## Natural Gas Hydrates: Technical Review and Prospects in Asia

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Abstract— Even as petroleum E&P activities increase to meet the ever-increasing global energy demand, there is need to address the environmental concerns associated with burning of fossil fuels. Natural gas is a cleaner fuel that has been identified as a strategic energy resource that will meet the present demand while minimizing carbon dioxide emissions. The presence of massive natural gas hydrate deposits widely distributed globally presents enormous potential that can be harnessed to attain energy sustainability. India, China and Japan have been at the forefront of research and exploration of gas hydrates in Asia. Though remarkable exploration and production results in the field tests have been observed, sustained efficient production, maintaining mechanical integrity of the formation and disposal of the produced water remain as challenges that must be addressed before commencing production at a commercial scale. This paper presents comprehensive insights on natural gas hydrates as an energy source and reviews the advancements made in exploring natural gas hydrates in Asia as well as the challenges encountered.

Keywords—Energy and Environmental sustainability, Hydrate dissociation, Hydrate structures, Natural gas hydrates

#### I. INTRODUCTION

The world still depends heavily on fossil fuels to supply its ever-increasing energy demand. In 2019, 84% of the global energy consumption, as represented in Fig. 1, was fossil-based [1]. This dependence on fossil energy is projected to continue beyond two decades from now [2]. In Asia, China and India stand out as major global contributors to the growing energy consumption with coal production supplying the largest share. On the flip side, burning of these fuels has led to an increase in global carbon dioxide emissions by 15% in the last ten years [1]. Asia contributes more than 50% to these emissions with China on the lead (Fig. 1). Because of the intense pressure to manage the carbon cycle, governments have enforced stringent regulations to reduce these emissions and placed emphasis on renewable sources of energy [3]. This has seen some growth in renewable energy though its contribution

to the global share is still limited, currently standing at just 5%. In this view, shifting dependence from coal to natural gas will help decelerate the increase of carbon dioxide emissions while sustainably supplying the current demand. Natural gas is a cleaner fuel because of its low carbon dioxide emissions, low residue and no oxides of sulphur or nitrogen are emitted when it is burned. The current global consumption of natural gas is 3929 billion cubic metres (BCM) which is a 33% increase over a decade. The highest consumers are the United States of America, Russia, China and Canada respectively [1]. It is worth noting that while natural gas consumption in the US has grown by 37% in the last decade, the country's carbon dioxide emissions have reduced by 6% over the same time period. It is therefore evident that by utilizing the available natural gas reserves, countries in Asia can effectively reduce their carbon emissions. It is estimated that there are sufficient natural gas resources (both conventional and unconventional) for over 200 years supply going by the current trends of demand [4]. Currently, the world relies on conventional natural gas resources but with the envisioned increase in demand, there is need to add unconventional sources like coal bed methane, shale gas, tight gas and natural gas hydrates to the energy mix [5]. Tapping into the enormous potential of natural gas hydrates can unlock the much-sought energy sustainability.

Since the first discovery of hydrates in 1967, efforts have been made to estimate the global gas hydrate reserves [6]. It is postulated that gas hydrates are the most abundant fossil fuels fairly evenly distributed across the world (Fig. 2). The initial reserve estimates were approximately 3053 x 10<sup>15</sup> cubic metres at standard temperature and pressure [6]. With increased understanding and accuracy for estimation of gas hydrate quantities, this value has reduced but still remains significantly higher that other conventional unconventional fossil fuel reserves worldwide. The United States Geological Survey (USGS) in 2001 estimated the global hydrate reserves to be in the range of 100,000 to 300,000,000 trillion cubic feet (TCF) [7]. Over the years, the paradigm has changed from estimation to extraction technologies which is the focus of this review. A detailed technical review of natural

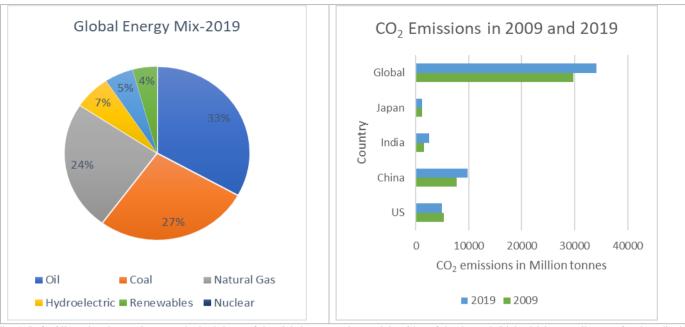


Fig. 1: Left: Oil, coal and natural gas are the back-bone of the global energy mix supplying 84% of the demand; Right: Major contributors of carbon dioxide emissions and the changes in emissions globally between 2009 and 2019 [1]

gas hydrates is presented and the hydrate potential of Asia discussed in subsequent sections.

#### II. NATURAL GAS HYDRATES: TECHNICAL REVIEW

The past two decades has seen tremendous advances in the study area of hydrate chemistry and engineering. This increased interest is fueled by the significance of hydrates in a wide array of disciplines. In the oil and gas industry, flow assurance issues were the primary driving force for the study of gas hydrates. It was necessary to detect and control hydrate formation in flowlines and pipelines, particularly in deep subsea conditions [8]. To reduce chances of hydrate formation, subsea pipelines were buried, insulated or thermodynamic inhibitors were constantly pumped into the pipeline [9]. Methanol was the most popular due to its ease of availability. In cases of already formed hydrates, depressurization, heating and chemical injection methods were applied. Hydrates have also been studied as a method of energy storage. Storage of natural gas in form of hydrates requires less space than Liquefied Natural Gas (LNG) and is safer [10]. The same principle can be applied for the storage of hydrogen gas [11]. In addition, by utilizing the heat of fusion of hydrates, they can be used to store cool energy [12], [13]. The game changing application of the knowledge of gas hydrates is the exploitation of hydrate bearing sediments as a source of energy. Gas hydrates may not be the energy source for the future but they are certainly strategically reliable in the transition from conventional carbon fuel to renewables.

