# The Influence of Geochemistry of Gas Hydrates on the Shear Strength and Stability of Marine Sediment Movement

J. Rajaraman[1(✉)], K. Thiruvenkatasamy[1], and S. Narasimha Rao[2]

[1] Department of Harbour and Ocean Engineering, AMET University,
Kanathur, Chennai, India
`rajaraman.usha44@gmail.com`, `swamy2667@gmail.com`
[2] Dredging Corporation of India (Govt. of India), Vishakhapatnam, India
`kuttyharirao@gmail.com`

**Abstract.** Methane obtained from hydrate will become a significant energy resource in the near future. It will become a critical sustainable source of energy possibly by 2025. In this inter-disciplinary research paper the influence of Environmental Geochemistry of gas hydrates on the shear strength and stability of marine sediment movement is discussed. Methane, $CH_4$, the most common form of natural gas associated with petroleum reservoirs, is in gaseous state at standard temperature and pressure conditions. But under high pressure and low temperature, it combines with water molecules to form an icy – white compound called methane hydrate. Taking a continental margin (continental shelf, slope and raise) and abyssal depth the geo environment is represented as four zones namely 1. Continental shelf has high temperature and low pressure 2. Continental slope has low temperature low pressure 3. Continental rise with low temperature high pressure 4. Abyssal depth with high temperature and high pressure (it does not exist in nature in the case of gas hydrates). The same zones can be classified geo-technically for sediments as 1. Continental shelf with high angle of internal friction ($\varphi$) and low cohesion (c) 2. Continental slope with low angle of internal friction ($\varphi$) and low cohesion (c) 3. Continental rise with low angle of internal friction ($\varphi$) and high cohesion (c) 4. Abyssal depth with high angle of internal friction ($\varphi$) and high cohesion (c) (which does not exist in nature). These four zones are analyzed geotechnically for stability of sediments in the sea floor environment. The inter-disciplinary equation of shear strength and gas hydrate environment is $\tau = c + \sigma \tan \varphi$ where $\tau$ = shear strength of the sediment, c and $\varphi$ are geotechnical parameters and $\sigma$ = to vertical stress of sea water depth and also sediment thickness above the point of consideration with geo thermal gradient. This paper also deals with the decomposition of gas hydrates which decreases the shear strength, making the sediment move towards failure. Basically soil is a three phase system consisting of solids of the soil, water and air. Gas hydrates will behave as solid or gas depending upon the environmental conditions. Gas hydrates will (1) change pore pressure, (2) cause dilation (3) weaken sediments and (4) break down initiates major slumps in continental slopes. The application of Skempton's pore pressure parameters A and B are verified through environmental considerations. The sediment movement from coastal areas to abyssal plain should be as natural as possible. The conclusion is that, accelerated sediment movement is dangerous to marine environment.

D.N. Singh and A. Galaa (eds.), *Contemporary Issues in Geoenvironmental Engineering*, Sustainable Civil Infrastructures,
DOI 10.1007/978-3-319-61612-4_18

# 1 Introduction

Methane ($CH_4$), the most common form of natural gas associated with petroleum reservoirs, is in gaseous state at standard temperature and pressure conditions. But under high pressure and low temperature, it combines with water molecules to form an icy-white compound called methane hydrate (Carroll 2001). Other gases such as ethane, propane, butane, $CO_2$, $H_2S$ etc. also form compounds with water and in general, they are called as gas hydrates. In nature such high pressure and low temperature conditions are prevalent in areas of permafrost (both offshore and onshore), on the outer continental margins and shelves, and beneath sea floors. Gas hydrates comprise more than 99 per cent of methane and in an ideally saturated gas hydrate the molar ratio of methane to water is about 1:6. Thus it contains huge volumes of gas e.g. 1 $m^3$ of solid hydrate (theoretically) contains up to 164 $m^3$ of methane gas at standard pressure and temperature. In nature, the more typical value is 40 $m^3$ of methane. Though the hydrates are least understood unconventional energy resource as of now, they hold the greatest volume of the global methane endowment (Carroll 2001). Methane produced from gas hydrates is truly unconventional because of its origin, trapping mechanism and production technologies. Unlike conventional traps, which are a prerequisite for the accumulation of oil and natural gas, gas hydrates can form their own trap within the pore space and expand themselves against the sediment load in the form of massive hydrates.

