



# Gas Hydrate and Climate Change

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Abstract: Energy demand after the industrial revolution is increasing exponentially but the supply of the same is not even close because of the diminishing fossil fuels. Since, the easy oil has been exploited, researchers are looking for potential crude generation in harsher environment. The harsher environment would mean usage of sophisticated technologies to extract and at deeper levels, which is not considered economical. Consequently, scientists and researchers are looking for alternative energy source such as Gas hydrates in order to meet the energy demand. The anthropogenic activities such as burning of fossil fuel, coal, wood etc has caused adverse effect on the environment like global warming. Therefore, unconventional source of energy like gas hydrates can be used as clean energy. Gas hydrate stability is controlled by several factors like, temperature, pressure, gas composition, ionic impurities in water, thickness of the zone. This paper pertains to study the phase behaviour of the gas hydrate with respect to pressure and temperature, furthermore, the environmental implications of gas hydrates which trigger catastrophic events like tsunami, submarine landslide ocean acidification etc. Special attention is also placed on the opportunities and challenges of gas hydrates policies in consideration to environmental impacts in order to push forward the global developments of the sustainable energy.

Keywords: Climate Change, Gas Hydrate, Environmental impact, Seafloor Instability.

## I. INTRODUCTION

 $\mathbf{T}$  he atmosphere and the ocean are the two element that acts as a Carbon sink and it is expected to undergo significant change due to the rise in the atmospheric CO<sub>2</sub> concentration due to increased anthropogenic activities viz, burning of fossil fuels like oil, wood, coal etc. [1,2]. Due to the increased anthropogenic activities, CO<sub>2</sub> levels have raised to a critical level, where all of the bio-diversity is getting affected, leading to an altered ecosystem, ocean circulation pattern, changes in the biotic diversity and temperature increase. The increase in temperature in the atmosphere means, increased surface temperature of the ocean, decrease in salinity, change in pH and ultimately the melting of polar ice leading to foreseen increase in the sea levels by 0.5m within next 50 to 100 years [3]. Some of the scientist working in this field believe that, the CO<sub>2</sub> produced can have an unwavering effect increase of sea level of 1m [4].

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The greenhouse gas like CO<sub>2</sub> produced from different sources can play havoc with nature like increase the average global temperature, resulting in sea level rise, extreme weather events, an increase in the spread of tropical diseases, eco-system change and even species extinction [5,6,7,8,9,10]. Since the ocean is the largest carbon sink, it can uptake anthropogenic CO<sub>2</sub> and may alter the seawater chemistry of the world's ocean with serious dire consequences of the marine biota. It includes decreased calcification process (mainly in corals), increased pH (acidity), decline of the phytoplankton (reduced oxygen levels in the ocean) thus changing the whole thermodynamics of the ocean [11,12,13,14,15].

The nature tends to work in mysterious ways and thus they tend to repair itself when subjected to any external changes but recent studies have suggested that the significant impacts will persist for hundreds of thousands of years after the CO2 emanation ceases [16.17].

But, due to rapid industrialization and high demand in energy, it has become the need of the hour of every Nation to produce as much as energy possible to keep the world running, without giving nature a second thought. Many anthropogenic activities which include conventional energy sources which are basically non-renewable in nature. Compared to the World Energy Council 2016, the current worldwide energy requirements are met 33% from oil, 29% from coal, 24% from natural gas and 10% from renewable and 4.0% from nuclear energy and a comparative study between 2005 and 2015 are done in the following figure 1[18].



Fig. 1: Comparative study of conventional energy between 2005 and 2015 [18].

As the easy oil has cease to exist engineers and scientist are working relentlessly to find hydrocarbon in extreme temperature and pressure zones as well as alternative energy resource. One such resource is called Gas Hydrates.

# II. COMPOSITION, STRUCTURE AND OCCURANCES OF GAS HYDRATES

Gas hydrates (CH $_4$  5.75H $_2$ O) are crystal structure with hydrogen bonded void water molecules that traps a guest molecule.



