Gas Hydrates at Minimum Stability Water Depths in the Gulf of Mexico: Significance to Geohazard Assessment

Alexei V. Milkov[1], Roger Sassen[1], Irina Novikova[2], and Eugeniy Mikhailov[2]

[1]Geochemical and Environmental Research Group,
[2]Department of Physics, Texas A&M University, College Station, Texas 77845, USA

Abstract

Gas hydrate stability is a function of water depth, bottom water temperature, pressure, and thermal gradient in sediments, pore water salinity, gas availability, and composition. The modeled minimum water depths at which gas hydrates crystallize at present in the Gulf of Mexico is 330-615 m, depending on the source gas composition. The minimum water depth at which gas hydrates have been found by shallow coring is about 440 m. Bottom water temperature is variable because of seasonal variations, and the propagation of warm core Loop Current eddies. The influence of heat flow associated with these two factors on gas hydrate stability is presented in the paper. Seasonal variations in bottom water temperature may affect gas hydrate stability only in the upper 1-2 m of sediments, depending on water depth. Warm core eddies also only affect the upper 1-2 m of sediments depending on the duration of their propagation. Our data imply a thin but extensive gas hydrate geohazard zone in the Gulf of Mexico at water depth ranging from ~440 m to ~720 m. Repetitive gas hydrate formation and decomposition could cause sediment deformation, slumps, and gas blowout craters, and increase the rate of oil venting to the water column. Such events may impact sub-sea petroleum exploitation within the Gulf of Mexico.

Introduction

Geological hazards are potentially damaging phenomena that may occur within a specified period of time and within a given area (e.g., volcanic activity, earthquakes, soil erosion) (Bell, 1999). Many geohazards including landslides, submarine gullies, mud flows, etc. have been identified in oceans around the world (Kou and Du, 1995; Orren, 1996). The Gulf of Mexico represents a complex petroleum province in which various geohazards are present.

Stauffer et al. (1999) distinguish two types of geohazards that may play a significant role on the Gulf of Mexico continental slope. Seabed geohazards include fault scarps, fluid expulsion features, diapiric structures, gas vents, unstable slopes, mudflow gullies and lobes, slumps, sand waves, mud lumps and mud volcanoes, collapse features, carbonate rock outcrops, pinnacles, reefs, and chemosynthetic communities. Subsurface geohazards include shallow faults, slumps, buried channels, salt intrusions, shallow gas-charged sediments and shallow water flow. Gas hydrates that outcrop on the seafloor (MacDonald et al., 1994), and which occur at shallow subbottom depths (e.g. Sassen et al., 1999a,b) are also potential geohazards (Stauffer et al., 1999).

Gas hydrates are minerals in which hydrocarbon and nonhydrocarbon gases are held within rigid cages of water molecules. Because the equilibrium conditions of gas hydrate formation/dissociation are close to P,T-conditions of shallow sediments at water depths in 300-700 m range (depending on bottom water temperature), gas hydrates may impact deep-water operations. The potential impact of gas hydrates as geohazards was recognized about 20 years ago (Taylor et al., 1980; McIver, 1982), and is now generally accepted by geologists and engineers (Bagirov and Lerche, 1998; Ergun and Cifci, 1999). However, little research has been done on the geohazard aspect of gas hydrates and "this area represents a major future challenge" (Sloan, 1998, p.577).

The present paper focuses on the relatively shallow water depths (300-700 m) in the Gulf of Mexico. In this zone, gas hydrates are thought to be relatively unstable and may impact drilling operations, sea-floor installations, and pipelines. The main objectives of this paper are (1) to estimate the minimum water depth of gas hydrate formation, and (2) to study the influence of bottom water temperature changes on gas hydrate stability.