# 2 Discovery of Gas Hydrate

Davy (1811) was the first to discover gas hydrate when chlorine gas and water reacted to give rise to a solid compound at cold weather conditions in the laboratory. A variety of other molecules are later found to form hydrates called as clathrates in which they are considered as guests while the water being the host molecule. In general, a clathrate is a compound formed by the inclusion of molecules of one kind (guest) within the cavities of the crystal lattice of another (host). Clathrates, also known as "inclusion or container compounds," display no chemical bonding between the host and the guest molecules. They can form spontaneously under certain pressure, temperature conditions when a host molecule (e.g., water) crystallizes into an open lattice structure and a guest molecule of suitable size (e.g., methane) fits into the lattice voids.

**Occurrence**

Gas hydrates occur ubiquitously in three distinct areas: Polar (permafrost) regions, shallow offshore sediments in Arctic and sub-arctic regions, and deep ocean sediments in tropical regions. Hydrates that occur naturally exist in disseminated or dispersed, nodular, layered and massive forms. Except layered hydrates, others occur in unconsolidated sediments (Kuldeep Chandra 1997). The most favourable conditions for occurrence of gas hydrates are:

(i) Areas of hemipelagic sedimentation of Pleistocene age,
(ii) Rapid sedimentation rate (> 3 cm/1000 years),
(iii) P & T conditions, pressure (> 50 atms) and temperature (4–6 °C) envelop,
(iv) Geothermal gradient (< 6°C/100 m), and

(v) Sediment organic carbon content (> 0.5 per cent) and methane concentration in porewater (> 10 ml/1)

### Crystal Structure

Methane (gas) hydrate is a crystalline ice-like solid compound. It occurs in three structures I, II and H, the most predominant being the structure I. In structure I, the cages are arranged in a body centered cubic packing, and are large enough to include methane, ethane and other gas molecules of similar molecular diameter such as $CO_2$ and $H_2S$. In structure II, some cages in the face centered (diamond) cubic packing are larger enough to include bigger molecules such as propane and isobutane. Structure H being least common in nature, contains cages still larger than structure II in a hexagonal crystallographic system (Sloan 1998).

### Physical Properties

Some typical physical properties of methane hydrate are given in Table 1. The density of methane hydrate (0.91 g/cm$^3$) is less than water. It may vary slightly depending on the methane saturation of the hydrate lattice and with the incorporation of other molecules such as $H_2S$ in the lattice. The heat of hydrate formation and the heat of hydrate dissociation are equal in magnitude but in opposite sign. When hydrate forms, heat is released from the exothermic system and when hydrate dissociates, heat is taken up into the endothermic system. The measured value of methane hydrate formation enthalpy at 273 °K is 54 kJ/mole (Sloan 1998).

**Table 1.** Some physical properties of methane hydrate

| Serial No: | Property | Magnitude |
|---|---|---|
| 1 | Bulk density (gms/cm$^3$) | 0.912 |
| 2 | Thermal conductivity at 263 °K (w/m-k) | 0.49 ± 0.02 |
| 3 | Adiabatic compressibility at 273 °K, 10–11 pa | 14 |
| 4 | Heat of fusion at 273 °K (KJ/mole) | 54 |
| 5 | Heat of dissociation at 273 °K (KJ/mole) | –54 |
| 6 | Heat capacity at constant pressure (KJ/mole) | 257 |
| 7 | Dielectric constant at 273 °K | 58 |
| 8 | Poisson’s ratio | 0.33 |

Source: Max 2000.

## 3 Stability of Gas Hydrates

The stability of a gas hydrate depends on pressure (P), temperature (T) and the solubility of gas as a function of P and T of the hydrate system. The stability is more susceptible to changes in temperature than to pressure. In addition to temperature, other physical properties such as thermal conductivity and thermal diffusivity are also critical which control the transfer of heat through hydrate reservoirs. Further, certain chemical and geological factors promote or inhibit hydrate stability. These include:

- Gas properties: presence of ethane, propane, $CO_2$/ $H_2S$ etc.
- Pore fluid properties: dissolved ions ($Na^+$ $K^+$ $Mg^{2+}$ $Ca^{2+}$)
- Sediment composition: fine grained sediments (clays)
- Geological processes: erosion, rate of sedimentation, slumping, subsidence, uplift, and earthquakes.