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Gas hydrates are characterised based on the type of gas molecule trapped by the water molecules.[19] On the molecular scale, a single guest molecule is en-clathrated by the hydrogen bonded voids in these non-stochiometric hydrates. Guest molecules of distinct sizes combine with the hydrogen bonded water molecules to form 3 distinct yet a well-defined structure SI, SII and SH [20]. The cubic structure I predominates the Earth and generally contains (0.4-0.55nm) guest, viz. methane, CO<sub>2</sub>, ethane etc. Whereas, SII is man-made having guest molecule of size 0.6-0.7nm, viz propane, iso-butane etc and SH are rare in nature with molecules of size 0.8-0.9 nm and contain molecules like Argon, Krypton, O2 and N2[21] as shown in figure 3.



Fig3. The five cavity types and three common unit crystal of methane hydrates. The numbers in coloured blocks represent the number of cage types and the water molecules in a unit lattice [22].

Gas hydrates are mainly spread in the slope of the seabed sediments with depth of 400 to 1000m at temperature below 10C, with pressure greater than 3.5 MPa (Fig 4). Gas hydrates are not only found in seabed, but also in the premafrost regions of Russia, Canada and other countries. But Ocean is the major depositional place for gas hydrates [23].



Fig 4 shows the methane hydrate spread in ocean and on land [24].

Even though other hydrates are also present in nature, methane hydrate is dominant of all. The global volume of methane bound gas is still uncertain but it was estimated tobe  $1.8 \times 10^{16} - 3.4 \times 10^{17}$  m3 in global submarine[25] gas hydrate reservoir with as high as 7600x10^15m3[26] and low as 0.2x10^15m3[27] It is also considered to be clean as it contains high purity of methane molecules and also when burnt produces very less residue, which makes it environmental friendly compared to other by products SOx, NOx and other carcinogenic gases which gets released as by-products from Coal, CBM, shale[28].

Gas hydrates are mainly formed in the permanently frozen regions and outer continental margins where the methane concentration exceeds its solubility limits [29].



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Figure 5. Phase diagram of gas hydrate with respect to temperature, pressure and depth. [30]

The methane which gets trapped as the hydrate compounds comes from the microorganism which gives out methane as the by-product, by consuming the detrital organic matter. The amount and the rate of supply depends on the methane supply. There are two known source of major methane hydrate formation in a Hydrate Stability Zone (HSZ). The HSZ occurs from around 530m depth from Northern latitudes and 250m of the Southern latitudes [31] (garg et al., 2008). The two-methane source include HSZ and deep methane influx. Deep methane influx is produced by the bacteria that decomposes organic rich sediments which provides a constant influx within the marine layer of 99.99% of pure methane with trace element of impurities like Ethane, propane, carbon-di-oxide, hydrogen sulphate [31]. In some areas, the influx rate of the natural gas has been estimated as high as 2.05Kgm2/yr at 12.3°C.

Hydrate formation is favoured in coarse sediments, and they help in decisive step in understanding the hydrate lithology, since coarse grain sediments have high permeability value than the fine grained. When the upwelling methane gas enters the HSZ, it gets dissolved in the pore space of the coarse sediments and exist in three phases as shown in the figure 5.viz., free gas, dissolved in solution and as solid hydrate. Thus, a precise temperature and pressure is required to convert methane to methane clathrate structure. The solubility of methane increases at elevated temperature and pressure, therefore the ascending fluid cools off as they rise and encounters the region of methane insolubility. At this point the methane crystallizes out of the solution becoming more insoluble [32].

Once the methane is saturated with the ocean water existing between he coarse sediment grains, at right temperature and pressure, the ice crystal starts to form in the crystal lattice and trap the methane molecules within the lattice. The guest and the host are not chemically involved rather by a weak Van der Waals force in the ice crystal that would make the entire lattice more stable [33]. Thus, the gas hydrates are formed and able to persist and build a large depositional layer, for the clathrates to be more stable than the ice or methane gas alone.

