Application of Thermodynamic Models to Hydrate Formation Prediction during Surface Production Well Testing Using the Ratio Factor Method

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Abstract — Hydrate formation, one of the problems encountered during surface production well testing, is governed by many factors including, the kinetics and thermodynamics of the system. In this paper, a thermodynamic model which centres on changes in the Langmuir constant of the guest molecule(s) under operating field conditions as crucial parameter in hydrate formation process is presented. Acquired surface production well testing data (pressure, temperature and choke size) from a hydrate well using a real time data acquisition system were used to determine the effect of choke size variation on Langmuir constant and thus on hydrate formation. A generalized correlation for evaluating Langmuir constant for large cage/cavity under field conditions was developed and expanded to incorporate variations on the choke sizes. The developed model shows that as the choke size increases, Langmuir constant decreases leading to decrease in the rate of hydrate formation. Since the driving force for hydrate formation is the product of fugacity and Langmuir constant, it then follows that as Langmuir constant approaches zero due to increasing choke size, this product also approaches zero thereby leading to zero hydrate formation.

Index Terms – Hydrate Formation, Thermodynamics Models, Langmuir constant, well testing, guest molecules.

1 INTRODUCTION

N Atural gas hydrates are solids that for when liquid water and natural gas are brought in contact at ambient temperature and high pressure, typically 5 - 15C and 50 -

100bar ^[1]. Such conditions are readily found in natural gas industry and in oil and gas production operations. Meanwhile, as exploration and production operations now concentrate on regions of deep-water (offshore) or lower temperature, more emphasis are now being laid on hydrate formation on production fercilities such as seperators, pipes, manifolds, etc., due to the hazard hydrates impose on the facilities, personnel and environment.

Plugging of surface production lines by hydrate during surface well testing has always imposed a serious problem to the oil and gas industry.

Hydrate formation process is a complex one involving gas, liquid and solid at low temperature and high pressure. Since it is a pressure – temperature process, its thermodynamics becomes imperative. In the oil and gas industry, well testing is an important aspect of well intervention that needs to be carried out for well's production optimization and profit maximization. However, hydrate formation is one of the numerous problems encountered during this activity; thus understanding its formation and proffering the necessary solutions becomes inevitable. This work takes a combined theoretical and pratical – oriented approach to solving this problem.

2 PROCEDURE

2.1 Theory of the Thermodynamic of Hydrate Formation Models

Gas hydrates are solid cystaline compounds that occur when water forms a cage like structurules. Gas hydrates of interest to the oil and gas industry are composed of water and eight molecules: methane, ethane, propane, isobutene, normal butane, nitrogen, carbon dioxide and hydrogen sulphide ^[2]. Three types of gas hydrates have been identified as structure I, structure II and structure H. However, it has been found that the structure I is the commonly formed hydrate during surface well testing. Militating against this problem using choke size variation based on thermodynamic principles became of interest.

The basis of the models for hydrate formation is the wellknown Van der Waals – Platteeuw model for the prediction of stability and gas filling for gas hydrate ^[3], which is based on classical statistical thermodynamics and has the following assumptions:

- i. Each cavity can contain at most one gas (guest) molecule.
- ii. The interaction between a gas and water molecule can be described by a pair of potential function, and the cavity can be treated as perfectly spherical.
- iii. The gas molecule can freely rotate within the cavity.
- iv. There is no interaction between gas (guest) molecule in different cavities, and the gas molecule interact only with the nearest water molecules; that is enclathration is described as Langmuir adsorption.
- v. The free energy contribution of the water molecules is dependent on the mode of dissolved gases, that is, the guest molecule does not distort the hydrate lattice.

The Van der Waals and Platteeuw model statistically treated hydrate cages as "adsorption sites" in which species become "adsorbed" or encaged. A concept paralleled to that of Langmuir adsorption theory.

The thermodynamics of the reaction product (hydrate) using the various equations and applying the conditions for phase equilibrium in terms of chemical potential, fugacity and activity coefficient of a mixture of gas and liquid to yield solid, can be applied to study the effect of Langmuir constant on hydrate formation during surface production well testing.