The phase equilibria shown in Fig. 1 apply to pure methane system and structure I gas hydrate in the presence of fresh or saline water. Presence of even a fractional percentage of ethane or propane that produce structure II hydrate, is stable at higher temperatures than structure I at a given pressure, thus increasing its stability. In contrast, the presence of dissolved ions ($Na^+$, K+ , $Ca^{2+}$, $Mg^{2+}$) in pore fluids inhibit the stability of gas hydrate. The inhibitory effect of ionic compounds on the stability of hydrate has critical implications, for the evolution and long term stability of hydrate deposits in areas characterized by salt tectonism, evolution of seafloor brine basins, and circulation of briny liquids as evident in the Gulf of Mexico (Sassen and McDonald 1997).

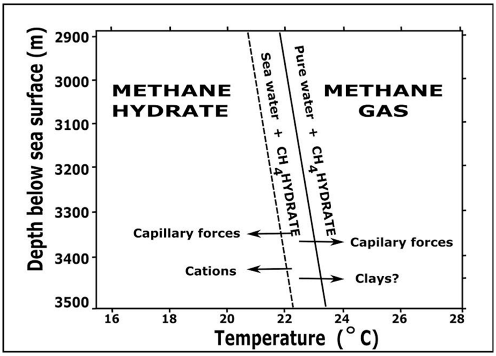


**Fig. 1.** Stability of marine hydrate for pure water (Solid Line) and sea water (Dashed Line) systems. Arrows schematically show various physical and chemical factors that affect stability of hydrate. (Source: Max 2000)

The composition of sediment matrix may exercise a strong influence on the temperature of hydrate dissociation in some settings. Clays appears to promote hydrate formation at higher temperatures. Physical properties of the sediment may play a critical role on the stability of hydrate as well. Large capillary forces that arise in fine grained sediments may inhibit the entry of fluids into the interstices between the grains and thus significantly inhibit hydrate stability, depressing its dissociation temperature.

Methane hydrates often form as disseminated grains and pore fillings in coarse grained sediments whereas in finer silt/clay deposits, they commonly appear as nodules and veins. In general, naturally occurring methane hydrates, form in two types of geological settings (Milkov and Sassen 2001):

(i) Structural accumulations associated with faults and mud volcanoes, where gas leaking from deeper subsurface petroleum system is rapidly transported (via faults, gas chimneys or other fluid conduits) to the gas hydrate stability zone (Cassassucem et al. 2004), and

(ii) Stratigraphically bound accumulations in relatively permeable sea floor sediments where bacterial methane generates in situ or slowly migrates from shallow depths into the gas hydrate stability zone.

## 4 Gas Hydrate Stability Zone (GHSZ)

Physical conditions that control the presence of methane hydrate are usually represented by a phase diagram in terms of temperature and depth fields as shown in Fig. 1.

It illustrates the phase of equilibrium among gas hydrate, free gas and aqueous solution, and physical parameters controlling the formation of gas hydrate (P, T and salinity). The phase boundary (dashed line) separates colder, higher pressure conditions where methane hydrate is stable to the left of the curve, from conditions to the right, where it is not stable (solid line) assuming a typical hydrothermal gradient in water and geothermal gradient in sediment. The figure shows the variation of temperature with depth of water and underlying sediment. The point where the solid line (representing the conditions in sediment) crosses the phase boundary represents the bottom of the zone where methane hydrate is stable (GHSZ). This phase boundary corresponds to a sediment depth of about 300–600 m below the sea floor (bsf) at a water depth of about 3,000 m along the Indian continental margins (Fig. 2). However, the hydrate zone in the water column is much shallower (about 750 m). When methane in water is of sufficient concentration (near saturation), it forms hydrate in the hydrate stability zone. However, being lighter than water, it floats upward and would dissociate when it crosses the depth where the hydrothermal gradient and the gas hydrate boundary curves intersect each other. On the other hand, if the gas hydrate forms within the sediment, it will be bound in place. The precise location of base of the GHSZ under known pressure and temperature conditions depends on several factors, the most important being the gas composition. Presences of higher hydrocarbons (ethane, propane etc.) allow the gas hydrates to form at lower pressure and higher temperature in shallow waters. The presence of salts (NaCl, KCl, $MgCl_2$ etc.), in pore waters shift the gas hydrate phase boundary to the left, low temperature and high pressure (in deep waters).

