the growth from right to left is consistent with a nucleation process for the initiation of hydrate followed by growth at the crystal face. These 2D images show that hydrate formed as a uniform band across the plug, rather than as separate, discrete clumps, again consistent with nucleation initiating hydrate growth at the right-hand side of the plug.

Similar results to what is reported in this paper using CO<sub>2</sub> were obtained using methane.

These preliminary experiments demonstrate the value of MRI to monitor the formation of hydrate and the difficulties, mostly unreported, involved in the process to intentionally form hydrate in significant quantities.

## **CONCLUSIONS**

Preliminary results showed that hydrate took several hours to form with the amount being consistent with the gradually decreasing gas saturation from the gas injection face rather than only in separate, discrete areas.

Permeability went to zero when less than half of the sample was filled with hydrate implying that selected, but not detected, areas were completely filled with hydrate before all of the pore volume was filled.

## ACKNOWLEDGEMENT

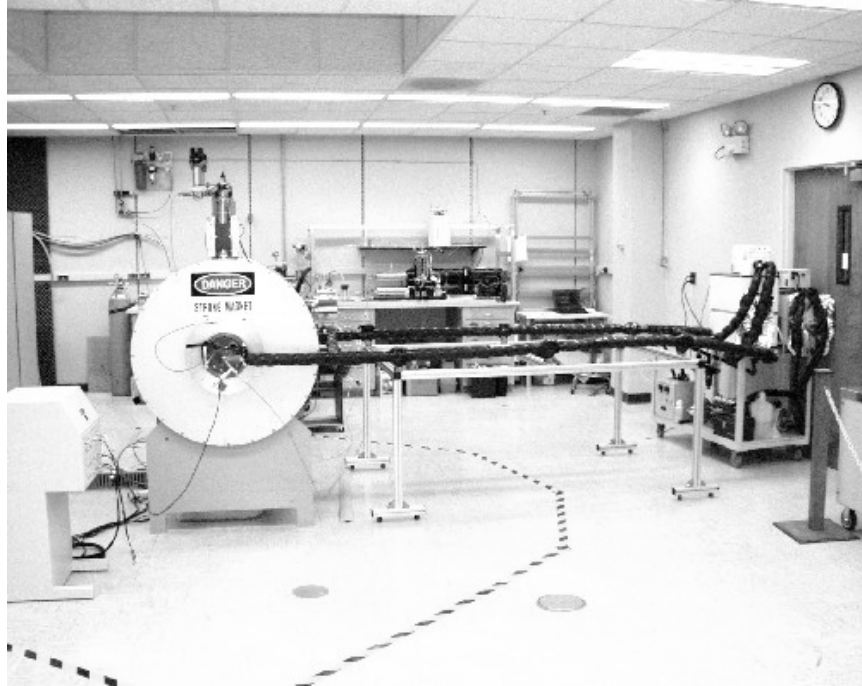
One of the authors is indebted for the support from the Norwegian Research Council.