Geology and Geochemistry of Gas Hydrates

The Gulf of Mexico continental slope is a complex petroleum province where both bacterial methane hydrates and thermogenic gas hydrate occur. As of today, gas

hydrates have been recovered from more than 50 sites at water depth in the ~440 to >2400 m range by piston coring, deep drilling and using submersibles (Sassen et al., 1999a,b). The strong spatial association between gas hydrates, petroleum seeps, and oil and gas discoveries is postulated (Fig. 1, Sassen et al., 1999b). In addition, it is well established that shallow gas hydrate accumulations tend to form along the rims of salt-withdrawal basins, over salt ridges, and near the leading edge of the Sigsbee Escarpment where active faults associated with salt bodies provide pathways for migration of fluids from deep subsurface (Sassen et al., 1999b). Although the distribution of gas hydrates at greater depth within the sediments of the continental slope is poorly studied, modeling of gas hydrate stability zone (GHSZ) indicates that thermogenic gas hydrates may occur in upper 1150 m of sediments at deepest gas hydrate sites (Milkov and Sassen, 2000).

Gas hydrates of all three known structures – I, II, and H – have been found in the Gulf of Mexico (Brooks et al., 1984, 1986; Sassen and MacDonald, 1994, 1997; Sassen et al., 1998, 1999b). Structure I hydrate is composed mainly of bacterial methane and is stable at greater temperature and pressure than structure II and H hydrates that contain heavy hydrocarbon gases (C_{2+}) originated from deep Earth's interior (Sassen et al., 1999a,b). The fraction of methane decreases and the fraction of ethane, propane and butane increases when gas hydrate forms from natural vent gas in the Gulf of Mexico. After that bacterial oxidation affects hydrate-bound methane and changes its isotopic composition (Sassen et al., 1999a).

Minimum Water Depth of Gas Hydrate Formation

The minimum water depth limit for gas hydrate formation is a function of bottom water temperature, water salinity, gas availability, and gas composition. A graphical method (e.g., MacLeod, 1982) was applied to estimate the minimum water depth of gas hydrate formation at the intersection of annual average hydrothermal gradient and gas hydrate stability curves (Fig. 2).

An annual average hydrothermal gradient was constructed using data from Wash et al. (1998a). Sloan's (1998) GSMHYD Hydrate Program was used to estimate gas hydrate stability conditions. We have calculated the equilibrium conditions of gas hydrate formation based on geochemical measurements of thermogenic vent gases and pure methane (Table 1) that represent the range of natural vent gases thus far studied in the Gulf of Mexico (Sassen et al., 1999a,b). We assumed standard water salinity (35‰).

The minimum water depth for stability of bacterial structure I gas hydrate (100% C_1) is estimated ~615 m, a value similar to Collet's (1995) estimate of 600 m. Thermogenic (structure II) gas hydrate is estimated to crystallize from natural vent gases at water depths in the ~330 (90.4% C_1) to ~420 m (95.9% C_1) range. However, the minimum water depth at which gas hydrates have been found by shallow coring is about 440 m (Sassen et al., 1999b). Anderson et al. (1992) assumed that thermogenic gas hydrate could exist in the Gulf of Mexico in water depth as shallow as 220 m. However, we believe this estimate assumed unrealistic natural gas compositions.

Temperature in the shallow sediments in the Gulf of Mexico is mainly affected by two mechanisms. These include heat flow into sediments from bottom water and movement of relatively warm fluids from the deep subsurface to the seafloor along salt-related fracture zones and along active faults. Bottom water temperature is a critical parameter that defines the minimum water depth of gas hydrate formation, and the thickness of GHSZ. However, water temperature is not constant. In the Gulf of Mexico water temperature varies seasonally, and because of the influence of warm-core Loop Current eddies (Walker et al., 1993; MacDonald et al., 1994; Roberts et al., 1999).