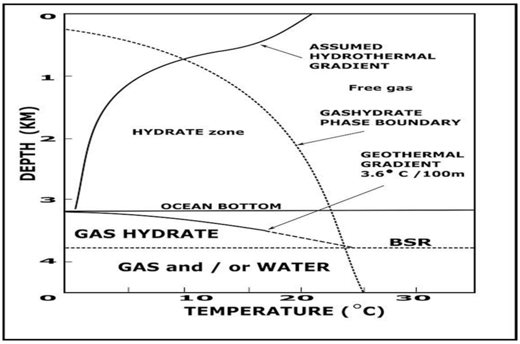


**Fig. 2.** Phase diagram of methane hydrate for indian continental margins. (Source: Hanumantha Rao et al. 1998)

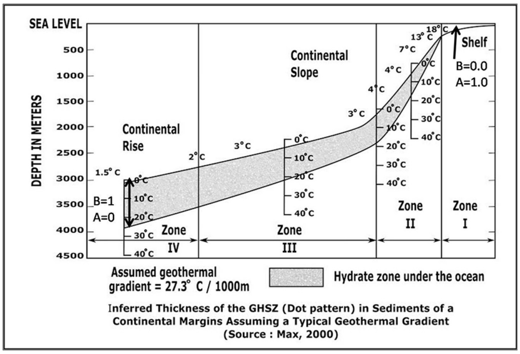
### Thickness of GHSZ

As stated above, the vertical extent of the sediment layer from sea floor to the intersection point of the phase boundary curve with the geo-thermal gradient curve in the sediment gives the thickness of GHSZ. In general, the thermal gradient tends to be uniform across broad regions where sediments do not vary. Therefore, for a given water depth, the sub-bottom depth to the base of the GHSZ will be quite constant. However, because a change in water depth causes changes in pressure, it is to be anticipated that the base of GHSZ will extend further below sea floor as water depth increases. It implies that the zone where gas hydrate exists, forms a more or less uniform layer below the sea floor, thickening towards greater depths (Fig. 3). Though this is commonly true, there are few exceptions because of disturbances of thermal structure in the sediments (Max 2000). These include:

(i) Sea floor landslides: They remove cooler near surface sediments, leaving warmer-than normal materials near the sea floor which cause local shallowing of the base of GHSZ.

(ii) Salt diapers: They produce warm spots since the salt has greater thermal conductivity than other sediments which forces the base of GHSZ to shallower regions.

(iii) Faults: Circulation of warm fluids up to shallow sub-bottom regions through faults as channel ways results in the disruption of gas hydrate formation or shift the base of GHSZ to shallow waters.



Inferred Thickness of the GHSZ (Dot pattern) in Sediments of a Continental Margins Assuming a Typical Geothermal Gradient (Source : Max, 2000)

**Fig. 3.** A and B appearing in the figure are Skempton's pore pressure Parameters

## 5 Gas Hydrates, Shear Strengths and Stability of Marine Sediment Movement (Fig. 3)

In zone 1 hyper pycnal flow adds more well graded sediments and the $\varphi$ is high with reasonable cohesion (c). This zone also represents high temperature and low pressure and therefore methane hydrates are not formed in sediments.

In zone 2 gas hydrates are formed in sediments but not much due to low pressure though the low temperature is favourable for the formation of gas hydrates.

Geo-technically this region has low $\varphi$ (rounded and weathered grain sizes) and low cohesion (c) due to loss fines.

In zone 3 the environmental conditions are favourable for the formation of gas hydrates. The high pressure and low temperature combination is the main reason. Due to sediment movement the sediments are highly weathered with low $\varphi$ and high cohesion. High cohesion indicates the production of clay.

In zone 4 as pointed out earlier in the abstract high temperature and high pressure does not exist in nature. This possibility is ruled out in marine environment. Similarly high friction $\varphi$ and high cohesion © cannot exist together.

