Review

Towards Commercial Gas Production from Hydrate Deposits

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Abstract: Over the last decade global natural gas consumption has steadily increased since many industrialized countries are substituting natural gas for coal to generate electricity. There is also significant industrialization and economic growth of the heavily populated Asian countries of India and China. The general consensus is that there are vast quantities of natural gas trapped in hydrate deposits in geological systems, and this has resulted in the emerging importance of hydrates as a potential energy resource and an accompanying proliferation of recent studies on the technical and economic feasibility of gas production from hydrates. There are then the associated environmental concerns. This study reviews the state of knowledge with respect to natural gas hydrates and outlines remaining challenges and knowledge gaps.

Keywords: natural gas hydrates; methane hydrate; unconventional resource; energy resource; natural gas

Nomenclature: G = Gas, guest molecule; N_H = Hydration number; H = Hydrogen; O = Oxygen

1. Introduction

In the 1930s, research into the clogging of oil and natural gas pipelines by a crystalline material, particularly in colder regions, led to the discovery that hydrates composed of water and natural gases such as methane, ethane, propane and/or butane was being formed in the lines [1,2]. This

hydrate-problem could be solved by dehydrating the gas prior to shipping, heating the pipelines to temperatures above the hydrate formation point and/or using chemical inhibitors to prevent their formation. Until the 1980s, with their discovery in the natural environment in very large quantities, hydrates were just regarded as a nuisance by the pipeline engineers, or at best a curiosity by the scientific community. This is evident by the fact that prior to 1975 few publications existed on natural gas hydrates [3]. Within the last two decades however the interest in natural gas hydrates have grown significantly as reflected by the increase in the number of publications, the increased level of funding for research and the hosting of gas hydrate conferences, the first being held in the U.S.A. in 1991. That conference was jointly hosted by the U.S. Department of Energy, the U.S. Geological Survey and the Naval Research Laboratory, and was held at the U.S. National Centre of the U.S. Geological Survey in Reston (VA).

The global estimates of gas contained in hydrate deposits at standard conditions range from 2×10^{14} m^3 to 3.053×10^{18} m^3 [4,5]. Even if the conservative estimates are considered, the consensus is that the worldwide quantity of natural gas hydrates are vast and begs to be evaluated both technically and economically as a potential energy resource. This interest is also augmented by: (i) the ever increasing global energy demand, (ii) the finite volume of conventional fossil fuels and (iii) the fact that natural gas is environmentally friendly when compared to solid and liquid fossil fuels.

Countries with limited conventional hydrocarbon resources such as Japan, China, India, U.S.A. and Korea have taken a leading role in the assessment of hydrates as a potential energy resource [5–8]. The government of Japan established a national hydrate research program in 1995 [9] while the government of India established their national hydrate research program in 1996 [10]. Other countries which are investigating the possibility of government sponsored research programs or which have recently embarked on such programs include Malaysia, Norway, Vietnam and Mexico. In addition, the European Union, Taiwan and Chile all currently show interest in natural gas hydrates [5,7].

This increasing worldwide interest also stems from the fact that gas hydrates are metastable and affected by pressure and temperature conditions. Changes in pressure and temperature of the sediments in which they occur can result in the release of the methane which in turn could impact oceanic and atmospheric chemistry and ultimately the global climate. This metastable characteristic of natural gas hydrates may also be able to explain major seafloor instabilities which result in submarine slides and slope failures [11]. Thus, naturally occurring gas hydrates are of societal concern in three areas, namely resources, hazards and climate. This study reviews the state of knowledge with respect to natural gas hydrates and outlines remaining challenges and knowledge gaps.

2. Physical and Chemical Properties

Hydrates is a subgroup of clathrates, that is solid compounds "in which molecules of one substance are enclosed and physically trapped in the cavities of a crystal lattice formed by the molecules of another substance" [12]. These clathrates form under conditions of low temperature and high pressure, with no chemical bonding between the host and guest molecules. The term hydrate refers specifically to the group of clathrates in which water is the host molecule, gas (G) is the guest molecule, and the general reaction equation is given by the expression:

$$G + N_H H_2O = G.N_H H_2O \tag{1}$$

in which the hydration number is given by N_H where N ranges between 5.75 and 7.2 [7,13].

Natural gas hydrates refer to the case where the guest gas molecule is a natural gas. In the case of methane hydrate, because the methane molecules are tightly packed in the crystalline lattice, methane in hydrate form has a high energy density of 184,000 btu/ft^3 [1]. This compares with 1150 btu/ft^3 for methane gas (CH_4) and 430,000 btu/ft^3 for liquefied natural gas (LNG), the cryogenic liquid form of methane. This makes it an attractive source of methane.

Three crystalline structures, namely Structure I (SI), Structure II (SII) and Structure H (SH), have been discovered in Nature [13]. SI methane hydrate is the most common one found to date and here the crystalline cages are arranged in the body-centered packing of the cubic crystallographic system, large enough to include molecules of the size of methane, ethane, carbon dioxide and hydrogen sulfide. SII, in which the cages are arranged in diamond packing in the cubic system, allows for larger molecules such as propane and isobutane, in addition to those mentioned for SI. SH is the least common structure found in Nature. Here the cage arrangement is hexagonal and some of the cages are smaller than those in structure II and require small molecules (such as methane), whereas the larger cages can take larger molecules such as neohexane.

While the various types of gas hydrates are stable under arctic and deep ocean conditions of pressure and temperature, SI methane hydrate is the dominant type comprising greater than 99% of all hydrates in the ocean floor [5,14]. As such the literature often refers to natural gas hydrates as methane hydrate. The maximum amount of methane in this type of hydrate is 164 volumes of methane at standard conditions to one volume of methane hydrate [11,15].

3. Geological Occurrences

Natural gas hydrates are found in two geological settings *i.e.*, (i) onshore, in and below areas of thick permafrost and (ii) offshore, in the marine sediments of the outer continental margins. They occur in a narrow zone, commonly referred to as the hydrate stability zone (HSZ) or the gas hydrate stability zone (GHSZ) which parallels the terrestrial surface in permafrost areas or the sea floor.