The Influence of Seasonal Variations of Bottom Water Temperature on Gas Hydrate Stability

Seasonal variation of bottom water temperature is restricted to relatively shallow water depths in the Gulf of Mexico (~700 m) (Fig. 3). The range of variation increases with decreasing water depth, and approaches 1 °C at 300 m water depth (Wash et al., 1998a). We model the heat flow as a one-dimensional problem. The heat flow may be described by the equation (Carslaw and Jaeger, 1959):

$$\frac{\partial^2 \Delta T(z,t)}{\partial z^2} = \frac{1}{\alpha^2}\frac{\partial \Delta T(z,t)}{\partial t} \tag{1}$$

where the function $\Delta T(z,t)$ represents the change in temperature due to seasonal variations, z is the depth dimension, α^2 is the thermal diffusivity of the sediments, and t is the time. The thermal diffusivity of the sediments derives from the empirical relation (Von Herzen and Maxwell, 1959):

$$\alpha^2 = 2.67K – 0.3 \times 10^{-3} \tag{2}$$

where K represents the thermal conductivity. Stoll and Bryan (1979) researched the thermal conductivity of
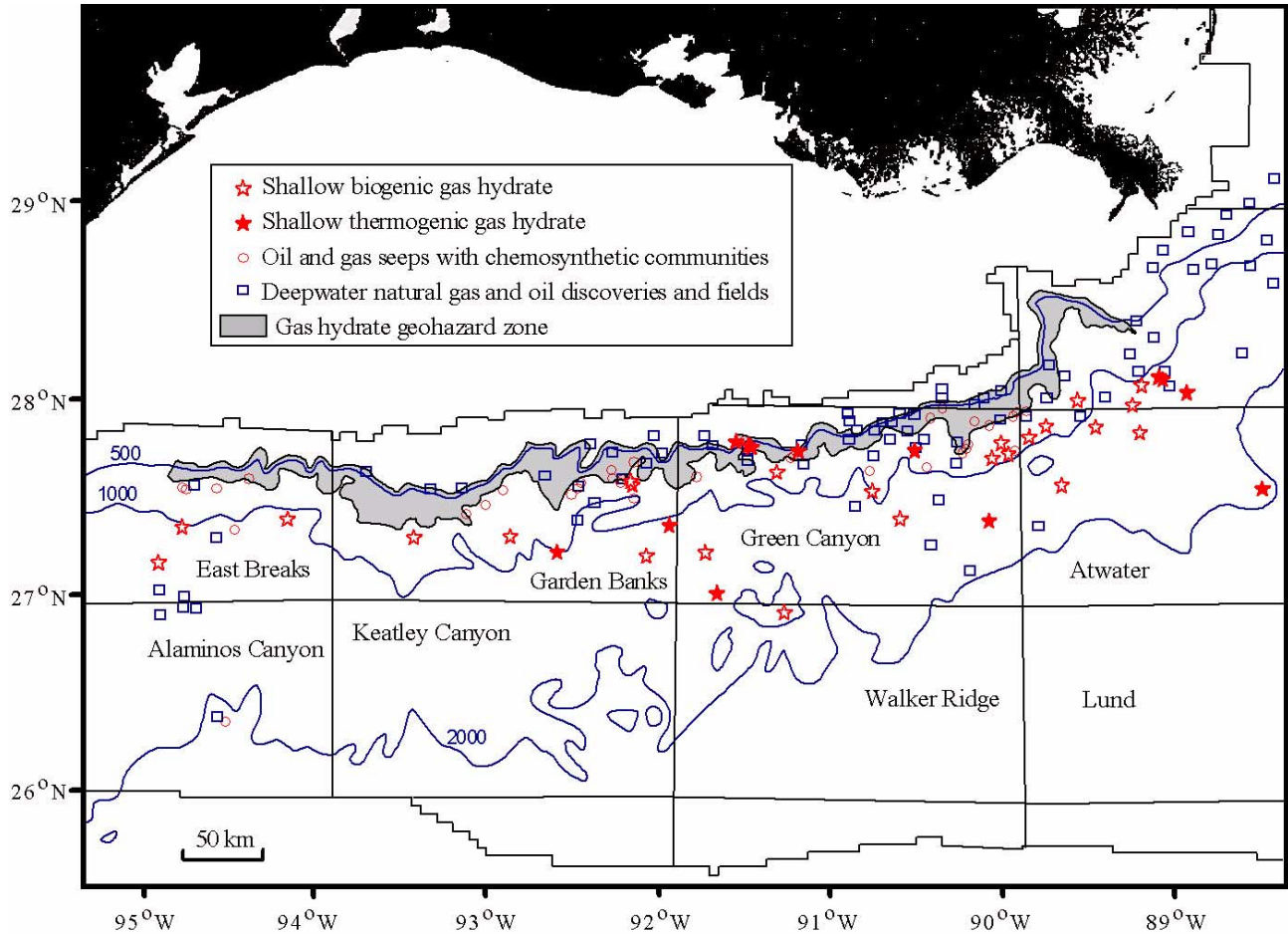
Figure 1. Location map showing distribution of gas hydrate sites, oil seeps, petroleum discoveries and fields, and potential hydrate geohazard zone in the Gulf of Mexico continental slope (modified from Sassen et al., 1999 a,b). Water depth contours are shown in meters.

