NMR-compatible Sample Cell for Gas Hydrate Studies in Porous Media

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ABSTRACT

The production of methane (CH_4) from natural-gas hydrate deposits via molecular replacement by injected, thermodynamically more favourable, carbon dioxide (CO_2) is a promising method of energy production and carbon sequestration. However, the viability of this technique is constrained by mass-transfer limitations, which are in turn associated with diffusion of the injected CO_2 into the hydrate-bearing sediment layers. Generally, the coupled heat- and mass-transfer phenomena associated with this replacement process in a complex heterogeneous porous media, are poorly understood. In order to facilitate the non-invasive pore-scale study of this replacement process (ultimately in sediment cores) using a range of Nuclear Magnetic Resonance (NMR) and Magnetic Resonance Imaging (MRI) techniques, a novel NMR-compatible sediment holder has been designed and constructed. Via the provision of centralised sample cooling, sample temperature control is afforded at high pressures whilst keeping the NMR magnet system at the required temperature. Hydrate formation and dissociation processes in model porous media were successfully investigated using a $\text{CH}_4/\text{C}_2\text{H}_6$ mixture and CO_2 respectively. Novel 1D MRI images of the residual liquid water and hydrocarbon gas were acquired during the hydrate formation and dissociation processes using a SPRITE MRI pulse sequence. Interleaved NMR T_2 relaxation measurements were also obtained to interrogate the pores sizes occupied by the residual water. From these results, the water distribution and subsequent hydrate-formation behaviour has been spatially and temporally resolved throughout the porous media.

Key words: porous media sample holder, hydrates, NMR, MRI, Finite Element Modelling

1. INTRODUCTION

Natural gas hydrates (NGHs) have been widely recognised as a vast hydrocarbon resource with an energy content much greater than that in all remaining conventional fossil fuels.¹⁻³ Gas hydrates are ice-like crystalline solids that occur when water and suitably sized gas molecules (typically less than 9.0 Å in diameter) are combined at high pressure and low temperature conditions.⁴ In nature, these hydrates form vast repositories of natural gas in both deep ocean sediment and shallow strata at depths ranging from 300 to 4000 m, where relevant thermodynamic conditions exist with a sufficient source of biogenic or thermogenic gases.⁵ As the world moves from liquid and solid fuels to a greater use of natural gas, the attractiveness of these NGHs is enhanced as a prospective energy resource.⁶ However, their viable development is still economically and technologically challenging.

The injection of carbon dioxide (CO₂) offers the possibility to recover natural gas from hydrate reservoirs via CH₄-CO₂ exchange with beneficial implications for CO₂ sequestration. In this process, high pressure CO₂ replaces CH₄ as the guest molecule in the hydrate crystal structure. Whilst this replacement process is thermodynamically favourable under a range of relevant conditions, and has been demonstrated on both a laboratory and field scale,^{7, 8} the commercial viability of this production technique is poor on account of limited CO₂ injectivity resulting in low CH₄ recovery rates.⁹ Mass transfer limitations, as conversion proceeds, are key and manifest as supercritical CO₂ being unable to substantially penetrate the product CO₂ hydrate surface to access the underlying natural gas hydrates. This mass transfer is clearly a function of a range of factors including hydrate distribution, permeability, porosity, as well as the pore space heterogeneity and wettability of the host sediments. Nonetheless, a detailed quantitative understanding of the replacement mechanism is still somewhat elusive.¹⁰ Extensive reviews of current knowledge regarding the properties and kinetics of the replacement reaction are provided by Komatsu et al.¹¹ and Koh et al.¹²

Non-invasive interrogation of this replacement process is possible using a range of tomographic techniques.¹³⁻¹⁵ Here, we focus on the application of nuclear magnetic resonance (NMR) and magnetic resonance imaging (MRI) methods. These have been widely applied across porous media studies, in particular with respect to petro-physics.^{16, 17} In order to facilitate such studies at relevant reservoir conditions, the use of a variety of rock core holders which are

compatible with NMR/MRI hardware has been reported.¹⁸⁻²² Located within NMR/MRI magnet systems, these holders are generally required to be constructed from non-metallic materials. In this regard, high-strength polymers (e.g. PTFE, PEEK and Polyimide) are typically employed.^{19, 20, 22} In the current application, the need for sub-zero sample cooling is significant in order for the required hydrates to form within a given porous media. This must be achieved whilst ensuring the surrounding magnet's temperature is tightly controlled at the required operational set point of, in our case, 35 °C.

In this work, we present the design and construction of a new NMR-compatible sample holder, which is suitable for low-field benchtop NMR hardware as is widely used in the context of rock core characterisation. Given the required formation of hydrates within a sediment bed, refrigerative cooling is provided to the sample from a central cylindrical channel, which when coupled with silica aerogel insulation minimises any thermal influence on the surrounding magnets in the NMR/MRI system. The mechanical design of the (predominately PEEK) sample holder as a function of temperature is interrogated using 3-D finite element method (FEM) simulations.^{23, 24} By way of validation, hydrate formation and dissociation processes are subsequently studied using both a methane/ethane mixture and CO₂. MRI 1D profiles are shown to be able to track the temporal evolution in the free water content through these processes, whilst NMR T_2 measurements are used to probe the evolution in the pore size distribution occupied by this free residual water. These collectively facilitate the future application of this hydrate sample holder to CH₄-CO₂ hydrate exchange experiments.