Thus, stability of gas hydrate hinges on the delicate balance between the temperature and pressure, which decides whether the gas hydrate be intact or dissociate and gets released into the environment. Even though gas hydrate is said to be clean energy, it is still considered potent when released into the atmosphere without proper aid. It is said to be 20 times more powerful that  $CO_2$ , and takes 8 years to disintegrate. Gas hydrates has natural tendency to escape through seeps, but as the temperature in the atmosphere raises, stability of the hydrate is hindered and the methane gas starts to get released from the bed to the atmosphere (fig 4).

# III. ENVIRONMENTAL CONCERNS DUE TO GAS HYDRATE

Ocean acts as the major carbon sink. Climate change has drawn increasing attention all around the globe in the past several decades. The raise in the ocean temperature has lead to the decline of oxygen concentration which has impact the marine life in many different ways. This climate change can affect the stability of the methane hydrate. As the temperature increases the methane hydrate loses its stability and it starts to dissociate into methane gas and water. The dissociated methane bubble starts to rise through the water column. The methane bubble undergoes anaerobic and aerobic oxidation process as it travels through the water column and forms respective by products which may be harmful to the marine and the benthic environment and can also cause subsidence.

Although when followed the regime of hydrate stability, the methane hydrate still remains a commercially feasible alternative energy source in the near future. Any gas production test from the methane hydrate should be based on the environmental impact assessment [34]. Natural or anthropogenic migration of methane into the marine environment and atmosphere will exert impacts on the marine ecosystem, global climate change and component balance. Thus, the phase diagram becomes an important tool in understanding the stability of the hydrate and the resultant weakening support to the sediments, which may cause seafloor instability, submarine landslide or even tsunami.

## 3.1 Factors of Methane Hydrate Instability

Methane hydrate stability hinges on a delicate balance between low temperature and high pressure, even a few degrees Celsius increase in the hydrate vicinity can cause instability and methane clathrate can dissociate [35]. This dissociate can bring pockmarks or holes in the ocean sediment surface and can even cause mechanical instability of the seafloor, and cause a significant release of the methane gas. The size of the bubble determines whether gas would diminish as it travels through the water column or would is reach the ocean surface and get exposed to the atmosphere. Approximately, 1-5 GtC of methane can get released in a single event, causing an increased radiative force upto 0.2Wm-2 to the atmosphere [36].

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Besides temperature variation in the deep ocean, the ocean circulation due to oscillatory currents can also promote dynamic release of methane through seepage [37].

## 3.2 Methane Hydrate Can Cause Global Warming

The methane hydrate is quite abundant on the permafrost and beneath the seabed regions. Nevertheless, this abundant energy when triggered can cause global warming. Methane is considered a greenhouse gas because, methane is 21 time more potent than CO2 and also take 8 years to disintegrate to from CO2 [38]. Due to lower concentration of methane in the atmosphere, the infra-red radiation absorption band is less saturated [39]. Therefore, when large amount of methane gas escapes can likely to cause a catastrophe globally.

As the climate change is persistent due to the global rise of temperature, the stability phase of methane shifts and causes ablation of the permafrost in Arctic regions. The climate change causes the ice in the Arctic to melt and it acts as a triggering mechanism to dissociate methane and water from the methane hydrate. The deep ocean has a long ventilation time almost 100 - 1000 years therefore, a new equilibrium methane hydrate can only be achieved in 1000-10,000 years. Besides, the fraction of methane from the deep ocean that reaches the atmosphere is uncertain and totally depends on the transport phenomenon of the methane bubbles [40]. The oxidation lifetime of methane dissolved in seawater is almost 50 years [41]. Therefore, it is like a vicious cycle of global warming with methane released from gas hydrates and rise in temperature. Necessary measures need to be taken in order to control the methane release from the hydrates and its release to the atmosphere.

