KINETIC STUDY OF METHANE HYDRATE FORMATION IN A
BED OF SILICA SAND PARTICLES USING MAGNETIC
RESONANCE IMAGING

by

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ABSTRACT

This thesis studies the formation and decomposition of methane hydrate crystal in an unconsolidated bed of silica sand particles. Hydrate processes were visualized by taking advantage of the $^1$H magnetic resonance imaging technique, and the integrated intensity of magnetic resonance images was used to quantify the rate and kinetics.

For all of the experiments, the initial pressure was 8 MPa and the temperature was kept constant at 1°C. Beds composed of 2 grams of sand were saturated with different amounts of water (0.44, 0.33, 0.22 and 0.11 mL) in order to examine the effect of water content of the bed on the kinetics of hydrate formation in porous media. Also, the effect of particle size was investigated by forming hydrate in beds with different particle size ranges (210-297, 125-210, 88-177 and <74 µm).

It was found that the hydrate formation process in a bed of silica sand particles can be divided into three stages: induction time, non-uniform growth and uniform growth. During the first stage, methane molecules dissolved and diffused in water. After formation of the first crystals of hydrate at the end of the induction period (nucleation point), hydrate formation proceeded through a combination and competition between nucleation and growth, and multiple nucleation occurred. During the last stage, no obvious nucleation was observed and hydrate formation continued only through the growth of the crystals which had already been formed during the previous stages.

The rate of hydrate formation was found to be faster in beds with smaller particles and lower water content.
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To my parents

and my brother
1 INTRODUCTION ON GAS HYDRATES

1.1 What is gas hydrate?

Gas hydrates (more precisely, clathrate hydrates) are ice-like crystalline compounds which have the capability of storing small guest molecules (known as hydrate former species) inside their well defined cages of hydrogen-bonded water molecules (known as host lattice). They form under favorable thermodynamic conditions; usually high pressure and low temperature, when water combines with hydrate former molecules and encages them (Davidson 1973; P. Englezos 1993; Kvenvolden 1993; Sloan 2003; Y. F. Makogon, Holditch, and T. Y. Makogon 2007). CH₄, C₂H₆, C₃H₈, H₂, N₂, CO₂ and tetrahydrofuran (THF: C₄H₈O) are examples of well-known hydrate formers.

![Figure 1.1. A methane molecule trapped in the small cage of sI hydrate (5₁₂; pentagonal dodecahedron)](http://www.hydratech.bham.ac.uk/introhydrates/intro1.htm)

It should be noted that there is no chemical bond between guest and host species and physical interactions that are responsible for holding the structure together are Van der Waals forces and sometimes weak, transient hydrogen bonds. The empty water network is thermodynamically unstable and it is the occupancy of cages by hydrate former molecules that leads to stabilization.
Figure 1.1 illustrates a methane molecule trapped in the small cage of structure I hydrate which will be introduced in the next section.

1.2 Hydrate structures

Depending on the size of the hydrate former molecule and geometrical constraints, the hydrogen-bonded water molecules form specific structures. There are three well known structures for hydrates, namely structure I (Von Stackelberg and Muller 1951), structure II (Claussen 1951) and structure H (J. A Ripmeester et al. 1987). They are basically different in geometry and size of the cages as well as number of water molecules participating in building the unit cell.

Table 1.1 summarizes the number and types of the cages and also the number of water molecules for each structure. The common $5^{12}$ cavity among these structures is called the pentagonal dodecahedron which consists of 12 pentagonal faces (Figure 1.1). Under normal condition, each cavity can be occupied by one molecule of hydrate former with a size at least equal or less than the diameter of the cavity. For instance, CH$_4$, C$_2$H$_6$, Xe, CO$_2$ and H$_2$S form sI and N$_2$, O$_2$ and THF form sII. sH is different from two other structures in the sense that it needs larger molecules, like methyl cyclohexane or t-butyl ether, to fill its large cavity in addition to a help guest, such as CH$_4$ or H$_2$S, to occupy the medium and/or small cages in order for stabilization and preventing the structure from collapsing.

Two practical parameters frequently used in hydrate literature are hydration number and cage occupancy. The former is defined as the ratio of the number of water molecules to that of hydrate former in a unit cell of hydrate. For instance, methane forms sI and each methane molecule can ideally occupy two small and six large cages, therefore:
\[ N_H = \frac{46}{6 + 2} = 5.75 \]

Table 1.1. Hydrate structures (adapted from P. Linga 2009, with permission from the author)

<table>
<thead>
<tr>
<th>Cavity type [average cavity radius, nm]</th>
<th>Structure (Formula)</th>
<th>Repeating Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Small (S)</td>
<td>Medium (M)</td>
<td>Large (L)</td>
</tr>
<tr>
<td>[0.395]</td>
<td>-</td>
<td>[0.433]</td>
</tr>
<tr>
<td>[0.391]</td>
<td>-</td>
<td>[0.473]</td>
</tr>
<tr>
<td>[0.391]</td>
<td>[0.406]</td>
<td>[0.571]</td>
</tr>
</tbody>
</table>

However, this is not always the case, because methane rarely occupies all small and large cages. So, cage occupancy is defined to reflect this fact and obviously has a value between zero and one. It is defined as the ratio of actual number of guest molecules occupying each cage to the case where cages are fully filled. Cage occupancy and hydration number are closely related and lower cage occupancy leads to higher hydration number. For example, the occupancy of small and large cages of methane hydrate at equilibrium conditions of 1°C and 2.9 MPa are 0.88 and 0.97, respectively (Sloan 1996). Hence, the hydration number would be:

\[ N_H = \frac{46}{(2 \times 0.88) + (6 \times 0.97)} \approx 6.1 \]
The difference in cage occupancy (incomplete filling of the cages) under different pressure and temperature conditions causes hydrate to be considered as non-stoichiometric substance.

1.3 Hydrate partial phase envelope

Figure 1.2 shows the equilibrium pressure and temperature at which methane hydrate forms upon availability of water and methane. Having accurate information about the equilibrium formation conditions of hydrate plays a key role in designing processes that are related to hydrates. The equilibrium curve in blue represents a typical partial phase envelope of hydrates.

![Partial phase equilibrium diagram of the methane hydrate. The overall shape of the equilibrium curve is the same for other hydrate formers, data from (Sloan 1996)](image)

The points on the solid blue curve determine the pressure and temperature conditions under which the two phases of liquid water and hydrate former are at equilibrium with an infinitesimal amount of solid hydrate phase. Above this curve is the hydrate stability zone whereas below it is the non-hydrate zone and hydrate decomposes to liquid water and hydrate former.

Driving force for hydrate formation is defined as deviation from equilibrium. It can be based either on pressure or temperature. Suppose the red point in Figure 1.2 has a pressure of $P$ and
temperature of $T$. Therefore, the intersections of red horizontal and vertical arrows with equilibrium curve will respectively have a pressure and temperature of $(P, T_{eq})$ and $(P_{eq}, T)$. So, driving force of hydrate formation in terms of pressure (over pressure) would be $\Delta P = P - P_{eq}$ and in terms of temperature (subcooling): $\Delta T = T - T_{eq}$.

### 1.4 History and significance of gas hydrates

The first discovery of hydrates, as a scientific curiosity in laboratory, dates back to 1811 when Davy observed the hydrates of chlorine (oxymuriatic acid). Over the next 125 years, the interest in hydrates was mainly academic and scientists were trying to identify more new hydrate formers, and to measure their formation pressure-temperature conditions. In 1934, Hammerschmidt reported plugging of the natural gas transmission lines by hydrates and that elucidated the importance of hydrates to the oil and gas industry and initiated a new research era in this field: **gas hydrate inhibition**. The next big event was the detection of hydrates in nature by Russians in 1960’s.

A list of scientific achievements during the early years of the development of hydrate science is given in Table 1.2.

Overall, attention towards hydrate has been changed over the years and now they are considered as a potential energy source for future, a factor in global climate change and a submarine geohazard (Kvenvolden 1999).
Table 1.2. The early international contributions on the hydrate science (personal communication with Dr. John A. Ripmeester)

<table>
<thead>
<tr>
<th>Scientist</th>
<th>Year (country)</th>
<th>achievement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Davy</td>
<td>1810 (U.K.)</td>
<td>reported chlorine in water froze more easily than water itself, thus identifying the first clathrate hydrate</td>
</tr>
<tr>
<td>Faraday</td>
<td>1823 (U.K.)</td>
<td>reported chlorine hydrate had 10 water molecules for every Cl$_2$ molecule</td>
</tr>
<tr>
<td>Lowig</td>
<td>1828 (Germany)</td>
<td>reported bromine hydrate</td>
</tr>
<tr>
<td>De la Rive</td>
<td>1829 (Switzerland)</td>
<td>discovered SO$_2$ hydrate</td>
</tr>
<tr>
<td>Berthelot</td>
<td>1856 (France)</td>
<td>synthesized first organic hydrates, methyl bromide &amp; chloride</td>
</tr>
<tr>
<td>Wroblewski</td>
<td>1882 (Poland)</td>
<td>discovered CO$_2$ hydrate</td>
</tr>
</tbody>
</table>

**Hydrate research emerged as a distinct discipline; Bakhuis Roozeboom, de Forcrand, Villard devoted most of their research careers to hydrates**

<table>
<thead>
<tr>
<th>Scientist</th>
<th>Year (country)</th>
<th>achievement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Le Chatelier</td>
<td>1884 (France)</td>
<td>applied Clausius-Clapeyron equation to hydrate formation, allowing heat of formation to be derived</td>
</tr>
<tr>
<td>Villard</td>
<td>1888-89 (France)</td>
<td>reported CH$_4$, C$_2$H$_6$ and C$_3$H$_8$ hydrates</td>
</tr>
<tr>
<td>De Forcrand</td>
<td>1890’s (France)</td>
<td>reported existence of double hydrates</td>
</tr>
</tbody>
</table>

**Liquid hydrates are now recognized as a separate species from gas hydrates**

<table>
<thead>
<tr>
<th>Scientist</th>
<th>Year (country)</th>
<th>achievement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Von Stackelberg</td>
<td>1932 (Germany)</td>
<td>initiated 25-year of research on composition and structure of hydrates</td>
</tr>
<tr>
<td>Hammerschmidt</td>
<td>1934 (U.S.)</td>
<td>suggested that hydrate rather than ice forms gas pipeline blockages; led to phase equilibrium studies and procedures to predict solid hydrate formation and recipes for prevention (1940–60; Deaton and Frost, Katz, Kobayashi).</td>
</tr>
<tr>
<td>Nikitin</td>
<td>1936-40 (Russia)</td>
<td>showed rare gases, Xe, Kr and Ar, can be separated by partitioning between solid hydrate and the liquid phase in contact with it</td>
</tr>
<tr>
<td>Wilcox, Carson, and Katz</td>
<td>1941 (U.S.)</td>
<td>developed the first method for estimation of hydrate formation conditions</td>
</tr>
<tr>
<td>Claussen, von Stackelberg, Pauling and Marsh</td>
<td>1951-52 (U.S., Germany, U.S., U.S.)</td>
<td>used X-ray diffraction to show that hydrate structures are clathrates</td>
</tr>
<tr>
<td>Van der Waals and Platteeuw</td>
<td>1957 (Netherlands)</td>
<td>formulated the statistical theory of clathrates, the foundation of most hydrate prediction procedures</td>
</tr>
<tr>
<td>U.S. Office of Saline Water</td>
<td>1960’s</td>
<td>initiated projects on desalination of sea water with hydrates; a new cycle of hydrate structural determinations by diffraction methods (Jeffrey, U.S.)</td>
</tr>
<tr>
<td>Parrish and Prausnitz</td>
<td>1960-70’s</td>
<td>Discovery of gas hydrates in nature. Scientists in the USSR and North America presented evidence for hydrate under permafrost and in offshore marine sediment</td>
</tr>
<tr>
<td></td>
<td>1972 (U.S.)</td>
<td>extended the van der Waals model for gas mixtures and presented the first computer aided algorithm</td>
</tr>
</tbody>
</table>

**Experimental and computational approaches to the science and engineering of hydrates are now in place, allowing rapid progress in knowledge generation on hydrates**
1.4.1 Hydrates as a potential energy source

The foremost component of natural gas hydrates is methane which forms sI. However due to the presence of some larger molecules like ethane, propane or butane, natural gas hydrate are usually found in the form of sII. So, ideally for each 24 moles of natural gas there will be 136 moles of water. Therefore, the equivalent volumetric ratio at standard conditions would be:

\[
\frac{V_{\text{N.G.}}}{V_W} = \left(\frac{n_{\text{N.G.}}}{n_W}\right) \left(\frac{ZRT}{P}\right) \left(\frac{M_W}{\rho_W}\right) = \left(\frac{16 + 8}{136}\right) \left(\frac{1 \times 8.314 \times 273.15/100000}{0.018/1000}\right)
\approx 222
\]

According to Kvenvolden (1993) if one cubic meter of gas hydrate dissociates, it will produce 0.8 m³ of water and 164 m³ of gas at standard pressure and temperature:

\[1 \text{ m}^3 (\text{gas hydrate})_{\text{solid}} + \text{Heat} \rightarrow 0.8 \text{ m}^3 (\text{water})_{\text{liquid}} + 164 \text{ m}^3 (\text{gas})\]

These numbers clearly show the potential of gas hydrate as an excellent candidate for energy source for future. It is not only due to their high methane concentration but also because methane is a relatively clean fuel. It has the lowest carbon to hydrogen ratio among hydrocarbons which means upon combustion it produces less carbon dioxide.

However, methane extraction from hydrate reserves is very challenging. Designing safe decomposition techniques which allow controllable methane recovery has still remained a big challenge. Additionally, although the global amount of trapped methane in hydrates is enormous, hydrate reservoirs are usually distributed over a wide area which makes their tapping very troublesome.

Accurate estimates of the amount of methane trapped in gas hydrates requires understanding of the fundamental aspects of “where-how-why” gas hydrates occur in nature. Natural gas hydrates can be found in two major natural porous environments: on-shore, under the permafrost region
of the earth at subsurface depths ranging from 130 to 2000 m, and off-shore along the continental margins, ranging from 100 to 1100 meters below the sea floor (Collett 2002), where the conditions are suitable for hydrate formation (pressure and temperature as well as the availability of methane and water).

Gas hydrate deposits (GHD) are distributed all around the planet and over 220 GHDs have been discovered (Y. F. Makogon, Holditch, and T. Y. Makogon 2007). Figure 1.3 shows a map of discovered GHDs throughout the world.

Figure 1.3. Map of the discovered GHDs. Reprinted from Y. F. Makogon, Holditch, and T. Y. Makogon (2007) with permission from Elsevier

Five of the best known marine and permafrost hydrate accumulations are located (1) on the Blake Ridge along the southeastern continental margin of the United States, (2) along the Cascadia continental margin off the pacific coast of Canada, (3) near the Nankai Trough off the eastern coast of Japan, (4) on the North Slope of Alaska and (5) in the Mackenzie River delta of northern Canada (Collett 2002).
These sites are detected using different techniques including seismic profile of the Bottom Simulating Reflectors (BSR), and well logging techniques (gamma ray, neutron porosity, chlorine concentration, electrical resistivity) and compressional and shear wave velocity measurements. Existence of hydrate is identified by anomalies in the obtained profile.

As mentioned before, formation of hydrates requires a certain combination of pressure and temperature. The theoretical hydrate stability zone (HSZ) of hydrates can be located by comparing geothermal and hydrostatic pressure gradients (the temperature and pressure profile of the earth or ocean) with the hydrate phase boundary, in which the pressure is converted to depth. Figure 1.4 shows the HSZ both in marine and permafrost. The intersections of the hydrate phase boundary and geotherm/ocean temperature profile determine the two ends of the HSZ.