Natural gas hydrates (NGHs) are solid compounds composed of gas molecules (guests) trapped within cage-like structures formed by water molecules (hosts) [14]. They are formed under low temperature and high-pressure conditions.

They differ from normal ice in that there must be a guest molecule present to form hydrates while ice can solidify in pure state. Besides, NGHs are crystalline and nonstoichiometric [13]. Natural gas hydrates fall under the clathrates group of solid gas-water mixtures in which the guest molecules are bound to the host lattice by Van der Waal's forces of attraction [9]. A single cage formed by water molecules has a maximum occupancy of one guest molecule. Some common guest molecules in gas hydrates are: methane, ethane, propane and carbon dioxide. In pure hydrates, adjacent cages have the same guest molecules while in mixed hydrates, adjacent cages may contain different types of guests. The proportion of the constituents of gas hydrates influence the stability of gas hydrates. It is expressed by the hydration number which is the number of host molecules per guest molecules present in a cage [14]. Cage occupancy and the structures formed by hydrates are discussed in subsection C of this article. Typically, 85% of a crystal of gas hydrate consists of water molecules. Gas hydrates are said to be gas concentrators due to their high energy content. When 1 unit of gas hydrate is broken down it releases 160 units of free natural gas in volume at standard temperature and pressure. Methane is a powerful greenhouse gas with 21 times more potential than carbon dioxide. By exploiting natural gas hydrates, direct methane gas emissions to the atmosphere can be avoided. In this sense, natural gas hydrates are strategic in attaining energy and environmental sustainability.

#### A. Occurrence of gas hydrates

Natural gas hydrate deposits are fairly evenly distributed in the world and can be found in two geological settings: marine or permafrost.

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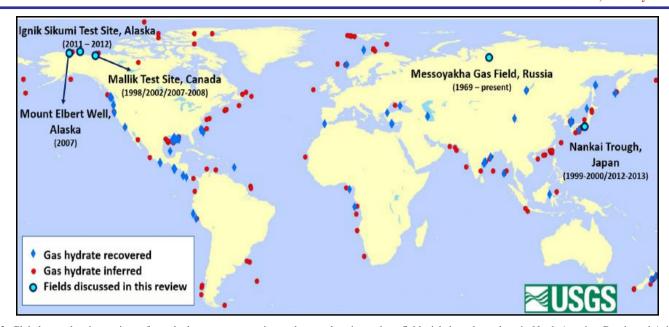


Fig. 2: Global map showing regions of gas hydrate occurrence sites and some locations where field trials have been done in North America, Russia and Asia, courtesy [2].

Marine reserves are estimated to be more than the permafrost reserves in more than two orders of magnitude[15]. In these two settings, the gas hydrate stability zones (GHSZ) differ due the geothermal gradients. The GHSZ is the envelope formed by the geothermal gradient line and the hydrate phase boundary as shown in Fig. 3. The intersection of the lines gives the upper and lower boundaries for gas hydrate existence. In marine settings, hydrates are found typically along the continental shelf at water depths between 300 and 800m due to increased sedimentation and high organic matter content[14]. From Fig. 3, it can be seen than hydrates occur at shallower depths in permafrost than in marine settings. It is noted also that the span of occurrence of hydrates beneath the ocean is quite limited due to the geothermal gradient that rapidly yields high temperatures as the depth increases. Apart from pressure and temperature, the gas composition of the hydrates influences the zone of stability. The presence of heavier components such as propane results in a shift of the phase boundary thus increasing the stability zone. Because of this reason, mixed hydrates can be found at deeper zones than methane hydrates but not exceeding 2000m due to the geothermal gradient[2]. Permafrost hydrates are largely found in Russia, Canada, Alaska China [16]. Marine hydrates on the other hand are found in many oceans across the globe. Some marine fields that have been studied include Nankai trough of Japan, The East and West coast of India, Black sea and Caspian seas of Russia and the South China Sea[7].

#### B. Formation of gas hydrates

Formation of natural gas hydrates requires the presence of both natural gas and water at low temperature and highpressure conditions. Similar to other fossil fuels, natural gas is a product of organic matter transformation[17]. The gas can either be of biogenic or thermogenic origin. Biogenic gas is formed by the action of methanogenic bacteria on organic matter at non-oxidizing conditions. This process of transformation is called diagenesis and the product is predominantly methane gas. At greater depths and higher temperatures, thermogenic gas is generated through thermocatalysis. This gas contains heavier gases including ethane and propane. To form hydrates, the generated thermogenic gas has to migrate through faults and fissures from deep high temperature zones to shallower cooler regions[14]. Due to this migration, most of the hydrates composed of thermogenic gas give a wide BSR response (discussed in subsection E) because of localized accumulations.

Within the hydrate stability zone and in the presence of formation water, hydrates then form in two stages: nucleation and growth. Nucleation is the initial stage in which small groups of water molecules combine with gas and grow to a size that can sustain propagation[18]. It is analogous to precipitation in a saturated solution. While in precipitation the driving force is supersaturation, the driving force for nucleation is equilibrium thermodynamics. The starting point for hydrate formation is supercooled water and it takes place at a microscopic level. Nucleation in nature is heterogenous i.e., takes place in presence of an impurity and is a random process. In coarse-grained sediments, hydrate formation starts at the grain boundaries and extends towards the pore space[19]. Such is the case with Nankai trough (Japan) and Mallik (Canada) sites. In fine sands, the hydrates cement the grains forming part of the rock matrix. These sediments have been observed in India, South China Sea (SCS) and Gulf of Mexico (Fig. 4). The second stage of hydrate formation is growth. It involves the propagation of crystal development into massive structures. Growth has been described by three models: mass transfer, heat transfer and intrinsic kinetics[14].