2.2 Chemical Potential of Water in the Hydrate Lattice Model

For The governing equation that predicts the chemical potential of water in the hydrate lattice $\mu_W H$ according to Van der Waals and Platteeuw is expressed as ^[4, 5].

$$\mu_{w}^{H} = \mu_{w}^{\beta} - RT \sum_{m} \mathcal{D}_{m} Ln \left(1 + \sum_{j} C_{j,m} f_{j,m} \right)$$
(1)

Where: $\mu_W B$ = chemical potential of the water in the hypothetical empty hydrate lattice (atandard hydrate) with no cage occupied by guest molecules. The hydrate structure with the lowest chemical potential of water (μ_W) will be the stable structure. The contributions of the water chemical potential are the hypothetical empty lattice $\mu_W B$ and the reduction in chemical potential due to occupancy of cages by guests.

 v_m = number of cavities of type 'm' per water molecule in the lattice. The summation over species j is necessary if multiple hydrate forming species are present ^[6].

For a pure component structure 1 (s1) hydrate system, the complete expression using equation 1 is;

$$\mu_{w}^{H} = \mu_{w}^{\beta} - \left[\frac{1}{23}RTLn(1+C_{j,1}f_{j}) + \frac{3}{23}RTLn(1+C_{j,2}f_{j})\right]$$

Since structure 1 and 2 has 2 small cavities $(6.5^{12}, 6^2) C_{j1}$ is the Langmuir constant for a type j guest within the pentagonal cavity (small cage, 5¹²), C_{j2} is the Langmuir constant for j guest within the tetra Kaidecahedral cavity (large cavity, 5¹², 6²) and fj is the equilibrium fugacity of component in the multiphase mixture.

Equation 2 holds for a two-caged structure 1 hydrate. A "twocaged occupancy" refers to structure 1 clathrate system in which the guest molecule occupies both large and small cavities while for "one-caged occupancy", the guest occupies only the small or large cavity ^[7]. Thus, for a one-caged occupancy for which it is the large cavity that is occupied, equation 2 reduces to:

$$\mu_{w}^{H} = \mu_{w}^{\beta} - \left[\frac{3}{23}RTLn(1+C_{j,2}f_{j})\right]$$
(2)

Equation 1 can also be rewritten as [8, 9 and 10]:

$$\mu_{w}^{H} = \mu_{w}^{\beta} + RT \sum_{m} \mathcal{D}_{m} Ln \left(1 - \sum_{j} \theta_{j,m} \right)$$
(3)

Where $\theta_{j,m}$ = the fractional occupancy of the jth guest molecule in the mth hydrate cavity, defined

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(This information is optional; change it according to your need.)

as
$$\theta_{j,m} = \frac{C_{j,m} f_{j,m}}{1 + \sum_{j} C_{j,m} f_{j,m}}$$
 (5)

The product of the Lagmuir constant and fugacity of the guest is the driving force for occupancy ^[11].

2.3 Chemical Potential of Water in the Aqueous Liquid Phase Model

The chemical potential of water in the aqueous liquid phase from classical thermodynamics, assuming ideal relationship for the water and dissolved gas phase is ^[8,4].

$$\mu_{w}^{L} = \mu_{w}^{\beta} - \frac{\Delta \mu_{w}^{0}}{RT_{0}} + RT \int_{T_{0}}^{T} \left(\frac{\Delta H_{w}}{RT^{2}}\right) dT - RT \int_{P_{0}}^{P} \left(\frac{\Delta V_{w}}{RT}\right) dP$$

$$+ RTLn(x_{w}y_{w})$$
(6)

But
$$x_w y_w = a_w$$
 (7)

 a_w is the activity of the water defined by: $a_w = \frac{f_w^L}{f_w^0}$ (8)

 $f_w^{\ L}$ is the fugacity of water – rich aqueous phase and $f_w^{\ 0}$ is the fugacity of water in the reference state, which is chosen to be a pure water at the T and P of the mixture; thus; $f_w^{\ L} = f_w^{\ L}$ (T, P, Pure) ^[10].

 x_m = the mole fraction of water in the water – rich phase and y_w is the mole fraction of water in the gaseous phase. $\Delta \mu_w^0$ = the difference in the chemical potential of water between the hypothetical empty hydrate lattice (standard hydrate) and liquid water at a reference temperature T₀ (273.15K) and zero absolute pressure; ΔH_w and ΔV_w are the enthalpy and volume difference.

