ABSTRACT
The hydrate mound in Mississippi Canyon Block 118 (MC 118) contains mostly Structure II thermogenic hydrates formed by gases upflowing along a nearly vertical fault system extending from a salt diapir that lies several hundred meters beneath the hydrate mound. Preliminary modeling studies were performed by representing the hydrocarbon gas mixture as a single gas. The one-dimensional THROBS simulator was used to model (1) the hydrate distribution above the shallowest BSR, (2) the presence of high salinity fluids within the hydrate stability zone, and (3) gas venting at the sea-floor.

A "compositional" (i.e. multi-gas) simulator is needed to account for the various gas components present in MC 118 hydrates, such a treatment for the gas composition is necessary for modeling phenomena such as molecular fractionation. Progress on the development of a multi-dimensional multi-component (methane, ethane, and propane) simulator is described.

Keywords: Natural Gas Hydrates, Gulf of Mexico, Structure II, Multi-component hydrates, Modeling
has been attributed by Sassen et al. [2] to molecular fractionation during hydrate formation. Prediction of hydrate equilibrium for multi-component systems such as that present at the MC 118 Hydrate Mound may be made by (1) the gas gravity method, (2) the Ki value method, and (3) the statistical thermodynamics method [3]. The gas gravity method can only determine the pressure and temperature conditions for hydrate formation; the Ki value approach also yields the hydrate composition. Only the statistical thermodynamics method provides both the hydrate composition and the fraction of each cavity occupied by molecules of different gases. Unfortunately, the latter method is too computationally intensive to be incorporated into a numerical simulator for modeling the formation and dissociation of hydrates. Consequently, it was decided to use the statistical thermodynamics method to generate data for the other two simpler (i.e. the gas gravity and the Ki value) methods for use in a numerical simulator.

We at first used an “equivalent gas” (i.e. the gas gravity method) to investigate aspects of hydrate formation and dissociation at the Hydrate Mound. These parametric calculations are described in the following section. Work is currently proceeding on developing a multi-dimensional multi-component simulator based on the Ki value method, the progress to-date is outlined.

Preliminary Modeling Calculations
Garg et al. [4] describe a one-dimensional numerical simulator (THROBS) for modeling the formation and dissociation of Structure I methane hydrate. For purposes of the calculations described in this section, THROBS was modified to include the stability curve for Structure II hydrate as deduced from the CSMHYD computer program [3]. We consider a three-component gas mixture (methane: 95%, ethane: 4.3%, and propane: 0.7% mole fractions) in equilibrium with gas hydrate and brine. Note that the assumed ethane and propane volume fractions (~mole fractions) differ somewhat from those reported for the vent gas at MC118; these volume fractions were adjusted in order to approximate the hydrate gas composition. The three-phase (gas phase in equilibrium with hydrate and pure water) equilibrium data, obtained using the CSMHYD program, was fit by the following expression:

$$\log(P) = A + BT + CT^2 + DT^3$$ (1)

In Equation (1), pressure P is in Pa, temperature T is in degrees Celsius, and the A, B, C and D coefficients are:

- $A = 6.15697$
- $B = 3.5522 \times 10^{-2}$
- $C = 1.4957 \times 10^{-3}$
- $D = -2.8245 \times 10^{-5}$

In the pressure range of interest (10 to 15 MPa) for MC 118 Hydrate Mound gas hydrates, the effect of pore salinity on equilibrium temperature can be represented adequately by the following relation:

$$\Delta T_{eq} = -6 \alpha_s$$ (2)

where $\alpha_s$ denotes the pore fluid salinity. Equation (2) implies that for normal seawater salinity, the hydrate equilibrium temperature is depressed by about 2°C.

Since the vent gas at the Hydrate Mound is mostly methane, it was decided to use the methane PVT properties for the “equivalent” gas phase. Other required hydrate properties (e.g. density, compressibility, thermal expansion coefficient, specific heat, heat of formation) were estimated based on published data.