In permafrost areas the extraordinary cold of the surface results in the stability zone being relatively close to the surface. In continental polar regions where surface temperatures average below 0 °C, the upper depth limit for methane hydrate is about 150 m below the surface [11].
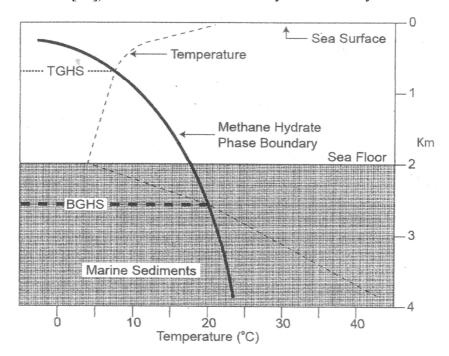
In oceanic sediments it is the pressure exerted by the overlying water and the low temperatures (<20 °C) at water depths generally in excess of 300 m which results in a stable zone. There the depth to the base of the stability zone is dependent on the increasing temperature related to the geothermal gradient of approximately 3–4 °C per 100 m in continental slope sediments [1], with the maximum lower limit being about 2000 m below the solid surface [11,16].

The change in water temperature with depth is termed the hydrothermal gradient, and this varies considerably depending on latitude and the local heating attributes of the specific body of water. The decline in temperature with depth is generally most rapid close to the surface and then reduces significantly at what is termed the "thermocline" [1]. Because of the very cold water in arctic regions, natural gas hydrates are stable at shallower depths than in the more temperate and open oceans.

The physical conditions that control the presence of methane hydrate in terms of the temperature/depth field, are also illustrated in Figure 1. Methane hydrate is stable to the left of the

phase boundary curve where the temperatures are lower and the pressures are higher. The sea water temperature, illustrated by the dashed line, declines from the surface and reaches a minimum at the sea floor; thereafter the temperature increases due to the geothermal gradient. In this schematic North Atlantic Ocean thermal conditions were used and for illustration purposes and the sea floor was placed at a water depth of 2000 m.

Figure 1. Schematic of the Pressure-Temperature (P-T) phase diagram for oceanic methane hydrate. A seafloor depth of 2000 m is used for illustration purposes (modified after Dillon and Max [14]). * BGHS—Base of Gas Hydrate Stability zone.

The base of the hydrate stability zone occurs where, because of geothermal gradient, the temperature of the sediments gets high enough such that the hydrate becomes unstable, even though the pressure continues to increase. At this point the local geothermal gradient intersects the hydrate phase boundary (Figure 1). In areas with similar geothermal pressure gradients, because the pressure at the sea floor increases with water depth, the thickness of the HSZ also increases with water depth [14,16].

The precise location of the base of the stability zone for any given pressure/temperature condition is also dependent on the composition of the gas. For example in the Gulf of Mexico, at a pressure equivalent of 2500 m, and if pure methane gas is present, the base of the hydrate stability zone will occur at 21 °C [14]. At the same pressure, if the gas concentration is 93% methane, 4% ethane and 1% propane with smaller amounts of higher hydrocarbons, the base of the stability zone will occur at 23 °C. For a gas concentration is 62% methane, 9% ethane and 23% propane along with some heavier hydrocarbons, the phase limit will be at 28 °C.

3.1. Source of Hydrocarbon Gases

The source of the methane in hydrate deposits is mainly biogenic activity (*i.e.*, due to bacterial methanogenesis) at relatively low temperatures and pressures and not through the high temperature high pressure thermogenic processes which are responsible for the generation of most of the conventional oil and gas deposits [14]. In some locations however the hydrate is comprised of thermogenically-formed hydrocarbon gases and other gases such as hydrogen sulfide and carbon dioxide, which form at depth and rise along faults to form gas hydrates at shallower depths. Geochemical analyses have indicated that the gases in hydrate deposits in the Gulf of Mexico, the Messoyakha field in the West Siberian Basin and the Prudhoe Bay-Kuparuk area North Slope Alaska are a mixture of both biogenic and thermogenic methane [11,17].

3.2. Classification of Deposits

Natural gas hydrates serve to cement sediments and occur as disseminated grains and pore fillings in coarse grain sediments and as nodules and veins in finer silt/clay deposits (see Table 1). They have also been observed in cores to exist as laminae along specific horizons apparently controlled by bedding porosity and in massive deposits as fracture fill [18,19]. Hydrate accumulations have also been subdivided into four (4) basic classes based on simple geological features [5,20]: Class 1 accumulations consist of a hydrate zone with an underlying fluid zone consisting of gas and liquid water; Class 2 deposits consist of a hydrate zone which overlies a zone of mobile water; Class 3 deposits consist of a single hydrate layer with no underlying mobile fluids; and Class 4 refers to disperse, low saturation deposits which occur in oceanic sediments and which lack confining geologic strata. Class 4 type deposits are in particular, considered to be unrecoverable at this time using available technology.

In recognition of the wide range of geological settings for gas hydrates, Boswell and Collett [21] used the concept of a resource pyramid to display the relative size and producibility of a variety of hydrate occurrences (Figure 2). In this schematic, the most promising resources are located at the top while the most technically challenging are located at the base.

4. Resource Assessment

Most of the estimates of the total amount of natural gas contained in the hydrate deposits involve extrapolation of localized geological data to a global level. The higher value is based on the assumption that hydrates will exist wherever favourable P-T conditions exist, while the minimum values accounts for factors such as CH_4 availability, porosity, amount of organic matter and thermal history of previous regimes. Klauda and Sandler [22], who estimated 120×10^{15} m^3 STP of CH_4 used a state of the art thermodynamic model which incorporated the effects of pores and salt, the intersection of geothermal gradients with the methane hydrate phase boundary and local organic content. Two recent independent estimates, having indicated that the volume of gas hydrates worldwide is approximately 21×10^{15} m^3, have led to this number being the current consensus [11,23–25].

Table 1. Various Locations of Hydrate Occurrence and Sample Descriptions [19].