## REFERENCES

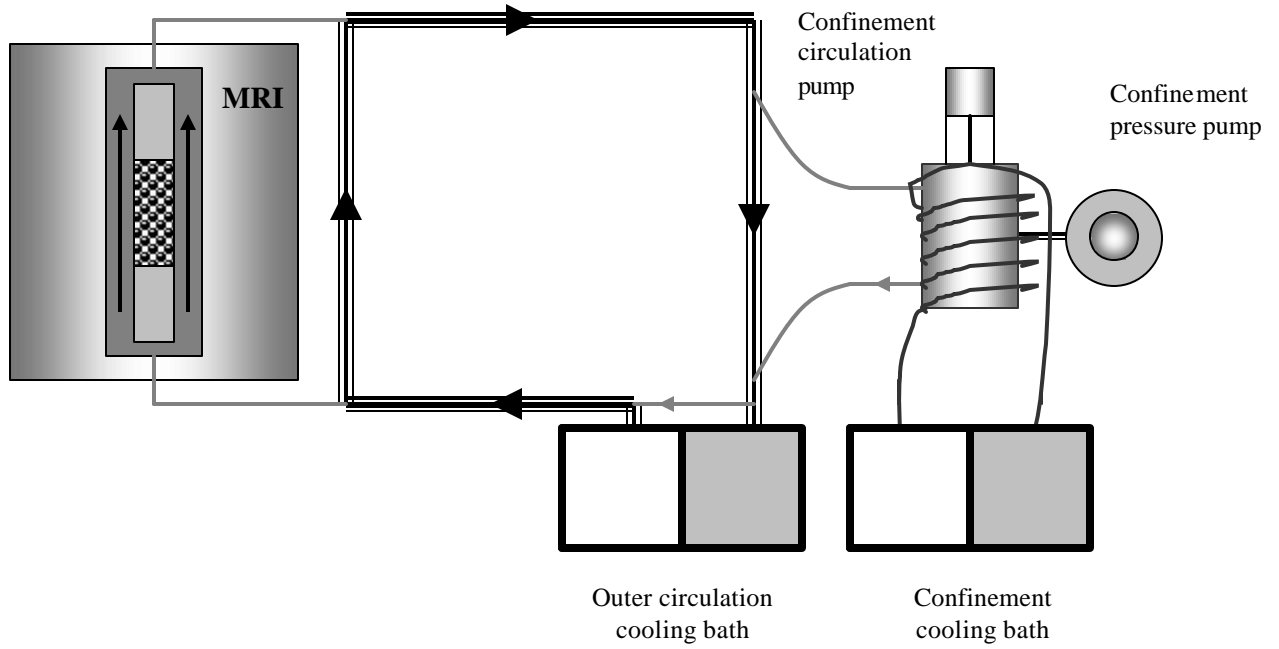
1. Moudrakovski, I.L., Ratcliffe, C.I. and Ripmeister, J.A.: "Application of Magnetic Resonance Microimaging (MRM) to Monitor the Formation of Gas Hydrate", Proc.: Fourth International Conference on Gas Hydrates, Yokohama, Japan, May 19-23, 2002.
2. Baldwin, B.A., Moradi-Araghi, A. and Stevens, J.C., "Monitoring Hydrate Formation and Dissociation in Sandstone and Bulk with Magnetic Resonance Imaging", Reservoir Technology Report (in process of issuing, May 2003).

DIAMETER	[cm]	3.8
LENGTH	[cm]	9.4
POROSITY		22.1
ABS. PERM	[Darcy]	1.1
GRAIN DENSITY	[g/cm <sup>3</sup> ]	2.65

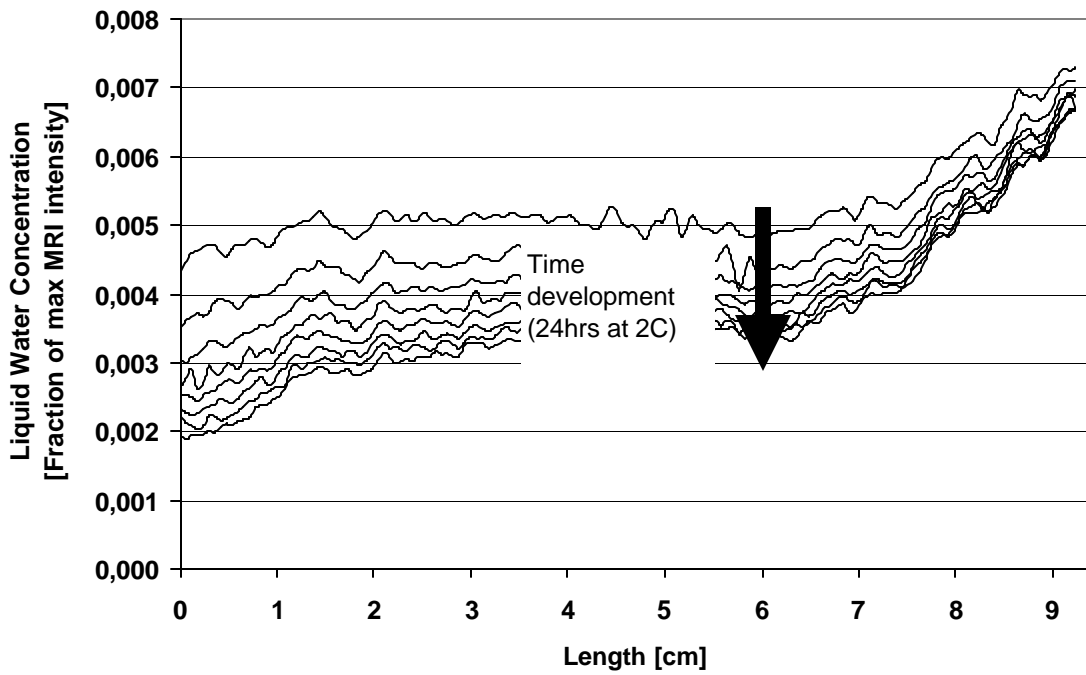
Fluid	Formula	Purity [%]	Viscosity @ 20°C/atm P [cP]	Density @ 20°C/82bar [g/cm <sup>3</sup> ]	Dew point @20 °C [bar]
Deionized Water	H <sub>2</sub> O	99.9	1.00	1.00	
Methane	CH <sub>4</sub>	99			
Carbondioxide	CO <sub>2</sub>	99		0,7	58
Flourinert FC-84		99			
Antifreeze		-			