**Facts About Stability of Gas Hydrates**

1. Stability of gas hydrates is a function of temperature (T) and pressure (P).
2. The stability is more susceptible to changes in temperature than pressure.
3. Clays appear to promote hydrate formation at higher temperature.
4. In fine grained soils large capillary forces that arise may inhibit the entry of fluids into the interstices between the grains.

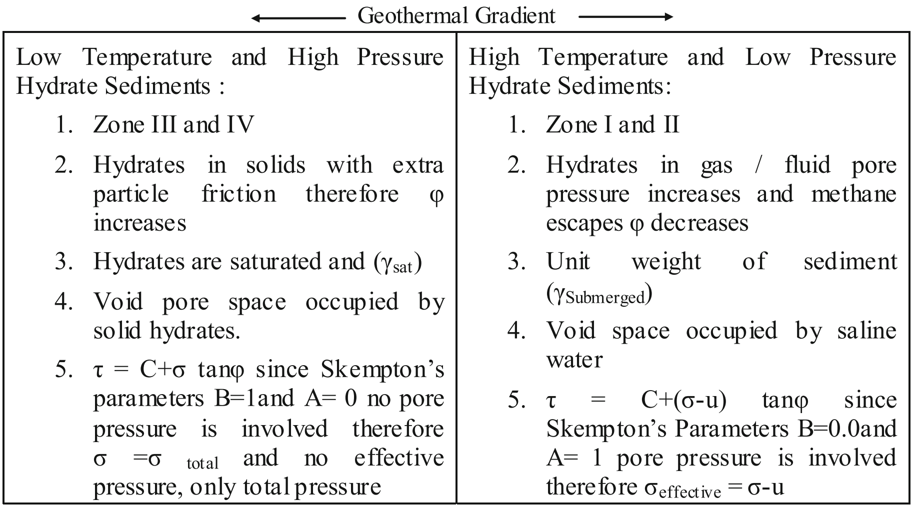
## 6 Interpretation of Skempton's Pore Pressure Parameters to Ocean Bottom Hydrate Sediments (Fig. 4)

The usual Skempton's pore pressure parameters are given by the following equation:

$$\Delta u = B[\Delta\sigma_3 + A(\Delta\sigma_1 - \Delta\sigma_3)] \tag{1}$$

where $\Delta\ \sigma_1$, $\Delta\ \sigma_3$ are major and minor (confined) principal stress increments and A and B are pore pressure parameters as given below:

$$B = \frac{\Delta u}{\Delta\sigma_3}, \qquad A = \frac{\Delta u}{\Delta\sigma_1 - \Delta\sigma_3}$$



← Geothermal Gradient →

| Low Temperature and High Pressure Hydrate Sediments : | High Temperature and Low Pressure Hydrate Sediments: |
|---|---|
| 1. Zone III and IV | 1. Zone I and II |
| 2. Hydrates in solids with extra particle friction therefore φ increases | 2. Hydrates in gas / fluid pore pressure increases and methane escapes φ decreases |
| 3. Hydrates are saturated and ($\gamma_{sat}$) | 3. Unit weight of sediment ($\gamma_{Submerged}$) |
| 4. Void pore space occupied by solid hydrates. | 4. Void space occupied by saline water |
| 5. τ = C+σ tanφ since Skempton's parameters B=1and A= 0 no pore pressure is involved therefore σ =$\sigma_{total}$ and no effective pressure, only total pressure | 5. τ = C+(σ-u) tanφ since Skempton's Parameters B=0.0and A= 1 pore pressure is involved therefore $\sigma_{effective}$ = σ-u |

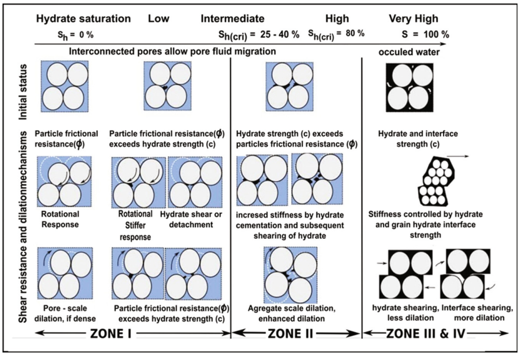


**Fig. 4.** A summary of the mechanisms controlling the shear strength of hydrate bearing sediments, where soil grains are shown in white, hydrate in black and water in blue (after Waite et al. 2009; modified from Yun et al. 2007). At high hydrate saturations effective stress becomes invalid and interpretations must be based on total stress.