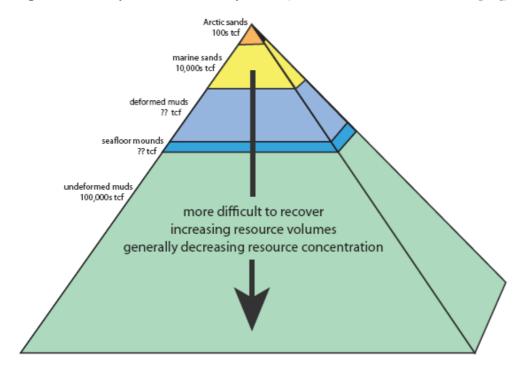| Geographic Location	Description
Middle America Trench (Costa Rica)	
-DSDP Leg 84, Site 565	Inclusions in mud and muddy sand.
-ODP Leg 170, Site 1041	Disseminated and sheets in microfractures.
Middle America Trench (Guatemala)	
-DSDP Leg 67, Site 497	Inclusion in sediment.
-Site 498	Cement in coarse vitric sand.
-DSDP Leg 84, Site 568	Inclusion in mudstone.
-Site 570	Laminated ash; massive core at 249 m (1.05m core).
Middle America Trench (Mexico)	
-DSDP Leg 66, Site 490	Laminated ash and mud.
-Site 491	Inclusions in mud.
-Site 492	Laminated ash.
Eel River Basin (California)	Layers, nodules in mud.
Cascadia Basin (Oregon)	
-DSDP Leg 146, Site 892	Aggregates, layers in silt.
-Hydrate Ridge	Layers, massive in carbonate crust.
P17 Okhotsk Sea (Russia)	
-Paramushir Island	Layers in ooze.
P18 Okhotsh Sea (Russia)	
-Sahkalin Island	Layers in silt and clay.
Japan Sea (Japan)	
-ODP Leg 127, Site 796	Crystals in sand with clay.
Nankai Trough (Japan)	
-ODP Leg 131, Site 808	Fragment in wash core.
Peru-Chile Trench (Peru)	
-ODP Leg 112, Site 685	Fragments in mud.
-Site 688	Grains in mud.
Gulf of Mexico (Texas and Louisiana)	
-DSDP Leg 96, Site 618	Nodules, crystals in mud.
-Green Canyon	Nodules, layers in rubble.
-Garden Banks	Nodules, layers in rubble.
-Mississippi Canyon	Pieces in coarse sediment.
-Bush Hill	Mounds at seafloor.
Haakon-Mosby Mud Volcano (Norway)	Inclusions and plates.
Niger Delta (Nigeria)	Nodules, dispersed in clay.
Black Sea (Russia)	Veinlets in silty clay.
Caspian Sea (Russia)	Laminated in clayey silt.
Lake Baikal (Russia)	Disseminated in sand, silts.
Mediterranean Sea (Kula Mud Volcano)	Not described.
Mackenzie Delta (Canada)	Dispersed in sand, gravel.

Figure 2. Gas Hydrate Resource Pyramid (modified after Boswell *et al.* [21]).

While none of the above estimates are well defined, even the most conservative one indicates an enormous amount of gas stored in hydrate reservoirs since by comparison, as at year end 2009 the remaining conventional gas reserves in the world were estimated at 1.9×10^{14} m^3 STP [26]. This is approximately 1% of the estimated volume of gas stored in hydrate deposits.

In 1995, Collett conducted a systematic assessment of the U.S. hydrate resource [5]. Probabilities were assigned to 12 geological attributes which are correlatable with the existence of hydrates and the mean estimate of the hydrate resource was subsequently determined to be 9×10^{15} m^3 STP of CH$_4$ with 5% and 95% probability values of 1.9×10^{16} and 3×10^{15} m^3 STP respectively. Estimates of the volume of natural gas stored globally in permafrost hydrate reservoirs have ranged from 0.31×10^{14} to 340×10^{14} m^3, while for the oceanic deposits, the volumes ranged from of 0.31×10^{14} to 760×10^{16} m^3 STP. These data indicate that the oceanic deposits contain approximately two orders of magnitude more gas than the permafrost deposits.

Based on the 2007 SPE/AAPG/WPC/SPEE Reserves and Resources Classification, Definitions and Guidelines, natural gas hydrate deposits may be classified as Contingent Resources, and further sub-classified as Development Not Viable or as Currently Unrecoverable in-place volumes [27,28]. This stems from the fact that: (i) while significant hydrate accumulations have been penetrated and mapped, and (ii) theoretical recovery methods have been identified, the economic criteria has not been satisfied since no commercial recovery methods have yet been developed.

5. Distribution of Natural Gas Hydrates

5.1. Arctic Accumulations

The confirmation of the occurrence of hydrates on the North Slope of Alaska came when a core containing gas hydrates was recovered from a well in the Prudhoe Bay area [29,30]. Also, based on the

well log data of 445 wells on the North Slope, 50 were deemed to contain natural gas hydrates. Many of the wells had multiple hydrate bearing units with individual thicknesses ranging from 3 to 31 m. Six lateral continuous sandstone and conglomerate units were delineated and in four of those units, large free gas accumulations were observed, stratigraphically trapped downdip [31]. The Prudhoe Bay-Kuparuk River area is estimated to contain approximately 1.0×10^{12} to 1.2×10^{12} m^3 STP of gas. Mud-log gas chromatographic data from 320 wells in the North Slope area indicate that methane is the dominant gas in the near surface sediments. Also the gas evolved from hydrate samples in the Prudhoe-Bay area consisted mainly of methane (87–99%) and thus methane gas chemistry was assumed for assessment of hydrate stability conditions.

For the Mackenzie Delta-Beaufort Sea Region of Canada [32–34], a database presented by Smith and Judge [34] indicated that 17% (25) of 146 wells examined were identified as possibly containing gas hydrates. The data also indicated that the formation gases consisted almost entirely of methane (99.2 to 99.5%) [29,34]. This further suggests that SI methane should be the dominant gas hydrate form in this area.