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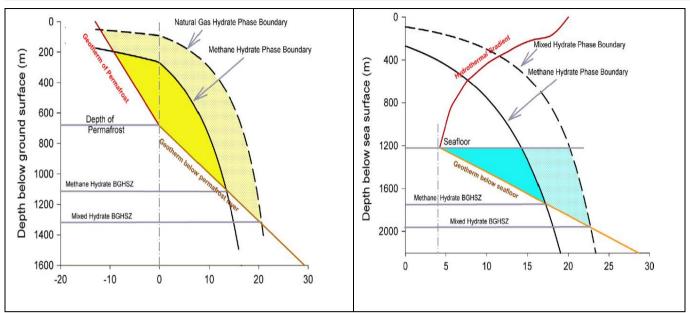


Fig. 3: Phase diagrams for natural gas hydrates in permafrost environment (left) and marine settings (right) showing zones of methane gas hydrates and mixed gas hydrates [2].

In sum, four conditions must be present for gas hydrates to form: Low temperatures; high pressure; presence of a small non-polar molecule such as methane; and presence of water molecules. The presence of methane is often an overlooked factor but it is absolutely important for hydrate stability as presented in the next subsection.

#### C. Structures of Gas Hydrates

NGHs fall under the clathrates class of solid gas-water compounds [9]. This class is distinguished from the semi clathrates by the nature of the bond between the host and guest molecules. In clathrates, guest molecules are held within host cages by Van-der-Waal forces of attraction while in semiclathrates, the guest molecules physically attach to the host molecules. Semi-clathrates are stable at atmospheric pressures while clathrates form under high pressure conditions. Natural gas hydrates occur in three different structures in nature: cubic structure I (sI), cubic structure II (sII) and hexagonal structure (sH) [2], [9] . To better understand these structures, it is important to first highlight on the types of cavities formed by water molecules in hydrates. There are five kinds of cages as detailed in Table 1. The faces are formed by water molecules bonded by hydrogen bonds that enclose a cavity in which the guest will reside.

A combination of these cavity types then forms the three basic structures of hydrates. It is worth noting that the pentagonal dodecahedron cavity type is common in all the three structures. The cavity size determines the type of guest molecule that can be accommodated by the structure with each cavity having a maximum occupancy of one guest molecule. It is the presence of the guest that stabilizes the hydrate. However, very small molecules (less than 3.5 Å) cannot stabilize any cavity.

# i. *Cubic structure I (sI):* The sI structure is described as primitive and is formed by small guest molecules, predominantly methane. It is made by the pentagonal dodecahedron and tetrakaidecahedron cavity types. This structure hosts molecules of sizes between 4.2 Å and 6 Å. Common guests of the sI structure are: methane, ethane, carbon-dioxide and hydrogen sulphide.

- ii. Cubic structure II (sII): The sII structure is formed by pentagonal dodecahedron and hexakaidecahedron cavity types and is often described as a face-centered structure. It forms the smallest cavity that accommodates guests of sizes lower than 4.2 Å. Gases with small molecular diameters such as argon, krypton, hydrogen, nitrogen and oxygen often form the sII structure. Propane and isobutane molecules also form sII hydrates and are hosted in its larger cavities that are formed by 28 water molecules per cavity.
- *Hexagonal structure (sH):* This structure is formed by pentagonal dodecahedron, irregular dodecahedron and icosahedron cavity types. It forms the largest cavities than can host both small and large guest molecules. Large cages have a higher occupancy because they can host both small and large guests. Large guest molecules can be fractions of oil or condensate such as isopentane and neohexene which are hosted in cavities of size 7-9 Å while smaller molecules of isobutane and propane are hosted in cavities of size 6-7 Å. These guest molecules exist in combination with methane, hydrogen sulphide and nitrogen molecules. The hexagonal structure is therefore common in mixed gas hydrates that occur in deeper reservoirs. The schematics of these structures and their formula are given in Table 2. There are other structures like Jeffrey structures III, IV, V, VI,VI, VII and T that are uncommon in natural gas hydrates and form at very high pressures in the range of Gigapascals [20].

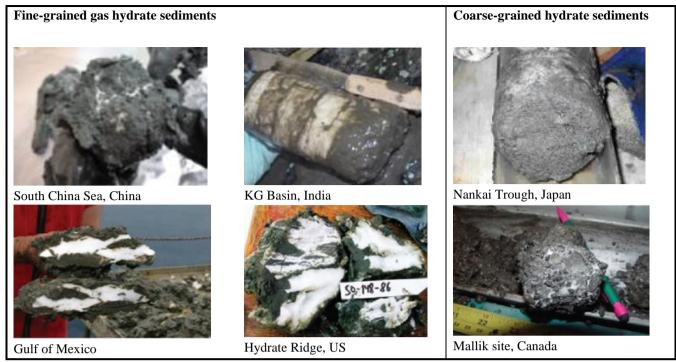


Fig. 4: Fine-grain and coarse grain samples of gas hydrate bearing sand from various drilling expeditions, courtesy [9]

#### D. Properties of gas hydrates

For successful exploration and production of gas hydrates, it is key to understand their properties. Mechanical, electromagnetic and thermal properties play the greatest role in hydrate exploration.

