SIMULATION STUDY ON INJECTION OF CO₂-MICROEMULSION FOR
METHANE RECOVERY FROM GAS HYDRATE RESERVOIRS

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METHANE RECOVERY FROM GAS HYDRATE RESERVOIRS**

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ABSTRACT

Gas-hydrates are crystalline substances in which a solid water lattice accommodates gas molecules, such as methane, in a cage-like structure. A simulation study was conducted, both on 1-D and 2-D reservoir models, using STOMP-HYD simulator to evaluate a set of optimum parameters for methane recovery with simultaneous CO₂ sequestration. A simple 1-D analysis supports the hypothesis of enhanced gas-hydrate recovery using a CO₂-microemulsion injection technique. A series of simulations carried out on the 2-D reservoir model, revealed that the temperature and concentration of CO₂-microemulsion as well as initial CH₄-hydrate saturation in the reservoir are the key parameters in the replacement of CH₄ with CO₂ in the hydrate phase. The results from the 2-D analysis indicated that the moderate microemulsion with a CO₂ concentration in the range of 40% to 50% show good methane recoveries for the reservoir under consideration. Preliminary energy requirement calculations were also carried out to demonstrate the advantages of using the CO₂-microemulsion injection over the thermal stimulation method. These calculations indicated that the energy requirement for CO₂-microemulsion injection is less than 1/10th of that required in case of thermal stimulation method. The results support the hypothesis of using CO₂-microemulsion injection technique for methane recovery from gas-hydrate reservoirs.

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CHAPTER ONE

INTRODUCTION

The world civilization needs a constant supply of energy to survive. Conventional energy sources such as coal, oil, flowing water, wind, bio-resources and nuclear sources help us in meeting our energy demands. However, it is now realized that all the fossil energy resources on the Earth are being depleted at an alarming rate and by the year 2050 these reserves will be almost exhausted (*Mishra; 2004*). Hence, it is imperative for the world to search for other energy sources. Unless new oil fields are discovered, the old reserves will be nearly consumed by 2010 (*Mishra; 2004*). As one source of energy disappears another appears. The most recent discovery of a new energy source, called gas hydrates, can be of great service to mankind in the future. They are of considerable interest for their potential as an energy resource and for their potential role in global climate change. For the present, exploration and study of these unusual compounds have generated hopes about their commercial exploitation in the near future.

It is noted that 1 m³ methane hydrate will release approximately 170 m³ of methane gas at standard temperature and pressure (STP) conditions (*Englezos and Lee; 2005*). Thus, one can understand immediately the potential of methane-hydrates in the Earth to become a source of natural gas. The worldwide estimates for the amount of natural gas in gas-hydrate deposits range from 5.0x10² to 1.2x10⁶ trillion cubic feet (TCFG) for permafrost areas and from 1.1x10⁵ to 2.7x10⁸ trillion cubic feet (TCFG) for oceanic sediments (*Kvenvolden; 1993*). If these estimates are valid, then the amount of methane in gas-hydrates is almost two orders of magnitude larger than the estimated total remaining recoverable conventional methane resources, estimated to be about 9x10³ trillion cubic feet (TCFG) (*Masters, et al.; 1991*).

The mean gas-in-place from hydrate resources onshore of Alaska are 590 Tcf (Collett; 1997). The Alaskan sites where gas hydrates are inferred or identified include the Prudhoe Bay Unit (PBU), Kuparuk River Unit (KRU), and the Milne Point Unit (MPU) areas on Alaska North Slope (ANS).

Until recently, the natural gas industry considered methane hydrates only a nuisance, something that occasionally plugs up pipelines or causes wellbores to collapse. Oil resources becoming more expensive and difficult to exploit in the next couple of decades creates the need to prospect for new fossil fuel deposits. Thus hydrates have sparked an interest among the energy experts around the world. Natural gas hydrates are crystalline solids, resembling snow, that form from mixtures of water and natural gas under certain temperature-pressure conditions. Unless natural gas has any associated water removed from it before being fed into a pipeline, gas hydrates may form and plug the pipeline. The hydrates sometimes have plugged the fittings placed at the heads of gas wells.

Conventional methods of methane recovery from gas hydrate deposits include thermal injection, depressurization, inhibitor injection, and injection of non-hydrate forming gases. The project, *"Injection of CO₂ for Recovery of Methane from Gas Hydrate Reservoirs"* involving the University of Alaska Fairbanks, Pacific Northwest National Laboratory (PNNL) in partnership with BP Exploration (Alaska) Inc. (BPXA) and United States Department of Energy (USDOE), aims to study the possibility of a new method of recovering methane from gas hydrates using CO₂. During this phase of the project, a prototype microemulsion injector was developed and tested successfully at PNNL; an Equation of State (EOS) module for modeling hydrate formation under different conditions was developed at UAF, and the task of incorporating the new EOS module into the simulator STOMP was undertaken at PNNL. As a result of this, a new simulator module, called STOMP-HYD, was developed at PNNL. STOMP-HYD can handle gas-hydrate formation/dissociation mechanisms under a wide spectrum of conditions. Along

with the current studies on gas-hydrate formation and dissociation in porous media and gas hydrate modeling, "*Production Modeling of Gas-Hydrate Reservoir using STOMP-HYD Module*" was one of the critical subtasks that needed to be completed at UAF.

Among the conventional hydrate dissociation methods, the thermal stimulation technique provides heat needed to dissociate the hydrates but with some unavoidable heat loss to the host rock. Depressurization of an adjacent free gas zone can effectively dissociate gas-hydrate but the endothermic nature of the hydrate decomposition will decrease reservoir temperature, which may temporarily lower production rate. Chemical inhibitors can effectively shift the hydrate stability field to produce free gas but the cost of the chemicals needs to be considered and the environmental concerns need to be addressed. An innovative technique has been proposed whereby methane will be recovered from gas-hydrates with simultaneous CO₂-hydrate formation. UAF and PNNL have been conducting studies to analyze the feasibility of this proposed method. A key aspect in the design and interpretation of the proposed injection experiments is numerical simulation. A successful demonstration of the proposed production method in the laboratory does not automatically guarantee a successful demonstration in the field, where heterogeneity in hydrate occurrence, sediment geochemistry, and geohydrology introduces complexity that is impossible to reproduce in the laboratory. Reservoir modeling provides the necessary linkage between the laboratory and field scale application of using CO₂ to economically produce gas-hydrate reservoirs along the ANS. The present study tries to verify the proposed method of recovering methane from gas-hydrates that uses CO₂ to extract methane gas while simultaneously forming a CO₂-hydrate. The 1-dimensional and 2-dimensional production modeling of methane recovery from a gas-hydrate reservoir will help in deciding the critical operating factors like pressure and temperature conditions of the injecting CO₂-slurry, the injecting flow rate of the slurry, and the concentration of the slurry.

CHAPTER TWO

LITERATURE REVIEW

2.1 Methane Gas Hydrate

Gas hydrates are crystalline substances composed of water and gas, in which a solid water lattice accommodates gas molecules in a cage-like structure, or clathrate. Among the hydrocarbon gas hydrates, methane hydrates are of particular interest because of their enormous gas storage potential. A hydrocarbon gas M will react with water to form hydrates at low temperature and high pressure conditions to form a solid hydrate lattice as per shown in the following reaction:

where, n_H is the hydration number.

The natural gas hydrates were first documented by Sir Humphrey Davy back in 1810 (*Sloan; 1998*). Chlorine hydrate discovered by Davy is generally credited as the first observance of gas hydrates. It is the result of the hydrogen bond that water can form hydrates. The water molecules through hydrogen bonding form a lattice structure with interstitial cavities. These cavities are occupied by gas molecules with molecular size smaller than the diameter of the cavities, thereby stabilizing the crystal lattice framework. The water molecules are referred to as the *host molecule*, and the other compounds, which stabilize the crystal, are called as the *guest molecules*. The stabilization resulting from the guest molecule is postulated to be caused by van der Waals forces. Another interesting thing about the gas hydrates is that no bonding exists between the guest and host molecules. The formation of a hydrate requires the following three conditions (*Carroll; 2003*):

1. The right combination of temperature and pressure. Hydrate formation is favored by low temperature and high pressure.

2. A hydrate former. Hydrate formers include gases like methane, ethane, and carbon dioxide, etc.

3. A sufficient amount of water - not too much, not too little.

It has been established that hydrates crystallize into two types of structures, commonly known as type I and type II, which have been investigated with X-ray diffraction methods by *von Stackelberg and Müller (1954)*. The unit cell of structure-I has 2 small and 6 large cavities and consists of 46 water molecules. The 2 small cavities are pentagonal dodecahedra (5^{12}) and the 6 large cavities are tetradecahedra ($5^{12}6^2$). When a guest molecule occupies each of the cages, then the theoretical formula for the type I hydrate is: $X.5 \frac{3}{4} \text{H}_2\text{O}$, where X is the hydrate former. In case of structure-II, the unit cell of the type II structure contains 16 smaller cavities in the shape of distorted pentagonal dodecahedra and 8 large cavities in the shape of hexadecahedra ($5^{12}6^4$). When a guest molecule occupies all of the cages, then the theoretical composition of type II hydrate is: $X.5 \frac{2}{3} \text{H}_2\text{O}$, where X is the hydrate former (*Carroll; 2003*). The methane hydrates have hydration number (N_H) ranging from 5.77 to 7.4.

In 1987, *Ripmeester et al.* proposed a new hydrate structure, called structure-H. According to the above authors, the unit cell has 34 water molecules forming a hexagonal lattice. The structure-H hydrate has three different types of cavities, three 5^{12} cavities which are common to all known hydrate structures, two new 12 face $4^35^66^3$ cavities and one new large $5^{12}6^8$ cavity. The first two types of cavities accommodate the small gas molecules. The large cavity in this structure can accommodate even larger molecules, so molecules in the size range of 7.5 to 8.6 Å can potentially form gas hydrates. In case of type H hydrates, two different formers are required to stabilize the hydrate structure. Because of this, it is difficult to determine the theoretical formula for type H hydrates. However, if it is assumed that the small molecule, X, occupies only the two smaller cages, then the theoretical formula is $Y.5X.34 \text{H}_2\text{O}$ (*Carroll; 2003*).

The structure formed is a function of the molecular size of the gas molecules, with smaller molecules such as methane, ethane, nitrogen, and carbon dioxide forming type I and larger gas molecules such as propane and iso-butene forming type II hydrates. The type H is formed from components of the light naphtha fraction or components of gasoline, thus indicating a hydrate structure that can participate in petroleum as well as natural gas processes. The arrangement of molecules in structures I, II, and H is shown in *Figure 2.1*.

Figure 2.1: Types of cavities in structures I, II, and H hydrate (Sloan; 1998)

The physical properties of different hydrate structures are given in the following *Table 2.1*.

Table 2.1: Physical properties of the three types of gas hydrates (Sloan; 1998)

	Structure I	Structure II	Structure H
Cavity Types	$5^{12}, 5^{12}6^2$	$5^{12}, 5^{12}6^4$	$5^{12}, 4^3 5^6 6^3, 5^{12}6^8$
Radius (Å)	3.91, 4.33	3.902, 4.683	3.91, 4.06, 5.71
Cages / Unit cell	2, 6	16, 8	3, 2, 1
Co-ordination number	20, 24	20, 28	20, 20, 36
Crystal Type	cubic	cubic	hexagonal

2.1.1 Importance of Natural Gas Hydrates

Vast amounts of hydrocarbons are trapped in hydrate deposits (*Sloan; 1998*). Such deposits exist in distinct geologic formations such as permafrost and deep marine sediments, where the thermodynamic conditions of low temperature and high pressure allow hydrate formation. The lower depth limit of hydrate deposits is controlled by the geothermal gradient. The majority of natural hydrocarbon gas hydrates contain CH_4 in overwhelming abundance under certain pressure-temperature conditions (*Figure 2.2*). One unit volume of methane hydrates can contain approximately 160-175 volumes of methane gas and less than one unit of water at standard conditions. Because of its huge quantities and the wide geographical distribution, methane hydrates represent a potentially enormous natural gas resource. The worldwide estimates of hydrate reserves are very high but somewhat uncertain. From an energy point of view, the enormous amounts of methane hydrate under the ocean and beneath arctic permafrost represent an estimated 53% of all fossil fuel (coal, oil, natural gas) reserves on earth. Current estimates of worldwide quantity of hydrocarbon gas hydrate range between 10^{15} to 10^{18} m^3 . Even the most conservative estimates of the total quantity of gas in hydrates may surpass by a factor of two the energy content of the total fossil fuel reserves recoverable by conventional methods (*Sloan; 1998*). *Figure 2.3* gives the relative magnitude of gas hydrates as a reservoir of organic carbon on earth.

The methane-water combination is a solid at low temperatures and high pressures (shaded). Adding inhibitors such as sodium chloride to the water shifts hydrate-gas phase boundary curve to the left, while adding carbon dioxide, hydrogen sulfide and other hydrocarbons moves the curve to the right. Different geothermal gradients also will cause a shift in the depth and width of the gas-hydrate stability zone.

Figure 2.2: Pressure vs. temperature phase diagram for simple methane-hydrate (Collett; 2000)

Figure 2.3: Distribution of organic carbon in the Earth's crust (excluding dispersed organic carbon such as kerogen and bitumen) (Lee and Holder; 2001)

Another important factor behind recovering methane from these methane gas hydrates is that methane is a less carbon-intensive fuel than coal or oil. Methane from hydrates (or other sources) produces only half as much carbon dioxide as coal per unit of combustion products. Two thirds of coal combustion products are CO₂ whereas only one third of the products are CO₂ from methane (*Lee and Holder; 2001*).

Thus, methane can reduce the amount of anthropogenic emissions of carbon dioxide gas, which causes a greenhouse effect. Therefore, the utilization of the methane contained in natural gas hydrate would not only ensure the adequacy of world energy resources, but would also mitigate potential global climate change.

2.1.2 The Hydrate Stability Zone

The formation and occurrences of gas hydrate in nature is controlled by formation temperature, formation pore pressure, gas chemistry, pore-water salinity, availability of gas and water, gas and water migration pathways, and the presence of reservoir rocks and seals. *Figure 2.4* depicts the three-phase hydrate-equilibrium line and identifies the area above the curve as the hydrate stability zone. In natural environments, low temperature and high pressure conditions could occur offshore in shallow depths below the ocean floor and onshore beneath the permafrost. The geothermal gradient of the Earth increases the pressure requirement for the stability of the hydrate at a much greater rate than the pressure increases due to the hydrostatic gradient. Therefore, there is a depth interval where hydrates may be stable.

Figures 2.5a and b are the examples of the depths of hydrate phase stability in permafrost and in oceans, respectively. In each figure, dashed lines represent the thermal gradients as a function of depth. The slopes of dashed lines are discontinuous

both at the base of the permafrost and at the water/sediment interface, where new sediment thermal conductivities cause new thermal gradients.

Figure 2.4: Schematic representation of the three-phase equilibrium curve and methods of hydrate decomposition

The solid lines are drawn from hydrate phase equilibrium data, with pressure converted to depth. As shown in the figure, in permafrost regions in which surface temperatures are well below freezing, gas hydrates can be present at depths between 150 and 2000 m (*Kvenvolden; 2001*). Under offshore conditions, gas hydrate stability conditions usually extend to depths 100 to 500 m below the ocean floor (*Collett et al.; 2000*), although gas hydrates have been recovered from the ocean floor in some cases.

Addition of salt, such as NaCl, to a gas hydrate system lowers the temperature at which gas hydrates form. The pore-water salts in contact with the gas during gas hydrate formation can reduce the crystallization temperature by about 0.06°C for each part per thousand of salt. Therefore, pore water salinity similar to that of seawater (32‰) would shift the gas hydrate stability curve to the left and reduce the thickness of the gas hydrate stability zone. *Zhu et al. (2005)* have developed a thermodynamic model in order to analyze the effect of salt concentration on hydrate equilibrium for CH_4 - and CO_2 -

hydrate systems. The results obtained from their study clearly indicate that much higher equilibrium pressures are required in the presence of salt as compared to the bulk hydrates. Continuing this study further, *Bhangale et al. (2006)* have recently developed a pore-freezing model that can be used to predict gas hydrate equilibrium for pure CH_4 , CO_2 and mixed CH_4 - CO_2 hydrate systems in saline pore waters for any given pore size distribution. The important feature of this model is that it considers the salting out phenomenon (increase in salt concentration due to gas hydrate and ice formation).

Figure 2.5: Hydrate stability zone for (a) arctic and (b) marine environments
(<http://www.usgs.doe.gov/>)

Figure 2.6 shows the effect of temperature and gas composition on the thickness of the gas hydrate stability zone (*Collett; 2002*). The mean annual surface temperature was assumed to be -10°C and varied depths to the base of the permafrost were used in the calculations. The two gas hydrate stability curves represent gas hydrates with different gas chemistries. One of the stability curves is for pure methane hydrate (100%),

and the other is for a hydrate that contains 98% methane, 1.5% ethane, and 0.5% propane.

Figure 2.6: The effect of permafrost depth, geothermal gradient and gas chemistry on the hydrate stability zone (assuming a 9.795 kPa/m pore-pressure gradient)
(Collett; 2002)

2.1.3 Worldwide Occurrences of Natural Gas Hydrate

The geologic occurrence of gas hydrates has been known since the mid-1960s when gas-hydrate accumulations were discovered in Russia (Makogon; 1981). Methane hydrates can be found in abundance in permafrost areas such as on the North Slope of Alaska and Canada and as well as in offshore continental marine environments throughout the world including the Gulf of Mexico and the East and West Coasts of the United States (Thomas; 2001). According to the estimates, approximately 200,000 trillion cubic feet (Tcf) of methane may exist in the form of hydrates in the U.S. permafrost regions and surrounding waters. On a worldwide basis, the estimate is 700,000 Tcf or

about two times the total carbon in coal, oil and conventional gas in the world. The worldwide distribution of gas hydrates is shown in the following Figure 2.7.

Figure 2.7: Location of known and inferred gas hydrate occurrences in oceanic sediments of outer continental margins and permafrost regions. (<http://geology.usgs.gov>)

Kvenvolden and McMenamin (1980) reported the presence of gas hydrates in permafrost regions and beneath the sea in the outer continental margins. Gas hydrates are known to be present in the western Siberian platform (*Makogon; 1981*) and are believed to occur in other permafrost areas of northern Russia, including the Timan-Pechora province, the eastern Siberian craton, and the northeastern Siberian and Kamchatka areas (*Cherskiy et al.; 1985*). Permafrost associated gas hydrates are also present in the Northern American arctic. Well-log responses attributed to the presence of gas hydrates have been obtained in about one-fifth of the wells drilled in the Mackenzie Delta, and in the Arctic Islands more than one-half of the wells are inferred to contain gas hydrates (*Bily and Dick; 1974*). Direct evidence for gas hydrates on the North Slope of Alaska comes from core tests, and indirect evidence comes from drilling and open-hole industry well logs, which suggest the presence of numerous gas-hydrate layers in the area of the Prudhoe Bay and Kuparuk River oil fields (*Collett and Ehlig-Economides; 1983*).

The combined information from Arctic gas hydrate studies show that in permafrost regions, gas hydrates may exist at subsurface depths ranging from approximately 150 to 2000 m. In oceanic sediment where the ocean is at least 300 m deep, methane hydrate exists at depths of about 0 - 1,100 m below the seafloor. Recently, *Thomas (2001)* and *Collett (2002)* have separately documented five of the best-known marine and on-shore permafrost-associated gas hydrate accumulations in the world. The estimates of the total amount of methane gas trapped inside these hydrate accumulations is given in *Table 2.2*.

Table 2.2: Estimated volume of gas within the downhole log-inferred gas hydrate accumulations (*Collett; 2002*)

Site Identification	Depth of Gas-Hydrates (m)	Hydrate Bearing Zone Thickness (m)	Volume of Gas within Hydrate per km ² (m ³)
1. Blake Ridge			
Site 994	212.0 – 428.8	216.8	669,970,673
Site 995	193.0 – 450.0	257.0	1,267,941,673
Site 997	186.4 – 450.9	264.5	1,449,746,073
2. Cascadia continental margin			
Site 889	127.6 – 228.4	100.8	466,635,705
3. Nankai Trough, Japan			
Hydrate Unit	207 - 265	16	755,712,000
4. North Slope of Alaska			
Unit C	651.5 – 680.5	29.0	1,030,904,796
Unit D	602.7 – 609.4	6.7	133,382,462
Unit E	564.0 – 580.8	16.8	346,928,811
5. Mackenzie River delta			
Hydrate Unit	888.8 – 1101.1	212.3	4,749,066,080

The following section discusses the occurrences of gas hydrate on the North Slope of Alaska.

2.1.4 Northern Alaska Gas Hydrate Resources

The occurrence of gas hydrates on the ANS was confirmed in 1972 in the northwest part of the PBU field (*Collett; 1993, Thomas; 2001*). On the North Slope, the methane hydrate stability zone is areally extensive beneath most of the coastal plain province and has thicknesses greater than 1000 m in the Prudhoe Bay area. *Figure 2.8* depicts the distribution of the Eileen and Tarn gas hydrate accumulations in the area of the Prudhoe Bay, Kuparuk River, and Milne Point oil fields on the North Slope of Alaska. Gas hydrates have been inferred to occur in 50 North Slope exploratory and production wells based on the well log responses. All of these gas hydrates are geographically restricted to the area overlying the eastern part of the Kuparuk River oil field and the western part of the Prudhoe Bay oil field. The estimated amount of gas within these gas hydrate accumulations is approximately 37 to 44 Tcf which is equivalent to twice the volume of conventional gas in the Prudhoe Bay field (*Collett; 1993*).

Most of the North Slope gas hydrates have been found to occur in six laterally continuous layers (Unit A, B, C, D, E, and F) of lower Tertiary sandstones and conglomerates. *Figure 2.9* depicts the cross section from the Prudhoe Bay – Kuparuk River area showing the lateral and vertical extent of gas hydrates. Recently, two large gas hydrate accumulations have been identified near the Prudhoe Bay oil field. The volume of gas estimated within the known gas hydrates of the Prudhoe Bay – Kuparuk River infrastructure area alone may exceed 100 trillion cubic feet of in-place gas.

Figure 2.9: Cross section showing lateral and vertical extent of gas hydrates and underlying free-gas in the Prudhoe Bay – Kuparuk River area. (Collett; 2002)

2.1.5 Production Methods of Gas Hydrates

Historically, the petroleum industry's interests in methane hydrates have primarily been related to safety issues such as wellbore stability while drilling, seafloor and formation stability, platform subsidence, and pipeline plugging. Gas hydrates as an energy commodity are commonly grouped with other unconventional hydrocarbon resources that are either expensive to extract or require specialized technology for extraction. Major technical hurdles in the process of making gas hydrate an energy source include: 1) methods to find, characterize, and evaluate the resources; 2)

technology to safely and economically produce natural gas from methane hydrate deposits; and 3) safety and seafloor stability issues related to drilling through gas hydrate accumulations to produce conventional oil and gas (Thomas; 2001).

