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Mathematical Modeling and Simulation of Hydrate Formation Conditions in Nigerian Oil and Gas Pipelines

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The transportation of production and processing of petroleum fluids in pipelines and other transport lines can be significantly affected by flocculation, deposition and plugging. This problem has tremendously affected Nigerian pipelines for oil and gas transport. In this paper, the flow assurance considered includes the prevention, mitigation and remediation of hydrate. A mathematical model for predicting the equilibrium conditions for hydrate formation is:

$$T = \frac{\Delta v_W \cdot P}{R \cdot \left[\frac{1}{T_O} \cdot \frac{\Delta h_W}{R} - \frac{1}{T_F} \cdot \frac{\Delta h_W}{R} + ln(X_W) - \frac{\Delta \mu_W^o}{R \cdot T_O} - \left[\sum v_j \cdot ln(1 - \sum \theta_{ji})\right]\right]}$$

and simulations carried out to compare with experimental data. This model would be used to predict the hydrate formation temperature for given operating pressure so as to determine the hydrate inhibition requirement for the pipeline.

Keywords Equilibrium conditions, flow assurance, hydrate formation

INTRODUCTION

Deep water offshore technology has advanced markedly in the last 10 years as the industry seeks to achieve oil production from over increasing depths. In the early years of offshore oil and gas exploration and production, the largest and the most accessible fields wear developed first. These fields presented only moderate technical challenges, and their large reserves base offered significant economics of scale, which made them commercially attractive.^[1] However, as these fields are being depleted, producers are being forced to look for replacement or reserves. This has led to increased interest in deeper waters, harsher and more difficult environment where operating conditions are not encouraging, most notable in the Gulf of Mexico, offshore Brazil, West Africa, and west of the Shetlands.^[2-13] As a result, there have now been a number of developments in deep water's in excess of 500 m water depth and a number that exceeds 1 km (e.g., SNEPCO's Bonga at 1030 m, Elf's Girasol at 1300 m, and Petrobras Recandor at 1500-2000 m). For these developments the capital investment required in the pipeline systems represents a significant proportion of the total field development cost, and, therefore, desirable that designs are optimal and efficient,

putting into consideration some of the challenges being faced by the industry as a result of these advancements.

As production moves into deeper, colder water and as we have less access to production facilities, the industry is beginning to face transport challenges for two reasons.^[14] The first is that most deep water development currently encourages the use of floating production systems or the use of subsea tiebacks to host platforms in shallow waters. In this case the production fluid has to be transported over long tie back distances from wells to processing facilities either on platforms or floating production systems. The second factor is that in most offshore location, the temperature gradient would encourage flocculation of materials that would impede the flow of oil and gas in transport facilities thus affecting production rates. Flow assurance strategies are being used to reduce this problem to minimum.

Flow assurance includes all issues important in maintaining the flow of oil and gas from reservoir to reception facilities. Flow assurance at the basic level means keeping the flow path open. The term was coined in the early 1990s in Portuguese as *gurantia de fluxo*, literally meaning as "Guarantia the flow," which was subsequently translated to give the now well–known expression "flow assurance." The term originally covered the thermal hydraulic and production issues encountered in oil and gas production; it is defined in a more comprehensive way following recent research and development in today's oil industry, including all issues important to maintaining the flow of oil and gas from reservoir to reception facilities.

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Flow assurance is a term that encapsulates a number of fluid flow, heat transfer, and production chemistry issues that have important implication for the transportation of hydrocarbons from reservoirs to processing facilities. It is a multidiscipline activity requiring engineers with detailed technical background to "follow the flow" from reservoir through to reception. Communication between various technical disciplines is essential for flow assurance. Flow assurance demands a diversity of skills in areas such as geochemistry, thermodynamics, production chemistry, heat transfer, multiphase fluid-dynamics subsea engineering, and operations.^[15]

Flow assurance should be taken very seriously as the economic implications of blockages (especially hydrates) in transportation process are tremendous, which is why predictive modeling is essential. The technique of modeling is based on observed and statically mathematical theories, continuous thermodynamics, transport phenomena, colloidal solution theory, and aggregation theory.

The objectives of this study are

- 1. to study the causes of potential blockages in pipeline and other transport facilities
- to evaluate the strategies for preventions mitigation and remediation of hydrates formation in pipelines as such blockages are known to reduce to zero flows leading to unplanned shutdown of production.
- 3. To develop a mathematical predictive model for hydrate formation in a pipeline system production.

The term is defined in a more comprehensive way following recent research and developments in today's oil industry.

MODELING OF EQUILIBRIUM CONDITION FOR HYDRATE FORMATION ASSUMPTIONS

Each cavity can contain at most one gas molecule.