2. BACKGROUND

2.1 Relevant NMR and MRI Theory

In the oil and gas industry, NMR relaxation measurements are routinely applied for reservoir characterization through both rock core analysis in the laboratory (occasionally at reservoir conditions) and well logging programs in the field.²⁵ These non-invasive measurements often consider the measured ¹H NMR signal transverse relaxation times (T_2). In particular, the derived probability distributions of T_2 , $P(T_2)$, are commonly utilized to estimate petro-physical properties such as porosity, permeability, pore size distribution and wettability.^{17, 26} The NMR signal intensity $M(t)$ is acquired using a standard Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence²⁷ and fit with the following expression to determine $P(T_2)$:

$$\frac{M(t)}{M_0} = \int P(T_2) \exp\left(-\frac{t}{T_2}\right) dT_2 \quad (1)$$

where $M(t)$ is the measured signal intensity at time t and M_0 is the initial magnetization at $t = 0$.

In the absence of significant diffusion through gradients in the magnetic field, the measured value of T_2 can be expressed as follows:²⁸

$$\frac{1}{T_2} \approx \frac{1}{T_{2B}} + \frac{1}{T_{2S}} \quad (2)$$

where T_{2B} is the bulk relaxation time of the relevant fluid and T_{2S} is the surface relaxation time. For fluids inside porous media, T_{2S} can be expressed as follows:^{29, 30}

$$\frac{1}{T_{2S}} = \rho_2 \left(\frac{S}{V} \right) \quad (3)$$

Here, ρ_2 is the transverse surface relaxivity and (S/V) represents the surface-to-volume ratio of the pore space. T_{2B} is usually much longer than T_{2S} , consequently it can be assumed that $1/T_2$ is equivalent to $1/T_{2S}$.¹⁶ A relationship can then be established between pore size and T_2 assuming the confining geometry to be perfectly spherical with a radius, r :

$$\frac{1}{T_2} \approx \rho_2 \left(\frac{3}{r} \right) \quad (4)$$

MRI techniques have found moderate application for the characterization of porous materials via determination of spatially-resolved fluid saturations in porous media.^{16, 31} In order to follow dynamic processes occurring between fluids contained within a porous medium, one-dimensional (1D) MRI measurements or axial profiles have been used to monitor displacement processes.^{22, 32} The most common approach is to employ a standard spin echo MRI method for such profiling purposes.^{33, 34} However Single-Point Ramped Imaging with T_1 Enhancement (SPRITE)³⁵ has been developed and proven to be more immune to NMR r.f. imperfections and signal relaxation effects, providing more quantitative rock fluid MR images than the spin echo

method.²² In this work, 1D SPRITE MRI measurements were employed to monitor the fluid signal (liquid water or hydrocarbon gases) during gas hydrate generation and dissociation processes.

2.2 NMR Studies of Hydrate Systems

Most NMR studies of gas hydrates in the literature employ high field NMR equipment. Solid-state NMR spectroscopy has been used to determine hydrate structure type and relative cage occupancies of various hydrate-former molecules.¹² Solid-state ^{13}C NMR spectra measurements were used to determine the phase equilibria of gas hydrates formed with CO_2 and CH_4 within heterogeneous porous materials.^{36, 37} These studies showed that the hydrate phase equilibrium was shifted to larger pressure values due to capillary effects. Lee et al.³⁸ conducted CO_2 replacement experiments through silica gel samples and developed a method based on solid-state ^{13}C NMR spectroscopy to estimate the expected CH_4 recovery and CO_2 concentrations in the hydrate phase after the substitution process. Cha et al.³⁹ employed both in situ ^1H and ^{13}C NMR spectroscopy to monitor the replacement kinetics in methane hydrates when subjected to mixtures of CO_2 and N_2 . A spontaneous exchange reaction was suggested, as there was no evidence of increased ^1H NMR signal due to the formation of free water molecules. Additionally, the replacement ratio was observed to slightly increase for the smallest hydrate cages, which may be attributed to the presence of N_2 . The replacement process for mixed hydrate crystals (sII and sH) using CO_2 has also been systematically studied using a combination of ^{13}C NMR and various other metrology modalities.⁴⁰⁻⁴²