2.4 The Langmuir Constant Model

However, for the purpose of this paper, the temperature dependence of the Langmuir constant modified by Munck et al ^[11] as reported by Smith et al ^[12] will be used:

$$C_{j,m}(T) = \frac{A_{j,m}}{T} \exp\left(\frac{B_{j,m}}{T}\right)$$
(9)

Where: $A_{j,m} \& B_{j,m}$ are experimentally fit parameters, and are dependent on which guest molecule j is present in cage m.

2.5 Fugacity Model using Peng Robinson Equation of State

The guest species fugacity can also be calculated using a suitable equation of state, such as the Peng Robinson equation of state. The generalized form of the Peng Robinson is ^[13 and 14].

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b) + b(V-b)}$$
(10)
Where: (11)

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$$b = \frac{0.07780RT_{c}}{P_{c}}$$
(12)
$$\alpha(T) = \left[1 + K\left(1 - \sqrt{\frac{1}{T_{c}}}\right)\right]^{2}$$
(13)

 $\begin{aligned} Ok &= 0.37464 + 1.54226\omega - 0.26992\omega^2 \qquad (14)\\ \omega &= \text{acentric factor, Tc} = \text{critical tempt., Pc} = \text{critical pressure}\\ \text{Equation 10 can be written as} \ ^{[14]}: \end{aligned}$

$$Z^{3} - (1 - B)Z^{2} + (A - 3B^{2} - 2B)Z - (AB - B^{2} - B^{3}) = 0$$
(15)

Where:
$$A = \frac{aP}{(RT)^2}$$
 (16)

$$B = \frac{Pb}{RT} \tag{17}$$

$$Z = \frac{PV}{RT}$$
(18)

Z is the compressibility factor, 'a'is the interaction (or the energetic) parameter and b, the molar co-volume ^[15].

When Peng Robinson equation of state is applied to fugacity calculation, the resulting equation is

$$Ln\left(\frac{f_i}{P}\right) = (Z-1) - Ln(Z-B)$$
(19)
Where: $\frac{f_i}{P} =$ fugacity coefficient

Where: $\frac{J_i}{P}$ = fugacity coefficient.

However, $f_{j,l}$ at the various pressure and temperatures on the different choke sizes utilized for this work were obtained using the program for thermodynamic properties calculation using the Peng Robinson cubic equation of state developed by Sandler ^[14]. The various methane parameters used for the fugacity computation were those found in Abboth and Vanness ^[16] and Sandler ^[14].

3 APPLICATION OF THERMODYNAMIC MODELS TO WELL TEST DATA

3.1 Hydrate Phase equilibrium

The phase equilibrium of clathrate hydrates can be described

by:
$$\mu_w^H = \mu_w^L$$
 (20)
Thus, $\mu_w^\beta - \mu_w^H = \mu_w^\beta - \mu_w^{\text{Lors}} = \Delta \mu_w^{\beta - \text{Lors}}$ (21)

Where: $\mu_w^{\beta-L \text{ or } S}$ is the chemical potential of water in the liquid phase (L) or soliod phase (S) depending on the stable phase at the given temperature and pressure.