#### Mechanical Properties

The presence of gas hydrates in sediments influences the strength of the formation and consequently impacts stability when extracted. How the hydrate forms in the formation determines its contribution to the mechanical strength of the sediments. This form is dictated by depositional environment and lithification process[14]. To describe the strength of the hydrates, various elastic moduli are measured including Young's modulus, bulk modulus, shear modulus of rigidity and Poisson's ratio. These are measured by Ultrasonic pulse transmission or Raman spectroscopy. Studies have shown that methane hydrates have higher compressive strength, creep and elasticity than pure ice[21]. The strength is influenced by the composition and structure; consolidation of the sediments; cage occupancy and temperature. Hydrates existing at low temperature have higher strength than those close to the phase boundary. Understanding how the mechanical properties of hydrates change with dissociation is key in ensuring the stability of subsea pipelines and production platforms.

#### Thermal Properties

Thermal conductivity is a measure of the ability of a material to conduct heat. NGHs exhibit anomalous heat conductivity behaviour, similar to glass. Transient Hot Wire (THW) and Transient Plane Source (TPS) techniques are used to measure the thermal conductivity of hydrates. The TPS is

preferred for in-situ measurements because it is adaptable to field setups as opposed to THW. Thermal diffusivity is a measure of the thermal inertia of the hydrates and is measured by similar methods. Another thermal property of importance is the calorific value. It is a measure of heat energy contained or can be extracted from a material due to temperature difference. Calorimetric analysis is done using specific enthalpy data and the mass fractions of hydrates, fluids and rock grains. This information is used to calculate the energy requirement for extraction and hence guide in deciding the economical method to be applied[22]. A heat flow calorimeter is used in measuring the calorific value of hydrates. The accuracy of the measurements depends on the vapor pressure of gas hydrates and the distribution of free water.

#### iii. Electromagnetic properties

The electrical conductivity of gas hydrates is lower than that of aqueous solutions. It depends on the occupancy of the pores and the concentration of ions. When conducting the resistivity log, a higher resistivity is recorded for hydrate zones compared to free gas or water zones. Impedance spectroscopy and Controlled Source electromagnetic (CSEM) methods are used in inferring hydrate saturation through application of the Archie's equation[23], [24].

#### E. Exploration of Gas Hydrates

Various methods have been used to determine where gas hydrates occur. Bottom Simulating Reflector (BSR) is a seismology technique that infers the bottom boundary of hydrate zone from the travel time recorded for acoustic waves emitted into the ocean[2]. Due to the acoustic impedance between the hydrate zone and an underlying free gas zone, a

No.	Cavity type	Formula	Description	Schematic
1	Pentagonal dodecahedron	512	Has 12 pentagonal faces/sides	
2	Tetrakaidecahedron	51262	Has 14 faces: 12 pentagonal face and 2 hexagonal.	
3	Hexakaidecahedron	51264	Has 16 faces: 12 pentagonal faces and 4 hexagonal.	
4	Irregular dodecahedron	435663	Has 12 faces: 3 squares, 6 pentagonal and 3 hexagonal	
5	Icosahedron	51268	Has 20 faces: 12 pentagonal and 8	MIT

hexagonal.

sharp decrease in velocity is recorded at the boundary. Seismic velocities of up to 2000m/s are recorded in the hydrate zones which sharply fall to 1500m/s in the free gas zone below the BSR. Whilst most oceanic hydrates have been identified through BSRs, some hydrate deposits have been known to exist without a BSR and vice versa [14], [25]. Since the BSRs only give the lower boundary of the hydrate reservoir below the ocean, more geological and petrophysical data is required to assess the extent of the reservoir and the hydrate content. Drilling and logging are done, which are also useful in permafrost hydrate exploration. The presence of hydrates can only be ascertained through correlation of a series of logs. Typical log records for gas hydrate zones are summarized in Table 3. Secondary methods of gas hydrate exploration involve core analysis done by X-ray Computed tomography (CT), Infra-red temperature sensing, pore water chlorinity and gas evolution tests. Pressurized cores give more accurate data as they preserve the initial condition of the hydrates but are difficult to handle and can fail due to sudden pressure variations.

#### F. Extraction of Gas Hydrates

Because gas hydrates are held immobile within cage patterns created by water molecules, extraction requires destabilizing the hydrate molecules by breaking the intermolecular forces between gas and water molecules to release the gas; and creation of flow channels for the gas to

flow to the wellbore. Dissociation can be achieved by changing the in-situ pressure- temperature conditions or shifting the equilibrium conditions so that the gas occurs free at the prevailing reservoir P-T conditions[19]. There are three primary methods of extraction of gas hydrates: depressurization, thermal stimulation and chemical inhibition. Dissociation is an endothermic process whose rate depends on the dynamics of heat transfer within the hydrate zone. Regardless of the method of extraction, dissociation of hydrates occurs in a radially not axially[14].

#### i. Depressurization

In depressurization, the gas is produced by lowering the pressure of the hydrate reservoir to stimulate dissociation. When a hydrate reservoir exists with an underlying free gas zone, depressurization is done by producing the free gas causing a reduction in pressure. This induces dissociation of hydrates occurring at the base of the hydrate zone to release gas into the free gas zone below. It is a slow and localized process because it is dependent on heat transfer dynamics through the hydrate reservoir but it is economical[26]. The heat required to sustain the endothermic dissociation process is obtained from the surrounding rocks. To accelerate production, an external source of heat may be incorporated in combination with lowering of pressure. This principle has been applied for producing gas from the Messoyakha field of North East Siberia[27].

Table 2: Schematic representation of hydrate cubic and hexagonal hydrate structures, courtesy [2], [9] [28]

Structure	Schematic	Unit Cell Formula
Cubic structure I (sI)	Representation	6(5 <sup>12</sup> 6 <sup>2</sup> ).2(5 <sup>12</sup> ).46H <sub>2</sub> O
Cubic structure II (sII)		8(5 <sup>12</sup> 6 <sup>4</sup> ).16(5 <sup>12</sup> ).136H <sub>2</sub> O
Hexagonal structure (sH)		1(5 <sup>12</sup> 6 <sup>8</sup> ).3(5 <sup>12</sup> ).2(4 <sup>3</sup> 5 <sup>6</sup> 6 <sup>3</sup> ).34H <sub>2</sub> O

This field has been producing hydrates from a permafrost setting for 17 years since 1971. Production of gas started from the free gas zone and after two years, dissociated gas from the overlying hydrate layer was produced. It is estimated that 36% of the gas production from this field is from the hydrate reservoir [14].

