A SIMULATION STUDY OF GAS HYDRATE DISSOCIATION ON THE NGHP-02 SITES

M. Tech. Thesis

by

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INDIAN INSTITUTE OF TECHNOLOGY ROORKEE
ROORKEE – 247 667 (INDIA)
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A THESIS

Submitted in partial fulfilment of the
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CANDIDATE’S DECLARATION

I hereby certifythatthe work which is being presented in the thesis entitled **"A SIMULATIONSTUDY OF GAS HYDRATE DISSOCIATION ON THE NGHP-02 SITES "** in partialfulfilment of the requirements for the award of the Degree of Master of Technology and submitted in the Department of Biotechnology of the Indian Institute of Technology Roorkee, Roorkee is an authentic record of my own work carried out during a period from May, 2018 to May, 2019 under the supervision of Dr. Chandrajit Balomajumder, Professor, Department of Chemical Engineering and Dr. Bijan Choudhury, Professor, Department of Biotechnology, Indian Institute of Technology Roorkee, Roorkee.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other Institution.

(NISHIKANT BHAUSAHEB SONAWANE)

This is to certify that the above statement made by the candidate is correct to thebest of my knowledge.

Prof. Bijan Choudhury,
Co-Supervisor

Prof. Chandrajit Balomajumder,
Supervisor

Date:

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Finally, I would like to express my warm thanks to all those authors who have either been consulted or quoted.

Nishikant Bhausaheb Sonawane

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Abstract

Gas hydrates are white compounds with crystalline and non-stoichiometric form. Formation of it occurs in the presence of water at low temperatures and high pressures with Methane, Ethane, Propane, Isobutane and number of other gases. A cage-like crystal structure gets formed through hydrogen bonding around the entrapped gas molecules.

The removal of methane from gas hydrates economically and environment friendly is necessary. The Methane gets produced from Gas Hydrates dissociation which occurs inside the marine sediment after applications techniques such as Depressurization, Chemical Inhibitor Injection, Thermal stimulation etc. So, there is need to predict the suitable technique which fulfil the requirement of producing Methane by avoiding hydrate reformation**.**The effectiveness of Dissociation Technique is dependent on the reservoir properties of Gas Hydrates. The behaviors of different chemical inhibitors in the reservoir can be studied through simulation. The simulation on the properties of National Gas Hydrate Programme (NGHP)-02 sites is carried using simulation on T+H. Therefore, the main objective of this thesis is to do comparative study between Inhibitors and 1TbS Test file; and then among Different Tests files namely 1P, 1P_ice, 1_Pk, 1T, 1_TbS and 1_TbSk with parameters on the selected site properties respectively. The cellulose content percentage in wheat straw sample is also calculated.

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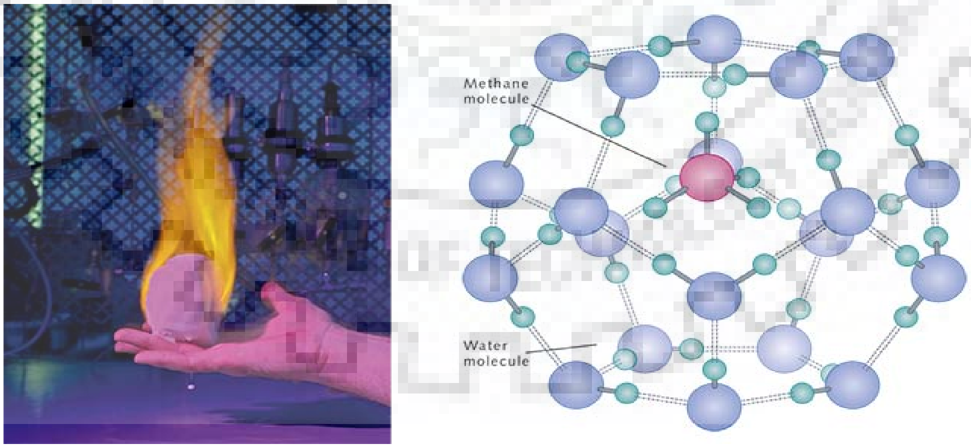
Chapter 1: Introduction

Methane Gas Hydrates are white crystalline substances found inside the earth's crust at marine sediments under the sea bed and in permafrost regions at slight depth than conventional oil and gas. The structure of Gas Hydrate consists of Methane molecules surrounded by Water molecules in a cage like structure. One cubic meter of Methane Gas Hydrate liberates 164 cubic meters of Methane Gas when brought to atmospheric condition. Gas hydrate have cages formed by bonding of hydrogen and water molecules in which gaseous molecules gets trapped.The Hydrate can be formed in aqueous solution even when the concentration of dissolved gas is 40 % lower than the peak concentration at which gas hydrate gets formed. Gas is taken by diffusion from the outer pore fluid as hydrate get form in porous medium.Hydrate growth is promoted by cooling process as gas get transferred from aqueous to hydrate phase.Highly concentrated gas molecules are present in hydrate structure but in liquid phase they are widely dispersed [12]. Gas hydrate remain stable up to temperature of 291 K after application of pressurization. Material density of gas hydrate is 0.91 g/cm^3. The gas hydrate properties vary according to texture, structure, permeability and source of supply of methane [19]. Methane Hydrates are stable slightly above or below 0˚C with high pressures [21].

1.1 The Structure of Methane Gas Hydrate



Source- Dietmar Gust, Berlin

Fig 1.1 Structure of Methane Hydrate

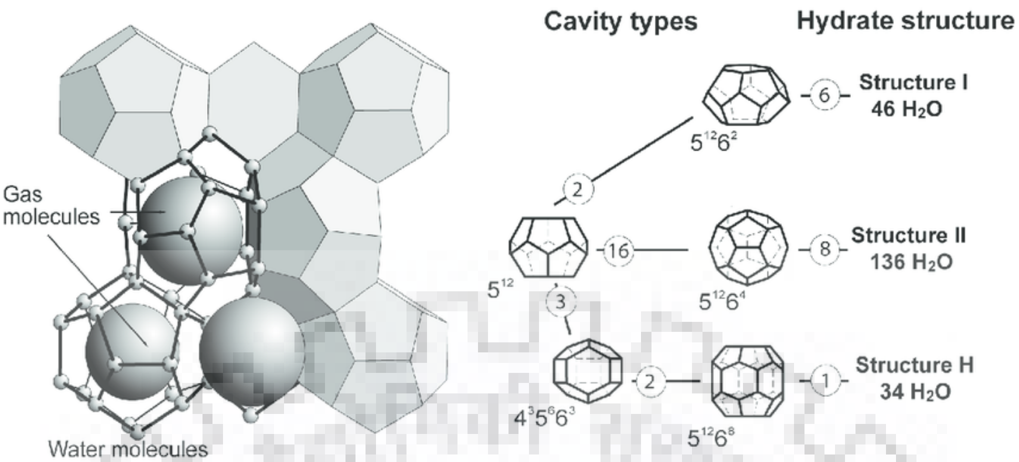


Fig 1.2 Types of Methane Hydrate Structure [20].

Gas Hydrates are mainly found in 3 structures- I (sI), II (sII), and H (sH). These are cubic structure I, Cubic structure II and Hexagonal structure(sH) which varies according to size and the nature of the guest molecule. The origin of Hydrate formation is either Thermogenic or Biogenic. Biogenic gas hydrates formed by Gas releases by bacterial community in sediment beneath the sea bed. Thermogenic gas hydrates gets formed by Hydrocarbon gases at high pressure and greater Temperature from kerogens (Organic matter) [21].

1.2 A Method to Detect Gas Hydrate in the Sea bottom sediments

The availability of Methane Gas Hydrate is determined by direct sampling and reflection technique named as Bottom Simulating Reflector which is based on seismic data acquisition. In Bottom Simulating Reflector (BSR) technique, seafloor topography inside the marine reflection data is mimicked by reflectors by crosscutting sedimentary data. Occurrence of BSRs is in margin sediments in the region of free Methane gas and Gas Hydrates [2]. Bottom simulating reflectors (BSRs) are able to identify the gas hydrate bearing sediments. It has negative polarity than seafloor reflection which implies decline of Seismic impedance. Partial exchange of pore water by solid gas hydrates inside sediments within Hydrate stability zone (HSZ) explains negative velocity contrast at the BHSZ. The appearance of Bottom simulating reflectors (BSRs) seismic reflection data is the best indication of identifying gas hydrates within marine sediments [10].

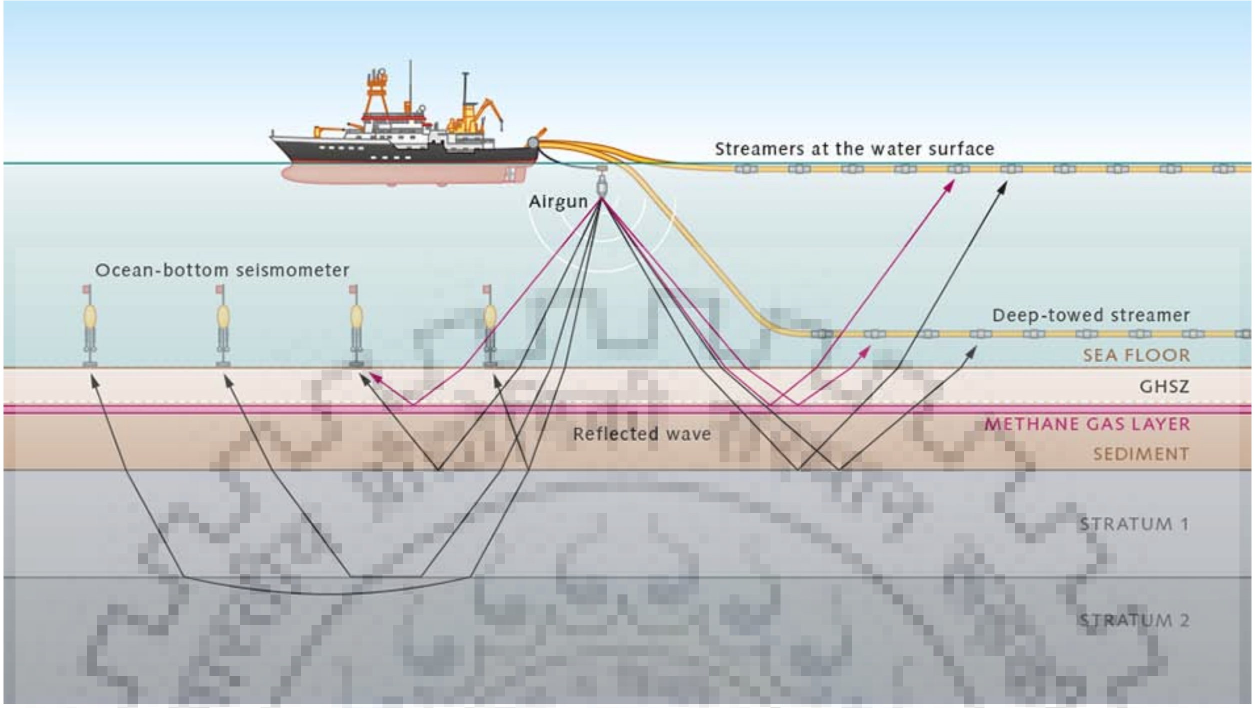


Fig 1.3 Schematic diagram of Bottom Simulating Reflector (BSR) technique.

In seismic method, acoustic waves are produced by airguns which penetrates within the seabed. These are reflected by the separate layers of the seabed at different strengths and/or refracted. Streamers are the receivers which records the reflected waves from the bottom. The seafloor image is created from the data obtained by the receivers. Multichannel seismics are used at the starting of prospecting. They can detect the bottom simulating reflectors (BSRs). It is a powerful reflection of the acoustic waves which is considered as a visible lighter layer into the seismic image. This effect is observed in different sediment types. For methane hydrate, the strong reflector is generated by free methane gas which lies below the gas hydrate stability zone (GSHZ). A very high temperature exists below the GSHZ where the collection of methane gas generating from higher depths of the sediments takes place.As methane gas gets clearly distinguished from other layers in the data of seismic image as it has very low density than the surrounding sediments or methane hydrate [11].

1.3 Occurrence Sites of Methane Hydrates

1.3.1 Details of Worldwide Sitesof Methane Hydrate

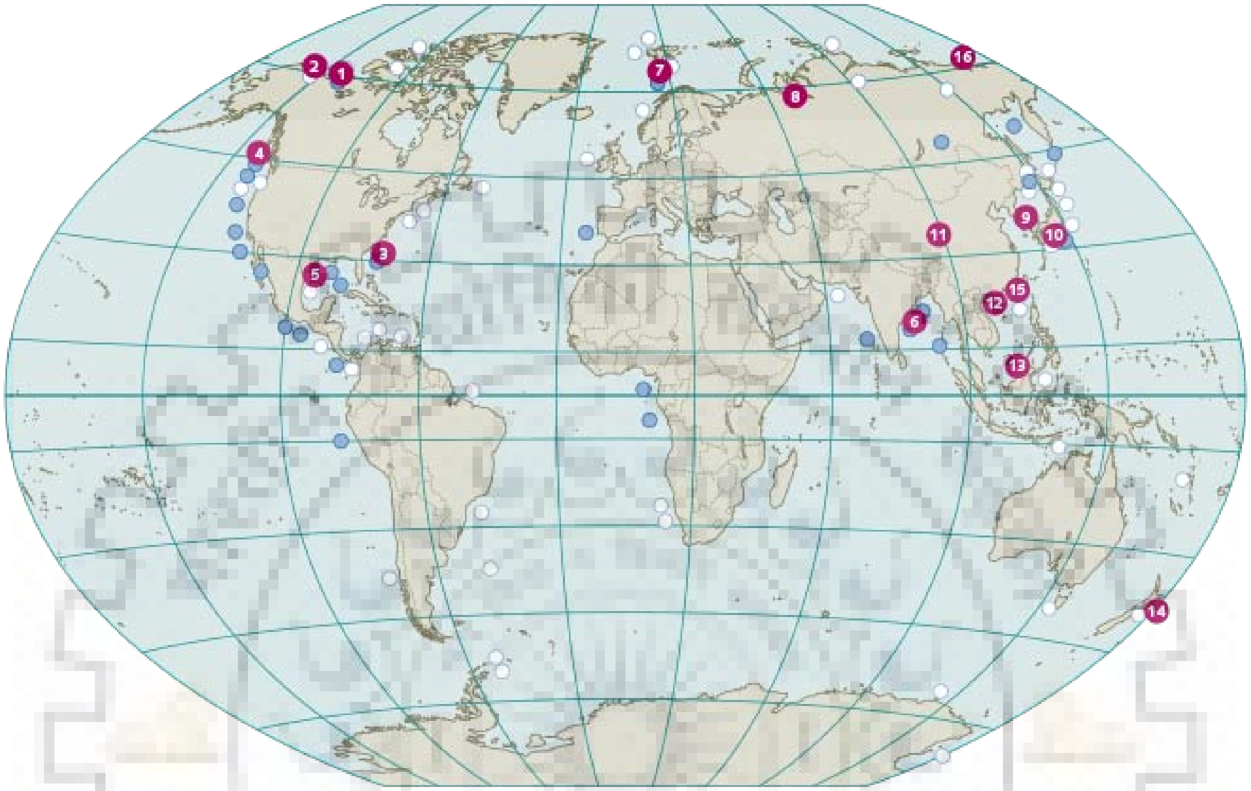


Fig 1.4 Global scenario of Methane Hydrate

1. Mallik- Richards Island in Canada documented highly concentrated gas hydrate at the Mallik site in 1972. Gas hydrate evaluation programme was carried in 1998,2002 and 2007-2008 in which Depressurizaton Method was found favorable.

2. North Slope- At #2 well of Northwest Eileen State gas hydrates were discovered within the North Slope region of Alaska. The magnitude of 16 Trillion cubic metres gas hydrates deposits were estimated at this site. The test of removal of gas hydrate was carried in 2011 at Purdhoe bay.

3. Blake Ridge- This site was one of the starting site for research of gas hydrate which is located at the continental slope off the coast of North Carolina. Seismic method of geologic survey was used for the discovery of gas hydrate deposits. Extensive deposits of gas hydrate were confirmed in 1995 by scientific drilling. 28.3 trillion cubic metres of gas hydrate were estimated at this site.

4. Cascadia Continental Margin- Ocean drilling program (ODP)wasused for this area which is located at Pacific coast of the united states. The objective was to gather new knowledge about the structure and history of earth. The “Hydrate ridge” was drilled in 2002 and 2005.

5. Gulf of Mexico - Gas hydrates were discovered in massive amount at Gulf of Mexico in 1995. These hydrates had interesting structures as special biological organisms were present there. A collaborative project involving researchers and industrialists directed safety view of deep-water drilling in 2005. Highly concentrated gas hydrates were discovered in 2009 under the second expedition of drilling.

6. Indian Ocean- NGHP executed expedition- 01 in 2006. A significant amount of gas hydrate was found at Krishna-Godavari, Mahanadi and Andaman basins [13]. These sites are expected to have second largest reservoirs of gas hydrates as per US Geological Survey and amount is estimated to be 100-130 trillion cubic feet [14].

7. Svalbard- Significant study was carried out at the Svalbard Island’s shelf off the western coast. Many active seeps were found at beginning of this century. According to Scientists, Dissociation of gas hydrate is occuring due to climate change at Svalbard.

8. Messoyakha- The oil and gas fieldlocated at western Siberia provided the first evidence of gas hydrates existence in nature. A natural gas production is contributed by gas hydrate in this area.

9. Ulleung-Basin- In 2007 and 2010,Deep SeaDrilling was carried in the Sea of Ulleung Basin off the coast of south Korea. The hydrates found in the pores of sand and inside of deformed muds.