Recovery of gas from hydrates requires the dissociation of the hydrates by changing the thermodynamic conditions to a state where the hydrate phase is unstable. Methane hydrate is composed of roughly six molecules of water for each molecule of methane. Therefore, the decomposition reaction can be represented by (Pooladi-Darvish, 2004):

Dissociation of gas hydrates can be accomplished in at least three ways. The first method is *depressurization*, the second is *thermal injection* and the last is *inhibitor injection*. Figure 2.10 depicts these proposed methods in detail.

Figure 2.10: Schematic of proposed gas hydrate production methods:
(a) Depressurization; (b) Thermal injection; (c) Inhibitor injection

The first technique is *depressurization*. It operates by lowering the pressure in a gas reservoir with embedded or adjacent zones of solid hydrate. When the pressure reaches the dissociation pressure, gas hydrates at the interface get converted to gas and water. This technique has been used in the Messoyakha gas field in the western Siberia hydrocarbon province (Max et al.; 1997).

In the *thermal injection* method, heat is added to the reservoir at constant pressure. When the heat is added, by either circulating hot fluids downhole or with the application of electric or sonic means, the system temperature increases until it reaches the hydrate dissociation temperature. At the dissociation temperature, all heat that is added is spent on hydrate dissociation. The main disadvantage of this method is that major portion of the added heat is lost to reservoir rock and water. In the absence of any heat loss to the surrounding rocks and water, the injected energy is about 10% of the recovered energy. But in the presence of heat loss, the injected energy can exceed the heating value of the gas. The second major drawback of this process is that the producing horizon must have good porosity, on the order of 15 percent or more, for the heat flooding to be effective. All these considerations make this process more expensive.

The third method is *inhibitor injection*, similar in concept to the chemical means presently used to inhibit the formation of water ice. This method seeks to displace the natural gas hydrate equilibrium condition beyond the hydrate stability zone's thermodynamic conditions through injection of a liquid inhibitor chemical (such as methanol, etc.) adjacent to the hydrate. The chemical inhibitor injection method is also expensive, although less so than the thermal stimulation method, owing to the cost of the chemicals and the fact that it also requires good porosity. Finally, the injection of either steam or inhibitor fluid tends to "flood out" the reservoir over time, which makes it even more difficult for liberated gas to flow to the producing wellbore.

2.1.6 Challenges Involved

Considering the fact that approximately 175 SCF of natural gas constitute one cubic foot of hydrate, there is certainly a serious safety hazard involved during drilling operations, since hydrates can decompose into gas under wellbore conditions. Conventionally, drilling through natural gas hydrates has been avoided since it introduces two external sources of heat, friction and circulated drilling muds, which can cause dissociation of hydrates immediately adjacent to the bore hole. Moreover, the free

gas underneath the hydrate cap can be over pressured, such that drilling into it without taking proper precautions can lead to a blowout. When not avoidable, the hydrate stability zone is drilled and cased as fast as possible to minimize the risk of wall failure, perhaps leading to loss of the hole. Collapsed tubing in the USSR has been attributed to hydrate dissociation (*Makogon; 1988*).

Drilling through the hydrate zone can lead to the dissociation of hydrates thereby releasing a large amount of gas. Under these conditions, the presence of gas provides the potential for explosions and fires. Preventive techniques such as the use of cold mix water at 42°F, reduced circulating rates, the use of smaller downhole motors, and mud weights at 10.0-10.5 pounds per gallon (ppg) rather than the usual 8.7-9.0 ppg, especially during drilling through the hydrate zone, have been successful in reducing the release of gas from hydrates throughout the Milne Point field.

The experiences with the Cascade discovery well in 1994 and the first six development wells in 1996 (*Schofield et al.; 1997*) have shown that at Cascade, every well encounters gas hydrates and the usual countermeasures have not proved effective. The maintenance of the hydrate formation temperature below 62°F with a 8.33 ppg gradient was critical from the hydrate stability point of view.

Gas hydrates could form in the drill string, BOP stack, choke and kill line. This could result in potentially hazardous conditions, i.e., flow blockage, hindrance to drill string movement, loss of circulation, and even abandonment of the well. As gas hydrates consist of more than 85% water, their formation could remove significant amounts of water from the drilling fluids, changing the properties of the fluid. This could result in salt precipitation, an increase in fluid weight, or the formation of a solid plug. *Grigg and Lynes (1989)* have shown that oil-based drilling fluids contain enough water to form hydrates, but under more stringent conditions than water-based fluids. This necessitates a combination of salts and chemical inhibitors, which could provide the required inhibition to avoid hydrate formation.

Mallik 2L-38, a 3773 ft (1150 m) deep gas hydrate research well drilling and coring operation, experienced problems (*Ohara et al.; 1999*) in the early stages of the well due to warm weather, crane rigging up in a very remote location, slow rigging, drilling mud control system with poor shakers, no desander, degasser and jet hopper mix and an extended time to assemble the BOP stack. The mud weight was gradually increased from 8.92 ppg to 9.93 ppg as a precautionary measure, with mud temperature held between 1-3°C during drilling of the main hole, with formation temperatures of 32°F at 2198 ft (670 m) and 57.2°F at 3773 ft (1150 m).

2.2 Rising Concentrations of CO₂

Prior to the Industrial Revolution, the energy needs were satisfied primarily by using wood. The increased energy needs due to rapid industrialization were met initially by using coal and later oil and natural gas. Thus, our global energy system is characterized by a gradual de-carbonization since it moved from wood to coal to oil and to natural gas. Concerns about rising concentrations of carbon dioxide (CO₂) in the atmosphere have led to considering the possible large-scale storage of anthropogenic CO₂ in near-surface geological formations. The concentration of CO₂, which is emitted to the atmosphere as a result of burning of fossil fuels, clearing of forests, and manufacture of cement, has increased from approximately 280 to 370 ppm today (*Orr, 2004*). That level is higher than the concentrations observed over the last 400,000 years.

Emissions of CO₂ are approximately 24×10^9 tonnes/yr (24 Gt/yr), or approximately 6.5 Gt/yr of carbon. Greenhouse gases such as CO₂ in the atmosphere influence the climate (*Hansen, 2004*). Rising concentrations of CO₂, and other greenhouse materials such as CH₄, N₂O, and black soot, raise the issue of interactions with global climate. Estimates of economic growth indicate that the concentrations of CO₂ in the atmosphere will continue to grow during this century unless significant steps are taken to reduce releases of CO₂ into the atmosphere.

Figure 2.11 shows the concentrations of individual greenhouse gases present in the atmosphere.

Figure 2.11: Concentrations of Greenhouse gases in the atmosphere

(<http://www.umich.edu/~gs265/society/greenhouse.htm>)

Obviously, the concentration of greenhouse gases such as CO₂ has to be reduced in order to prevent the catastrophic climate change. *Englezos and Lee (2005)* have summarized four broad options for reducing anthropogenic emissions of greenhouse gases and CO₂:

- (a) Improvement in energy efficiency in generation or in end-use,
- (b) Switching to fuels containing less carbon (e.g. natural gas or coal),
- (c) Substitution of electricity from carbon-free sources (e.g. renewable or nuclear),
- (d) Capture and storage of carbon dioxide.

Realistically, it is unlikely that any single approach would be used alone. A combination of these four options will most likely be adopted to meet particular needs. It is also noted that by using CO₂ removal and storage technology it is conceivable that hydrogen can be produced almost free of emissions from fossil fuels.

Hoffert et al. (2002) concluded that one technology that could contribute to meeting the challenge of reducing CO₂ concentrations is the capture and storage of CO₂ that would otherwise be emitted to the atmosphere. At least three options exist for geologic storage of CO₂ (*Parson and Keith, 1998; Holt et al., 2000; Gale, 2003; van der Meer,*

2003): oil and gas reservoirs, deep saline aquifers, and unmineable coalbeds. These options are discussed in detail in the following section.

2.2.1 Options for Geological Storage of CO₂

As discussed earlier, there are three options available for geologic storage of CO₂. The following *Table 2.3* summarizes the estimates of the capacity of the three storage options made by *Parson and Keith (1998)* and by the International Energy Agency (IEA) Greenhouse R and D Program (*Gale, 2003*).

Table 2.3: Estimated storage capacities of geologic formations (Gt CO₂)

Storage Option	Parson and Keith	Gale
Oil and Gas Reservoirs	740 to 1850	920
Deep Saline Aquifers	370 to 3700	400 to 10,000
Coalbeds	370 to 1100	40

2.2.1.1 Oil and Gas Reservoirs

Oil reservoirs are appealing as storage locations because they are known to have a geological seal that trapped hydrocarbons. Thus, as long as oil-production operations have not damaged that seal, the reservoir should be able to hold injected CO₂ indefinitely. Because oil (and gas) reservoirs have known seals and because there is a regulatory structure that has experience in permitting gas-injection operations, existing oil fields will likely be the first places to undertake CO₂ sequestration, if it is done on a large scale.

CO₂ can be stored in zones in which CO₂ replaces reservoir oil or water. CO₂ is soluble in water, and it is approximately 10 times more soluble in undisplaced oil. A separate CO₂-rich phase also can occupy significant pore volume.

CO₂ injection into gas reservoirs has been proposed but not attempted. CO₂ could be used for pressure maintenance or for condensate vaporization, but the cost of purchasing CO₂ has made these applications uneconomical in the absence of incentives

for CO₂ storage. If CO₂ injection is used to store CO₂ and maintain pressure in a gas reservoir, a key issue will be the mixing of the injected CO₂ with the CH₄ in the reservoir and the resulting concentration in the produced gas. CO₂ is more viscous than CH₄, but well-to-well flow will still be dominated by reservoir heterogeneity. In reservoirs with good vertical communication, it may be possible to take advantage of the higher density of CO₂ to design injection strategies and well completions that place CO₂ low in the reservoir, with production taken from the top.

2.2.1.2 *Deep Saline Aquifers*

In this type of setting, the gravity segregation caused by the density difference between the injected CO₂ and brine will cause preferential flow at the top of the aquifer. Aquifers with large volume, reasonable permeability and thickness, and good pressure communication over long distances will be most attractive such that large volumes could be injected without raising aquifer pressure significantly. The key questions for aquifer-injection projects will involve aquifer characterization.

2.2.1.3 *Coalbeds*

In oil and gas reservoirs and aquifers, injected CO₂ occupies the pore space as a separate phase or is dissolved in water or oil. Deep, unmineable coalbeds offer a different storage mechanism, the same mechanism that is the source of coalbed methane. Such gases as CH₄ or CO₂ get adsorbed on the surfaces of coal particles at high pressure. Significantly more CO₂ adsorbs on coal at a given pressure and temperature than CH₄ or N₂. Flow in coalbeds will occur primarily in the fracture network (cleats in coal). According to *Zhu et al. (2003)* injected CO₂ will flow through the cleats, diffusing into matrix blocks and replacing adsorbed CH₄. Thus, CO₂ injection into the coalbeds can be used to enhance CH₄ recovery.

Thus, it can be seen that geologic storage of CO₂ can contribute to reductions in emissions of CO₂ into the atmosphere. Recently, a new idea has come forward for CO₂ sequestration. The basic concept is to inject CO₂ in the form of microemulsion into the

natural gas hydrates and extract CH_4 , thereby storing CO_2 in the form of CO_2 -hydrates. The following section discusses this innovative method in more detail.

2.3 Replacement of Methane in CH_4 -hydrates with CO_2 -hydrates

The large global rates of carbon dioxide (CO_2) release during fossil fuel consumption can increase the greenhouse effect and thus are believed to promote global climate change. Attention has recently been focused on several environmental problems including global warming and destruction of the ozone layer and the countermeasures to deal with these problems. Concerns about the potential effects of rising carbon dioxide levels in the atmosphere have stimulated interest in a number of carbon dioxide sequestration studies. Scientists and researchers all over the world are trying to find new ways of solving the problem of the increasing amount of CO_2 in the atmosphere. One interesting and innovative suggestion is the sequestration of carbon dioxide as clathrate-hydrates by injection of carbon dioxide into methane-hydrates. The simultaneous sequestration of carbon dioxide and the production of methane by injection of carbon dioxide into deposits of natural gas hydrates, if possible, represents a potentially efficient and cost effective option for the carbon dioxide sequestration. This concept has several attractive features (*McGrail et al., 2005*):

- 1) CO_2 is thermodynamically favored over CH_4 in hydrate,
- 2) The heat released by formation of CO_2 -hydrate is 20% greater than the heat needed for dissociation of CH_4 -hydrate,
- 3) Refilling pore space with CO_2 -hydrate is expected to maintain mechanical stability of the hydrate-bearing formations during production, and
- 4) The process is environmentally friendly, removing CO_2 from the atmosphere while simultaneously producing clean-burning natural gas.

The idea of swapping CO_2 for CH_4 in gas hydrates was first advanced by *Ohgaki et al. (1996)* for methane hydrates and then by *Nakano et al. (1998)* for ethane hydrates. More information about their work is described in the following section. As discussed

earlier, depressurization is the most often considered method for commercial production of hydrates (Sloan, 1998), but combined depressurization and thermal stimulation have been used recently to produce a small amount of gas from the Mallik 5L-38 research well located on the Mackenzie Delta, Northwest Territories, Canada.

2.3.1 Original Idea

Some of the early work in the field of gas-hydrates involves the proposed technology for storing CO₂ in the form of hydrates under the ocean floor, the idea put forth by Ohgaki and Inoue (1994). Their procedure involved pumping the stored gas through a pipe at high pressure, and storing it in the basins which are located on the bottom of the ocean. The authors proposed that at a certain depth, tiny gas-hydrate particles will be formed at the contact surface between the sea water and the compressed gas, which has a higher density and which aggregates, forming a solid layer of hydrate. Figure 2.12 shows the pressure-temperature diagram of three-phase coexisting curves.

Δ : triple point (pure), • : critical end point, ○ : critical point (pure)
 □ : quadruple point, — : two-phase line (pure), : critical locus
 — . — : three-phase line

Figure 2.12: Pressure-temperature diagram of three-phase coexisting curves for the system of H₂O (1) CO₂ (2) Involving gas-hydrates.

All published literature prior to Ohgaki and Inoue's work had mentioned only two four-phase coexistence points and two three-phase coexistence curves (ice-hydrate-gas and hydrate-water-gas).

2.3.2 First Experimental Evidence

A vast quantity of hydrate of natural gas (mainly CH_4) is observed under the bottom of the ocean floor. *Ohgaki et al. (1996)* presented the first experimental evidence for the possibility of CH_4 exploitation combined with CO_2 isolation. As discussed earlier, The three-phase coexistence line (pressure and temperature relation) of gaseous methane-saturated water-methane hydrate was also measured in addition to the measurement of CO_2 solubilities in liquid water and the pressure-temperature relation of gaseous CO_2 -liquid water- CO_2 hydrate.

Based upon their experimental data, the authors constructed the pressure-temperature relations for the CO_2 -water-hydrate and CH_4 -water-hydrate systems which are depicted in *Figure 2.13*.

Figure 2.13: Three-phase coexisting lines of CO_2 - CH_4 mixed hydrate system.
 (L1: H_2O -rich phase; L2: CO_2 -rich phase; G: gas phase; H: hydrate phase;
 q: quadruple point in the CO_2 - H_2O system)

From the above figure, it is clear that there is an interesting zone where CO_2 -hydrate can grow up although methane hydrate is dissociated at a given temperature and pressure. It can be observed that the formation pressure of CO_2 -hydrate is lower than that of CH_4 -hydrate; therefore, it is presumed that CO_2 -hydrate is more stable than CH_4 -hydrate below 283 K. The existence of the shaded zone in *Figure 2.13* is essential to

study the operational conditions of replacement of natural gas (methane) by CO₂ in a gas-hydrate field.

The proposed process of natural gas-hydrate replacement with CO₂-hydrate is schematically shown in *Figure 2.14*. CO₂ recovered from the electric power stations and other sources can be transported by tankers to the marine station and introduced into an exploitation cave, where the temperature and pressure conditions can be regulated to maintain the three-phase coexisting conditions.

Figure 2.14: Schematic diagram of natural gas exploitation and CO₂ isolation process
(<http://www.cheng.es.osaka-u.ac.jp/ohgakilab/main-e.html>)

The CO₂ in this process also serves one more important function of heat supply. It has been pointed out that the methane hydrate has self-protection ability for pressure instability because of the large enthalpy change of hydrate dissociation (Handa, 1986). The heat of CO₂ hydration (exothermic reaction) exceeds the heat of methane hydrate dissociation (endothermic reaction), that is, the methane exploitation becomes possible by use of the heat of CO₂ hydration.

2.3.3 Subsequent Studies

Following the study by *Ohgaki et al. (1996)*, *Nakano et al. (1998)* investigated high-pressure phase behavior for the ethane hydrate system in a high pressure cell up to a maximum pressure of 100 MPa. In this study, they measured the phase equilibrium relationship of an ethane hydrate-water-liquid ethane mixture in the temperature range from 290.4 to 298.4 K and over a pressure range of 19.48 to 83.75 MPa. The authors concluded that the results obtained from their experimental study can be used for natural gas exploitation combined with CO₂ isolation.

Ohgaki and Nakano (1997) extensively studied the three-phase coexisting lines (pressure-temperature relation) of gases-saturated water-gas hydrates for CO₂, CH₄ and C₂H₆ pure hydrates. They investigated the decomposition rate of CO₂ and CH₄ pure gas hydrates under isothermal isobaric and three-phase coexisting conditions. Their study concluded that the averaged distribution coefficient of CH₄ between the gas phase and the hydrate phase was about 2.5, meaning CH₄ in the hydrate phase was selectively replaced by CO₂ and the mole fraction of CH₄ in the gas phase was larger than that of mixed hydrate phase. In the case of CO₂-CH₄ mixed hydrate decomposition, the authors noticed that CH₄ was selectively driven out to the gaseous phase while CO₂ was saved as hydrate. All the results from this experimental study support the possibility of CH₄ exploitation from natural-gas fields by use of CO₂ stored as gas hydrates.

Hirohama et al. (1996) investigated the possibility of segregating CO₂ from the biosphere and storing it as CO₂-hydrate in the hydrate layers under the bottom of the ocean. The aim is to convert CH₄-hydrate to CO₂-hydrate while sustaining the total pressures near the hydraulic pressure at the bottom of the ocean, so as not to destroy thin cap rocks which segregate the hydrate from the biosphere. The total pressure must be kept above the CH₄-hydrate forming pressure. The temperature must be sustained below 283 K because CO₂-hydrate is not stable above this temperature.

Hirohama and co-workers carried out an experimental study on the conversion of CH₄-hydrate into CO₂-hydrate using liquid CO₂. The investigators measured the recovery rate of methane from CH₄-hydrate soaked in liquid CO₂ in the temperature range of 274–277 K and in the pressure range of 4–5 MPa. The composition of the hydrate measured at the end of the experiment indicated that the formation of CO₂-hydrate consumed all H₂O which had been encaging the recovered CH₄. The results from this study also indicated that the recovery rate of CH₄ from CH₄-hydrate soaked in liquid CO₂ was much lower than that in gaseous N₂.

In-situ observation of the replacement of CH₄-hydrate by CO₂-hydrate was conducted by *Uchida et al. (2001)* using a Raman Spectroscopy method. The authors measured the Raman spectra in two regions: near the C-H stretching mode (2890–2930 cm⁻¹) and near the C-O stretching mode (1250–1450 cm⁻¹). Before replacing CH₄ vapor with CO₂ vapor, the ratio of the intensity of the larger peak to the intensity of the smaller peak was approximately 3.5. After replacing CH₄ vapor with CO₂ vapor, it was observed that the intensity ratio gradually decreased. Since CO₂ molecules occupy mainly the large cage of the clathrate structure, the authors concluded that this change of the intensity ratio must have come from a relatively larger decrease in the intensity of the larger peak; that is, CO₂ molecules in the vapor phase replaced CH₄ molecules in the large cages of the hydrate.

To address the issue of the rate of the replacement reaction of CH₄-hydrate by CO₂-hydrate, *McGrail et al. (2004)*, conducted a series of experiments to directly measure the rate of penetration of CO₂ into bulk methane hydrate. They investigated the method of CH₄ replacement in CH₄-hydrate using CO₂ and validated the key steps in the process using laboratory-scale experiments. The authors used Scanning Laser Raman Spectroscopy to track the penetration depth of CO₂ into the methane hydrate layer as a function of time and temperature. The results obtained from this study validated the thermodynamic favorability of swapping CO₂ for methane but the investigators

observed very slow exchange rates deeper into the gas hydrate. The calculated rates of CO₂ penetration into the methane hydrate were only about 0.25, 0.55 and 1.3 mm/hr at 0, 2.5 and 4.5°C, respectively.

White (2003) carried out a mass transfer study on CO₂ penetration through methane hydrates using CO₂-microemulsion. The author also studied the methane hydrate dissociation upon CO₂-microemulsion injection using Raman Spectroscopy. The results indicated that CO₂ can penetrate into a methane hydrate zone through a molecular mining process by dissociating the CH₄ from a hydrate phase and stabilizing the mixed CO₂-CH₄ hydrate at temperatures that are out of the pure CH₄ hydrate stability zone.

Hirohama *et al.* (1997) studied the recovery rate of CH₄ from CH₄-hydrate immersed in CO₂-CH₄ mixtures. The authors carried out an experimental study to analyze the effect of two different compositions of liquid CO₂-CH₄ mixture on the rate of the conversion at 274 K. They observed that as the initial mole fraction of CH₄ in the liquid phase increased, the rate of the conversion decreased dramatically. The ultimate CH₄ recoveries obtained in this study (8% and 2%) were small as compared to the earlier study (Hirohama *et al.*, 1996).

Recently, Komai *et al.* (2002) studied the formation and dissociation of CH₄- and CO₂- hydrates as well as the phenomenon of interchange of CH₄ and CO₂ as a function of time, temperature and pressure conditions. They used Raman Spectroscopy technique to carry out their study. The study confirmed that both CH₄ and CO₂ gas hydrates can coexist in the structure of the replaced hydrate sample. From their observations, it was found that the reformation of carbon dioxide hydrate occurred at the surface and inside the sample of methane hydrate as well as producing ice crystals. Figure 2.15 shows the trend of CO₂/CH₄ components in the solid hydrate after CO₂ introduction as a function of time.

Figure 2.15: Change in gas hydrate components of during the replacement experiment

The above figure shows that the proportion of CO₂-hydrate in the sample increased with time. Because the transport of CO₂ gas should be fast in porous media, the in-situ replacement of CO₂ gas hydrate may be used for the extraction of methane from CH₄-hydrate reservoirs.