![Figure 1.4. The hydrate stability zone.](image)

The estimated amount of methane trapped in GHDs ranges from 14 to 34,000 trillion cubic meters (TCM) in permafrost and from 3,100 to 7,600,000 TCM in oceanic sediments (Collett 2002) and the total global estimate is now converged on 15,000 TCM at standard conditions.
The Council of Canadian Academies (2008) reported the data of Milkov (2004) as the global estimate of methane hydrate, 1000-5000 TCM. However, they mentioned that even this stringent estimate is 2 to 10 times larger than the global estimate of the conventional natural gas reserves (4400 TCM) and technically recoverable undiscovered resources. Recalling that the natural gas consumption of the United States in 2008 was 0.65 TCM, further demonstrates that the global estimates of methane in the form of hydrates are indeed significant.

1.4.2 Hydrates as a factor in global climate change and geohazard

Methane is one of the greenhouse gases, which is 20 times more active than the equivalent weight of carbon dioxide over a 100-year time span (Kvenvolden 1993). So, formation and decomposition of natural gas hydrates deposits as big storehouses of methane can significantly influence the global climate. Increase in the temperature of HSZ as a result of global warming can lead to decomposition of hydrates which consequently brings more greenhouse gas to the atmosphere and accelerates global warming through positive feedback. This may lead to the occurrence of a runaway greenhouse effect (RGE) (see Figure 1.5). However, as noted by Kvenvolden (1999), released methane gas experiences several obstacles on its way to reach the atmosphere. Hatzikiriakos and Peter Englezos (1993) assessed the possibility of the occurrence of RGE and found that the temperature at the top of a methane hydrate zone will begin to increase within the next 100 years under the catastrophic scenario of global warming.

Moreover, gas hydrate can act as a geohazard particularly in the ocean where the stability and strength of the ocean floor greatly depends on the presence of hydrates. Dissociation of hydrates in these regions can lead to an enhanced fluidized layer at the base of the hydrate zone, slope
failure, debris flows, slumps (Kvenvolden 1993) and thus collapse of the engineering structures, if they exist at that location.

Figure 1.5. The Runaway greenhouse effect. Reprinted from Peter Englezos and Ju Lee (2005) with permission from the Korean Institute of Chemical Engineering

1.5 Other aspects of gas hydrates

Exclusive properties of hydrates have enabled them to be used in a variety of technological applications. Examples in separation technology include concentrating aqueous organic solutions, desalination, fractionation of gases and liquids, and CO₂ separation from flue gas. Their ability in forming hydrate with some certain molecules in addition to having preference toward a hydrate former over the other has given them this applicability. Moreover, their relatively high energy density has made it feasible to utilize them as a means of gas transportation and storage (P. Englezos 1993).

1.6 Methane recovery techniques

In order to extract methane from gas hydrate deposits, we need to find a way to decompose them by bringing the thermodynamic conditions (pressure and temperature) below the equilibrium curve, to the non-hydrate zone. On this basis, three methods have been proposed (Holder, Kamath, and Godbole 1984):
1. **Thermal stimulation:** The purpose of this method is to raise the temperature (at a constant pressure) until reaching the equilibrium value and then crossing the equilibrium curve. The process pathway is shown by the red horizontal arrow in Figure 1.2.

2. **Depressurization:** In this technique we reduce the pressure (at a constant temperature) to a value below the equilibrium curve in order to enter into the non-hydrate zone. The red vertical arrow in Figure 1.2 shows the path of such process.

3. **Inhibitor injection:** The idea of this method is to shift the equilibrium curve to higher pressures and lower temperatures instead of changing the prevailing pressure/temperature of the hydrate phase. For instance, injection of methanol, as a chemical inhibitor, can move the equilibrium curve to the more severe thermodynamic conditions (higher $P$ and lower $T$). The dashed green arrow in Figure 1.2 illustrates the schematic of this operation.

Unfortunately, each of the abovementioned methods has its own disadvantage. Since hydrate decomposition reaction is highly endothermic ($\sim 55 \text{ kJ mol}^{-1}$ at $273 \text{ K}$ for pure methane hydrate) depressurization might lead to temperature drop, even below $0^\circ \text{C}$ and consequently ice formation, as well as a possibility of hydrate reformation which obviously hampers decomposition. On the other hand, heating and pumping large quantities of hot fluid, such as hot water or steam, in cold regions makes thermal stimulation energetically inefficient and uneconomic. Also, injecting large volume of chemicals, like methanol or glycol, required to alter the equilibrium condition is neither cost-effective nor environmentally friendly. Perhaps, a production technology which enjoys a combination of these techniques may turn into an efficient method of recovery of gas from hydrate reservoirs.
The other major issue that must be taken into account when considering a hydrate reservoir for gas recovery is the flow characteristics of the hydrate containing sediment. Properties such as porosity and permeability play a very crucial role in providing the essential flow of the product of decomposition reaction (water and gas) to the production well.

### 1.7 Thermodynamics and kinetics of hydrates

#### 1.7.1 Thermodynamics

The state of the art of hydrate thermodynamic is satisfactory for most engineering applications and has reached its mature level and as noted by Sloan (2004), prediction accuracy of available models is sufficiently close to the experimental accuracy. The first thermodynamic model for hydrate phase equilibria was proposed by Van der Waals and Platteeuw (1959) based on the statistical thermodynamical approach, often referred to as the solid solution theory to account for the cage occupancies and non-stoichiometric nature of clathrate hydrates (J. Ripmeester and Ratcliffe 1999). It assumes that the free energy difference between hypothetical empty lattice and occupied lattice is $\Delta \mu$ and is related to the cage occupancies by the following correlation:

$$\Delta \mu = kT \sum_{i} v_i \ln(1 - \theta_i)$$  \hspace{1cm} \text{Eq. 1.1}

Where:

$v_i$ is the number of cages of type $i$ per water molecule

$T$ is the absolute temperature

$k$ is the Boltzmann’s constant

$\theta_i$ is the fractional cage occupancy of hydrate former in cage type $i$
Other assumptions are that free energy difference is guest independent and that there is no
guest-guest interaction.

The fractional occupancies are related by a Langmuir adsorption-like expression to the
minimum partial pressure of the guest ($P_D$) under which the hydrate is stable:

$$P_D = \left( \frac{\theta_i}{1 - \theta_i} \right) C_i \quad \text{Eq. 1.2}$$

Where $C_i$ is the Langmuir constant.

A number of modifications were done by different researchers on this simple model to increase
its prediction ability and accuracy and are available in literature (see Koh 2002 and references
therein).

1.7.2 Kinetics

In hydrate jargon, kinetic study refers to the investigation of time dependent changes in hydrate
processes including, but not limited to, gas uptake measurement (number of moles of gas
consumed for hydrate formation), gas release measurement (number of moles of gas released
upon hydrate decomposition), rate of hydrate formation/dissociation, hydrate nucleation/growth
and structural changes. Despite the great progress which has been made so far in
thermodynamic (time-independent equilibrium properties of hydrates), kinetic is still a
challenging topic and an open area of research which needs more fundamental understanding
and further investigation both at macroscopic and microscopic levels.
Hydrate formation is viewed as a crystallization process (Vysniauskas and Bishnoi 1983; P. Englezos et al. 1987; P. Englezos, Kalogerakis, and Bishnoi 1990; Bishnoi and Natarajan 1996) which is known to occur in two steps: Nucleation and Growth.

During nucleation process clusters of water and hydrate former is forming from aqueous solution. These clusters are unstable and may break or grow until reaching the critical size. The clusters of critical size are stable and act as site for further growth which immediately leads to the formation of crystals of hydrate (Bishnoi and Natarajan 1996). The time elapsed until the appearance of the first crystals is called the induction period and is known to be a stochastic (unpredictable) parameter. It is also referred to as nucleation point or turbidity point since the presence of crystals in fluid phase makes it to appear turbid.

Although considering a nucleation event as the predecessor of hydrate crystal growth enjoys a considerable support, it has not yet been fully understood and there are different hypotheses for the nucleation mechanism: Labile cluster nucleation hypothesis (Sloan and Koh 2008), Nucleation at the interface hypothesis (Long 1994) and Local structuring nucleation hypothesis (Birkedal 2009).

\[
\text{aq.soln.} \xrightarrow[\text{Nucleation}]{} \left\{ \text{clusters of water and hydrate former molecules} \right\} \rightarrow \left\{ \text{stable hydrate nuclei of critical size} \right\} \rightarrow \left\{ \text{hydrate crystals} \right\} \quad \text{Growth}
\]

**Figure 1.6. Representation of the hydrate formation as a crystallization process**

The second stage is hydrate growth which does not have the complexity of the nucleation process and, simply, stable nuclei grow as solid hydrates during this period.

Figure 1.7 shows a typical gas uptake curve from a hydrate formation experiment. It can be divided into three events. The first event is induction period (time zero to induction time) in
which molecules of gas dissolve in water. At the end of the induction period nucleation happens and immediately after that hydrate formation (growth) is verified by a catastrophic increase in the consumed number of moles of gas. From this time onwards, hydrate formation continues and the rate gradually decreases. This can be either due to the creation of a solid hydrate layer as a mass transfer barrier at the interface of gas and water phase which considerably slows down the gas diffusion toward the water phase or due to the shortage of one of the reactants (water and/or hydrate former gas) as a result of the progress of the formation reaction.

![Figure 1.7. A typical uptake curve for the hydrate formation from bulk water. Adapted from Sloan and Koh (2008) with permission from Elsevier](image)

Hydrate growth can be modeled by considering the fugacity difference as the driving force (P. Englezos et al. 1987) and the rate of growth per particle can be expressed as below:

$$\left( \frac{dn}{dt} \right)_p = K^* A_p \left( \frac{f_b - f_{eq}}{\text{driving force}} \right)$$  \hspace{1cm} \text{Eq. 1.3}

Where:

$K^*$ is the combined rate constant
\( A_P \) is the surface area of each particle.

\( f_b \) is fugacity of dissolved gas in bulk water

\( f_{eq} \) is the equilibrium fugacity of dissolved gas at the particle surface

On the other hand, hydrate decomposition, as the counterpart of formation, is considered to be a sequence of lattice destruction followed by desorption of gas to the fluid phase (Kim et al. 1987). A similar approach can be implemented to express the rate of decomposition as the following:

\[
- \left( \frac{dn}{dt} \right)_p = K_d A_P \left( \frac{f_{eq} - f_d^V}{Driving\ force} \right)
\]

Eq. 1.4

Where:

\( K_d \) is the decomposition rate constant

\( A_P \) is the surface area of each particle.

\( f_{eq} \) is the equilibrium fugacity of released gas at the particle surface

\( f_d^V \) is the fugacity of the evolved gas phase
2 FUNDAMENTALS AND BASIC PRINCIPLES OF MAGNETIC RESONANCE IMAGING

2.1 Introduction

The Nuclear Magnetic Resonance (NMR) is a very versatile technique which has a broad application in chemical structure determination of materials in all three phases of gas, liquid and solid. It was discovered in the 40’s by physicists (Bloch, Hansen, and Packard 1946; Purcell, Torrey, and Pound 1946); however, it was soon realized to be a very flexible technique and rapidly was applied to other fields of science such as synthetic chemistry, biochemistry, medicine and material science.

A very important and promising advancement in the seventies (Lauterbur 1973) was the realization of the ability of this technique to map the spatial distribution of a particular NMR nucleus in an object via NMR images (Veeman 1997).

NMR imaging has various synonyms. In medicine it is normally called “Magnetic Resonance Imaging” (MRI); however, “NMR Imaging” and “Spatially Resolved Nuclear Magnetic Resonance” are also common. For resolutions up to $100\times100\times1000 \ \mu m^3$ the term “Mini-Imaging” is used and for higher resolutions “Micro-Imaging” or “NMR-Microscopy” is applied (Kuhn 1990).

2.2 Fundamentals and basic concepts of MRI

The fundamentals and physical principles on which the MRI is based are complicated; however, considering some basic concepts of NMR including magnetization, RF pulse excitation, relaxation times, free induction decay, spin-echo sequence and magnetic field gradient could be
very helpful in developing a better understanding of the process (Coates, Xiao, and Prammer 2001).

### 2.3 Magnetization

NMR is based on the magnetic property of many atomic nuclei such as $^1\text{H}$, $^2\text{H}$, $^{13}\text{C}$, $^{15}\text{N}$, $^{17}\text{O}$, $^{31}\text{P}$, etc. Due to an odd number (unpaired) of protons or neutrons they have a net charge on their nucleus. Rotation of this charged nucleus around a certain axis (spinning) generates a magnetic field or magnetic dipole moment ($\vec{\mu}$) which is proportional to the angular momentum ($\vec{J}$). The proportionality constant is called the gyromagnetic ratio ($\gamma$) and is a specific property of each nucleus.

$$\vec{\mu} = \gamma \vec{J} \quad \text{Eq. 2.1}$$

Magnetization is defined as the sum of the individual magnetic dipole moments:

$$\vec{M} = \sum \vec{\mu} \quad \text{Eq. 2.2}$$

In the absence of an external magnetic field, the nuclei are randomly aligned and there is no net magnetization.

As opposed to the macroscopic world where a bar magnet can only have two equilibrium orientations, either parallel (stable situation with lower energy level) or antiparallel (unstable situation with higher energy level) in an external magnetic field, in the atomic world there are $2I + 1$ allowed orientations for a nuclear magnet where $I$ is a property of the nucleus called nuclear spin quantum number (Veeman 1997).
### Table 2.1. Gyromagnetic ratio and nuclear spin quantum number of some important NMR nuclei

<table>
<thead>
<tr>
<th>NMR nuclei</th>
<th>Relative sensitivity (μ/μ₀)</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>¹H</td>
<td>1.00</td>
<td>1/2</td>
</tr>
<tr>
<td>¹³C</td>
<td>1.75 × 10⁻⁴</td>
<td>1/2</td>
</tr>
<tr>
<td>¹⁵N</td>
<td>3.82 × 10⁻⁶</td>
<td>1/2</td>
</tr>
<tr>
<td>¹⁷O</td>
<td>1.11 × 10⁻⁵</td>
<td>5/2</td>
</tr>
</tbody>
</table>

Placing these nuclei in a relatively strong static external magnetic field (B₀z) will exert a torque on them and therefore forces them to rotate about the direction of the external magnetic field according to the Newtonian physics. The precessional frequency (f) of this motion is called *Larmor frequency* and is expressed by the following equation:

\[
f = \frac{\gamma}{2\pi} B₀z \quad OR \quad \omega = \gamma B₀z
\]

Eq. 2.3

Let’s consider ¹H as our nucleus of interest for the rest of the discussion. ¹H has a nuclear spin quantum number of 1/2 and gyromagnetic ratio of 42.58 MHz T⁻¹. It is one of the NMR nuclei which is very widely used in MRI experiments due to its high natural abundance and high sensitivity.

Under thermal equilibrium conditions the number of hydrogen nuclei which align themselves along the external field is greater than those who are in the opposite direction and therefore there will be a net bulk magnetization, M₀, in the direction of the external magnetic field.

### 2.4 RF pulse excitation

After placing the NMR nuclei in a strong external static magnetic field, the next step in performing an MRI experiment is to excite the magnetization from its equilibrium state into the transverse plane.
This is possible through the application of an RF pulse using a special electrical coil which produces an oscillating magnetic field ($B_1$) perpendicular to the external static field. The “resonance” component of Nuclear Magnetic Resonance comes from the fact that this oscillating field has to be in exact synchrony with the NMR nuclei. The reason for that is because once the magnetization vector loses its equilibrium state as a result of excitation it starts to precess at the Larmor frequency and in order to be able to continue excitation the RF pulse must follow the precessing nuclei with the same frequency (Anon. 2009). The tipping angle ($\theta$) of the magnetization is proportional to the magnitude of the oscillating field and duration of the time ($\tau$) over which it is applied and the proportionality constant is again the gyromagnetic ratio.

$$\theta = \gamma B_1 \tau$$  \hspace{1cm} Eq. 2.4

### 2.5 Relaxation times

Imposing a 90° pulse flips the equilibrium magnetization vector to the transverse plane (x-y plane). After turning off the oscillating field, the external static field is still present and under its influence, magnetization starts to precess until it loses its extra energy and reestablishes the equilibrium state.

During this precession the magnetization comes out of the x-y plane and the tip of magnetization vector moves on a converging helical path on the outer surface of a sphere (see figure 2.2 in (Birkedal 2009)).