- 1. The gas molecule can freely rotate within the cavity.
- 2. There is no interaction between the gas molecules in different cavities and the gas molecules interact only with the nearest neighbour water molecules.
- 3. The free energy contribution of the water molecules is independent of the mode of dissolved gases (i.e., the gas does not distort the hydrate lattice).
- 4. Only structure II hydrates occur in oil and gas system.

DEVELOPMENT OF THE MODEL EQUATION

Considering that the hydrate was formed from a singlephase water-rich liquid containing dissolved hydrate former, the conditions where the hydrate phase is in equilibrium with the water-rich liquid phase are needed. At these conditions, the chemical potential of the species in various phases must be equal in all phases.^[2] At equilibrium, the chemical potential of water in the hydrate phase is equal to the chemical potential of water in the water rich or ice phase. Mathematically,

$$\mu_{\rm H} = \mu_{\rm W} \qquad [1]$$

where μ_H is the chemical potential of water in the hydrate phase and μ_W is the chemical potential of water in the water phase.

The condition for the equilibrium can be rewritten as

$$\Delta \mu_{\rm W} = \Delta \mu_{\rm H}$$
 [2]

and

$$\Delta \mu_{\rm W} = \mu_{\beta} - \mu_{\rm W} \tag{3}$$

$$\Delta \mu_{\rm H} = \mu_{\beta} - \mu_{\rm H} \tag{4}$$

where μ_{β} is the chemical potential of an unoccupied hydrate state, used as the reference state.

In Equation (3), $\Delta \mu_w$ is the difference in chemical potential between water in an empty hydrate lattice and pure water and in Equation (4), $\Delta \mu_H$ is the difference in the chemical potential between an empty hydrate water lattice and one occupied by a guest molecules.

Assuming an ideal solution relationship for the water and dissolved gas phase,

$$\frac{\Delta \mu_{\rm W}}{\mathbf{R} \cdot \mathbf{T}} = \frac{\Delta \mu_{\rm W}^{\rm o}}{\mathbf{R} \cdot \mathbf{T}_{\rm O}} - \int_{\mathbf{T}_{\rm O}}^{\mathbf{T}_{\rm F}} \frac{\Delta h_{\rm W}}{\mathbf{R} \cdot \mathbf{T}^{2}} d\mathbf{T} + \int_{0}^{P} \frac{\Delta \mathbf{v}_{\rm W}}{\mathbf{R} \cdot \mathbf{T}} d\mathbf{P} - \ln(\mathbf{X}_{\rm W})$$
[5]

where

$$\Delta h_W = \Delta h_W^o + \int_{T_O}^T \Delta C_{pw} dT \qquad \qquad [6]$$

 h_w is the enthalpy of water, C_{pw} is the heat capacity of water, T is the temperature, T_o is the reference temperature, T_F is the hydrate formation temperature, R is the universal gas constant, v_w is volumetric differences between water in an empty hydrate lattice and pure water, and

$$\Delta C_{pw} = \Delta C_{pw}^{0} + b \cdot (T - T_{O})$$

b = 0.141 [7]

where $\Delta \mu_W^o$ is the experimentally determined reference potential treated as a constant whose value can change according to the gas specie present; Δh_W^o is an experimentally determined reference enthalpy difference between the empty hydrate lattice and pure water phase at the reference temperature; ΔC_{pW}^o is an experimentally determined reference enthalpy difference; x_w is the mole fraction of water in the water rich phase.