Lee *et al.* (2003, 2004) carried out an experimental study, using a solid state NMR technique, on methane recovery from solid methane hydrate with carbon dioxide. To observe favorable exchange between CO₂ and CH₄ hydrate, there must be preferential partitioning of CO₂ and CH₄ between the gas and the solid hydrate phases. Since the large cages outnumber the small cages by a factor of three, if CO₂ has a preference for the large cage in the hydrate, then it will lead to a favorable exchange between CO₂ and methane hydrate. The authors investigated this hypothesis in their study. Their observations showed that the ratio of the cage occupancies in the large and small cages for CH₄ ($\theta_{L,CH_4}/\theta_{S,CH_4}$) goes on decreasing with increasing concentration of CO₂ in the gas mixture. The molecular diameter to cavity diameter ratio is 1.00 for CO₂ whereas it is 0.855 for CH₄. When CO₂ competes with CH₄ in occupying the small cage of the sI hydrate, CO₂ being a relatively poorer guest for occupying the small cages, the occupancy ratio for CH₄ becomes lower at higher CO₂ compositions because CO₂ preferentially occupies the large 5¹²6² cage in the mixed CH₄/CO₂ hydrate.

The authors concluded that the replacement of CH_4 by CO_2 is favored both from the point of view of equilibrium thermodynamics and kinetics. Reaction rates and the total yield of the replacement reaction in actual natural gas hydrate deposits will depend on a variety of factors, such as the degree of hydrate dispersion in sediments, hydrate particle size and the gas transport.

It has been shown that destabilization of the hydrate in the sediments under the ocean floor could trigger catastrophic slope failures (*Gunn et al., 2002*) and thus decomposition processes for CH_4 recovery could lead to weakening of the ocean floor. Further, if CH_4 -hydrate decomposes rapidly, it is probable that the released CH_4 from the hydrate could transfer to the air and significantly add to the greenhouse effect (*Levieveld and Crutzen, 1992*).

Replacement of CH_4 in the hydrate with high pressure CO_2 is a potential candidate for recovering CH_4 gas from its hydrates under the ocean. *Ota et al. (2005a)* studied the dynamics of CH_4 replacement in the CH_4 -hydrate with saturated liquid CO_2 at 273.2 K and 3.6 MPa using a high pressure optical cell. The results obtained from the replacement experiments showed that the mole fraction of CH_4 in hydrate phase decreased whereas that of CO_2 in the hydrate phase increased with respect to time. The study also showed that the amount of the decomposed CH_4 -hydrate was almost the same as that of the formed CO_2 -hydrate. This close relation between the CH_4 -hydrate decomposition and the CO_2 -hydrate formation implied that the guest molecule was replaced in the hydrate. This study also revealed that the decay in the S-cage (small cage) was much slower than that in the M-cage (medium cage). The quantitative analysis from this study showed that CH_4 in the hydrate gradually moved the liquid CO_2 phase while CO_2 in the liquid phase penetrated into the hydrate phase.

In a similar study, *Ota et al. (2005b)* experimentally examined the CH_4 - CO_2 replacement in CH_4 -hydrate with a high-pressure optical cell over temperatures ranging from 271.2 to 275.2 K and at an initial pressure of 3.25 MPa. The authors also measured

the kinetics of CH₄-hydrate decomposition and CO₂-hydrate formation during the replacement with a laser Raman technique.

The results from the study showed that the amounts of decomposed CH₄-hydrate ($Q_{\text{CH}_4, \text{Dec}}$) and the formed CO₂-hydrate ($Q_{\text{CO}_2, \text{Form}}$) increased rapidly in the early stages (time < 10 hr) of the replacement reaction. After that, the slopes of each Q changed and the rates increased slowly (time > 10 hr). These results are shown in *Figure 2.16* below.

Figure 2.16: Amount, Q , of the (a) decomposed CH₄ hydrate ($Q_{\text{CH}_4, \text{Dec}}$) and (b) the formed CO₂ hydrate ($Q_{\text{CO}_2, \text{Form}}$) as a function of time.

The authors also plotted a graph of $Q_{\text{CH}_4, \text{Dec}}$ against $Q_{\text{CO}_2, \text{Form}}$ which is shown in *Figure 2.17*. From this figure, it is clear that the $Q_{\text{CH}_4, \text{Dec}}$ was slightly larger than $Q_{\text{CO}_2, \text{Form}}$ up to 20 mmol decomposition, but after that became lower than $Q_{\text{CO}_2, \text{Form}}$. However, the $Q_{\text{CH}_4, \text{Dec}}$ was almost proportional to $Q_{\text{CO}_2, \text{Form}}$ over the period studied. This close relation between $Q_{\text{CH}_4, \text{Dec}}$ and $Q_{\text{CO}_2, \text{Form}}$ suggested that the guest molecule probably underwent actual replacement in the hydrate phase.

Figure 2.17: Plot of decomposed CH₄-hydrate ($Q_{CH_4, Dec}$) vs. formed CO₂-hydrate ($Q_{CO_2, Form}$) at 3.25 MPa

Most of the studies discussed so far show that the conversion of bulk CH₄-hydrates into CO₂-hydrates is possible. But in nature, the gas hydrates are found in the arctic and sub-seafloor formations embedded in porous sediments. Therefore, the results from the studies of conversion of CH₄-hydrates into CO₂-hydrates can not be directly applied to naturally occurring hydrates. The thermodynamics of any potential conversion of CH₄-hydrate to CO₂-hydrate will be affected by the size of the pores in which the conversion of CH₄-hydrate to CO₂-hydrate would take place.

To analyze this problem, *Wilder et al. (2002)* developed a thermodynamic model to explain and predict the equilibria in porous media for any pore size distribution. The results from this study allowed an assessment of the thermodynamic feasibility of converting CH₄-hydrate to CO₂-hydrate in porous media involving various size pores. The results showed a significant decrease in the difference between the enthalpies of dissociation for CH₄ and CO₂ hydrates as the pore size in the sediment decreases. This suggested that the replacement of CH₄ by CO₂ in the hydrate lattice was less thermodynamically favored as the pore size of the sediment decreased.

CHAPTER THREE

PROBLEM STATEMENT

As discussed in Chapter 2, methane can be produced from natural gas-hydrates using the conventional methods such as depressurization, thermal stimulation or inhibitor injection. However, as it has been discussed in Chapter 2, all of these methods are associated with some disadvantages which make them a less viable option for field application. It has also been discussed that CO₂ injection can be used as an alternate method to produce methane from the hydrate reservoirs while simultaneously sequestering CO₂ from the atmosphere.

The main objective of this study was to demonstrate the feasibility of the CO₂ injection technique in the form of microemulsion to produce CH₄ from the natural gas-hydrate reservoirs. To achieve this objective, a simulation study was conducted in 1-dimensional (1-D) and 2-dimensional (2-D) models using the STOMP-HYD simulator. The STOMP simulator and its features are discussed in more detail in the next chapter.

The different types of simulation runs with their primary objectives are outlined here:

3.1 Simulation Study on 1-Dimensional Reservoir Model

The primary aim of this exercise was to demonstrate the feasibility of the CO₂-microemulsion injection technique for methane production using a simple 1-D reservoir model. In this part of the study, different cases were studied to examine the effects of CO₂-microemulsion temperature and concentration along with the effect of the formation permeability on methane recovery. Since the main purpose of this part of the study was to assess the viability of the proposed process, the reservoir properties such as absolute formation permeability values used under this exercise were taken as hypothetical. The performance of the CO₂-microemulsion injection technique was

evaluated against that of the thermal stimulation method, which was the reference case in this part of the study.

3.2 Simulation Study on 2-Dimensional Reservoir Model

The main purpose of this part of the study was to evaluate the performance of the CO₂-microemulsion injection method in terms of the effect of temperature, concentration of CO₂-microemulsion, and the initial CH₄-hydrate saturation on methane recovery using a 2-D reservoir model. In this part of the study, a number of production scenarios were tested with varying injection temperatures and concentrations of CO₂-microemulsion to determine the optimized parameters for the reservoir under consideration. These production scenarios are discussed in details in Chapter 8.

Along with the operational parameter optimization, it was also necessary to compare the methane production obtained under the CO₂-microemulsion injection technique against that obtained under the conventional production methods, to demonstrate the importance and feasibility of the microemulsion injection technique. Therefore, a conventional method, thermal stimulation, was selected for this exercise for the comparison purpose.

In this part of the study, it was also important to examine the energy input requirements for the CO₂-microemulsion injection technique as compared to those of a conventional method such as thermal stimulation. Therefore, calculations were carried out to determine the heat input requirements and energy efficiency for the microemulsion injection technique as well as for the thermal stimulation method. A detailed explanation of these calculations is given in Chapter 8.

CHAPTER FOUR

STOMP-HYD MODULE OF STOMP SIMULATOR

4.1 Introduction

Reservoir simulation combines physics, mathematics, reservoir engineering and computer programming to develop a tool for predicting reservoir performance under various operating conditions. The need for reservoir simulation stems from the requirement for petroleum engineers to obtain accurate performance predictions for any hydrocarbon/gas-hydrate reservoir under different operating conditions. This need arises from the fact that in a hydrocarbon recovery project (which possibly involves a capital investment of hundreds of millions of dollars), the risk associated with the selected development plan must be assessed and minimized (*Ertekin et al., 2001*). The second reason behind the need of a reservoir simulator is the inability of the experimental techniques to simply match the scale of actual reservoirs. Factors contributing to this risk include the complexity of the reservoir because of heterogeneous and anisotropic rock properties; regional variations of fluid properties and relative permeability characteristics; and the applicability of other predictive methods with limitations that may make them inappropriate. Therefore, the reservoir simulator serves the purpose of making very reliable and accurate reservoir performance predictions as compared to the experimental as well as analytical techniques.

At present, there are very few reservoir simulators which can handle a gas-hydrate reservoir system, STOMP being one of them. The following section gives the details about the simulator STOMP and its features.

4.2 Simulator STOMP and Latest STOMP-HYD Module

STOMP-HYD is the latest module of the simulator STOMP, an acronym for Subsurface Transport Over Multiple Phases, which has been developed by the Pacific Northwest National Laboratory (PNNL) situated in Richland, WA. STOMP is a multifluid subsurface flow and reactive transport simulator. The simulator module STOMP-HYD uses the Newton-Raphson iteration scheme to solve the coupled non-linear governing equations, describing the conservation of water, methane, carbon dioxide and sodium chloride mass and thermal energy for a geologic system comprising aqueous, liquid carbon dioxide, gas, hydrate, ice and solid matrix phases.

The STOMP simulator has been designed with a variable source code, where source code configurations are referred to as operational modes (*White and Oostrom, 2003*). Operational modes are classified according to the solved governing flow and transport equations and constitutive relation extensions. Therefore, the appropriate operational mode must be selected for dealing with the particular subsurface system of interest.

The STOMP simulator solves transient flow and transport problems in the subsurface environment in one, two and three dimensions. The simulator is capable of handling orthogonal, Cartesian, tilted Cartesian and cylindrical co-ordinate systems. The simulator solves steady-state problems either directly or through false-transients starting from a user specified initial state. Direct solutions to steady-state problems are possible for initial conditions sufficiently close to the solution; therefore, transient solutions to steady-state conditions are the recommended approach. Coupled flow solutions can be obtained for selected one-, two-, or three-phase systems under isothermal or non-isothermal conditions. The STOMP simulator allows considerable control over simulation parameters related to convergence, time stepping, solution techniques and execution limits.

The latest operational mode in the family of STOMP operational modes is STOMP-HYD, which deals with hydrate formation/dissociation at subsurface conditions. As discussed earlier the different components in this operational mode include water, CH_4 , CO_2 and NaCl mass. The hydrate saturation at the subsurface conditions is computed from the ratio of hydrate equilibrium pressures *in-situ* and *ex-situ*, assuming the hydrate phase is completely occluded by aqueous phase. The relative permeabilities of the mobile phase are computed using multifluid constitutive relations. This operational mode assumes the following wettability order: aqueous, liquid carbon dioxide, gas. Kinetics of hydrate formation/dissociation and hydrate molecular exchange are also included during the coding of this operational mode. The following sections describe the various transport as well as constitutive equations used in the STOMP-HYD module.

4.3 Multifluid Transport Equations (*White et al., in preparation*)

Four mass conservation and one energy conservation equations are used in the STOMP simulator to describe the subsurface hydrate system, in which the conserved mass components are water, CH_4 , CO_2 , and salt. Transport is assumed to occur over three mobile phases, aqueous, liquid CO_2 , and gas; and four immobile phases, hydrate, ice, precipitated salt, and host porous media. The aqueous phase comprises liquid water, dissolved CO_2 , dissolved CH_4 , and dissolved salt. The gas phase comprises water vapor, gaseous CO_2 , and gaseous CH_4 . The hydrate phase comprises water, CO_2 , and CH_4 in a crystalline clathrate structure. The liquid CO_2 phase is considered a nonaqueous phase liquid comprising only liquid CO_2 , where dissolution of CH_4 in liquid CO_2 is ignored. Ice and precipitated salt phases are single component phases comprising water and salt, respectively.

4.3.1 Energy Conservation Equation

Energy transport occurs over all the seven mobile and immobile phases. This can be represented using following energy conservation equation, expressed in differential form:

$$\begin{aligned} \frac{\partial}{\partial t} \sum_{\gamma=l,g,n,h,i,p} (\phi \rho_{\gamma} S_{\gamma} u_{\gamma}) + \frac{\partial}{\partial t} (1-\phi) \rho_s u_s = & - \sum_{\gamma=l,g,n} [\nabla (h_{\gamma} F_{\gamma})] - \sum_{\zeta=w,a,o} \nabla (h_g^{\zeta} J_g^{\zeta}) \\ & - \nabla (k_e \nabla T) + \sum_{\gamma=l,g,n} (h_{\gamma} \dot{m}_{\gamma}) + \dot{q} \end{aligned} \quad \text{----- (Eq.4.1)}$$

The above Eq. (4.1) states that the accumulation of energy in the mobile and immobile phases in a control volume is balanced with the energy advected into the control volume by the mobile phases, diffused into the control volume via the gas phase, and conducted into the control volume, plus the energy associated with mobile phase sources and thermal energy sources.

4.3.2 Mass Conservation Equation

Mass transport of the conserved components (i.e. water, CO₂, CH₄, and salt) occurs over the three mobile phases and three immobile phases, excluding the host porous media. This can be explained using the following mass conservation equation:

$$\begin{aligned} \frac{\partial}{\partial t} \sum_{\gamma=l,g,n,h,i,p} (\phi \rho_{\gamma} S_{\gamma} \omega_{\gamma}^{\zeta}) = & - \sum_{\gamma=l,g,n} \nabla \omega_{\gamma}^{\zeta} F_{\gamma} - \sum_{\gamma=l,g} \nabla J_{\gamma}^{\zeta} + \sum_{\gamma=l,g,n} \omega_{\gamma}^{\zeta} \dot{m}_{\gamma} \\ & \text{for } \zeta = w,a,o,s \quad \text{----- (Eq. 4.2)} \end{aligned}$$

The mass conservation equation states that the accumulation of component mass is balanced with the component mass advected into the control volume via mobile phases, diffused into the control volume via the aqueous and gas phases, and the component mass associated with mobile phase sources. Sorption of component on the host porous medium is ignored, which eliminates the porous medium phase from the

governing equations for component mass. Diffusion transport through the liquid CO₂ phase is also ignored.

4.3.3 Advective and Diffusion-Dispersive Fluxes

The advective mass flux for the mobile phases occurs in response to the gradients in phase pressure and gravitational body forces (i.e. buoyancy force):

$$F_{\gamma} = - \frac{\rho_{\gamma} k_{r\gamma} k_i}{\mu_{\gamma}} (\nabla P_{\gamma} + \rho_{\gamma} g z_g); \text{for } \gamma = l, g, n \text{ ----- (Eq. 4.3)}$$

Diffusive component mass flux for the aqueous and gas phases occurs in response to the gradients in the component mole fraction:

$$J_{\gamma}^{\zeta} = - \tau_{\gamma} \phi \rho_{\gamma} S_{\gamma} \frac{M^{\zeta}}{M^{\gamma}} D_{\gamma}^{\zeta} (\nabla \chi_{\gamma}^{\zeta}); \text{for } \gamma = l \text{ and } \zeta = w, a, o, s \text{ ----- (Eq. 4.4)}$$

for $\gamma = g$ and $\zeta = w, a, o$

Flux variables such as advective mass flux, diffusive component flux and thermal energy flux are computed at the surface centroids between two grid cells.

4.4 Constitutive Equations (*White et al., in preparation*)

The constitutive equations serve the function of relating the variables in the governing conservation equations. The governing energy and component mass conservation equations are solved for five primary variables. The constitutive equations close the system of equations by relating the primary variables to the secondary variables. The constitutive equations, for some but not all of the variables, are discussed below:

4.4.1 Phase Saturation

Phase saturation can be defined as the fraction of the pore volume occupied by a phase. Phase saturation relations depend on a phase distribution and wettability conceptual model. The phase distribution conceptual model used in the simulator STOMP is assumed to follow the model proposed by *Clennell et al. (1999)*. According to

this model, the hydrate is assumed to be totally occluded by aqueous phase and the wettability order is aqueous, liquid CO₂, followed by gas. Following this conceptual model, the apparent total liquid saturation can be given as the sum of the effective liquid CO₂ saturation and the apparent aqueous saturation, which in turn is given as the sum of the effective hydrate and effective aqueous saturations. From this exercise, the effective gas saturation can be obtained as one minus the apparent total liquid saturation.

$$\overline{s_t} = \overline{s_n} + \overline{s_l} \quad \text{----- (Eq. 4.5)}$$

where, $\overline{s_l} = \overline{s_l} + \overline{s_h} \quad \text{----- (Eq. 4.6)}$

Therefore,

$$\overline{s_g} = 1 - \overline{s_l} \quad \text{----- (Eq. 4.7)}$$

The apparent total liquid saturation is a function of the scaled interfacial pressure difference between the gas and liquid CO₂ phases; and the apparent aqueous saturation is a function of the scaled interfacial pressure difference between the liquid CO₂ and aqueous phases. More information about these saturation functions has been documented somewhere else.

4.4.2 Hydrate Saturation

The hydrate saturation in simulator STOMP is computed using the ratio of *in-situ* equilibrium pressure and *ex-situ* equilibrium pressure. The *ex-situ* equilibrium pressure can be computed from the mole fraction of hydrate formers (excluding water) and the temperature, from tabular data generated from Sloan, whereas the *in-situ* equilibrium pressure is computed as the sum of the gas-phase partial pressures of CO₂ and CH₄. Now, knowing the *in-situ* and *ex-situ* equilibrium pressures, the hydrate-aqueous interfacial radius can be computed as shown below:

$$\frac{p_{eq}^{in}}{p_{eq}^{ex}} = 1 + \frac{a}{1 + \exp \frac{\ln(r_{hl}) + b}{c}} \quad \text{----- (Eq. 4.8)}$$

where, $a = 0.1145$, $b = 17.09$ and $c = 0.8817$

The above functional form was derived from the computer code developed by *Klauda and Sandler (2003)* which computes the equilibrium pressure ex-situ and in-situ, over a range of temperature and CH_4 gas phase mole fractions. Eq. (4.8) provides a relationship between the equilibrium pressure ratio and the hydrate-aqueous interfacial radius, needed to compute the capillary pressure difference between the hydrate and aqueous phases. The capillary pressure difference between the hydrate and aqueous phases can be computed as shown in the following equation:

$$(P_h - P_l) = \frac{2 \sigma_{hl}}{r_{hl}} \quad \text{----- (Eq. 4.9)}$$

The capillary pressure difference computed as per Eq. (4.9) was then used in the specified soil moisture retention function to calculate hydrate saturation. Now, the apparent aqueous saturation can be calculated as a function of the scaled capillary pressure difference between the hydrate phase and aqueous phase.

$$\overline{s_l} = \text{func}[(P_h - P_l)] \quad \text{----- (Eq. 4.10)}$$

Now, knowing the apparent aqueous saturation ($\overline{s_l}$) and the effective aqueous saturation ($\overline{s_l}$), the effective hydrate saturation can be computed as:

$$\overline{s_h} = \overline{s_l} - \overline{s_l} \quad \text{----- (Eq. 4.11)}$$

4.4.3 CO_2 and CH_4 Thermodynamic and Transport Properties

The properties like density, enthalpy, internal energy and fugacity of pure liquid and vapor CO_2 , and vapor CH_4 were determined from bilinear interpolation on temperature and pressure using the two-dimensional thermodynamic property data tables based on temperature and pressure. The authors have also discussed calculating

the viscosity and thermal conductivity of pure liquid and vapor CO_2 as well as that of pure vapor CH_4 .

4.4.4 Hydrate Composition, Density, Enthalpy and Thermal Conductivity

Three-dimensional hydrate property data tables were generated from Sloan based on temperature, gas-phase mole fraction (excluding water) of CH_4 , and aqueous phase mass fraction of salt. A trilinear interpolation scheme was used on this tabular data to generate the ex-situ equilibrium pressure, hydrate mole fraction (excluding water) of CH_4 , CO_2 small- and large-cage occupancy numbers, and CH_4 small- and large-cage occupancy numbers. The authors have illustrated a systematic procedure for carrying out these calculations.

The authors have also given a detailed explanation in their paper about many other properties such as water thermodynamic and transport properties, aqueous-phase thermodynamic and transport properties, gas-phase thermodynamic and transport properties, ice saturation, and ice thermodynamic and transport properties.

4.5 Input File

The STOMP simulator is controlled through a text file, which must be entitled *input* for proper execution. This input file has a structured format composed of cards, which contain associated groups of input data. Depending on the operational mode, input cards may be required, optional, or unused. Required cards must be present in an input file. Optional cards are not strictly required to execute the simulator, but may be required to execute a particular problem. Unused cards are treated as additional text that is unrecognized by the simulator. Cards may appear in any order within the input file; however, the data structure within a card is critical and must follow the formatting directives. The readers interested in knowing more about the working and the features of the simulator STOMP can refer to the STOMP: User's Guide (*White and Oostrom, 2003*).

Recently, *Stone (2006)* conducted a simulation study using STOMP-HYD module to analyze the effect of capillary pressure on CH₄ production from gas-hydrate reservoirs. The study showed that the soils with higher capillary pressures resulted in higher aqueous saturations in the formation, thereby causing a rapid heat transfer through the formation, which ultimately results in rapid dissociation of CH₄-hydrates and fast CH₄ production from the reservoir.