Table 1. Molecular composition (vol. %) of vent gases used to estimate gas hydrates stability conditions.

Study area	C_1	C_2	C_3	i-C_4	n-C_4	i-C_5	n-C_5	Reference
	100	–	–	–	–	–	–	
GC 184/185	95.9	2.4	1.2	<0.1	0.3	0.2	<0.1	Sassen et al., 1999a
GC 184/185	90.4	4.5	3.7	0.6	0.6	0.2	<0.1	Sassen et al., 1999a

hydrate-bearing sediments. They found that the presence of gas hydrates decreases the thermal conductivity of sediments by about 20 percent. In this study, we assume a constant thermal conductivity (0.002 cal/$^\circ$C/cm/sec) that is 80 percent of thermal conductivity of ocean sediments with 60-70 percent porosity (0.0025 cal/$^\circ$C/cm/sec; Stoll and Bryan, 1979).

The temperature at given subbottom depth and given time may be defined by the equation:

$$T(z,t) = T_0 + \lambda z + \Delta T e^{-\sqrt{\frac{\omega}{2a^2}}z} sin\left(\omega t - \sqrt{\frac{\omega}{2a^2}}z\right)$$ (3)

where T_0 is the annual average temperature, λz represents the average geothermal gradient, the last term describes seasonal variations in water temperature, and ΔT and ω are
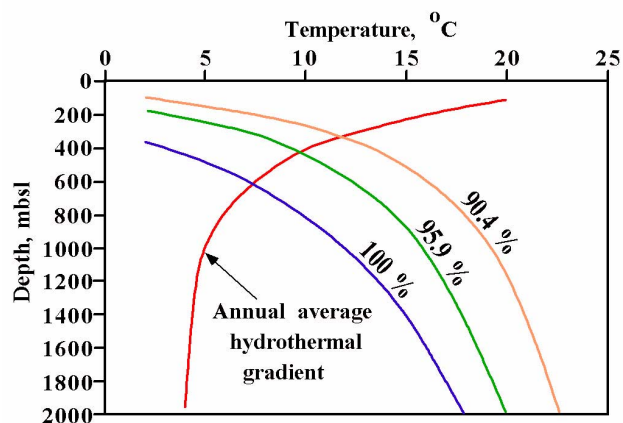
Figure 2. Annual average hydrothermal gradient in the Gulf of Mexico (after data of Wash et al., 1998a) and gas hydrate stability curves for vent gases containing 100, 95.9 and 90.4 percent methane (see Table 1 for complete gas compositions). Depth is shown in meters below sea level (mbsl).

the amplitude and the frequency of the temperature oscillation, respectively.