#### ii. Thermal Stimulation

In thermal stimulation, heat is introduced in the hydrate zone by injecting steam or hot water; by electric or by acoustic means to raise the temperature above the stability phase causing the hydrates to dissociate and release gas. As discussed in hydrate properties, the amount of heat required is estimated based on the thermal conductivity of the hydrate bearing sediments. Some heat sources that have been experimentally investigated for thermal stimulation are: injection of hot water, In-situ combustion of methane and electromagnetic heating through microwave energy[2]. Thermal stimulation has not been applied in many field trials as it is considered inefficient due to huge losses of heat energy[6]. In addition, release of gas after dissociation results in an increase in reservoir pressure consequently shifting the equilibrium conditions.

#### iii. Chemical inhibition

Chemical inhibition works by shifting the gas hydrate phase boundary. When chemicals are introduced into the reservoir, the phase boundary is shifted to higher-pressure-lower-temperature so that gas occurs free at the existing reservoir conditions. Salts, alcohols and glycols are commonly used thermodynamic inhibitors used to dissociate hydrates. They act by competing for water molecules by forming hydrogen bonds. Gas production rate by this method depends on the concentration and injection rate of the chemical inhibitor; temperature; pressure and interfacial interaction between the hydrate and inhibitor[2]. Methanol is the most popular of all the alcohols used for chemical inhibition

because it is readily available and cheap. Over time, methanol has lost its popularity because of high handling costs as it has a low flash point that poses a safety threat and it is difficult to recover from the produced hydrocarbons[14]. Ethylene glycol is the preferred alternative because of ease of handling and is less toxic [29]. Other inhibitors used are mono-ethylene glycol (MEG), diethylene glycol (DEG) and tri-ethylene glycol (TEG) because of their ease of recovery. Salts have also been used as inhibitors[30]. They ionize when in solution and interact with the dipoles of the water molecules of the hydrates. These water molecules are more attracted to the ions than to the hydrates thus stimulating dissociation. The main challenge they pose, however, is salting out when applied at a higher concentration which limits the rate of recovery that can be attained when extracting using salt. Chemical inhibition has not applied in many fields but was tried at initial stages of production from Messoyakha[27]. The anticipated results were not achieved by using methanol leading to a shift to production through depressurization.

Besides these three primary methods of extraction of gas hydrates, CO<sub>2</sub> injection has been studied[31]. It is considered as a variation of chemical injection that involves substitution [32]. As established earlier, methane and carbon dioxide gases both form the cubic structure I of hydrates. Injection of CO<sub>2</sub> into methane hydrate formations results in an exchange process where methane gas is liberated and CO2 replaces it forming CO<sub>2</sub> hydrates. In this method the heat released by CO<sub>2</sub>- hydrate formation is simultaneously used to stimulate CH<sub>4</sub>- hydrate dissociation making it a potentially selfsustaining process[2]. In addition, the exchange process maintains the geo-mechanical integrity of the subsurface strata eliminating chances of collapsing and unintended methane gas release. It was tried in a field test at Ignik-Sikumi field, Alaska in 2012 where it resulted in production of 855MSCF of methane gas with injection of 48.6 MSCF of CO2 over a 6week period [6], [33]. Other combination methods that have been suggested are the huff-and-puff method, hot brine and a combination of depressurization and chemical inhibition[34], [35].

#### III. FIELD CASES IN ASIA

This section provides a review of gas hydrate exploration in India, China and Japan focusing on the outcomes of the expeditions carried out and the challenges holding back commercial production.

#### A. India

The economic potential of natural gas hydrates in India was established in 1997 and since then three exploration expeditions have been done under the National Gas Hydrate Programme (NGHP). Significant reserves were established in NGHP01 at the Krishna-Godvari (KG) basin, Mahanadi & Andaman basins along the East coast and Kerala-Konkan

Table 3: Typical well log responses for gas hydrate bearing zones [14]

No.	Type of Log	Response in hydrate zones
1	Mud log	Increase in gas content of return mud due to dissociation of hydrates.
2	Resistivity Log	Increase in both shallow and deep resistivity compared to free gas zone.
3	Spontaneous Potential Log	Less negative than free gas zone
4	Caliper log	Larger diameter borehole due to dissociation of hydrates
5	Acoustic log	Decreased travel time than both water and free gas zones
6	Neutron log	Similar to response in water zones
7	Density log	Lower density than water zones but close to ice.
8	NMR	Used to infer hydrate concentration indirectly from porosity readings.
9	Rate of Penetration (ROP)	Decreased compared to zones filled with fluids

basin on the West coast. Of these basins, KG basin contains the highest amount of hydrate reserves estimated at 134 TCF deposited in 130m thick hydrate-bearing zones [36], [37], [38]. In 2015 under NGHP02, 42 wells were drilled, cored and logged in four areas (A, B, C & E) and formation pressure tests done [7]. Of the four areas studied in this expedition areas B and C in KG basin were identified as the as prime locations for the planned production testing in the third expedition. NGHP03 is planned to be executed in three phases. In the first phase, the geologic, reservoir, flow and geo-mechanical models will be prepared to carve the plan of action for production testing. It will also cover cost projections, environmental impact assessments and tendering for rig services. Phase two will entail further logging and core analysis to validate the developed models before actual production testing is done in the third phase. The third phase will finalize the evaluation of the resource potential of natural gas hydrates in India by production testing paving way for commercial production if successful [39].