CHAPTER FIVE

1-D SIMULATION STUDY

The STOMP-HYD module is in an early stage of development and it had some limitations in terms of handling a complex reservoir model at the time when this study was conducted. The current version of STOMP-HYD was not capable of handling real field-scale reservoir geometries involving complex 3-D models. To tackle this problem, initially a study was carried out on a simple 1-dimensional (1-D) reservoir models to test the hypothesis of CO₂-microemulsion injection for methane recovery from the gas hydrate reservoirs. Based on the 1-D simulation, the feasibility of using CO₂-microemulsion injection for methane recovery was studied by more complex 2-dimensional (2-D) reservoir models.

Execution of 1-D and 2-D simulations would impose considerable demand on the available computing power (a desktop PC with Intel® Pentium® 4 processor, 512 MB RAM, running the Windows® XP Professional Operating System). To reduce the execution time of the simulation runs, University of Alaska Fairbanks' Supercomputing service (Arctic Region Supercomputing Center) was used during the entire study.

The present chapter discusses the 1-D simulation runs involving various scenarios. The input data used in all the simulations and the results obtained from this part of the study along with the discussion of those results are given subsequently.

5.1 1-D Simulation Experiments

The effects of various parameters such as CO₂-microemulsion temperature, concentration of CO₂-slurry and absolute permeability of the formation rock were analyzed with a simple 1-D horizontal reservoir model. The primary objective of these 1-D simulations was to support the hypothesis of CO₂-microemulsion injection for methane recovery from gas-hydrate reservoirs. The following section gives the details

about initialization of the model with the help of grid geometry and defining initial and boundary conditions.

5.1.1 Initialization of 1-D Model

This section describes some of the parameters from the *input* file, such as grid system, initial conditions, etc., along with the properties used under each of these systems.

5.1.1.1 Grid System:

A Cartesian coordinate system was chosen for 1-D simulation experiments. A horizontal 1-D grid system (20x1x1) containing 20 grid-blocks was considered. As shown in *Figure 5.1*, this reservoir model had 20 grid-blocks in the x-direction. The dimensions of each grid-block are mentioned below:

X-direction: 5 m

Y-direction: 1 m

Z-direction: 1m

Thus the total length of this reservoir model was 100 m. A schematic of this horizontal system is shown below:

Figure 5.1: Schematic representation of the 1-D reservoir model

For the above system, CO₂-microemulsion injection was considered from the west boundary (grid-block#1) of the system whereas methane production was assumed from the east boundary (grid-block#20) of the system.

5.1.1.2 Hydraulic Properties:

The hydraulic properties in the *input* file give the user an option for specifying either intrinsic permeability or hydraulic conductivity. For the current study, intrinsic permeability was specified in the *input* file. Basically, all the 1-D simulation runs were carried out using two different values of absolute permeability for the reservoir model. The absolute permeability value was set to 1 Darcy or 10 Darcy during the study. In reality, it is impossible to find a gas-hydrate reservoir with such a high permeability. Since the primary objective of the 1-D simulation study was just to support and demonstrate the possibility of the CO₂-microemulsion injection method for methane recovery, the selection of unrealistic values for some of the reservoir properties such as absolute permeability is justified.

5.1.1.3 Initial Conditions of Reservoir Model:

The initial conditions such as aqueous pressure and temperature as well the hydrate saturation were specified uniform across the reservoir model. As discussed in Chapter 2, the hydrate stability zone for the arctic region lies approximately between the temperatures of -8°C to 14°C and from a depth of 200 m up to 1100 m. *Figure 2.10* in Chapter 2 gives more information about this. Considering these facts, a uniform initial temperature of 3°C was chosen for the reservoir system. Table 5.1 shows the different initial conditions.

Table 5.1: Initial conditions across the 1-D reservoir model

Aqueous Pressure	6 MPa
Temperature	3°C
Hydrate Saturation	50%
Mass Fraction of CH ₄ in Hydrate Phase	100%

The mass fraction of CH₄ in hydrate phase was assumed 100% meaning that pure CH₄-hydrates were considered to be present in the reservoir under consideration.

5.1.1.4 Boundary Conditions:

As discussed earlier, CO₂-microemulsion injection was assumed from the west boundary of the reservoir model (grid-block#1) whereas the methane production was considered from the east boundary (grid-block#20). For this study, it was assumed that CH₄ gas production was carried out at a pressure of 6 MPa which is same as the initial pressure of the reservoir system. The CO₂-microemulsion injection was assumed to be injected at a higher pressure of 7 MPa from the West boundary. Table 5.2 gives the details of the boundary conditions applied at these two boundaries. The CO₂-microemulsion concentration is taken as the volume fraction of liquid CO₂ in the microemulsion.

Table 5.2: Boundary conditions for 1-D reservoir model

West Boundary (Gridblock: 1,1,1)	East Boundary (Gridblock: 20,1,1)
Aqueous Pressure = 7 MPa	Temperature = 3°C
Liquid CO ₂ Pressure = 7 MPa	Aqueous Pressure = 6 MPa

Excluding these mentioned parameters, all other properties of reservoir model as well as the boundary conditions were kept constant in all 1-D simulation runs. The detailed descriptions of various simulation runs along with the different parameters used in the individual case are given in the next section.

5.1.2 Production Scenarios

The different types of production scenarios tested on the 1-D horizontal reservoir model were designed in order to analyze the effect of CO₂-microemulsion temperature as well as the concentration of CO₂-slurry on methane production. The sensitivity of the reservoir model in terms of the absolute permeability of the formation was also tested during these simulation runs.

It was important to compare the CH₄ recovery obtained from the CO₂-microemulsion injection technique against some reference method. To achieve this, a

conventional production method, thermal stimulation, was selected for comparing the results. A total of 7 different simulation cases were completed on the 1-D reservoir model. Out of the 7 cases, Case No. 1 through 3 involved a formation permeability of 1 Darcy, whereas Case No. 4 through 7 used a formation permeability of 10 Darcy. The important parameters that were used in these 1-D simulation runs are given in Table 5.3.

As is clear from Table 5.3, Case No. 1 is the thermal stimulation method in which warm water at a temperature of 50°C was injected into the formation. The concentration of CO₂-microemulsion in the injection stream was 0% under this case. In a similar way, Case No. 4 was the base case scenario for the formation permeability of 10 Darcy, where warm water at a temperature of 50°C was injected into the formation without CO₂ in the injection stream.

Table 5.3: Different simulation cases studied during 1-D simulation experiments

Case No.	CO ₂ -microemulsion Temperature [°C]	CO ₂ -microemulsion Concentration	Formation Permeability [D]
1	50 (Base Case)	0%	1
2	15	50%	1
3	25	50%	1
4	50 (Base Case)	0%	10
5	25	25%	10
6	25	50%	10
7	25	75%	10

The rest of the parameters were kept constant and are outlined in the previous sections. The initial conditions used during the simulation experiments were kept the same as discussed previously in section 5.1.1.4. The boundary conditions including aqueous and liquid CO₂ pressure on the west boundary and aqueous pressure and temperature on the east boundary were kept the same as shown earlier in Table 5.2.

The results obtained from the 1-D simulation study along with the discussion of these results have been presented in the following Chapter 6.

CHAPTER SIX

RESULTS AND DISCUSSION: 1-D SIMULATION STUDY

6.1 1-D Simulation Experiments

As discussed earlier, a total of 7 different cases were studied in this section in order to demonstrate the feasibility of a CO₂-microemulsion injection method for CH₄ recovery. The total amount of CH₄ gas recovered and the total amount of CO₂-microemulsion injected into the reservoir were the two most important variables to be monitored. Along with these two variables, temperature and pressure of the reservoir system, CH₄-CO₂ mixed hydrate saturation as well as individual CH₄ and CO₂ hydrate saturations within the reservoir were observed under each case.

The different production scenarios tested during this stage are outlined in detail in section 5.1.2 of the earlier chapter. A total of 7 simulation cases were run in the 1-D simulation study. The results obtained from this study are discussed below.

6.1.1 Case 1: Thermal Stimulation – Warm Water @ 50°C and 1 Darcy (Base Case)

This case was designed to analyze the effect of injection of warm water on the CH₄-hydrate dissociation and compare the results with the CO₂-microemulsion injection technique used in the rest of the cases. The injection temperature of water was set to 50°C and the aqueous CO₂ volume fraction in the injection stream was set to 0%, thereby simulating a condition of only hot water injection into the formation. The formation permeability was assumed as 1 Darcy.

Figure 6.1 shows the temperature profiles within the reservoir system at different simulation times. It was expected that the heat introduced into the formation by hot water will be utilized to dissociate the CH₄-hydrates in the reservoir. As a result, we can observe a steady increase in the temperatures on the injection side of the system. However, the temperature at the west boundary did not rise to the injection temperature

of 50°C indicating that the heat in the form of hot water is getting utilized for CH₄-hydrate dissociation. The CH₄-hydrates on the west side of the system underwent dissociation and with the continuation of hot water injection, more and more heat was transmitted, from the injection site towards the production side, into the reservoir increasing the temperatures progressively. Figure 6.1 also shows that at the end of 200 days, the temperature in the first half portion of the system increased from its initial value of 3°C to approximately 10°C. Figure 6.2 shows the aqueous pressure variation inside of the reservoir at different simulation times.

Figure 6.1: Case 1 - Temperature profiles at different simulation times
(thermal stimulation @ 50°C, 1 Darcy)

Figure 6.2: Case 1 – Aqueous pressure profiles at different simulation times
(thermal stimulation @ 50°C, 1 Darcy)

The total hydrate saturation profiles are shown in the following *Figure 6.3*, whereas *Figure 6.4* represents the CH₄-hydrate saturations in the reservoir at different simulation times. Under the present base case, since the liquid CO₂ concentration was zero in the injection stream, therefore there will not be formation of any CO₂-hydrates in the system. Hence, the total hydrate saturation represented in *Figure 6.3* is the same as the CH₄-hydrate saturations shown in *Figure 6.4*. As discussed before, the temperature at the west boundary of the reservoir system increased steadily from its initial temperature. As it can be seen from *Figure 6.4*, the CH₄-hydrate saturation at the west boundary decreased to a value of 11% after 50 days of warm water injection. As the hydrates on the west side of the reservoir underwent dissociation, the released CH₄ gas migrated towards the east side under the pressure differential. But due to the low temperature – high pressure conditions in that part of the reservoir, this free CH₄ gas again underwent a hydrate formation process resulting in an increase in the hydrate saturation. Therefore in some portion of the reservoir, the hydrate saturations became greater than the initial value of 50%.

**Figure 6.3: Case 1 – Total hydrate saturation at different simulation times
(thermal stimulation @ 50°C, 1 Darcy)**

Figure 6.4: Case 1 - CH₄-hydrate saturation at different simulation times (thermal stimulation @ 50°C, 1 Darcy)

A detailed methodology for calculating the CH₄ recovery efficiency has been given in section 8.1.1. Using this methodology, the recovery efficiency calculations were carried out for different production scenarios studied under 1-D simulation study. In the present scenario, there was no CH₄ production over the entire simulation time of 4800 hours (200 days). Hence, the recovery efficiency for this case was zero. The CH₄-hydrates on the west side of the reservoir underwent dissociation, but the released CH₄ gas underwent hydrate formation process during its passage towards the production well on the east side of the reservoir. Hence, no CH₄ production was observed from the production well.

6.1.2 Case 2: CO₂-microemulsion Injection – 50%, 15°C and 1 Darcy

In this scenario, CO₂-microemulsion with a temperature of 15°C was injected into the reservoir having a formation permeability of 1 Darcy. The concentration of liquid-CO₂ in the injected microemulsion stream was 50% on the volume basis. The results have been shown for the following simulation time periods: 0 days (initial condition), 50 days, 100 days, 150 days, and 200 days (end of the simulation time).

Figure 6.5 shows the temperature profile in the reservoir system at different simulation time periods. As it can be seen from this figure, upon CO₂-microemulsion injection, the temperature of the reservoir started increasing from its initial temperature of 3°C. After the 50 days, the temperature at the west boundary of the reservoir increased up to 13°C, but after that, the temperature at this location went on decreasing. The main reason for the rise and then decrease in temperature can be attributed to the hydrate dissociation/formation phenomena. As we can see from Figures 6.7 and 6.8 which represent individual CH₄- and CO₂-hydrate saturations up to 50 days of injection time, CH₄-hydrate dissociation and CO₂-hydrate formation processes were going on simultaneously at the west boundary. That resulted in increasing the temperature at this end of the system. But after 50 days, the CH₄-hydrate saturation at the west boundary was negligible. The CO₂ injected into the formation after this time period continued to go into the hydrate phase at the west end of the system resulting in lowering the temperature as hydrate formation is an endothermic process. As more and more CO₂-microemulsion was injected into the reservoir, it helped in increasing the temperature of the system resulting in a higher amount of CH₄-hydrates being dissociated.

Figure 6.5: Case 2 - Temperature profiles in the reservoir system (50% CO₂-microemulsion @ 15°C, 1 Darcy)

Figure 6.6: Case 2 - Aqueous pressure profiles in the reservoir system (50% CO₂-microemulsion @ 15°C, 1 Darcy)

Figure 6.6 shows the aqueous pressure profile inside of the reservoir at different simulation times. As discussed earlier, up to 50 days of simulation time, most of the CH₄-hydrates at the west boundary of the reservoir underwent dissociation, with the simultaneous process of CO₂-hydrate formation at this end. After 50 days, the CO₂-hydrate formation process dominated the CH₄-hydrate dissociation in this region resulting in very high hydrate saturations which are shown in Figure 6.9. Therefore, these high hydrate saturations offered an appreciable amount of resistance to the flow in the region near to the injection well. With the increase in the hydrate saturation in this region, the aqueous pressure gradient became steeper as shown in Figure 6.6.

Figure 6.7 depicts the CH₄-hydrate saturation in the reservoir. As discussed earlier, most of the CH₄-hydrates in the region near to the injection well underwent dissociation in 50 days. After 50 days of injection, the CH₄-hydrate saturation at the west boundary decreased drastically and was close to 7%. As the CH₄-hydrates underwent dissociation, the released CH₄ gas migrated towards the production well. But due to temperature-pressure conditions in that part of the reservoir are favorable for CH₄ to

form hydrate; it underwent a CH₄-hydrate formation process resulting in CH₄-hydrate saturations greater than the initial value of 50%.

Figure 6.7: Case 2 - CH₄-hydrate saturation at different simulation times (50% CO₂-microemulsion @ 15°C, 1 Darcy)

The individual CO₂-hydrate saturations are shown in *Figure 6.8* at different simulation times. As discussed before, the CO₂-hydrate saturations in the region close to the injection well increased rapidly to higher values in the range of 65% to 85% during the simulation. These high CO₂-hydrate saturations might have offered a great resistance to the flow of microemulsion, which results in low injectivity.

Figure 6.9 shows the total CH₄-CO₂ mixed hydrate saturations in the reservoir which is the sum of individual CH₄- and CO₂-hydrates as discussed before.

Figure 6.8: Case 2 – CO₂-hydrate saturation at different simulation times (50% CO₂-microemulsion @ 15°C, 1 Darcy)

Even though most of the released CH₄ gas again underwent hydrate formation process during its passage towards the production well as shown in *Figure 6.7*, the CH₄ recovery was only about 0.45% under the present case at the end of 4800 hours (200 days) of fluid injection. The CH₄ recovery profile has been shown in *Figure 6.10*.

Figure 6.9: Case 2 - Total CO₂-CH₄ hydrate saturation at different simulation times (50% CO₂-microemulsion @ 15°C, 1 Darcy)

The pore volume of the reservoir system under consideration can be calculated by the following equation:

$$V_p = V_b * \phi \quad \text{----- (Eq. 6.1)}$$

where,

V_p = Pore volume, m^3

V_b = Bulk volume, m^3

ϕ = Porosity, fraction

The bulk volume of the reservoir system can be computed using the grid dimensions and the total number of grids as:

$$\begin{aligned} V_b &= (5 \times 1 \times 1) \times 20 \\ &= 100 \text{ m}^3 \end{aligned}$$

The porosity of the reservoir model was considered as 30% for the 1-D simulation study. Therefore, the pore volume can be calculated as:

$$\begin{aligned} V_p &= 100 \times 0.30 \\ &= 30 \text{ m}^3 \end{aligned}$$

The volume of liquid CO₂ can be calculated using the values of mass of liquid CO₂ and its density. In the CO₂-microemulsion injection technique, two different injection temperatures of 15°C and 25°C have been used in the study as shown in Table 5.3. The densities of liquid CO₂ at 15°C and 25°C were taken as 855 kg/m³ and 725 kg/m³, respectively (*Span and Wagner, 1996*). From the knowledge of the density and the mass of liquid CO₂ in each production scenario, the volume of liquid CO₂ being injected into the reservoir under each production scenario was calculated. The pore volume (PV) of liquid CO₂ being injected into the reservoir can be calculated using the following equation:

$$\text{PV of liquid CO}_2 \text{ injected} = \frac{\text{Volume of liquid CO}_2 \text{ injected}}{\text{Pore volume}} \quad \text{----- (Eq. 6.2)}$$

Figure 6.10 shows the profiles of pore volumes of liquid CO₂ injected into the reservoir as well as CH₄ recovery over the entire simulation time. This figure clearly shows that approximately 0.05 pore volumes of liquid CO₂ needed to be injected into the reservoir before any CH₄ gas production started.

Figure 6.10: Case 2 - The profiles of pore volumes of CO₂ injected and CH₄ recovery (50% CO₂-microemulsion @ 15°C, 1 Darcy)

6.1.3 Case 3: CO₂-microemulsion Injection – 50%, 25°C and 1 Darcy

In this present case, the effect of a CO₂-microemulsion with higher injection temperature on CH₄-hydrate dissociation, and thereby on CH₄ gas recovery was analyzed. The concentration of microemulsion was kept similar to the previous case (50%) whereas its temperature was increased to 25°C. Figures 6.11 through 6.16 show the results for this particular case.

Figure 6.11 shows the temperature profile at various simulation times. Again in this case, the temperature profiles are similar to those observed in Case No. 2. As can be seen, the temperature at the west boundary initially increased from its original value of 3°C upto 13°C at the end of 50 days. During this time period, as discussed in the earlier case, both processes of CH₄-hydrate dissociation and CO₂-hydrate formation occurred in the region close to the injection well, raising the temperature in that region. After 50

days of microemulsion injection, most of the CH_4 -hydrates in this region underwent dissociation and the remaining CH_4 -hydrate saturation was low, around 7-8% as shown in Figure 6.13. At the same time, the CO_2 -hydrate saturations in this region increased to approximately 55% as shown in Figure 6.14.

Figure 6.11: Case 3 - Temperature profiles at different simulation times (50% CO_2 -microemulsion @ 25°C , 1 Darcy)

CH_4 -hydrates continued to undergo dissociation throughout the simulation time; but after around 100 days, a substantial amount of CO_2 -hydrates also underwent dissociation in the region closer to the injection well due to the high injection temperature of the microemulsion. This resulted in a relatively small decrease in temperature after around 150 days of injection time, as shown in Figure 6.11. In the region away from the injection well, we can observe the temperature profile shifting from the west side towards the east side.

Figure 6.12 presents the aqueous pressure profiles in the reservoir at different simulation times. These pressure profiles did not show the type of behavior that was observed in Case No. 2. In this case, the pressure profile after 50 days of microemulsion injection was similar to the one observed in Case No. 2. But as discussed earlier, after around 100 days of injection time, the CO_2 -hydrates in the region close to the injection

well also started to undergo dissociation because of the higher temperatures in this region. As shown in *Figures 6.14*, it is clear that the CO₂-hydrate saturations in the region close to the injection well were close to 50%, which will not introduce additional resistance to the flow of CO₂-microemulsion into the reservoir.

Figure 6.12: Case 3 - Aqueous pressure profiles at different simulation times (50% CO₂-microemulsion @ 25°C, 1 Darcy)

Figure 6.13: Case 3 – CH₄-hydrate saturation at different simulation times (50% CO₂-microemulsion @ 25°C, 1 Darcy)

Figure 6.14: Case 3 – CO₂-hydrate saturation at different simulation times (50% CO₂-microemulsion @ 25°C, 1 Darcy)

Figures 6.13 and 6.14 depict the individual CH₄- and CO₂-hydrate saturations inside of the reservoir at different simulation times. As discussed previously, the CH₄-hydrate saturation near the injection well decreased to approximately 7% at the end of 50 days and it went down to zero around 150 days. The free CH₄ gas released from the CH₄-hydrate traveled towards the production well, but because of the low temperature and high pressure conditions, it again went into the hydrate phase resulting in higher CH₄-hydrate saturations. Figure 6.14 indicates that the CO₂-hydrate saturations in the region close to the injection well increased in the early time. But as time progressed, some portion of CO₂-hydrates underwent dissociation due to the higher temperatures in this region. This resulted in the decrease in the CO₂-hydrate saturations.

Figure 6.15 shows the total CH₄-CO₂ mixed hydrate saturations, which is the sum of individual CH₄- and CO₂-hydrates inside of the reservoir. As is clear from the earlier discussion, almost all the CH₄-hydrates as well as some portion of CO₂-hydrates were dissociated in the region close to the injection well, which resulted in a decrease in the overall hydrate saturations in that region as shown in Figure 6.15.

Figure 6.15: Case 3 - Total CO₂-CH₄ hydrate saturation at different simulation times (50% CO₂-microemulsion @ 25°C, 1 Darcy)

Figure 6.16: Case 3 - The profiles of pore volumes of CO₂ injected and CH₄ recovery (50% CO₂-microemulsion @ 25°C, 1 Darcy)

Figure 6.16 shows the pore volumes of liquid CO₂ injected into the reservoir and the CH₄ recovery as a function of time. The injection of CO₂-microemulsion at high temperature resulted in more CH₄-hydrate dissociation and higher CH₄ gas recovery as

compared to the Case No. 2. A cumulative CH₄ recovery of approximately 6% was observed in this case at approximately 0.08 pore volumes of CO₂ injected.

Figure 6.17 summarizes the results of CH₄ recovery efficiency at the end of 200 days for all the three cases discussed so far. Examining these results, it can be found that the CO₂-microemulsion injection technique resulted in much higher CH₄ recovery as compared to Case No. 1 which was the thermal stimulation only.

Figure 6.17: Summary of CH₄ recovery efficiency for all the cases with formation permeability of 1 Darcy

6.1.4 Case 4: Thermal Stimulation–Warm Water @ 50°C and 10 Darcy (Base Case)

Similar to the earlier Case No. 1, the effect of injecting warm water with increased permeability was analyzed in this case. The concentration of CO₂-microemulsion was set to zero. Figure 6.18 shows the temperature profiles in the reservoir system at different time steps. Under the present case, the formation permeability was 10 Darcy as compared to the previous three cases in which the

formation permeability was 1 Darcy. It was expected that the increased permeability would be helpful in allowing easy flow of warm water as well as CO₂-microemulsion across the reservoir. As expected, the high injection temperature of warm water and high formation permeability resulted in rapid CH₄-hydrate dissociation in the region close to the injection well, as shown in *Figure 6.21*. Therefore, after 50 days of the warm water injection, the temperature at the injection well becomes injected water temperature (50°C). Thereafter, the temperature profile moves from the west towards east side of the reservoir with an increase in time.