$$\mu_w^{\ \beta} - \mu_w^{\ H} = -RT \sum_m \upsilon_m Ln \left(1 - \sum_j \theta_{j,m} \right) = \Delta \mu_H$$
(22)

$$\mu_{w}^{\beta} - \mu_{w}^{L} = \frac{\Delta \mu_{w}^{0}}{RT_{0}} - RT \int_{T_{0}}^{T} \left(\frac{\Delta H_{w}}{RT^{2}}\right) dT +$$

$$RT \int_{P_{0}}^{P} \left(\frac{\Delta V_{w}}{RT}\right) dP - RTLn(x_{w}y_{w}) = \Delta \mu_{L}$$
(23)

At equilibrium, $\Delta \mu_{\rm H} = \Delta \mu_{\rm L}$; hydrate can exist; that is (24):

$$-RT\sum_{m} \upsilon_{m} Ln \left(1 - \sum_{j} \theta_{j,m}\right)$$
$$= \frac{\Delta \mu_{w}^{0}}{RT_{0}} - RT \int_{T_{0}}^{T} \left(\frac{\Delta H_{w}}{RT^{2}}\right) dT + RT \int_{P_{0}}^{P} \left(\frac{\Delta V_{w}}{RT}\right) dP - RTLn(x_{w}y_{w})$$

For this paper, the hydrates formed are assumed to be a structure 1 (s1) single hydrate of methane species.

The last term of equation 24 which accounts for the effect of dissolved gas (methane) using the mole fraction of water in the liquid phase is eliminate by assuming that the well testing is taking place in a well of known basic sediment and water (BS&W); thus, the concentration of water is very close to unity

 $(x_w = 1)$ in water rich solutions and also, because the solubil-

ity of methane in water is low; hence $a_w = 1$.

The first two terms on the right hand side of equation 24 represents $\Delta \mu_L$ (T, P, = 0), the chemical potential difference at a fix temperature and zero pressure.

From equation 23 when $a_w = 1$ or $x_w = 1$

$$\frac{\Delta\mu_{L}}{RT} = \frac{\Delta\mu_{w}}{RT} (T, P) = \frac{\Delta\mu_{w^{0}}}{RT_{0}} - \frac{\Delta H_{w^{0}}}{R} \left[\frac{1}{T_{0}} - \frac{1}{T} \right] + \frac{\Delta V_{w^{0}}}{RT} \left[P - P_{0} \right]$$
(25)

Once the reference state value for

$$\Delta \mu_w^{\ 0} \equiv \Delta \mu_w^{\ \beta-L}(T_0) \equiv \Delta \mu_w^{\ \beta-S}(T_0),$$

$$\Delta H_w^{\ 0} \equiv \Delta H_w^{\ \beta-L}(T_0) \equiv \Delta H_w^{\ \beta-S}(T_0) \text{ and}$$

$$\Delta V_w^{\ \beta-L}(T_0) = \Delta V_w^{\ \beta-S}(T_0) \text{ are known}, \Delta \mu_w^{\ \beta-H}(T, P) \text{ can}$$

be computed at the various temperature and pressure of interest.

Taking the following thermodynamic reference state properties of structure1 (s1) hydrate as givwn by literature as: $\Delta \mu_w^0$ ($T_0 = 273.15$ k, $P_0 = 0$) = 1263 Jmol⁻¹;

 ΔH_w^{0} (T₀, P₀) = 1389 Jmol⁻¹ and $\Delta V_w = 3.0 \times 10^{6} \text{m}^3$ /Jmol and the following steps were taken to develop an excel program to solve equation 25 by calculating;

1. The values of the various $\frac{\Delta \mu_w^{\beta-L}}{RT}$ at the various temperatures and pressures obtained while testing

the hydrate well were calculated. β_{-L} β_{-H}

2. At equilibrium,
$$\frac{\Delta \mu_w}{RT} = \frac{\Delta \mu_w}{RT}$$
, hence the vari-

ous values of $\frac{\Delta \mu_w^{\beta-L}}{RT}$ obtained from step 1 were equated to equation 22.