Figures 4 and 5 demonstrate the temperature distribution in sediments at 330 and 615 m water depth in January and in July, and gas hydrate stability curves. At 330 m water depth thermogenic gas hydrates could theoretically crystallize from vent gas containing 90.4% C_1 in January to depths as great as 2.1 meters below seafloor (mbsf) (Fig. 4). These gas hydrates should decompose before July as water temperature increases (Fig. 4). However, in July *P,T*-conditions for crystallization of gas hydrates occurs at

depths from 2.8 m to 4.2 mbsf. There is only a small probability that gas hydrates will form in this particular case because significant overcooling is needed to nucleate crystallization (Clennell et al., 1999). At 615 m water depth, the stability zone of bacterial methane hydrate may reach 1.2 m in January and then decreases to zero in July (Fig. 5). Therefore, seasonal variations of bottom water temperature could influence the gas hydrate stability zone in a thin veneer of sediments.

The Influence of Loop Current Eddies on Gas Hydrate Stability

Warm-core eddies associated with the Loop Current (the main current in the Eastern Gulf of Mexico) propagate on the continental slope and significantly change bottom water temperature (e.g., Walker et al., 1993). The eddy shedding occurs every 11 ± 3 months, on average (Vukovich, 1995). The modeling of the variability of Loop Current eddies indicates that the speed of eddy propagation is 3-5 km/day; eddy sizes are 200-400 km, and eddy lifetimes approximate 100-200 days (Oey, 1996). MacDonald et al. (1994) noted that large eddies can raise sea water temperatures to 14 °C at 500 m water, whereas the average bottom water temperature at this depth is 8.5 °C (Wash et al., 1998a). In addition, bottom water temperature in the Gulf of Mexico may change on the order of 3 °C at 540 m water depth even without the influence of Loop Current eddies (Roberts et al., 1999).
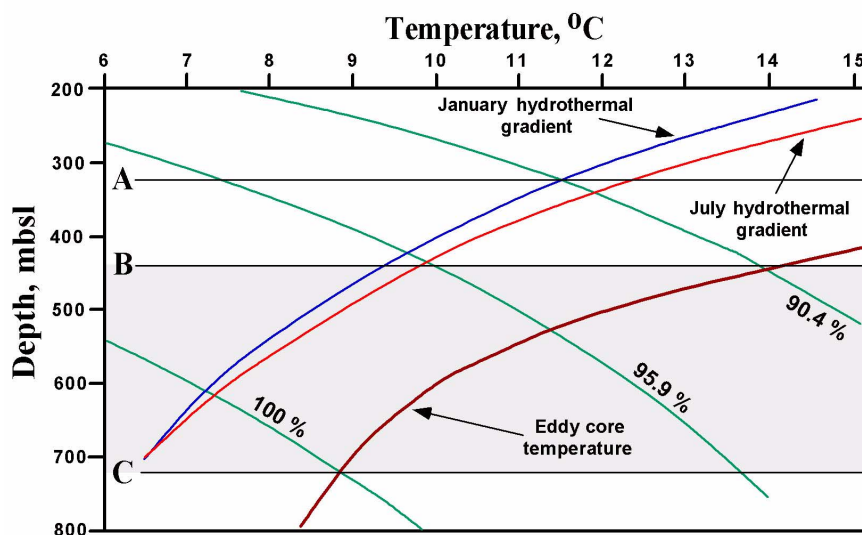

Figure 3. January and July hydrothermal gradients (after data of Wash et al., 1998a), eddy core temperature (after data of Elliot, 1982), and gas hydrate stability curves. Line A represents the modeled minimum water depth at which gas hydrates crystallize at present, line B represents he minimum water depth at which gas hydrates have been found by shallow coring. The shaded area between lines B and C is a potential hydrate geohazard zone.

In our study we assume that warm-core eddies propagate along the continental slope where gas hydrates exist in shallow sediments. The initial water temperature at a given water depth is shown in Figure 2. We assume that warm-core eddies influence the bottom water temperature for 30 days and 90 days, and that the maximum temperature at specified water depth occurs at the 15th day and the 45th day, respectively. Figure 3 shows the water temperature profile in the core of a warm eddy measured in June 1967 in the central Gulf of Mexico (Elliott, 1982). This profile has been used to estimate the maximum water temperatures subject to influence of an eddy.