**Figure 6.18: Case 4 - Temperature profiles at different simulation times
(thermal stimulation @ 50°C, 10 Darcy)**

Figure 6.19 gives the details about the aqueous pressure profiles in the reservoir at different time steps. There is no liquid-CO₂ being injected from the injection well in the present case and the absolute formation permeability is also high. The high formation permeability helped the injection rate resulting in rapid dissociation of CH₄-hydrates. This rapid dissociation results in maintaining a flat aqueous pressure profile at the injection pressure value of 7 MPa for some part of the reservoir as shown in *Figure 6.19*.

Figure 6.20 shows the total hydrate saturation profiles at different time steps. Due to no liquid CO₂ in the injection stream from the injection well, the total hydrate saturations presented in Figure 6.20 are the pure CH₄-hydrate saturations shown in Figure 6.21.

Figure 6.19: Case 4 – Aqueous pressure profiles at different simulation times (thermal stimulation @ 50°C, 10 Darcy)

As we can see from these two figures, the high formation permeability helps in allowing rapid flow of warm water across the reservoir and the high temperatures of the water result in rapid dissociation of the CH₄-hydrates. The CH₄-hydrates in half of the reservoir on the injection side underwent dissociation resulting in zero hydrate saturations at the end of 200 days of simulation time.

Figure 6.20: Case 4 - Total hydrate saturation at different simulation times (thermal stimulation @ 50°C, 10 Darcy)

As the released CH_4 gas moved across the reservoir towards the production well, some fraction of it went back into the hydrate phase resulting in higher CH_4 -hydrate saturations that are seen in the region close to the production well while the remaining portion of the free CH_4 gas was produced from the production well.

Figure 6.21: Case 4 - CH_4 -hydrate saturation at different simulation times (thermal stimulation @ 50°C, 10 Darcy)

Figure 6.22 shows the CH₄ gas recovery from the reservoir as a function of time under the present case. The CH₄ gas breakthrough was observed much earlier in this case (around 75 days or 1800 hours), as compared to 1 Darcy case (Case No. 1) with the cumulative CH₄ recovery of approximately 33%.

Figure 6.22: Case 4 - The profiles of pore volumes of hot water injected and CH₄ recovery (thermal stimulation @ 50°C, 10 Darcy)

6.1.5 Case 5: CO₂-microemulsion Injection – 25%, 25°C and 10 Darcy

This case discusses the injection of a 25% CO₂-microemulsion with a formation permeability of 10 Darcy. The injection temperature of CO₂-microemulsion was assumed to be 25°C. Figure 6.23 shows the temperature profiles in the reservoir at different simulation times. As a result of high formation permeability, the flow of the CO₂-microemulsion across the system was much easier. The high formation permeability and warmer injection temperatures of the microemulsion resulted in the dissociation of all the CH₄-hydrates at the injection well after just 50 days of simulation time as shown in Figure 6.25. At the same time, the CO₂-hydrate saturation at this location was around 14% as depicted in Figure 6.26. As a result of high injectivity accompanied by CO₂-hydrate formation at this location resulted in increasing the temperature from the initial value of 3°C to around 11°C at the end of 50 days. As shown in Figures 6.25 and 6.26, the

CO₂-hydrates in the region close to the injection well progressively underwent dissociation after 50 days due to the heat associated with CO₂-microemulsion. This CO₂-hydrate dissociation led to the decrease in the temperatures in the region a little away from the injection well location, as shown in *Figure 6.23* below. Again, as the released CH₄ gas moved across the reservoir towards the production well, some portion of that went into the hydrate phase as shown in *Figure 6.25*. This phenomenon again resulted in increasing the temperature in the reservoir. These entire processes of hydrate dissociation-formation ultimately led to ups and downs in the temperature profiles as shown in *Figure 6.23*.

Figure 6.24 shows the aqueous pressure profiles in the reservoir at various simulation times. As shown in this figure, the aqueous pressure profiles remained flat in the regions near the west boundary of the system, due to the CH₄- as well as CO₂-hydrates undergoing dissociation with increase in time.

Figure 6.23: Case 5 - Temperature profiles at different simulation times (25% CO₂-microemulsion @ 25°C, 10 Darcy)

But in the regions away from the injection well, there was substantial amount of CO₂-hydrate formation and therefore the aqueous pressures dropped due to the resistance offered by these hydrate saturations to the flow of microemulsion through the pore spaces.

Figures 6.25 and 6.26 represent the individual CH_4 - and CO_2 -hydrate saturations inside of the reservoir at different simulation times. As has been discussed before, the CH_4 -hydrate saturations at the injection well decreased to zero at the end of 50 days. As time progressed, more and more CH_4 -hydrates underwent dissociation due to the heat associated with the microemulsion and the heat released from the CO_2 -hydrate formation. At the end of 150 days, the total CH_4 -hydrate saturation within the reservoir was approximately 4%, which even went down at the end of 200 days of simulation time, as depicted in Figure 6.25.

Figure 6.24: Case 5 – Aqueous pressure profiles at different simulation times (25% CO_2 -microemulsion @ 25°C , 10 Darcy)

Figure 6.25: Case 5 - CH_4 -hydrate saturation at different simulation times (25% CO_2 -microemulsion @ 25°C , 10 Darcy)

Figure 6.26 below represents the CO₂-hydrate saturations across the reservoir at different simulation times. As said earlier, the CO₂-hydrate saturations initially increased in the region close to the injection well but later underwent dissociation due to the heat associated with the microemulsion. High CO₂-hydrate saturations can be observed in the reservoir away from the injection well at the end of 150 days and 200 days of microemulsion injection. From Figure 6.23, it is clear that the temperatures in this region were close to 12.5°C at the end of 150 days and 200 days. The pressure-temperature equilibrium curve for CO₂-hydrate presented in Figure 2.13 shows that the equilibrium pressure for CO₂-hydrates at 12.5°C is 5.8 MPa. In the present case, the aqueous pressures in the reservoir away from the injection well were in the range of 6.1 MPa to 6.6 MPa as shown in Figure 6.24. Thus, it is clear that the conditions in the region away from the injection well were still favorable for CO₂ to form hydrate. Figure 6.27 shows the total CH₄-CO₂ hydrate saturations across the reservoir, which is nothing but the combination of individual CH₄- and CO₂-hydrate saturations as discussed before.

Figure 6.26: Case 5 – CO₂-hydrate saturation at different simulation times (25% CO₂-microemulsion @ 25°C, 10 Darcy)

Figure 6.27: Case 5 - Total CO₂-CH₄ hydrate saturation at different simulation times (25% CO₂-microemulsion @ 25°C, 10 Darcy)

The high formation permeability resulted in the high injection rates of CO₂-microemulsion, thereby getting an early CH₄ gas recovery. This ultimately resulted in more CH₄ gas production as shown in Figure 6.28. The CH₄ gas breakthrough was observed around 900 hours of injection time. The CH₄ gas recovery observed in this case was approximately 90%, which was much higher than Case No. 4.

Figure 6.28: Case 5 - The profiles of pore volumes of CO₂ injected and CH₄ recovery (25% CO₂-microemulsion @ 25°C, 10 Darcy)

6.1.6 Case 6: CO₂-microemulsion Injection – 50%, 25°C and 10 Darcy

The present case is similar to the previous case with the exception of the concentration of CO₂-microemulsion. In the present scenario, the concentration of CO₂-microemulsion was increased from 25% in the earlier case to 50% in the present case; with an injection temperature of 25°C and formation permeability of 10 Darcy. *Figure 6.29* shows the details of the temperature profiles in the reservoir system at different times. The increased CO₂-microemulsion concentration is helpful in the CH₄-CO₂ replacement in the hydrate phase. Under the present scenario, the microemulsion with higher liquid CO₂ concentration helps in faster dissociation of CH₄-hydrates within the reservoir, as shown in *Figure 6.31*. As is clear from *Figure 6.31*, as soon as CO₂-microemulsion enters into the reservoir from the west boundary, it leads to the dissociation of almost all the CH₄-hydrates in the region near the injection well. This results in maintaining a flat temperature profile in that region at the end of 50 days of injection. From *Figure 6.32*, which represents the CO₂-hydrate saturations across the reservoir, it was found that the CO₂-hydrate saturations increased to a level of around 55% in the areas away from the injection well. This process of CO₂-hydrate formation also introduced heat in the reservoir, further increasing the reservoir temperatures as shown in *Figure 6.29*. The increase in the reservoir temperatures at different simulation times is the combined result of CO₂-hydrate formation and CH₄-hydrate dissociation.

Figure 6.30 shows the aqueous pressure profiles inside the reservoir at different simulation times. The aqueous pressure profiles observed in Case No. 2 are also similar to those obtained in the present case. An explanation similar to that given for Case No. 2 is valid for the present case as well. From *Figures 6.31* and *6.32*, we can observe that the CH₄-hydrate saturations in the region close to the injection well were zero at the end of 50 days of simulation time; whereas at the same time, the CO₂-hydrate saturations increased to approximately 75% in that region.

**Figure 6.29: Case 6 - Temperature profiles at different simulation times
(50% CO₂-microemulsion @ 25°C, 10 Darcy)**

Such high hydrate saturations must have offered a great opposition to the flow of CO₂-microemulsion across the reservoir, which ultimately resulted in a sudden drop in the aqueous pressures in this region. With an increase in the time, CO₂-hydrate saturations closer to the injection well went on increasing, which offered more resistance leading to a further drop in the aqueous pressure across that region, as shown in *Figure 6.30*.

**Figure 6.30: Case 6 – Aqueous pressure profiles at different simulation times
(50% CO₂-microemulsion @ 25°C, 10 Darcy)**

Figures 6.31 and 6.32 represent the individual CH₄- and CO₂-hydrate saturations across the reservoir at different simulation times. As discussed earlier, Figure 6.31 clearly shows that higher concentrations of CO₂-microemulsion helped in rapid dissociation of CH₄-hydrates within the reservoir. This was indicated by 50 days of injection time, after which all of the CH₄-hydrates in the region close to the injection well were completely dissociated. After 100 days of simulation time, the CH₄-hydrate saturations across most of the reservoir were less than 6 to 8%, as shown in Figure 6.31. Comparing the results obtained under the present scenario with those obtained in Case No. 5, it indicates that higher CO₂-microemulsion concentration is helpful in higher CH₄ recovery.

Figure 6.31: Case 6 - CH₄-hydrate saturation at different simulation time (50% CO₂-microemulsion @ 25°C, 10 Darcy)

Figure 6.32 shows the CO₂-hydrate saturations across the reservoir at different simulation times. As discussed before, higher CO₂-microemulsion concentrations help in the dissociation of CH₄-hydrates from the reservoir, simultaneously forming more CO₂-hydrates.

Figure 6.32: Case 6 – CO₂-hydrate saturation at different simulation times (50% CO₂-microemulsion @ 25°C, 10 Darcy)

Figure 6.33: Case 6 - Total CO₂-CH₄ hydrate saturation at different simulation times (50% CO₂-microemulsion @ 25°C, 10 Darcy)

Figure 6.33 illustrates the total CO₂-CH₄ hydrate saturations across the reservoir. The high total hydrate saturations in the region near the injection well are a direct result of high CO₂-hydrate saturations depicted in Figure 6.32. A close analysis of Figures 6.29 and 6.30 reveals that the temperature and pressure near the injection side were approximately 10.5°C and 7 MPa, respectively. At these P-T conditions, the CO₂-hydrates are stable (Ohgaki *et al.*, 1996) and this has already been discussed in section

2.3.2. Due to the presence of favorable P-T conditions for CO₂-hydrate stability in the region close to the injection well, high CO₂-hydrate saturations are observed in that region, which ultimately result in high total hydrate saturations.

Figure 6.34 shows the pore volumes of CO₂ injected and CH₄ gas recovery as a function of time for the present case. It is clear from Figure 6.34 that the CH₄ gas breakthrough was observed much earlier than in any of the cases discussed so far and the total CH₄ gas recovery was also high. Approximately 95% of CH₄ gas recovery was observed at the end of 4800 hrs (200 days) of CO₂-microemulsion injection. Comparing the CH₄ recoveries obtained in the present case and in Case No. 5, it can be concluded that the 50% CO₂-microemulsion injection with temperature of 25°C was more favorable for CH₄ recovery.

Figure 6.34: Case 6 – The profiles of pore volumes of CO₂ injected and CH₄ recovery (50% CO₂-microemulsion @ 25°C, 10 Darcy)

6.1.7 Case 7: CO₂-microemulsion Injection – 75%, 25°C and 10 Darcy

In the present scenarios, the injection temperature of microemulsion as well as the formation permeability was kept same as used in Cases 5 and 6, but the concentration of CO₂-microemulsion was increased to 75% in the present case.

Figure 6.35 below shows the temperature variations along the reservoir system at different simulation times. In this case, the temperature profiles showed similar patterns progressively moving across the reservoir from the injection side towards the production side. The injection of the microemulsion at 25°C resulted in increasing the temperature near the injection well, as seen in *Figure 6.35*. The increase in the reservoir temperature away from the injection well is due to the heat evolved from the CO₂-hydrate formation, as shown in *Figure 6.38*.

Figure 6.36 depicts the aqueous pressure profiles across the reservoir at different simulation times. The nature of these pressure profiles is much similar to those obtained in Case No. 6. In the present scenario 75% CO₂-microemulsion was injected into the formation which carried more liquid CO₂ into the reservoir. The availability of more CO₂ from the injection stream is one of the reasons for higher CO₂-hydrate saturations near the injection well, as shown in *Figure 6.37*. But the main reason for higher CO₂-hydrate saturations in the region close to the injection well is due to appropriate pressure-temperature conditions at this location. It can be noticed from *Figure 6.35* that the reservoir temperature near the injection well is approximately 10.5°C. The reservoir pressure in the region near the injection well is close to 7 MPa which can be seen from *Figure 6.36*. As discussed in Case No. 6, these P-T conditions fall in the CO₂-hydrate stability region. The favorable P-T conditions lead to high CO₂-hydrate saturations in the region close to the injection well, as shown in *Figure 6.38*.

Figure 6.35: Case 7 - Temperature profiles at different simulation times (75% CO₂-microemulsion @ 25°C, 10 Darcy)

From Figure 6.38 we can observe that the CO₂-hydrate saturations in the region near the injection well increased well beyond 90% which blocked the pore space available for the microemulsion flow across the reservoir. Due to this, we observe a sudden drop in the aqueous pressure profiles near the injection well, as shown in Figure 6.36. The CO₂-hydrate saturations in this region remained the same throughout the simulation time, which resulted in similar aqueous pressure profiles with an increase in time.

Figures 6.37 and 6.38 show the individual CH₄- and CO₂-hydrate saturations across the reservoir at different simulation times, respectively. As discussed before, along with the higher concentration of CO₂-microemulsion in the injection stream, the suitable P-T conditions in the region close to the injection well is the primary reason for higher CO₂-hydrate saturations in that region, as shown in Figure 6.38. The higher CO₂-hydrate saturations close to the injection well ultimately led to decreasing the flow of microemulsion from the injection well into the reservoir, which caused the dissociation of lower amounts of CH₄-hydrates away from the injection well, as shown in Figure 6.37. At the end of 200 days of simulation time, substantial amounts of CH₄-hydrates underwent dissociation only in the west half of the reservoir, unlike the earlier case.

From these results it can be concluded that very high CO₂-microemulsion concentrations are not helpful for maximizing the CH₄ recovery, because of higher concentrations of microemulsion result in higher CO₂-hydrate saturations near the injection well, thereby opposing the flow of microemulsion into the reservoir.

Figure 6.36: Case 7 – Aqueous pressure profiles at different simulation times (75% CO₂-microemulsion @ 25°C, 10 Darcy)

Figure 6.37: Case 7 - CH₄-hydrate saturation at different simulation times (75% CO₂-microemulsion @ 25°C, 10 Darcy)

Figure 6.38: Case 7 - CO₂-hydrate saturation at different simulation times (75% CO₂-microemulsion @ 25°C, 10 Darcy)

Figure 6.39 below represents the total CO₂-CH₄ hydrate saturations across the reservoir at different simulation times.

Figure 6.39: Case 7 - Total CO₂-CH₄ hydrate saturation at different simulation times (75% CO₂-microemulsion @ 25°C, 10 Darcy)

Figure 6.40 shows the pore volumes of CO₂ injected and the CH₄ gas recovery as a function of time under the present case. As said before, a higher amount of CO₂-hydrates were formed near the injection boundary of the reservoir, which might have affected the

relative permeability for the flow of CO₂-microemulsion. That is why the CO₂ injection profile started becoming flat only few hours after starting the injection. These overall processes affected the cumulative CH₄ recovery, which was reduced to around 40% at the end of 200 days of simulation time.

Figure 6.40: Case 7 - The profiles of pore volumes of CO₂ injected and CH₄ recovery (75% CO₂-microemulsion @ 25°C, 10 Darcy)

Figure 6.41 summarizes the results for CH₄ recoveries vs. pore volumes of fluid injected for Case Nos. 4 through 7. Examining the results, it was found that much lower pore volumes of CO₂-microemulsion were needed to be injected over the 200 days of injection time as compared to the pore volumes of warm water injection over the same injection time. It can be observed that, even after injection of 1 pore volume of warm water, the cumulative CH₄ recovery was less than 20%. However, in all the CO₂-microemulsion injection scenarios, the CH₄ production started after injecting approximately 0.06 pore volumes of CO₂-microemulsion. The cumulative CH₄ recovery obtained in the case of warm water injection was much less than any of the CO₂-microemulsion injection scenario.

Figure 6.41: CH₄ recovery vs. pore volumes of fluid injected for all the cases with formation permeability of 10 Darcy

From the results, it can also be noted that the CH₄ production profiles are much similar in cases 5 through 7. In order to analyze CH₄ recovery in a detailed manner, the results for cases 5 through 7 were plotted separately in Figure 6.42.

Figure 6.42: CH₄ recovery vs. pore volumes of CO₂ injected for cases 5 through 7 with formation permeability of 10 Darcy

Examining the results presented in *Figure 6.42*, it was observed that the CH₄ breakthrough occurred approximately at the equivalent CO₂-microemulsion PV injection in cases 5 through 7. In Case No. 7, injection of 75% CO₂-microemulsion with 25°C temperature resulted in much higher CO₂-hydrate saturations near the injection well resulting the lower injectivity for the microemulsion. The low injectivity ultimately resulted in low CH₄ recovery as compared to Case Nos. 5 and 6. The low CO₂-hydrate saturations in the region near the injection well in cases 5 and 6 led to the higher CH₄ recoveries.

The results from 1-D simulation study also showed that very high CO₂-microemulsion concentrations are not favorable for maximizing CH₄ production and therefore it is clear that the operating parameters of CO₂-microemulsion such as temperature and concentration need to be optimized for the better performance of this technique. The 2-D simulation study discussed in the next couple of chapters focuses on this issue.

CHAPTER SEVEN

2-D SIMULATION STUDY

7.1 2-D Simulation Experiments

After completing the 1-D simulation study, the next step was to carry out 2-D simulation runs with the model conditions representing the reservoir conditions. The effect of different CO₂-microemulsion concentrations and temperatures was tested and analyzed during the 2-D simulation experiments. A number of simulations were carried out using different values of CO₂-microemulsion concentration in the range of 10% to 90%. The critical temperature of liquid-CO₂ is 31°C; therefore, in order to analyze the effect of liquid-CO₂ injection on CH₄ recovery, the CO₂-microemulsion injection temperature was varied from 6°C up to 28°C. A detailed description of these input conditions is given in the following section. Some of the properties of the *input* file used for the 2-D simulation study have been described in the earlier chapter.

7.1.1 Initialization of 2-D Model

This section describes some of the properties of the *input* file that were not discussed in detail in the earlier section.

7.1.1.1 Grid System:

It was decided to use a single layer gas-hydrate reservoir. Therefore, a Cartesian coordinate system was selected for 2-D simulation experiments. A horizontal 2-D grid system (10x10x1) containing 100 grid-blocks was considered. As shown in *Figure 7.1*, this reservoir model had 100 grid-blocks in the x-y plane. The dimensions of each grid-block are mentioned below:

X-direction: 10 m

Y-direction: 10 m

Z-direction: 1m

Thus the total length and width of this reservoir model was 100 m in each direction. A schematic of this horizontal system is shown in *Figure 7.1*. CO₂-microemulsion injection was considered from the west boundary [Grid-block # (1,5,1)] of the system, whereas methane was produced from the east boundary [Grid-block # (10,5,1)] of the system.

Figure 7.1: Schematic representation of the 2-D reservoir model

7.1.1.2 Initial Conditions of Reservoir Model:

The initial conditions such as aqueous pressure and temperature were specified uniform across the reservoir model. The initial hydrate saturation was varied over the reservoir model as depicted in *Figure 7.2*. *Table 7.1* shows the different initial condition parameters and the values assigned for each of those parameters. The mass fraction of CH₄ in hydrate phase was again assumed 100% in this case which means that pure CH₄-hydrates were considered to be initially in the reservoir.

7.1.1.3 Boundary Conditions:

During this study, the effect of depressurization was also analyzed with simultaneous CO₂-microemulsion injection. The aqueous pressure on the production side was reduced to 3 MPa while the gas pressure was kept around 3.65 MPa in the production well. CO₂-microemulsion injection pressure was kept at 7 MPa. *Table 7.2* shows the boundary conditions used on the west and east boundary of the reservoir.

Figure 7.2: Initial hydrate saturation used in 2-D simulation runs

Table 7.1: Initial conditions across the 2-D reservoir model

Aqueous Pressure	6 MPa
Temperature	4°C
Hydrate Saturation	Figure 7.2
Mass Fraction of CH ₄ in Hydrate Phase	100%

Table 7.2: Boundary conditions for 2-D reservoir model

West Boundary (Gridblock: 1,5,1)	East Boundary (Gridblock: 10,5,1)
Aqueous Pressure = 7 MPa	Aqueous Pressure = 3 MPa
Liquid CO ₂ Pressure = 7 MPa	Gas Pressure = 3.65 MPa

Excluding these parameters, the rest of the properties and the boundary conditions of the reservoir were kept constant in each simulation run. The detailed descriptions of various simulation runs along with the different parameters used in the individual case are given in the next section.