The modified THROBS simulator was used to perform parametric calculations to examine the following aspects of hydrate formation/decomposition at Hydrate Mound:

1. Gas influx rates required for hydrate formation.
2. Effect of salinity on hydrate distribution.
3. Effect of temperature gradient.
4. Conditions required for the co-existence of three phases (hydrate, gas, liquid) and for gas venting at the sea-floor.

These parametric calculations are described in the following.

Gas Supply
Hydrate formation and distribution is controlled by pore fluid pressure, temperature, salinity, and the
available gas supply. To determine the gas supply required to create three-phase conditions near the seafloor, a series of five calculations were run. At Hydrate Mound MC 118, the water depth is about 880 meters and the seafloor temperature is about 5.5 °C [1]. For present purposes, it is assumed that sedimentation is negligible on a time scale of 1000 to 10,000 years. Other sediment and fluid properties (e.g. porosity, heat capacity, thermal conductivity, compressibility, permeability, relative permeabilities, diffusivities of methane, sulfate and salt in water, etc.) are similar to those used by Garg et al. [4]. The spatial grid consists of 50 blocks. The initial height of the grid is ~361 meters; the latter value did not change much (less than 2 meters) with the formation/dissociation of gas hydrate in any of the cases described in this section. A fixed time step of 1 year was employed, and each case was run for a total of 10,000 time steps.

The inflowing fluid is essentially all gas (99.99% by mass). A series of 5 calculations were run with total upward mass flux ranging from 10^-8 to 5 x 10^-8 kg/s-m^2 at a temperature of about 20.5 °C. Assuming a gas density of ~100 kg/m^3, the inflow yields a superficial gas velocity of ~ (3 – 16) mm/year. The interstitial gas velocity can of course be much higher.

The distributions of hydrate at t = 2000, 5000, and 10,000 years are displayed in Figure 1. It is apparent from Figure 1 that for the lowest two gas upflow rates, the top of the hydrate zone remains below the seafloor even at t = 10,000 years. For the remaining three cases, the top of the hydrate zone reaches the seafloor at various times. For the highest gas upflow, the hydrate reaches the seafloor at about 3200 years. The time for the hydrate to form near the seafloor decreases with an increase in the gas upflow rate. It should be reiterated that the formation of hydrate at or close to the seafloor and the creation of 3-phase conditions (free gas, liquid, solid hydrate) is essential for gas venting at the seafloor.

The effect of gas upflow rate on hydrate formation is further illustrated in Figure 2 which shows the hydrate distribution with depth after the injection of an equal amount of gas. Depending on the gas upflow rate, the profiles shown in Figure 2 correspond to different elapsed times. Thus, the profile for the lowest upflow rate is plotted at t = 10,000 years, and the one at the highest upflow rate is at 2000 years. It is clear from Figure 2 that the hydrate distribution does not only depend on the total gas supply; it also is a strong function of the gas upflow rate.

Total Mass Upflow

The calculations presented in the preceding subsection illustrate the effect of the gas upflow rate on hydrate formation. Of course, there is little reason to assume that the upflow consists of only gas. To investigate the effect of a two-phase upflow (i.e. brine and free gas) on hydrate formation, a series of four calculations were run. Case m1 is identical with the high gas upflow case discussed in the preceding section. The upward gas mass flux is the same in all the four cases; the amount of brine upflow (and hence gas mass fraction of the total upflow) varies from case to case. The salinity of the upflowing liquid is assumed to be twice the normal sea-water salinity, and the temperature of the fluid influx is 20.5 °C.

Results for this series of calculations are displayed in Figures 3 and 4. Higher brine upflow tends to smooth out salinity profiles (compare cases m1 and m4, Figure 4). For case m4, at t = 10,000 years, the salinity within the hydrate zone is only slightly higher than in the hydrate-free zone beneath it. Another effect of the higher mass upflow is to shoal up the bottom of the hydrate stability zone (Figure 3). The latter effect is a direct consequence of the salinity and to a lesser degree temperature distributions; below a depth of about 150-200 m, the salinity increases with increasing upflow rate.
Figure 1: Hydrate distribution with depth at t = 2000, 5000, and 10,000 years. Calculations are parameterized by the upward gas mass flux ($10^{-8}$, $2 \times 10^{-8}$, $3 \times 10^{-8}$, $4 \times 10^{-8}$, and $5 \times 10^{-8}$ kg/s-m$^2$).