 TABLE 1

 Experimental and simulated results with percentage errors for pure water

TABLE 2
Experimental and simulated results with percentage errors
for sea water

S/N	Experimental results (K)	Simulated results (K)	Percentage errors	S/N	Experimental results (K)	Simulated results (K)	Percentage errors
1	271.9000	272.2285631	-0.1208	1	271.9000	272.2868	-0.1423
2	272.8000	272.2285631	0.2095	2	272.8000	272.2868	0.1881
3	273.7000	272.0571327	0.6002	3	273.7000	272.1283	0.5742
4	274.7000	271.9714175	0.9933	4	274.7000	272.0491	0.9650
5	275.6000	271.7999871	1.3788	5	275.6000	271.8906	1.3459
6	276.5000	271.6285567	1.7618	6	276.5000	271.7321	1.7244
7	277.4000	271.4571262	2.1423	7	277.4000	271.5736	2.1003
8	278.4000	271.2856958	2.5554	8	278.4000	271.4151	2.5089
9	279.3000	271.0285502	2.9615	9	279.3000	271.1774	2.9082
10	280.2000	270.6856894	3.3955	10	280.2000	270.8604	3.3332
11	281.2000	270.3428285	3.8610	11	281.2000	270.5435	3.7897
12	282.1000	269.9999677	4.2893	12	282.1000	270.2265	4.2090
13	283.0000	269.5713917	4.7451	13	283.0000	269.8303	4.6536
14	283.9000	269.0571004	5.2282	14	283.9000	269.3548	5.1233
15	284.9000	268.457094	5.7715	15	284.9000	268.8001	5.6511
16	285.8000	267.7713723	6.3081	16	285.8000	268.1662	6.1700
17	286.7000	266.9142202	6.9012	17	286.7000	267.3738	6.7409
18	287.6000	265.9713529	7.5204	18	287.6000	266.5021	7.3359
19	288.6000	264.77134	8.2566	19	288.6000	265.3927	8.0413
20	289.5000	263.3141814	9.0452	20	289.5000	264.0456	8.7926
21	290.4000	261.5998773	9.9174	22	291.3000	260.4796	10.5803
22	291.3000	259.4569971	10.9313	21	290.4000	262.4607	9.6210
23	292.3000	256.8855408	12.1158	23	292.3000	258.1024	11.6995
24	293.2000	253.8855085	13.4088	24	293.2000	255.3289	12.9165
25	294.1000	250.2854698	14.8978	25	294.1000	252.0007	14.3146
26	295.0000	243.8568291	17.3367	26	295.0000	246.0575	16.5907

Further,

$$\frac{\Delta \mu_{\rm H}}{\mathbf{R} \cdot \mathbf{T}} = -\left[\sum \mathbf{v}_{\rm j} \cdot \ln \cdot \left(1 - \sum \theta_{\rm ji}\right)\right]$$
[8]

and

$$\theta_{ji} = \frac{C_{ji} \cdot f_i}{1 + \sum C_{ji} \cdot f_i}$$
[9]

where v_j is the ratio of j type cavities present to the number of water molecules present in the hydrate phase; f_i is the gas phase (and hydrate phase) fugacity of the i type hydrate forming species which can be calculated by the Peng Robinson equation of state; C_{ji} is the Langmuir constant for species i in cavity j; θ_{ji} is the fraction of j type cavities, which are occupied by i type gas molecules.

From Equation (2), since

$$\Delta \mu_{\rm W} = \Delta \mu_{\rm H} \tag{10}$$

then,

$$\frac{\Delta\mu_{\rm W}}{\mathbf{R}\cdot\mathbf{T}} = \frac{\Delta\mu_{\rm H}}{\mathbf{R}\cdot\mathbf{T}}$$
[11]

Since RT = RT

So, Equations (5) and (8) yield

$$\begin{split} \frac{\Delta \mu_{W}^{o}}{R \cdot T_{O}} &- \int_{T_{O}}^{T_{F}} \frac{\Delta h_{W}}{R \cdot T^{2}} dT + \int_{0}^{P} \frac{\Delta v_{W}}{R \cdot T} dP - \ln(X_{W}) \\ &= - \left[\sum v_{j} \cdot \ln \cdot \left(1 - \sum \theta_{ji} \right) \right] \end{split}$$
[12]

Equation (12), becomes, after evaluating

$$\frac{\Delta \mu_{W}^{o}}{\mathbf{R} \cdot \mathbf{T}_{O}} - \int_{\mathbf{T}_{O}}^{\mathbf{T}_{F}} \frac{\Delta h_{W}}{\mathbf{R} \cdot \mathbf{T}^{2}} d\mathbf{T} + \frac{\Delta \mathbf{v}_{W} \cdot \mathbf{P}}{\mathbf{R} \cdot \mathbf{T}} - \ln(\mathbf{X}_{W})$$

$$= -\left[\sum \mathbf{v}_{j} \cdot \ln \cdot \left(1 - \sum \theta_{ji}\right)\right]$$
[13]

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which is the same as

$$\begin{split} \frac{\Delta v_W \cdot P}{R \cdot T} &- \int_{T_O}^{T_F} \frac{\Delta h_W}{R \cdot T^2} dT + \ln(X_W) - \frac{\Delta \mu_W^0}{R \cdot T_O} \\ &- \left[\sum v_j \cdot \ln \cdot \left(1 - \sum \theta_{ji} \right) \right] \end{split}$$
[14]

$$\frac{\mathbf{R} \cdot \mathbf{T}}{\Delta \mathbf{v}_{\mathrm{W}} \cdot \mathbf{P}} = \frac{1}{\int_{T_{\mathrm{O}}}^{T_{\mathrm{F}}} \frac{\Delta h_{\mathrm{W}}}{\mathbf{R} \cdot \mathbf{T}^{2}} \mathrm{dT} + \ln(\mathbf{X}_{\mathrm{W}}) - \frac{\Delta \mu_{\mathrm{W}}^{\mathrm{o}}}{\mathbf{R} \cdot \mathbf{T}_{\mathrm{O}}}} \qquad [15]$$