The Mallik L-38 well in the Mackenzie area encountered 100 m of hydrate bearing sandstone within the depth interval from 820 to 1103 m [29,34]. In 1998, the JAPEX/JNOC/GSC Mallik 2L-38 well was drilled near the site of the Mallik L-38 well to conduct extensive scientific studies on the occurrence of natural gas hydrates [29,33]. The hydrate bearing zone was 150 m thick within the depth interval of 889–1101 m and gas hydrates were observed in a 37 m core sample which was comprised of unconsolidated sands and gravels. High electrical resistivities and rapid acoustic velocities were exhibited by the cored and downhole logged hydrate intervals. Estimates of gas in this area range from 9.3×10^{12} to 2.7×10^{13} m^3 [29,34,35].

The occurrence of natural gas hydrates has been inferred in several provinces of Russia including the West Siberian Basin, Lena-Tunguska, Timan-Pechora and several sedimentary basins in northeastern Siberia and the Kamchatka area [29]. In the West Siberian Basin, reservoirs contain mostly methane (92.5–99.0%) and as such the pure methane chemistry is assumed for gas hydrate stability calculations. In this area, the depth to the top and base of the hydrate stability zone ranges from zero to 1000 m respectively [29,36].

Natural gas hydrates have been associated with the Messoyakha field in the northeastern corner of the West Siberian Basin based on production and geological data. Gas is found in the Dolgan Formation at depths between 720 and 820 m. Of note is that the upper section of this formation (approximately 40 m) lies within the gas hydrate stability zone, while within the lower 40 m there is free gas. Total gas reserves within this formation is estimated at 80×10^9 m^3, one-third of which occur within the hydrate bearing zone [6,29,37].

When production began from this field in 1969, the reservoir pressure decline followed the predicted path. In 1971 however the observed pressure deviated from the predicted values. This deviation was attributed to the liberation of gas from the overlying hydrate bearing zone due to dissociation associated with the decline in pressure from the underlying free gas zone. It was estimated that about 36% (5.17×10^9 m^3) of the gas produced was from the hydrate zone [29,38].

While a review of available geological, geochemical and production data by Collett and Ginsburg [29,39] indicated that the overlying gas hydrates may not have been contributing significantly to gas production, in a more recent numerical simulation study of the Messoyakha field,

results similar to the actual reported flow rates and pressure behaviour were observed [40]. The results of the numerical simulation study indicated that as much as 15–20% of the gas produced from the Messoyakha field came from dissociation.

5.2. Oceanic Accumulations

Oceanic accumulations of natural gas deposits have been identified in several areas including Japan, India, Gulf of Mexico, Blake Ridge, China, Korea and Trinidad and Tobago. Japan initiated a national hydrate research program in 1995 based on the occurrence of BSRs on 2-dimensional and 3-dimensional (2D/3D) seismic profiles [9]. Since then, the presence of methane hydrate has been confirmed by exploration wells drilled in water depths of 945 m. The data indicate that 1800 Tcf of gas may exist off the southeastern coast at depths between 1135 and 1213 m below mean sea level (MSL). Thirty two wells have since been drilled offshore Japan to assist with characterizing the occurrence of methane hydrate and estimating the amount of methane hydrate resources.

In August 2006, a 4-month expedition to explore for hydrate deposits offshore India was successfully completed [41]. An international group of scientists, led by the Indian Directorate General of Hydrocarbons and the USGS, explored four offshore basins including the Kerala-Konkan, the Krishna-Godavari and the Mahanadi Basins along with the Andaman Islands. Significant gas hydrate accumulations were discovered, including one of the world's richest marine gas hydrate accumulations in the Krishna-Godavari Basin, and a 600-metre deep gas-hydrate-bearing volcanic ash layer in the Andaman Sea. Some 2850 metres of core were recovered and techniques for infrared core imaging and pressure coring data processing were further developed.

Gas hydrate deposits were confirmed in the Shenhu Area in the South China Sea during the GMGS-1 drilling expedition [8,42]. The hydrates occurred in a disseminated form in foram-rich clay sediments in layers 10–25 metres thick, located about 200 m below the sea floor. Core tests indicated hydrate saturations in the range of 26%–48% with methane being the predominant gas (>99%). Geochemical studies indicated that the source of the methane is mainly *in situ* microbial activity. The geophysical data showed a BSR extending over an area of 15 km^2 and it is estimated the total amount of methane trapped in this accumulation is 160×10^8 m^3 at a 50% probability [8].

Surveys conducted by the Korea Institute of Geoscience and Mineral Resources between 2000 and 2004 suggested that there is significant potential for hydrate occurrence in the Ulleung Basin in the Korea East Sea [7]. This is based on the many gas related features which have been identified in the area including a shallow gas zone, gas seepage on the continental slope, and gas-related structures such as pockmarks and domes. Hydrate samples have been collected from depths of up to 7.8 m below the sea floor in water depths of approximately 2000 m and in which a 2-metre hydrate layer was found with a methane content of 99%. The hydrates were intercalated in clayey sediments.

In 2004, natural gas hydrates were observed in at least 12 cores recovered in water depths from 714 to 28,386 m in the Atlantic continental margin offshore Trinidad and Barbados [43,44]. The 6-metre piston cores were taken during surface geochemical exploration (SGE) coring studies. Deville *et al.* [45] in studies of mud volcanism in the Trinidad-Barbados area, also noted the presence of bottom simulating reflectors (BSRs) on seismic cross sections and alluded that these were as a result of gas hydrate bearing sediments. Subsequent detailed analysis of three-dimensional (3D) seismic data from

eastern offshore also showed the presence of several positive indicators which suggest that natural gas hydrates are present in the oceanic sediments [46]. The dataset covered an area of transition between the continental shelf and slope in the Columbus Basin. Bottom simulating reflectors (BSRs) were observed over an areal extent of 516.8 km^2 or approximately 29% of the area of the mapped seafloor.
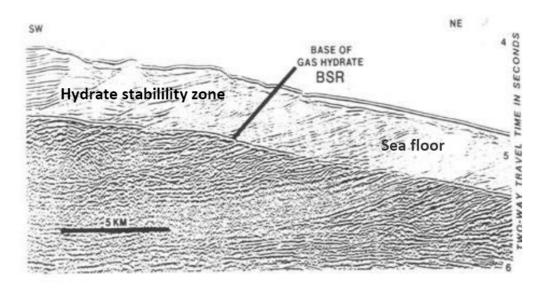
6. Delineation

The occurrence of natural gas hydrates is inferred from: (i) seismic reflection profiling, (ii) well logs and (iii) direct sampling. Hydrate samples have already been recovered from at least three locations in permafrost and 20 in ocean sediments [5].