10. Nankai Trough- In 1999, the first resource-grade gas hydrate was found in marine sands at area off Japan. The estimated amount of gas hydrate deposits is 1.1 trillion cubic metres.

11. Qilian Mountains: It is located in Tibetan Plateau at western China up which has permafrost up to depths of 100 metres. Gas Hydrates occured in fractured sandstones and mudstones as per drilling project in 2008 and 2009.

12. Shenhu Basin- It is a part of South China sea and was explored by marine geological mapping under a Chinese state institute for marine geology, Guangzhou Marine Geological Survey (GMGS). Higher concentration of gas hydrate was found in fine-grained sediment layers.

13. Gumusut-Kakap- Commercial ventures encountered with geohazards of subsurface gas hydrates, low seismicity, shallow faulting, steep seafloor slopes in this oil field off the shore of eastern Malaysia. The study of this site was started in 2005.

14. New Zealand- Under the seafloor investigation at Hikurangi Trough, strong seismic signals of BSR were noted. This region off the coast of New Zealand was studies by different types of measurements.

15. Taiwan- It has continental plate coverage where methane bearing water get expelled off the sediments. Hence, favorable condition is available for the formation of methane hydrates. This zone of tectonic drilling was studied in 2004 by drilling. The gas hydrates are expected to spread across the area of 11,000 square kilometres of seafloor area.

16. East Siberian Shelf- This is a coastal area where permafrost region underlies below it. Highly concentrated methane was discovered in upper layer of seafloor by using scientific studies. It is expected to have gas hydrates in the permafrost region from which methane gets generated [15].

Table 1.1 Gas Hydrate Field Testing details of different reservoirs

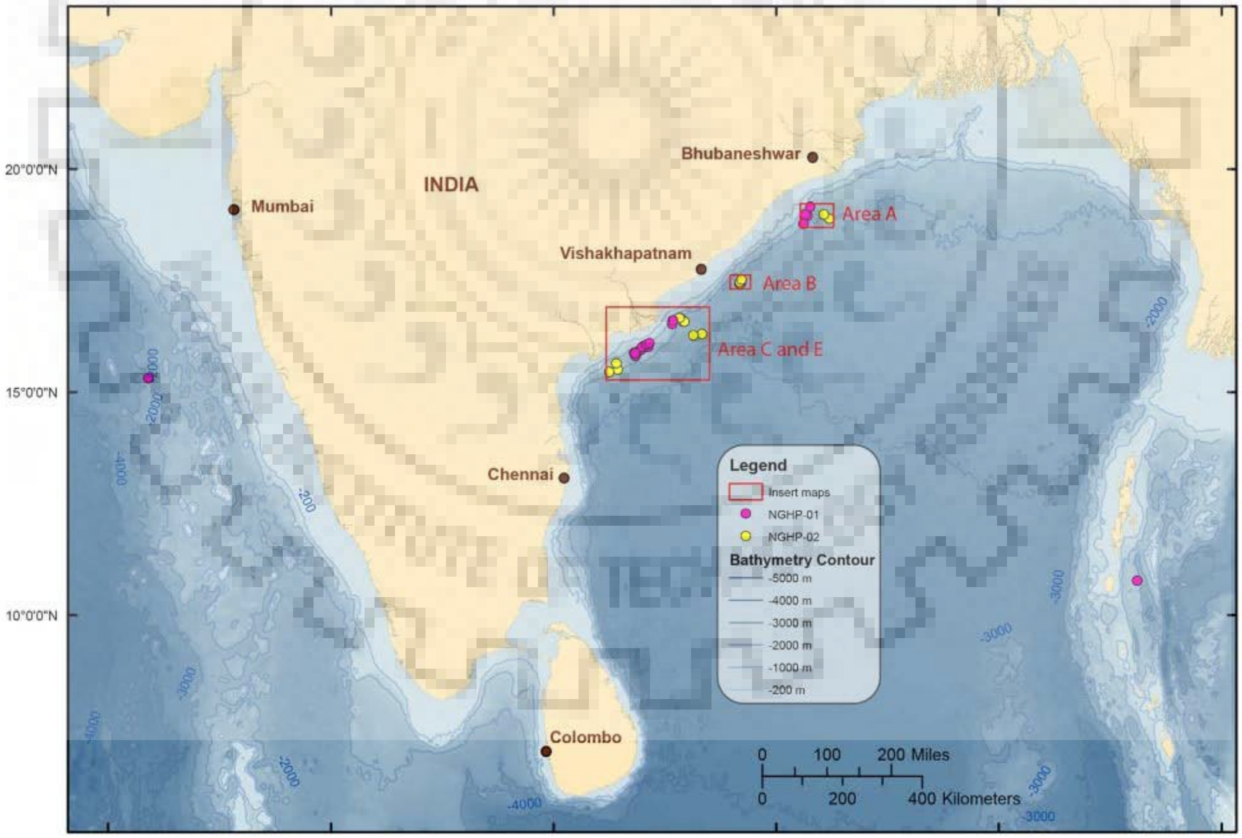
Site area	**Well height**	**Volume**	**Temperature**	**Pressure**	**Sediment porosity**	**Sediment permeability**	**Hydrate saturation**	**Dissociation technique**	**Extraction rate**
Mallik Gas Hydrate In Mackenzie Delta in Canada, April 2007 Dallimore et al. (2008, July)	1160 meter	40 TCF	272.9 K	2.563 MPa	0.30 to 0.40	0.01-1	70 to 83 %	Thermal stimulation	2000 to 4000 m3/day
Nankai trough in Daini Atsumi Knoll, off the coasts of Atsumi and Shima peninsulas March 12-18th, 2013 Boswell, R. (2013).	1240 meter	16 to 27 trillion cubic meter	283.15 K	The pressure was lowered from 13.5 MPa to 4.5 MPa	62% to 43%	MH ZONE 0.05-1.23	1 to 12%	Depressurization method	(20,000 cubic meters per day) 120,000 cubic meters of methane gas were produced
Iġnik Sikumi Alaska North Slope 2012 Schoderbek, D., et al. (2012)	1900 feet below sea level	85 TCF	(1 to 1.5 °C)	1,420 (9.8 MPa) to 1,200 psi (8.27 MPa)	0.40	0.06-1.12	70 to 60%	CO2–CH4 Exchange	(24,210 m3) 175,000 scf/d
Atsumi/Shima peninsula April and June 2017 Oyama et al. (2017).	1300 meter	20 to 25 TCF	284.77 K	2.98 MPa	0.50 T0 0.77	0.02-0.004	20-25%	Depressurization technique	12 days and 200,000 m3
South China Sea May 2017 Jin, G et al. (2017)	1266 meter	10-15 TCF	274.15–281.15 K	Initial formation pressure of 14.4 MPa	33% to 48%	0.07-0.002	40 -60%	Depressurization technique	300000 cubic meters of natural gas from the gas hydrate reservoir 200 mbsf, for 60 consecutive days

1.3.2 Details of Indian Sites of Methane Hydrate

The Ministry of Petroleum and Natural Gas (MoP&NG) initiated The National Gas Hydrate Programme (NGHP) in India in 1997. Under the coordination of the Directorate General of Hydrocarbons (DGH)., NGHP was reestablished by the MoP & NG in the year 2000. By a Memorandum of Understanding with DGH, the USGS participation in the NGHP was enabled.

1.3.2.1 NGHP-02 Objective

The NGHP-02 Expedition was carried from 3rd March 2015 to 28th July 2015 off the eastern coast of India. The primary objective of NGHP-02 expedition was the exploration and discovery of highly saturated gas hydrate occurrences in sand reservoirs that would be aim of testing of future production.



Source- Collet et al.

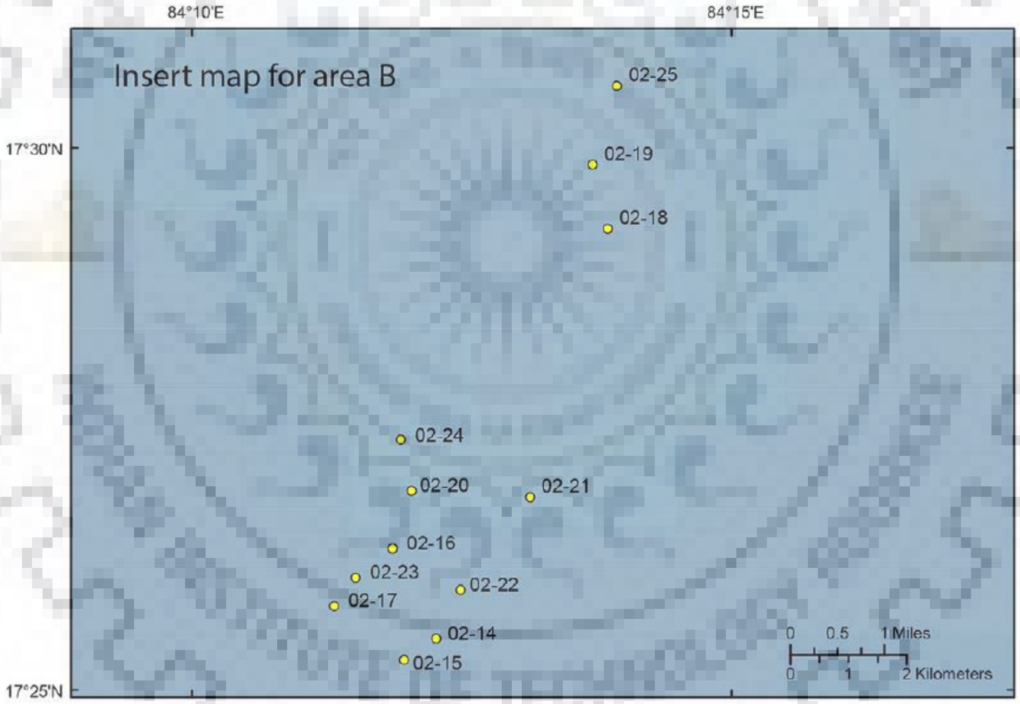
Fig1.5 Location Maps for sites drilled during Expeditions NGHP-01 and NGHP-02 [17].

The logging (LWD) operations were carried out in first 2 months of the expedition in which 25 holes were drilled and logged. The coring operation was performed in next 3 months at most promising 10 sites.

1.3.2.1 NGHP-02 Operations

The analysis of more than 80 sites from different offshore basins of India was included in NGHP-02 pre-expedition drill site review. After analysis, 29 sites from the Mahanadi and Krishna-Godavari Basins were finalized for drilling project under NGHP-02.

Oil and Natural Gas Corporation Limited (ONGC) of India on the behalf of NGHP and the MoP&NG planned and managed the NGHP-02. The drilling platform was the research D/S Chikyu, operated by the Japanese Drilling Company (JDC) and the shipboard science program was managed by the Japan Agency for Marine-Earth Science and Technology (JAMSTEC). LWD, wireline logging, and formation testing services were provided by Schlumberger. Pressure coring tools were supplied by JAMSTEC and shipboard pressure core operations and analysis were supplied by Geotek Coring. Additional operational and scientific support was supplied by



Source- Collet et al.

Fig 1.6 Enlargement of site regions for NGHP-02 in fig 1.5

the USGS, the U.S. Department of Energy (US-DOE), the National Institute of Advanced Industrial Science and Technology (AIST), and the Japan Oil, Gas and Metals National Corporation (JOGMEC) [16].

Table 1.2 Details of NGHP-02 Expedition

WELL	DEPTH	THERMAL GRADIENT mK/m	GRAIN DENSITY g/cm3	P WAVE	PERMEABILITY mD	BULK DENSITY g/cm3	POROSITY	SHEAR MODULUS Mpa	S wave m/sec	SHEAR STRENGTH Mpa	METHANE HYDRATE (% PORE VOLUME)	THERMAL CONDUCTIVITY W/mK	ELECTRICAL RESISTIVITY OHM	x-ray	MAGNETIC SUCEPTIBILITY
NGHP-02-23		61	2.78	1500			0.7 in non hydrate zone						01 TO 2 increases in gas hydrate zone	prominent pebbles and muddy matrix	
	270-290											1.2			
165.3-198.5	282			2839	0.0036 AT 0.5 Mpa		0.45	643	554		52				
271-288.6	284.65			3089	0.008 at 0.2 Mpa						43				
	284.7			3030							62				
NGHP-02-22		64	2.6-2.8			1.6	65%					0.65-1.4	1.5 AND DEC IN ZONES		
70.6-197.8														NEAR VERTICAL FACTURES	
207.7-290.2						1.6-2.75	3-70%								
	240			1844	0.001 AT 1.7 Mpa			425	450		48				
NGHP-02-19		58	2.6-2.8			1.7	0.8-0.6					0.65-1.3		HONEYCOMB STRUCTURE WITH VERTICAL FRACTURES	
305.2-372							0.5								
	317			1899							60				
	317.6			1642	0.01 AT 0.97 MPA			407	400						
NGHP-02-17		70	2.7-2.6				0.8-0.6					0.8-1.1	15 OHM IN GAS HYDRATE ZONE	HUGE MASS OF GS HYDATE, PEBBLE SIZE STRUCTURE SEEN	
58.9-246			2.8			8/1/2002									
	270			1594	64 at 1.72 mpa			321	385	0.55	0				
	285.12			1583	0.00066 at 1.7 mpa			457		0.46	8.6				
NGHP-02-16													01 to 11	honey comb structures developed inlayers	
142.4-195.8						1.58									
272.5-296.8						2.1	0.67-0.42								
	273.19			2417	15 at 2 mpa			972	649		66				
	278			2693	74 at 1.6 mpa			1393	766		76				
NGHP-02-09		70	2.7-2.9			1.65-1.95	0.6 TO 0.5							FRACTURES DUE TO GAS HYDRATE DISSOCIATION	
213.2-271.5															
	215.11			2094	1.83 AT 1.7 MPA			1771	876	2	33				
	236.63			2448	18.82 AT 0.7 MPA						83				
	214.66			1598	0.0004 AT 1.7 MPA			242	331		0				

Table 1.2 Details of NGHP-02 Expedition (Continue…)

WELL	DEPTH	THERMAL GRADIENT mK/m	GRAIN DENSITY g/cm3	P WAVE	PERMEABILITY mD	BULK DENSITY g/cm3	POROSITY	SHEAR MODULUS Mpa	S wave m/sec	SHEAR STRENGTH Mpa	METHANE HYDRATE (% PORE VOLUME)	THERMAL CONDUCTIVITY W/mK	ELECTRICAL RESISTIVITY OHM	x-ray	MAGNETIC SUCEPTIBILITY
NGHP-02-08		60	2.6-2.8			1.2-1.9	2.7								50-100 X 10^-5
49.6-103.2												80-100	6 TO 11		
246.8-272													50		
	247.81			1712	0.002 AT 1.96 MPA			254	333	0.8	0				
	249.2			1609				200	302	0.4	0.1				
NGHP-02-07		70	2.7			1.65-1.95	0.6-0.5					0.85-1.1			<200x10^-5
64.8-110.7						1.54-2.05									
181.1-207.6															
	107.61			1626							0				
NGHP-02-05		43	2.6-2.85												<50x10^-5
91.5-172.5						2.2-2.9									
171.5-479.4															
479.4-504.8															
	502.7			2096	0.002 at 1.95 mpa			1260	742		26				
NGHP-02-1		57	2.65-2.9			1.6-2	0.5-0.6						1		
124.8-174.5															
196-260															
	205.9			1685	0.0004 at 1.46 mpa					0.45	6.3				

(Source-GHRTC, ONGC Panvel)

Table 1.3 Site-specific parameters for NGHP-02 Sites [17].

Site NGHP-02	Water Depth (m)	Thermal Gradient (˚C/m)	Seafloor Temperature (˚C)	Salinity (ppt)
01	1760.00	4.0	4.0	31.3
05	2814.50	2.2	2.2	27.0
07	1914.00	3.3	3.3	32.0
08	2167.50	3.3	3.3	33.3
09	2219.50	3.3	3.3	31.4
16	2546.50	2.6	2.6	18.8
17	2557.50	2.3	2.3	20.0
19	2519.50	2.4	2.4	23.0
22	2557.00	2.3	2.3	23.8
23	2553.50	2.6	2.6	18.8

1.4 Methods for Production of Methane from Gas Hydrates

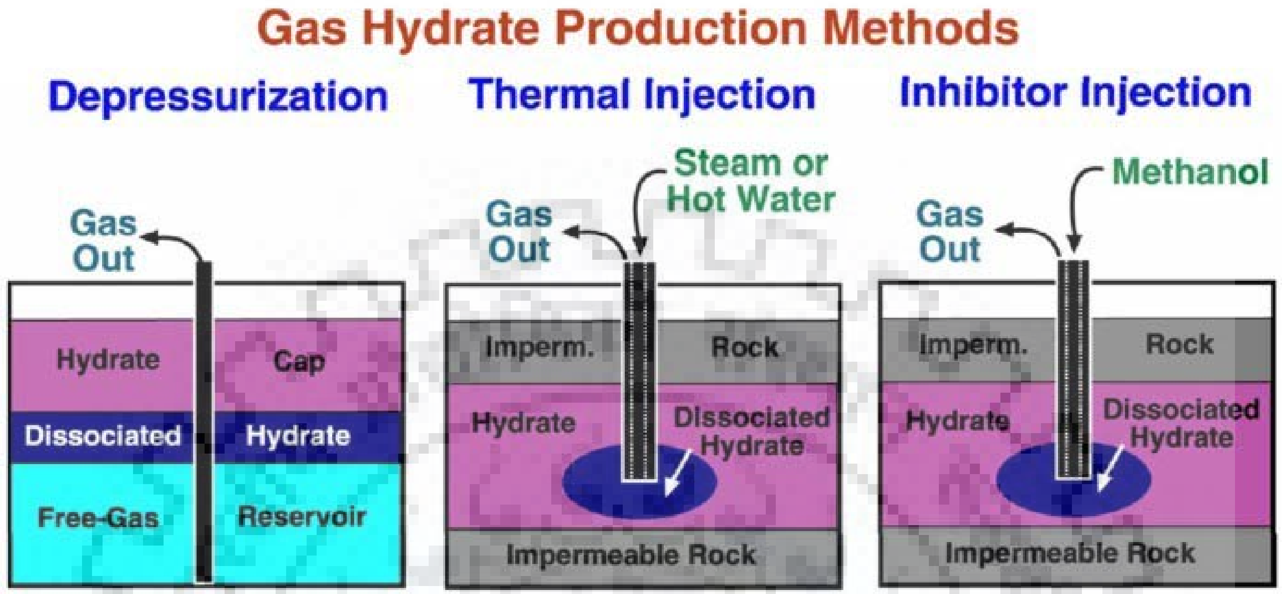


Fig 1.6. Different techniques of Gas Hydrate Exploitation

1.4.1 Depressurization: In this technique, reservoir pressure is decreased below Hydrate equilibrium of Hydrate. Dissociation of Hydrate takes place with drop in pressure.