The magnitude of the longitudinal (projection on z axis) and transverse (projection on x-y plane) projections of magnetization changes exponentially with time. The time constant for the growth of z-component is called the spin-lattice or longitudinal relaxation time ($T_1$) and the time
constant of the decay of x-y component is called the spin-spin or transverse relaxation time ($T_2$). They both are correlated to the mobility of the molecules containing nuclear spins (Kuhn 1990).

\[
\begin{align*}
M_z(t) &= M_0(1 - e^{-t/T_1}) \\
M_{xy}(t) &= M_0 e^{-t/T_2}
\end{align*}
\]

Eq. 2.5

Where,

$M_0$ is the magnitude of the equilibrium magnetization

This special motion of the magnetization vector is very important because according to the Faraday’s law of induction, movement of the transverse magnetization in a closed circuit can induce electrical current. In fact, the signal that we obtain as the response of our system is nothing but this detected induced current.

As a result of the relaxation process the amplitude of this signal decreases as transverse magnetization decays in time and the obtained signal is called Free Induction Decay (FID). Figure 2.1 shows a typical signal in an FID experiment.

![Figure 2.1](image-url)

Figure 2.1. Following a 90° pulse the signal decays as a result of the relaxation and is called the FID (Free Induction Decay) signal. Reprinted from Talagala and Lowe (1991) with permission from John Wiley and Sons

It should be noted that inhomogeneity of the external magnetic field as well as chemical shift effects (spin spin interactions) affect the magnitude of the external magnetic field which is being
sensed by each nucleus. Because of this deviation in the external field the individual nuclear moments precess at different Larmor frequency and therefore lose their phase coherency in x-y plane and consequently the signal decays very much faster.

The common solution for this problem is the application of a $180^\circ$ pulse which forms the basis of the so-called *spin-echo pulse sequence* method in MRI.

### 2.6 Spin-echo pulse sequence

Upon the application of a $180^\circ$ pulse, all of the spins flip around the y-axis and move in exactly the opposite path that led them to dephase. So, they again gradually gain their phase coherency which produces a growing signal in the receiver coil. This shows up as an echo in the detected signal. It should be noted that due to relaxation the magnitude of this echo is smaller than that of the previous signal and therefore the application of the $180^\circ$ pulse can be repeated until the complete relaxation of transverse magnetization. In order to initiate another sequence we need to apply a new $90^\circ$ pulse to excite the magnetization again.

![Figure 2.2. Creation of a spin-echo signal using 180° pulse. Reprinted from Talagala and Lowe (1991) with permission from John Wiley and Sons](image)
2.7 Magnetic field gradient

The key concept and heart of the MRI which gives it the ability to spatially resolve the NMR nuclei is the utilization of magnetic field gradients. The applied gradients are usually constant over a specific time period which means their magnitude is linearly changing with position. Therefore, the total magnetic field sensed by each nucleus would be the sum of the external field and the gradient field:

\[ B_z = B_{0,z} + B_z(x) \hspace{1cm} \text{\&} \hspace{1cm} \frac{dB_z(x)}{dx} = G_x: \text{const}. \]

Eq. 2.6

Hence, according to the Larmor’s equation, the frequency at which each nucleus precesses would depend on position:

\[ B_z = B_{0,z} + G_x x \Rightarrow \omega(x) = \omega_0 + \gamma G_x x \]

Eq. 2.7

Gradient coils are specially designed to produce these gradient fields.

The idea of using magnetic field gradients, but with different approaches, can be utilized to spatially resolve the NMR nuclei in an object in all three dimensions. Slice selection, phase encoding and frequency encoding are the common procedures used in MRI.

2.7.1 Slice selection

In order to do a three dimensional imaging experiment, instead of exciting all the nuclei, we need to do a selective excitation which excites the equilibrium magnetization of a narrow slice of NMR nuclei within the object without interacting with the nuclei outside of this thin slice.

This requires that the profile of the excitation pulse in the frequency domain approaches a rectangle in order to uniformly excite the nuclei within the slice and negligible excitation
outside it. The Fourier transform of the \textit{sinc} function extended for a reasonable amount of time has a well-defined rectangular shape. Such an RF pulse is shown in Figure 2.3.

![Figure 2.3. A truncated sinc function pulse in time domain (top) which gives a reasonable rectangular profile in the frequency domain (bottom) in order to uniformly excite a narrow slice of NMR nuclei in an object with negligible interactions with nuclei outside this region. Reprinted from Talagala and Lowe (1991) with permission from John Wiley and Sons](image)

Now, if we have a gradient along the \( z \) axis we can excite a narrow band which its thickness depends on the magnitude of the gradient applied:

\[
G_z = \frac{dB_z}{dz} : \text{const} \Rightarrow \Delta B_z = G_z \Delta Z \Rightarrow \Delta F = \frac{2\pi}{\gamma} G_z \Delta Z \Rightarrow \Delta Z = \frac{2\pi}{\gamma G_z} \Delta F \quad \text{Eq. 2.8}
\]

This procedure can subsequently be followed by performing frequency encoding and phase encoding schemes in order to implement the \( x \) and \( y \) spatial information on the response of the system as well. The reader is referred to Talagala and Lowe (1991) for detailed explanation on these schemes.
2.8 The obtained signal

The obtained signal as the response of the system, \( S(t) \), is the sum of the contribution of all individual spins:

\[
S(t) = \int \int \rho(x, y)e^{-i(k_xx + k_yy)}dxdy = FT[\rho(x, y)] \Rightarrow \rho(x, y) = FT^{-1}[S(t)]
\]

Eq. 2.9

Where \( k_x = \gamma G_x t \) and \( k_y = \gamma G_y t \) and are called spatial frequencies.

As can be seen, the spin density (\( \rho \)) can be obtained by performing an inverse Fourier transform on the obtained signal and then properly assigned to its corresponding point in x-y plane (I. L. Moudrakovski, Ratcliffe, and J. A. Ripmeester 2002).
3 LITERATURE REVIEW AND RESEARCH OBJECTIVES

The formation of gas hydrates in natural porous environments (sediment in permafrost and the ocean) is a complex process and it still remains a big question on how nature mediates hydrate processes. Since the recovery of natural gas hydrate involves difficulties and expenses, samples of natural gas hydrates are not readily available for research work (Siriwardane and D. H Smith 2002). There is also the concern whether or not the recovered sample properly represents the hydrates in a reservoir as there are changes in pressure and temperature during the recovery operation.

Therefore, proper inspection of natural gas hydrates requires comprehensive laboratory investigations of hydrates in porous media. Kinetics and fluid transport in hydrate-containing sediments are among the subjects that need further examination. So far, a huge amount of work has been devoted to the investigation of hydrate from bulk water. However, mechanisms of formation and decomposition of hydrates in porous media and also their interactions with host sediment are not as yet very well understood.

The information gathered from hydrate studies in porous media can be beneficial in a variety of aspects including the provision of more accurate data for hydrate detection in nature, development of a safe gas recovery technique, and improving and extending the existing analytical/numerical models for hydrates.

So, the literature review of this thesis mainly focuses on the works done on the investigation of hydrates in porous media with a particular emphasis on the application of MRI in studying the kinetic.
3.1 Hydrate in porous media

Cheng and Pinder (1976) examined consolidation of sand by forming hydrates of freon-11 in the interstices of a sand bed. They assumed consolidation was complete when the sample (sand bed+hydrate) could withstand at least a pressure gradient of 1357 kPa/cm. The conclusions of their work were: (a) A subcooling of about 5 to 6 °C is needed for effective consolidation and (b) After the injection of hydrate former it takes considerable time for hydrates to grow and block the pores.

Stoll and Bryan (1979) were among the first who formed hydrates in porous media to study the changes in physical properties of hydrate containing sediments. Interestingly, they observed a decrease, rather than increase, in the thermal conductivity of sediment upon hydrate formation. Also, acoustic wave velocity measurements confirmed conversion of the water-bearing sediment to a stiff elastic mass after formation of a sufficient amount of hydrates.

Mechanical strength test of Parameswaran, Paradis, and Handa (1989) on soil samples containing THF hydrate showed that the compressive strengths of the samples were higher than that of frozen sand containing ice.

Tohidi et al. (2001) studied formation and decomposition of gas hydrate in a synthetic glassy micromodel (grain size range: 70-500 µm) of porous media in order to visually observe the interaction between hydrates and porous media. They formed hydrate from three different hydrate formers: THF (water soluble), CH₄ (free gas), CO₂ (dissolved gas). In all cases, hydrates tended to concentrate in the center of the pores and did not adhere to the grain surfaces due to the presence of a thin layer of free water. Cementation only occurred in regions with small grains or where the hydrate saturation was large.
The THF hydrate pattern in their porous media suggested that nucleation and growth of clathrate is not favored on the silica surface because silica glass surface is water wetting and does not promote heterogeneous nucleation. In the case of methane gas, hydrate formation began at the gas (bubble)-water interface and proceeded inward. Since no movement was observed, they speculated that changes in the structure of surrounding water might spread hydrate formation throughout the media rather than migration of nuclei. Hydrate formation from dissolved CO$_2$ gas in water provided a definitive confirmation of hydrate formation in the absence of free gas.

Finally, they concluded that hydrate growth was a competition between kinetic and transport limitations (dominant in the case of sparingly water soluble hydrate former) and the requirement of minimization of surface energy by agglomeration of hydrate crystals into large masses (dominant in the case of soluble hydrate former).

Waite, Winters, and Mason (2004) performed a set of experiments to investigate the interaction of the hydrate with its host sediment. As was reported by Cheng and Pinder (1976) hydrate formation in the interstices of a sand bed will consolidate the sand, but the question is whether hydrates form in pore fluids (becoming load-bearing members) or they will cement the grains. Dvorkin et al. (2000) proposed four different pore-scale hydrate distributions (see Figure 3.1).

The authors formed methane hydrate using their Gas Hydrate and Sediment Test Laboratory Instrument (GHASTLI) in the interstices of partially water-saturated Ottawa sand. Comparison of the results of a rock physics model, which predicts the compressional wave speed for different modes of hydrate/sediment interactions, with experimental measured values of laboratory-made hydrate-bearing sediment were used to determine the mode of hydrate/sediment interaction. Based on experimental results, they concluded that hydrate formation in gas-rich environments mimics surrounding and cementing the sediment grains.
Winters et al. (2004) measured physical properties (shear strength and acoustic velocity) of sediments containing natural and laboratory-formed methane hydrate. Their main finding from acoustic modeling was that natural gas hydrate (samples from Malik 2L-38 well, Mackenzie Delta, Northwest Territories) does not cement sediment grains and acts as a part of the sediment frame while laboratory-formed gas hydrates and frozen Ottawa sand cement their sandy environments. It was also consistent with results of strength test and velocity measurement. They attributed this difference to some yet-unknown factors including formation mechanism, mineral phases and location of the water molecules that might control hydrate sediment interaction. Finally they pointed out models that use laboratory-derived properties of hydrates must be adjusted to account for the difference between the behavior of the lab-made hydrates and natural gas hydrates.

A series of experiments were done by Kumar (2006) on the formation of CO₂ hydrates at 2.76 MPa and 4°C in a porous medium represented by a column of glass beads with a diameter range of 89-150 µm, porosity of 0.33 and absolute permeability of 66.44 D. Permeability was also experimentally determined in presence of hydrates. Formation of hydrates was verified by
pressure and temperature data recording. Experimental results indicated that for initial water saturations less than 35%, hydrate tends to form on the grain surfaces. However, pore filling is favored for initial water saturations greater than 35%. A one dimensional numerical model was also developed for hydrate dissociation by depressurization, assuming kinetic, heat transfer and fluid flow mechanisms involved. Kinetic and heat transfer from the surroundings were found to be the controlling steps, especially for the high permeability system.

Waite et al. (2008) employed three different techniques (X-ray Computed Tomography imagery, thermal conductivity, and shear strength and acoustic compressional speed measurements) to investigate the changes in the physical properties of a laboratory-formed methane hydrate-cemented sand due to depressurization and subsequent repressurization. The motivation for this study came from the fact that during sampling and recovering hydrate from natural environments, they will be exposed to the atmosphere, at least once, in order to be transferred to the storage vessel. So, it is concerned that this excursion from in-situ condition to the storage condition might change physical properties of hydrates. In other words, can this sample reasonably represent the undisturbed one?

They formed methane hydrate in Ottawa sand, depressurized it to atmosphere for a short period of time and then repressurized it. CT was used to map the hydrate distribution of initial and repressurized sample. A density decrease near the perimeter and increase near the central axis of the sample was observed. They attributed the density changes to hydrate redistribution and also hydrate growth from previously unreacted water. For the short period of depressurization, hydrate started to dissociate near the perimeter of the sample where the heat is readily available for this endothermic reaction. Then, during repressurization water was drawn back to the
hydrate formation front (inward migration) by capillary forces to form hydrates near the central part of the sample (Gupta et al. 2006; Kneafsey et al. 2007a).

Thermal conductivity ($\lambda$), which depends on the pore-space hydrate saturation (Waite et al. 2002), was measured using an axially positioned thermal probe heater and the results showed an increase of $\lambda$ near the sample’s central axis due to increased hydrate saturation near the central part.

Compressional and shear wave measurements indicate how rigid the sand grains are linked together. They observed a large increase in shear wave speed and suggested that it could be due to the hydrate redistribution and also new hydrate growth which increased the stiffness of the sample near the central axis by cementing the sand particles.

Finally, the authors concluded that even a brief depressurization induces hydrate redistribution which can significantly change the physical properties of the sample.

### 3.2 Thermodynamics of hydrate in porous media

The following researchers studied the thermodynamics (equilibrium conditions) of gas hydrates in porous media and unanimously agreed on the “inhibiting effect” of restricted (confined) geometry. It means for a given temperature hydrates form at a higher pressure and for a given pressure they form at a lower temperature compared to the case where hydrates form from bulk water (Handa and Stupin 1992; Clarke, Pooladi-Darvish, and Bishnoi 1999; Uchida, Ebinuma, and Ishizaki 1999; Klauda and Sandler 2001; Seshadri, Wilder, and D. H Smith 2001; Wilder et al. 2001; Ostergaard et al. 2002; Uchida et al. 2002; Anderson et al. 2003a; Anderson et al. 2003b; Llamedo, Anderson, and Tohidi 2004).
According to the solid-solution theory, stability conditions of clathrate depend directly on the activity of water. As water activity decreases, formation of hydrates requires higher pressure and lower temperature (i.e. phase boundary moves to the more severe conditions). So, based on this theory, the above researchers justified their observations by the fact that the activity of water is reduced in porous media as a result of capillary forces. It is well known that the inhibition can also be caused by electrolyte solutions, since presence of ions in the aqueous phase reduces the activity of water.

Clarke, Pooladi-Darvish, and Bishnoi (1999) developed a method to predict phase behavior of hydrates in porous media. The basic necessity for the equilibrium is the equality of chemical potential of different components present in each phase:

\[
\begin{align*}
\mu^L_i &= \mu^V_i \quad (i = 1, \ldots, N) \\
\mu^H_j &= \mu^V_j \quad (j = 1, \ldots, NH)
\end{align*}
\]

Eq. 3.1

Where, \(N\) is the total number of components and \(NH\) is the number of hydrate formers. \(L\), \(V\) and \(H\), respectively, represent liquid, vapor and hydrate phases. The chemical potential in liquid and vapor phase are usually obtained from the corresponding fugacity which can be computed using a proper equation of state. Whereas, the fugacity of water in hydrate phase is generally calculated from the model of Van der Waals and Platteeuw; a statistical thermodynamic model based on the three dimensional generalization of localized adsorption:

\[
\Delta \mu^H_W = \mu^\beta_W - \mu^H_W = -RT \sum_i v_i \ln \left( 1 - \sum_j \Theta_{ij} \right)
\]

Eq. 3.2

Where, \(\mu^H_W\) and \(\mu^\beta_W\) are the chemical potentials of water in the hydrate phase and metastable hypothetical empty hydrate lattice. \(v_i\) is the number of cages of type \(i\) per water molecule. \(R\) is
the universal gas constant and $T$ is the absolute temperature. $\Theta_{ij}$ is the fractional cage occupancy of hydrate former $j$ in cages of type $i$ and is given by:

$$\Theta_{ij} = \frac{C_{ij}f_j}{1 + \sum_j C_{ij}f_j}$$  \hspace{1cm} \text{Eq. 3.3}$$

In which, $C_{ij}$ is the Langmuir constant of component $j$ in cage type $i$ and $f$ is fugacity.