6.1. Geophysical Sensing

Available geophysical data (quite often from the petroleum sector) is initially used to delineate prospective methane hydrate deposits using a framework similar to that of the petroleum-system concept. In the permafrost regions, significant data were available as a result of the exploitation of conventional oil wells. These included 3-D seismic data, drilling and logging data. In the marine environment, indirect indicators from low quality 2-D seismic data have been widely used to delineate hydrate deposits. More recently 3-D data have been used [5,46].

Most of the oceanic hydrate deposits have been inferred based on the appearance of an anomalous bottom simulating reflector (BSR) (Figure 3) on seismic reflection profiles [11]. This BSR parallels the sea floor form and increases in sediment depth with water depth. It cuts across reflections which represent sedimentary layers, and is characterized by reflection polarity reversals and negative reflection coefficients. Of note is that this reflector occurs at a depth which coincides with the base of the gas hydrate stability zone.

Figure 3. Schematic of Oceanic Seismic Section Showing a Strong Bottom Simulating Reflector (BSR) and Overlying Hydrate Stability Zone. (Modified after Kvenvolden [23]).

The BSRs thus mark the interface between high-velocity hydrate-cemented sediments and low-velocity uncemented sediments (which contains free gas below). Compressional velocity values of 1700–2400 m/s are known to be typical for gas-hydrated sediments [47]. Blanking above this BSR is also associated with an increase in the hydrate concentration in the sediments.

One shortcoming of using industry seismic data is that they are typically acquired with a deeper target depth in mind. The vertical and horizontal resolution within the hydrate stability zone is thus less than if the survey was designed specifically for the shallow methane hydrate targets. This compromises identification and quantification of the hydrate resource.

Remote sensing techniques which allow for detection of methane hydrate deposits at a scale that provides for geologic confidence are still needed, and in this regard new geophysical tools and techniques continue to be developed [48]. Multicomponent seismic attributes, new rock physics models and *in situ* data are being combined to provide estimates of methane hydrate concentrations in deep water strata. Non-standard seismic techniques such as ocean bottom cables (OBCs) are also being advanced to better understand methane hydrate in marine sediments [48,49]. Efforts are also being focused on the use of controlled source electromagnetic (CSEM) imaging for methane hydrate delineation. CSEM techniques while widely used in exploration for conventional deposits also have considerable promise for methane hydrate detection because of the electrical resistivity contrast between methane hydrate-bearing and water-saturated rocks [48,50,51]. It is also envisaged that the combined use of seismic and CSEM has the potential to minimize ambiguity compared to the use of either technique alone.

6.2. Downhole Logs

The three main advantages associated with the use of logs are: (i) data are obtained at reservoir conditions of temperature and pressure, (ii) the data are obtained as a continuous profile across the interval of interest with no gaps and (iii) data are sampled at a scale intermediate between core and seismic measurements.

Sonic logs provide data on the elastic wave properties of the formation. For example, in the presence of free gas, sonic velocity decreases sharply but increases in the presence of hydrates. Velocity data also provides information on the shear strength of the formation which increases in the presence of hydrates. These data assist with the determination of the nature of the BSR, the interpretation of VSP and seismic data, and also in estimating the concentration of methane hydrate and free gas [52,53].

Porosity measurements are estimated using neutron, sonic and density log data. The neutron porosity log measures neutron scattering which is controlled by the total hydrogen content. It is however adversely affected by hydrogen bonding in clay rich sediments. The density log on the other hand measures the electron and bulk density of the formation and once the average grain density of the formation is assumed, bulk density and porosity can be computed. The density log derived porosity values are however sensitive to grain density. By combining the results from these two logs and reducing the sensitivity to either the hydrogen bound and/or grain density, the porosity estimate can be improved [53,54].

Resistivity logs can be used to estimate porosity along with hydrate concentration [53,55,56]. These logs however must be carefully corrected since the Archie formulation may overestimate hydrate concentration [57].

With logging while drilling (LWD), sensors placed just above the drill bit provide the source of data and an intermediate resolution of 0.5 m is achieved [53]. Estimates of porosity may be more representative than that from wireline logs and lab cores test since the measurements are obtained from just above the drill-bit and with minimum of drilling disturbance.

Logs provide the link for core data with regional seismic data and as such a multidisciplinary strategy is needed to allow for the integration of core, log and regional geophysical and seismic data. The multiple scales of investigation complement each other extremely well with the scale ratio of core to log being greater than 2×10^3 while that for log to seismic may be 10^6 to 10^7 times larger.

7. Laboratory Studies

Data on methane hydrate growth and dissociation kinetics, physical and thermal properties, and geomechanical and geophysical data are all required for numerical simulation and calibration of remote geophysical measurements. These data include geophysical properties of hydrate bearing sediments (HBS) (elastic wave properties), geomechanical properties (stress and strain relationships, Modulus of elasticity, Poisson's ratio, internal friction angle), relative permeability data (absolute, effective and relative permeability data along with relative permeability end points), capillary pressure, and thermal properties of the hydrate and the HBS (pure and porous media, thermal conductivity and thermal diffusivity) [5]. These data serve to assist with modelling and predicting the relationship between the sediment fabric, the natural environment and the existence of gas hydrates.

Reviews of laboratory based experimental projects have noted that the major limitation is the nature of the samples being analysed [48,58]. In most studies the samples were synthesized from free gas plus water plus sediments and available data indicate that the properties of the samples varied with synthesis method. There is thus concern about the accuracy and the reproducibility of the data, particularly if measurements are to be scaled and extended to naturally occurring deposits. On the other hand, while *in situ* measurements would be ideal, these are not often practical and cannot be conducted as systematically and extensively as laboratory measurements. A few studies have however been done using pressure-core samples.