#### B. China

China has both permafrost and marine gas hydrates [40]. Permafrost hydrates are found in the Qinghai-Tibet Plateau with estimated gas reserves of 0.12 trillion cubic metres (TCM). In 2008, the China Geological Survey (CGS) drilled

four exploratory wells in Qilian mountains establishing abundant mixed gas hydrates of cubic structure II. Marine hydrates, on the other hand, are found in South China Sea (SCS). The Guangzhou Marine Geological Survey (GMGS) has undertaken to explore and develop this resource since 2007. In the first expedition, GMGS1, gas hydrates were confirmed by the BSR technique in the Shenzu area of SCS. GMGS2 explored the Pearl River mouth basin discovering gas hydrates accumulated in a coarse sand reservoir of two zones with total thickness of 49m. A simulation study done following this survey projected an expected gas recovery of 6700 cubic metres/day [41]. The third expedition, GMGS3 was done in 2015 in collaboration with China Geological Survey in the Shenzu area of South China Sea. The hydrate bearing zones were identified between 183m and 201m below the seafloor at a water depth of 1245m. The gas hydrates in this region are of thermogenic origin with structure sI and sII, methane hydrates being the most predominant.

#### C. Japan

The Methane Hydrate Research and Development Program (MHRDP) was formed in 1995 by Japan Oil Gas and Metals National Corporation (JOGMEC) to carry out gas hydrate surveys in the South East coast of Japan. The estimated resource potential of Nankai trough is 40 trillion cubic feet which is equivalent to more than a decade of supply of the country's natural gas import [42]. Three exploration phases have been executed under MHRDP. In the first phase, seismic surveys were done and exploration wells drilled. This phase led to the characterization of the hydrate reservoir, estimation of the producible reserves and proposal of depressurization as the suitable method for production testing. This recommendation was made by JOGMEC following the production tests that the company had done in Mallik field, Canada that established that depressurization was more effective than thermal stimulation [42]. The first production test was done during the second phase of MHRD in 2013. In the production test done continuously for six days, the reported cumulative gas production was 119,500 cubic metres while water production rate was 20,000 cubic metres per day. Following this success, the third phase was started and two more production tests done in 2017. Two wells, AT1-P3 and AT1-P2 were successfully tested for longer periods. AT1-P3 produced 40,000 cubic metres of gas in 12 days after which there was excessive sand production. The water production was 922 cubic metres. AT1-P2 produced 220,000 cubic metres of gas in a continuous 24-day flow test.

Of the three field cases discussed, Japan is leading having done two production tests, in 2013 and 2017. It is projected by the USGS that Japan will be the first country globally to commercially extract hydrates from marine settings.

### IV. CHALLENGES FACING GAS HYDRATE EXTRACTION CASES

#### A. Maintaining mechanical integrity

Mechanical integrity issues that arise with hydrate extraction are a major concern. As earlier discussed, when hydrates form part of the rock matrix, they contribute to the strength of the formation. Dissociation of gas hydrates results in weakening of the subsurface strata which could potentially cause subsidence, landslides and methane release. During the production testing at Malik site, there were collapsed casings and conduits caused by a reduction in stability of the formation [42]. With drilling and production, the geomechanical changes must be well understood and proper engineering design adopted. Technologies such as CH<sub>4</sub>-CO<sub>2</sub> exchange can aid in maintaining the mechanical integrity of the formation[31]. This method has been tested for extraction of methane hydrates in Ignik Sikumi field resulting in production of 855 million SCF of methane gas with injection of 48.6 million SCF of CO<sub>2</sub> for 6 weeks [2]. Of the injected CO<sub>2</sub> volume, 40% was permanently sequestered as CO<sub>2</sub> hydrates. Despite such encouraging results, the technical details of the exchange process, its applicability in mixed hydrate reservoirs and logistical plans for CO2 injections have to be well investigated and planned in order to implement successfully [2].

#### B. Environmental Issues

There are concerns about direct methane emissions in case hydrate dissociation is not appropriately controlled. Given the global warming potential of methane, such leakages must be prevented. It should be noted that shallow hydrate deposits can contribute greatly to methane emissions due to oceanic warming caused by climate change. However, such shallow deposits are dispersed and the hydrate quantities in them are not significant for economic extraction. Researchers are thus faced with a challenge of distinguishing emissions from such shallow deposits and quantifying them. In planned productions, proper engineering design must be done to prevent any leakages during extraction including gas contained in drilling cuttings.

#### C. Produced water disposal

As noted earlier, water is produced alongside gas after dissociation of hydrates. Though actual quantities produced depend on the structure of the hydrates, the amounts are significant. This water is contaminated and must be properly treated and disposed safely to prevent any health or environmental hazards [43], [44]. This requires adequate understanding of the constituents of the produced water. Methods such as re-injection to depleted reservoirs can be considered though the cost implication of the handling facilities must be evaluated.

#### D. Economic justification

Beyond the confirmed quantities of extractable reserves, economic returns from a production project must exceed the production costs to justify undertaking it. When compared with the conventional resources, production of gas hydrates is costlier. It is estimated that conventional gas production costs \$2.00-\$9.00 per million BTU while producing hydrates may cost between \$4.65 and \$9.08 per million BTU. This cost is even higher than that projected for shale gas (approximately \$3.00-\$7.00 per million BTU) [2]. Therefore, justification of a gas hydrate production project currently may be anchored on the environmental benefits to be accrued or rely on policy changes. Ultimately though, as we increase dependence on natural gas and exhaust the easier conventional sources, extraction of hydrates will be a viable alternative.