On the other hand, chemical potential of water in bulk liquid phase would be:

$$\frac{\Delta \mu_W^L}{RT} = \frac{\Delta \mu_W^0}{RT_0} - \int_{T_0}^{T} \frac{\Delta H_W^L}{RT^2} dT + \int_{P_0}^{P} \frac{\Delta V_W^L}{RT} dP - \ln(a_w)$$  \hspace{1cm} \text{Eq. 3.4}$$

In which, $\Delta \mu_W^L$ and $\Delta \mu_W^0$ are the chemical potential difference of water between pure liquid phase and empty hydrate lattice at temperature and pressure of $(T, P)$ and $(T_0, P_0)$, respectively. $\Delta H_W^L$ and $\Delta V_W^L$ are the molar enthalpy and volume difference between pure liquid water and empty hydrate lattice. $a_w$ is the activity of water at bulk condition.

However, as a result of capillary forces there would be an extra term to account for the confined geometry. According to the Young-Laplace equation there is a pressure difference between the liquid phase and the gas phase in a capillary of radius $r$:

$$\Delta P = P_g - P_w = \frac{2\sigma_{gw}}{R_p \cos \theta}$$  \hspace{1cm} \text{Eq. 3.5}$$

![Figure 3.2. Water in a capillary of radius $R_p$](image)
Where, \( \sigma_{gw} \) is the surface tension of water in contact with gas, \( R_p \) is the pore radius and \( \theta \) is the contact angle.

From thermodynamic relations we know that (at constant \( T \)):

\[
\frac{d\mu_w}{RT} = \frac{V_w}{RT} dP \Rightarrow \int_{bulk}^{cappillary} \frac{d\mu_w}{RT} = \int_{P,W,bulk}^{P,W,cappillary} \frac{V_w}{RT} dP \\
= \frac{V_w}{RT} \int_{R_p \to \infty}^{R_p} -d\left( \frac{2\sigma_{gw}}{R_p} \cos \theta \right) = -\frac{V_w}{RT} \left( \frac{2\sigma_{gw}}{R_p} \cos \theta \right)
\]

Eq. 3.6

Hence,

\[
\frac{\Delta \mu_w}{RT} = \frac{\Delta \mu_w^0}{RT_0} - \int_{T_0}^{T} \frac{\Delta H_w^L}{RT^2} dT + \int_{P_0}^{P} \frac{\Delta V_w^L}{RT} dP - \ln(a_w) + \frac{V_w}{RT} \left( \frac{2\sigma_{gw}}{R_p} \cos \theta \right)
\]

Eq. 3.7

Therefore, from the equality of the chemical potential of water:

\[
RT \sum_i v_i \ln \left( 1 - \sum_j \Theta_{ij} \right) + \frac{\Delta \mu_w^0}{RT_0} - \int_{T_0}^{T} \frac{\Delta H_w^L}{RT^2} dT + \int_{P_0}^{P} \frac{\Delta V_w^L}{RT} dP - \ln(a_w) + \frac{2V_w \sigma_{gw}}{RRT_P} \cos \theta = 0
\]

Eq. 3.8

This equation can be iteratively solved for \( P \) at a given \( T \).

According to the calculations of Uchida et al. (2002) using Gibbs-Thomson equation, the pore size that can shift the equilibrium temperature by \(-0.5\) K for methane hydrate is about 100 nm.

### 3.3 Kinetics of hydrate processes in porous media

The conventional method of kinetic investigation of hydrate processes is monitoring pressure, temperature and the amount of hydrate forming substance consumed during the course of experiment. But the results obtained from these macroscopic studies do not give us a complete picture of the phenomenon since they are not capable of spatially resolving the process and they are devoid of any information at the microscopic level. As noted by I. L Moudrakovski et al.
(2004) the observation of gradual conversion of water to hydrates obtained from pressure recoding is only a result of an averaging over many local environments in which the process is occurring, because in a closed system as a result of hydrate formation the pressure drops regardless of the location of the reaction.

The more sophisticated methods of studying hydrates, especially in porous media, are the ones which are capable of visualization of the process and therefore spatially resolving them. They can be very beneficial in providing more fundamental insight about the mechanism of hydrate formation or dissociation. Magnetic Resonance Imaging and X-ray Computed Tomography are among these methods. As suggested by J. Ripmeester and Ratcliffe (1999), the application of NMR imaging in clathrate science, especially hydrate formation and decomposition processes, provides space-resolved and time-resolved images which can contribute a great deal of information.

Kinetics of hydrate can also be studied at molecular level using spectroscopy techniques such as Nuclear Magnetic Resonance, X-Ray Diffraction and Raman. They are very useful in providing information about structural properties of hydrates.

However, none of the above methods is solely sufficient and if one wants to obtain a more fundamental and more comprehensive understanding of the kinetic and mechanism of hydrate processes, one has to utilize multiple means of measurements (Kneafsey et al. 2007b).

3.3.1 Macroscopic kinetic studies

Yousif et al. (1990) were among the first who worked on the recovery of methane gas from hydrate deposits, through laboratory measurements. They formed hydrates in Berea sandstone core and measured the rate of dissociation by taking advantage of electrical resistivity
measurements to monitor the dissociation front. They also formulated an analytical model (a moving boundary model) for the depressurization scheme.

Buffett and Zatsepina (2000) carried out a set of experiments on the formation of hydrates from dissolved gas in natural porous media. They claimed they were the first who showed hydrate can form in porous media under realistic conditions when the free gas is absent. This justified the commonly proposed explanation for the formation of marine hydrates by migration of methane-bearing fluid from the deeper depth. They used CO₂ as the hydrate former gas in Lane Mountain sand with grain size of 0.4 to 0.6 mm. The authors also showed that electrical resistance measurements could be a sensitive and reliable means for hydrate formation detection from a solution where the gas concentration is low.

But it should be noted that solubility of CO₂ in water is much higher than methane and therefore the results from CO₂ experiment may not necessarily be correlated to the case where methane is the hydrate former.

Kono et al. (2002) performed a systematic study of the reaction engineering kinetics of formation and decomposition of methane gas hydrate in various custom-designed porous sediments. Based on the experimental results, they found that the formation reaction was first order with respect to methane concentration (no. of moles) and calculated the reaction rate constants. During decomposition they observed two different behaviors depending on the sediment type: zero- and first-order reaction. The authors pointed out that these types of apparent rate constants are not the same as the intrinsic chemical reaction rate constants and they represent the combined effect of reaction, heat transfer and mass transfer.
Sung and Kang (2003) experimentally investigated the production behavior of methane hydrate in porous rock using depressurization and methanol injection schemes. A Berea sand stone core was saturated with 1.5 wt% NaCl aqueous solution and methane gas. Pressure, temperature and electrical resistances were recorded during the experiments. They tested their experimental apparatus by measuring equilibrium condition and found excellent match with reported values in the literature. From the formation experiments, they observed that as hydrate started to form, the pressure decreased rapidly with a simultaneous increase in resistance.

For depressurization, a pulse type response was observed in pressure and resistance profiles. During dissociation the amount of produced water was greater than that of released gas, therefore the relative permeability of gas was low and it was difficult for the gas to flow. The gas would not migrate until its amount increased to a critical limit as dissociation continued.

Methanol injection did not show a pulse-type behavior, since methanol changed the equilibrium conditions remarkably and imposed a high driving force for decomposition.

Liang et al. (2005) studied the decomposition behavior of methane hydrates formed in 5 cm$^3$ of wet activated carbon in a closed system in the temperature range of 275.8 to 264.4 K and estimated the decomposition rate constant. They also measured the decomposition rate for hydrates formed from 5 cm$^3$ of pure water and an aqueous solution of 650 g.cm$^{-3}$ sodium dodecyl sulfate (SDS). Comparison of the results showed that methane hydrate dissociated more rapidly in porous activated carbon. In addition, a 3-parameter mathematical model was developed to describe the decomposition kinetic behavior below the ice point based on an ice-shielding mechanism. According to this model the kinetic process could be described as the following:
1. Destruction of clathrate hydrate lattice at the surface of hydrate particle and desorption of methane molecule from the surface of hydrate particle

2. Diffusion of the methane molecule through a porous ice layer and release to the vapor phase

A new apparatus was designed to accommodate three beds with different diameter for studying hydrate formation in a silica sand matrix and the effect of sample size was investigated (S. C Nam et al. 2008; C. Haligva 2009; Praveen Linga et al. 2009a; Praveen Linga et al. 2009b; C. Haligva et al. 2010). The initial unconsolidated bed consisted of silica sand with the mesh size in range of 50 to 70, was completely saturated with water. The ratio between water and sand for complete filling of interstitial spaces was found to be 0.217 mL of water per gram of sand. Pressure of the gas phase and temperature profiles were recorded using 6 thermocouples planted at different locations inside the bed. Then hydrate-containing silica sand matrix was subsequently undergone a decomposition experiment using depressurization and thermal stimulation.

Formation experiments were conducted at 8 MPa and temperatures of 1, 4 and 7°C. Temperature spikes at different times and at different locations inside the bed during the experiments at 1 and 4°C demonstrated the occurrence of “multiple nucleation”. The authors considered this multiplicity of hydrate nucleation as a factor responsible for obtaining a relatively high percentage of water conversion to hydrate at 1 and 4 °C compared to the experiment at 7°C where no multiple nucleation happened. The rate of hydrate formation was also dramatically enhanced compared to forming hydrate from bulk water in a stirred tank reactor because of the higher degree of water dispersion. Formation of hydrates in the interstices of a silica sand matrix was also verified independently by Raman spectroscopy and morphology observations. As the
authors pointed out, 6 thermocouples cannot precisely and completely locate the position of the hydrate formation reaction inside the bed. This is due to the fact that the response of a particular thermocouple could be either a signature of a sudden liberation of heat as a result of hydrate nucleation at the location of the tip of thermocouple or as a result of heat transfer from the neighboring area. So, it was not very clear that how multiple nucleation happened throughout the bed. With the current experimental set up it is not possible to visualize the process in order to see hydrate formation patterns inside the bed. Further understanding of the formation mechanism needs a visualization technique that can enable us to resolve the process spatially.

After formation, hydrates were decomposed by thermal stimulation and more than 95% of methane was recovered. Dissociation proceeded at two stages where the rate of the first stage was dependent on the bed size; however, no dependency was observed for the rate during the second stage.

In the case of hydrate decomposition by depressurization, more than 80% of methane was recovered. It was concluded that the dissociation occurred at three steps where the rate of the first step was strongly and the rate of the second step was weakly dependent on the bed size. The rate of the third step was more or less the same for all three bed sizes. The data was also fitted to an exponential function and it was observed that the time constant was a linear function of the bed size.

But, one concern about this work is that it can be argued whether the difference in the rate of decomposition is a result of change in the sample size or it is due to heat transfer effects. Heat transfer calculations show that when we replace water/sand mixture with Copper cylinder in order to reduce the diameter of the bed, we are considerably changing the heat transfer characteristic of the set up. As illustrated in appendix A, the heat conduction resistance between
the bed with smallest diameter (when CC1 and CC2 are both present) and external water bath is approximately 5% (1/20) and 10% (1/10) of the cases when we replace CC2 and then both CC2 and CC1 with a water/sand mixture.

### 3.3.2 Microscopic kinetic studies (visualization methods)

I. L Moudrakovski et al. (1999) used $^1$H NMR microimaging to show that the ice which is encapsulated by hydrate is able to melt at its usual melting point as opposed to the suggestion that hydrate layer can keep the encapsulated ice in a superheated state.

Mork, Schei, and Larsen (2000) studied hydrate formation in quartz sand, with a particle size distribution of 210-295 µm, using three different techniques: NMR imaging, X-ray computer tomography (CT) and mechanical strength and deformation measurements. Stoichiometric aqueous solutions of THF and R-11 were chosen for hydrate formation in order to simplify the study.

As opposed to the NMR imaging experiments, the authors gained no useful information from their CT test due to the very small density difference between the THF hydrate and the THF-water mixture. The NMR images showed that hydrate formation started almost simultaneously in many interior locations in the sample and the deviation from stoichiometric solution (for example evaporation of THF) led to excess fluid remaining between neighboring lumps of hydrates. For the R-11/sand system, hydrate formation was not spatially-homogeneous throughout the sample and the authors considered the lack of widespread nucleation as the responsible factor.

It was also found that the R-11-hydrated-sediment was stronger than the THF-hydrated one.
I. L. Moudrakovski, Ratcliffe, and J. A. Ripmeester (2002) presented an experimental protocol for conducting magnetic resonance microimaging (MRM) to monitor hydrate formation. They pointed out that understanding of the mechanism of hydrate formation and decomposition, especially in porous media, requires some information at the molecular level with both space and time resolution. In this work, they formed CO₂ hydrate from ice particles and methane hydrate in a mixture of water/sand/silica gel. Hydrate formation was qualitatively verified by the observation of the darkening of the lighter areas of the MRI image. No quantitative analysis was presented.

Baldwin, Moradi-Araghi, and Stevens (2003) employed MRI to monitor hydrate formation and dissociation in a THF/water-saturated Berea sandstone plug and in the bulk. ¹H MRI produces images with a large contrast between hydrogen in the liquid phase and hydrate, ice or sandstone due to the shorter relaxation time in the solid state. They used a solution of water and THF with a molar ratio of 16:1 and called it stoichiometric solution, while the correct ratio is 17:1.

They observed no significant effect of porous rock on hydrate dissociation since the dissociation curve of the bulk hydrate and hydrate saturated rock were similar. They acquired six slices along the length of the core. For formation experiments in porous rock the slice which was closer to the entrance of the cooling liquid first showed intensity loss (hydrate formation). As formation proceeded the left side of the images converted completely to hydrate whereas the right side still showed signal from the water/THF solution. It was not clear for them whether it was because of nucleation processes or merely the flow path of the coolant (the coolant entered the system from the left side). Following complete conversion to hydrate, the conditions were set to dissociate hydrate. Unlike the intensity gradient observed during formation experiment along the sample, the intensity uniformly increased with time during dissociation. The authors attributed this
uniformity to the slow heating process. They would expect to observe the dissociation front as a ring starting from outside edge of the sample growing inward at a faster rate of warming.

MRI images of the bulk formation experiments showed that hydrate formed predominantly from the wall of the vessel toward the center. The formation rate was 1.2-1.7 cm/h. As opposed to the sand stone experiment, they observed the inverse pattern of formation in dissociating the bulk sample.

I. L Moudrakovski et al. (2004) have used spatially resolved $^1$H magnetic resonance microimaging measurements to probe methane and carbon dioxide hydrate formation in dispersed water droplets. They showed that quantitative spatially resolved kinetic information became available by following the disappearance of the $^1$H spin density associated with water. The authors formed hydrates of methane gas in water droplet, hydrates of CO$_2$ gas in ice particles and also hydrates of methane in water droplet from dissolved methane in perdeuterated liquid isooctane.

Unlike the gradual conversion of water to hydrate reported in most of the macroscopic studies, they observed quite inhomogeneous and stochastic conversion of water to hydrate, some drops converted quickly, others requiring hours or days. They postulated that averaging over many local environments in bulk samples is the only reason for the observation of gradual behavior. The quantitative measurements in the smaller sub-portions of images showed that the process becomes more inhomogeneous as we focus on a smaller portion of the sample.

The images did also show a sudden conversion of droplets to hydrates at random times and hydrate formation at the droplet’s center instead of at the hydrate-water interface. The authors explained this observation by pointing out that the growth rate at the interface was slow enough
to allow the buildup of the diffused gas in water phase which thus resulted in nucleation at the center away from the interface.