The application of MRI methods for the study of visually opaque hydrates systems is comparatively less mature. Baldwin et al.⁴³ imaged the spatial distribution of THF hydrates in rock cores during hydrate formation/dissociation experiments. Using MRI measurements, Bagherzadeh et al.⁴⁴ found that hydrate formation occurs at a uniform rate within unconsolidated sediment independent of grain size employed. By analysing the variations in the MRI signal intensity, Husebø et al.⁴⁵ investigated the effects of salinity on the thermodynamic stability of CH_4 hydrates in rock cores. It was observed that CH_4 hydrate saturation was controlled by the total brine salinity rather than brine distribution within the pore network. Focused on CO_2 storage in NGH deposits, Kvamme et al.^{46, 47} employed MRI to monitor free water and hence permeability reduction while CO_2 hydrates were formed in various sandstones. Ersland et al.^{18, 48} provided tomographic evidence regards the conversion of CH_4 hydrates into CO_2 hydrates within a Bentheimer sandstone core plug. These

tomographic images resolved the liquid water distribution and indicated that little hydrate dissociation was occurring during the CH₄-CO₂ exchange process. Song et al.⁴⁹ imaged water distributions in a porous medium during NGH dissociation as pressure was decreased and temperature was increased.

In addition to NMR spectroscopy and MRI, the use of NMR relaxometry has also been applied in various studies of hydrate systems relevant to CO₂-CH₄ exchange. Kleinberg et al.^{28, 50} for example, showed the applicability of NMR relaxometry in permafrost and deep ocean sediments to evaluate various petro-physical properties such as pore size, permeability and phase saturations (hydrate, water, free gas). Minagawa et al.^{51, 52} estimated both the pore size distribution and permeability of hydrate-bearing sandstones whilst Komai et al.⁵³ assessed the reduction in porosity and permeability as methane hydrate formed in various sandstones. Recently, 2D T_1 - T_2 NMR measurements have been conducted to resolve different phase compositions in a variety of porous media during hydrate generation and dissociation in porous media.^{54, 55}

3. MATERIALS AND METHODS

3.1 Materials

Figure 1 shows the NMR-compatible hydrate sample holder designed and constructed in this work. This cylindrical sample holder has a 46 mm outer diameter, 34 mm inner diameter, and a length of 163 mm. This cell readily fits inside desktop NMR spectrometers that are routinely used for rock core analysis, and can accommodate a sample volume of 56 mL. In the current application, it was accommodated within a benchtop Oxford Maran Ultra 12.9 MHz rock core analyser from Oxford Instruments, UK.

Figure 1. NMR-compatible hydrate sample holder. (a) Cross-sectional schematic of the sample holder assembly, showing the assembly of the middle chilling tube and the fluid flow channels through the end-caps (b) Photograph of the hydrate sample holder without thermal insulation, and (c) complete assembly with an aerogel coating for thermal insulation.

The hydrate sample holder requires two end-caps to seal the sample, these include three connections which provide access for the process fluid inlet/outlet, safety pressure relief and the inner coolant fluid respectively (Figure 1.a). The core holder body and the end-caps were constructed using Polyether-ether-ketone (PEEK) (E-Plas, Western Australia, Australia), which is NMR compatible, as well as reasonably wear and chemical resistant. Internal to the core holder is a chilling tube with the following dimensions: 9.53 mm OD, 4.76 mm ID, and 90.55 mm length (Figure 1.b). This connects concentrically to both end-caps and it is made from a reinforced PEEK matrix (Ensinger, Nufringen, Germany), which is a composite of PEEK, carbon fibre (CF), (PTFE) and graphite. This modified PEEK composite was selected as it has an improved thermal conductivity ($0.82 \text{ W m}^{-1} \text{ K}^{-1}$) relative to standard PEEK ($0.28 \text{ W m}^{-1} \text{ K}^{-1}$). The chilling tube allows for coolant at atmospheric pressure to be circulated through the core holder and thus for the provision of cooling from its central region. The

coolant mixture used consisted of an equal volume of water and ethylene-glycol¹ (Chem-Supply, SA, Australia) dosed with 1.68 wt% Manganese chloride (MnCl₂), which served as a paramagnetic agent to eliminate the ¹H NMR signal from the mixture. (MnCl₂ decreased the ¹H NMR T_2 of the mixture from 1 s to 0.0008 s at which point it is practically undetectable in the experiments conducted). The physical interfaces between the cooling tubing and the end-caps, as well as the seal between the main core holder body and the end-caps used Kalrez O-rings (Dupont, TN, USA) which are CO₂ compatible as required. The final assembly is able to accommodate sample pressures up to at least 100 bar.

The outside of the core holder is treated and coated with thermally insulating silica aerogel (Tec Corporation LTD, Korea) to an average thickness of 2.5 mm (Figure 1.c) The provision of internal cooling coupled with this thermal insulation allowed for adequate temperature control of the surrounding magnet assembly at the required temperature of 35 °C. The aerogel coating also serves to reduce condensation on the core holder, this was further reduced by a continuous flow of dry air over the aerogel layer during experiments – this also served to assist in magnet temperature regulation.