7.1.2 Production Scenarios

7.1.2.1 Effect of Temperature and Concentration of CO₂-microemulsion:

In this section, the different types of production scenarios were tested on the 2-D horizontal reservoir model. These were designed to analyze the effect of CO₂-microemulsion temperature as well as the concentration of CO₂-slurry. The CO₂-microemulsion temperatures as well as concentrations were varied over the ranges as given below:

1. CO₂-microemulsion Injection Temperature = 6°C to 28°C
2. CO₂-microemulsion Concentration = 10% to 90%

The rest of the parameters were kept constant and are outlined in the previous sections. Along with the effect of CO₂-microemulsion temperature and concentration, the effect of initial hydrate saturation on the performance of the microemulsion injection technique was also studied.

7.1.2.2 Effect of Initial Hydrate Saturation:

A few simulation experiments were designed to investigate the effect of initial hydrate saturation in the reservoir on CH₄ recovery. Unlike the non-uniform hydrate saturation, the initial hydrate saturation was kept uniform throughout the reservoir system. One more important thing to remember here is that the temperature of injected CO₂-microemulsion was kept at 25°C throughout this exercise. The different values of CO₂-microemulsion concentration analyzed during this study are given in Table 7.3.

Table 7.3: CO₂-microemulsion concentrations used for 2-D simulation experiments

No.	CO ₂ -microemulsion Concentration [%]
1.	15
2.	30
3.	50
4.	80

The initial hydrate saturation was changed over a wide range of values for each value of CO₂-microemulsion. The different values of hydrate saturation are given in Table 7.4.

Table 7.4: Different values of initial hydrate saturations used in 2-D simulation runs

No.	Initial Hydrate Saturation [%]	No.	Initial Hydrate Saturation [%]
1.	30	5.	55
2.	35	6.	60
3.	45	7.	65
4.	50	8.	80

7.1.2.3 CH₄ Production: CO₂-microemulsion Injection vs. Conventional Method

An exercise was also carried out to compare the CH₄ production obtained with the CO₂-microemulsion injection technique to that obtained from the conventional methods. As the conventional method, thermal stimulation was selected. To examine the performance of the CO₂-microemulsion injection technique, two different scenarios were considered, which will be explained in detail later in Chapter 8.

In this exercise, the pressure at the production well was kept equal to 2.5 MPa. In case of the thermal stimulation method, warm water injection is at a temperature of 50°C. The values of CO₂-microemulsion temperature and concentration are listed in the following Table 7.5. In this section, all the three scenarios were run for 1250 days (30000 hours) of simulation time.

Table 7.5: Operating parameters for the CO₂-microemulsion

No.	CO ₂ -microemulsion Concentration	CO ₂ -microemulsion Temperature [°C]
1	30%	25
2	50%	28

7.1.2.4 Energy Efficiency Calculations

Following the simulation study described in section 7.1.2.3 above, an exercise was carried out to analyze the effectiveness of these methods in terms of the total energy requirement as well as the energy efficiency of these techniques.

The enthalpy values of liquid CO₂ and water at 7 MPa pressure (injection pressure) were used to calculate the total energy supplied to the reservoir for the cases discussed in earlier section. These enthalpy values and the results obtained from this exercise are given in the next chapter.

CHAPTER EIGHT

RESULTS AND DISCUSSION: 2-D SIMULATION STUDY

8.1 2-D Simulation Experiments

The 2-D simulation experiments were designed to analyze the performance of CO₂-microemulsion technique in a natural gas-hydrate reservoir under a wide range of temperature and concentration conditions. In the later part of this study, it was realized that the initial hydrate saturation might have significant influence on the selection of the optimized values for CO₂-microemulsion temperature and concentration. Therefore, some more 2-D simulation experiments were performed to investigate this possibility. As discussed in section 7.1.2.1 earlier, the effect of different CO₂-microemulsion concentrations and temperatures on methane production was analyzed. Along with the effect of microemulsion concentration and temperature, the effect of initial hydrate saturation on methane recovery was also analyzed. The energy requirement calculations were carried out in brief for the CO₂-microemulsion injection technique as well as the thermal stimulation method (conventional technique), to emphasize the importance and advantages of the microemulsion injection technique over the conventional process. The following sections summarize the results obtained from this part of the study.

8.1.1 Effect of Temperature and Concentration of CO₂-microemulsion

8.1.1.1. *Effect of Temperature with 30% CO₂-microemulsion Injection:*

In this case, a 30% CO₂-microemulsion was injected into the reservoir. The injection temperature of the microemulsion was varied over the range between 6°C to 28°C. The initial CH₄-hydrate saturation across the reservoir is shown in *Figure 7.2*. The total methane production was monitored for each of these cases. Table 8.1 summarizes the cumulative CH₄ gas produced at the end of total simulation time of 2000 days (48000

hours) for those different cases. The effect of the injection temperature on CH₄ recovery can be seen from the results given in the table.

**Table 8.1: Total amount of methane produced at the end of 2000 days (48000 hours):
30% CO₂-microemulsion injection**

Temp [°C]	CH ₄ Recovery [kg]	CH ₄ Recovery [%]
6	4414.25	2.00
10	4883.73	2.21
15	25502.76	11.55
18	63126.62	28.58
22	91210.27	41.30
25	92190.83	41.74
28	86939.25	39.36

**Figure 8.1: Effect of microemulsion temperature on methane recovery:
30% CO₂-microemulsion injection**

The cumulative CH₄ production observed in each case is plotted as a function of time and is shown in *Figure 8.1* above. From the results given in *Figure 8.1*, it is clear that

the CH₄ recovery was poor at low CO₂-microemulsion injection temperatures such as 6°C and 10°C. The reason for such low CH₄ recoveries at low injection temperature can be attributed to the insufficient amount of heat supplied to the reservoir formation to cause the dissociation of CH₄-hydrates. Even though CO₂-hydrate formation also is a source of heat for CH₄-hydrate dissociation, the energy supplied by CO₂-hydrate formation is not sufficient to cause the dissociation of large amounts of CH₄-hydrates. As can be seen from this figure, with an increase in CO₂-microemulsion injection temperature, there is an increase in CH₄ recovery.

8.1.1.2 Effect of Temperature with 50% CO₂-microemulsion Injection:

In this case, the CO₂-microemulsion concentration was fixed at 50%. The injection temperature of the microemulsion was varied over a range between 6°C to 28°C. The initial CH₄-hydrate saturation across the reservoir is shown in *Figure 7.2*. Table 8.2 gives the results of cumulative CH₄ produced as well as percentage recovery of CH₄ over the total simulation time at the different CO₂-microemulsion injection temperatures discussed here.

**Table 8.2: Total amount of methane produced at the end of 2000 days (48000 hours):
50% CO₂-microemulsion injection**

Temp [°C]	CH ₄ Recovery [kg]	CH ₄ Recovery [%]
6	4437.14	2.01
10	4913.28	2.22
15	17538.01	7.94
18	25443.58	11.52
22	45691.94	20.69
25	94757.80	42.90
28	175293.70	79.37

The results shown in Table 8.2 are plotted as a function of time and are shown in *Figure 8.2* below. As discussed before, these results again indicate that the low CO₂-microemulsion injection temperatures are not really beneficial in the CH₄-CO₂ replacement process as the microemulsion does not carry a sufficient amount of heat

along with it to result in large amounts of CH_4 -hydrate dissociation. Therefore, the cases studied with low CO_2 -microemulsion injection temperatures did not result in high CH_4 recoveries.

**Figure 8.2: Effect of microemulsion temperature on methane recovery:
50% CO_2 -microemulsion injection**

As discussed in section 7.1.2.1, in the present analysis of the effects of CO_2 -microemulsion concentration and injection temperature, the concentration was varied over the range of 10% to 90% whereas the injection temperature was varied between 6°C and 28°C. The analysis of the results obtained in this part of the study revealed that the maximum CH_4 recovery was obtained for the CO_2 -microemulsion injection case with a 50% concentration and 28°C as the injection temperature. The maximum of 79.37% of CH_4 recovery was observed under that case. Therefore, the results obtained under this case such as total hydrate saturation as well as individual hydrate saturations (CO_2 - and CH_4 -hydrate) are discussed in a more detailed fashion. For the results of cumulative CH_4 production obtained for the rest of the cases studied, please refer to Appendix.

Figure 8.3: CH₄-hydrate saturation in the reservoir at t = 0 days (initial condition)

Figures 8.3 through 8.6 represent the total hydrate saturation (CO₂- and CH₄-hydrate saturations combined) variation across the reservoir at different simulation times. The locations of the injection as well as production wells are shown in these figures. The changes in the hydrate saturations taking place in the reservoir before and after the CO₂-microemulsion injection process are noticeable from these figures.

Figure 8.4: Total hydrate saturation in the reservoir at t = 50 days

Figure 8.5: Total hydrate saturation in the reservoir at $t = 500$ days

Figure 8.6: Total hydrate saturation in the reservoir at $t = 2000$ days

To get a clearer idea of how the individual hydrate saturations (CO_2 - and CH_4 -hydrate) are changing within the reservoir, the individual hydrate saturations were calculated using the simulation results. The individual CO_2 - and CH_4 -hydrate saturations are plotted at different simulation times and are shown in Figures 8.7 through 8.13. There were no CO_2 -hydrates present in the reservoir at the initial

conditions. The CO₂-hydrate saturation was zero across the entire reservoir for time $t = 0$ days. As the CO₂-microemulsion injection started from the injection well on the west side of the reservoir, we can observe the CH₄-hydrates dissociating in the small region close to the injection well. Therefore, the CH₄-hydrate saturations in this region decreased in the range of 20% to 35% at the end of 50 days of simulation time, as shown in *Figure 8.8*. At the same time, the CO₂-hydrates started to form in the same region as a result of the CO₂-microemulsion entering the reservoir and therefore, the CO₂-hydrate saturations started to increase in this region, as shown in *Figure 8.9*. It can be observed that at the end of 50 days, the CO₂-hydrate saturation close to the injection well was about 35% and then progressively decreased in the area away from the injection well.

Figure 8.7: CH₄-hydrate saturation across the reservoir at $t = 0$ days (initial condition)

Figure 8.8: CH₄-hydrate saturation across the reservoir at t = 50 days

Figure 8.9: CO₂-hydrate saturation across the reservoir at t = 50 days

As the time progressed, more and more CO₂-microemulsion was injected into the reservoir formation causing the CH₄-hydrate dissociation in the area away from the

injection point. As depicted in *Figure 8.10*, the CH_4 -hydrate dissociation front has moved well into the reservoir at the end of 500 days of injection time, but it has not reached the end of the reservoir yet. The CH_4 -hydrate saturations in the right side of the reservoir are very similar to the initial conditions. When the CH_4 -hydrates are undergoing dissociation in the area close to the injection well, as well as some distance from it, simultaneously the CO_2 -hydrates are being formed. *Figure 8.11* represents the CO_2 -hydrate saturations across the reservoir at time $t = 500$ days. As it can be noticed from this figure, the CO_2 -hydrate saturations are lowered to 30% - 40% in the region close to the injection well because of the continuous supply of heat in the form of microemulsion from this location. But as it moves away from the injection well inside of the reservoir, the CO_2 -hydrate saturations increased to the range of 50% to 60%, partly because of the low reservoir temperatures as compared to the injection site.

Figure 8.10: CH_4 -hydrate saturation across the reservoir at $t = 500$ days

For most of the right side of the reservoir, the CO₂-hydrate saturations remain zero because the microemulsion hasn't reached there yet, as shown in *Figure 8.11*.

Figure 8.11: CO₂-hydrate saturation across the reservoir at $t = 500$ days

Figure 8.12: CH₄-hydrate saturation across the reservoir at $t = 2000$ days

Figure 8.13: CO₂-hydrate saturation across the reservoir at t = 2000 days

Figures 8.12 and 8.13 show the CH₄- and CO₂-hydrate saturations across the reservoir at the end of total simulation time (t = 2000 days), respectively. The results presented in Figure 8.12 clearly show that the CH₄-hydrate saturation decreased to almost zero for most of the region in the left side of the reservoir. Because of the lower pressure at the production well, as compared to the overall reservoir conditions, the CO₂-microemulsion preferred a direct route from the injection well towards the production well and did not reach to the corners of the reservoir on the right side. Therefore, the CH₄-hydrates in this region did not undergo dissociation, resulting in higher CH₄-hydrate saturations in this region as compared to the entire reservoir. In a similar way, the CO₂-hydrate saturations in these two locations can be found to be lower than the rest of the reservoir area. This is depicted in Figure 8.13 above.

8.1.1.3 Effect of CO₂-microemulsion Concentration:

As discussed in section 7.1.2.1, the CO₂-microemulsion concentration was varied over the range of 10% to 90% to analyze its effect on CH₄ recovery from the reservoir under consideration. The initial CH₄-hydrate saturation across the reservoir has been shown earlier in *Figure 7.2*. The results for methane recovery as well as methane recovery efficiency for all the production cases studied so far in the 2-D study are presented in *Table 8.3*. The results for methane recovery efficiency are also presented in a graphical form in *Figure 8.14*.

There was not a clear pattern observed in terms of the effect of CO₂-microemulsion concentration on CH₄ recovery for the reservoir conditions under consideration. The results indicate that low CO₂-microemulsion concentrations, in the range of 10% to 30%, showed poor CH₄ recoveries. The CO₂-microemulsions with high concentrations, in the range of 75% to 90%, also resulted in low CH₄ production, whereas the CO₂-microemulsion with moderate concentrations in the range of 35% to 60% showed considerably higher CH₄ recoveries with the maximum CH₄ production occurring for the case with 50% CO₂-microemulsion concentration and 28°C injection temperature. The low CO₂-microemulsion concentrations (< 35%) did not show good CH₄ recoveries at all injection temperatures, suggesting that the heat evolved as a result of CO₂-hydrate formation with such low microemulsion concentrations is not sufficient for the dissociation of large amounts of CH₄-hydrates.

From the results presented in *Figure 8.14*, it can also be noticed that with the CO₂-microemulsion concentrations in the range of 40% to 50%, the CH₄ recoveries increased substantially compared to the rest of the cases. It suggests that with CO₂-microemulsion concentration of 40% to 50%, more CO₂-hydrates are getting formed in the reservoir, leading to the release of more heat to the surroundings, which ultimately causes dissociation of more CH₄-hydrates. This entire process is also helped with the increase in

CO₂-microemulsion injection temperatures. And therefore, higher CH₄ recoveries are observed in the present case.

Figure 8.14: Results for methane recovery efficiency as a function of microemulsion temperature at different concentrations

Poor CH₄ recoveries were observed for the cases having high CO₂-microemulsion concentrations (> 75%). The low CH₄ recoveries might have caused by the high CO₂-hydrate saturations in the region near to the injection well, because of the appropriate P-T conditions for CO₂-hydrate stability as well as sufficient amounts of CO₂ available for CO₂-hydrate formation in this region. The high CO₂-hydrate saturations might have resulted in poor injectivity of the rest of the CO₂-microemulsion from the injection well into the formation. Examining the results, it was found that higher CO₂-microemulsion concentrations are not necessarily resulting in high methane production. With the conditions in this 2-D study, a CO₂-microemulsion with 50% concentration proved to be the most effective in terms of methane recovery for the reservoir with initial CH₄-hydrate saturation as shown in Figure 7.2. Figure 8.15 depicts a surface plot showing the methane recovery as a function of CO₂-microemulsion concentration and temperature.

Figure 8.15: Surface plot showing the variation of methane recovery as a function of CO₂-microemulsion temperature and concentration

The behavior of different CO₂-microemulsion concentrations with different initial hydrate saturations will be discussed in detail in section 8.1.2.

During this entire simulation study, the effective porosity of the reservoir formation was taken to be 36%. The entire reservoir was divided into 100 grid-blocks and the dimensions of each grid-block are (10 m × 10 m × 1 m). Therefore, the bulk volume of each grid-block in the reservoir can be given as:

$$\begin{aligned} \text{Bulk Volume of a single grid-block} &= 10 \text{ m} \times 10 \text{ m} \times 1 \text{ m} \\ &= 100 \text{ m}^3 \end{aligned}$$

The initial hydrate saturation was assumed across the reservoir as shown in Figure 7.2 before. Therefore, from the knowledge of bulk volume of a single grid-block, effective porosity and initial hydrate saturation in that grid-block, the total amount of CH₄ in that grid-block can be computed. Similar calculations can be repeated for all the

grid-blocks present in the reservoir to yield the total amount of CH₄ gas within the entire reservoir.

An example calculation is shown here considering a single grid-block. The initial reservoir pressure and temperature conditions are 6 MPa and 4°C, respectively. Consider 1 m³ of methane gas-hydrate at these initial reservoir conditions. The density of methane gas-hydrate was taken as 900 kg/m³. Therefore, the mass of methane gas-hydrate can be calculated as:

$$\begin{aligned}\text{Mass of CH}_4\text{-hydrate} &= \text{Volume of CH}_4\text{-hydrate} \times \text{Density of CH}_4\text{-hydrate} \\ &= 1 \text{ m}^3 \times 900 \text{ kg/m}^3 \\ &= 900 \text{ kg}\end{aligned}$$

Assuming CH₄ gas molecule occupies each of the cages in the hydrate structure, the theoretical formula for the CH₄-hydrate becomes: CH₄•5.75 H₂O. From this molecular formula, the molar ratio of CH₄ : H₂O can be written as 1 : 5.75. The molecular weight of the CH₄ molecule is 16 kg/kmol whereas that of the H₂O molecule is 18 kg/kmol. Knowing the molar ratio of CH₄ : H₂O and the molecular weights of CH₄ and H₂O, the weight ratio of CH₄ : H₂O in the CH₄-hydrate structure can be calculated as :

$$\begin{aligned}\text{Wt. (CH}_4\text{)} : \text{Wt. (H}_2\text{O)} &= 1 \times 16 : 5.75 \times 18 \\ &= 16 : 103.50\end{aligned}$$

The mass fraction of CH₄ in the hydrate structure can be computed using the weight ratio of CH₄ : H₂O as shown below:

$$\begin{aligned}\text{Mass fraction of CH}_4 &= \frac{16}{16 + 103.50} = \frac{16}{119.50} \\ &= 0.1339\end{aligned}$$

The mass of CH₄-hydrate has been calculated before to be 900 kg. The density of CH₄ at the reservoir conditions (6 MPa and 4°C) is taken to be 47 kg/m³ (*Setzmann and Wagner, 1991*). Therefore, the volume of CH₄ gas under reservoir conditions can be computed as:

Volume of CH₄ trapped in the hydrate structure at 6 MPa and 4°C

$$= \frac{900 \text{ kg} \times 0.1339}{47 \text{ kg/m}^3}$$

$$= 2.5640 \text{ m}^3/\text{m}^3 \text{ of CH}_4\text{-hydrate}$$

The CH₄-hydrates will undergo a dissociation process at standard temperature-pressure (STP) conditions and thereby will release CH₄ gas. The volume of the released CH₄ gas at STP conditions can be computed using the ideal gas law as shown below:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad \text{----- (Eq. 8.1)}$$

where,

P₁ = Pressure at the reservoir conditions = 6 MPa

V₁ = Volume of CH₄ at the reservoir conditions = 2.5640 m³/m³ of CH₄-hydrate

T₁ = temperature at the reservoir conditions = 4°C = 277.16 K

P₂ = Pressure at the surface conditions = 0.101325 MPa

V₂ = Volume of CH₄ at the reservoir conditions = unknown

T₂ = temperature at the reservoir conditions = 25°C = 298.16 K

Substituting above values in Eq. 8.1 and rearranging the equation:

$$V_2 = \frac{P_1}{P_2} \times \frac{T_2}{T_1} \times V_1 \quad \text{----- (Eq. 8.2)}$$

$$V_2 = \frac{6}{0.101325} \times \frac{298.16}{277.16} \times 2.5640$$

$$V_2 = 163.33 \text{ m}^3/\text{m}^3 \text{ of CH}_4\text{-hydrate}$$

The above calculations indicate that 1m³ of gas-hydrate will release 163.33 m³ of CH₄ gas at standard conditions upon its dissociation. The density of CH₄ gas at STP conditions is taken to be 0.65 kg/m³. From the knowledge of the volume and density of CH₄ gas at STP conditions, the mass of CH₄ gas at STP conditions can be calculated:

$$\text{CH}_4 \text{ mass} = 163.33 \text{ m}^3/\text{m}^3 \text{ of CH}_4\text{-hydrate} \times 0.65 \text{ kg/m}^3$$

$$= 106.16 \text{ kg/m}^3 \text{ of CH}_4\text{-hydrate}$$

From the above calculations it is clear that 1 m³ of CH₄-hydrate will release CH₄ gas at the surface having a total mass of 106.16 kg.

Now, consider a grid-block having an initial hydrate saturation of 70%. Therefore, the total amount of CH₄ in-place in this grid-block at the reservoir conditions can be calculated as:

Total Amount of CH₄ @ Reservoir Conditions =

$$\begin{aligned} & \text{Volume of grid-block} \times \text{Effective Porosity} \times \text{Initial Hydrate Saturation} \\ &= 100 \text{ m}^3 \times 0.36 \times 0.70 \\ &= 25.2 \text{ m}^3 \end{aligned}$$

It has already been shown that 1 m³ of gas-hydrate at the reservoir conditions upon dissociation will release CH₄ gas having a total mass of 106.16 kg. Therefore, the total CH₄ mass that will be released upon dissociation of 25.2 m³ of gas-hydrates is:

$$\begin{aligned} \text{Mass of CH}_4 \text{ that will be released} &= 25.2 \text{ m}^3 \times 106.16 \text{ kg/m}^3 \text{ of CH}_4\text{-hydrate} \\ &= 2675.23 \text{ kg} \end{aligned}$$

Similar calculations were performed for all the grid-blocks in the reservoir and the total amount of CH₄ was calculated to be 220859.51 kg.

The CH₄ recovery efficiency for the individual CO₂-microemulsion injection case was calculated as follows. Consider the CO₂-microemulsion injection case with 50% microemulsion concentration and an injection temperature of 28°C, for which the maximum CH₄ recovery was observed among all the cases discussed. In this case, the total CH₄ production was 175293.70 kg. Therefore, the recovery efficiency for this case can be given as:

$$\begin{aligned} \text{Recovery Efficiency} &= \frac{\text{Actual CH}_4 \text{ Production}}{\text{Total CH}_4 \text{ in Place}} \quad \text{----- (Eq. 8.3)} \\ &= \frac{175293.70}{220859.51} = 79.37\% \end{aligned}$$

Similar calculations were performed for all the cases studied and the results are tabulated in Table 8.3.