Gao, Chapman, and House (2005) applied the MRI technique and $T_1$ (spin-lattice relaxation time) measurement to monitor hydrate formation and dissociation patterns of THF/D$_2$O solution. Formation of hydrates for the first time showed spatially-homogeneous nucleation along the perimeter of the sample with an inward growth. Dissociation was found to follow an inverse pattern. In reformation experiment, the induction time was shorter; however, hydrate locally nucleated at a point near the wall of the vessel. The authors attributed this to the residual clathrate hydrate structure which acted as nucleation site. Their MRI images demonstrated that once hydrate nucleated, it grew only at the water/hydrate interface.

From the $T_1$ measurement experiments, they concluded that structured liquid water at the hydrate interface plays a key role in both hydrate growth and dissociation. $T_1$ values of THF in liquid phase during hydrate formation and dissociation fall far low from the linear relationship between $\ln(1/T_1)$ and temperature. Also, as the amount of liquid phase diminished, the higher $T_1$ was observed. The authors justified this observation by the possibility that as more hydrate is present the higher percentage of liquid phase gets structured through the hydrogen bonding with the partial cages on the hydrate surface. However, this is in contrary with the fact that relaxation time is proportional to the mobility. If the higher portion of liquid phase gets structured the $T_1$ must decrease instead of increasing.

Y. T Seo et al. (2005) worked on the separation of CO$_2$ from flue gas using hydrate formation in porous silica gel with nominal diameter of 30 nm. They obtained a water conversion to hydrate of better than 85% in about 1 hour and 90% of this yield was achieved in the first 20 min. $^1$H NMR microimaging showed that formation of hydrates started from the bottom of the bed and
then propagated to the top. The authors attributed the rapid rate of growth to the high degree of dispersion of water which provided a larger contact between water and gas compared to the bulk water. Also, a thin layer of water on the wall of the hydrophilic surface of the pores, known as bound water which does not undergo the usual freezing transition, functioned as transportation path for CO₂ to diffuse into the pores and contribute to hydrate formation throughout the bed.

Susilo et al. (2006) studied kinetics of deuterated methane sI and sH formation and decomposition from ice particles using nuclear magnetic resonance spectroscopy and imaging. Three large molecule guest substances (LMGS) were used: tert-butyl methyl ether, neo-hexane and methyl cyclohexane. The effect of a non-hydrate former (n-heptane) was also studied. Spectroscopy measurements revealed the following order for the rate of growth:

\[
\text{ice} - \text{TBME} - \text{CD}_4 > \text{ice} - \text{CD}_4 > \text{ice} - \text{NH} - \text{CD}_4 > \text{ice} - \text{MCH} - \text{CD}_4 > \text{ice} - n\text{C}_7 - \text{CD}_4
\]

NMR imaging showed that TBME had a strong affinity toward ice and although the diffusion rate of methane in NH and TBME were of the same order, the better wetting property of TBME played an important role in speeding up the hydrate crystallization.

Kneafsey et al. (2007b) conducted a series of experiments on methane hydrate formation and dissociation in a partially saturated silica sand (100-200 µm) sample. Pressure and temperature measurements as well as X-ray computed tomography (CT) scanning were employed to observe the system behavior.

The results indicated that hydrate formation did not proceed at a constant rate but occurred in fits and starts. Temperature increases were coincident with sudden pressure decline as the second verification of hydrate formation. 65% of water converted into hydrate based on a hydrate number of 5.75.
Local density variations in CT scans could be caused by one or combination of the following processes: hydrate formation/decomposition, water saturation changes (migration), mechanical changes (compaction) and gas pressure changes. Comparison of the voxel density change as a result of each of these processes showed that water migration was the dominant process. The authors proposed a conceptual model for hydrate formation in a partially water-saturated water-wetting porous medium: Hydrate formation consumes a portion of the water present in interstices, thus partially or fully fills the pores with solid hydrates and leads to the pores with smaller sizes. Assuming hydrate as a water wetting substance, water will flow toward the smaller pores as a result of capillary forces. Therefore, a moving formation or dissociation front will drag a water saturation front along. The model is schematically illustrated in Figure 3.3.

![Figure 3.3. Capillary-driven migration of water towards the smaller pores as a result of hydrate formation. Reprinted from Kneafsey et al. (2007b) with permission from Elsevier](image)

They also observed an unexpected phenomenon that the rate of hydrate formation could be increased by reducing the driving force (reducing pressure or increasing temperature towards the equilibrium condition). They suggested two possible explanations. Decreasing the pressure or increasing the temperature reduces equilibrium saturation of methane in water. In one way it can lead to supersaturation of water with respect to methane and accelerate hydrate formation. On the other hand, this dissolved methane might release and break the hydrate wall around the
possible isolated pockets of water containing dissolved gas and thus improve the communication between the gas and water phase.

Seol and Kneafsey (2009) utilized X-ray computed tomography along with pressure and temperature measurement to study the effect of bed heterogeneity on the formation and decomposition of methane hydrate as well as water flow through the hydrate-bearing sand. A bed with a prescribed distribution pattern of sand with two different grain sizes was prepared for this purpose.

They started forming methane hydrate at 4°C and 4.8 MPa but because hydrate did not form even after two days they changed the conditions to 3°C and 5.5 MPa in order to facilitate the process and finally after 12 hour hydrate began to form. Formation of hydrates was verified by concomitant pressure drop and temperature rise. Similar to their previous work (Kneafsey et al. 2007b) several temperature peaks, as large as 3.5°C, were observed.

Hydrate saturation was more uniform in the coarse sand while it was more highly localized in the fine sand. In terms of hydrate saturation, three contrasting regions were observed along the length of the column: circular-band-shaped as half ring, locally concentrated and disseminated patterns.

The observation of hydrate formation and dissociation suggested that availability of water and gas, heat transfer, capillary force, grain size, initial water saturation and relative permeability are the factors that affect the process.

A number of publications from the Department of Physics and Technology of the University of Bergen (Allegaten 55, 5007 Bergen, Norway), ConoPhillips (OK, USA) and Green Country Petrophysics LLC (OK, USA) illustrated the usefulness of MRI technique in monitoring and
visualizing methane hydrate formation and subsequent methane release by depressurization or CO\textsubscript{2} sequestration in a consolidated Bentheim sandstone core. Conventional pressure and volume monitoring were also employed as independent evidences of hydrate processes. Changes in permeability were also measured as hydrate formed or dissociated (Ersland et al. 2008; Husebo et al. 2008; Husebo, Graue, and Kvamme 2008; Stevens, Howard, et al. 2008; Stevens, Baldwin, et al. 2008; Baldwin et al. 2009; Ersland et al. 2009; Birkedal 2009).

The sandstone was characterized by a quartz-rich framework with small amount of clay with an average pore diameter of 125 µm, porosity of 0.22-0.23 and absolute permeability of 1100 mD. The operating pressure and temperature were kept constant in the range of 1200 psi and 4°C.

Two different geometries of core plugs were used in these studies. The first one was a cylindrical core plug for investigating of methane hydrate formation and subsequent methane release by depressurization under constant P or V condition. For CO\textsubscript{2} sequestration experiments a POM (polyoxymethylene) spacer was placed between two halves of a cylindrical core to simulate a fracture opening which enhanced fluid flow throughout the porous media. Release of methane upon CO\textsubscript{2}-exchange was monitored by following the accumulation of methane in the liquid CO\textsubscript{2} in the spacer.

Standard 2D and 3D spin-echo acquisition sequences were run with sufficient signal averaging up to 9 hours. They mentioned that the most useful information was collected from the decrease in the integrated intensity of the whole plug in the 3D image with a field of view of 6×6×11 cm. However, it should be noted that acquiring data over such a big volume, which takes a considerable time, is not an efficient and accurate way of collecting data, because during the 9 hours of data acquisition, even for a slow process, some changes will definitely occur which will be masked by averaging the data over this 9 hours.
In formation experiments, the trend of signal loss was very similar to that of volume increase in the supply methane pump (due to conducting hydrate formation under constant pressure in a closed system). There was no specific pattern in hydrate formation and it formed uniformly throughout the core in most of the cases (average behavior).

Effects of initial water saturation and water salinity were also investigated. The results showed that the rate of formation in cores with lower water saturation was faster. Higher salinity of water resulted in slower kinetic in addition to a lower extent of water conversion to hydrate. The authors justified the faster rate of formation compared to the bulk experiments by considering the fact that the abundance of menisci in the partially water-saturated pores provided sufficient available gas-water interfaces for hydrate formation without creating a solid rind that hindered the subsequent growth (Stevens, Baldwin, et al. 2008).

In CO2 sequestration, after formation stopped, the sample was exposed to liquid CO2 at 1200 psi and the build up of methane in liquid CO2 phase was followed by MRI imaging. They performed two flushes to recover 60-70% of trapped methane. This procedure maintained the hydrate stability in the core with no evidence of the excess water production.

In depressurization, the pressure was reduced below equilibrium to start the dissociation. Methane production under constant volume and constant pressure was examined. The buildup of methane in the gas phase and release of water was monitored by the MRI signal which showed the same trend as that of increase in methane mole fraction in the gas phase (average behavior).

From their preliminary study they concluded that methane can be recovered at an acceptable quantity from porous media within the same timescale using pressure reduction and CO2-exchange. However, in applying these schemes one should be aware of the advantages and
disadvantages of each method. Although depressurization can lead to almost complete recovery, methane production is associated with free water as the by product and the system also has to be driven out of the thermodynamic stability zone. On the other hand, sequestration has the benefits of maintaining the structural integrity of the sedimentary reservoir with little or no change in the residual free water during production. Also, the thermodynamic conditions do not necessarily need to be close to equilibrium. The main disadvantages are relatively slower rate and lower level of recovery of trapped methane (Husebo, Graue, and Kvamme 2008). It should also be noted that, the recovered methane is a mixed CO₂-CH₄ phase which requires a post-operation to be separated from CO₂.

The authors should also mention that pumping large quantity of liquid CO₂ in sediments can considerably increase the compression costs. In a CO₂-exchange process, flow characteristics of the reservoir are also very important and properties such as porosity and permeability play crucial roles.

Husebo et al. (2008) studied the effect of water salinity on the methane hydrate formation pattern in sand stone. For every salinity used, a series of patterns was observed and there was no specific trend. However, the initial brine distribution was found to affect the pattern. MRI profiles along the core showed that formation events occurred at an equal rate for a core with a homogeneous initial brine distribution. Heterogeneity in initial brine distribution led to different rates along the core and it was faster at locations where there was more accessible water.

Induction times as long as 30 hours were observed (they regarded it as a variable of unknown origin (Baldwin et al. 2009)). After the conversion of most of the water to hydrate, they removed the remaining methane in the spacer by pushing it out through the injection of liquid CO₂. The spacer was then monitored by MRI to follow the exchange process between CH₄ and
CO₂. No evidence of dissociation or melting of hydrates was observed, at least within the resolution and sensitivity of the MRI. After the signal increase from the release of methane reached a plateau in time, second and third flush with CO₂ also performed to make sure that the maximum amount of methane had been recovered. The signal increase during the second and third stages indicated that not all of the methane was recovered following the first flush.

Furthermore, measurement of permeability in the core showed a quick reduction once hydrate began to form and in no experiment it dropped below 1 mD. Hydrate then dissociated by depressurization and it was verified by an increase in MRI signal. There was not a concomitant increase in permeability upon hydrate dissociation.

The point that needs to be taken into account here, is that Kvamme and co-workers never addressed thermodynamic limitations of the CO₂-exchange process as discussed by Huen Lee et al. (2003). Lee et al showed that in the formation of hydrate from a mixed CH₄-CO₂ gas there is a limit for the occupancy of large cages by CO₂, i.e. even when the composition of the feed gas approached 100% CO₂, the ratio of methane occupancy between the large and small cages was not zero (about 0.23). The authors also pointed out that the rate and yield of the exchange process in natural deposits depend on a variety of factors, such as the degree of dispersion of hydrate in sediment, hydrate morphology, particles size, and gas transport.

### 3.4 Research objectives

Following the recent work in our laboratory (C. Haligva 2009; Praveen Linga et al. 2009a; Praveen Linga et al. 2009b; C. Haligva et al. 2010) and in order to extend our understanding of the hydrate formation mechanism and the occurrence of multiple nucleation in porous media we propose to employ the MRI technique. MRI has the capability of visualizing and spatially resolving the hydrate processes.
Although a number of papers have been published in the literature that prove the suitability of the MRI technique in visualizing hydrate processes, none of them has accurately and completely utilized the unique feature of spatial resolution to quantify the kinetics of hydrate in both time- and space-resolved fashions.

The specific objectives of this research work are summarized below:

1. To obtain a better and deeper understanding of hydrate formation mechanism in porous media
2. To verify the occurrence of multiple nucleation in formation of hydrates in porous media
3. To investigate the effect of particle size on the rate of hydrate formation
4. To examine the effect of water saturation on the hydrate formation trend in porous media
4 MATERIALS AND METHODS

The experimental part of this work has been conducted in two parts. A few macroscopic experiments were conducted first by following the procedure reported by C. Haligva (2009).

The main experimental effort was concerned with the investigation of the kinetics of hydrate formation and dissociation in a bed of silica sand particles using Magnetic Resonance Imaging to monitor these processes. Since, the MRI experiment requires a specialized NMR spectrometer, I went to the National Research Council of Canada, Ottawa, and I was given the opportunity to perform my experiments using their 200 NMR spectrometer which has the imaging capability as well.

4.1 Materials

Ultra High Purity (UHP) methane of grade 3.7 from PraxAir, silica sand supplied by Sigma-Aldrich (product no. 274739) with a mesh size range of 50 to 70, equivalent to particle size range of 210-297 µm, and distilled water were used.

In order to produce sand with smaller particle size, the original sand from Sigma-Aldrich was ground using a mortar and pestle and then sieved to the following ranges:

<table>
<thead>
<tr>
<th>Silica sand</th>
<th>Mesh size</th>
<th>Particle size range (diameter in µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50-70</td>
<td>210-297</td>
</tr>
<tr>
<td>2</td>
<td>70-120</td>
<td>125-210</td>
</tr>
<tr>
<td>3</td>
<td>80-170</td>
<td>88-177</td>
</tr>
<tr>
<td>4</td>
<td>&gt;200</td>
<td>&lt;74</td>
</tr>
</tbody>
</table>
4.2 Macroscopic experiments

4.2.1 Apparatus

A detailed description of the apparatus used in this section is provided by C. Haligva (2009). A brief description is given below.

The heart of the apparatus is a 316 SS cylindrical reactor (internal diameter of 10.16 cm and height of 15.24 cm) which is immersed in a water bath. The temperature of the bath is controlled using an external refrigerator (ER). Depending on the bed height, 8 and 7 Omega copper-constantan thermocouples are positioned inside the reactor in order to monitor the temperature (see Figure 4.2). The pressure of the gas phase is also recorded by a Rosemount smart pressure transducer (model 3051). The data are saved using a National Instrument data acquisition system (DAQ) connected to a computer (PC). The schematic of the apparatus is illustrated in Figure 4.1.

![Figure 4.1. Schematic of the apparatus used for macroscopic experiments. Modified from C. Haligva (2009) with permission from the author](image-url)
4.2.2 Procedure

An unconsolidated bed of silica sand which was fully saturated with water was prepared. The reactor was filled with sand and water up to the desired height. 914.1 gr of sand and 198.5 mL of water were required to fill the reactor up to the height of 7 cm. The corresponding values for a bed with a height of 4 cm were 522.3 gr and 113.4 mL. It was previously found that the ratio between the mass of sand and the volume of water for a fully water-saturated bed is 0.217 mL/gr (C. Haligva 2009). In a fully water-saturated bed, water completely fills the interstitial spaces between sand particles.

Once the bed was set up, thermocouples were inserted and the reactor was closed. It was then placed in the water bath and purged with methane three times at a pressure lower than the equilibrium formation pressure of methane hydrate in order to remove the maximum amount of air from the gas phase above the bed.
After reaching the desired experimental temperature, 4°C, methane was introduced into the reactor at a pressure of 8 MPa. Because methane was at ambient temperature, the thermocouples showed an increase in temperature; however, they quickly went back to their set point (approximately 5 min after methane introduction) and that was set as time zero for the experiment. The data were subsequently recorded at a time interval of 20 seconds. The experiment was stopped when there was no significant change in pressure.