To form gas hydrates in the sample holder, deionized water was used along with two different gas hydrate formers: (1) a mixture of methane and ethane (molar fractions: x_{CH_4} = 0.68 and $x_{C_2H_6}$ = 0.32); and (2) CO₂ (both supplied by Coregas at purities of 99.995%). The model host porous media used was a random packing of spherical glass ballotini, comprising a grain size distribution from 500 µm to 850 µm (with a mean diameter of 660 µm) and a gravimetrically determined porosity of 36%. It had a density of ~ 2.4 g cm⁻³, and a thermal conductivity of 1.09 Wm⁻¹K⁻¹.⁵⁹

3.2 Experimental Setup

The complete experimental apparatus is schematically shown in Figure 2. This system involves two flow loops:

¹ In traditional core flooding a per-fluorinated compound is usually employed, however a water-MEG mixture was selected in this case as it presents an approximately 10-fold increase in thermal conductivity (~ 0.40 W m⁻¹ K⁻¹,⁵⁶ versus ~0.057 W m⁻¹ K⁻¹,^{57, 58}).

(1) The high-pressure sample fluid, which enables the direct injection of relevant fluids to the sample using the end-cap injection ports. The porous media sample (glass ballotini packing) was placed in the core holder around the central chilling tubing. Following this, sample fluids (water, CO₂ or CH₄/C₂H₆ mixture) were circulated through the core holder under high pressure using two syringe pumps (Teledyne ISCO Pump 260D, USA). Two pressure relief valves were included in the high-pressure flow loop such that a maximum working pressure of 100 bar was not exceeded.

(2) The atmospheric pressure coolant mixture via the central chilling tube. The coolant mixture was pumped through the chilling tubing using a thermostatic bath (Lauda Alpha RA8, Germany) at a flowrate of 15 L/min.

Figure 2. Schematic of the complete experimental apparatus for gas hydrate formation/dissociation monitored by NMR and MRI measurements. Two distinct flow loops are used for the sample fluid (high pressure) and the cooling fluid (atmospheric pressure) respectively.

3.3 Thermomechanical Analysis of the new Sample Holder

Given the use of different materials of construction and the use of high pressure and low temperatures, the following mechanical analysis of the sample holder was completed. A geometrically consistent 3D model for the sample holder was developed in Solidworks™ (Dassault Systems, France). Subsequently, the thermal and mechanical response of the core holder to high pressure and low temperature regimes was numerically simulated using ANSYS Multiphysics™ (ANSYS, USA). The required material mechanical and thermal properties are

listed in Table 1. Finite element modelling (FEM) was used to determine the coupled induced stresses and temperature distribution within the core holder in 3D as a function of temperature and pressures (covering a range from 40 to 100 bar and 10 to -25 °C, respectively).

Table 1. Principal properties of materials employed in the 3D FEM Model

Component	Material	Density [g/cm ³]	Thermal Conductivity [W/ m K]	Young's Modulus [MPa]	Tensile Yield Strength [MPa]	Elongation at Break [%]
Thermal Insulation	Silica Aerogel	0.16	0.0442 ¹	-	-	-
Core Holder Body	PEEK	1.32	0.28	4400	110	20
End-Caps	PEEK	1.32	0.28	4400	110	20
Sample (Porous Medium)	Glass Ballotini	2.23	0.2 - 0.36 ²	-	-	-
Chilling Tubing	PEEK Composite	1.44	0.82	5500	102	3

1. The thermal conductivity of the aerogel estimated for a layer with 2.5 mm of thickness.

2. This range corresponds to the sample volume being fully saturated with air or water. The temperature profile was relatively insensitive to this range (< 0.9 °C)

Temperature distribution results are shown in Figure 3. A 3D simulation of the temperature distribution through the sample space is shown in Figure 3(a) for the case when the coolant mixture is at -25 °C and the sample is fully water-saturated. The external temperature of the sample holder is consistently above 20 °C, which is adequate for temperature control of the surrounding magnet. The sample can readily reach temperatures down to -5 °C. Figure 3(b) shows the mean sample temperature, as predicted by the simulation platform, as a function of the coolant temperature recorded at the glycol bath. (Note that the coolant temperature will rise prior to entering the sampler holder cooling tube – this is minimised to less than 5 °C via extensive insulation on the supply line.) Validation measurements of the sample temperature were also performed as a function of coolant temperature using a RS PRO Digital Thermometer inserted into the sample volume of the holder through one of the injection ports (this was done outside of the magnet environment). The corresponding data are also plotted in Figure 3(b) – there is excellent agreement with the simulation predictions across the temperature range considered with a maximum discrepancy of 0.8 °C.

Figure 3 (a) Thermal simulation using 3D FEM model of the sample holder using a coolant temperature of -25 °C. (b) Sample temperature versus coolant temperature – both as predicted by the simulation and via measurement with a thermocouple located in the sample volume.