1.4.2 Thermal Stimulation: This technique consists of injection of steam or hot brine solution which causes increase in temperature of hydrate reservoir. This destabilizes Gas hydrate and methane gas gets released.

1.4.3 Inhibitor Injection: In this technique, chemical inhibitor such as methanol, ethylene glycol is injected into hydrate reservoir which causes disturbance of gas hydrate equilibrium condition.

1.4.4 Carbon Dioxide Sequestration: This technique involves swapping of methane with carbon dioxide. This process is proved thermodynamically and kinetically feasible.

1.4.5 Microwave Heating: In this technique, electromagnetic energy is converted to thermal energy. Microwave can be passed by its molecular interaction with electromagnetic fields directly to materials. This leads to dissociation of Gas hydrate [18].

Table 1.4 Economics of various dissociation processes of Gas Hydrates [18].

Parameter	**Thermal Stimulation Method**	**Depressurization**	**Conventional Gas Production**
Investment in millions of Rs.	254200	166000	157500
Annual cost in millions of Rs.	160000	125500	100000
Total Production (million m^3/year)	1274.26	1557.43	1557.43
Production cost (Rs./million m^3)	6356.6	4025.9	3213.6
Break-even wellhead price (Rs./million m^3)	7945.8	2523.3	3972.9

Chapter 2: Literature Review

Sr. No.	Author	Article	Method	Description
1	Jeonghwan LeeEt al. (2010)	An experimental study on the productivity of dissociated gas from gas hydrate by depressurization scheme	Depressurization	In Depressurization, decreasing the reservoir pressure below the pressure of hydrate formation takes place. According to results, inlet pressure is almost equal to the outlet pressure during formation and dissociation of Gas Hydrates.
2	Annick Nago Et al. (2011)	Natural Gas Production from Methane Hydrate Deposits Using CO_2 Clathrate Sequestration: State-of-the-Art Review and New Technical Approaches	CO_2 Clathrate Sequestration	By Experiment, it is proved that CO2 is preferably trapped against methane into the Gas hydrate phase. Here, Gas hydrate molecule swaps between CO2 and Methane in the hydrate phase. The main driving force for converting from Gas hydrate into CO_2 hydrate is diffusion.
3	Pierrick Bouffaron Et al. (2013)	Methane Hydrates, Truths and Perspectives		The transfer rate of methane in marine sediments is dependent on the bacteria activity in the marine sediments. Stability of sediment containing gas hydrate is based on Hydrate reservoirs. CO2 hydrates have more thermodynamic stability than Gas hydrates.
4	Hyery KangEt al. (2014)	Nondestructive natural gas hydrate recovery driven by air and carbon dioxide	1. Sample preparation and gas injection procedures. 2. Mixed-phase gas hydrate sampling using liquid nitrogen quenched helium gas 3. Spectroscopic analysis	Inhibitor injection revers chemical environment of gas hydrate to inhibit its stability of formation. Methane exploitation from gas hydrate is decided by Critical methane concentration (CMC) which is influenced by depth of Gas hydrate, sediment geochemistry, saturated pore water and geothermal gradient.
5	Jiafei Zhao Et al. (2014)	Analysis of heat transfer effects on gas production from methane hydrate By Depressurization	Depressurization	Hydrate dissociation get facilitated while increase in C_{ps} of core material increases initial sensible heat in the core. Pressure in the core can be increased by high water production and high thermal conductivity can inhibit dissociation process which is an endothermic process. Increase in Cumulative gas production observed with the thermal conductivity of porous media.

Sr.	Author	Article	Method	Description

No.				
6	Jong Min Lee Et al. (2015)	Insights into the Kinetics of Methane Hydrate Formation in a Stirred Tank Reactor by in Situ Raman Spectroscopy		Change of molecular interaction between methane and water from solute and solvent to guest and host molecules of Gas hydrates leads to entering of guest molecules to different chemical environments of small and large cages, where both play key role for observing Raman peak via its unique wavelength.
7	Yongchen Song Et al. (2015)	Evaluation of gas production from methane hydrates using depressurization, thermal stimulation and combined methods	1. Depressurization 2. Thermal Stimulation	Combination of Pressure and heat transfer initially drives the hydrate dissociation. Temperature of Hydrate sediments get increased with transfer of heat from surrounding to environment, and hydrate dissociate slowly. Formation of ice is effectively avoided by warm water injection technique.
8	Jong Min Lee Et al. (2015)	Insights into the Kinetics of Methane Hydrate Formation in a Stirred TankReactor by in Situ Raman Spectroscopy		From macroscopic and microscopic data, Initiation of Methane Hydrate growth shows strict occupation of large cages containing dissolved Methane.Change of molecular interaction between methane and water from solute and solvent to guest and host molecules of Gas hydrates leads to entering of guest molecules to different chemical environments of small and large cages, where both play key role for observing raman peak via its unique wavelength.
9	Jiafei Zhao (2015) Et al.	Analyzing the process of gas production for natural gas hydrate using depressurization	Depressurization	Methane Hydrate saturation is determined with the help of formation and dissociation equation, hydration number, volume of components, pore size etc. The gas production rate increases as production pressure decreases. Gas production percentage increases when gas production pressure get reduced.
10	L Chen Et al. (2016)	Study of methane hydrate as a future energy resource: low emission extraction and power generation		The consideration of CO_2 recovery and re-injection would help increase the storage rate and substitute of the underground methane hydrate cages. The optimized system is estimated to be able to achieve power efficiency about 35% for the proposed system. The physical model is a horizontally operated cylinder core, where an axis is applied for simplicity of model.

Sr.	Author	Article	Method	Description

No.				
11	Dong-Yeun Koh a Et al. (2016)	Energy-efficient natural gas hydrate production using gas exchange	Gas Exchange	Geo-mechanical stability of Gas hydrate sediments via carbon dioxide sequestration in crystalline methane hydrate phase is enhanced by Gas exchange method.
12	Vishnu Chandrasekh-aran NairEt al. (2016)	Influence of thermal stimulation on the methane hydrate dissociation in porous media under confined reservoir	Thermal stimulation	The grain size of the porous media is an important factor affecting the formation and dissociation characteristics of hydrates. The formation of hydrate is detected by a sharp increase in the temperature and by drop of the pressure of the reactor. The pressure of the reactor tends to decrease due to the gas uptake into the hydrate phase in porous medium.
13	Pavel Serov Et al. (2017)	Postglacial response of Arctic Ocean gas hydrates to climatic amelioration		Gas hydrate occur stable in the Gas Hydrate Stability zone (GSHZ). It is a function of sub bottom geothermal gradient, pore water salinity, bottom water temperature, hydrostatic and lithostatic pressure. Thickness of GHSZ increases in with increase in water depth.
14	Mingjun Yang Et al. (2017)	Gas recovery from depressurized methane hydrate deposits with different water saturations		Acceleration of Gas Hydrate dissociation is affected by difference in its dissociation and production rate. Rapid GH dissociation is observed in areas of excess deposition of water under variation of backpressure. After comparison, greater mobility observed in excess water deposits.
15	Lin Yang Et al. (2018)	Influence of Reservoir Stimulation on Marine Gas Hydrate Conversion Efficiency in Different Accumulation Conditions		With increase in initial saturation of NGH, sensitivity of variable stimulation effect on it get decreased. For higher conversion of NGH, different stimulation effect required as per accumulation condition. Greater conversion efficiency NGH occur due to low saturation of NGH.
16	Stian Almenningen Et al. (2018)	Salinity Effects on Pore-Scale Methane Gas Hydrate Dissociation		Morphologies observed are porous NGH shells with encapsulated gas and nonporous crystalline NGH. Reformation of NGH take place due to local salinity gradients. Freshening of pore water causes self-preservation effect which leads to increase in stability of NGH.

Table 2.1 Characteristics of Methanogenic Bacteria

Species	Location	Morphology	Temperature (Optimum ˚C)	pH Range (Optimum)	Metabolism	Comments	Ref.
Methanogenium frigidum	Ace Lake in the Vesfold Hills of Antarctica	Irregular, nonmotile coccoids	15°C	6.5 - 7.9	Me	cells were slightly halophilic	Franzmann PD et al. (1997) [4]
Methanolobus psychrophilus	Zoige wetland of the Tibetan plateau	Coccoid Cells, loosely aggregates, flagella	0–25 ˚C (18 ˚C)	6.0 – 8.0	Me	Biotin required as growth factor	Guishan Zhang et al. (2008) [5]
Methanosarcina acetivorans	Marine canyon sediments evolving Methane	Nonmotile cell but has a single fimbria-like structure	35- 40°C	6.5 - 7.0	Me	Required for growth is NaCl and Mg^{2+}	KEVIN R. SOWERS et al. (1984) [6]
Methanoculleus submarinus	Nankai Trough off the eastern Methane Hydrate sediments at the coast of Japan	Nonmotile and irregular coccoids cells (average diameter range 0.8 - 2 μm)	Most rapid growth at 45°C (no growth at <10°C or >55°C).	5.0 and 8.7 but did not grow at pH 4.7 or 9.0.	Me	Cells required acetate as a carbon source.	Jill A. Mikucki et al. [7]
Methanospirillum stamsii	anaerobic expanded granular sludge bed (EGSB) bioreactor	Gently motile Cellsby using tufted flagella	5– 37 °C (optimum at 20–30 °C)	pH 6.0–10 (optimum 7.0–7.5)	Me	Methane production with H_2/CO_2 and very weak growth with formate	Sofiya N. Parshina et al. [8]

2.1Research Gap

1. The current existing methods of exploitation of methane from Methane Gas Hydrates are very expensive. They can be harmful to environment. So, there is need to find better approach for removalof Methane from Gas Hydrates
2. Although depressurization method is cheapest among them but reformation of hydrate starts in it after some time. To avoid this problem, other techniques are needed to be discovered in addition to depressurization.
3. Need to find better chemical inhibitor for chemical Inhibitor Injection Technique for Dissociation of Gas Hydrates.

2.2Objectives

1. Study of Simulation on Dissociation Techniques to produce Methane from Gas Hydrates.
2. To compare different Methods to produce Methane by simulation using reservoir rock properties of NGHP-02 Sites.
3. Determination of Cellulose percentage in acid pre-treated wheat straw sample.

Chapter 3: Material and Method

3.1 Equipment Specifications

1. **Gas booster**: It is used for increasing gas pressure. (5000psi). with the help of nitrogen gas and methane gas cylinder, it can increase pressure up to 2000psi.
2. **Gas Hydrate Cell**: It's a reactor which is made of stainless and provides proper condition (high pressure and low temperature) for formation of methane gas hydrate.
3. **Cooling system**: Ethylene glycol (-30˚C) bath which maintain the reactor at low temperature.
4. **Controller: PID**
5. **Raman Spectroscopy**: Determine Methane Hydrate structure
6. **Methane Gas cylinder**

Chapter 4: Simulation of System Behavior in Gas Hydrate Bearing Reservoir

4.1 Introduction

Non-isothermal gas release, flow and phase behavior of fluids and heat within complex geologic media can be modelled using T+H by solving coupled equations of heat and mass balance. The simulation by this code is used to study production of or formation of natural gas hydrate deposits at the subsurface (i.e., in deep marine sediments/in the permafrost region), along with laboratory scale experiments of formation/dissociation of hydrates in fractured/porous media. If the volume of domain and its sub-division follows (a) a defined representative volume (b) Darcy’s law is applicable, the behavior of hydrate bearing geological sediments can be predicted using T+H.

T+H covers both an equilibrium and kinetic model of formation and dissociation of Hydrate. An equilibrium hydration model includes heat and maximum four components of mass, i.e., CH4, H2O, and inhibitors soluble in water such as salts/alcohol. The additional component of CH4(Methane)-Hydrate is introduced in Kinetic model, which is considered as an individual component. These components are subdivided into for possible phases namely liquid phase, gas phase, ice phase and hydrate phase respectively.

4.2 Modeled Processes and Underlying Assumptions

The following phenomena and processes in Hydrate bearing geological systems can me modelled by T+H:

1) The flow of liquids and gases in geological systems

2) The relevant transport and heat flow.

3) The subdivision of mass components between possible phases

4) Exchange of heat due to

   a. Conduction

b. Convection/advection

c. Radiation

d. Dissociation/Formation (Hydrate reaction)

e. Latent heat corresponding to phase changes (water fusion or ice melting, vapor condensation/water evaporation),

5) Equilibrium or kinetic reaction of hydration (Dissociation/Formation)

6) The transport of inhibitors (salts/alcohols) and water soluble gases responsible for molecular diffusion and advection

7) The impact of water soluble inhibitor on the behavior of hydrate

8) Any Technique of dissociation of hydrate (such as depressurization, thermal stimulation method and chemical inhibitor injection) and their combinations

4.3 Components and Phases

The amount of CH4 (Methane) gas released or CH4-Hydrate formed is calculated from the reaction below-

$$CH_4 + N_H H_2O \qquad CH_4 \cdot N_H H_2O \longrightarrow$$

where:

N_H = hydration number,

subscript m = methane.

The natural gas hydrate may include one or more additional gases in addition to simple CH4-hydrate. All natural hydrates comprise of hydrate forming gases which can play important role in their behavior and nucleation.

The hydration/formation of binary (Composite) hydrates is

$$\chi_m[CH_4 \cdot N_H H_2O] + \chi_G[G \cdot N_G H_2O] \longrightarrow \chi_m\, CH_4 + \chi_G G + (\chi_m\, N_H + \chi_G N_G)\, H_2O$$

Where:

G= second hydrate-forming gas

N_G= hydration number of the G-hydrate

χ= mole fraction in the binary hydrateand $\chi_m+\chi_G= 1$.

subscripts*G*and *m*shows the second gas and methane respectively.

The gas *G* can be one of CO_2, H_2S, N_2, or another gaseous alkane C_nH_{2n+2} (m=2,3,4).

4.4 The Mass and Energy Balance Equation

Following *Pruess et al.* [1999], mass and heat balance considerations in every subdomain (gridblock) into which the simulation domain is been subdivided by the integral finite difference method dictates that

$$\frac{d}{dt}\int_{Vn} M^{k} dV = \int_{\Gamma n} \mathbf{F}^{k}\cdot\mathbf{n}\, d\tilde{A} + \int_{Vn} q^{k} dV,$$

where,

$\boldsymbol{V}, \boldsymbol{V_n}$volume, volume of subdomain n [L^3];

M^kmass accumulation term of component k [kg m^{-3}];

$\boldsymbol{A}, \boldsymbol{\Gamma_n}$surface area, surface area of subdomain n[L^2];

$\mathbf{F}^k$Darcy flux vector of component k [kg m^{-2}s^{-1}]

ninward unit normal vector;

q^{κ} source/sink term of component k [kg m^{-3} s^{-1}];

$t$time [T].

4.5 Mass Accumulation Terms

Under kinetic conditions, the equation describing the behavior of the hydrate masscomponent and phase is provided by the model of [*Kim et al.*, 1987] as

$$Q_H = \frac{\partial M}{\partial t} = -K_o \exp(\frac{\Delta Ea}{RT})F_A A(f_{eq}-f_v)$$

where,

K_0 intrinsic hydration reaction constant [kg m^{-1} Pa^{-1} s^{-1}];

ΔE_a hydration activation energy [J mol^{-1}];

R universal gas constant [8.314 J mol^{-1} K^{-1}];

T temperature [K];

F_A area adjustment factor [dimensionless];

A surface area participating in the reaction [m^2];

f_{eq} fugacity at equilibrium at temperature T (Pa)

f_v fugacity in the gas phase at temperature T (Pa) [9].