The U.S. Geological Survey has developed laboratory equipment to simulate pressures and temperatures encountered in gas hydrate stability regions. The Gas Hydrate and Sediment Test Laboratory Instrument (GHASTLI) system can be used to form gas hydrates in reconstituted sediments of various types, and preserve core samples containing gas hydrates while their physical properties are measured [59–61]. This system is made up of a number of separate pressure and temperature control systems to model *in situ* conditions and is designed for a core specimen of 71-mm diameter and 140 mm in height. The system can exert pressures of up to 25 MPa and simulate temperature conditions of 3 to 25 °C. Instrumentation and sensors placed in close proximity to the test specimen provides measurements which are logged.

The main types of data recorded include compression and shear waves, acoustic properties, shear strength, permeability and electrical resistivity. Properties of the host sediment prior to hydrate formation, after hydrates have formed and after dissociation can be determined.

8. Production Methodologies

Proposed methods of exploiting hydrate deposits are all based on inducing dissociation and include: (i) thermal stimulation in which the reservoir temperature is increased above the hydration temperature for the given reservoir pressure; (ii) depressurization in which the reservoir pressure is lowered to below the hydration pressure for the given reservoir temperature; (iii) use of inhibitors which shift the pressure-temperature equilibrium conditions so that the hydrates become unstable [62] and (iv) the exchange of methane molecules in the hydrate structure for carbon dioxide molecules *in situ*. Combinations of these techniques have also been proposed.

Depressurization is currently considered the most economically attractive recovery technique and is suited to Class 1, 2 and 3 type deposits [5]. Because of its technical effectiveness and simplicity, it also appears to be the only long-term practical option. Care must be taken as this strategy may be adversely affected by the reformation of hydrates or the formation of ice as a result of the inherent endothermic nature of gas hydrate dissociation. The production from the Messoyakha field of West Siberia (a Class 1 type deposit) has been attributed to simple depressurization of natural gas hydrates overlying a free gas zone which was on production [63,64].

While thermal numerical simulation models have been developed and indicate that recovery of hydrate gas solely by hot water injection or steam stimulation is technically feasible, the cost of projects of this nature will be prohibitive as there is need to heat both the hydrates and the porous medium [5,13]. There would also be heat losses through the boundaries which would further contribute to the inefficiency of the process. For Class 3 deposits, numerical simulation studies indicated that simple thermal stimulation via electrical heating and warm water injection appeared to be a slow and inefficient method with low production rates of 4–12 MSCFD [64]. This strategy is however recommended for use in conjunction with the depressurization for Class 1, 2 and 3 deposits to prevent secondary hydrate and ice formation.

The use of more advanced production schemes with new well designs is also being considered. One such design combines depressurization with localized thermal stimulation [65]. The process is cyclic with one stage of gas production followed by a second stage which involves destruction of the secondary hydrate mainly by warm water injection. Numerical simulation studies have shown that long production periods (months to years) can be maintained interspersed with short periods (days to weeks) of thermal stimulation.

The use of chemical inhibitors such as methanol and glycol has also been shown to be technically feasible. However the large volumes required, the rapid reduction in effectiveness as a result of the dilution of the inhibitor by the H_2O released from dissociation, high costs and environmental concerns associated with the use of these chemicals, all make this technique unattractive [5].

Another hydrate production methodology which has been simulated in the laboratory using artificial media involves the exchange of methane molecules in the hydrate structure for carbon dioxide molecules *in situ* with the methane molecules then being produced [48]. This production scheme has a

desirable attribute in that it will reduce the greenhouse gas footprint of hydrates by sequestering carbon dioxide while the methane is being produced. Several significant challenges are envisaged with this technique including complex well completions and operational procedures [48,66].

Class 4 sediments most likely may not be recoverable under any combination of any current production techniques, since it is highly unlikely that the low permeability clay rich unconsolidated marine sediments possess the mechanical strength necessary for the generation of the flow paths to allow for the movement of dissociated gas to the well bore.

9. Numerical Simulation

Several methane hydrate simulators have been developed including TOUGH+HYDRATE, HYDRES, MH21, STOMP-HYD, CMG STARS and Hydrate ResSim [48,67,68]. These have been used to provide production forecasts for hydrate bearing formations, to aid in the interpretation of laboratory data, and to determine physical property parameters, such as thermal conductivity and relative permeability for heterogeneous hydrated samples.

TOUGH+HYDRATE and MH21 were calibrated against thermal dissociation data from the Mallik test well [5]. While there was good agreement with the observed data, there were significant deviations when predicting long term production forecasts and so both codes are enhanced.

STOMP-HYD has been used to simulate methane hydrate production by means of CO_2 injection [68], and more recently, Phirani and Mohanty [69] developed a thermal compositional and kinetic simulator for use in the design and interpretation of both laboratory and field scale CO_2 flooding experiments. Preliminary results indicated that to dissociate methane hydrate by CO_2 injection, either relatively low operating pressures (<6 MPa at 5 °C) are required, or the CO_2 mole fraction in the fluid phase (*i.e.*, dissociated methane plus injected CO_2) must be kept very high.

Most of the models listed previously also took part in a code comparison study. The participants felt that the models accounted for the general physics of the recovery process, but that validation and calibration would be constrained by the fact that there are no reliable and well documented long term production data sets [5].

Of note is that a likely hydrate deposit close to the PBU L-106 site, North Slope Alaska is being evaluated for a long-term field test of 18–24 months [70]. This Class 3 deposit which occurs at depth of 678.5 m, has a net sand thickness of 36 m and high hydrate saturation (75%), porosities (40%) and intrinsic permeabilities (1–5 Darcys). This study, led by the U.S. Department of Energy has indicated that production from horizontal wells may be orders of magnitude larger than that from vertical wells with the cumulative volume of methane produced reaching 5.27×10^6 ST m^3 over a production period of approximately two years from a horizontal well of length 1000 m. A stable production high of 9×10^3 ST m^3/day was also predicted. The much needed data to improve the production forecasting capability of the available numerical simulators could also be provided by such a field test.