Figure 4 presents the results obtained from the mechanical simulation. Figure 4(a) shows the equivalent stress in the holder (in 3D) for the maximum working conditions (pore fluid pressure 100 bar, coolant fluid temperature -25 °C) - the highest equivalent stress generated is 47.8 MPa. To assess the mechanical integrity, the ratio between the tensile yield strength of the relevant material (reported in Table 1) and the equivalent stress was calculated (hereafter referred to as the ‘safety factor’). The mean safety factor for the various sample holder components is reported in Figure 4(b) as a function of pressure for a cooling fluid temperature of -25 °C. In all cases and at all locations the safety factor exceeded a value of 2.5. In terms of elastic properties, PEEK and its composites are regarded as being comparatively susceptible.⁶⁰ Using the 3D analysis, the resultant elastic strain in the sample holder assembly were compared against the elongation-at-break parameter for each material (as reported in Table 1) - this property reflects the ability of polymers to resist changes of shape without crack initiation.⁶² The 3D equivalent elastic strain distribution is shown in Figure 4(c) for the maximum working conditions (100 bar, -25 °C) – the maximum strain value was 0.011 mm mm⁻¹ which occurs in the contact zone between the main holder body and the end-caps. The mean value of elastic strain is expressed as a % in Figure 4(d) as a function of pressure for the various holder components – these are consistently lower than the elongation-at-break parameters listed in Table 1.

Figure 4. Structural analysis of the sample holder assembly using the 3D FEM model. (a) Equivalent stresses, according to Von Mises yield formulae. The maximum stress developed is 47.8 MPa at -25°C and 100 bar. (b) Safety factor as a function of pressures for the various components. (c) Equivalent elastic strains of the sample holder. The maximum strain was 0.011 mm mm⁻¹, which represents a structural deformation of 0.1mm. (d) Equivalent elastic strain of the sample holder components as a function of pressure.

3.4 NMR Methods Used

A variety of interleaved NMR and MRI methodologies were employed to systematically monitor gas hydrate formation and dissociation processes in the glass ballotini packing contained within the new hydrate sample holder:

- (i) Standard simple free induction decay (FID) measurements were used to determine the saturations of the different phases (water, hydrocarbon gas, and hydrate) in the ballotini packing as well as the mean value of T_2^* for the NMR signal bearing species.

- (ii) A standard CPMG pulse sequence²⁷ was used to periodically determine the total signal intensity (from all ^1H containing fluids in the ballotini packing) as well as the probability distribution of T_2 relaxation times in the sample (which is related to the pore size distribution).
- (iii) MRI measurements, specifically those using the Single Point Ramped Imaging with T_1 Enhanced (SPRITE)³⁵ pulse sequence, were applied in 1D along the sample axis to determine the fluid content profile as hydrate formation and dissociation proceeded.

The experimental parameters employed in the CPMG and SPRITE acquisitions are summarised in Table 2.

Table 2. NMR and MRI measurement parameters

CPMG PULSE SEQUENCE			
90° pulse length (μs)	14.4	Number of averages	16
180° pulse length (μs)	29.5	Echo time (μs)	2000
Relaxation delay (s)	15	Number of echoes	4096
1D SPRITE MRI			
RF pulse length (μs)	1.5	Total number of pixel in profile	64
RF pulse flip angle (deg)	9	Resolution (mm)	1.7
Encoding time (μs)	94	Repetition delay (s)	3
Field of view (cm)	10.7	Number of averages	64

3.5 Experimental Campaign

Initial testing of the assembled equipment utilised the formation and subsequent thawing of ice at atmospheric pressure in the water-saturated ballotini packing in the sample holder (the water content of the packing was gravimetrically determined to be 20 ml) whilst sequentially executing the NMR measurements detailed above. Average sample temperatures of 20, 4.0, 0.5, and -2.5 °C were systematically studied by varying the temperature of the coolant mixture. Ice thawing was then realised by increasing the sample temperature back to 20 °C.

Hydrate formation was then monitored in the water-saturated glass ballotini in two subsequent series of experiments using (i) CO_2 and (ii) a mixture of 0.68 CH_4 + 0.32 C_2H_6 (mole fraction basis); water was always the limiting reactant with the relevant gas in excess.

Water was displaced from the saturated glass ballotini packing by flowing the relevant hydrate former fluid at low pressure from above, with water allowed to freely drain from the bottom of the sample holder. In both cases, this resulted in a reduction of the water saturation from 100% to 44% (9.0 ml of water retained). In the case of the CO₂ displacement, the pressure was then increased to 40 bar and maintained at this value throughout the experiment. Whilst repeatedly executing the series of NMR/MRI measurements detailed above, the mean sample temperature was gradually changed according to the following profile: 20 °C, 3.5 °C, 0 °C, -2.2 °C, 3.5 °C and 20 °C, respectively. This entire measurement campaign was then repeated using the CH₄ + C₂H₆ mixture as the hydrate former at a pressure of 60 bar with the following temperature profile: 20 °C, 3.5 °C, -2.2 °C, 3.5 °C and 20 °C. The conditions of these various measurement points are summarised in Figure 5 relative to their respective hydrate phase envelopes: the low temperature measurements are all comfortably within the hydrate forming region.