Chapter 5: Result and Discussion

5.1 Chemical Inhibitors for Gas Hydrate Dissociation

Table 5.1Properties of Chemical Inhibitors

Chemical	Mol. Wt. (g/mol)	Density (kg/m^3)	Dissolution Enthalpy	A_0 coeff in $C_p = A_0 + A_1T + A^2T^2$ (J/mol/K)	A_1 coeff in $C_p = A_0 + A_1T + A^2T^2$ (J/mol/K^2)	A_2 coeff in $C_p = A_0 + A_1T + A^2T^2$ (J/mol/K^3)
Brine	5.84480E+01	2.60000E+03	6.64790E+04	4.12930E+01	3.36070E-02	-1.39270E-05
Ethanol	4.6069E+01	7.89000E+02	6.02096 E+06	5.93420E+01	3.63580E-01	-1.21640E-03
Ethylene Glycol	6.20680E+01	1.09700E+03	7.41125 E+06	7.5878E+01	6.41820E-01	-1.6493E-03
Methanol	3.20420E+01	7.92000E+02	7.44023 E+06	4.0152E+01	3.1046E-01	-1.0291E-03

Source- Wikipedia (Data Page)

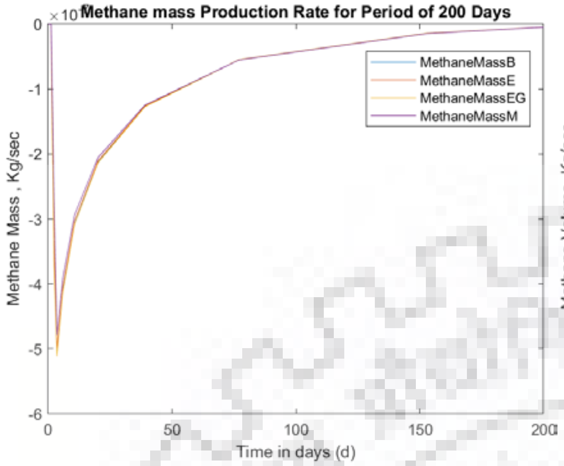
5.2 Simulation of Hydrate Dissociation for NGHP Site 2_08

Table 5.2.1 Properties of Site 2_08

Site	Grain Density (Kg/m^3)	Permeability (m^2)	Porosity	Thermal Conductivity (W/mK)
2_08	2.8×10^3 Kg/m^3	1.973×10^{-18} m^2	0.48	100

Table. 5.2.2 Chemical Inhibitor Vs Parameters for Test 1TbS on NGHP Site 2_08

Inhibitor	Time(d)	CH4 Mass Rate (kg/s)	CH4 Vol Rate (m3/s)	Cum CH4 Mass (kg)	Cum CH4 Vol (m3)	Free CH4 in Res (m3)	Remain Hydrate (kg)
Brine	2.0000000E+02	-4.8026747E-09	-7.0947031E-09	-9.7518392E-01	-1.4405807E+00	1.0777287E+01	7.5456008E+00
Ethanol	2.0000000E+02	-4.8239485E-09	-7.1261297E-09	-9.6620219E-01	-1.4273125E+00	1.0780571E+01	7.4761036E+00
Ethylene Glycol	2.0000000E+02	-4.8009346E-09	-7.0921326E-09	-9.7715686E-01	-1.4434952E+00	1.0776591E+01	7.5608667E+00
Methanol	2.0000000E+02	-4.8725849E-09	-7.1979774E-09	-9.4660553E-01	-1.3983635E+00	1.0787451E+01	7.3244721E+00



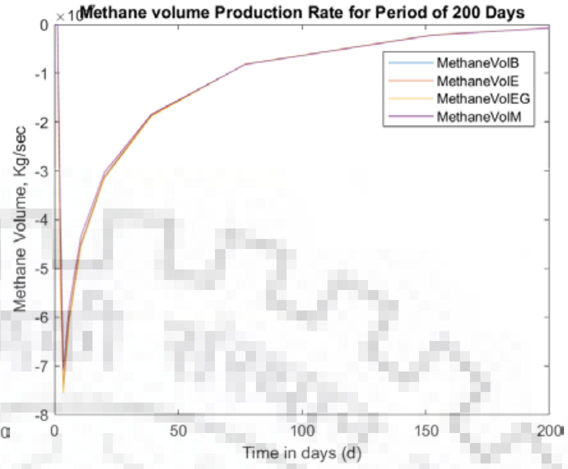
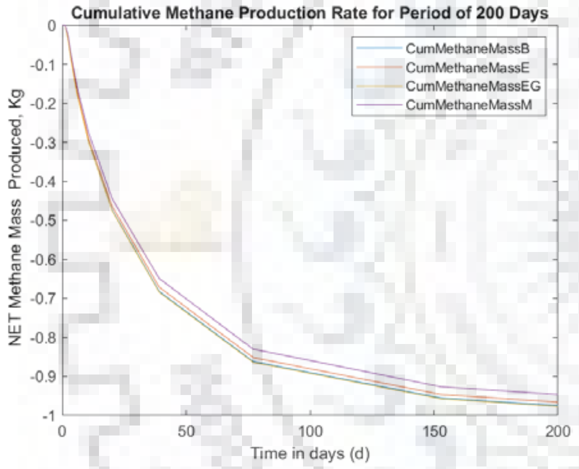


Fig 5.2.1(a) Methane Mass Comparison **Fig 5.2.1(b)** Methane Volume Comparison



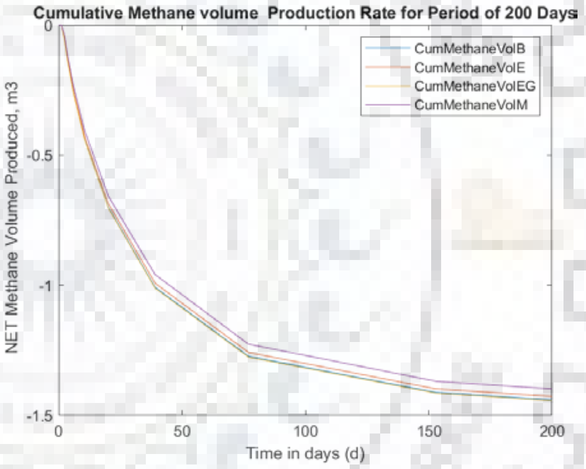
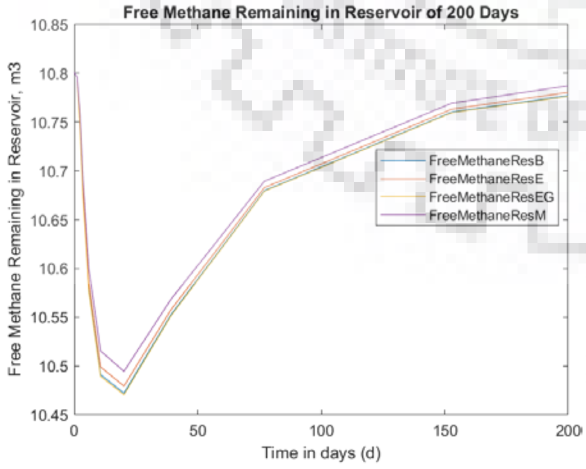


Fig 5.2.1(c) Cumulative Methane MassComparison **Fig 5.2.1(d)** Cumulative Methane Volume Comparison



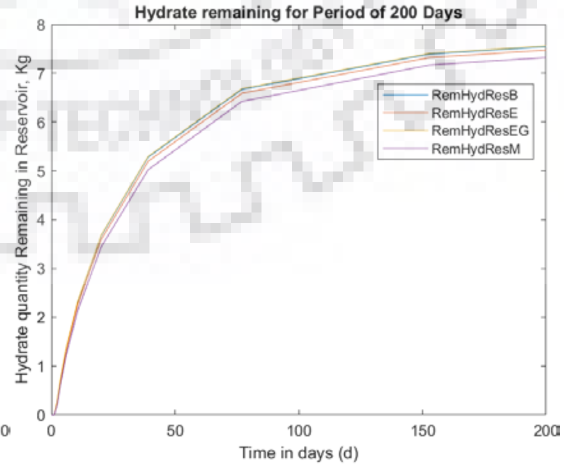


Fig 5.2.1(e) Free Methane Mass Comparison **Fig 5.2.1(f)** Remaining Hydrate in Reservoir

Fig. 5.2.1 Inhibitor Vs Parameters site 2_08

From Table. 5.2.2 and plots in Fig. 5.2.1, the increasing order of efficiency in Test 1TbS for NGHP Site 2_08 is **Brine < Ethylene Glycol < Ethanol< Methanol**. So, Methanol inhibitor is used in Test TbS for its comparison with other tests.

Table 5.2.3 Tests Vs Parameters for Different Tests on site 2_08

Test	Time(d)	CH4MassRate (kg/s)	CH4 Vol Rate (m3/s)	Cum CH4 Mass (kg)	Cum CH4 Vol (m3)	Free CH4 in Res (m3)	Remain Hydrate (kg)
1P	1.1423633E+00	0.0000000E+00	0.0000000E+00	1.1615077E+00	1.7158256E+00	1.2576617E+00	2.1047780E+02
1P_ice	1.1828157E+00	0.0000000E+00	0.0000000E+00	1.2044373E+00	1.7792430E+00	1.2070041E+00	2.1163323E+02
1Pk	3.0137335E-01	4.5398145E-06	6.7063955E-06	4.3687796E-01	6.4537360E-01	6.4505450E-02	2.1608471E+02
1T	1.8989899E-02	0.0000000E+00	0.0000000E+00	-1.7615398E-03	-2.6022170E-03	0.0000000E+00	2.2087084E+02
1TbS_m	2.0000000E+02	-4.8725849E-09	-7.1979774E-09	-9.4660553E-01	-1.3983635E+00	1.0787451E+01	7.3244721E+00
1TbSk_m	1.2507953E+02	-3.4584667E-09	-5.1089854E-09	-9.7470512E-01	-1.4398734E+00	1.0789584E+01	7.5418960E+00

Where

1P = Depressurization, Equlibrium Dissociation, No Inhibitor

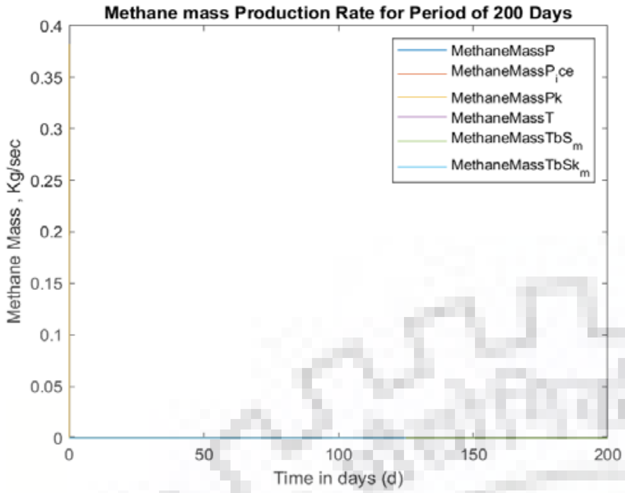
1P_ice = Thermal Stimulation, Kinetic Dissociation, No Inhibitor

1Pk = Depressurization, Kinetic Dissociation, No Inhibitor

1T= Thermal Stimulation, Equilibrium Dissociation, No Inhibitor

1TbS = Hydrate formation, Equilibrium Hydration Reaction, Inhibitor

1TbSk = Hydrate formation, Kinetic Hydration Reaction, Inhibitor



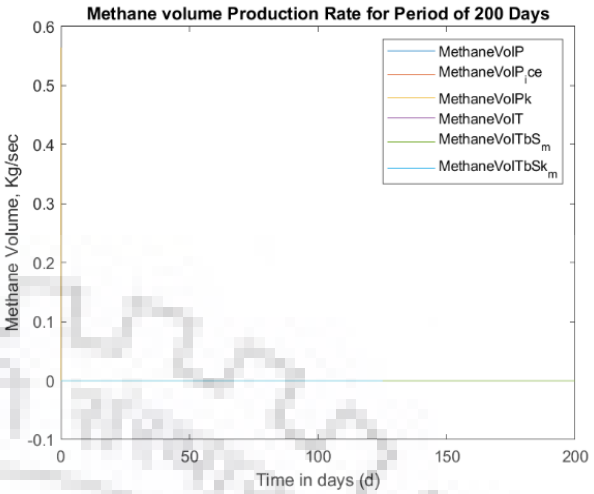
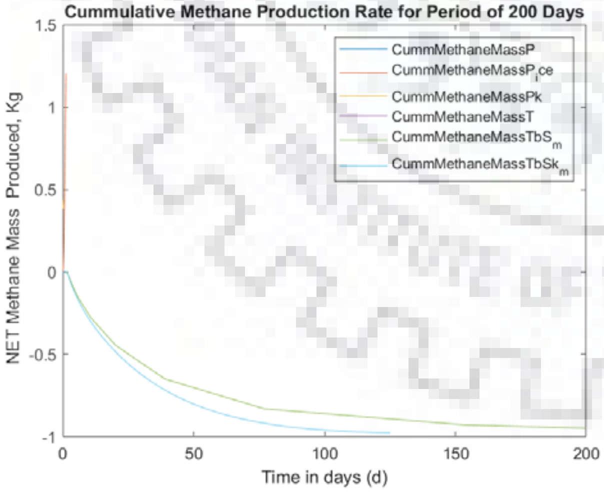


Fig 5.2.2 (a) Methane Mass Comparison**Fig 5.2.2(b)** Methane Volume Comparison

In fig 5.2.2 (a), Methane Mass production for 1P, 1P_ice and 1T is absent and negligible amount of Methane mass get produced for 1T method. Negative Methane mass production for 1TbS_m and 1TbSk_m indicates formation of hydrate.

In Fig 5.2.2 (b)Methane Volume production for 1P, 1P_ice and 1T is absentand negligible amount of Methane volume get produced for 1T method. Negative Methane volume production for 1TbS_m and 1TbSk_m indicates formation of hydrate.



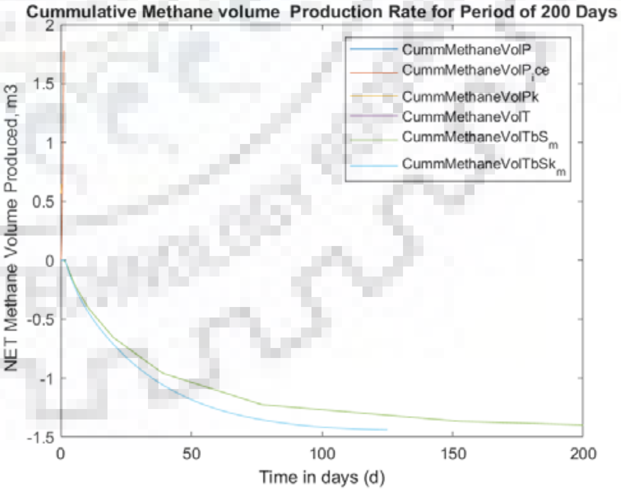


Fig 5.2.2 (c) Cumulative Methane MassComparison**Fig 5.2.2 (d)**Cumulative Methane Volume Comparison

In Fig 5.2.2 (c),CumulativeMethane Mass production for 1P, 1P_ice and 1T stops in approx. 2 days. Negative Cumulative Methane mass production for 1TbS_m and 1TbSk_m indicates formation of hydrate. In fig 5.2.2 (d), A continuously decreasing Trend is observed for 1TbS_m and 1TbSk_m. Approx. 11.7 m^{3}cumulative volume gets produced for 1P and 1P_ice case.

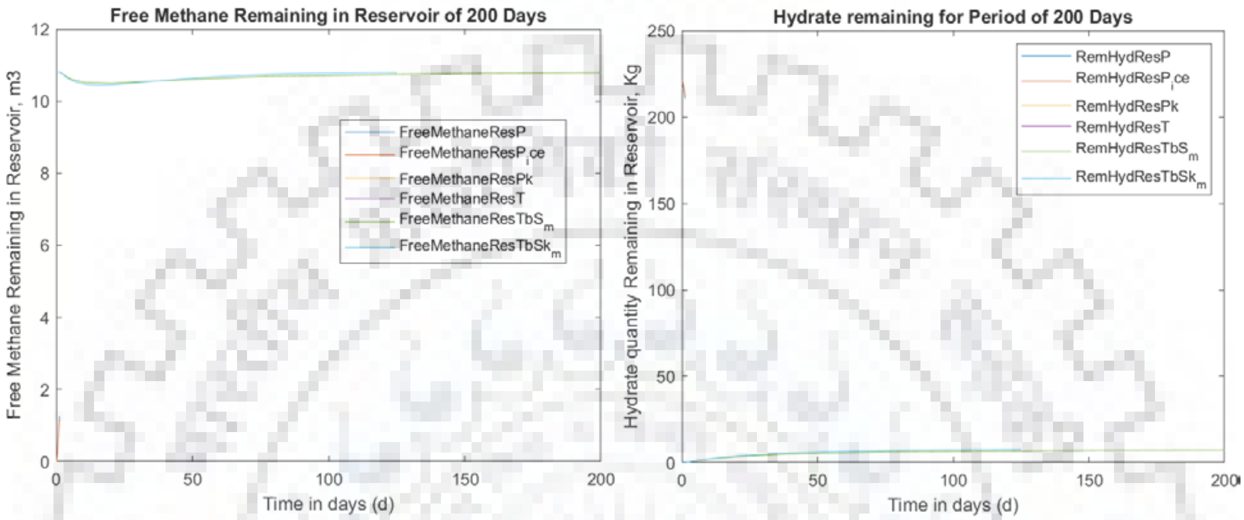


Fig 5.2.2 (e) Free Methane Mass Comparison**Fig 5.2.2 (f)**Remaining Hydrate in Reservoir

Fig. 5.2.2 Test Vs Parameters for site 2_08

In fig 5.2.2(e), Maximum amount of free Methane in seen in the case of 1TbSk_m where production lasts for 125 days. In fig 5.2.2(f), A minimum amount of Remaining Hydrate is observed for 1TbS_m.