Figure 2: Comparison of hydrate distribution with depth for the same total mass of gas upflow but different rates.
Figure 3: Hydrate distribution with depth at $t = 2000$, 5000, and 10,000 years. Calculations are parameterized by the gas mass percentage of the upward fluid (free gas plus brine) mass flux. Although the upward gas mass flux is the same in all the cases, the total mass flux (and hence gas mass percentage) varies from case to case.

Figure 4: Relative salinity distribution with depth at $t = 2000$, 5000, and 10,000 years. Calculations are parameterized by the gas mass percentage of the upward fluid (free gas plus brine) mass flux. Although the upward gas mass flux is the same in all the cases, the total mass flux (and hence gas mass percentage) varies from case to case.
Salinity of Upflowing Brine
Hydrate Mound at MC 118 is underlain by a salt diapir. Addition of salt from the diapir to the upflowing brine could increase its salinity. To study the impact of upflowing brine salinity on hydrate formation, a series of five calculations (cases s1 to s5) was run; note that case s2 is the same as case m4 described in the preceding subsection. The upward gas mass flux, brine mass flux, and gas mass fraction are the same for all the five cases, the salt mass fraction of the upflowing brine, however, is taken to vary from 100% (case s1) to 500% (case s5) of normal sea-water.

Computed distributions of hydrate and salinity are shown in Figures 5 and 6, respectively. By $t = 10,000$ years, the volume of inflowing brine is enough to replace the fluid in place in the sediment column at $t = 0$ years. Interestingly, the salinity distribution with depth at $t = 10,000$ years (Figure 6) is not uniform. Below the hydrate zone, the salinity ($t = 10,000$ years) is equal to the salinity of the upflowing fluid; within the hydrate zone, the salinity differs from that beneath the hydrate due to hydrate formation/decomposition and salt diffusion in the pore water. At $t = 2000$ and 5000 years, the hydrate distribution with depth does not vary much from case to case. The bottom of the hydrate stability zone tends to get shallower at late times (Figure 5) due to an increase in salinity and consequent hydrate melting. Continued upflow of high salinity fluid (salinity = 5 x normal sea-water) will eventually melt most if not all of the solid hydrate.

Conductive Temperature Gradient
Hydrate formation is controlled by the pore pressure, temperature, and salinity in addition to gas supply. In the preceding, we considered the role of salinity and gas supply on hydrates present beneath the Hydrate Mound MC 118. Since the pressure distribution with depth is in the main governed by the sea-level, it is not necessary to carry out parametric calculations by varying formation pressure. In this subsection, we will investigate the effects of temperature by considering a range of conductive temperature gradients. For these calculations, case s2 (same as case m4) with a temperature gradient of 30°C/km is adopted as the base case. Additional calculations were carried out for temperature gradients of 20°C/km, 25°C/km, 35°C/km, and 40°C/km; the remaining model parameters were left unchanged from the base case.

Computed distributions of hydrate saturation and temperature are illustrated in Figures 7 and 8, respectively. Not surprisingly, an increase in conductive temperature gradient results in an increase in pore fluid temperatures (Figure 8) which in turn leads to a shoaling of the base of the hydrate stability zone (Figure 7).

Summary of Parametric Calculations
The parametric calculations reported herein were designed to investigate the effect of major variables (gas supply, upward fluid flux, salinity, temperature gradient) that are likely to govern the distribution of gas hydrates beneath the Hydrate Mound MC 118. The presence of gas venting and high salinity fluids indicates the existence of three-phase (solid hydrate, free gas, and liquid brine) conditions at or near the sea-floor. The free gas supply from beneath the Hydrate Mound must be sustained for a sufficiently long period to create such a three-phase zone; the length of time depends on the gas upflow rate. If the upflow is essentially all gas, hydrate formation results in high salinities within the hydrate zone. On the other hand if the upflow contains a large fraction of brine, the salinity distribution tends to get smoothed. Both the high salinity brine upflow and high conductive temperature gradient result in a shoaling of the bottom of the hydrate stability zone.