Figure 5. Hydrate phase equilibrium diagrams for a mixture of CH₄ /C₂H₆ (molar fractions $x_{CH_4}=0.68$ and $x_{C_2H_6}=0.32$) and for pure CO₂, as calculated using Multiflash™ (KBC Advanced Technologies, UK). Experimental measurement points for both CH₄/C₂H₆ (◇) and CO₂ (□) are also shown. The vertical dashed lines indicates the freezing point in the absence of dissolved gas. In the case of CO₂ saturation of the aqueous phase this results in a freezing point depression of 1.5 °C.

3.6 Calculation method for phase saturations

Phase saturations (water (S_w), gas (S_g), and hydrate (S_{hyd})) were directly determined *in situ* using the following series of mass balance equations:

$$HI_w S_w + HI_g S_g = I_{\text{NMR}} \quad (5)$$

$$(\eta_w^{t=0} - \eta_w) - N\eta_h = 0 \quad (6)$$

$$S_w + S_g + S_{\text{hyd}} = 1 \quad (7)$$

where HI is the hydrogen index of the phase denoted by the subscript. I_{NMR} is the NMR signal intensity normalised to the signal intensity for the fully water saturated glass ballotini sample ($S_w=1$), corrected for the influence of sample temperature. $\eta_w^{t=0}$ is the initial number of moles of water when $t = 0$, prior to gas hydrate formation; η_w and η_h are the numbers of moles of water and hydrate, respectively. N is the hydration number, whose value depends on the hydrate former molecule. The value reported by Subramanian et al.⁶³, $N = 6.62$, is used for the $\text{CH}_4/\text{C}_2\text{H}_6$ hydrate whilst a value of $N = 6.0$ is used for the CO_2 hydrate.⁶⁴

4. RESULTS AND DISCUSSION

4.1 Ice validation measurements.

Figure 6 shows the interleaved FID and CPMG NMR signal intensities (normalised to the intensity at the point of ice nucleation) for a fully saturated glass ballotini sample, as well as the mean T_2^* and T_2 relaxation times, as a function of time through the full freeze-thaw cycle. The corresponding mean sample temperature is also shown. In both cases the increase in NMR signal up to 7 hours can be attributed to the Boltzmann effect⁶⁵ as the temperature is progressively decreased. Ice nucleation is clearly evident at 7 hours (after approximately two hours of supercooling – note NMR signal is received only from the liquid water phase) leading to rapid ice growth and consequential loss of NMR signal via both measurement protocols (CPMG and FID). Ice formation is complete after approximately 4 hours; the system is clearly heat transfer controlled. Given the thermal mass of the sample holder and the ballotini, using the 3D FEM model and the latent heat associated with ice formation we estimate that a mean overall sample temperature rise of $\sim 0.1^\circ\text{C}$ is to be expected. Residual signal is evident but is less than 2% of the original signal intensity – this will be discussed below. Increasing the temperature back to 20°C restored the expected NMR signal intensities.

The mean T_2^* is constant until the onset of nucleation at which point it increases substantially before decreasing precipitously as ice formation nears completion. T_2^* is very sensitive to

background magnetic field gradients due to susceptibility differences: these are greater for water-silica as opposed to water-ice. Presumably water-ice interfaces significantly influence the T_2^* during initial ice growth, but water-silica interfaces dominate near the end. In contrast, the mean T_2 is observed to marginally decrease as temperature is sequentially lowered before decreasing significantly and more rapidly as ice growth occurs.

Figure 6. Ice generation and thawing test. Evolution of the (a) FID and (b) CPMG signal intensity and the mean values of the transverse relaxation times, T_2^* and T_2 , respectively.

More instructive, however, is to consider the evolution in the distribution of T_2 relaxation times. These are shown in Figure 7(a) as a function of time. Two distinct populations are evident—these are converted to an approximate pore size using Eq. (4) and a ρ_2 value of 28.5 $\mu\text{m s}^{-1}$.^{66, 67} The rate of ice formation (loss of signal) in both populations is approximately the same with the larger peak trending to slightly smaller T_2 values (greater confinement due to ice formation albeit the effect is minor). The small amount of residual water (~1.5 wt%, 0.3 ml) present once ice formation is complete is located in both peaks. The distributions were restored once the ice thawed. Figure 7(b) shows the signal distribution from the liquid water phase as a function of axial position and time. This distinctly shows that the residual water (once ice formation is complete) is located at both extremities of the ballotini packing in contact with the end caps. This very small amount of fluid is presumably not below 0 °C in this specific location – its relatively small size is however reassuring. The data in Figure 6 and Figure 7 provide a

reasonable reference against which to compare the hydrate formation experiments that are now detailed.

Figure 7. (a) Evolution of T_2 relaxation time distributions (and estimated pore size distribution) and (b) 1-D SPRITE profiles during ice generation and thawing in glass beads in the core holder. Approximately 98% of the available water turned into ice. Ice formation and thawing process occurred similarly in all pores within the ballotini packing.