5.3Simulation of Hydrate Dissociation for NGHP Site 2_17

Table 5.3.1 Properties of Site 2_17

Site	Grain Density (Kg/m^3)	Permeability (m^2)	Porosity	Thermal Conductivity (W/mK)
2_17	2.7×10^3 Kg/m^3	6.316×10^{-14} m^2	0.8	1.1

Table 5.3.2 Chemical Inhibitor Vs Parameters for Test 1TbS on NGHP Site 2_17

Inhibitor	Time(d)	CH4 Mass Rate (kg/s)	CH4 Vol Rate (m3/s)	Cum CH4 Mass (kg)	Cum CH4 Vol (m3)	Free CH4 in Res (m3)	Remain Hydrate (kg)
Brine	2.0000000E+02	-2.7742372E-07	-4.0982141E-07	-3.1533470E+01	-4.6582503E+01	1.2289338E+01	2.4399395E+02
Ethanol	2.0000000E+02	-2.7643821E-07	-4.0836558E-07	-3.0148403E+01	-4.4536427E+01	1.2524410E+01	2.3327683E+02
Ethylene Glycol	2.0000000E+02	-2.6901435E-07	-3.9739875E-07	-3.1755686E+01	-4.6910770E+01	1.2258209E+01	2.4571337E+02
Methanol	2.0000000E+02	-2.5451837E-07	-3.7598472E-07	-2.7425201E+01	-4.0513604E+01	1.3028458E+01	2.1220573E+02

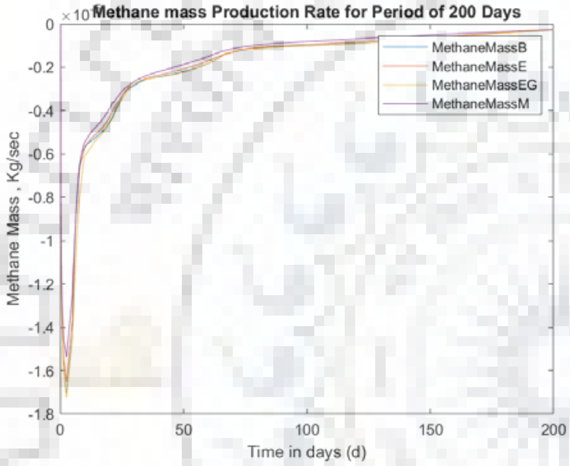


Fig 5.3.1(a) Methane Mass Comparison

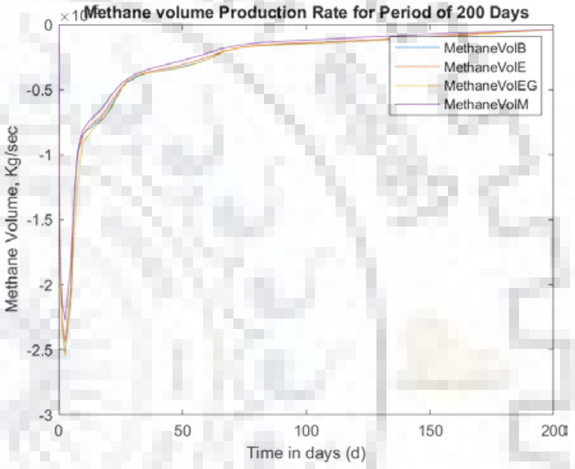


Fig 5.3.1(b) Methane Volume Comparison

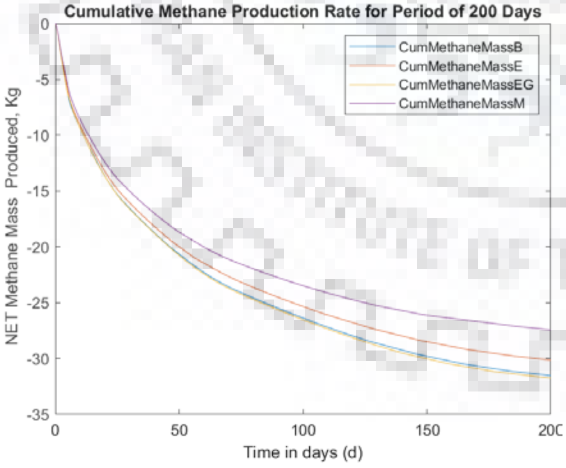


Fig 5.3.1(c) Cumulative Methane MassComparison

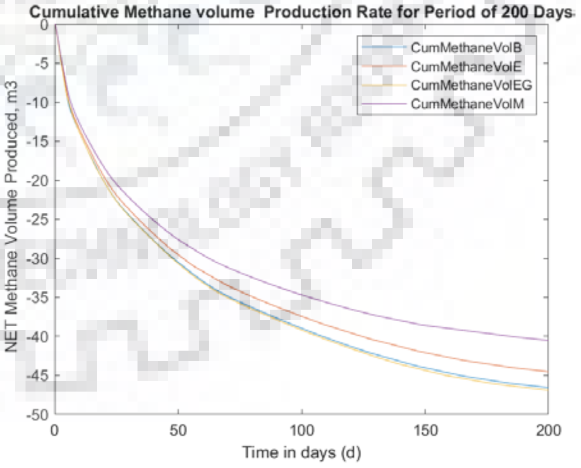


Fig 5.3.1(d) Cumulative Methane Volume Comparison

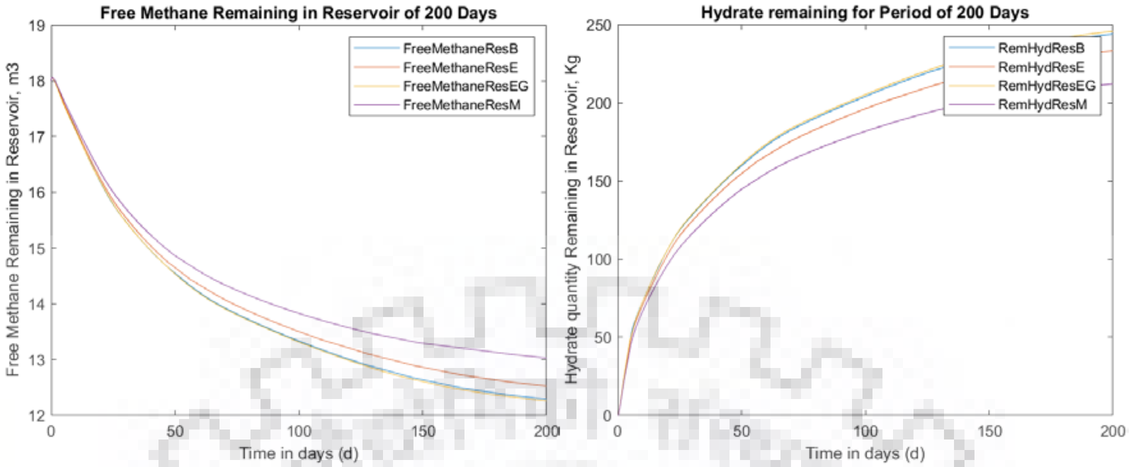


Fig 5.3.1 (e) Free Methane Mass Comparison **Fig 5.3.1 (f)** Remaining Hydrate in Reservoir

Fig. 5.3.1 Inhibitor Vs Parameters for site 2_17

From Table. 5.3.2 and plots in Fig. 5.3.1, the increasing order of efficiency in Test 1TbS for NGHP Site 2_17 is **Brine < Ethylene Glycol < Ethanol< Methanol**. So, Methanol inhibitor is used in Test TbS for its comparison with other tests.

Table 5.3.3 Tests vs Parameters for Different Tests on site 2_17

Method	Time(d)	CH4 Mass Rate (kg/s)	CH4 Vol Rate (m3/s)	Cum CH4 Mass (kg)	Cum CH4 Vol (m3)	Free CH4 in Res (m3)	Remain Hydrate (kg)
1P	1.0000000E+01	4.1081002E-06	6.0686499E-06	9.2719250E+00	1.3696858E+01	2.1665463E+00	2.9403256E+02
1P_ice	2.0000000E+02	0.0000000E+00	0.0000000E+00	4.7592749E+01	7.0305912E+01	1.6437830E-01	0.0000000E+00
1_Pk	2.0000000E+02	4.1313044E-07	6.1029281E-07	2.2935519E+01	3.3881265E+01	1.7156775E+00	1.8830889E+02
1T	4.2202546E+01	0.0000000E+00	0.0000000E+00	4.7572179E+01	7.0275525E+01	3.4683374E+00	0.0000000E+00
1_TbS_m	2.0000000E+02	-2.5451837E-07	-3.7598472E-07	-2.7425201E+01	-4.0513604E+01	1.3028458E+01	2.1220573E+02
1_TbSk_b	1.0173684E+02	-9.7891881E-07	-1.4460980E-06	-2.6684981E+01	-3.9420121E+01	1.3263809E+01	2.0647819E+02

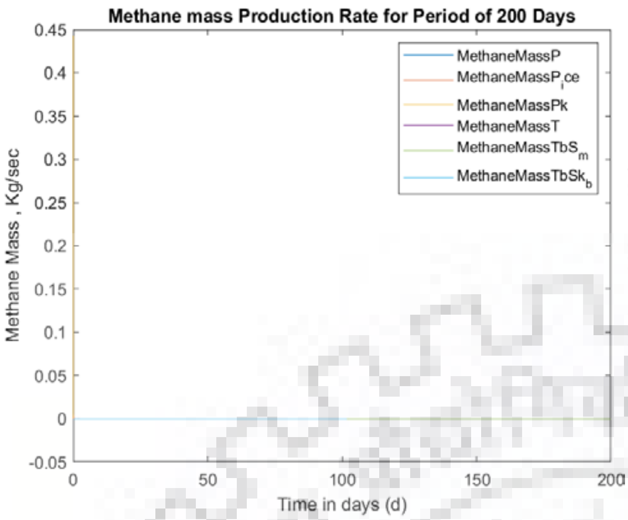


Fig 5.3.2 (a) Methane Mass Comparison

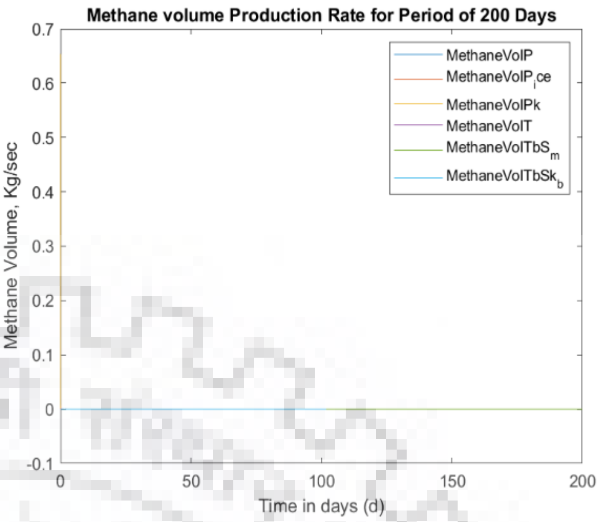
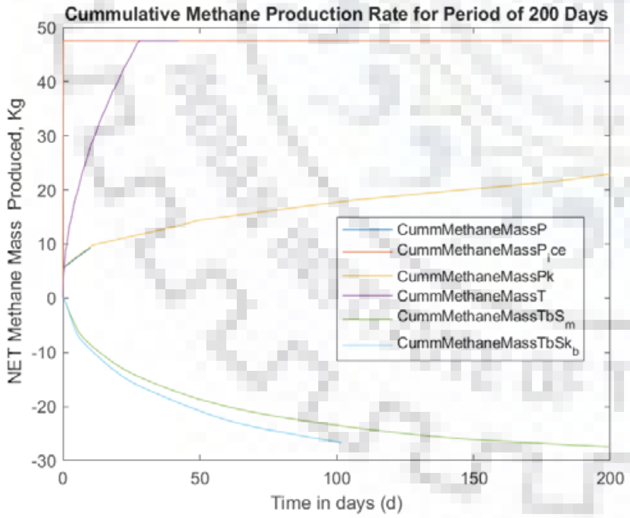


Fig 5.3.2 (b) Methane Volume Comparison

In fig 5.3.2 (a**)**, Methane production is absent for 1T case. Negative Methane production for 1TbS_ and 1TbSk_ m indicates formation of Hydrates. In fig 5.3.2 (b), Similar trend is observed for Methane Volume comparison for all the cases as in in fig 5.2.2 (a).



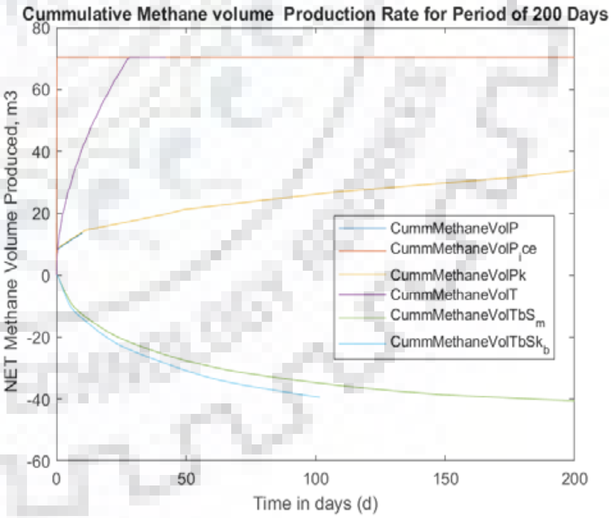


Fig 5.3.2(c) Cumulative Methane MassComparison**Fig 5.3.2 (d)** Cumulative Methane VolumeComparison

In fig 5.3.2 (c), Maximum amount of Cumulative Methane Mass production take place for 1P_ice Case. In fig 5.3.2 (d), Similarly, Maximum amount of Cumulative Methane Volume production is seen for 1P_ice case which lasts for 200 days.

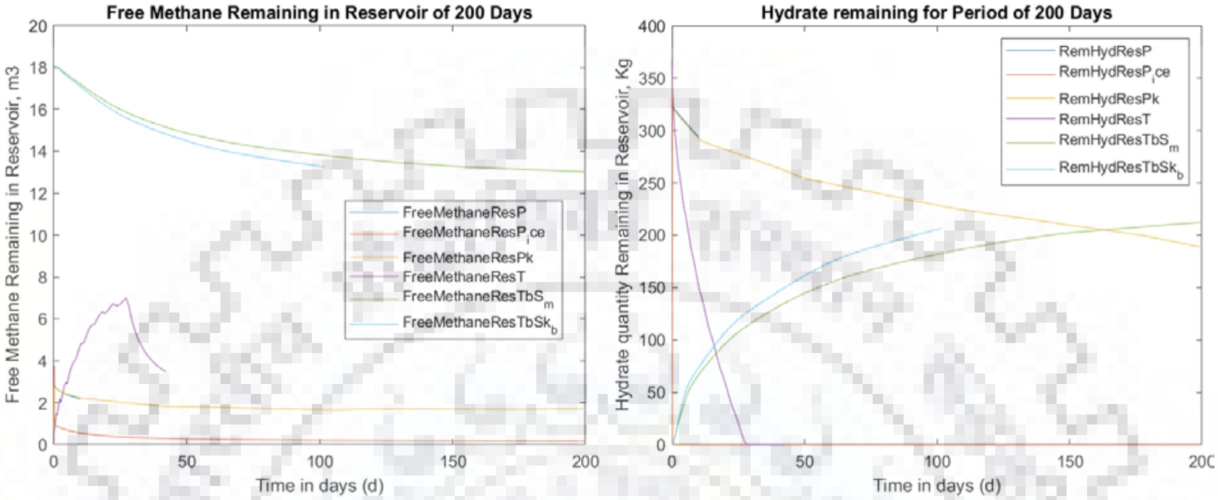


Fig 5.3.2 (e) Free Methane Mass Comparison**Fig 5.3.2 (f)** Remaining Hydrate in Reservoir

Fig. 5.3.2 Test Vs Parameters for site 2_17

In fig 5.3.2(e), Maximum Amount of free Methane is seen for 1_TbSk_b case where subscript b indicates brine which is used as an inhibitor to avoid hydrate formation. In fig 5.3.2(f), 1P case shows higher amount of Remaining Hydrate in Reservoir.