$$T = \frac{\Delta v_{W} \cdot P}{R \cdot \left[\int_{T_{O}}^{T_{F}} \frac{\Delta h_{W}}{R \cdot T^{2}} dT + \ln(X_{W}) - \frac{\Delta \mu_{W}^{o}}{R \cdot T_{O}} - \left[\sum v_{j} \cdot \ln \cdot \left(1 - \sum \theta_{ji} \right) \right] \right]$$
[1]

Solving the term in T² symbolically gives,

$$T = \frac{\Delta v_{W} \cdot P}{R \cdot \left[\left(\frac{-1}{T_{F}} \cdot \frac{\Delta h_{W}}{R} + \frac{1}{T_{O}} \cdot \frac{\Delta h_{W}}{R} \right) + \ln(X_{W}) - \frac{\Delta \mu_{W}^{o}}{R \cdot T_{O}} - \left[\sum v_{j} \cdot \ln \cdot \left(1 - \sum \theta_{ji} \right) \right] \right]}$$
[17]

Rearranging finally results to

$$\begin{split} \Gamma = & \frac{\Delta v_{W} \cdot P}{R \cdot \left[\left(\frac{1}{T_{O}} \cdot \frac{\Delta h_{W}}{R} - \frac{1}{T_{F}} \cdot \frac{\Delta h_{W}}{R} \right) + \ln(X_{W}) - \frac{\Delta \mu_{W}^{o}}{R \cdot T_{O}} \right. \\ & \left. - \left[\sum v_{j} \cdot \ln \cdot \left(1 - \sum \theta_{ji} \right) \right] \right] \end{split}$$

$$[18]$$

RESULTS AND DISCUSSION

Experimental and Simulated Results

The objective of the research work centered on ensuring flow assurance in oil and gas pipeline systems and the development of a mathematical predictive model to predict the equilibrium condition (equilibrium temperature) for hydrate formation.

The model was developed theoretically from the basic principles of thermodynamics of hydrate formation. A computer simulation was carried out on the model using experimental data collected from the Shell Nigeria Exploration and Production Company Ltd. (Port Harcourt, Nigeria) MATCAD was used to carry out the simulations. The experimental data as shown in Tables 1 and 2 was used to carryout were obtained the simulations for both pure water and sea water. Hydrate formation temperature for pressure conditions ranging from 9 bar to 445 bar for both pure water and sea water giving 26 results.

The result obtained for pure water produced deviation from experimental data in percentage error as can be seen in table 4.5 ranging from -0.1208% for hydrate formation temperature of 271.900 K, increasing as temperature increases to 17.3367% with the highest hydrate formation temperature of 295.000 K. The results shows that the model has an average error of 6.0158%. In the case of sea water the percentage error ranges from -0.1423 for hydrate formation temperature of 271.9000 K, increasing as temperature increased to 16.5907 with the highest predicted hydrate formation temperature of 295.000 K. The results show that the model has an average error of 5.8360% for pure water. From the experimental data the sea bed temperature is approximately 4°C during a shut down, any pressure greater than 18 bar will result in the potential for hydrate formation. From the simulated results, it can be shown that hydrate would form at higher temperature up to 243.857 K for pure water and 246.058 K for sea water provided the pressure is high, that is, at 340 bar for pure water and 345 bar for sea water. Comparing the results shows that hydrates formation temperature decreases with salinity. Hence, this model would be useful in predicting the hydrate formation temperature for given operating pressure and it finds application in hydrate inhibition requirements for oil and gas pipelines, thus optimising the use of chemical inhibitors for hydrate control.

CONCLUSION

From the results it can be concluded that the postulated model below is a good representation of the equilibrium condition for hydrate formation since the average percentage error of the model is 5.9259%

$$\begin{split} T = & \frac{\Delta v_W \cdot P}{R \cdot \left[\frac{1}{T_O} \cdot \frac{\Delta h_W}{R} - \frac{1}{T_F} \cdot \frac{\Delta h_W}{R} + \ln(X_W) - \frac{\Delta \mu_W^o}{R \cdot T_O} \right.} \\ & \left. - \left[\sum v_j \cdot \ln \cdot \left(1 - \sum \theta_{ji} \right) \right] \right] \end{split}$$

Thus, this should be used to determine hydrate inhibition requirements of oil and gas pipeline.

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