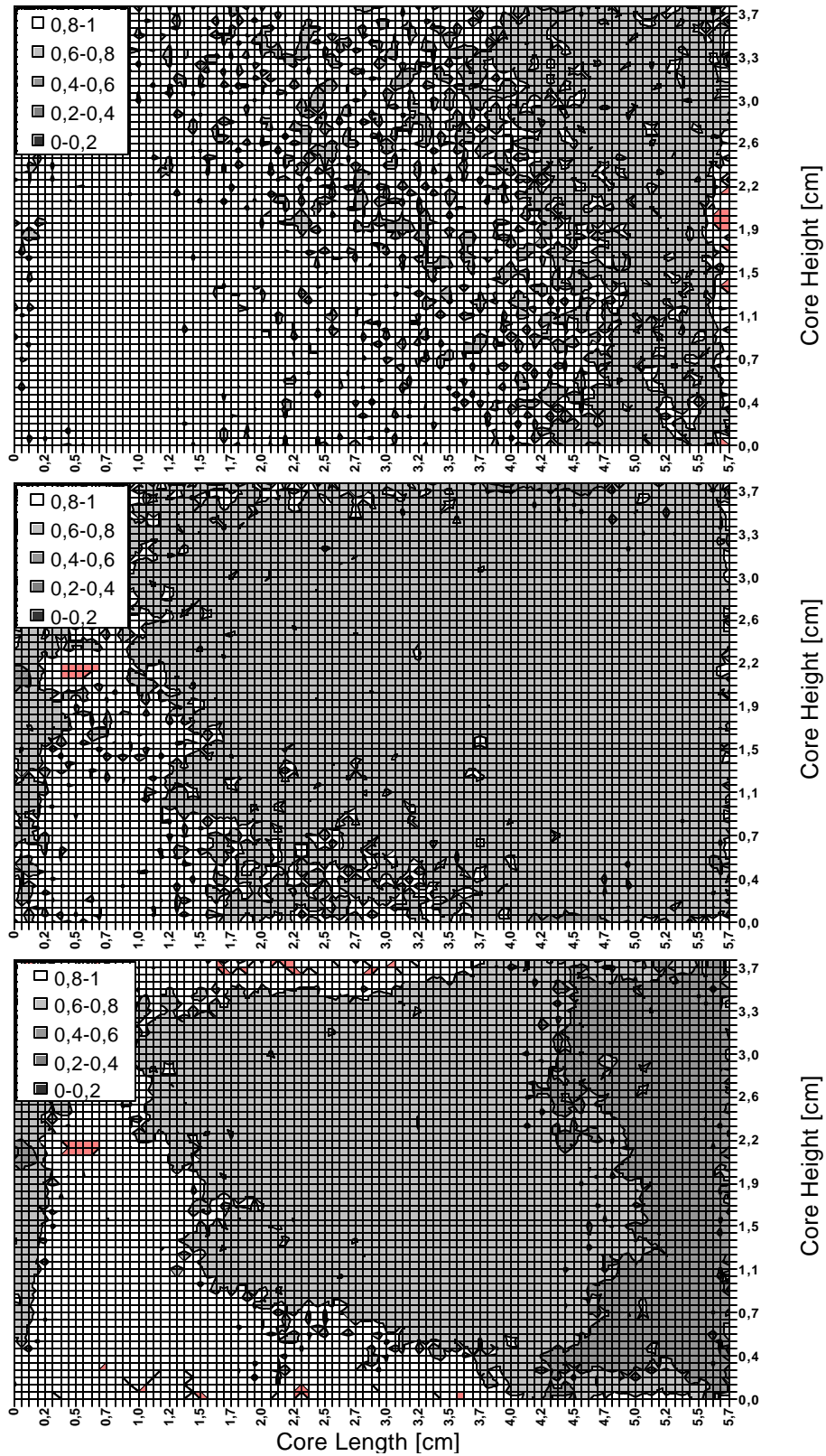
**Figure 1. MRI with cooling system**



**Figure 2. Schematics of MRI and cooling system.**



**Figure 3. Formation of CO<sub>2</sub> hydrate along the core as function of time.**



**Figure 4. Sequence of 2D images of CO<sub>2</sub> hydrate formation as function of time. Top: when cooled to 2°C. Center: After 30 minutes at 2°C. Bottom: After 8 hours at 2°C. Gray scale indicates fraction of water not bound in hydrate.**