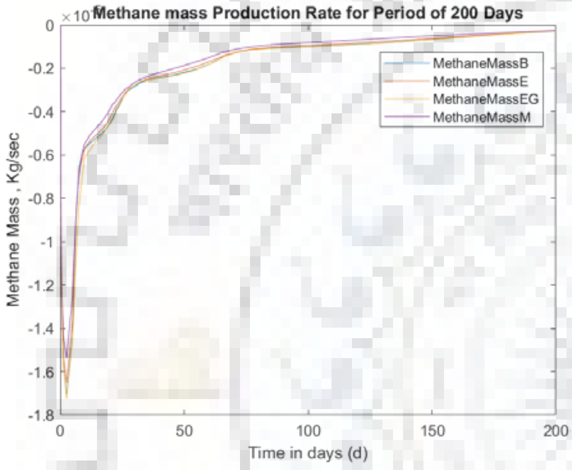
5.4 Simulation of Hydrate Dissociation for NGHP Site 2_19

Table 5.4.1 Properties of Site 2_19

Site	**Grain Density (Kg/m^3)**	**Permeability (m^2)**	**Porosity**	**Thermal Conductivity (W/mK)**
2_19	2.8×10^3 Kg/m^3	9.869×10^{-18} m^2	0.8	1.1

Table 5.4.2 Chemical Inhibitor Vs Parameters for Test 1TbS on NGHP Site 2_19

Inhibitor	Time(d)	CH4 Mass Rate (kg/s)	CH4 Vol Rate (m3/s)	Cum CH4 Mass (kg)	Cum CH4 Vol (m3)	Free CH4 in Res (m3)	Remain Hydrate (kg)
Brine	2.0000000E+02	-3.9031997E-07	-5.7659627E-07	-1.9932205E+01	-2.9444651E+01	1.6466569E+01	1.5422779E+02
Ethanol	2.0000000E+02	-3.6436635E-07	-5.3825654E-07	-1.9157148E+01	-2.8299705E+01	1.6548929E+01	1.4823069E+02
Ethylene Glycol	2.0000000E+02	-3.9562182E-07	-5.8442838E-07	-2.0078881E+01	-2.9661326E+01	1.6450910E+01	1.5536271E+02
Methanol	2.0000000E+02	-3.1590838E-07	-4.6667249E-07	-1.7719377E+01	-2.6175772E+01	1.6699261E+01	1.3710577E+02



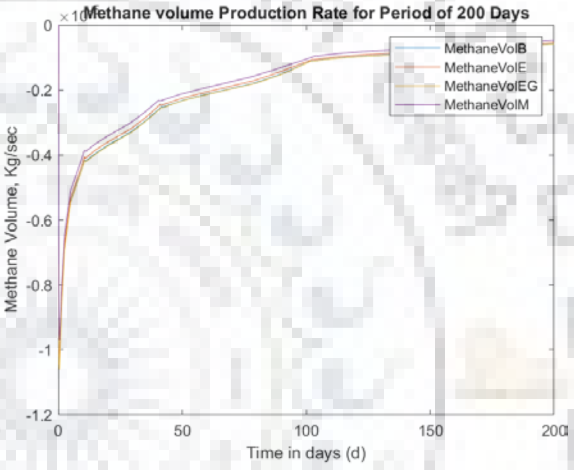
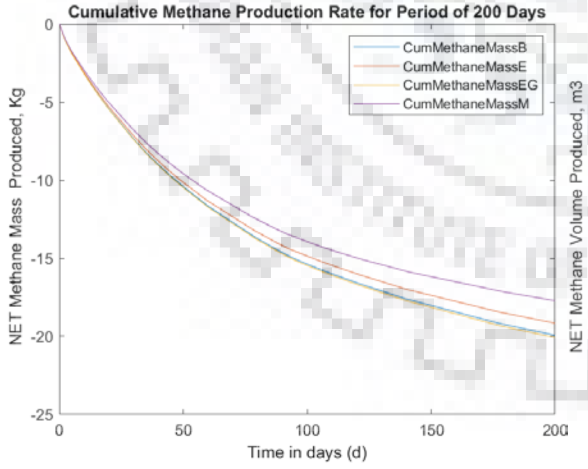


Fig 5.4.1(a) Methane Mass Comparison **Fig 5.4.1(b)** Methane Volume Comparison



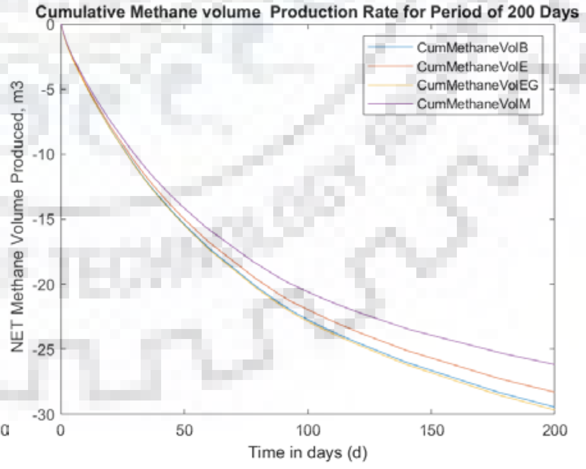


Fig 5.4.1(c) Cumulative Methane MassComparison **Fig 5.4.1(d)** Cumulative Methane Volume Comparison

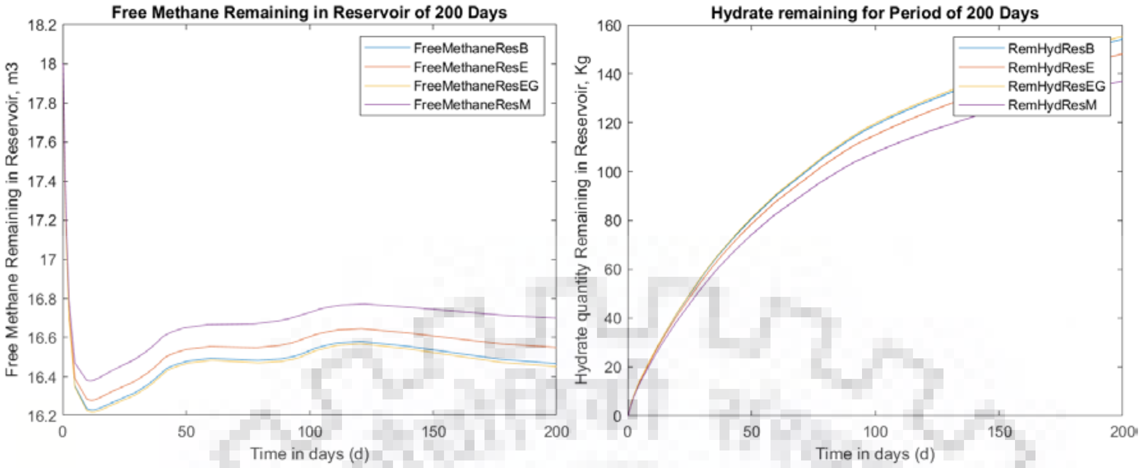


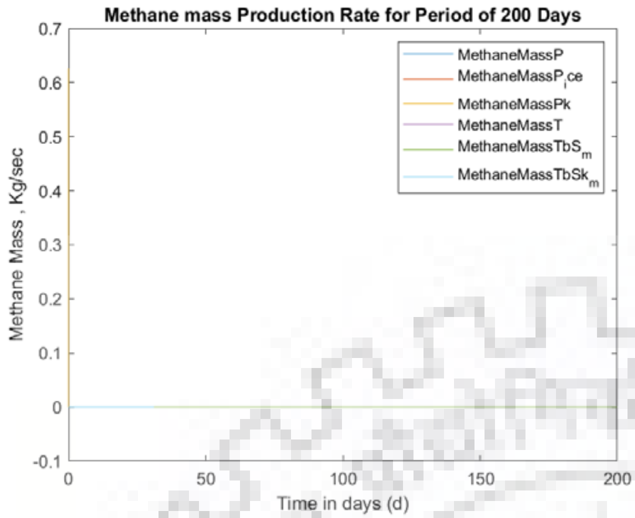
Fig 5.4.1 (e) Free Methane Mass Comparison **Fig 5.4.1 (f)** Remaining Hydrate in Reservoir

Fig. 5.4.1 Inhibitor Vs Parameters for site 2_19

From Table. 5.4.2 and plots in Fig. 5.4.1, the increasing order of efficiency in Test 1TbS for NGHP Site 2_19 is **Ethylene Glycol <Brine < Ethanol< Methanol**. So, Methanol inhibitor is used in Test TbS for its comparison with other tests.

Table 5.4.3 Tests vs Parameters for Different Tests on site 2_19

Method	Time(d)	CH4MassRate (kg/s)	CH4VolRate (m3/s)	Cum CH4 Mass (kg)	Cum CH4 Vol (m3)	FreeCH4inRes (m3)	RemainHydrate (kg)
1P	1.0000000E+01	-9.4234736E-08	-1.3920732E-07	-1.7916084E-01	-2.6466355E-01	0.0000000E+00	3.6716145E+02
1P_ice	6.5075908E+01	0.0000000E+00	0.0000000E+00	1.4108167E+01	2.0841148E+01	9.3674635E-01	2.5909091E+02
1_Pk	3.9412245E-01	-5.6295868E-07	-8.3162508E-07	5.9537110E-01	8.7950601E-01	0.0000000E+00	3.6116842E+02
1T	6.8258102E+01	0.0000000E+00	0.0000000E+00	4.7572179E+01	7.0275525E+01	9.4562137E+00	0.0000000E+00
1_TbS_m	2.0000000E+02	-3.1590838E-07	-4.6667249E-07	-1.7719377E+01	-2.6175772E+01	1.6699261E+01	1.3710577E+02
1_TbSk_m	3.1128565E+01	-1.9065700E-06	-2.8164615E-06	-7.1293552E+00	-1.0531769E+01	1.6536420E+01	5.5164229E+01



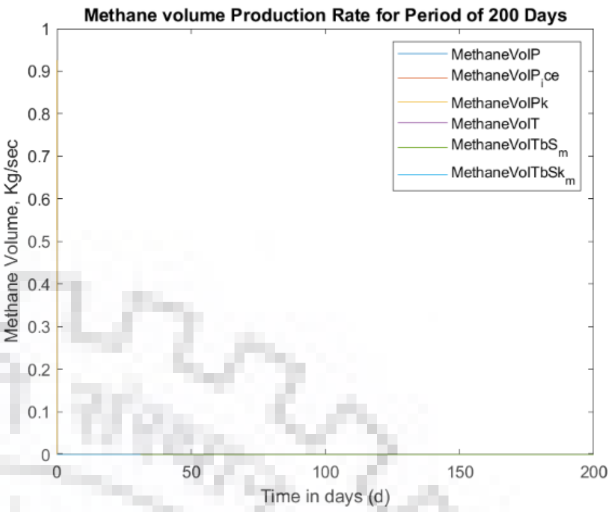
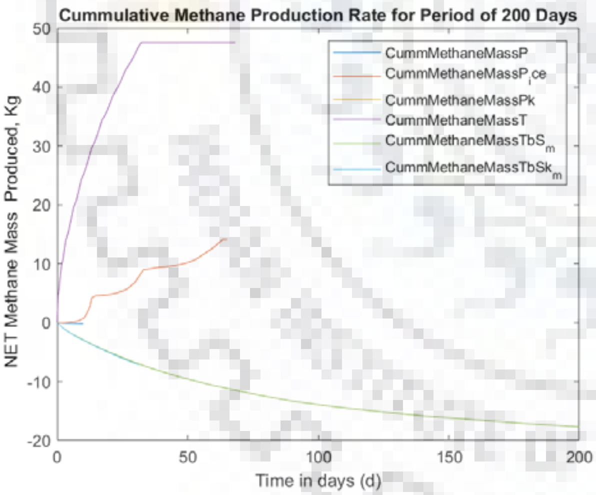


Fig 5.4.2(a) Methane Mass Comparison**Fig 5.4.2(b)** Methane Volume Comparison

In fig 5.4.2(a), Methane Mass production is absent for 1P_ice and 1T case while other cases show negative trends. In fig 5.4.2(b), Similar trend is observed for 1P_ice and 1T case and Negative Methane Volume production signifies formation of Hydrates.



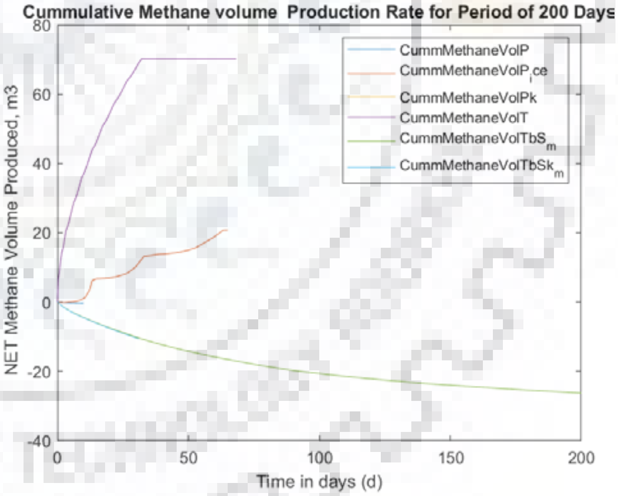


Fig 5.4.2(c) Cumulative Methane Mass Comparison**Fig 5.4.2(d)** Cumulative Methane Volume Comparison

In fig 5.4.2(c), A continuous increase of Cumulative Methane Mass is seen in 1T case which remains constant for next interval of days. Negative slope is observed for 1TbS_m case. In fig 5.4.2(d), Similar trend as fig 5.4.2(c), is observed for all the cases for Cumulative Methane Volume production.

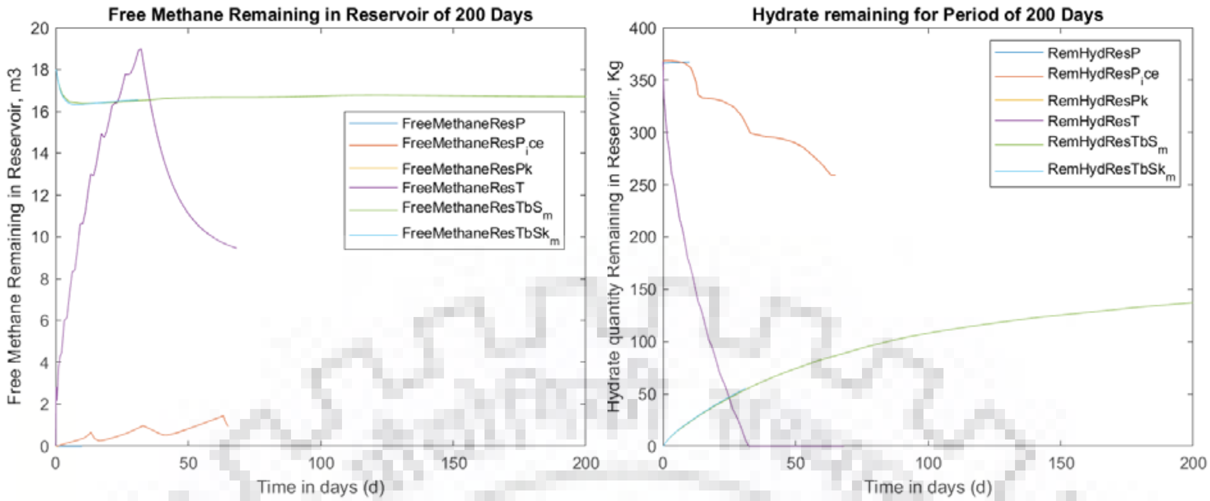


Fig 5.4.2(e) Free Methane Mass Comparison **Fig 5.4.2(f)** Remaining Hydrate in Reservoir

Fig. 5.4.2 Test Vs Parameters for site 2_19

In fig 5.4.2(e), Maximum Amount of free Methane is seen for 1_TbS_m case where subscript m indicates Methanol which is used as an inhibitor to avoid hydrate formation. Free Methane is absent in the cases 1P and 1Pk.In fig 5.4.2(f), Higher value of Remaining hydrate for 1P case shows that this method is not suitable for site 2_19.

5.5Simulation of Hydrate Dissociation for NGHP Site 2_22

Table 5.5.1 Properties of Site 2_22

Site	Grain Density (Kg/m^3)	Permeability (m^2)	Porosity	Thermal Conductivity (W/mK)
2_22	2.8×10^3	9.869×10^{-19}	0.8	1.3

Table 5.5.2 Chemical Inhibitor Vs Parameters for Test 1TbS on NGHP Site 2_22

Inhibitor	Time(d)	CH4 Mass Rate (kg/s)	CH4 Vol Rate (m3/s)	Cum CH4 Mass (kg)	Cum CH4 Vol (m3)	Free CH4 in Res (m3)	Remain Hydrate (kg)
Brine	2.0000000E+02	-2.7542299E-07	-4.0686585E-07	-6.2365512E+00	-9.2128829E+00	1.2933759E+01	4.8256052E+01
Ethanol	2.0000000E+02	-2.6578957E-07	-3.9263498E-07	-6.0771687E+00	-8.9774367E+00	1.2994546E+01	4.7022811E+01
Ethylene Glycol	2.0000000E+02	-2.7735086E-07	-4.0971378E-07	-6.2696994E+00	-9.2618507E+00	1.2921264E+01	4.8512540E+01
Methanol	2.0000000E+02	-2.4758535E-07	-3.6574298E-07	-5.7649043E+00	-8.5161473E+00	1.3109957E+01	4.4606628E+01

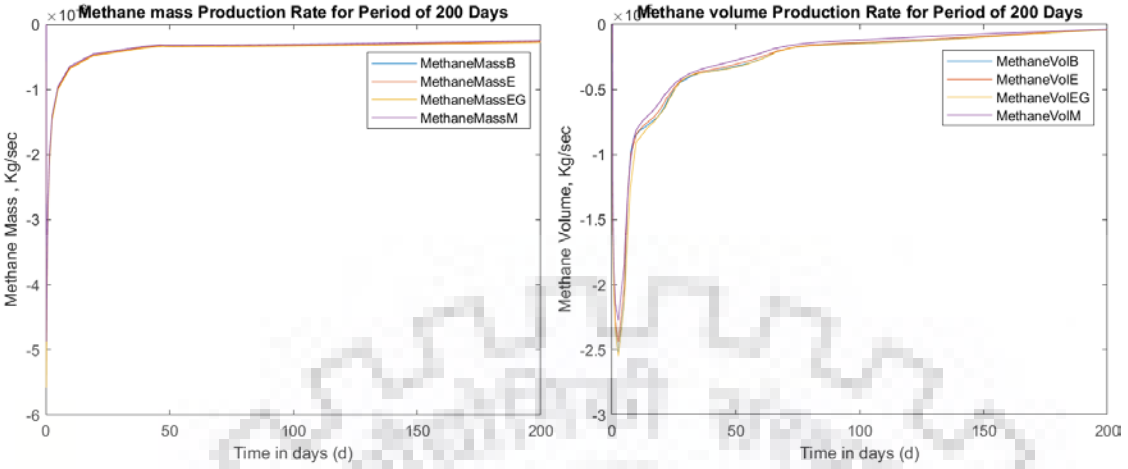


Fig 5.5.1(a) Methane Mass Comparison **Fig 5.5.1(b)** Methane Volume Comparison

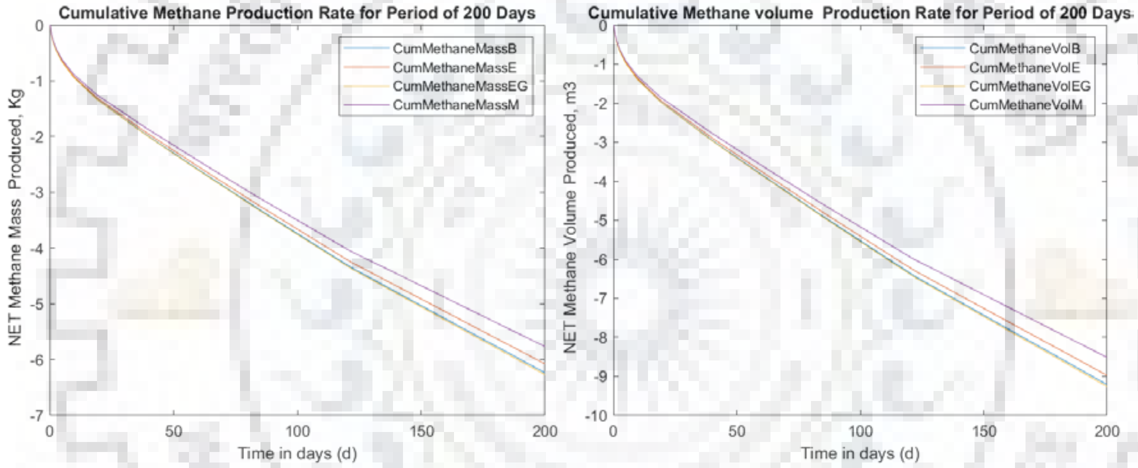


Fig 5.5.1(c) Cumulative Methane Mass Comparison **Fig 5.5.1(d)** Cumulative Methane Volume Comparison