The numerical results presented in this section suggest that in order to characterize the hydrates beneath the Hydrate Mound MC 118, it is necessary to obtain reliable estimates of at least (1) gas and brine upflow rates, (2) pore fluid salinity distribution with depth, (3) salinity of upflowing brine, and (4) temperature distribution with depth. A borehole is absolutely essential for making the necessary measurements of sediment properties (e.g. porosity and compaction coefficient), pore fluid properties (e.g. salinity and gas content), and hydrate distribution.
Figure 5: Hydrate distribution with depth at $t = 2000$, $5000$, and $10,000$ years. Calculations are parameterized by the salinity of the upward flowing brine. The salinity varies from $100\%$ to $500\%$ of normal sea-water.

Figure 6: Relative salinity distribution with depth at $t = 2000$, $5000$, and $10,000$ years. Calculations are parameterized by the salinity of the upward flowing brine. The salinity varies from $100\%$ to $500\%$ of normal sea-water.
Figure 7: Hydrate distribution with depth at $t = 2000$, $5000$, and $10,000$ years. Calculations are parameterized by the conductive temperature gradient.

Figure 8: Temperature distribution with depth at $t = 2000$, $5000$, and $10,000$ years. Calculations are parameterized by the conductive temperature gradient.
MULTI-COMPONENT HYDRATE SIMULATOR

As previously mentioned, a “compositional” (i.e. multi-gas) simulator is needed to account for the various gas components present in MC 118 hydrates; such a treatment for the gas composition is necessary for modeling phenomena such as molecular fractionation and multiple BSRs. We seek to describe a system consisting of up to three hydrocarbon gases (principally methane, with smaller amounts of ethane and propane) together with a saline brine in the pressure/temperature range at which hydrates may form (generally between 0ºC and 35ºC temperature and between 1 MPa and 100 MPa pressure). Two methods for calculating hydrate/liquid/gas equilibrium conditions for aqueous/hydrocarbon systems are available in the literature. The first is a statistical thermodynamic approach described by Sloan [3]. This procedure has been embodied in a stand-alone computer program called CSMHYD [3]. The second approach is the much simpler and more heuristic “distribution coefficient” or “K-value” method, which permits equilibrium conditions to be estimated using algebraic formulae [3].

It had been our original intent to employ the “K-value” approach in the development of the constitutive description for the three-component hydrocarbon case. To this end, we first undertook to use the formulation of Mann et al. [5] to try to estimate equilibrium conditions as a function of temperature for a non-saline aqueous system in equilibrium with a gaseous phase consisting of 96% methane (CH\textsubscript{4}), 3% ethane (C\textsubscript{2}H\textsubscript{6}) and 1% propane (C\textsubscript{3}H\textsubscript{8}) by volume. This composition is representative of the vent gases emanating from the Mississippi Canyon 118 hydrate site [2]. Structure II hydrate was assumed. These “K-value” results were then compared to those from similar calculations using the more general-purpose CSMHYD program of Sloan [3]. Unfortunately these comparisons suggested that the “K-value” approach, while useful for preliminary estimation purposes, is insufficiently robust for use in a general-purpose simulator. Figure 9 illustrates the results of this comparison for \( P_{eq} \), the “equilibrium pressure” at which all three phases may coexist, as a function of temperature. The two methods produce comparable results over a pressure range extending from approximately 2 MPa to 20 MPa, but outside that range the “K-value” method diverges markedly from the CSMHYD representation. For pressures less than about 1.7 MPa the “K-value” P/T relationship has a negative derivative, and the equilibrium temperature appears to diverge completely for pressures exceeding 50 MPa or so.