4.2.3 Calculations

The gas phase of the reactor is a closed system. Therefore, as methane combines with water and forms hydrate the number of methane molecules in the gas phase decreases and this leads to the pressure reduction.

The number of moles of methane consumed for hydrate formation is calculated from pressure data and temperature of the gas phase. Since the system is closed any reduction in the number of moles of methane in the gas phase should be equal to the number of moles of methane captured in hydrate phase. Hence:

\[
\Delta n_{H_1} = n_{G,0} - n_{G,t} = \left(\frac{PV}{zRT}\right)_{t=0} - \left(\frac{PV}{zRT}\right)_t
\]

Eq. 4.1

Where:

\(\Delta n_{H_1}\) is the number of moles of methane consumed for hydrate formation

\(n_{G,0}\) is the number of moles of methane in the gas phase at time zero

\(n_{G,t}\) is the number of moles of methane in the gas phase at time \(t\)

\(P\) is the pressure of the gas phase

\(V\) is the volume available for methane gas

\(R\) is the universal gas constant
\( T \) is the absolute temperature of the gas phase

\( z \) is the compressibility factor calculated from Pitzer’s correlation (J. M. Smith, Van Ness, and Abbott 2005).
4.3 MRI experiments

4.3.1 Apparatus

Imaging was performed on a Bruker Avance 200 NMR spectrometer (magnetic field of 4.7 Tesla) using multislice spin-echo pulse sequences with Gaussian selective pulses. Three vertical slices and three horizontal ones were chosen to acquire images on a 128×128 acquisition matrix (the configuration of slices is illustrated in Figure 4.5 and summarized in Table 4.2). 8 scans were accumulated to achieve a good signal-to-noise ratio.

<table>
<thead>
<tr>
<th></th>
<th>No. of slices</th>
<th>Slice thickness (mm)</th>
<th>Distance between slices (mm)</th>
<th>Field of View (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Horizontal</td>
<td>3</td>
<td>1</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>Vertical</td>
<td>3</td>
<td>1</td>
<td>2.2</td>
<td>3</td>
</tr>
</tbody>
</table>

4.3.2 Procedure

For all MRI experiments, 2 grams of sand was carefully mixed with the desired volume of water (0.44, 0.33, 0.22 or 0.11 mL) on a weighing plate and maximum uniformity in water distribution was ensured (the first MR image showed acceptable uniformity in water distribution). Then, the sand/water mixture was loaded into the high pressure Sapphire cell (the hydrate formation reactor). It was placed in the imaging probe inside the NMR spectrometer and then connected to the methane cylinder. In order to remove air from the gas phase, the system was exposed to vacuum (at 2-3 psia) and then purged with methane at a low pressure. After reaching the desired temperature, 1°C, methane was introduced at a pressure of 8 MPa and it was set as time zero for the experiment.

The set up is schematically illustrated in Figure 4.3 and Figure 4.4.
Figure 4.3. Schematic of the setup for the MRI experiments

Figure 4.4. Schematic of the NMR spectrometer (imager) connected to a PC for data transfer
Figure 4.5. Slice configuration, (a) Vertical slice, (b) Horizontal slice. The red rectangle and circle are typical Region of Interests (ROI) used to obtain the integrated intensity of images. It should be noted that the vertical image is upside down which means the top of the bed is at the bottom of the image and vice versa.
Horizontal and vertical images were alternatively acquired every 5 minutes (64 seconds for each scan and waiting time of 236 seconds). Pressure was also recorded at a time interval of 1 minute using a pressure transducer (Swagelok, model PTI-S-NG1500-27AQ) and Omega data acquisition system.

4.3.3 Calculations

The intensity of Magnetic Resonance images is proportional to the number density of hydrogen nuclei in the liquid phase (water). Formation of hydrate converts the liquid water to solid hydrate and because the relaxation time for hydrogen nuclei in the solid phase is very short, they become undetectable. So, hydrate formation can be followed by monitoring the decrease in the intensity of MR images, using this unique feature of the MRI technique in contrasting hydrogen nuclei in liquid and solid phases.

The intensity of MR images was integrated over a pre-defined region of interest (see Figure 4.5) using ParaVision software. Hydrate formation was verified via the expected decrease in the intensity of images as a result of conversion of liquid water to solid hydrate. The experiment was stopped when there was no significant change in the intensity of the images.

The uptake curve was also calculated using the same method described in the macroscopic experiments. The reduction in pressure which is equivalent to increase in the number of moles of methane consumed for hydrate formation was secondary and independent evidence for the formation of hydrates.

In order to calculate the percentage of water conversion to hydrates, the intensity of images for each slice was normalized by the intensity of the first image (at time zero). Since the intensity of the image is proportional to the number of hydrogen nuclei in the liquid phase and consequently
to the number of liquid water molecules, the hydrate conversion can be computed as the following:

\[
I \propto n_W \Rightarrow \frac{I}{I_0} = \frac{n_W}{n_{W0}} \Rightarrow 1 - \frac{I}{I_0} = \frac{n_{W0} - n_W}{n_{W0}} \Rightarrow 100 \times \left(1 - \frac{I}{I_0}\right) = 100 \left(\frac{n^H_W}{n_{W0}}\right) \text{: percentage of water molecules which has been converted to hydrate}
\]

Eq. 4.2

Where:

- \(I\) and \(I_0\) are the intensities of images at time \(t\) and time 0
- \(n_W\) and \(n_{W0}\) are the numbers of water molecules in the liquid phase at time \(t\) and time 0
- \(n^H_W\) is the number of water molecules in hydrate phase at time \(t\)

Also, in order to make sure that reducing the particle size does not dramatically change the porosity (\(\varepsilon\)) of the bed, \(\varepsilon\) was estimated by the method of McCabe, Smith, and Harriott (2001). They tabulated the porosity as a function of the ratio of particles’ diameter to the bed diameter. A linear interpolation through their data would result in the following relation:

\[
\varepsilon = 0.34 + 0.4 \left(\frac{d_{\text{particle}}}{D_{\text{bed}}}\right) ; \quad r^2 = 0.998
\]

Eq. 4.3

The porosities of the beds were calculated using this correlation and are given in Table 4.3.

As it can be seen the porosities are in the range of 0.35±0.01 which is in the acceptable range of experimental error. Therefore, the void volumes of the beds composed of the same mass of these sands are equal the within experimental error. Consequently, the initial water saturation would not vary considerably if these beds are saturated with the same volume of water.
Table 4.3. Porosity of the beds composed of the original and ground-sieved silica sands

<table>
<thead>
<tr>
<th>PSD (µm)</th>
<th>Porosity (ε)</th>
</tr>
</thead>
<tbody>
<tr>
<td>210-297</td>
<td>0.351-0.356</td>
</tr>
<tr>
<td>125-210</td>
<td>0.347-0.351</td>
</tr>
<tr>
<td>88-177</td>
<td>0.345-0.350</td>
</tr>
<tr>
<td>&lt;74</td>
<td>0.340-0.344</td>
</tr>
</tbody>
</table>

Finally, in order to compare the rate of hydrate formation a parameter was defined as the following:

\[
\text{Rate} \left( \frac{mL}{min} \right): R = \frac{\text{water content} \times \text{avg. conversion in vertical slices}}{t_{\text{total}} - t_{\text{induction time}}} \tag{4.4}
\]

Since in MRI experiments the water content of the beds differs, the total time cannot solely be interpreted as a criterion to compare the rate. It is very obvious that the higher amount of water needs more time to be converted to hydrate. But the defined parameter \( R \) takes this fact into account and it is basically a measure of the volume of water which has been converted to hydrate in a unit of time.
5 RESULTS AND DISCUSSIONS

5.1 Macroscopic experiments

For these three experiments the initial pressure is 8 MPa, temperature is 4 °C and the silica sand particle size distribution is 210 to 297 µm. Total time (duration of experiment), induction time and percentage of the conversion of water to hydrate are given in Table 5.1.

Table 5.1. Experimental results for the macroscopic experiments. The initial pressure is 8 MPa, the temperature is 4 °C and the sand PSD is 210-297 µm

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Bed height (cm)</th>
<th>Total time (min)</th>
<th>Induction time (min)</th>
<th>Water conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7</td>
<td>3900</td>
<td>252.0</td>
<td>79.5</td>
</tr>
<tr>
<td>2</td>
<td>7</td>
<td>6850</td>
<td>67.0</td>
<td>74.6</td>
</tr>
<tr>
<td>3</td>
<td>4</td>
<td>2100</td>
<td>30.3</td>
<td>79.3</td>
</tr>
</tbody>
</table>

Hydrate conversion was calculated based on a hydration number of 6.0 (Sloan 1996).

Normalized uptake curve and temperature profiles for these experiments are plotted in Figure 5.1, Figure 5.2 and Figure 5.3.

The number of moles of methane consumed for hydrate formation after the induction time was normalized by the total number of moles consumed at the end of experiment.

Hydrate formation is verified by the concomitant decrease in pressure and increase in temperature. Because the system is closed, as hydrates form, methane from the gas phase goes into the solid hydrate phase and due to the decrease in the number of methane molecules in the gas phase the pressure reduces. Also, hydrate formation is exothermic and therefore the released heat of reaction causes the temperature to go up. But, because the bed is immersed in a
temperature-controlled water bath the heat will be dissipated and temperature goes back to the set point. This can be seen as a peak in the temperature profile.

![Normalized uptake curve and temperature profiles](image)

Figure 5.1. The normalized uptake curve and temperature profiles for experiment 1 in Table 5.1 (initial $P = 8$ MPa, $T = 4^\circ C$, PSD = 210-297 µm, bed height = 7 cm)

The width and height of this peak depends on a number of factors: the amount of water converting to hydrate, the rate at which this reaction happens and heat is released and finally the rate at which the heat is removed from the bed to the bath.

It is interesting to note that after the first sharp temperature peak at the beginning of the experiment (the nucleation point), there are several other peaks detected by thermocouples at different locations inside the bed and at different times. It can be seen that whenever these peaks occur the uptake curve is steeper and therefore the rate of methane consumption is faster as compared to the situation where the temperature remains constant.
This certainly suggests that the nature of hydrate formation is different during these two situations. It can be postulated that when the temperature remains constant and the number of moles of methane consumed for hydrate formation increases slowly and almost linearly, the crystals of hydrate are growing at a rate at which the heat transfer from the bed to the bath is fast enough to remove the heat of reaction and maintain the temperature at its set point.

On the other hand, when hydrate formation occurs faster, probably due to the nucleation of new crystals and sudden conversion of the pockets of water in the interstices and most likely the connected neighboring area to hydrate, the rate of heat release is large enough to overwhelm that of heat dissipation and this generates peaks in the temperature profiles.

So, it can be concluded that as opposed to hydrate formation in bulk water in which it is believed only one nucleation event happens at the induction time (nucleation point), “multiple
nucleation” occurs during hydrate formation from the water which is dispersed in a bed of sand particles. Multiple nucleation is a term which describes the occurrence of several nucleation events at different locations inside the bed and at different times. It should be noted that in a stationary system there may be multiple nucleation but no one has tried to measure it till now.

These results are in excellent agreement with the recent work of C. Haligva (2009).

For experiment 3 where the height of the bed was reduced to 4 cm, it can be seen that 80% of the hydrate formation occurs right after the induction time. The temperature profiles in the inset of Figure 5.3 shows complex peaks which means nucleation events happen fast enough such that before all of the heat from the previous nucleation dissipated a new crystal nucleates and releases heat.
This can be attributed to the fact that reducing the height of the bed will decrease the diffusion length (mass transfer resistance) for methane and therefore methane would be more readily available for hydrate formation all over the bed. When the height of the bed is 7 cm, it is probable that due to the relatively slow rate of diffusion, before methane reaches the bottom of the bed, hydrate forms in the middle or upper part of the bed. This slows down the rate of methane diffusion and consequently hydrate formation rate because diffusion through solid phase (hydrate) is slower than that of liquid phase (water). So, nucleation may occur at totally different times.
5.2 MRI experiments

Experimental conditions of the experiments performed are given in Table 5.2. The initial pressure was 8 MPa for all experiments and temperature was kept constant at 1°C.

In the beginning it was attempted to form hydrate at temperatures of 4 and 7°C as well, but hydrate did not form even after 4 days. So, it was decided to do all of the experiments at 1°C. But forming hydrate even at 1°C in a bed which was completely saturated with water, with a water to sand ratio of 0.22 mL/g, was not successful. It was probably due to the very small direct contact area between water and methane at the interface on top of the bed, a circle with a diameter of 7.5 mm. Also, having a smaller bed (compared to the macroscopic experiments) which obviously has a lower amount of water and sand, can decrease the probability of nucleation and subsequent hydrate formation. It seems reasonable that as the volume of the bed increases, the more reactant (water) will be available for hydrate formation which consequently increases the probability of hydrate formation. It should be noted that nucleation as the trigger of hydrate formation is a stochastic process.

In order to increase the area of direct contact between water and methane, the amount of water present in the bed was reduced. Decreasing the water content of the bed facilitates hydrate formation by providing some pathways and channels for the gas to penetrate readily through them and be in direct contact with water almost all over the bed.

In a fully water-saturated bed, hydrate formation, especially at the bottom of the bed, is diffusion-controlled, i.e. methane has to dissolve in water and diffuse through liquid phase which is a relatively slow process. However, in a partially water-saturated bed, the gas is able to freely communicate through tortuous channels of the bed which is much faster than diffusion.
Table 5.2. Experimental conditions for the MRI experiments. The initial pressure is 8 MPa and the temperature is 1 °C

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Water content (mL)</th>
<th>Particle Size Range (µm)</th>
<th>Total time (min)</th>
<th>Induction time (min)</th>
<th>Hydrate conversion* (%)</th>
<th>Rate×10^5 (mL/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>0.11</td>
<td>210-297</td>
<td>4030</td>
<td>810</td>
<td>77.3</td>
<td>2.11</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td></td>
<td>2680</td>
<td>40</td>
<td>78.3</td>
<td>3.21</td>
</tr>
<tr>
<td>6</td>
<td>0.22</td>
<td>210-297</td>
<td>5390</td>
<td>110</td>
<td>90.6</td>
<td>3.70</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td></td>
<td>5700</td>
<td>210</td>
<td>91.0</td>
<td>3.51</td>
</tr>
<tr>
<td>8</td>
<td>0.33</td>
<td>210-297</td>
<td>8070</td>
<td>300</td>
<td>91.1</td>
<td>3.72</td>
</tr>
<tr>
<td>9</td>
<td>0.44</td>
<td>210-297</td>
<td>19210</td>
<td>120</td>
<td>85.8</td>
<td>1.96</td>
</tr>
<tr>
<td>10</td>
<td>0.22</td>
<td>88-177</td>
<td>730</td>
<td>180</td>
<td>81.2</td>
<td>24.47</td>
</tr>
<tr>
<td>11</td>
<td>0.33</td>
<td>88-177</td>
<td>930</td>
<td>30</td>
<td>89.4</td>
<td>31.73</td>
</tr>
<tr>
<td>12</td>
<td></td>
<td></td>
<td>1240</td>
<td>70</td>
<td>90.4</td>
<td>24.06</td>
</tr>
<tr>
<td>13</td>
<td>0.44</td>
<td>88-177</td>
<td>2630</td>
<td>10</td>
<td>93.9</td>
<td>15.71</td>
</tr>
<tr>
<td>14</td>
<td>0.33</td>
<td>&lt;74</td>
<td>250</td>
<td>60</td>
<td>65.8</td>
<td>86.81</td>
</tr>
<tr>
<td>15</td>
<td>0.44</td>
<td>&lt;74</td>
<td>520</td>
<td>50</td>
<td>83.6</td>
<td>70.72</td>
</tr>
<tr>
<td>16</td>
<td>0.22</td>
<td>(210-297)+(&lt;74)</td>
<td>930</td>
<td>40</td>
<td>85.2</td>
<td>20.16</td>
</tr>
<tr>
<td>17 (D†)</td>
<td>0.22</td>
<td>(210-297)+(&lt;74)</td>
<td>1640</td>
<td>-</td>
<td>96.4**</td>
<td>-</td>
</tr>
<tr>
<td>18 (Re-F‡)</td>
<td>0.22</td>
<td>(210-297)+(&lt;74)</td>
<td>2330</td>
<td>0</td>
<td>83.2</td>
<td>7.76</td>
</tr>
<tr>
<td>19</td>
<td>0.22</td>
<td>125-210</td>
<td>1190</td>
<td>20</td>
<td>87.5</td>
<td>16.18</td>
</tr>
<tr>
<td>20</td>
<td>0.33</td>
<td>125-210</td>
<td>7940</td>
<td>110</td>
<td>92.4</td>
<td>3.84</td>
</tr>
<tr>
<td>21</td>
<td>0.44</td>
<td>125-210</td>
<td>11390</td>
<td>40</td>
<td>91.1</td>
<td>3.52</td>
</tr>
<tr>
<td>22 (D†)</td>
<td>0.44</td>
<td>125-210</td>
<td>210</td>
<td>-</td>
<td>96.2**</td>
<td>-</td>
</tr>
</tbody>
</table>

*: the avg. between vertical slices †: Decomposition, ‡: Re-formation, **: % of recovery
The general behavior of the system is the same for all experiments. Below is a detailed analysis of experiments 4 and 9 which are typical representatives of the hydrate formation habits in a bed of silica sand particles.