To study the flux of heat associated with the eddy into the sediments, we model the heat flow as a one-dimensional problem (see Equations 1 and 2 in the previous section). In this case the boundary conditions are defined by the water temperature distribution $f(z=0,t)=F(t)$. Analysis of the measured data (Elliot, 1982) allows us to fit the bottom temperature distribution using Gaussian function:

$$F(t) = A exp\left[-\frac{(t - t_0)^2}{\tau^2} \right]$$

(4)

where A is maximum temperature variation, τ is the effective duration of the eddy propagation, t_0 is the time from the beginning of measurements to the temperature peak. Equation (1) was solved using Fourier transformation method. The final equation for the temperature distribution in sediments can be obtained in the form of integral expression:

$$T(z,t) = T_0 + \lambda z + \frac{A\tau}{\sqrt{\pi}} \int_0^{+\infty} e^{-\frac{\omega^2 \tau^2}{4}} e^{-\sqrt{\frac{\omega}{2a^2}}z} cos\left(\sqrt{\frac{\omega}{2a^2}}z - \omega(t - t_0) \right) d\omega$$
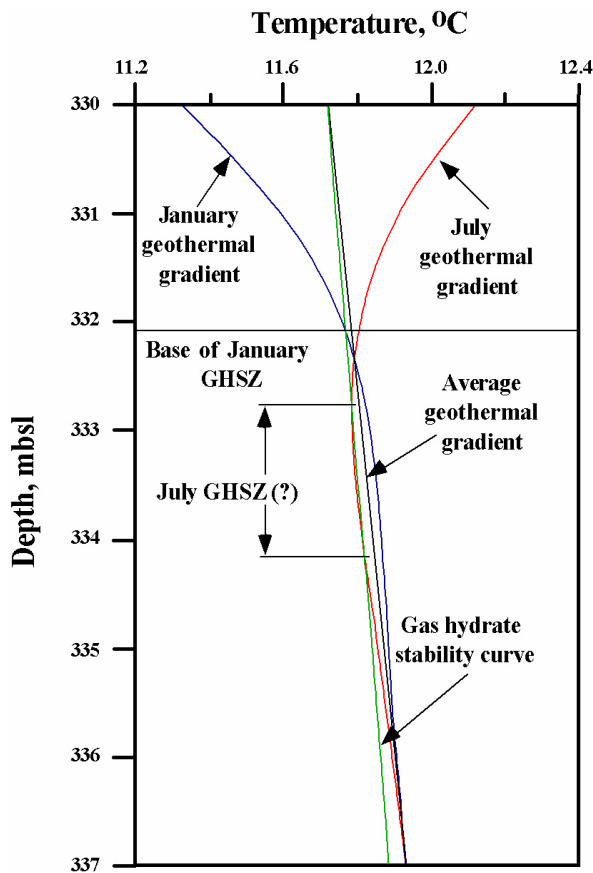
(5)