The clear superiority of the CSMHYD results mandated that this more general-purpose approach would be required for the development of our new constitutive model. But direct use of CSMHYD (or an equivalent statistical thermodynamics program) within a hydrate simulator would be much too computationally inefficient for practical calculations. Accordingly, we adopted an intermediate approach. The CSMHYD program was exercised extensively to characterize three-phase equilibrium conditions for a three-component hydrocarbon gas (CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{6} and C\textsubscript{3}H\textsubscript{8}) in equilibrium with H\textsubscript{2}O as a function of temperature. The composition of the gaseous phase is specified by the values of two dimensionless parameters \( H \) and \( G \):

\[
H = \frac{<\text{Ethane}> + <\text{Propane}>}{<\text{Methane}> + <\text{Ethane}> + <\text{Propane}>}
\]

\[
G = \frac{<\text{Propane}>}{<\text{Ethane}> + <\text{Propane}>}
\]

where:

\(<\text{Methane}> = \text{number of moles of CH}_4 \text{ in the gaseous phase},\)

\(<\text{Ethane}> = \text{number of moles of C}_2\text{H}_6 \text{ in the gaseous phase}, \text{ and}\)

\(<\text{Propane}> = \text{number of moles of C}_3\text{H}_8 \text{ in the gaseous phase}.\)

CSMHYD calculations were carried out for temperature \( T = 0ºC, 5ºC, 10ºC, ..., 35ºC \), for \( H = 0.00, 0.02, 0.04, ..., 0.10 \) and for \( G = 0, 0.125, 0.25, 0.375, 0.5 \) and 1.0. The calculated results for each of the 248 cases considered (equilibrium pressure \( P_{eq} \) and the equilibrium composition of the hydrocarbon mixture in the solid hydrate phase) were recorded.

The CSMHYD calculations described above were carried out for four-component systems (H\textsubscript{2}O, CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{6} and C\textsubscript{3}H\textsubscript{8}) without dissolved salt (NaCl). Of course, in reality the “equilibrium pressure” (the pressure at which all three phases –
hydrocarbon gas, solid hydrate, and aqueous brine with dissolved hydrocarbons (can coexist) may be regarded as depending upon temperature, brine-phase salinity, and the composition of the gaseous phase. Defining brine salinity as:

\[ S = \frac{\text{dissolved NaCl mass}}{\text{dissolved NaCl mass} + \text{liquid H}_2\text{O mass}} \]

it is useful to define an “adjusted temperature” \( T_{\text{adj}} \) by:

\[ T_{\text{adj}} = T + 60 \times S \]

where both \( T_{\text{adj}} \) and \( T \) (the actual measured temperature of the system) are expressed in degrees Celsius. The effect of non-zero salinity upon the equilibrium relations is to raise the equilibrium pressure [3] [4], so that the equilibrium pressure at \( (T, S) \) is essentially the same as that for pure water at \( (T_{\text{adj}}, S = 0) \). So, the equilibrium conditions (equilibrium pressure, and the composition of the solid hydrate phase) may be regarded as a function of \( T_{\text{adj}} \) and the composition of the gaseous phase or “feedgas”.

Using the above relation for \( T_{\text{adj}} \), mathematical fits were formulated to the computed CSMHYD results which yield equilibrium pressure and the hydrate hydrocarbon composition (molar ratios of \( \text{CH}_4 : \text{C}_2\text{H}_6 : \text{C}_3\text{H}_8 \)) as functions of \( T_{\text{adj}} = T + 60 \times S \) and the values of \( H \) and \( G \) describing the composition of the feedgas. These fits employ smooth interpolations (with continuous partial derivatives) among the values obtained from CSMHYD.

Figure 10 shows the behavior of the resulting smooth fit to the CSMHYD data for the equilibrium pressure \( P_{\text{eq}} \) as a function of the adjusted temperature \( T_{\text{adj}} = T + 60 \times S \) for various representative values of the feedgas composition parameters \( H \) and \( G \). At any fixed value of \( T_{\text{adj}} \), the equilibrium pressure tends to increase as the feedgas methane (\( \text{CH}_4 \)) content increases relative to the other hydrocarbons (decreasing values of \( H \)), and also increases with decreasing propane (\( \text{C}_3\text{H}_8 \)) content (decreasing values of \( G \)). Thus, as the mean molecular weight of the feedgas mixture increases, the equilibrium pressure tends to decline and the region in which solid hydrate is stable becomes larger (i.e. extends down to lower pressures).