## **OCEAN ACIDIFICATION**

The release of methane from the hydrate in oceanic regions can cause ocean acidification and oxygen depletion in the surrounding region. If the hydrate release is from a low oxygen environment then the ecosystem can be severely affected. More than 50% of the dissolved methane could be retained inside the seafloor by microbial anaerobic oxidation of methane (AOM) [42, 43]. The AOM converts methane and oxygen into the carbon-di-oxide, causing an imbalance in the pH of the ocean [44]. Ocean acts as a biggest carbon sink and if there is an increase in the formation of carbon-dioxide in the ocean and also in atmosphere, it can be catastrophic globally.

# 3.3 Gas Impact On Marine Organisms

The gas which dissociates from the bottom of the sea bed gets partly dissolved in the ocean before coming to the surface. Marine animals can get severely affect when it comes in contact with direct gas bubbles and also dissolved in ocean. Gas can rapidly penetrate into the fish through gills and disturb their main functional systems like respiration, nervous system, blood formation, enzyme formation etc. External symptoms include common behavioural changes like fish excitement, increased activity etc.

Furthermore, prolonged exposure can lead to chronic poisoning i.e. at this stage the cumulative effects if physiological and biochemical occurs depending on the nature of the toxin and its concentration. Gas emboli can cause rupture of the tissues, enlarging of bladder, abnormalities in circulatory system and other pathological changes.

Three main types of intoxication by methane gas has been given by the Medical Toxicology viz.,

- Light: Reversible and the effect on central nervous 1. and cardiovascular system will disappear quickly
- Medium: Can cause a deeper and permanent 2 functional change in the central nervous and cardiovascular systems also can increase the number of leukocytes in the peripheral blood.
- Heavy: Permanent damage to the cerebrum, heart 3. tissue and alimentary canals and also acute form of leucocytosis.

The above description gives a general pattern of how a vertebrate would behave when it is exposed to those situations.

Correspondingly, the release of methane can also reduce the oxygen content in the surrounding and this will affect the surrounding marine ecology.

# 3.4 Seafloor Instability Caused By Methane Hydrate

Methane hydrates form a solid structure when they are containing sediment pore space [45]. Due to the fact that the water can't be expelled in a consolidated sediment, this in fact adds a stress to the sediment. The methane hydrate being fragile can be consequential even when there is a slight deviation of temperature and pressure. The methane clathrate would collapse into water and gas as soon as the hydrate bearing sediments become under-consolidated. Furthermore, the seafloor deforms and could cause a submarine landslide or an earthquake beneath the seabed leading to tsunami.

Similar incident of methane hydrate was observed at the off coast of Norway about 7000 years ago. 25m high mega tsunami hit Norway and Scotland, which was thought to be triggered by the Storegga submarine landslide with enormous amount of sediments gliding down up to 800kms down the continental slope. Also, the Russian researchers found that the unstable hydrate slid in 1997 too. The thickness of the tsunami deposited is 20 to 100 cms [46].

Maslin et al. stated that the mass failure event of the Amazon Fan was mostly generated by the calamitous failure of the continental slope, which was later correlated with the climate induced changes of sea level. The rapid decrease of the sea level exposed the gas hydrates and de-stabilised the gas hydrate at the continental slope triggering slope failure and causing the massive glacial mass transport of sediment deposits [47]

It is been said that the slope become susceptible to fail with increase in the thermal diffusivity, water depth and gas saturation and decreases in the pressure diffusivity, water depth and gas saturation.



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Figure 6: Dissociation of hydrate continental slope[48]

Reduction of the sea level and varying temperature and pressure combination has said to initiate the dissociation of the hydrate along the base, which would cause a large volume of gas being released into the atmosphere (Figure 6). The increasing pore fluid volume, reduces the slope stability. It was studied that the disruption of continental slope in Beaufort Sea was induced by the hydrate decomposition within the impermeable clayey sediments [49]

# IV. PROSPECT AND CHALLENGES

Gas hydrate is considered a potential future energy as it would discharge the least amount of carbon per energy unit produced [50]. The carbon emission is of a prime concern as it will affect not only the human lives but also disturb the natures balance. Even though the ocean would act as the largest carbon sink, but over addition of the carbonic ions can cause ocean acidification.