#### V. CONCLUSION

Natural gas hydrates evidently have enormous potential as a sustainable energy source to meet the exponentially rising demand in Asia and reduce the carbon emissions. Given the massive deposits that are fairly evenly distributed globally and the developments made so far in extraction technologies, hydrates are the most promising prospect of the unconventional resources. Of the methods applied so far in field tests, depressurization has been identified as the most efficient. It requires the least energy and results in higher cumulative production though at low rates. With most governments strongly supporting research and collaborations, it is anticipated that full-scale field production will commence in this coming decade. Upon reviewing the trends of field tests done, it is expected that Japan will be at the forefront of commercial production from Nankai trough. Before then, further investigations need to be carried out to ensure higher gas production rates sustained over long time periods. Besides, management of produced water, ensuring geo-mechanical stability and methane gas leakage prevention are milestones that have to be achieved before commercialization of a hydrate production project.

#### REFERENCES

- [1] B. Looney, "Statistical Review of World Energy, 2020 | 69th Edition," *Bp*, vol. 69, p. 66, 2020, [Online]. Available: https://www.bp.com/content/dam/bp/business-sites/en/global/corporate/pdfs/energy-economics/statistical-review/bp-stats-review-2020-full-report.pdf.
- [2] Z. R. Chong, S. H. B. Yang, P. Babu, P. Linga, and X. Sen Li, "Review of natural gas hydrates as an energy resource: Prospects and challenges," *Appl. Energy*, vol. 162, pp. 1633–1652, 2016, doi: 10.1016/j.apenergy.2014.12.061.
- [3] U. E.I.A., "Carbon dioxide emissions coefficients," Washington D.C.: U.S., 2013.
- [4] E.I.A US, "Annual energy outlook 2012. Washington D.C," 2012.
- [5] I.E.A., "World energy outlook special report: are we entering the golden age of gas?," Paris, France:, 2011.
- [6] C. T. Boswell R, "Current perspectives on gas hydrate resources," Energy Environ. Sci., 2011.
- [7] T. Collett, "Natural Gas Hydrates—Vast Resource, Uncertain

ISSN: 2278-0181

- Future," *Usgs*, no. March, pp. 2–3, 2001.
- [8] E. D. Sloan, Natural gas hydrates in flow assurance. Gulf Professional Publishing, 2010.
- [9] A. Hassanpouryouzband et al., "Gas hydrates in sustainable chemistry," Chem. Soc. Rev., vol. 49, no. 15, pp. 5225–5309, 2020, doi: 10.1039/c8cs00989a.
- [10] A. Gudmundsson, J.S., Borrehaug, "No Title," in *Proc. Second International Conference on Gas Hydrates*, 1996, p. 415.
   [11] J. Andersson and S. Grönkvist, "Large-scale storage of hydrogen,"
- [11] J. Andersson and S. Grönkvist, "Large-scale storage of hydrogen,"

  International Journal of Hydrogen Energy, vol. 44, no. 23. Elsevier
  Ltd, pp. 11901–11919, May 03, 2019, doi:
  10.1016/j.ijhydene.2019.03.063.
- [12] Y. Z. Wendy L Mao 1, Ho-Kwang Mao, Alexander F Goncharov, Viktor V Struzhkin, Quanzhong Guo, Jingzhu Hu, Jinfu Shu, Russell J Hemley, Maddury Somayazulu, "Hydrogen clusters in clathrate hydrate," *Science* (80-. )., 2002.
- [13] W. Ke, T. M. Svartaas, and D. Chen, "A review of gas hydrate nucleation theories and growth models," *Journal of Natural Gas Science and Engineering*, vol. 61. Elsevier B.V., pp. 169–196, Jan. 01, 2019, doi: 10.1016/j.jngse.2018.10.021.
- [14] C. A. Koh, E. D. Sloan, A. K. Sum, and D. T. Wu, "Fundamentals and applications of gas hydrates," *Annu. Rev. Chem. Biomol. Eng.*, vol. 2, no. July, pp. 237–257, 2011, doi: 10.1146/annurevchembioeng-061010-114152.
- [15] Klauda Jeffer; Sandler Stanley, "Global Distribution of Methane Hydrate in Ocean Sediment," Energy & Fuels, vol. 19, no. 2, 2005.
- [16] Y. Zhao, Jiafei & Yu, Tao & Song, Yongchen & Liu, Di & Liu, Weiguo & Liu, Yu & Yang, Mingjun & Ruan, Xuke & Li, "Numerical simulation of gas production from hydrate deposits using a single vertical well by depressurization in the Qilian Mountain permafrost, Qinghai-Tibet Plateau, China," *Energy, Elservier*, vol. 52, no. C, pp. 308–319, 2013.
- [17] et al. Kirschke S, Bousquet P, Ciais P, Saunois M, Canadell JG, Dlugokencky EJ, "Three decades of global methane sources and sinks," *Natl. Geosci.*, vol. 6, pp. 813–823, 2013.
- [18] J. S. P. B. Parent, "Investigations into the Nucleation Behaviour of Methane Gas Hydrates," *Chem. Eng. Commun.*, vol. 144, no. 1, pp. 51–64, 1996.
- [19] A. Hassanpouryouzband et al., "Gas hydrates in sustainable chemistry," Chem. Soc. Rev., vol. 49, no. 15, pp. 5225–5309, 2020, doi: 10.1039/c8cs00989a.
- [20] R. K. Jeffrey, G.A., McMullan, "The Clathrate Hydrates," Prog. Inorg. Chem., vol. 8, p. 43, 1967.
- [21] C. J. Circone, S., Stem, L.A., Kirby, S.H., Durham, W.B., Chakoumakos, B.C., Rawn and Y. Rondinone, A.J., Ishii, "Clathrate Hydrates of Natural Gas," *J. Phys. Chem. B*, vol. 107, 2003.
- [22] R. M. Rueff, E. D. Sloan, and V. F. Yesavage, "Heat capacity and heat of dissociation of methane hydrates," Am. Inst. Chem. Eng. J., vol. 34, no. 9, 1988.
- [23] S. R. Mondal and K. K. Chopra, "Petrophysical evaluation of gashydrate formations in national gas hydrates programme Expedition 02 in India," *Proc. Annu. Offshore Technol. Conf.*, vol. 2019-May, 2019, doi: 10.4043/29614-ms.
- [24] A. E. Cook and W. F. Waite, "Archie's Saturation Exponent for Natural Gas Hydrate in Coarse-Grained Reservoirs," *J. Geophys. Res. Solid Earth*, vol. 123, no. 3, pp. 2069–2089, 2018, doi: 10.1002/2017JB015138.
- [25] T. S. Collett, "Detection and evaluation of natural gas hydrates from well logs, Prudhoe Bay, Alaska," University of Alaska Fairbanks, 1983
- [26] and H. O. Yoshihiro Konno, Yoshihiro Masuda, Yosuke Hariguchi, Masanori Kurihara, "Key Factors for Depressurization-Induced Gas Production from Oceanic Methane Hydrates," *Energy & Fuels*, vol. 24, no. 3, pp. 1736–1744, 2010.
- [27] G. G. Collett TS, "Gas hydrates in the Messoyakha gas field of the West Siberian Basin - A re-examination of the geologic evidence," *Int. J. Offshore Polar Eng.*, vol. 8, 1998.
- [28] J. Siažik, M. Malcho, and R. Lenhard, "Proposal of experimental device for the continuous accumulation of primary energy in natural gas hydrates," *EPJ Web Conf.*, vol. 143, pp. 4–9, 2017, doi: 10.1051/epjconf/201714302106.
- [29] L. D. Fan S, Zhang Y, Tian G, Liang D, "Natural gas hydrate dissociation by presence of ethylene glycol.," *Energy & Fuels*, vol. 20, 2005.
- [30] L. Ma, P. Luo, Y. He, L. Zhang, Y. Fan, and Z. Jiang, "Ultra-stable