Figure 4. January, July and annual average geothermal gradients and gas hydrate stability curves for gas containing 90.4 percent of C1 (gas hydrates are stable to the left of the curve). Water depth is 330 m.
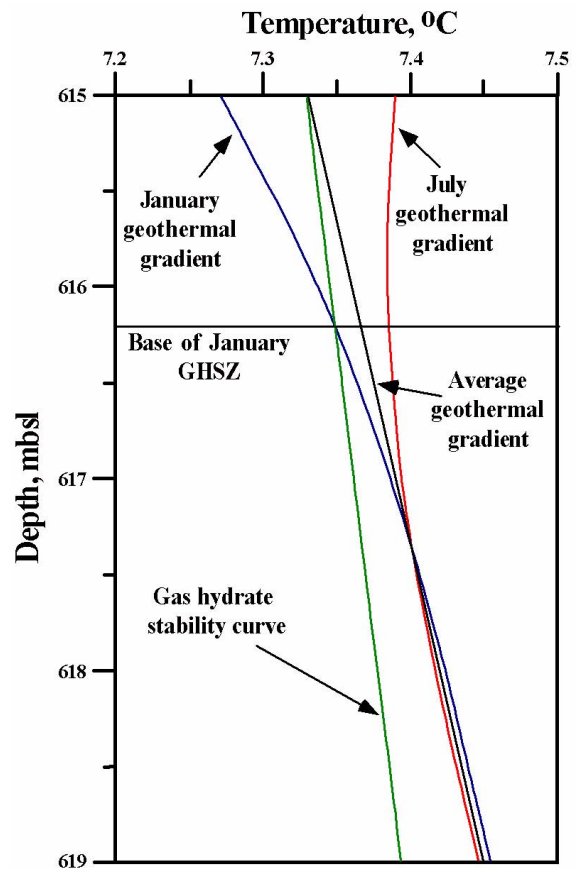

Figure 5. January, July and annual average geothermal gradients and gas hydrate stability curve for pure methane gas (gas hydrates are stable to the left of the curve). Water depth is 615 m.

The numerical results of the temperature distribution modeling and gas hydrate stability curve for natural vent gas containing 95.9 % C_1 are shown in Figures 6 and 7 for 450 m water depth. With this vent gas composition, water depth, and average geothermal gradient of 30 $^{\circ}$C/km, gas hydrates may form as deep as 54 mbsf. If an eddy lasted 30 days, gas hydrates should start to decompose immediately below seafloor by the end of 5th day (Fig. 6). The zone of gas hydrate instability increases in the shallow sediment section, and may reach a thickness about 1 m. After 25 days, gas hydrates are stable again immediately below seafloor but there is the zone of unstable gas hydrates at some depth within the GHSZ. For example, after 30 days, this zone occurs at depth 0.25 mbsf to 1.15 mbsf. Then this zone decreases, and by the 60th day, the shallow sediment is characterized by P,T-conditions favorable for gas hydrate stability. The same scenario is true for an eddy lasting 90 days, but in this case the zone of unstable gas hydrates is thicker and may reach 2 m (Fig. 7).

The Hydrate Geohazard-Risk Zone

Figure 3 suggests that gas hydrates may repeatedly crystallize and decompose because of bottom water temperature variations at water depth ranging from ~ 320 m (where the January hydrothermal gradient line intersects 90.4% C_1 gas hydrate stability curve), to ~ 720 m (where the eddy core temperature profile intersects the 100% C_1 gas hydrate curve). At shallower water depths, gas hydrates cannot form, and at deeper water depths bottom water temperature variations do not affect gas hydrate stability. However, the minimum water depth where gas hydrates actually occur is greater than the modeled water depth, about 440 m (Sassen et al., 1999b). The lack of coincidence is assumed to occur because thermogenic gas containing 90.4% C_1 (Table 1) is not widely distributed in the Gulf of Mexico petroleum system. An area at water depths in the 440-720 m range could be classified as a potential hydrate geohazard zone in the Gulf of Mexico (Fig. 1). This area encompasses ~14,000 km^2 within the northwestern continental slope. The average width is around 20 km. About 30% of active deepwater leases in the Gulf are located within this geohazard-risk zone (Mineral Management Service; www.gomr.mms.gov).