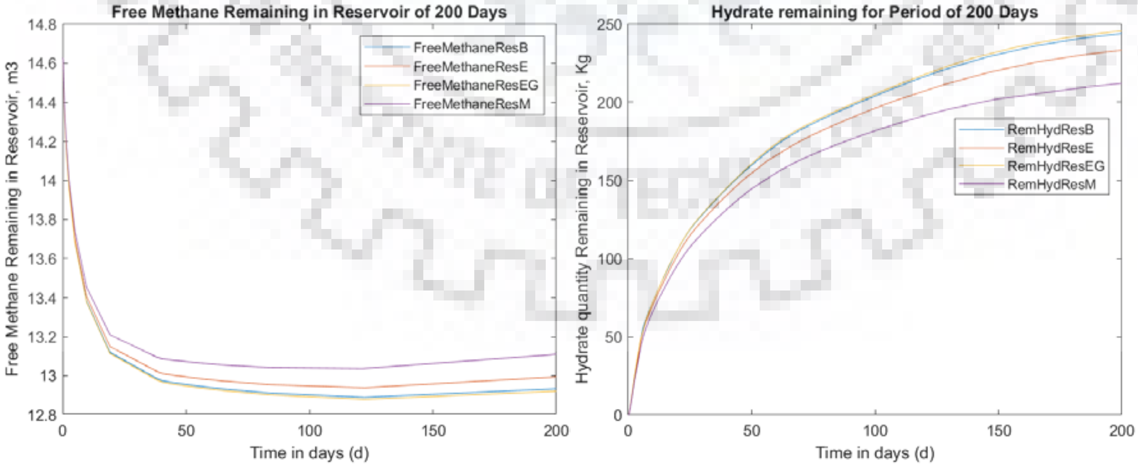


Fig 5.5.1 (e) Free Methane Mass Comparison **Fig 5.5.1(f)** Remaining Hydrate in Reservoir

Fig. 5.5.1 Inhibitor Vs Parametersfor site 2_22

From Table5.5.2 and plots in Fig. 5.5.1, the increasing order of efficiency in Test 1TbS for NGHP Site 2_22 is **Ethylene Glycol <Brine < Ethanol< Methanol**. So, Methanol inhibitor is used in Test TbS for its comparison with other tests.

Table 5.5.3 Tests vs Parameters for Different Tests on site 2_22

Method	Time(d)	CH4 Mass Rate (kg/s)	CH4 Vol Rate (m3/s)	Cum CH4 Mass (kg)	Cum_CH4_Vol (m3)	FreeCH4inRes (m3)	Remain Hydrate (kg)
1P	1.0000000E+01	-7.5765138E-08	-1.1192329E-07	-1.4949501E-01	-2.2084001E-01	0.0000000E+00	2.9834906E+02
1P_ice	2.0000000E+02	1.9219190E-07	2.8391357E-07	4.3799549E+00	6.4702446E+00	4.5744947E-01	2.6531638E+02
1_Pk	1.9277823E-01	-7.1580561E-07	-1.0574167E-06	4.9493831E-01	7.3114266E-01	0.0000000E+00	2.9336268E+02
1T	6.7850694E+01	0.0000000E+00	0.0000000E+00	3.8652395E+01	5.7098864E+01	2.1189314E+01	0.0000000E+00
1_TbS_m	2.0000000E+02	-2.4758535E-07	-3.6574298E-07	-5.7649043E+00	-8.5161473E+00	1.3109957E+01	4.4606628E+01
1_TbSk_m	4.5473900E+01	-3.0284038E-07	-4.4736792E-07	-2.0589539E+00	-3.0415691E+00	1.3049524E+01	1.5931399E+01

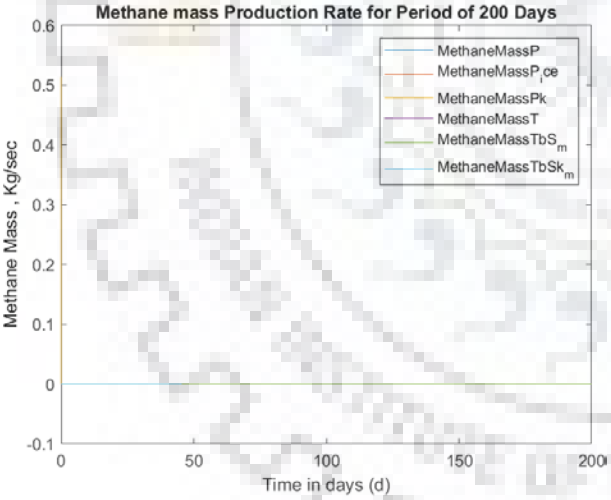


Fig 5.5.2 (a) Methane Mass Comparison

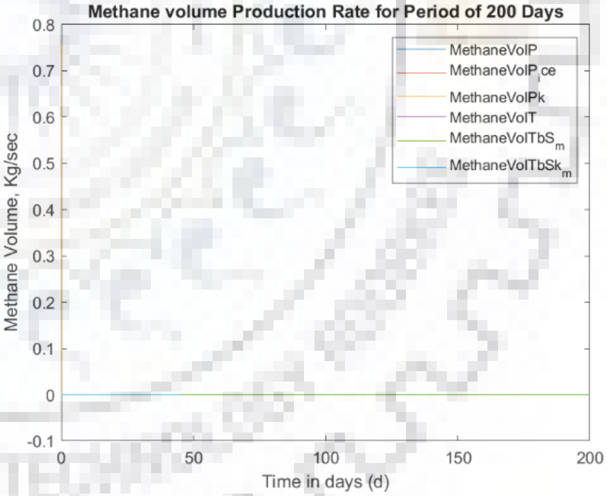


Fig 5.5.2 (b) Methane Volume Comparison

In fig 5.5.2(a), Methane production is absent for 1T case. Negative Methane production for 1P, 1Pk, 1TbS_ and 1TbSk_ m indicates formation of Hydrates. In fig 5.5.2(b), Similar trend is observed for Methane Volume comparison for all the cases as in in fig 5.5.2(a).

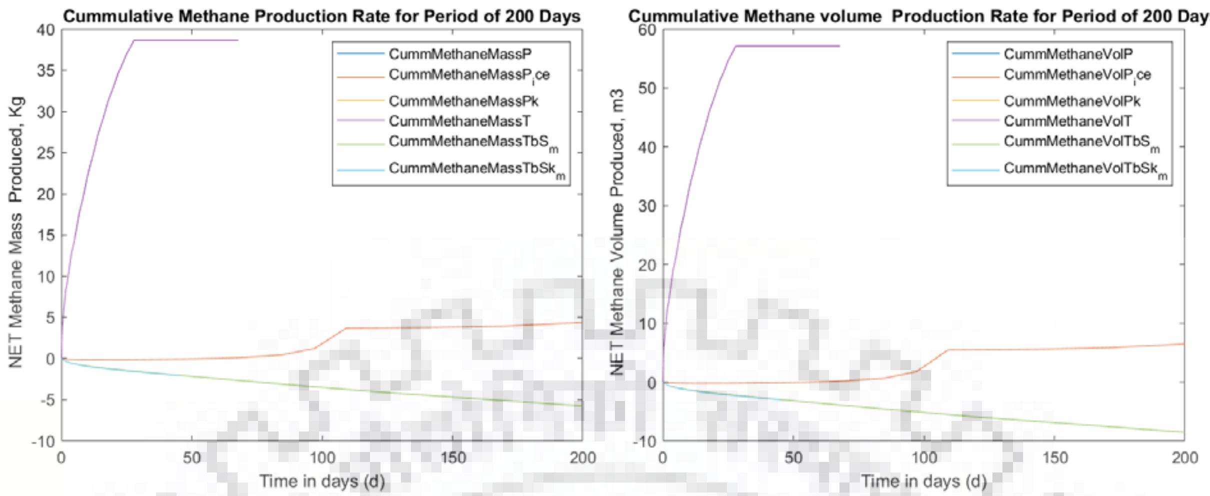


Fig 5.5.2 (c) Cumulative Methane MassComparison**Fig 5.5.2 (d)** Cumulative Methane VolumeComparison

In fig 5.5.2(c), A continuous increase of Cumulative Methane Mass is seen in 1T case which remains constant for next interval of days while 1P_ice and 1TbS_m cases show it lasts for complete 200 days. In fig 5.5.2 (d), Similar trend as in fig 5.5.2(c), is observed for all the cases for Cumulative Methane Volume production.

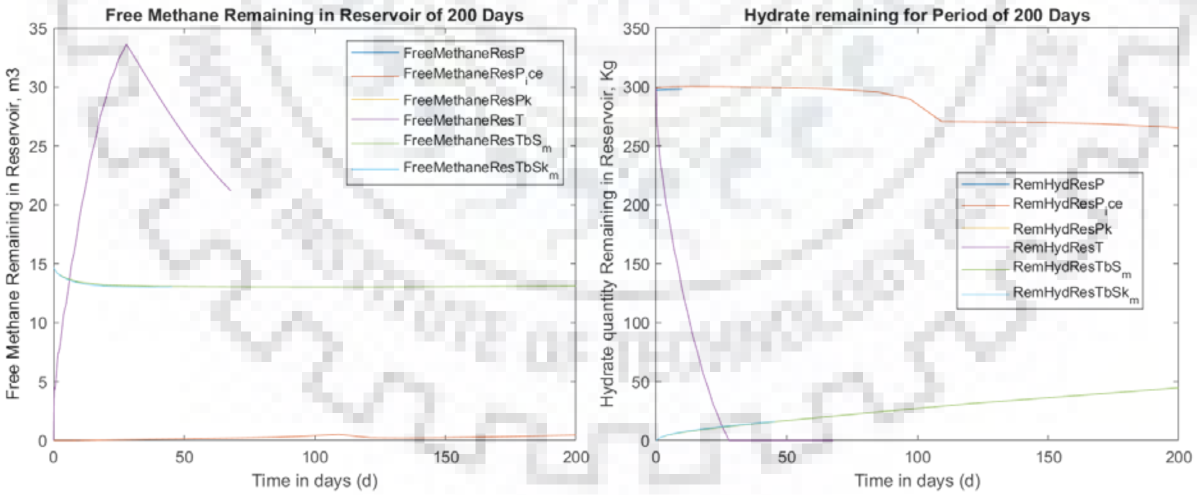


Fig 5.5.2 (e) Free Methane Mass Comparison **Fig 5.5.2** (f) Remaining Hydrate in Reservoir

Fig. 5.5.2 Test Vs Parametersfor site 2_22

In fig 5.5.2(e), Free Methane Mass Continuously increases for 1T case then decrease in quantity is observed which stops in 67 days. Maximum quantity is observed for 1_TbSk_m case. In fig 5.5.2(f), Higher value of Remaining hydrate for 1P shows that this method is not suitable for site 2_22.

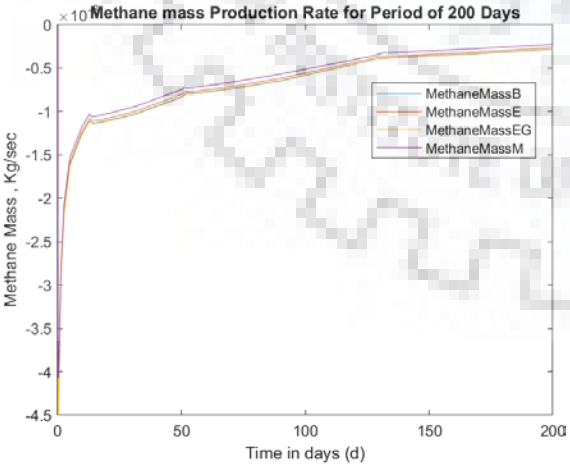
5.6Simulation of Hydrate Dissociation for NGHP Site 2_23

Table 5.6.1 Properties of Site 2_23

Site	Grain Density (Kg/m^3)	Permeability (m^2)	Porosity	Thermal Conductivity (W/mK)
2_23	2.78×10^3 Kg/m^3	3.552×10^{-18} m^2	0.8	1.2

Table 5.6.2 Chemical Inhibitor Vs Parameters for Test 1TbS on NGHP Site 2_23

Inhibitor	Time(d)	CH4 Mass Rate (kg/s)	CH4 Vol Rate (m3/s)	Cum CH4 Mass (kg)	Cum CH4 Vol (m3)	Free CH4 in Res (m3)	Remain Hydrate (kg)
Brine	2.0000000E+02	-2.8089438E-07	-4.1494841E-07	-1.0502989E+01	-1.5515436E+01	9.2075421E+00	8.1268119E+01
Ethanol	2.0000000E+02	-2.6156128E-07	-3.8638879E-07	-1.0116603E+01	-1.4944651E+01	9.2565312E+00	7.8278413E+01
Ethylene Glycol	2.0000000E+02	-2.8416627E-07	-4.1978177E-07	-1.0585479E+01	-1.5637294E+01	9.1982381E+00	8.1906398E+01
Methanol	2.0000000E+02	-2.2561928E-07	-3.3329383E-07	-9.3748904E+00	-1.3848963E+01	9.3490777E+00	7.2539322E+01



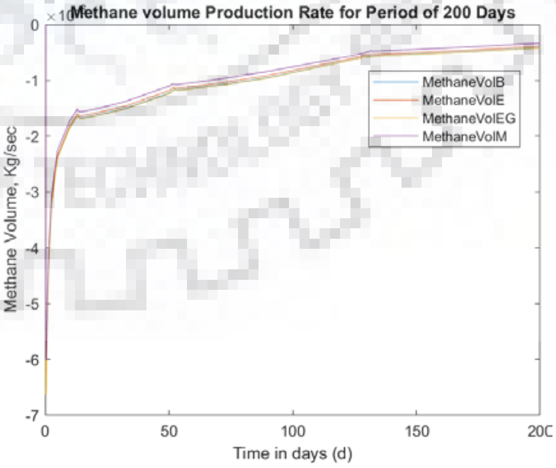


Fig 5.6.1(a) Methane Mass Comparison **Fig 5.6.1(b)** Methane Volume Comparison

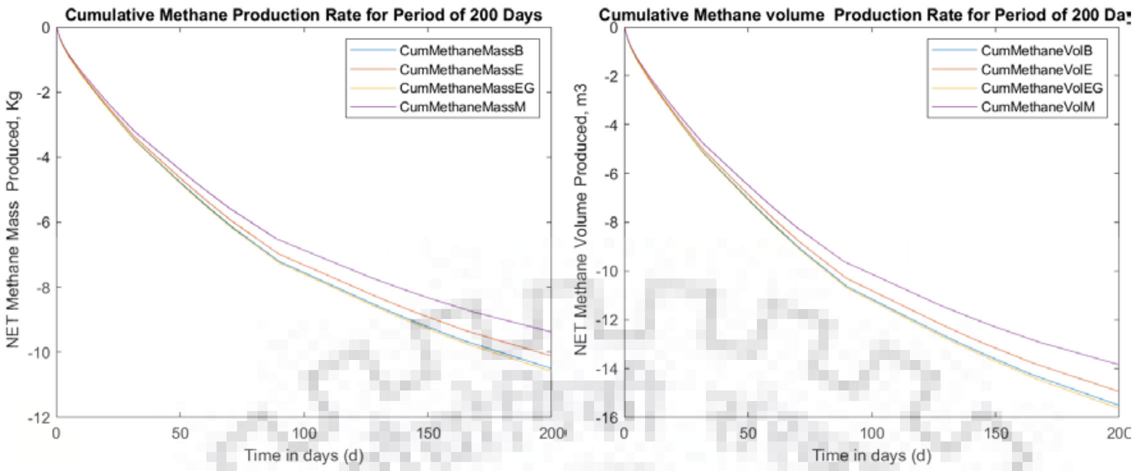


Fig 5.6.1(c) Cumulative Methane Mass Comparison **Fig 5.6.1(d)** Cumulative Methane Volume Comparison

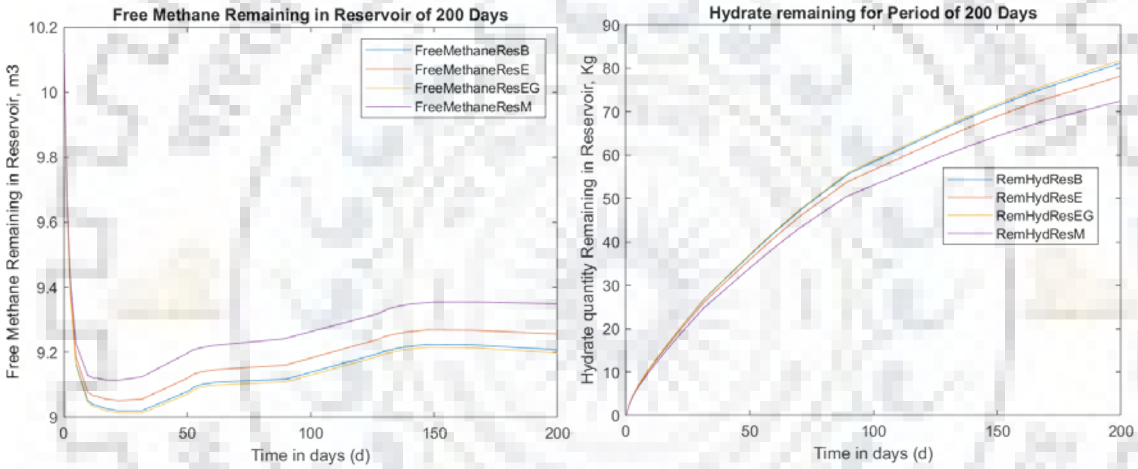


Fig 5.6.1 (e) Free Methane Mass Comparison **Fig 5.6.1 (f)** Remaining Hydrate in Reservoir

Fig. 5.6.1 Inhibitor Vs Parametersfor site 2_23

From Table5.6.2 and plots in Fig. 5.6.1, the increasing order of efficiency in Test 1TbS for NGHP Site 2_23 is **Ethylene Glycol <Brine < Ethanol< Methanol**. So, Methanol inhibitor is used in Test TbS for its comparison with other tests.