- silica nanoparticles as nano-plugging additive for shale exploitation in harsh environments," *Nanomaterials*, vol. 9, no. 12, 2019, doi: 10.3390/nano9121683.
- [31] S. N. Kazunari Ohgaki, Kiyoteru Takano, Hiroyuki Sangawa, Takuya Matsubara, "Methane Exploitation by Carbon Dioxide from Gas Hydrates—Phase Equilibria for CO2-CH4 Mixed Hydrate System," J. Chem. Eng. Japan, vol. 29, no. 3, pp. 478–483, 1996.
- [32] A. Demirbas, "Processes for Methane Production from Gas Hydrates," *Green Energy Technol.*, vol. 34, pp. 161–181, 2010, doi: 10.1007/978-1-84882-872-8\_5.
- [33] P.-D. Anderson BJ, Kurihara M, White MD, Moridis GJ, Wilson SJ and et al. M, "Regional long-term production modeling from a single well test, Mount Elbert Gas Hydrate Stratigraphic Test Well, Alaska North Slope," *Mar. Pet. Geol.*, vol. 28, pp. 493–501, 2011.
- [34] T. T. Falser S, Uchida S, Palmer AC, Soga K, "Increased gas production from hydrates by combining depressurization with heating of the wellbore," *Energy Fuels*, vol. 26, no. 6259–6267, 2012.
- [35] C. Z. Li XS, Yang B, Li G, Li B, Zhang Y, "Experimental study on gas production from methane hydrate in porous media by huff and puff method in pilot-scale hydrate simulator," *Fuel*, vol. 94, pp. 486–494, 2012.
- [36] V. K. Sahay and A. H. Johnson, "Gas hydrate deposits of Krishna Godavari Basin, India: Issues and potentiality in exploration and commercial production," *Proc. Annu. Offshore Technol. Conf.*, vol. 1, pp. 628–633, 2014, doi: 10.4043/25137-ms.
- [37] DGH, "Natural Gas Hydrates." dghindia.gov.in (accessed Oct. 31, 2020).
- [38] ONGC, "Gas Hydrates." https://www.ongcindia.com/wps/wcm/connect/en/about-ongc/new-initiatives-in-energy/gas-hydrates/ (accessed Nov. 15, 2020).
- [39] NDR, "Natural gas hydrates." https://www.ndrdgh.gov.in/NDR/(accessed Jan. 17, 2021).
- [40] Y. Song *et al.*, "The status of natural gas hydrate research in China: A review," *Renew. Sustain. Energy Rev.*, vol. 31, pp. 778–791, 2014, doi: 10.1016/j.rser.2013.12.025.
- [41] Y. Wang, J. C. Feng, X. Sen Li, Y. Zhang, and G. Li, "Evaluation of gas production from marine hydrate deposits at the GMGS2-site 8, pearl river Mouth Basin, South China Sea," *Energies*, vol. 9, no. 3, pp. 1–22, 2016, doi: 10.3390/en9030222.
- [42] JOGMEC, "Gas Production from Methane Hydrate Layers Confirmed."
  http://www.jogmec.go.jp/english/news/release/release0110.html (accessed Oct. 30, 2020).
- [43] A. Oyama and S. M. Masutani, "A review of the methane hydrate program in Japan," *Energies*, vol. 10, no. 10, 2017, doi: 10.3390/en10101447.
- [44] J. K. Y. K. S. X. W. T. M. I. N. Yoshihiro Nakatsuka and Yoneda, "The Second Offshore Product ion Test of Meth ane Hydrates in the Eastern Nankai Trough and Site Charact erization Efforts," Methane Hydrate News, vol. 19, no. 1, pp. 9–15, 2019.