4.2 CO_2 Hydrate Formation and Dissociation

After these ice validation experiments, the equivalent NMR and MRI measurements were conducted to monitor CO_2 hydrate formation and dissociation. The phase saturations as a function of time, calculated using equations 5-7, are shown in Figure 8. The pressure was kept at 40 bar throughout the CO_2 hydrate formation and dissociation process. In this experiment, the NMR signal is solely provided by the liquid water content.

Figure 8. Phase saturations during the CO₂ hydrate formation/dissociation experiment. The S_{hyd} increased to 50.4% when the temperature decreased to 3.5 °C at 20 hour. Fluid saturations, S_w and S_{CO_2} , were 1.9% and 47.7% respectively. From 0.9 to 22.8 hour, the hydrate phase volume increased by an average rate of 0.008 ml min⁻¹.

Following a reduction in temperature from 20 °C to 3.5 °C, the initial water content rapidly decreased as the hydrate formation proceeded – this reached completion in ~25 hours and shows three distinct kinetic regions (rapidly between 0.9 and 2 hours, comparatively slowly between 2 and 19 hours and very slowly between 19 and 25 hours). These observations are broadly consistent with those reported by, for example, Yang et al.⁶⁸ who observed CO₂ hydrate formation in ballotini packings at similar conditions. Only the last region presents a kinetic rate that is not constant, consistent with diffusion-limited hydrate formation control. From the water saturation value S_w , approximately 25% of the water is converted to hydrate during the initial growth phase (up to 2 hours), and approximately 95% overall (after 25 hours). The initial hydrate growth rate up to 2 hours was 0.022 ml/min, which corresponds to a fractional rate of $1.1 \times 10^{-3} \text{ min}^{-1}$ in terms of hydrate saturation. This then reduced to 0.006 ml/min ($3 \times 10^{-4} \text{ min}^{-1}$ in terms of hydrate saturation) and an average of $8.47 \times 10^{-5} \text{ min}^{-1}$ during the final diffusion-controlled region. Cheng et al.⁶⁹ observed an initial fractional rate of $1.6 \times 10^{-3} \text{ min}^{-1}$ when performing a similar measurement; in good agreement with our data. Yang et al.⁷⁰ observed an average fractional rate of $3.2 \times 10^{-3} \text{ min}^{-1}$ for CO₂ hydrate formation in partially saturated 100 µm ballotini whilst Yang et al.⁷¹ observed an average fractional rate of $2 \times 10^{-4} \text{ min}^{-1}$ averaged over thirty hours of hydrate formation for a full saturated sand sample; again these are broadly consistent with our results.

The residual S_w value of 1.9% after hydrate formation (when the temperature was 3.5 °C) was subtly reduced to 0.83% and 0.2% when the temperature was reduced to 0 and -2.2 °C, respectively. However the reduction from 0.83% to 0.2% is likely to reflect the formation of ice in the residual water as the S_w value is restored upon elevation of the temperature back to 3.5 °C. As discussed below, the residual 0.2 % is located at the periphery of the sample holder. Note the algorithm used to allocate phase saturations from the NMR signals acquired would result in ice being erroneously allocated to the hydrate phase, as is evident in [Figure 8](#). After approximately 115 hours the sample was warmed and the hydrate was observed to dissociate through the return of the water saturation signal. Due to temperature gradients within the cell during warming it wasn't possible to compare the dissociation temperature with the expected hydrate equilibrium.

[Figure 9\(a\)](#) shows the time-resolved T_2 (and estimated pore size) distribution for the residual water. The corresponding 1D axial profiles of residual water saturation are shown in [Figure 9\(b\)](#). In [Figure 9\(a\)](#), consistent with the ice formation experiment, two peaks are evident, albeit that they are less distinct. Preferential earlier CO₂ hydrate formation is clearly evident in the larger pores; the distribution is fully restored upon hydrate dissociation. With respect to [Figure 9\(b\)](#), the effect of the initial drainage process prior to sample cooling is immediately obvious in that it has resulted in greater water accumulation in the lower portion of the ballotini packing. Note that throughout the experiment, no pressure drop was observed across the sample holder indicating that the gas phase remained well connected. Initial hydrate formation is distinctly more rapid in the bottom of the sample holder (as shown in [Figure 9\(c\)](#)). This we attribute to the significantly larger water saturation, resulting in a larger local thermal conductivity. This is consistent with the observation of heat transfer control as discussed above. Residual water is observed to be evenly distributed through the ballotini packing upon the completion of hydrate formation (~25 hours). The residual water left at sub-zero temperatures (commencing after 67 hours) is again observed to form at the axial edges of the sample volume, consistent with the ice validation experiments discussed above.