Currently, the gas hydrates with conventional hydrocarbon recovery techniques are being study to extract the gas hydrates and transport the free gases. In the recent study, the most cost-effective option is depressurization method. Even though the gas hydrates need to be extract, but one must maintain the geo-mechanical integrity of the gas hydrate and limit the production of formation water [51]. Exploration and production research have been going on extensively before commercial production is carried out. Reservoir stability and its integrity needs to be the prime motive behind the study as unlike petroleum reservoirs, gas hydrates stability is very fragile and even a smallest disturbance gone unnoticed can be catastrophic. Due to never ending demand of energy of the country and diminishing fossil resource has created a societal decision rather than economic or technological decision for alternate energy sources [52]

## V. ENVIRONMENTAL CHALLENGES AND OPPORTUNITIES

Natural seeps are estimated to release 0.4-12.2 million metric tons of methane gas from the hydrates every year. So, even the methane which is being released naturally is a big concern to the researchers to study the climate change [53].

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Furthermore, the dissociation of gas hydrates would cause global warming, increasing the pH level of sea causing loss of oxygen [54]. Thus, the causes and implication from methane clathrates is a critical measure to minimalize impact on the environment. The release of methane hydrate would increase the presence anaerobic oxidation which can lead to the disturbance in benthos also can lead to mass extinction of rare species which are living in less oxygenated environment. Universally well recognized tools are being used to analyse and monitor the potential environmental problems about the exploitation of the resource like [52]:

- 1) Environmental Impact Assessment (EIA);
- 2) Strategic Environmental Assessment (SEA);
- 3) Ecosystem Approach to Management (EAM); and
- 4) Marine Spatial Planning (MSP)

## **Environmental Impact Assessment (EIA)**

It was first introduced by the International Association for Impact which "process of categorizing, forecasting, assessing and mitigating the bio-physical, social and other relevant effects of developmental proposal before any major decision is taken". EIA study is first and foremost study which needs to be carried by all the organisation before any production activity is started [55]

## Strategic Environmental Assessment (SEA)

This aims to ensure that the policies and the national plans associated with the resource exploitation take other users of land, air, sea and other shared assets into account [56]

## **Eco-system Approach to Management (EAM)**

1992 the United Nations Convention on Biological Diversity aims in the conservation of the biological diversity, fair and equitable sharing of the benefits arising from the utilization of the genetic resources [57,58]. It also states the maintenance of biological richness and ecological processes to sustain the composition, structure and functionality of the habitants

# Marine Spatial Planning (MSP)

MSP is designed to manage the usage of marine area multiple times which reduces the environmental impacts by analysing the current and anticipated usage of ocean and the eco-system.

The gas hydrate being in the pressurized state can hold more methane gas in small volumes and when dissociated and utilized properly could provide safe green energy [52]. The use of this alternating energy source could be used as a secure source for the country and if the consumption of the energy usage is to increase in the near future, fossil fuels could be replaced with gas hydrate. However, the proper policies need to be issues with no loopholes which could cost more for the country.



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## VI. CONCLUSION

Due to the industrial revolution, anthropogenic activities have boomed and its activities are ever increasing in a rapid pace. Discovery of crude oil and natural gas was considered more of a blessing in the modern world but the easy oil got diminished soon and researchers are looking for energy in most harsher conditions. Also, the energy requirement keeps increasing due the luxury of human living and it is very difficult for the engineers to meet the demand and therefore, we need to look for alternate energy source, one such source is Gas Hydrates which occurs beneath the seabed and in permafrost conditions. Number of nations are coming forward to study this bundle of energy and making significant efforts in securing and efficient utilization. Countries like USA, Japan, China, India etc are taking a serious interest towards this energy. Even though there are various implications involved proper monitoring system needs to be employed in order to curb the situation and safely exploited. Various opportunities and challenges for commercial gas recovery from gas hydrates are discussed with respect to the environmental impact.

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