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3. Since methane hydrate is a two-cage occupancy structure, the following equation holds:

$$-\sum_{\substack{\nu_m Ln(1-\sum_{j,m})=\\-\left[\nu_s Ln(1-\theta_{j,s})+\nu_l Ln(1-\theta_{j,l})\right]}^{\nu_m Ln(1-\sum_{j,m})}$$

4. Putting $v_s = \frac{1}{23}$, $v_l = \frac{3}{23}$ in equation 26 and as-

suming $\theta_{j,s} = 0.920$ from literature, the values of

 $\theta_{j,l}$ were obtained.

- 5. The various fugacity values were obtained in equation 5 for field datad by using the Sandler's software.
- 6. By substituting the various values of the fugacity obtained from step 5, the values of the Langmuir constant field data $[C_{j,l}]_{FD}$ using equation 5 erwe obtained.
- 7. Equating the various field data Langmuir constant, $\begin{bmatrix} C_{j,l} \end{bmatrix}_{FD}$ to equation 9, gives $\begin{bmatrix} -1 & A_{j,l} & B_{j,l} \end{bmatrix}$

$$b\left[C_{j,l}\right]_{FD} = \frac{A_{j,l}}{T} \ell x p \frac{B_{j,l}}{T}.$$
(27)

8. Taking the natural log and re-arranging equation 27,

gives
$$Ln[T \times C_{j,l}]_{FD} = \frac{B_{j,l}}{T} - Ln\left[\frac{1}{A_{j,l}}\right]_{FD}$$
 (28)

9. Equating 28 has $\begin{bmatrix} B_{j,l} \end{bmatrix}_{FD}$ oas the slope and

$$Ln\left[\frac{1}{A_{j,l}}\right]_{FD}$$
 as the intercept.

10. Taking the respective values of 0.02335 and 2653 for $A_{j,l}$ and $B_{j,l}$ for large cavity of methane hudrate, the values of the Langmuir constant for pure methane at various operating field conditions were calculated us-

ing the equation
$$\begin{bmatrix} C_{j,l} \end{bmatrix}_{PM} = \frac{A_{j,l}}{T} \ell x p \begin{bmatrix} \frac{B_{j,l}}{T} \end{bmatrix}$$
 (29)

Taking the natural log and re-arranging

$$Ln[T \times C_{j,l}]_{PM} = \frac{B_{j,l}}{T} - Ln\left[\frac{1}{A_{j,l}}\right]$$
(30)

3.2 Model Formulation

Plots of $L_n(T \times C_{j1})$ vs T⁻¹ for pure methane and those of field gases as guest molecules respectively, had the same linear profile but only differed in their values of slope and intercepts – $(B_{j,1} \text{ and } (A_{j,1})$ of the line. The variation in the magnitude of these differences at various temperatures were evaluated and a ratio factor method used to derived a gaeneralizes expression that could enable the prediction of the Langmuir constant for well testing under field conditions, when its values for pure methane are known.

3.2.1 The Ratio Factor Method

Introducing a ratio Ω , defined as

$$\Omega = \frac{Ln[T \times C_{j,l}]_{PM}}{Ln[T \times C_{j,l}]_{FD}}$$
(31)

And rewriting equation 29, we obtain equation 32 for a given

choke size:
$$\left[C_{j,l}\right]_{FD} = \frac{1}{T} \left[A_{j,l} \ell x p \left(\frac{B_{j,l}}{T}\right)\right]_{PM}^{\Omega}$$
 (32)

If variation of the ratio (equation 31 with choke sizes, is a known function, such as $\Omega = f(s) + k$ (33) We can incorporate choke size variation into the derived expression by putting equation 33 into equation 32, to obtain

$$\begin{bmatrix} C_{j,l} \end{bmatrix}_{FD} = \frac{1}{T} \begin{bmatrix} A_{j,l} \ell x p \left(\frac{B_{j,l}}{T} \right) \end{bmatrix}_{PM}^{\left(\left(f(s) + K \right)^{-1} \right)}$$
(34)

4 RESULTS AND DISCUSSION

From the excel program developed and using equation 28, a plot of the natural log of the product of temperature and Langmuir constant for field data versus the reciprocal of temperature. Figure 1 yields $[B_{j,l}]_{FD}$ = 1941.6 as the slope and

$$Ln \begin{bmatrix} 1 \\ A_{j,l} \end{bmatrix}_{FD} = 2.7763$$
 as the intervept, thus giving $A_{j,l}$ for

field data to be equals to 0.06227.