Table 8.3: Summary of the results for methane recovery (kg) and recovery efficiency (%) at different CO₂-microemulsion temperature and concentrations

Concentration →	10%		20%		30%	
Temperature ↓ (°C)	CH ₄ Recovery		CH ₄ Recovery		CH ₄ Recovery	
	[kg]	[%]	[kg]	[%]	[kg]	[%]
6	4394.56	1.99	4403.32	1.99	4414.25	2.00
10	4872.65	2.21	4883.60	2.21	4883.73	2.21
15	30543.50	13.83	39002.39	17.66	25502.76	11.55
18	21262.54	9.63	49720.22	22.51	63126.62	28.58
22	27379.64	12.40	55877.32	25.30	91210.27	41.30
25	27164.29	12.30	55071.18	24.93	92190.83	41.74
28	27956.57	12.66	54207.11	24.54	86939.25	39.36

Table 8.3: Methane recovery and recovery efficiency - continued

Concentration →	35%		45%		50%	
Temperature ↓ (°C)	CH ₄ Recovery		CH ₄ Recovery		CH ₄ Recovery	
	[kg]	[%]	[kg]	[%]	[kg]	[%]
6	4407.45	2.00	4434.75	2.01	4437.14	2.01
10	4889.62	2.21	4906.34	2.22	4913.28	2.22
15	21731.26	9.84	18344.46	8.31	17538.01	7.94
18	42143.06	19.08	28388.70	12.85	25443.58	11.52
22	111019.90	50.27	58274.76	26.39	45691.94	20.69
25	111988.70	50.71	152932.70	69.24	94757.80	42.90
28	105562.30	47.80	150890.20	68.32	175293.70	79.37

Table 8.3: Methane recovery and recovery efficiency - continued

Concentration →	60%		75%	
Temperature ↓ (°C)	CH ₄ Recovery		CH ₄ Recovery	
	[kg]	[%]	[kg]	[%]
6	4461.87	2.02	4527.92	2.05
10	4926.91	2.23	4985.40	2.26
15	16448.05	7.45	15497.75	7.02
18	22213.45	10.06	19834.86	8.98
22	34133.86	15.46	27467.35	12.44
25	52356.74	23.71	36360.93	16.46
28	117653.00	53.27	53836.34	24.38

Table 8.3: Methane recovery and recovery efficiency - continued

Concentration →	85%		90%	
Temperature ↓ (°C)	CH ₄ Recovery		CH ₄ Recovery	
	[kg]	[%]	[kg]	[%]
6	4613.40	2.09	4684.41	2.12
10	5062.20	2.29	5138.56	2.33
15	15077.35	6.83	15011.51	6.80
18	18935.70	8.57	18598.77	8.42
22	25272.45	11.44	24508.59	11.10
25	31967.73	14.47	30512.26	13.82
28	43136.11	19.53	39951.52	18.09

The results clearly indicate that the higher CO₂-microemulsion concentrations are not effective for the dissociation of CH₄-hydrates in the production of CH₄ gas from the natural gas hydrates. The reason for the ineffectiveness of higher CO₂-microemulsion

concentrations can be attributed to high CO₂-hydrate saturations in the region close to the injection well, which reduce relative permeability. Another important conclusion that can be drawn from these results is that, for the cases with low CO₂-microemulsion injection temperatures, methane recoveries are low as compared with the higher injection temperatures. Obviously, low injection temperature (< 20°C) does not help in raising the temperature of the entire reservoir system to above the CH₄-hydrate stability zone. At low temperatures, the freezing-memory effect also plays an important role in the dissociation/reformation process of methane hydrates. The freezing-memory effect suggests that when ice melts, a particular substance or structure exists in water or remains on the walls after melting from ice if the melted water is not heated to a temperature around 25°C (298 K). When the melted water is heated to a temperature around 25°C (298 K) or beyond, that particular substance no longer has the tendency of sticking to the walls and the freezing-memory effect appears to be vanishing. In the present case, the CH₄-hydrates get dissociated as water and CH₄ molecules due to CO₂-microemulsion injection. But if the microemulsion temperature is not high enough, it will result in CH₄ molecules retaining the tendency of sticking to the walls of surrounding rock and can again undergo a hydrate formation process if the favorable pressure-temperature conditions exist. Therefore, it is certain that with low CO₂-microemulsion injection temperatures, free CH₄ gas molecules exhibit the freezing-memory effect, and hence they have a higher tendency toward nucleation and returning to the hydrate phase, forming CH₄-hydrates.

8.1.2 Effect of Initial Hydrate Saturation

The results obtained so far in the 2-D simulation study are indicative of the effect of CO₂-microemulsion at different temperature and concentration conditions on methane hydrate dissociation and thereby on methane recovery. The results show that the maximum CH₄ recovery did not occur at higher CO₂-microemulsion concentrations. Under the appropriate temperature-pressure conditions, the ideal hydration number for

CO₂-hydrate will be 5.75, which results in a volume fraction of around 26.5% (equivalent to a mass fraction of approximately 29.8%) for liquid CO₂ in a liquid CO₂/water microemulsion. But the results obtained in section 8.1.1 indicate that the CO₂-microemulsion with concentration of 50% seems to be the best option for the methane-hydrate dissociation from the reservoir. It is important to note that a variable initial hydrate saturation, as shown in *Figure 7.2*, was considered across the reservoir for the results presented in section 8.1.1. From *Figure 7.2*, it was found that the initial hydrate saturations in the majority of the reservoir were in the range of 55% to 75%. The results presented in section 8.1.1 show that the best option for methane recovery from a gas-hydrate reservoir is the injection of CO₂-microemulsion with 50% concentration. The results presented in *Figure 8.16* show that for the reservoirs with initial hydrate saturation in the range of 30% to 50%, CO₂-microemulsion with low concentrations (15% and 30%) resulted in higher CH₄ recoveries. For the reservoirs with higher initial hydrate saturation (> 60%), CO₂-microemulsion with 50% concentration seemed to be the best option. This led me to believe that the initial hydrate saturation also has an important impact on the effect of CO₂-microemulsion displacement process.

Figure 8.16: Effect of initial hydrate saturation on methane recovery at different CO₂-microemulsion concentrations

To investigate this possibility, the 2-D simulation study was extended further to analyze the effect of initial hydrate saturation on methane production. The results obtained from this exercise are presented in *Figure 8.16*. This figure clearly indicates that the low CO₂-microemulsion concentrations can be effective for the production of the methane hydrates in the case of low hydrate saturation reservoirs. Their effectiveness, however, decreases drastically with an increase in the initial CH₄-hydrate saturation. For the reservoirs with low initial hydrate saturation values (30%), low CO₂-microemulsion concentrations (15% and 30%) show the best results for methane recovery while in the same low hydrate saturation region, high concentrations of CO₂-microemulsions show poor performance in terms of methane recovery. But as the initial CH₄-hydrate saturation increases, roughly above the 60% mark, the low concentrations of microemulsion are no longer effective. One of the reasons for this type of behavior could be the replacement mechanism between CO₂ and CH₄ in the hydrate phase. On the dissociation of CH₄-hydrates, the CH₄ gas molecules become free. It is a well-known fact that these CH₄ molecules released as a result of the decomposition of CH₄-hydrates and CO₂ molecules from the microemulsion compete with each other in order to occupy the empty lattice spaces. But at higher initial hydrate saturations, the free CH₄ gas molecules simply outnumber the CO₂ molecules for the lower concentrations of CO₂-microemulsion. This causes more released CH₄ gas molecules to go back into the hydrate phase.

For the reservoirs having low initial CH₄-hydrate saturations (30%), CO₂-microemulsions with lower concentrations seem to be an attractive choice for the replacement process. The high CO₂-microemulsion concentration of 80% showed very poor CH₄ recovery as compared to the rest of the cases. The high viscosity of such a concentrated microemulsion might have caused poor injectivity. The results obtained earlier as well as the results from this part of the study clearly indicate that higher CO₂-

microemulsion concentrations will not be helpful for the production of natural gas-hydrates.

The results shown in *Figure 8.16* also indicate that as the initial hydrate saturation approaches higher values, the technique of CO₂-microemulsion injection for methane recovery is no longer effective. For this part of the study, we have considered the absolute permeabilities of the reservoir formation to be 400 md and 200 md in the x- and y-directions, respectively. At high initial hydrate saturation, the permeability of the medium decreases drastically, which offers a great resistance for the movement of the microemulsion through the reservoir. In addition to that, as the CO₂-microemulsion enters into the reservoir formation from the injection well, the CO₂-hydrates are formed in the region close to the injection well. The formation of CO₂-hydrates additionally blocks some void space resulting in more resistance for the microemulsion injection. Therefore, it can be concluded that the present technique is not a good option for the reservoirs having a low permeability with high hydrate saturation. The solution to this problem might be to increase the permeability by some external means such as hydraulic fracturing.

8.1.3 Special Cases-Effect of CO₂-microemulsion Temperature

The results discussed in section 8.1.2 showed that different concentrations of CO₂-microemulsion have different effects on methane recovery, depending on the initial CH₄-hydrate saturation. The results presented in section 8.1.2 showed that two different CO₂-microemulsion concentrations, 30% and 50%, have significant differences in terms of their effect on methane recovery. The results indicated that the 30% CO₂-microemulsion performed well in the low (< 55%) initial hydrate saturation reservoirs, whereas the 50% CO₂-microemulsion was more effective for CH₄ recovery in high (> 55%) initial hydrate saturation ones. Therefore, these two concentration values were selected to study the effect of CO₂-microemulsion temperature on methane recovery.

The initial hydrate saturation was kept constant throughout the reservoir under the individual cases. These values are listed in Table 8.4.

Table 8.4: Initial hydrate saturations used for special cases

CO ₂ -microemulsion Concentration	Initial Hydrate Saturation
30%	45%
50%	60%

A number of simulations were carried out varying CO₂-microemulsion temperature between 10°C up to 28°C, to investigate the effect of CO₂-microemulsion temperature on methane recovery. In section 8.1.1, it has already been shown that 1 m³ of CH₄-hydrate will release 106.16 kg of CH₄ gas at the standard conditions upon its dissociation. Following the procedure demonstrated in section 8.1.1, the total amount of CH₄ in place for both the cases was calculated. The total amount of CH₄ is 171979.20 kg for the reservoir system having an initial hydrate saturation of 45%, and 229305.60 kg with an initial hydrate saturation of 60%. The methane recovery efficiency (%) was computed using Eq. 8.4. The results for total methane recovery (kg) as well as methane recovery efficiency (%) for individual cases are tabulated in Table 8.5.

$$\text{Recovery Efficiency} = \frac{\text{Actual CH}_4 \text{ Production}}{\text{Total CH}_4 \text{ in Place}} \quad \text{----- (Eq. 8.4)}$$

The methane recovery efficiencies obtained in these two scenarios are plotted against CO₂-microemulsion temperature as shown in *Figure 8.17*. Examining the results presented in *Figure 8.17*, it is evident that high CH₄ recoveries were observed for the reservoir with 45% initial hydrate saturation and 30% CO₂-microemulsion concentration. The CH₄ recoveries increased with an increase in CO₂-microemulsion injection temperature. Under this case, a steep increase in CH₄ recoveries can be observed until the microemulsion temperature reaches around 22°C.

Table 8.5: Total methane recovery obtained for the special cases discussed

CO ₂ -microemulsion Conc. = 30%			CO ₂ -microemulsion Conc. = 50%		
CO ₂ -microemulsion Temperature [°C]	Methane Recovery		CO ₂ -microemulsion Temperature [°C]	Methane Recovery	
	[kg]	[%]		[kg]	[%]
10	4014.06	2.33	10	4148.76	1.81
15	24714.07	14.37	15	11790.20	5.14
18	58710.12	34.14	18	16695.16	7.28
22	134727.30	78.34	22	28572.88	12.46
25	138056.70	80.28	25	53139.84	23.17
28	135620.60	78.86	28	77817.41	33.94

Figure 8.17: Effect of CO₂-microemulsion temperature on methane recovery for special cases discussed

As it can be seen from *Figure 8.17*, the curve for methane recovery reaches a plateau at a temperature of around 20°C. These results show that about 78% to 80% of

total recoverable CH_4 can be produced with CO_2 -microemulsion injection temperatures of 20 to 25°C . In order to increase the recovery efficiency, increasing injection temperatures might be a good option. On the other hand, the methane recoveries observed for the second scenario with 50% concentrated microemulsion are low compared to the ones obtained in the first scenario. The methane recoveries obtained under this scenario show a steady increasing trend, but the total amount of methane produced is much lower compared to the earlier scenario. The maximum amount of methane produced under this scenario is approximately 34% under the simulation conditions. This is probably due to the higher concentration of microemulsion results in higher CO_2 -hydrate saturations in the region near to the injection well which creates a great resistance for microemulsion injection.

8.1.4 CH_4 Production: CO_2 -microemulsion Injection vs. Conventional Method

As discussed in section 7.1.2.3, a simulation study was carried out to compare the performance of the CO_2 -microemulsion injection technique to that of the conventional method. Thermal stimulation was the conventional method selected for this study. All simulations were completed over a total time period of 1250 days (30000 hours). For this part of the study, the initial CH_4 -hydrate saturation in the reservoir was considered to be the same as shown in *Figure 7.2*. The total amount of CH_4 that can be recovered from this reservoir has already been calculated in section 8.1.1 to be 220859.51 kg. Using this value and the actual CH_4 production observed in each case, the CH_4 recovery efficiency was calculated. The results for the cumulative CH_4 recovery [%] versus pore volumes of fluid injected for these cases are plotted in *Figure 8.18*.

Figure 8.18: Cumulative methane production: CO₂-microemulsion injection vs. thermal stimulation method

The results shown in *Figure 8.18* clearly indicate that the cumulative CH₄ production observed with the thermal stimulation method was much lower as compared to the CO₂-microemulsion injection technique.

Examining the results presented in *Figure 8.18*, it is very clear that CO₂-microemulsion injection technique worked well and resulted in high CH₄ recoveries as compared to the thermal stimulation method. In case of thermal stimulation method, approximately 0.45 PV of warm water at 50°C was injected over 1250 days of injection time which resulted in cumulative CH₄ recovery of less than 20%. For 50% CO₂-microemulsion injection scenario, approximately 0.35 PVs of microemulsion was injected over the same injection time resulting in approximately 94% of methane recovery. In the case of 30% CO₂-microemulsion injection at 25°C, the cumulative CH₄ recovery of 60% was observed at the expense of approximately 0.17 PVs of CO₂ injection. In the case of thermal stimulation, the high temperature (50°C) of warm water resulted in higher injectivity causing higher PVs of warm water injection. The higher temperature (28°C) of 50% CO₂-microemulsion might have caused low hydrate saturations in the region near the injection well resulting in higher injectivity for CO₂-microemulsion

injection. Due to the higher injectivity, higher CH₄ recovery was obtained in 50% CO₂-microemulsion (28°C injection temperature) case. Comparing the results obtained in case of 30% and 50% CO₂-microemulsion techniques, it can be seen that, at 0.17 PVs of fluid injection, 30% CO₂-microemulsion injection showed good CH₄ recovery. The results also show that the higher CO₂-microemulsion injection temperatures may help in higher CH₄-hydrate dissociation. Thus, the results obtained from this exercise demonstrate the advantages of using CO₂-microemulsion injection technique over the thermal stimulation method for maximizing CH₄ recovery from a gas-hydrate reservoir.

8.1.5 Energy Efficiency Calculations

As discussed in section 7.1.2.4, the heat input calculations were carried out for the production scenarios discussed in section 7.1.2.3. In this section, the thermal stimulation method was considered as base case. Two CO₂-microemulsion injection scenarios were compared with the thermal stimulation method. The main objective of the energy requirement calculations presented here is just to serve as comparison purpose in order to give the readers a rough idea of the effectiveness of CO₂-microemulsion injection technique. There are various factors that are not considered in the present study. Therefore, much more detailed and complicated calculations would be required to compare their actual success before implementing them in a field scale application. The readers are advised to consider this exercise as a crude guideline for making the comparison between the different production techniques mentioned here.

In the case of the thermal stimulation method, the warm water was injected into the reservoir formation at a temperature of 50°C. The two CO₂-microemulsion injection scenarios considered injection of the microemulsions with injection temperatures of 25°C (and a 30% concentration) and 28°C (and a 50% concentration), respectively. From the results presented in section 8.1.1, it was found that the maximum CH₄ recovery was observed for the CO₂-microemulsion injection case with a concentration of 50% at an injection temperature of 28°C. Therefore, a CO₂-microemulsion with these parameters

was selected for the present study. The CO₂-microemulsion with a 30% concentration and 25°C injection temperature was considered as representative of the production scenarios with low CO₂-microemulsion concentration.

Table 8.6 shows the enthalpy values for liquid CO₂ and water that were used in these calculations. These values are taken at a reference pressure of 7 MPa which is the same as that of the injection pressure used in the simulation study. It was assumed that water at 4°C (277.16 K) and atmospheric pressure is available for preparing the CO₂-microemulsion. The enthalpy of water at 4°C and 1 atmosphere pressure is 16.90 kJ/kg. The difference in the enthalpies (ΔH) of water at different temperatures was used in calculating the total heat supplied to the reservoir.

$$\Delta H = H_{(\text{temperature, } T \text{ K})} - H_{(\text{temperature, } 277.16 \text{ K})}$$

For an example,

$$\begin{aligned}\Delta H &= 214.73 \text{ kJ/kg}_{(323 \text{ K})} - 16.90_{(277.16 \text{ K})} \\ &= 197.83 \text{ kJ/kg}\end{aligned}$$

Table 8.6: Enthalpies of liquid CO₂ and water at different temperatures (P = 7 MPa)

Liquid CO ₂			Water	
Temperature (K)	Enthalpy (kJ/kg)		Temperature (K)	Enthalpy (kJ/kg)
295	-250.47		298	110.67
300	-228.34		301	123.16
301.83	-212.9		323	214.73

From the simulation results it was found that in the case of thermal stimulation, a total of 1.56×10^6 kg of warm water at a temperature of 50°C (323 K) was introduced into the reservoir formation. Using the net enthalpy value of 197.83 kJ/kg for water as calculated above, the total amount of heat introduced into the reservoir comes out to be 3.08×10^8 kJ for the thermal stimulation method. In a similar manner, the calculations were carried out for the two CO₂-microemulsion injection techniques, considering the total amount of liquid CO₂ and water injected into the formation at the respective injection temperatures. Table 8.7 shows the total amount of liquid CO₂ and water injected into the reservoir under each production scheme. The last column in Table 8.7

represents the total amount of heat added to the reservoir system. The cumulative CH₄ production obtained in each production scenario is shown in *Figure 8.18*. These values are tabulated in Table 8.8 below.

Table 8.7: Total heat input under different production scenarios

Production Method	Amount of CO ₂ Injected [kg]	Amount of Water Injected [kg]	Total Heat Input [kJ]
Thermal Stimulation (50°C)	0.00	1.56×10^6	3.08×10^8
CO ₂ Injection_30% and 25°C	4.16×10^5	1.60×10^6	5.24×10^7
CO ₂ Injection_50% and 28°C	7.71×10^5	2.18×10^6	6.79×10^7

Table 8.8: Total CH₄ production under different production scenarios

Production Method	CH ₄ Produced [kg]
Thermal Stimulation (50°C)	42384.99
CO ₂ Injection_30% and 25°C	128337.20
CO ₂ Injection_50% and 28°C	206571.90

Based upon the data given in Tables 8.7 and 8.8, we calculated the values of heat added to the reservoir per kg of CH₄ recovered. For the thermal stimulation method, the total heat input value was 3.08×10^8 kJ whereas only 42384.99 kg of CH₄ was recovered in this process. This gives a value of 7277.07 kJ/kg as the amount of heat added to the reservoir per kg of CH₄ produced. In the similar manner, the calculations were done for the two CO₂-microemulsion injection scenarios. The calculated values are tabulated in Table 8.9. The results presented in Table 8.9 are also shown in *Figure 8.19*.

Table 8.9: Amount of heat required for producing one kg of CH₄

Production Method	Heat Added per kg of CH ₄ Produced [kJ/kg]
Thermal Stimulation (50°C)	7277.07
CO ₂ Injection_30% and 25°C	408.29
CO ₂ Injection_50% and 28°C	328.68

Figure 8.19: Heat added to the reservoir for producing one kg of CH₄ under different production scenarios

The results presented in *Figure 8.19* clearly indicate that very high heat input is necessary in the thermal stimulation method to produce a single kilogram of CH₄, as compared to the CO₂-microemulsion injection techniques. The energy requirement of the CO₂ injection method is less than 1/10th of what is required for thermal stimulation.

Now using the heating value of CH₄, we can calculate the total amount of heat that can be recovered from produced CH₄ in each production scenario. These heating values of CH₄ are given in Table 8.10 below.

Based upon the data given in Table 8.10, we used an average heating value of 52,775 kJ/kg for CH₄ in the calculations. Using the CH₄ production data from Table 8.8, the total amount of heat that can be recovered in each production scenario can be calculated. In the thermal stimulation method, a total of 42384.99 kg of CH₄ was produced.

Therefore, the total amount of heat recovered under this method is:

$$\begin{aligned}
 &= 42384.99 \text{ kg of CH}_4 \times 52775 \text{ kJ/kg of CH}_4 \\
 &= 2.24 \times 10^9 \text{ kJ}
 \end{aligned}$$

Table 8.10: Heating values for CH₄

	Heating Value [kJ/kg]
Lower Limit	50,200
Upper Limit	55,530

In a similar manner, the calculations were done for the two CO₂-microemulsion injection techniques. The results are presented in Table 8.11. The energy efficiency was defined as shown below:

$$\text{Energy Efficiency} = \frac{\text{Heat Recovered in the form of CH}_4}{\text{Heat Added to the Reservoir}}$$

Table 8.11: Total amount of heat recovered under different production scenarios

Production Method	Heat Recovered [kJ]
Thermal Stimulation (50°C)	2.24×10^9
CO ₂ Injection_30% and 25°C	6.77×10^9
CO ₂ Injection_50% and 28°C	1.09×10^{10}

Now, based upon the results reported in Tables 8.9 and 8.11, the energy efficiencies were calculated for each production scenario considered in this study. The results obtained are tabulated in Table 8.12.

Table 8.12: Energy efficiency ratios for different production scenarios

Production Method	Total Heat Added [kJ]	Heat Recovered [kJ]	Energy Efficiency Ratio [kJ/kJ]
Thermal Stimulation (50°C)	3.08×10^8	2.24×10^9	7.25
CO ₂ Injection_30% and 25°C	5.24×10^7	6.77×10^9	129.26
CO ₂ Injection_50% and 28°C	6.79×10^7	1.09×10^{10}	160.57

Figure 8.20: Energy efficiency ratios for different production scenarios

Figure 8.20 shows that the energy efficiency for the thermal stimulation method is very poor as compared to the CO₂-microemulsion injection technique. Again, it should be noted that the energy calculations presented here are preliminary and should not be considered for practical application. For the CO₂-microemulsion injection technique, these values are more than 10 times greater than for the thermal stimulation case.