Decomposition of gas hydrates may change some physical properties of sediments (e.g., density), increase water and gas content, increase pore pressure, and decrease the shear strength of the sediments (Campbell, 1991). This could develop zones of weakness within the
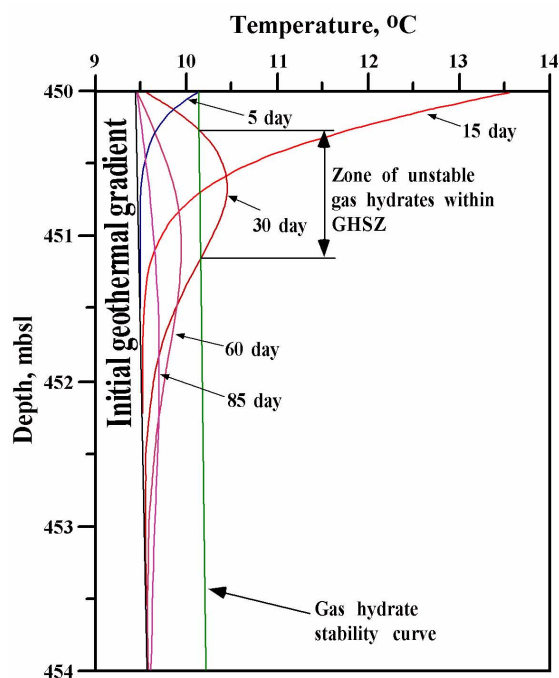

Figure 6. Gas hydrate stability curve for gas containing 95.9 percent of C1 (gas hydrates are stable to the left of the curve), and temperature distribution in sediment affected by 30-days eddy propagation. Water depth is 450 m.
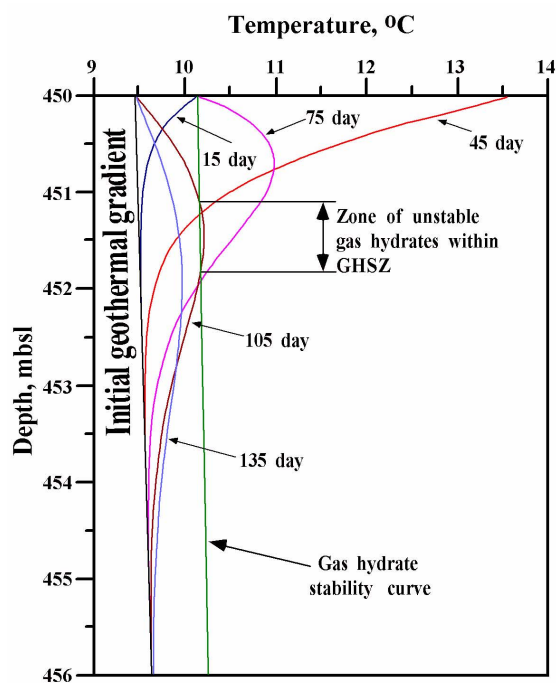

Figure 7. Gas hydrate stability curve for gas containing 95.9 percent C1 (gas hydrates are stable to the left of the curve), and temperature distribution in sediment affected by 90-days of eddy propagation. Water depth is 450 m.

very upper section of sediments, and trigger local land-slides and slumps. Various authors suggest that large regional slides worldwide have been caused by gas hydrate decomposition (see review in Haq, 1998). Gas hydrate formation/dissociation may also cause changes in foundation conditions and should be taken into account by engineers working in deep-sea sediments. In addition, decomposition of gas hydrates could release gas and oil physically trapped beneath continuous gas hydrate lenses to the water column.

Conclusions

In the Gulf of Mexico slope, where large volumes of gas hydrates are concentrated in sediments near the seafloor starting at water depth 440-615 m, bottom water temperature varies because of seasonal changes and because of the propagation of warm core Loop Current eddies across the slope. We have modeled the influence of heat flow from seawater on gas hydrate stability. The results of modeling indicate that both seasonal and short-term variations of bottom water temperature may affect gas hydrate stability only in the upper 1-2 m of sediments. However, the zone where repetitive gas hydrate formation and decomposition occur because of bottom water temperature change is very extensive in area, encompassing much of the Gulf slope. Gas blowouts, oil ejection into water column, sediment slumps, and other geohazards triggered by gas hydrate decomposition could occur in this zone, and impact sub-sea operations.

Acknowledgments

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