Fig.1. Variation of natural log product of Temperature and Langmuir constant field data with reciprocal of temperature.

The slope and intercept values found in literature are 2653 and 0.02335 respectively. The slope and intercepts values are empirically determined values that depend on the nature of the gas molecules (guest) that occupies the hydrate cavities.

The $A_{i,l}$ and $B_{i,l}$ obtained from this work differs from

 $A_{j,l}$ and $B_{j,l}$ for large cavity of structure 1 hydrate occupied by pure methane found in the in the literature. The difference

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gives

in $A_{j,l}$ and $B_{j,l}$ shows that the guest component(s) of the hydrate formed during well testing is not puer component(s) but rather it is a mixture of component(s), that is, methane and other hydrocarbons. Also the host molecule of the hydrate formed in the field is not pure but rather water with some dissolved salts. The presence of non-hydrcarbon gases such as CO₂ also affects the values of $A_{j,l}$ and $B_{j,l}$ hence the Langmuir constant.

4.1 Ratio Factor Determination

From the plot of natural log of the product of temperature and Langmuir constant for pure methane versus the reciprocal of temperature obtained by using the values from equation 29 and comparison with the plot of the natural log of the product of temperature and Langmuir constant field data versus the reciprocal of temperature, figure 2, the ratio factor is calculated to be 1.376. (Table 1) Hence;

$$\left[C_{j,l}\right]_{FD} = \frac{1}{T} \left[A_{j,l} \ell x p \left(\frac{B_{j,l}}{T}\right)\right]_{PM}^{0.7274}$$
(35)

TABLE 1:

The Result Difference between the Plots of Methane Hydrates using Aij and Bij as Pure Methane and Field Data for Ratio Factor Determination within the Tested Temperature Range.

$1/T(k^{-1})$	$Ln T \times C_{j,l}$	$Ln[T \times C_{j,l}]_{FD}$	$Ln[T \times C_{j,l}]_{PM}$
	(k/bar)	(k/bar)	$Ln[T \times C_{j,l}]_{FD}$
0.0033	4.9977	3.6310	1.3764
0.00335	5.1304	3.7281	1.3761
0.0034	5.2630	3.8251	1.3759
0.00345	5.3957	3.9222	1.3757
			Average =
			1 3760





Fig. 3. Normalization of Ln [T * C_{II}]_{F0} (large cavity) by multiplying with 1.376.



4.2 Effect of Choke Size Variation on Ratio Factor

The Ratio Factor was found to be a function to be a function of choke size (Table 2), which gave equation of the best fit (figure 5), as

 $\Omega = 0.1302 \text{ Ln}(s) + 0.9856$ (36) This shows that Langmuir constant for the field data when applied to different choke sizes, will give the expression.

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$$\left[C_{j,l}\right]_{FD} = \frac{1}{T} \left[A_{j,l} \ell x p \left(\frac{B_{j,l}}{T}\right)\right]_{PM}^{\frac{1}{0.1302 Ln(s)+0.9856}}$$
(37)

From the above model equation, as the choke size increases, the Langmuir constant for large cavity decreases.

The Ratio Ω varies with choke sizes as shown in Table 2. TABLE 2:

Average Values of Ratio Factor for the Various Choke Sizes Tested

S/No	Choke Size (1/16")	Ω	Remark (s)
1	12	1.2037	Test on 12/64" Choke
2	16 (1)	1.2559	First Test on 16/64" Choke
3	20	1.3491	Test on 20/64" Choke
4	24 (1)	1.3956	First Test on 24/64" Choke
5	32	1.7741	Test on 32/64" Choke
6	40	1.3679	Test on 40/64" Choke
7	44	1.3447	Test on 44/64" Choke
8	36	1.3774	Test on 36/64" Choke
9	24 (2)	1.4199	Second Test on 24/64"
			Choke
10	16 (2)	1.4305	Second Test on 16/64"
			Choke

4.2 Model Comparison

From Table 3, when the values of Langmuir constants from field data using the existing equation from literature were compared with the generalized proposed model, equation 37 gives a good approximation.