10. Economics

The viability of an energy resource is most often solely based on economics and in this regard several studies on the economic viability of hydrates as an energy resource have been conducted. In one such study the preliminary economics of two hypothetical onshore natural gas hydrate projects

were evaluated [67,71]. The 1st reservoir, a Class 1 reservoir consisted of a hydrate layer with 30.3×10^6 ST m^3 of gas initially in place (GIIP) and a free gas layer with 6.5×10^6 ST m^3 GIIP. The second accumulation, a Class 2 type deposit, contained 30.3×10^6 ST m^3 GIIP in the hydrate layer. It was proposed that each field be developed with seven wells, *i.e.*, five production wells and two water disposal wells, and that depressurization be used to produce the gas. CMG-STARS [72], a commercial numerical simulator was used to model the gas and water production rates. For the Class 1 deposit, initial free gas production resulted in an initial plateau production rate of 3.5×10^6 ST m^3 D. This rate was maintained for approximately 5 years, after which the production declined.

For the Class 2 type reservoir, initial production was low, but increased steadily to a peak production rate of approximately 2×10^6 ST m^3 D after which production declined. In this reservoir, a substantial volume of water had to be produced prior to the start of significant dissociation and subsequent gas production, hence the slow build up in gas production rate (even though not as high as in the case of the Class 1 type accumulation). To achieve a 15% rate of return, a gas price of $6.50 per MMBtu in 2009 dollars was required for the Class 1 deposit, while for the Class 2 reservoir, a gas price of $12.00 was required primarily due to the low initial production rates. It was assumed that the cost to develop conventional onshore gas reservoirs would be more attractive.

To study the economics of offshore gas hydrate development, a deep water (1524 km water depth) Class 3 gas hydrate reservoir (*i.e.*, no overlying free gas or underlying water) was considered. For comparison, the development of a conventional gas reservoir was also considered. For both accumulations a floating production facility was considered along with a 121 km pipeline and wells were added to maintain a 14.2×10^6 ST m^3 D plateau production and a cumulative recovery of 56.7×10^6 ST m^3 D over 20 yrs. The production forecast for the Class 3 Type hydrate accumulation was based on a study by Moridis and Reagan [64]. The gas hydrate accumulation required 48 wells while the conventional gas reservoir required 18 wells. The results indicated that to achieve a 15% (pre-tax, pre-royalty) rate of return, a gas price of approximately $3.50 per MMBtu was required for the conventional gas accumulation, while $7.00 was required for the gas hydrate accumulation.

These studies indicated that stand alone conventional gas accumulation will always be more attractive than a gas hydrate stand alone accumulation. But while in most cases the viability of an energy resource is based purely on economics, there are cases where the viability is based on local economic and non-technical factors. For example, countries with little or no domestic energy production rely on imported hydrocarbons which often create additional expenses. Also to provide energy security, resource poor countries often invest in relatively expensive unconventional energy resources. In this regard Japan and India have been investing in hydrate research programmes because they both have little local energy resources and pay a high price for imported hydrocarbon. For example the Japan National Oil Corporation (JNOC) has ongoing studies to assess their domestic hydrate resource potential, and along with the Geological survey of Canada in the Mackenzie Delta of northern Canada, JNOC in 1998 drilled the Mallik 2L-38 hydrate research well [33].

In general, onshore accumulations may be favourable if conventional gas is not available, and where gas is required for local communities or industries. Offshore accumulations on the other hand may prove to be attractive if there are no conventional nearby accumulations, but security of supply is a major concern. Even so significant work needs to be done to reduce the risk associated with these

developments including validation of reservoir performance using extended wells tests and improved accuracy of cost estimates, capital costs and recovery.

11. Gas Recovery

Based on economic considerations, it can be expected that the first recovery from hydrate reservoirs would be from sources which are concentrated, within quality reservoir rock, and easily accessible with existing infrastructure such as exists at the Eileen gas hydrate accumulation North Slope, Alaska, USA [5]. The second source would be hydrate deposits which are concentrated as well as being in good quality reservoir rock but away from existing infrastructure such as the Mallik gas hydrate accumulation in the Mackenzie Delta, Canada. The third frontier is envisaged to be moderate to highly concentrated deposits which occur within quality sandstone reservoirs in the marine environment. Accumulations of this nature would be in some of the basins in the Gulf of Mexico, the Nankai Trough offshore Japan, the eastern margin of India and offshore Vancouver Island [30,33,62]. For other deposits which occur in fine grain muds and shales, massive hydrate mounds and fine grain sediments, extraction is expected to be poor or very problematic at best without major technological advances in production systems.

12. Environmental Considerations

12.1. Climate Impact

The significance and role of methane hydrate in the global carbon cycle and in the radiative forcing of climate, or (as more commonly referred to) the greenhouse effect, has become a major societal concern. It has been suggested that since hydrate deposits occur in sediments in continental margins where hydrostatic pressures exceed 5 bar and temperatures are lower than 20 °C, a reduction in hydrostatic pressure and/or an increase in ambient temperature may result in the dissociation of methane—a greenhouse gas [24,73]. It is however heavily debated as to whether these changes will cause significant release of methane gas into the water column and ultimately the atmosphere since there are several other issues to be considered [74,75]. These include: (i) the quantity and transfer rate of methane from the sediments to the water column, (ii) the volume of methane which dissolves in the water column, and (iii) the volume of methane which eventually escapes to the atmosphere [24]. Furthermore, the change in atmospheric temperature occurs at the sea surface, and must be diffused to great depths in order to have any impact on the stability of the hydrates in the sediments.

In arctic regions, an increase in the mean temperatures can also potentially result in the release of methane into the atmosphere as a result of dissociation of the hydrates. The produced methane is of particular concern since while it will eventually react with the hydroxyl radical (OH) in the atmosphere, and be oxidized into water and carbon dioxide—both of which also contribute to climate forcing, the global warming potential of methane is 20 times that of CO_2.