Table 5.6.3 Tests vs Parameters for Different Tests on site 2_23

Method	Time(d)	CH4 Mass Rate (kg/s)	CH4 Vol Rate (m3/s)	Cum CH4 Mass (kg)	Cum_CH4_Vol (m3)	FreeCH4inRes (m3)	Remain Hydrate (kg)
1P	1.0000000E+01	-7.5765138E-08	-1.1192329E-07	-1.4949501E-01	-2.2084001E-01	0.0000000E+00	2.9834906E+02
1P_ice	2.0000000E+02	1.9219190E-07	2.8391357E-07	4.3799549E+00	6.4702446E+00	4.5744947E-01	2.6531638E+02
1_Pk	1.9277823E-01	-7.1580561E-07	-1.0574167E-06	4.9493831E-01	7.3114266E-01	0.0000000E+00	2.9336268E+02
1T	6.7850694E+01	0.0000000E+00	0.0000000E+00	3.8652395E+01	5.7098864E+01	2.1189314E+01	0.0000000E+00
1_TbS_m	2.0000000E+02	-2.4758535E-07	-3.6574298E-07	-5.7649043E+00	-8.5161473E+00	1.3109957E+01	4.4606628E+01
1_TbSk_m	4.5473900E+01	-3.0284038E-07	-4.4736792E-07	-2.0589539E+00	-3.0415691E+00	1.3049524E+01	1.5931399E+01

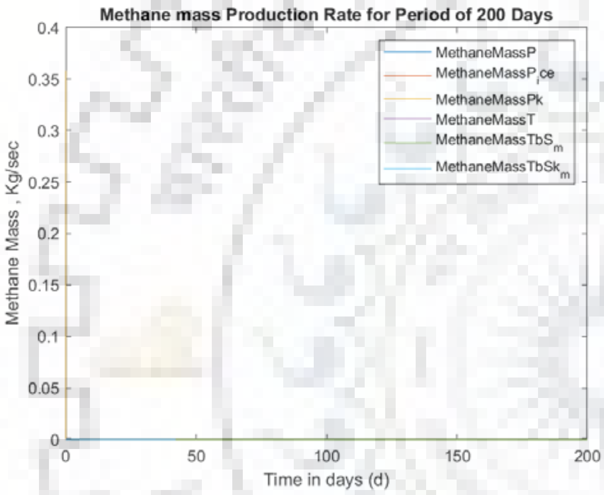


Fig 5.6.2(a) Methane Mass Comparison

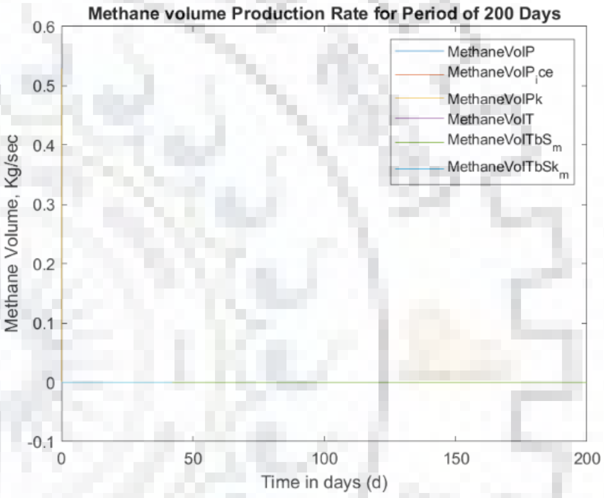


Fig 5.6.2(b) Methane Volume Comparison

In fig 5.6.2(a), Methane mass production is absent for 1T case while maximum value is observed for 1P_ice case. In fig 5.6.2(b), Maximum Methane volume production rate is observed for 1P_ice case while negative value is some cases shows formation of Hydrates.

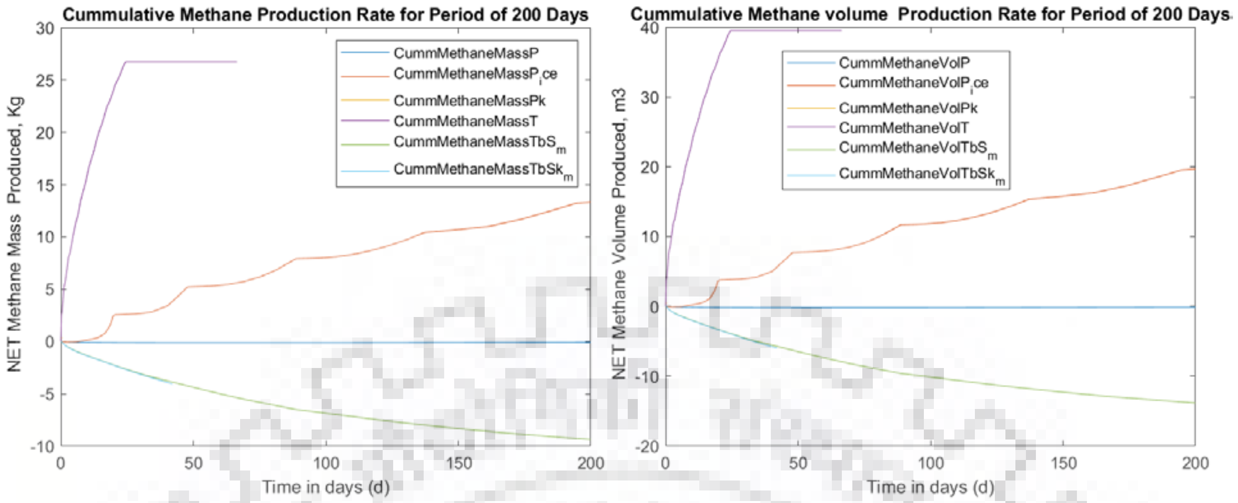


Fig 5.6.2 (c) Cumulative Methane MassComparison**Fig 5.6.2 (d)** Cumulative Methane Volume Comparison

In fig 5.6.2(c), A continuous increase of Cumulative Methane Mass is seen in 1T case which remains constant for next interval of days while 1P_ice and 1TbS_m cases show it lasts for complete 200 days. In Fig 5.6.2(d), Similar trend as in fig 5.6.2(c), is observed for all the cases for Cumulative Methane Volume production.

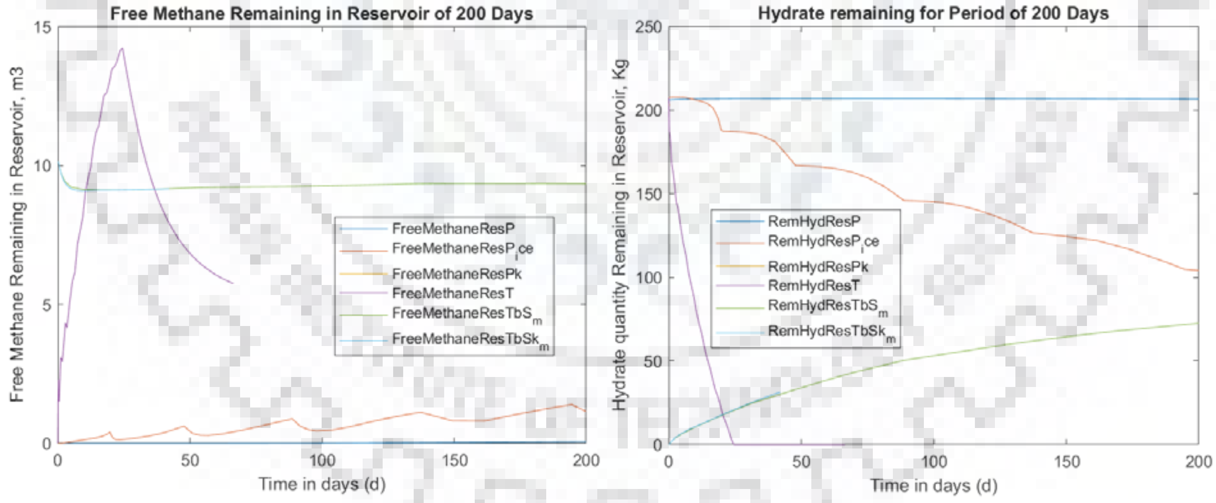


Fig 5.6.2(e) Free Methane Mass Comparison **Fig 5.6.2(f)** Remaining Hydrate in Reservoir

Fig. 5.6.2 Test Vs Parametersfor site 2_23

In Fig 5.6.2(e) Maximum amount of Free Methane Mass is seen for 1T case which lasts for 68 days while it is absent for 1P case. In fig 5.6.2(f) Remaining Hydrate in Reservoir is absent for

1T case while maximum quantity is observed for 1P case which is not suitable to produce methane easily from Gas Hydrates.

5.7 Determination of Cellulose percentage in acid pre-treated Wheat Straw

5.7.1 Materials and Methods

1. Purchased the wheat straw from the local market of town. Taken a sample of 50 g and measure its initial weight (Wet weight). Dry it using oven at 70 °C for 5 hours. Measure the weight of dried wheat straw sample.
2. Calculated the moisture content.

$$\text{Moisture content} = [(w-d)/w] \times 100 = 12.18\%$$

w = wet weight
d = weight after drying

3. Convert the dried wheat straw into powdered form using grinder. After which it was sieved through mesh sieves [22].

5.7.2 Chemical Pretreatment

Inorganic acid H_2SO_4 has been used for pretreatment of wheat straw to improve downstream enzymatic hydrolysis.

1. For dilute acid pre-treatment of wheat straw, low-concentration acids such as 1%, 2%, 3%, 4% and 5% were prepared.
2. Soaked the 2 gm of biomass i.e. wheat straw powder in each of the 2 sets of above mentioned acid samples of 20 ml. Then, autoclaved it for 60 and 90 minutes separately.
3. Then, it was neutralized it to pH 7 using 1M NaOH.
4. The sample was dried again and then FTIR analysis of acid pretreated wheat straw was carried out.

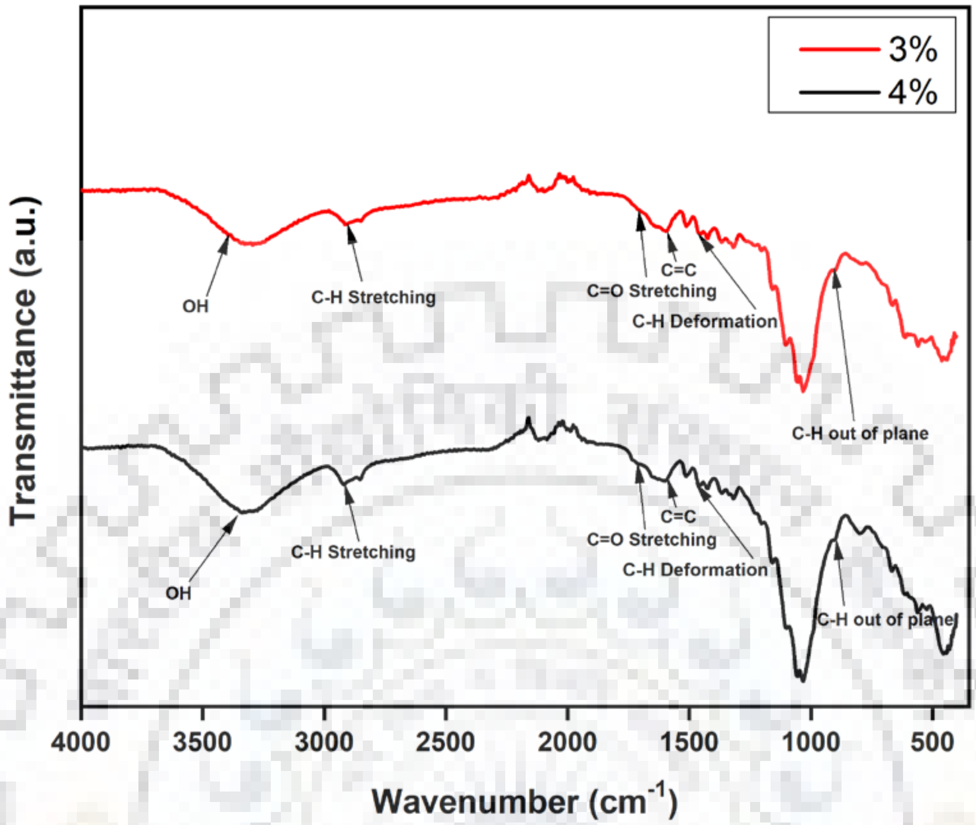


Fig. 5.7.1 FTIR Spectra of 3% and 4% acid pretreated wheat straw for 90 min.

Table 5.7 Assignment and description of peaks corresponding to functional groups of biomass components by FTIR analysis.

Wave number cm^{-1}	**Functional Group assignment**	**Related Biomass Component**
3400–3200	O-H stretching (hydrogen bond)	Cellulose
2910	C-H stretching	Cellulose
1720	C=O stretching	Hemicellulose/lignin
1650–1515	C=C aromatic skeletal vibration	Lignin
1465	C-H deformation	Lignin
900	C-H out of plane	Cellulose

After this process, Calculation of Cellulose percentagein 3% and 4% acid pretreated wheat straw sample for 90 minutes was carried out.

Fig. 5.7.2 Sample preparation step of 3% and 4% acid pretreated samples in the flasks for HPLC

5.7.3 Percentage of Cellulose in Samples

For 3%(1) sample, the calculated cellulose percentage= 47.27%

For 3%(2) sample, the calculated cellulose percentage= 50.98%

For 4%(1) sample, the calculated cellulose percentage= 53.57%

For 4%(2) sample, the calculated cellulose percentage= 52.26%

Hence, Highest percentage of cellulose is found in 4%(1) H_2SO_4 pretreated sample in which Hemicellulose and Lignin got Solubilized. So, our main focus is on conversion of cellulose to glucose.

5.8 Discussion

Methanol used as an inhibitor is Test 1TbS and 1TbSk gives better results as compared to other inhibitors namely Ethanol, Brine and Ethylene Glycol for 4 sites out of 5.

The comparison of Tests 1P, 1P_ice,, 1Pk 1T,1TbS, 1TbSk with respect to parameters namely Methane Mass Production Rate, Methane Volume Production Rate, Cumulative Methane Mass Production Rate, Cumulative Methane Volume Production, Free Methane Mass in Reservoir and

Remaining Hydrate gives complete scenario of Methane and Gas hydrate quantities inside the reservoir.

For NGHP site 2_08, only 1TbS_m test runs for complete time interval of 200 days. Similarly, for site 2_17 it is tests 1P_ice, 1Pk, 1TbS_m; for site 2_19 it was 1TbS_m; for site 2_22, it is 1P_ice, 1TbS_m and for site 2_23, it is 1P_ice and 1TbS_m tests which runs for selected time duration of 200 days.

Analysis of plots gives the complete coverage for different test on the specific reservoirs according to its properties.

Conclusion

1. The increasing order of efficient inhibitor in Test 1TbS for Free CH_4 in the reservoir cumulative CH_4 production in mass and volume for NGHP Site 2_08 and 2_17 is Brine < Ethylene Glycol < Ethanol< Methanol. For NGHP SITE 2_19, 2_22 and 2_23, it is found as Ethylene Glycol < Brine < Ethanol< Methanol.

2. Methane Mass Production Rate, Methane Volume Production Rate, Cumulative Methane Mass Production Rate, Cumulative Methane Volume Production, Free Methane Mass in Reservoir and Remaining Hydrate in the Reservoir are predicted by T+H simulation and compared with different Tests for NGHP-02 sites 2_02, 2_17, 2_19, 2_22 and 2_23 respectively.

3. The properties of reservoirs such as Grain Density, Permeability, Porosity and Thermal Conductivity plays significant role in dissociation of Methane from Gas Hydrate. So, a suitable Method must be chosen according to properties of the reservoir.

4. High permeability of rock inside the methane hydrate sediment leads to higher production of Methane and vice-versa. The Hydrate reformation condition occurs when free gas released after dissociation of gas hydrates is not taken out.

5. Cost factor must be considered for production of Methane from Gas hydrates while selecting Technique for its dissociation.

6. The 4% H_2SO_4 acid pretreated sample autoclaved for 90 minutes had highest percentage of cellulose (i.e., 53.57%) as compared to others. Hence, it can be considered for further procedure.

Future Work

1. More studies are needed to predict and analyze the dissociation of gas hydrates at different reservoirs and conditions.
2. Synthesis ofeconomic and environment-friendly Inhibitor for dissociation of Methane from Gas Hydrates.

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