TABLE 3

Values of A_{ji} and B_{ji} for the various Choke Sizes Tested

Choke size (1/64")	$A_{j,l}$	$B_{j,l}$	Pres. (bar)	Temt. (K)
12	5.1296-E12	9147.8	106.7	303.5
16(1)	1.80615	1039.6	128.4	298.3

20	38638.3	-1999.7	183.7	296.2
24(1)	5999.9	-1436.7	202.9	292.6
32	1.51892	1000.9	193.3	290
40	0.25684	1536.5	177.3	291
44	0.01209	2445.6	164.9	291.9
36	4.5234-E9	6746.6	185.8	292.4
24(2)	0.43089	1333	221.9	294.3
16(2)	0.22773	1509.1	233.8	298.6

As the various choke sizes B_{ji} increases, A_{ji} decreases and vice versa (Table 3). From chokes 20/64", B_{ji} increases as the choke size is increased, the flow rate is increased, more hydrocarbons are entrained in the system; thus, the higher the flow rate, the greater the tendency of higher molecular hydrocarbons joining in the formation of the hydrate. From literature, the higher the molecular mass of the hydrocarbon the higher the molecular mass of the hydrocarbon the higher the molecular mass of the hydrocarbon, the lower the A_{ji} value for large cages of methane hydrate structure 1 (s1) hydrate.

For chokes 12, 16(1), 20 and 24(1), the well may be said to be undergoing a clean-up operation hence the pressure-choke size data are not inversely proportional. This is a condition normally associated with clean-up operations. Thus during clean-up operations, impurities are higher, which in turn affects A_{ji} and B_{ji} values. Besides the first four choke sizes tested (that is, during the cleanup operation) from choke 32/64", the realationship between pressure and choke size became inverse, which is in conformity with literature.

5 CONCLUSIONS

The following conclusions can be drawn from this study.

- 1. The Langmuir constant for a large cavity/cage of a simple hydrate when occupied by pure methane under the same process (hydrate forming) conditions is about 1.37 times greater than the Langmuir constant (field data) of the guest molecule(s) that actually forms the hydrate under studies. Thus, confirming that hydrate formation component(s) under field conditions can never be a pure component.
- 2. A generalized correlation for Langmuir constant was developed which encompassed thee ratio factor between when structure I (s1) hydrate large cavity is assumed to be occupied by pure methane (guest) molecules and when the large cavity is actually occupied as in the field case, giving the expression;

$$\left[C_{j,l}\right]_{FD} = \frac{1}{T} \left[A_{j,l} \ell x p \left(\frac{B_{j,l}}{T}\right)\right]_{PM}^{0.7274}$$

3. Specific correlation was developed from the generalized correlation to determine the effect of choke size variation on Langmuir constant during surface production well testing using the test parameters (pressure, temperature and choke size) acquired from a hydrate well using a real time data acquisition system, has the form

$$\left[C_{j,l}\right]_{FD} = \frac{1}{T} \left[A_{j,l} \ell x p \left(\frac{B_{j,l}}{T}\right)\right]_{PM}^{\frac{1}{0.1302 Ln(s) + 0.9856}}$$

- 4. Choke size has an inverse relationship with Langmuir constant at a given temperature and pressure.
- 5. Increasing choke size during surface production well testing has been found to be an operating panacea for hydrate formation. As the Langmuir constant decreases, the product of Langmuir constant and fugaci-

ty $\left[C_{j,l}f_{j,l}\right]$ decreases, thereby leading to a decrease

in hydrate formation. This shows that at higher choke sizes, the possibility of hydrate forming and plug-ging/clogging the testing facilities is reduced.

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