A study of ice cores from Greenland and Antarctica revealed that there is a correlation between climate warming and increase in atmospheric methane and carbon dioxide [24,73], and it has been suggested that the rapid climate change observed in the past may be due to the catastrophic release of methane from hydrate sources which occurred as a result of the reduced hydrostatic pressure

associated with periods of lower sea levels. Dillon and Paul [76] suggested that a drop in the sea level of about 120 m during the last glacial maximum was sufficient to reduce the hydrostatic pressure sufficiently to raise the lower limit of the hydrate stability zone by 20 m. The conversion from solid hydrate to water and gas would have resulted in a reduction in the mechanical strength of the sediments, which in turn could have produced a zone of weakness where sediment failure could take place resulting in low-angle faulting with resultant slumping on the seafloor. Major slumps of Pliestocene age and which have been ascribed to these mechanisms, have been identified along continental margins around the world. In this scenario, significant quantities of methane from below the level of the slump could have been released. Paul *et al.* [77] suggested that such occurrences during the glacial periods would encourage a reversal and termination of the glacial cycle.

Another model suggests that once deglaciation begins, liberation from one or more arctic gas pools could liberate huge quantities of methane leading to accelerated warming [24]. Thorpe *et al.* [78] however when modelling the effect of release of a realistic volume of methane in the atmosphere at the end of the glacial cycle, concluded that the direct radiative effects of the methane emissions alone were too small to account for the reversal in the glacial cycle. Combinations of methane, carbon dioxide and heat transport inputs are required to simulate changes of the same magnitude. Haq [24] suggested that the significance of natural degassing can only be resolved by further simultaneous study of hydrated sediments and ice cores and measurement of: (i) the methane flux rate from the seafloor, (ii) what percentage is dissolved in the water column and (iii) the percentage which escapes to the atmosphere as these are all unknown at present [24,48]. Furthermore, the potential enhanced impact associated with the commercial production of methane hydrate has not yet been addressed. The environmental impact of natural degassing and degassing associated with commercial development has been widely discussed. A clearer understanding of what might occur if there is a catastrophic release of methane is also needed [24].

12.2. Geohazards—Slope Stability and Failure

The formation and dissociation of natural gas hydrates significantly affect the mechanical properties of marine sediments [79]. When liquid water and dissolved gas combine to form solid hydrates, the shear strength of the sediments is increased. Zhang *et al.* [80] have shown that the mechanical strength of hydrated sediments is approximately 10 times stronger than ice. Subsequent to the formation of a hydrated zone, a reduction in the pressure or an increase in the temperature of the formation would result in the hydrate becoming unstable and decomposing into water plus gas. This transformation from a solid to a liquid and gaseous state creates a decrease in the shear strength of the formation. Thus if the sediments are well sealed, since the water and gas released into the pore space exceed the volume originally occupied by the gas hydrates, the net effect will be an increase in pressure. If the system pressure exceeds the overlying hydrostatic pressure, the increased pore pressure can then weaken the sediment. There will now be a horizon along which the potential for slope failure is increased and so landslides can occur.

In the US Atlantic Margin, the majority of over 200 slump scars have been found to occur within the current up-dip limit of hydrate stability [81]. Intermittent BSRs have also been mapped along the entire margin implying that hydrates are common within these sediments. Bondevik *et al.* [82] noted

that one of the largest submarine slides (the Storrega Slide) in the Norwegian Continental margin, which extends over 800 km downslope, and which transported approximately 5500 km^3 of material, is flanked by sediments that contain a BSR. The sole of the slide is also coincident with the level of the BSR on its sides and suggests that the base of the hydrate stability zone was coincident with the failure surface.

Seismic reflection profiles, multi-beam bathymetric data, and long range side scan sonar images allow for the easy delineation of submarine slope failures. These techniques however provide no data on the cause of the failure. There are also a lot of challenges that make investigating the cause of the slide difficult including the fact that known slide scars are not fresh, environmental conditions would have changed since the slope failed, and access to the deepsea is limited. Any mitigation would be expensive.

In areas with conventional petroleum production, the geohazards associated with the occurrence of hydrate deposits and the geohazards and geomechanics associated with production from hydrate deposits still needs to be better understood, and more specifically, the response of the seafloor and shallow formations to the extraction of methane from the deposits, and the associated stability of the wellbore and pipelines.

13. Conclusions

Natural gas hydrates represent a vast resource with deposits in permafrost and oceanic sediments. There is a concerted effort by a number of governments to assess the technical and economic feasibility of these deposits as evidenced by the acceleration in the study of natural gas hydrates with several nationally funded research programs and more detailed field studies.

Remote sensing techniques which allow for detection of methane hydrate deposits at a scale that provides for geologic confidence need to be developed and in this regard new geophysical tools and techniques continue to be developed. It is envisaged that the combined use of seismic and controlled source electromagnetic (CSEM) imaging has the potential to minimize ambiguity compared to the use of either technique alone.

Numerical simulation will play an important role in assessing the production potential of the accumulations. Several numerical simulators have been developed which can provide estimates of production performance from hydrate deposits under different production scenarios and will serve to clarify and identify the dominant factors affecting the recovery of natural gas from hydrate bearing sediments. So far the numerical studies indicate that conventional techniques can be used to produce some of these deposits and new well designs have been proposed. These results need to be validated however, since there are no well documented long term production data sets.

Further thought will have to be given to production operations given the fact that these deposits occur in hostile environments of the arctic and deep ocean, and no wells exist to test and evaluate potential technologies.

The geohazards and geomechanics associated with commercial production from hydrate deposits need to be better understood and more specifically, the response of the seafloor and shallow formations to the extraction of methane from the deposits, and the associated stability of the wellbore and pipelines.

No major breakthrough has been made to date with regards to the possible roles of methane hydrate degassing as it relates to the carbon cycle and climate change, and so further research is required. Research is required on the role of commercial production as opposed to natural degassing on the environment along with methods of mitigating any environmental impact of natural degassing and degassing associated with commercial development of natural gas hydrates.

Acknowledgements

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