Figure 9. (a) Evolution of T_2 relaxation time (and approximate pore size) distributions and (b) 1-D SPRITE MRI profiles of residual water saturation during the CO₂ hydrate formation/dissociation experiment. (c) Based on Figure 9(b), the change in hydrate saturation in the bottom and top 40% of the sample holder as a function of time.

4.3 $\text{CH}_4 + \text{C}_2\text{H}_6$ Hydrate Formation and Dissociation

Figure 10 shows the phase saturations (water, gas and hydrate) through the hydrate formation /dissociation experiment conducted using a mixture of 0.68 $\text{CH}_4 + 0.32 \text{C}_2\text{H}_6$ (mol fraction) in the partially water saturated glass ballotini packing as a function of time. The temperature profile in the sample is superimposed. The pressure was kept at 60 bar throughout the experiment. In contrast to the previous experiments discussed above, it is important to highlight that NMR signal in these measurements arises both from the water and the gaseous hydrocarbon content. The sample temperature was reduced from 20 °C to 3.5 °C at 5.7 °C/hour. In this case hydrate formation commenced at a temperature of approximately 11 °C. The mean hydrate formation rate was 0.004 ml/min ($2.05 \times 10^{-4} \text{ min}^{-1}$ in terms of hydrate saturation with an initial rate of $1.17 \times 10^{-4} \text{ min}^{-1}$ and a maximum rate of $6.67 \times 10^{-4} \text{ min}^{-1}$) – this rate is within the ranges observed by Zhang et al.⁷² ($6.6 \times 10^{-5} - 7 \times 10^{-4} \text{ min}^{-1}$) and Zhang et al.⁵⁵ ($1.31 \times 10^{-4} \text{ min}^{-1}$) albeit both used pure methane but for a similar particle size porous media host and initial water saturation. The hydrate formation curve presents a number of complex transitions, most prominently a comparatively slow initial period before a fast formation rate which has been observed previously for mixed gas compositions as demonstrated in literature.^{73,74} It has also been observed to occur in studies with pure methane hydrate⁷⁵ and is often associated with a change (increase) in interfacial area between the gas and aqueous phase that results from the earlier hydrate formation. Figure 10 shows that residual water saturation was 1.3% when the hydrate formation was complete; this residual water was found to freeze upon the imposition of sub-zero temperatures. After approximately 115 hours the sample was heated and the initial water saturation signal returned fully.

Figure 10. Phase saturations during the hydrate formation/dissociation experiment using methane and ethane (molar fractions $x_{CH_4} = 0.68$ and $x_{C_2H_6} = 0.32$).

Figure 11 shows the corresponding T_2 relaxation time distributions as well as 1-D MRI SPRITE profiles for hydrate formation and dissociation as a function of time from this methane + ethane mixture. In agreement with the CO_2 hydrate data presented above, two distinct T_2 populations are evident – however these are a combination of the original pore size distribution convoluted with the different fluids providing signal: residual water and the hydrocarbon gas. Consequentially allocation to a specific pore size is not possible although the following observations can however be made. Once hydrate formation commenced, signal loss occurred from both peaks whose mean T_2 values remained essentially unchanged. A single peak was left when hydrate formation was complete – this was evenly distributed through the packing and resulted from the hydrocarbon gas content. Preferential formation of hydrate in the lower region of the packing is evident and results in a comparatively flat signal profile that gradually decreases. Future work will focus on deconvolution of this rich T_2 data from both phases via the acquisition of 2D T_2 - D data (where D is the self-diffusion coefficient), as well as on delivering a more homogeneous initial water saturation in the vertical direction.

Figure 11. (a) Evolution of T_2 relaxation time distributions and (b) 1-D SPRITE profiles during the gas hydrate formation/dissociation experiment using a methane and ethane mixture (molar fractions $x_{\text{CH}_4} = 0.68$ and $x_{\text{C}_2\text{H}_6} = 0.32$).

5. CONCLUSIONS

A novel hydrate sample holder has been constructed that is compatible with benchtop NMR/MRI hardware typically applied for rock core analysis. The unique central cooling channel operating at ambient pressure allows temperature to be controlled without affecting the operation of the magnet system. Mechanical integrity and the temperature distribution through the sample holder was investigated using 3D FEM and found to be satisfactory over the process conditions required. By way of demonstration, hydrate formation and dissociation in a partially saturated random packing of glass ballotini was successfully performed using both CO_2 and a mixture of CH_4 and C_2H_6 as the hydrate formers. In these experiments phase saturations (liquid water, gas, hydrate), pore size distributions and axial concentration profiles (both of the residual unsolidified water) were quantified through a hydrate formation-dissociation cycle. Future work will consider the use of more sophisticated multi-dimensional

T_2 - D measurements to better resolve the signal contribution from the residual water and the hydrocarbon gas/fluid phase, and detail a series of experiments using these techniques together with the hardware developed to monitor the gradual replacement of CH_4 hydrates by CO_2 in a range of porous media support structures.

ACKNOWLEDGEMENTS

This work was funded by the Australian Research Council through Discovery Project: DP170101108.

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