The results from the energy input and energy efficiency calculations show that a conventional production method such as thermal stimulation is an energy extensive process as compared to the proposed CO₂-microemulsion injection technique. All these results suggest that the CO₂-microemulsion injection technique is far more effective in producing CH₄ than the thermal stimulation method. In summary, it can be concluded that the results positively support the hypothesis of using the CO₂-microemulsion injection technique for CH₄ recovery from gas-hydrate reservoirs.

CHAPTER NINE

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

9.1 Conclusions

A simulation study was carried out using the STOMP-HYD module from the STOMP simulator in order to test the feasibility of a newly proposed CO₂-microemulsion injection technique for methane recovery from natural gas-hydrate reservoirs. A simple 1-D reservoir system was used under different conditions of formation permeability, CO₂-microemulsion temperature and concentration to demonstrate the application of this technique. Then, a 2-D reservoir system was built using reservoir property data such as porosity, permeability, and initial hydrate saturation, etc. A series of simulations were carried out in order to analyze the effects of temperature and concentration of injected CO₂-microemulsion on methane recovery. In addition, the effect of initial hydrate saturation on methane recovery was also analyzed at different CO₂-microemulsion concentrations. Preliminary energy requirement calculations were also carried out to demonstrate the advantages of using the CO₂-microemulsion technique over the thermal stimulation method. These calculations also very well support the hypothesis of using the microemulsion injection technique for methane recovery from gas-hydrate reservoirs. The following conclusions are drawn based upon the results obtained in the present study:

1. A simple 1-D analysis supports the hypothesis of enhanced gas-hydrate recovery using a CO₂-microemulsion injection technique. The results from the 1-D analysis showed that nearly pure methane was produced at the outlet boundary, which is consistent with the observations from laboratory experiments.
2. The results from the 1-D simulation study indicate that higher hydraulic conductivity results in much earlier methane production and higher CH₄ recovery. Therefore, hydraulic fracturing of the formation to improve injectivity

may be an effective option for improving methane production rate with CO₂-microemulsion injection technique.

3. The results from the 1-D analysis showed that the technique of CO₂-microemulsion injection produces more CH₄ than warm water injection alone.
4. From the 2-D analysis, it was clear that the moderate microemulsion with a CO₂ concentration in the range of 40% to 50% resulted in good methane recoveries for the initial hydrate saturation depicted in *Figure 7.2*. This analysis also pointed out that the freezing-memory effect might play a significant role at low injection temperatures.
5. The study showed that a microemulsion with 30% CO₂ concentration will be a good choice for the exploitation of reservoirs with relatively low hydrate saturation (< 50%). If the initial hydrate saturation is in the range of 55% to 75%, then using a 50% CO₂-microemulsion will be a logical option.
6. This analysis also led to a conclusion that the technique of CO₂-microemulsion injection for methane recovery from a reservoir with high hydrate saturation may not be a good choice due to the low effective permeability. Some external method such as hydraulic fracturing should be applied to increase the formation permeability.
7. The results obtained in this study also showed that the thermal stimulation method is not efficient for CH₄ recovery as compared to the microemulsion injection method for a CH₄-hydrate reservoir.
8. The energy requirements as well as energy efficiency calculations indicate that the thermal stimulation method is a highly energy intensive process as compared to the CO₂-microemulsion injection technique, which again supports the hypothesis of using the latter technique for methane recovery from gas-hydrate reservoirs.

9.2 Recommendations for Future Work

Some modifications in the approach followed in the present study would make it more useful in working towards the implementation of this process on a field scale. Here are some of the recommendations to extend the simulation study.

1. Because of the limitations of the STOMP-HYD module at the time of this study, the present analysis deals only with 1-D and 2-D reservoir models in order to demonstrate the feasibility of the proposed method and to analyze the effects of various parameters on methane production. But a simulation study completed on the actual reservoir scale will give more insight into the potential of this technique.
2. The future work should consider different production scenarios such as multiple injection/production wells in combination with horizontal well configuration to maximize CH₄ recovery.
3. The injection pressure of the CO₂-microemulsion can also be an important parameter affecting the methane recovery. Therefore, a future study analyzing the effect of the microemulsion injection pressure would provide some valuable information about the proposed technique.
4. Even though the proposed technique looks promising, a thorough economic analysis of the entire project will help in determining the economic viability of this process.

REFERENCES:

- Bhangale, A.Y., Zhu, T., McGrail, B.P., and White, M.D.: "A Model to Predict Gas Hydrate Equilibrium and Gas Hydrate Saturation in Porous Media Including Mixed CO₂-CH₄ Hydrates", SPE 99759, presented at the 2006 SPE/DOE Symposium on Improved Oil Recovery, Tulsa, OK, April 22-26, 2006.
- Bily, C. and Dick, J.W.L.: "Naturally Occurring Gas Hydrates in the Mackenzie Delta, N.W.T.", *Bulletin of Canadian Petroleum Geology*, 22, pp. 320-352, 1974.
- Carroll, J.J.: "Natural Gas Hydrates: A Guide for Engineers", Gulf Professional Publishing, Boston, MA, 2003.
- Cherskiy, N.V., Tsarev, V.P., and Nikitin, S.P.: "Investigation and Prediction of Conditions of Accumulation of Gas Resources in Gas-Hydrate Pools", *Petroleum Geology*, 21, pp. 65-89, 1985.
- Clennell, M.B., Hovland, M., Booth, J.S., Henry, P., and Winters, W.J.: "Formation of Natural Gas Hydrates in Marine Sediments 1. Conceptual Model of Gas Hydrate Growth Conditioned by Host Sediment Properties", *Journal of Geophysical Research*, 104(B10), pp. 22,985-23,003, 1999.
- Collett, T.S. and Ehlig-Economides, C.A.: "Detection and Evaluation of the In-Situ Natural Gas Hydrates in the North Slope Region, Alaska", SPE 11673, presented at the 1983 California Regional Meeting of the Society of Petroleum Engineers of AIME, Ventura, California, March 23-25, 1983.
- Collett, T.S.: "Natural Gas Hydrates of the Prudhoe Bay and Kuparuk River Area North Slope, Alaska", *The American Association of Petroleum Geologists Bulletin*, 77(5), pp. 793-812, May 1993.
- Collett, T.S.: "Gas Hydrate Resources of Northern Alaska", *Bulletin of Canadian Petroleum Geology*, 45(3), pp. 317-338, 1997.
- Collett, T.S., Lewis, R., and Uchida, T.: "Growing Interest in Gas Hydrates", *Oilfield Review*, pp. 42-57, Summer 2000.
- Collett, T.S.: "Energy Resource Potential of Natural Gas Hydrates", *AAPG Bulletin*, 86(11), pp. 1971-1992, 2002.
- Collett, T.S.: "Alaska North Slope Gas Hydrate Energy Resources", USGS Open File Report 2004-1454, pp. 1-6, 2004.
- Englezos, P. and Lee, J.D.: "Gas Hydrates: A Cleaner Source of Energy and Opportunity for Innovative Technologies", *Korean Journal of Chemical Engineering*, 22(5), pp. 671-681, 2005.

- Ertekin, T., Abou-Kassem, J.H., and King, G.R.: Basic Applied Reservoir Simulation, SPE Textbook Series Vol. 7, Richardson, TX, 2001.
- Gale, J.: "Geological Storage of CO₂: What's Known, Where Are the Gaps, and What More Needs to Be Done", Greenhouse Gas Control Technologies, Vol. I, Elsevier, Amsterdam, pp. 207-212, 2003.
- Grigg, R.B., and Lynes, G.L.: "Oil-Based Drilling Mud as a Gas Hydrate Inhibitor", SPE 19560, presented at the 1989 SPE Annual Technical Conference and Exhibition, San Antonio, Texas, October 8-11, 1989.
- Gunn, D.A., Nelder, L.M., Rochelle, C.A., Bateman, K., Jackson, P.D., Lovell, M.A., Hobbs, P.R.N., Long, D., Rees, S.P., Roberts, J., and Francis, T.: "Towards Improved Ground Models for Slope Instability Evaluations Through Better Characterization of Sediment-Hosted Gas Hydrates", Terra Nova, 14, pp. 443-450, 2002.
- Handa, Y.P.: "Compositions, Enthalpies of Dissociation, and Heat Capacities in the Range 85 to 270 K for Clathrate Hydrates of Methane, Ethane, and Propane, and Enthalpy of Dissociation of Isobutane Hydrate, as Determined by Heat-Flow Calorimeter", J. Chem. Thermodyn., 18, pp. 915-921, 1986.
- Hansen, J.: "Defusing the Global Warming Time Bomb", Scientific American, pp. 68-77, March 2004.
- Hirohama, S., Shimoyama, Y., and Wakabayashi, A.: "Recovery Rate of CH₄ from CH₄-hydrate Immersed in CO₂-CH₄ Mixtures", Preprints of Papers, 42(3), pp. 794-798, 1997.
- Hirohama, S., Shimoyama, Y., Wakabayashi, A., Tatsuta, S., and Nishida, N.: "Conversion of CH₄-Hydrate to CO₂-Hydrate in Liquid CO₂", Journal of Chemical Engineering of Japan, 29, pp. 1014-1020, 1996.
- Hoffert, M.I. et al.: "Advanced Technology Paths to Global Climate Stability: Energy for a Greenhouse Planet", Science, 298, pp. 981-987, 2002.
- Holt, T.J., Lindeberg, E.G.B., and Taber, J.J.: "Technologies and Possibilities for Larger-Scale CO₂ Separation and Underground Storage", SPE 63103, presented at the 2000 SPE Annual Technical Conference and Exhibition, Dallas, Texas, October 1-4, 2000.
- Klauda, J.B. and Sandler, S.I.: "Phase Behavior of Clathrate Hydrates: A Model for Single and Multiple Gas Component Hydrates", Chemical Engineering Science, 58, pp. 27-41, 2003.
- Komai, T., Kawamura, T., Kang, S., Nagashima, K., and Yamamoto, Y.: "In Situ Observation of Gas Hydrate Behavior under High Pressure by Raman Spectroscopy", Journal of Physics: Condensed Matter, 14, pp. 11395-11400, 2002.

- Kvenvolden, K.A.: "Gas Hydrates as a Potential Energy Resource – A Review of Their Methane Content", Howell, D.G., ed., *The Future of Energy Gases: U.S. Geological Survey Professional Paper 1570*, pp. 555-561, 1993.
- Kvenvolden, K.A., and McMenamin, M.A.: "Hydrates of Natural Gas: A Review of their Geologic Occurrence", U.S. Geological Survey Circular, 825, pp. 11, 1980.
- Kvenvolden, K.A., and Lorensen, T.D.: "The Global Occurrence of Natural Gas Hydrates", in *Natural Gas Hydrates – Occurrence, Distribution and Detection*, Paul, C.K. and Dillion, W.P. (eds.), Geophysical Monograph 124, 2001.
- Lee, H., Seo, Y., Seo, Y-T., Kim, D.Y., Moudrakovski, I.L., and Ripmeester, J.A.: "Replacement of Methane Hydrate by Carbon Dioxide: ^{13}C NMR Study for Studying a Limit to the Degree of Substitution", *Studies in Surface Science and Catalysis*, 153, pp. 495-500, 2004.
- Lee, H., Seo, Y., Seo, Y-T., Moudrakovski, I.L., and Ripmeester, J.A.: "Recovering Methane from Solid Methane Hydrate with Carbon Dioxide", *Angew. Chem. Int. Edit.*, 42, pp. 5048-5051, 2003.
- Lee, S.Y. and Holder, G.D.: "Methane Hydrates Potential as a Future Energy Source", *Fuel Processing Technology*, 71, pp. 181-186, 2001.
- Levieveld, J. and Crutzen, P.J.: "Indirect Chemical Effects of Methane on Climate Warming", *Nature*, 355, pp. 339-342, 1992.
- Makogon, Y.F. (Cielewicz, W.J.): "Hydrates of Natural Gas", Penn-Well, Tulsa, Oklahoma, 1981.
- Makogon, Y.F.: "Natural Gas Hydrates: The State of Study in the USSR and Perspectives for Its Use", 1988 Third Chemical Congress of North America, Toronto, June 5-10, 1988.
- Masters, C.D., Root, D.H., and Attanasi, E.D.: "Resource Constraints in Petroleum Production Potential", *Science*, 253, pp. 146-152, 1991.
- Max, M.D., Pellanbarg, R.E., and Hurdell, B.G.: "Methane Hydrate, a Special Clathrate: Its Attributes and Potential", Naval Research Laboratory, February 28, 1997.
- McGrail, B. P., Schaef, H. T., White M. D., Zhu T., and Hunter R. B.: "A New Method for Enhanced Production of Gas Hydrates with Carbon Dioxide", Poster Presentation at the AAPG Annual Meeting, Calgary, Alberta, June 16-19, 2005.
- McGrail, B.P., Zhu, T., Hunter, R.B., White, M.D., Patil, S.L., and Kulkarni, A.S.: "A New Method for Enhanced Production of Gas Hydrates with CO_2 ", AAPG Conference on Gas Hydrates: Energy Resource Potential and Associated Geologic Hazards, pp. 1-4, Vancouver, Canada, September 12-16, 2004.

- Mishra, P.: "Methane in its Hydrate Form – A Wonderful Future Energy Source", *Everyman's Science*, 39(2), 2004.
- Nakano, S., Yamamoto, K., and Ohgaki, K.: "Natural Gas Exploitation by Carbon Dioxide from Gas Hydrate Fields – High Pressure Phase Equilibrium for an Ethane Hydrate System", *Proc. Instn. Mech. Engrs.*, 212(A), pp. 159-163, 1998.
- Ohara, T., Dallimore, S.R., and Fercho, E.: "Drilling Operations, JAPEx/JNOC/GSC Mallik 2L-38 Gas Hydrate Research Well", in *Geological Survey of Canada Bulletin 544: Scientific Results from JAPEx/JNOC/GSC Mallik 2L-38 Gas Hydrate Research Well, Mackenzie Delta, Northwest Territories, Canada*, edited by Dallimore, S.R. et al. Geological Survey of Canada, Ottawa, 1999.
- Ohgaki, K. and Inoue, Y.: "A Proposal for Gas Storage on the Bottom of the Ocean, using Gas Hydrates", *International Chemical Engineering*, 34(3), pp. 417-419, 1994.
- Ohgaki, K. and Nakano, S.: "Methane Exploitation by Carbon Dioxide from Gas Hydrates", *Recent Res. Devel. in Chemical Engg.*, 1, pp. 1-15, 1997.
- Ohgaki, K., Takano, K., Sangawa, H., Matsubara, T., and Nakano, S.: "Methane Exploitation by Carbon Dioxide from Gas Hydrates – Phase Equilibria for CO₂-CH₄ Mixed Hydrate System", *Journal of Chemical Engineering of Japan*, 29(3), pp. 478-483, 1996.
- Orr, F. M. Jr.: "Storage of Carbon Dioxide in Geologic Formations", paper SPE 88842, *Distinguished Author Series*, pp. 90-97, September 2004.
- Ota, M., Morohashi, K., Abe, Y., Watanabe, M., Smith, R.L. Jr., and Inomata, H.: "Replacement of CH₄ in the Hydrate by Use of Liquid CO₂", *Energy Conservation and Management*, 46, pp. 1680-1691, 2005a.
- Ota, M., Abe, Y., Watanabe, M., Smith, R.L. Jr., and Inomata, H.: "Methane Recovery from methane hydrate using pressurized CO₂", *Fluid Phase Equilibria*, 228-229, pp. 553-559, 2005b.
- Parson, E.A. and Keith, D.W.: "Fossil Fuels Without CO₂ Emissions", *Science*, 282, pp. 1053-1054, 1998.
- Pooladi-Darvish, M.: "Gas Production From Hydrate Reservoirs and Its Modeling", paper SPE 86827, *Distinguished Author Series*, pp. 65-71, June 2004.
- Ripmeester, J.A., Tse, J.S, Ratcliffe, C.I., and Powell, B.M.: "A New Clathrate Hydrate Structure", *Nature*, 325, pp. 135, 1987.
- Schofield, T.R., Judzis A., and Yousif, M.: "Stabilization of In-situ Hydrates Enhances Drilling Performance and Rig Safety", SPE 38586, presented at the Annual Technical Conference and Exhibition, San Antonio, Texas, October 5-8, 1997.

- Setzmann, U. and Wagner, W.: "A New Equation of State and Tables of Thermodynamic Properties for Methane Covering the Range from Melting Line to 625 K at Pressures up to 1000 MPa", J. Phys. Chem. Ref. Data, 20(6), pp. 1061-1155, 1991.
- Sloan, E.D.: Clathrate Hydrates of Natural Gases, Marcel Dekker, Inc., New York, NY, 1998.
- Span, R. and Wagner, W.: "A New Equation of State for Carbon Dioxide Covering the Fluid Region from the Triple-Point Temperature to 1100 K at Pressures up to 800 MPa", J. Phys. Chem. Ref. Data, 25(6), pp. 1509-1596, 1996.
- Stone, C.L.: "The Effect of Capillary Pressure on Methane Gas Recovery from Gas Hydrates: A Simulation Study", M.S. Thesis, University of Alaska Fairbanks, May 2006.
- Thomas, C.P.: "Methane Hydrates: Major Energy Source for the Future or Wishful Thinking?", SPE 71452, presented at the Annual Technical Conference and Exhibition, New Orleans, Louisiana, September 30 – October 3, 2001.
- Uchida, T., Takeya, S., Ebinuma, T., and Narita, H.: "Replacing Methane with CO₂ in Clathrate Hydrate: Observations using Raman Spectroscopy", Proceedings of the Fifth International Conference on Greenhouse Gas Control Technologies, pp. 523-527, CSIRO Publishing, Collingwood, Australia.
- van der Meer, L.G.H.: "CO₂ Storage in the Subsurface", Greenhouse Gas Control Technologies, Vol. I, Elsevier, Amsterdam, pp. 201-206, 2003.
- von Stackelberg, M. and Müller, H. R.: "Feste Gas Hydrate", Z. für Elektrochemie, 58, 25, 1954.
- White, A.N.: "Mass Transfer Study on CO₂ Penetration Through Methane Hydrates Using CO₂ Vapor and A CO₂ Nucleated Microemulsion", M.S. Thesis, University of Alaska Fairbanks, December 2003.
- White, M.D. and Oostrom, M.: "STOMP – Subsurface Transport Over Multiple Phases", Version 3.0 User's Guide, 2003.
- White, M.D., McGrail, B.P., Zhu, T. and Phale, H.A.: "Numerical Studies of Methane Hydrate Production at Moderate Temperatures via Carbon Dioxide Exchange", *In Preparation*
- Wilder, J.W., Seshadri, K., and Smith, D.H.: "Thermodynamics of the Sequestration of Carbon Dioxide in Methane Hydrates in Porous Media", Fuel Chemistry Division Preprints, 47(1), pp. 17-19, 2002.
- Yezdimer, E.M., Cummings, P.T., and Chialvo, A.A.: "Determination of the Gibbs Free Energy of Gas Replacement in Clathrate Hydrates by Molecular Simulation", J. Phys. Chem. A, 106, pp. 7982-7987, 2002.

Zhu, J. et al.: "Analytical Theory of Coalbed Methane Recovery by Gas Injection", SPE 87338, SPE Journal, pp. 371-379, December 2003.

Zhu, T., McGrail, B.P., Kulkarni, A.S., White, M.D., Phale, H.A., and Ogbe, D.O.: "Development of a Thermodynamic Model and Reservoir Simulator for the CH₄, CO₂, and CH₄-CO₂ Gas Hydrate System", SPE 93976, presented at the SPE Western Regional Meeting, Irvine, CA, March 30 – April 1, 2005.

NOMENCLATURE:

Roman

D_{γ}^{ζ}	Diffusion-Dispersion tensor of component ζ in phase γ , m^2/s
F_{γ}	Advective mass flux vector in phase γ , kg/s m^2
G	Gas phase
g	Gravitational acceleration, (9.81 m/s^2)
H	Hydrate phase
h	Enthalpy, J/kg
J_{γ}^{ζ}	Diffusive mass flux vector of component ζ in phase γ , kg/s m^2
k_e	Equivalent thermal conductivity tensor, W/m K
k_i	Intrinsic permeability tensor, m^2
$k_{r\gamma}$	Relative permeability of phase γ
L_1	H_2O -rich phase
L_2	CO_2 -rich phase
•	
$\dot{m}$	Phase mass source rate, kg/s
M	Molecular weight, kg/kmol
P_{γ}	Pressure of phase γ , Pa
q	Quadruple point in the CO_2 - H_2O system
•	
q	Energy source rate, J/s
r_{hl}	radius of curvature for the hydrate-aqueous interface, m
s	Phase saturation
$\bar{s}$	Effective phase saturation
$\hat{s}$	Apparent phase saturation
t	Time, s
T	Temperature, K
u	Internal energy, J/kg
z_g	Gravitational unit vector

Greek

- ∂ = Differential operator
 ϕ = Porosity
 μ_γ = Dynamic viscosity of phase γ , Pa s
 ρ_γ = Density of phase γ , kg/m³
 σ_{hl} = Hydrate-aqueous interfacial tension, N/m
 τ_γ = Tortuosity factor of phase γ
 ω_γ^ζ = Mass fraction of component ζ in phase γ
 χ_γ^ζ = Mole fraction of component ζ in phase γ
 ∇ = Gradient operator, 1/m

Subscripts

- g = Gas phase
 h = Hydrate phase
 i = Ice phase
 l = Aqueous phase
 n = Liquid CO₂ phase
 p = Precipitated salt phase
 t = Total-liquid
 γ = Phase indicator

Superscripts

- a = CO₂ component
 ex = *ex-situ* (i.e., laboratory conditions)
 in = *in-situ* (i.e., porous media conditions)
 o = CH₄ component
 s = Salt component
 w = Water component
 ζ = Component indicator

APPENDIX

Figure A.1: Effect of microemulsion temperature on methane recovery:
10% CO₂-microemulsion injection

Figure A.2: Effect of microemulsion temperature on methane recovery:
20% CO₂-microemulsion injection

Figure A.3: Effect of microemulsion temperature on methane recovery:
35% CO₂-microemulsion injection

Figure A.4: Effect of microemulsion temperature on methane recovery:
45% CO₂-microemulsion injection

Figure A.5: Effect of microemulsion temperature on methane recovery:
60% CO₂-microemulsion injection

Figure A.6: Effect of microemulsion temperature on methane recovery:
75% CO₂-microemulsion injection

Figure A.7: Effect of microemulsion temperature on methane recovery:
85% CO₂-microemulsion injection

Figure A.8: Effect of microemulsion temperature on methane recovery:
90% CO₂-microemulsion injection