Normalized intensity of vertical and horizontal images as well as the normalized uptake curves for other experiments are given in appendix B.

Figure 5.4. Normalized intensity profiles of horizontal slices for experiment 9 (water content: 0.44 mL, PSD: 210-297 µm). Hydrate formation process can be divided into three stages which are separated by dashed lines: Induction period, non-uniform growth and uniform growth. The arrows typically indicate different nucleation events occurring during non-uniform growth period.
According to the intensity profiles hydrate formation process can be divided into three stages: the common *induction period*, *non-uniform growth* and *uniform growth*.

During the induction period, methane molecules dissolve in water and at the end of this period which is known as the induction time the first crystal of hydrate forms. It can be identified by the first sudden drop in the intensity of MR images.

Non-uniform growth refers to the period where there are several abrupt drops in the intensity of images, as typically indicated by arrows in Figure 5.4 and Figure 5.5. They reflect the nucleation events which occur at different positions in the bed and at different times. Overall,
during this period hydrate formation proceeds through a combination and competition between nucleation and growth (the accolades in Figure 5.5 represent growth). In fact, multiple-nucleation happens in this stage. A time-lapse series of difference images of vertical slices is given in Table 5.3. A difference image is an image which is obtained by subtracting the first image at time 0 from the original image at time t. In these images, the dark areas are indicative of hydrates. So, the sudden appearance of the purple spots in different positions in each slice and at different time proves the occurrence of multiple nucleation in hydrate formation in a water-saturated bed of silica sand.

It is very probable that hydrate nucleates on the surface of a sand particle which acts as the nucleation site. This leads to the quick conversion of the pocket of water in the interstitial space and most likely the connected interstices to hydrate. Therefore, an abrupt decrease in the intensity of MR images occurs and suddenly a dark spot appears in the difference image.

On the other hand, uniform growth refers to the period in which only the growth of the crystals that are already produced during the previous stage happens. There is no sudden drop and the intensity profile shows a uniform decay trend.

These periods are separated by dashed lines in Figure 5.4, Figure 5.5 and Figure 5.6. The bed with the same PSD and water contents of 0.22 mL (exp. 6 & 7) and 0.33 mL (exp. 8) show the same behavior (see Figures B.3, B.4 and B.5 in appendix B).
Table 5.3. Time lapse series of the difference images of experiment 9 (water content: 0.44 mL, PSD: 210-297 µm) [Vertical slices]. The darker areas represent hydrate. The sudden appearance of the purple spots at different positions in each slice and also at different times is a proof for the occurrence of multiple nucleation when hydrates form in a water-saturated bed of silica sand particles.

<table>
<thead>
<tr>
<th>t (min)</th>
<th>130</th>
<th>180</th>
<th>810</th>
<th>1680</th>
<th>2850</th>
<th>4050</th>
<th>4260</th>
<th>11770</th>
<th>15380</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slice 1</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
<td><img src="image9.png" alt="Image" /></td>
</tr>
<tr>
<td>Slice 2</td>
<td><img src="image10.png" alt="Image" /></td>
<td><img src="image11.png" alt="Image" /></td>
<td><img src="image12.png" alt="Image" /></td>
<td><img src="image13.png" alt="Image" /></td>
<td><img src="image14.png" alt="Image" /></td>
<td><img src="image15.png" alt="Image" /></td>
<td><img src="image16.png" alt="Image" /></td>
<td><img src="image17.png" alt="Image" /></td>
<td><img src="image18.png" alt="Image" /></td>
</tr>
<tr>
<td>Slice 3</td>
<td><img src="image19.png" alt="Image" /></td>
<td><img src="image20.png" alt="Image" /></td>
<td><img src="image21.png" alt="Image" /></td>
<td><img src="image22.png" alt="Image" /></td>
<td><img src="image23.png" alt="Image" /></td>
<td><img src="image24.png" alt="Image" /></td>
<td><img src="image25.png" alt="Image" /></td>
<td><img src="image26.png" alt="Image" /></td>
<td><img src="image27.png" alt="Image" /></td>
</tr>
</tbody>
</table>
Pressure profile and normalized uptake curve for experiment 9 is plotted in Figure 5.6. It is very important to note that uptake curve does not show any non-uniformity in its shape during non-uniform growth period. But, it can be seen that the profile shows a two step process after induction period.

So, as noted by Kneafsey et al. (2007b) it is very crucial to utilize different technique to investigate hydrate formation if one wants to gain a more complete picture of the process.

It was also pointed out by I. L Moudrakovski et al. (2004) that the smooth behavior observed in uptake curve is only the result of averaging over many local environments in which hydrate formation is happening.
Intensity profiles and uptake curve for experiment 4 (water content: 0.22 mL, PSD: 210-297 µm) are plotted in Figure 5.7. Unlike the previous experiment (water content: 0.44 mL, PSD: 210-297 µm), there is no non-uniform growth period. Since the initial water content of the bed is lower, most of the water is dispersed on the surface of the sand particles and the interstitial spaces between sand particles are not fully filled with water. Therefore, there will be some channels and pathways available for the gas to communicate through them and be in direct contact with water all over of the bed, from the top to the bottom (with the reasonable assumption that these pathways are evenly distributed throughout the bed). As a result and as it can be observed in Figure 5.7 and Table 5.4, hydrate formation follows almost the same trend in each slice group. This can suggest that hydrate formation in a porous medium, where the initial
water saturation is low, happens homogenously throughout the medium. As mentioned before, the main reasons are the availability and ease in the transportation of the gas all over the bed.

Table 5.4. Time lapse series of the images of experiment 4 (water content: 0.11 mL, PSD: 210-297 µm) [Vertical slices]. The darker areas represent hydrate. The gradual darkening of each slice shows that hydrate formation occurs uniformly when the initial water content of the bed is low. Here the water content is one fourth of the value corresponding to the fully water-saturated bed.

<table>
<thead>
<tr>
<th>t (min)</th>
<th>820</th>
<th>900</th>
<th>1050</th>
<th>1400</th>
<th>1740</th>
<th>2370</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slice 1</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
</tr>
<tr>
<td>Slice 2</td>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
<td><img src="image9.png" alt="Image" /></td>
<td><img src="image10.png" alt="Image" /></td>
<td><img src="image11.png" alt="Image" /></td>
<td><img src="image12.png" alt="Image" /></td>
</tr>
<tr>
<td>Slice 3</td>
<td><img src="image13.png" alt="Image" /></td>
<td><img src="image14.png" alt="Image" /></td>
<td><img src="image15.png" alt="Image" /></td>
<td><img src="image16.png" alt="Image" /></td>
<td><img src="image17.png" alt="Image" /></td>
<td><img src="image18.png" alt="Image" /></td>
</tr>
</tbody>
</table>

Table 5.4 depicts the time-lapse series of difference images for experiment 4. One can see that hydrate formation proceeds homogeneously as the intensity of difference images gradually and uniformly increases as time goes on. The absence of sudden darkening of various spots in the images suggests that no obvious multiple nucleation happens in this bed with low initial water saturation. Experiment 5, which is a duplication of this experiment, shows the same behavior (see Figure B.2 in appendix B).
One thing that has to be noted here is that hydrate formation can be followed to a larger extent through the decrease in the intensity of vertical slices as compared to horizontal slices. This is due to the fact that the area which is being imaged in vertical slice is almost 4 times greater than that of the horizontal one. Since the MRI signal intensity obtained is proportional to the number of water molecules in the liquid phase and there is more water in the vertical slice, therefore the signal to noise ratio is better for vertical slices. This means that for horizontal slices after a shorter time the signal reaches the noise level and from that time onwards remains almost constant. The image is thus controlled by noise which does not allow us to follow hydrate formation over a longer time. This difference between horizontal and vertical slices becomes smaller as the water content of the bed increases as there is more water in horizontal slices and thus the signal to noise ratio improves.

5.3 Effect of water content

In order to study the effect of the water content of the bed, the intensity of vertical slice 2 (as a typical representative of intensity profiles) and uptake curves are plotted in the same figure for each PSD. Since these experiments finished on very different time scales, for the purpose of better representing the time it is normalized by the following relation:

\[ \text{Normalized time} = \frac{t - t_{\text{Induction}}}{t_{\text{total}} - t_{\text{Induction}}} \]

Eq. 5.1
Figure 5.8. Comparison of the normalized intensity profiles of vertical slice 2 for experiments with different water contents and PSD of 210-297 µm.

Figure 5.9. Comparison of the normalized uptake curves for experiments with different water contents and PSD of 210-297 µm.
Figure 5.10. Comparison of the normalized intensity profiles of vertical slice 2 for experiments with different water contents and PSD of 125-210 µm

Figure 5.11. Comparison of the normalized uptake curves for experiments with different water contents and PSD of 125-210 µm
Figure 5.12. Comparison of the normalized intensity profiles of vertical slice 2 and normalized uptake curves for experiments with different water contents and PSD of 88-177 µm

Figure 5.13. Comparison of the normalized intensity profiles of vertical slice 2 and normalized uptake curves for experiments with different water contents and PSD of <74 µm
Comparison of the intensity profile and uptake curve for each PSD shows that hydrate formation happens faster in a bed with lower water content. The reason for this observation is that as the water content of the bed is reduced more channels become available for the gas to communicate through and participate in hydrate formation all over the bed. It is very well known that diffusion through the liquid phase is much slower than the free transportation of the gas through the tortuous pathways of the bed.

Figure 5.8 shows that when the water content of the bed composed of sand with the PSD of 210-297 µm is 0.11 mL, hydrate formation happens uniformly and there is no sudden drop in the intensity profile. The corresponding water content for the beds with PSD’s of 125-210, 88-177 and <74 µm are 0.22, 0.22 and 0.44 mL, respectively. So, it can be concluded that when the water content of the bed is lower than a specific value, depending on the PSD, hydrate formation occurs uniformly and there is no obvious multiple nucleation.

On the one hand, as water content of the bed decreases lower amount of water fills the interstices and the water is mostly distributed over the surface of the sand particles. Therefore, formation of hydrate and conversion of water to hydrate in an interstice and most probably the water in the connected interstices cannot impose a sudden drop in the intensity profile of the MR images.

On the other hand, as the PSD becomes smaller the size of the interstices decreases accordingly. So, again formation of hydrate in an interstice and the connected interstices will result in a smaller sudden drop in the intensity profile. This also explains why the lower limit of water content for observing a uniform behavior is higher in a bed with smaller PSD.
It can also be seen that as the sand particle size becomes smaller, the hydrate formation behavior in beds with different water contents becomes more similar. The intensity profiles in Figure 5.12 and Figure 5.13 show more similarity in the hydrate formation behavior in beds with different water contents as compared to the intensity profiles in Figure 5.8 and Figure 5.10.

5.4 Effect of particle size

The intensity profile of vertical slice 2 and the uptake curve for experiments with the same water content and different PSD’s are plotted below. As can be seen, the rate of hydrate formation is faster in a bed which is composed of smaller sand particles.

Since the specific area of the bed (a, area/volume) is inversely proportional to the diameter of the sand particles, \(d_p\), a bed with smaller particle size will have a larger surface area. If we presume that hydrate formation starts by nucleation at the surface of particles, therefore, a smaller particle size facilitates hydrate formation by providing more nucleation sites (larger surface area).

\[
a = \frac{\text{total surface area of particles}}{\text{total volume of the bed}} = a_p(1 - \varepsilon) = \frac{\text{total surface area of particles}}{\text{total volume of particles}/(1 - \varepsilon)} \quad \text{Eq. 5.2}
\]

Also, we know that:

\[
a_p = \frac{4\pi d_p^2}{4} = \frac{6}{d_p} \quad \Rightarrow \quad a = \frac{6(1 - \varepsilon)}{d_p} \quad \Rightarrow \quad a \propto \frac{1}{d_p} \quad \text{Eq. 5.3}
\]

One can see that the initial drop in the intensity profile (as a result of the first nucleation at the induction time) in Figure 5.14, Figure 5.16 and Figure 5.18 is larger for the bed with smaller particle. This is consistent with the fact that hydrate formation is overall faster in a bed composed of smaller particles.
Figure 5.14. Comparison of the normalized intensity profiles of vertical slice 2 for experiments with different PSD’s and water content of 0.44 mL.

Figure 5.15. Comparison of the normalized uptake curves for experiments with different PSD’s and water content of 0.44 mL.
Figure 5.16. Comparison of the normalized intensity profiles of vertical slice 2 for experiments with different PSD’s and water content of 0.33 mL.

Figure 5.17. Comparison of the normalized uptake curves for experiments with different PSD’s and water content of 0.33 mL.
Figure 5.18. Comparison of the normalized intensity profiles of vertical slice 2 for experiments with different PSD’s and water content of 0.22 mL.

Figure 5.19. Comparison of the normalized uptake curves for experiments with different PSD’s and water content of 0.22 mL.
A comparison of the rate of hydrate formation in beds with different water contents and different PSD’s is given in Figure 5.20. It can be seen that the effect of particle size is more profound compared to the effect of water content in the sense that the degree of increase in the hydrate formation rate is much higher when the particle size is smaller compared to the case where water content is lower.

![Figure 5.20. Comparison of the rate of hydrate formation in beds with different particle sizes and different water contents](image)

5.5 **Hydrate formation in a bed with bimodal PSD**

In experiment 16, 1.75 grams of the original sand (PSD: 210-297 µm) was mixed with 0.25 grams of sand with a PSD of <74 µm in order to investigate hydrate formation in a bed with has a broad range of particle size (bimodal particle size distribution). Adding 0.44 mL of water resulted in an over saturated mixture of water/sand and when 0.22 mL of water was added the water/sand mixture, in appearance, was very similar to a fully saturated mixture of sand/water.
The reduction in the volume of water needed for fully saturating the sand is because of the fact that the finer particles were small enough to partially fill the interstitial space between coarser particles which consequently decreased the void volume of the bed. It was observed that the rate of hydrate formation, \(20.16 \times 10^{-5}\) mL/min, was much faster than the rate in a fully saturated bed (exp. 6, water content: 0.44 mL), \(1.96 \times 10^{-5}\) mL/min, and partially (exp. 9, water content: 0.22 mL), \(3.70 \times 10^{-5}\) mL/min, saturated bed of original sand (2 grams of sand with a PSD of 210-297 µm).

This suggests that the particle size is a very influencing factor on the rate of hydrate formation in porous media. Even though replacing 0.25 grams of the coarse sand (PSD: 210-297 µm) with finer particles (PSD: <74 µm) in a bed with the water content of 0.22 mL largely reduced the void volume and filled most of the tortuous channels inside the bed, the rate of hydrate formation was considerably increased as compared to the bed with the same water content and 2 grams of the coarser sand (PSD: 210-297 µm).