Under global warming due to excess temperature even deeper sediments are subjected to high temperature and low pressure and therefore the solid hydrates break and the $\varphi$ value decreases rapidly. The effect can be illustrated by a conceptual model example: in a ten meter high marine slope of 40° the soil has cohesion; void ratio and angle $\varphi$ were found to be 2.5 tons/$m^2$, 0.81 and 14° respectively. When the temperature alters find the new factor of safety for the hydrate infested area for G = 2.7 and for 40° slope the stability number for different values of $\varphi$:

| φ | *n* |
|---|---|
| 6° | 0.122 |
| 7° | 0.116 |
| 14° | 0.074 |

From the given data γ saturated = 1.94 gm/cc and γ submerged 0.94 gm/cc. The factor of safety (F) is c/γ submerged x h x n that is = 3. 59. When the temperature alters the solid gas hydrates becomes pore pressure and escapes. Therefore the new $\varphi$ value is $\varphi' = 0.94/1.94 \times 14 = 6.78^{\circ}$. Therefore the geothermal gradient alters the $\varphi$ value from 14° to 6.78° which clearly indicates the effect of geothermal gradient on the stability of gas hydrate sediments. On the whole the sediments move towards ocean down the slope to reach the low temperature environment where the sliding sediments are stopped by the sediments with higher $\varphi$ values manifested as resistive force to stop the submarine slump. As a consequence the sea level rise inundates coastal areas.

## 7 Conclusions

1. Climate change impacts on methane hydrates. Huge amounts of methane are stored around the world in the sea floor in the form of solid methane hydrate. These hydrates represent a large energy reserve for humanity. Global warming could cause

the hydrate to destabilize. The methane, a potential green house gas could escape unused into atmosphere and could even accelerate climatic changes.

2. Methane hydrates located directly at the boundaries of the stability zones would be primarily affected because in these locations, a temperature increase of 1 °c (Celsius) would be sufficient to release large amounts of methane from the hydrates.
3. Methane should not become silent weapon for invisible, quiet wars.
4. Methane should not become lethal to mankind.
5. Dual nature of Methane hydrates is responsible for change in shear strength. It can exist in solid form or in gaseous form depending upon the temperature, pressure and environment.
6. If a strategic area is bombed will initiate the release of methane. The released methane will take care of the rest of the destruction, leading to catastrophe.

## References

Carroll, J.: Natural Gas Hydrates. Gulf Publishing, Boston (2001)

Cassassucem, F., Rector, J., Hoverstain, M.: Study of gas hydrates in the deep sea gulf of mexico from seismic data. Lead. Edge **23**, 366–372 (2004)

Davy, H.: On combination of oxymuriatic gas and oxygen gas. Philos. Trans. Royal Soc. **101**, 155 (1811)

Rao, Y.H., Reddy, S.L., Khanna, R., Rao, T.G., Thakur, N.K., Subrahmanyam, C.: Potential distribution of methane hydrates along the indian continental margins. Curr. Sci. **74**, 466–468 (1998)

Chandra, K.: Non – conventional hydro carbon resources like coal bed methane and gas hydrates: exploration imperatives for india. indian. J. Geol. **69**, 261–267 (1997)

Max, M.D.: Gas hydrate potential of the indian sector of the NE arabian sea and northern indian ocean. In: Max, M.D. (ed.) Natural Gas Hydrates. Kluwer Academic Publishers, London, pp. 213–224, 414 pp (2000)

Milkov, V.A., Sassen, R.: Economic geology of off-shore gas hydrate accumulations and provinces. Mar. Petrol. Geol. **19**, 1–11 (2001)

Sassen, R., McDonald, I.R.: Hydrocarbons of experimental and natural gas hydrates, Gulf of Mexico continental slope. Org. Geochem **26**, 289–293 (1997)

Sloan, E.D.: Clathrate Hydrates of Natural Gases, 2nd edn. Marcel- Dekker, New York (1998). 705 pp.