At equilibrium, the relative abundances of the heavier components (ethane and propane) are significantly higher in the solid hydrate phase than in the gaseous phase (the “feedgas”), and the hydrate-phase methane abundance is correspondingly reduced relative to that of the gaseous phase. For the solid hydrate phase, we define a quantity corresponding to \( H \) as follows:

\[ H^* = \frac{(<\text{Ethane}^*> + <\text{Propane}^*>)}{(<\text{Methane}^*> + <\text{Ethane}^*> + <\text{Propane}^*>)} \]

where in this case the mole fractions refer to the solid hydrate phase:

\[ <\text{Methane}^*> = \text{the number of moles of } \text{CH}_4 \text{ in the solid hydrate}, \]

\[ <\text{Ethane}^*> = \text{the number of moles of } \text{C}_2\text{H}_6 \text{ in the solid hydrate}, \]

\[ <\text{Propane}^*> = \text{the number of moles of } \text{C}_3\text{H}_8 \text{ in the solid hydrate}. \]

Representative results for \( H^*(T_{\text{adj}}, G, H) \) are displayed in Figure 11. There is a general tendency for \( H^* \) to decrease somewhat with increasing temperature, at least up to 25°C - 30°C or so, but note that in all cases \( H^* >> H \), that is, the population of the heavier components is significantly larger in the hydrate phase than in the gas phase with which it is in equilibrium. Furthermore, for a particular value of \( H \), the value of \( H^* \) tends to increase if the gas-phase propane fraction increases relative to the ethane fraction (that is, for increasing values of gas-phase \( G \)).

Figure 12 displays the composition of the non-methane portion of the hydrocarbons present at equilibrium in the solid hydrate phase, and illustrates how the relative propane content of the solid hydrate is substantially enhanced compared to that of the feedgas. This is described by the dimensionless quantity \( G^* \), defined as:

\[ G^* = \frac{<\text{Propane}^*>}{(<\text{Ethane}^*> + <\text{Propane}^*>)} \]

The value of \( G^* \) depends significantly upon the value of \( G \) itself and is relatively insensitive to \( H \). For small values of \( G \), the hydrate-phase propane fractionation effect is quite pronounced. If the gas-phase \( G \) value is 0.10, the corresponding hydrate-phase \( G^* \) value will be at least 0.46 and can be as high as 0.68.
Figure 9. Comparison of equilibrium pressure / temperature relationship for a salt-free system with Structure II hydrate and with a feedgas composition of 96% CH₄, 3% C₂H₆ and 1% C₃H₈ (mole fractions), according to algebraic fits (red symbols) of Mann et al. [5], and to the CSMHYD program (blue symbols) of Sloan [3].
Figure 10. Influence of feed-gas composition, brine salinity and temperature upon equilibrium pressure where three hydrocarbon-containing phases (gaseous, aqueous and solid hydrate) may coexist.
Figure 11. Influence of feed gas composition, brine salinity and temperature upon solid hydrate CH$_4$ content relative to other hydrocarbons.
Figure 12. Influence of feed-gas composition, brine salinity and temperature upon solid hydrate $C_3H_8$ content relative to $C_2H_6$. 

Gaseous phase composition:

\[ G = \frac{\langle \text{Propane} \rangle}{\langle \text{Ethane} \rangle + \langle \text{Propane} \rangle} \]

\[ H = \frac{\langle \text{Ethane} \rangle + \langle \text{Propane} \rangle}{\langle \text{Methane} \rangle + \langle \text{Ethane} \rangle + \langle \text{Propane} \rangle} \]

where `$<\text{Gas}>$' denotes the moles of 'Gas' in gaseous phase.
FUTURE WORK
Work is proceeding on incorporating the new constitutive description into the one-dimensional THROBS [4] and multi-dimensional STAR [6] simulators, and will be reported in a future publication.

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