A time-lapse series of images for this experiment is given in Table 5.5 and Table 5.6. In these images the brighter area represents the liquid water phase and the darker area represent all of the non-liquid water phases including the silica sand particles and the solid hydrate phase.

The intensity (brightness) of the MR image is proportional to the number density of hydrogen nuclei in the liquid water phase. Once hydrate forms, the liquid water converts to solidhydrate and hydrogen nuclei become undetectable due to the very short relaxation time in the solid phase. Therefore, hydrate formation can be verified by the transformation of the brighter areas of the image into the darker areas.
Table 5.5. Time lapse series of the images of experiment 16 (water content: 0.22 mL, PSD: (210-297)+(<74) µm) [Horizontal slices]. The brighter areas represent the liquid water phase and darker areas represent the solid hydrate phase and sand particles. As time passes and hydrate forms, brighter areas transform into the darker areas.

<table>
<thead>
<tr>
<th>t (min)</th>
<th>50</th>
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<th>70</th>
<th>90</th>
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</thead>
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<td>7966</td>
<td>7942</td>
<td>7928</td>
<td>7901</td>
</tr>
</tbody>
</table>

Slice 1

![Slice 1 Image](image1)

Slice 2

![Slice 2 Image](image2)

Slice 3

![Slice 3 Image](image3)
Table 5.6. Time lapse series of the images of experiment 16 (water content: 0.22 mL, PSD: (210-297)+(<74) µm) [Vertical slices]. The brighter areas represent the liquid water phase and the darker areas represent the solid hydrate phase and sand particles. As time passes and hydrate forms, brighter areas transform into the darker areas.

<table>
<thead>
<tr>
<th>t (min)</th>
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<tbody>
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<td>P (kPa)</td>
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<td>7928</td>
<td>7900</td>
<td>7871</td>
</tr>
</tbody>
</table>

Slice 1

Slice 2

Slice 3
5.6 Dissociation runs

At the end of experiment 16, the temperature was increased to 13°C in order to dissociate hydrates (the equilibrium temperature at 8 MPa is 11.4°C). As soon as the temperature crossed the phase boundary, hydrate started to decompose and the MRI signal reappeared in the images. The intensity of images is plotted in Figure 5.21. In order to ensure maximum recovery, the pressure was also reduced to 460 kPa at t=1400 minutes. At this point (460 kPa, 13°C) the recovery was about 80%. However, the point that needs to be taken into consideration is that the MRI signal is inversely temperature-dependent, which means the higher the temperature the lower MRI signal. So, in order to find the actual recovery temperature was reduced back to 1°C and it was observed that 96.4% of hydrate had been recovered.

Since the driving force for decomposition was relatively high all of the hydrates dissociated very quickly and the first MR image after reaching a temperature of 13°C showed almost a complete return of the signals.

The system was subsequently repressurized with methane to reform hydrates. Although no induction time was observed, the rate of reformation (exp. 18, 7.76×10^{-5} mL/min) was almost one third of the first formation run (exp. 16, 20.16×10^{-5} mL/min).

For the last experiment, a decomposition run (exp. 22) was also conducted at a temperature of 11.5°C. Since, the driving force for decomposition was smaller compared to the previous decomposition experiment the intensity profile started to build up gradually. This can be seen in the time-lapse series of MR images in Table 5.7 and Table 5.8.
The horizontal images show that dissociation starts from the perimeter of the bed and propagates inwards. This is consistent with the fact that the required heat for the decomposition reaction is supplied from the perimeter of the bed.

On the other hand, vertical images show that hydrate begins to decompose from the top of the bed and the dissociation front moves downwards. This is likely because of the fact that the temperature is slightly higher on the upper parts of the bed (due to the design of the cooling system of the imaging probe) which facilitates hydrate dissociation.

**Figure 5.21.** Normalized intensity profiles and uptake curve for experiment 17 (water content: 0.22 mL, PSD: (210-297)+(<74) µm)
Table 5.7. Time lapse series of the images of experiment 22 (water content: 0.44 mL, PSD: 125-210 µm [Horizontal slices]. The brighter areas represent liquid water phase and darker areas represent the solid hydrate phase and sand particles. As time passes and hydrate decomposes, darker areas transform into the brighter areas.

<table>
<thead>
<tr>
<th>t (min)</th>
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<th>50</th>
<th>60</th>
<th>70</th>
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<td>P (kPa)</td>
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<td>7810</td>
<td>7836</td>
<td>7905</td>
<td>460</td>
</tr>
</tbody>
</table>

Slice 1

Slice 2

Slice 3
Table 5.8. Time lapse series of the images of experiment 22 (water content: 0.44 mL, PSD: 125-210 µm) [Vertical slices]. The brighter areas represent the liquid water phase and the darker areas represent the solid hydrate phase and sand particles. As time passes and hydrate decomposes, darker areas transform into the brighter areas.

<table>
<thead>
<tr>
<th>t (min)</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>70</th>
<th>200</th>
</tr>
</thead>
<tbody>
<tr>
<td>P (kPa)</td>
<td>7719</td>
<td>7810</td>
<td>7836</td>
<td>7905</td>
<td>460</td>
</tr>
</tbody>
</table>

Slice 1

Slice 2

Slice 3
6 CONCLUSIONS AND RECOMMENDATIONS

Methane hydrate formation and dissociation in a water-saturated bed of silica sand particles were visualized by taking advantage of the $^1$H Magnetic Resonance Imaging technique. Hydrate formation in porous medium was investigated by following the changes in the intensity of magnetic resonance images. The effects of water content of the bed and particle size of the silica sand were also examined.

The conclusions are summarized below. Also, a number of recommendations have been made for future work. Obtaining a definitive mechanism for hydrate formation in porous media still needs further investigations and requires to be studied in greater detail.

6.1 Conclusions

1. According to the results of MRI experiments, the process of hydrate formation in a bed of silica sand can be divided into three stages: induction period, non-uniform growth and uniform growth. During the first stage methane molecules dissolve and diffuse in water and at the end of this period (nucleation point) the first crystals of hydrate appear.

2. Hydrate formation proceeds through a combination and competition between growth and nucleation during the non-uniform growth stage. This proves the occurrence of “multiple nucleation” when hydrates are forming in the interstices of a water-saturated bed of silica sand. No nucleation happens during the last stage and hydrate formation continues through the growth of the crystals which are already formed in previous stages.

3. It was observed that there is a lower limit for water content of the bed for which no non-uniform growth happens (0.11 mL for PSD of 210-297 µm, 0.22 mL for PSD of 88-177 µm). It is because of the fact that in these partially saturated beds, the amount of water in
the interstices is not enough to make a significant drop in the intensity profile as a result of nucleation and formation of hydrates. Also, the gas is freely available in tortuous channels of the bed and this leads to an almost uniform formation of hydrates all over the bed.

4. Hydrate formation was found to occur faster in a bed with lower water content. Decreasing water content of the bed will provide some pathways and channels for the gas to freely transport through them and participate in hydrate formation all over the bed thus facilitating hydrate formation. The dominant mechanism of methane supply for hydrate formation in a bed with higher water content is diffusion which is known to be much slower than free transportation of the gas.

5. Hydrate formation in a bed composed of smaller particles resulted in a faster rate of hydrate formation. If we presume that sand particles serve as nucleation site for hydrate formation, therefore, a bed with smaller particles will accelerate hydrate formation by providing larger area for nucleation and subsequent growth of hydrates (the specific area of the bed is inversely proportional to the diameter of the sand particles).

6.2 Recommendations

1. In this study, only one type of sand was used as the porous medium. Testing other material such as silica gel would determine if the general behavior of hydrate formation remains the same in a different porous environment.

2. The temperature was kept constant at 1 °C in MRI experiment. Macroscopic experiments of C. Haligva (2009) showed that no multiple nucleation happened at temperature of 7°C. So, it would be interesting to check if MRI experiment results in the same observation.
3. Since increasing the temperature changes the driving force for hydrate formation, it would also be of interest to test the effect of pressure. Because changing the pressure also alters the driving force for hydrate formation which may consequently affect the hydrate formation habit in porous media.

4. Macroscopic experiment showed that the size (height) of the bed can also have an influence on the hydrate formation habit. Conducting MRI experiment in beds with different height would certainly provide more information about the effect of bed height.

5. Even though the foremost hydrate former of the natural clathrate is methane, there are other components in the natural gas such as ethane and propane. Delineating the role of these substances in hydrate formation habit in porous media is of great importance as such components are known to modify the rate of hydrate processes significantly.

6. Pure water is rarely found in nature. So, it would be closer to the real conditions if one forms hydrate from brine solution with a concentration close to that of sea water.

7. Molecular Dynamics simulation of the formation of methane hydrate in presence of silica sand can also provide a great deal of information on the molecular level about the mechanism of hydrate formation in porous media. Phenomena such as cage formation and molecular arrangement of methane and water during hydrate formation can be studied precisely thus revealing fundamental details about the mechanism of hydrate formation in porous media.
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APPENDICES

Appendix A: Heat transfer calculations

The main mechanism of heat transfer from a water-saturated bed of silica sand to the outer surface of the reactor is conduction. The heat would subsequently be taken off from the outer surface of the Stainless Steel crystallizer by convection through water circulation in the water bath.

The heat conduction resistance for a cylindrical shell is defined as the following (Holman 1981):

\[ q = \frac{\Delta T}{R} \quad \text{and} \quad R = \frac{\ln\left(\frac{R_o}{R_i}\right)}{2\pi kL} \quad \text{Eq A.1} \]

Where:

- \( q \): is the heat flux through the cylindrical shell
- \( \Delta T \): is the temperature difference across the cylindrical shell along the r-direction
- \( R_o \): is the outer radius
- \( R_i \): is the inner radius
- \( k \): is the thermal conductivity
- \( L \): is the length of the cylinder

![Top view of the Copper Cylinder configuration](image)

Figure A.1. Top view of the Copper Cylinder configuration, reprinted from C. Haligva et al. (2010) with permission from American Chemical Society
Now, if we focus on the heat transfer from the inner core of the bed (white area in Figure A.1) we can compare the heat transfer rate by calculating the corresponding heat conduction resistance. Actually, when we are changing the bed size, we are replacing the Copper cylinders with water/sand mixture.

Thermal conductivity of the sand/water mixture was estimated by assuming a wt% average:

\[ k_{WS} = \left( \frac{0.217}{1 + 0.217} \right) k_W + \left( \frac{1}{1 + 0.217} \right) k_{quartz} = (0.178 \times 0.58) + (0.822 \times 1.4) = 1.25 \frac{W}{m\cdot K} \]

**Case I: CC1+CC2**

Since, the heat transfer resistances are in series, the total resistance would the sum of the individual resistances:

\[
R = R_{CC2} + R_{CC1} + R_{CR} = \frac{1}{2\pi L} \left[ \ln \left( \frac{R_{CC2,0}}{R_{CC2,i}} \right) k_c + \ln \left( \frac{R_{CC1,0}}{R_{CC1,i}} \right) k_c + \ln \left( \frac{R_{CR,0}}{R_{CR,i}} \right) k_{SS} \right]
\]

\[
R = \frac{1}{2\pi L} \left[ \ln \left( \frac{3.81}{2.54} \right) \frac{400}{400} + \ln \left( \frac{5.08}{3.81} \right) \frac{400}{400} + \ln \left( \frac{8.89}{5.08} \right) \frac{19}{19} \right] = \frac{1}{2\pi L} (0.00101 + 0.00072 + 0.02945) = \frac{0.03118}{2\pi L}
\]

**Case II: CC1**

\[
R = R_{WS2} + R_{CC1} + + R_{CR} = \frac{1}{2\pi L} \left[ \ln \left( \frac{R_{CC2,0}}{R_{CC2,i}} \right) k_{WS} + \ln \left( \frac{R_{CC1,0}}{R_{CC1,i}} \right) k_c + \ln \left( \frac{R_{CR,0}}{R_{CR,i}} \right) k_{SS} \right]
\]
\[ R = \frac{1}{2\pi L} \left[ \ln \left( \frac{3.81}{2.54} \right) + \ln \left( \frac{5.08}{3.81} \right) + \ln \left( \frac{8.89}{5.08} \right) \right] = \frac{1}{2\pi L} (0.32437 + 0.00072 + 0.02945) \]

\[ = \frac{0.35454}{2\pi L} \]

**Case III:** No CC

\[ R = R_{WS2} + R_{WS1} + R_{CR} = \frac{1}{2\pi L} \left[ \ln \left( \frac{R_{CC2,o}}{R_{CC2,i}} \right) + \ln \left( \frac{R_{CC1,o}}{R_{CC1,i}} \right) + \ln \left( \frac{R_{CR,o}}{R_{CR,i}} \right) \right] \]

\[ R = \frac{1}{2\pi L} \left[ \ln \left( \frac{3.81}{2.54} \right) + \ln \left( \frac{5.08}{3.81} \right) + \ln \left( \frac{8.89}{5.08} \right) \right] = \frac{1}{2\pi L} (0.32437 + 0.23015 + 0.02945) \]

\[ = \frac{0.58397}{2\pi L} \]

Hence:

\[ \frac{0.35454/2\pi L}{0.03118/2\pi L} \approx 11.4 \quad \text{and} \quad \frac{0.58397/2\pi L}{0.03118/2\pi L} \approx 18.7 \]

Therefore, when we have no CC in the bed the heat transfer resistance from the inner core of the bed is approximately 20 times of the case when we insert both CC1 and CC2 in the bed. Similarly, when we have only CC1 present in the system, it is approximately 10 times greater.
Appendix B: Normalized intensity profiles and uptake curves

This appendix contains the normalized intensity profile of the horizontal and vertical slices as well as normalized uptake curve for experiments reported in Table 5.2.

The concurrent occurrence of decrease in the intensity and increase in the number of moles of methane in the uptake curve provide independent proofs for formation of hydrates. The sudden drops in the intensity profiles can be interpreted as nucleation and smooth decays are indicative of the growth of hydrate crystals.

Because the signal to noise ratio is better for vertical slices, hydrate formation can be followed to a larger extent as compared to the horizontal slices.

Figure B.2. Normalized intensity profiles and uptake curve for experiment 5 (water content: 0.11 mL, PSD: 210-297 µm)
Figure B.3. Normalized intensity profiles and uptake curve for experiment 6 (water content: 0.22 mL, PSD: 210-297 µm)

Figure B.4. Normalized intensity profiles and uptake curve for experiment 7 (water content: 0.22 mL, PSD: 210-297 µm)
Figure B.5. Normalized intensity profiles and uptake curve for experiment 8 (water content: 0.33 mL, PSD: 210-297 µm)

Figure B.6. Normalized intensity profiles and uptake curve for experiment 10 (water content: 0.22 mL, PSD: 88-177 µm)
Figure B.7. Normalized intensity profiles and uptake curve for experiment 11 (water content: 0.33 mL, PSD: 88-177 µm)

Figure B.8. Normalized intensity profiles and uptake curve for experiment 12 (water content: 0.33 mL, PSD: 88-177 µm)
Figure B.9. Normalized intensity profiles and uptake curve for experiment 13 (water content: 0.44 mL, PSD: 88-177 µm)

Figure B.10. Normalized intensity profiles and uptake curve for experiment 14 (water content: 0.33 mL, PSD: <74 µm)
Figure B.11. Normalized intensity profiles and uptake curve for experiment 15 (water content: 0.44 mL, PSD: <74 µm)

Figure B.12. Normalized intensity profiles and uptake curve for experiment 16 (water content: 0.22 mL, PSD: (210-297)+(<74) µm)
Figure B.13. Normalized intensity profiles and uptake curve for experiment 18 (water content: 0.22 mL, PSD: (210-297) + (<74) µm)

Figure B.14. Normalized intensity profiles and uptake curve for experiment 19 (water content: 0.22 mL, PSD: 125-210 µm)
Figure B.15. Normalized intensity profiles and uptake curve for experiment 20 (water content: 0.33 mL, PSD: 125-210 μm)

Figure B.16. Normalized intensity profiles and uptake curve for experiment 21 (water content: 0.44 mL, PSD: 125-210 μm)