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Hydrate formation and its influence on natural gas pipeline: Simulation study

ABSTRACT

This study simultaneously studied the twin problem of hydrate and corrosion that occurs in natural gas pipeline, establishing their interdependent using a simulation approach. CO_2 corrosion was simulated using NORSOK M-506 standard model in matlab. Major factors considered are the relationship between corrosion rate and temperature, corrosion rate and P^H , corrosion-temperature relationship for varying CO_2 mole percent, and P^H values. The result from this study established that both type I and type II hydrates could form at the operating conditions of 5°C and 60 bar. The obtained result also shows that rate of corrosion decreases and increases with increase in P^H values and temperature respectively to a certain temperature of approximately 78 °C, then a dip in rate of corrosion. The result for corrosion-temperature relationship for varying P^H values and CO₂ mole percent shows a decrease in corrosion rate with an in increase in P^H , and an increase with increase in CO_2 mole percent t. Furthermore, the obtained results highlight a rise as high as 5.7 mm/year at a 3 mole percent CO_2 . This value and trend portray a bad omen for the affected pipeline. This study recommends that natural gas to be transported by pipeline should be sweetened and processed to remove H_2S , CO_2 and mercaptans if present. **Keywords:** CO_2 corrosion, model, simulation, hydrate, MATLAB

1. INTRODUCTION

Currently there are global guest ably led by the most advanced economies of the world on the utilization of a more environmentally friendly fuel. The essence which is to cut-down on the volume of emission of dangerous gaseous by-products of combustion of dirty fossil fuel that causes global warming with the propensity of causing environmental pollution and ecological disturbances or destruction. In all these, natural gas boldly stands in the gap as a transition energy source, because it emits relatively lower quantity of pollutants when combusted, compared to the other fossil fuels. The high demand of natural gas has led to large deplovment of exploration and exploitation technologies and the building of massive infrastructure for gas processing, treatment and transportation. Among the transportation modes of natural gas is pipeline transportation, and the most popular because its technology is easily understood, and it can be easily adapted to different environment [1]. These appealing features of pipeline transportation has led to a remarkable global rise in its network.

Study by Mokhatab et al. [2] revealed an addition of twelve thousand miles (12,000 miles) of pipeline yearly to the global pipeline infrastructure in the last decade. However, pipeline transportation of natural is faced with the flow assurance problem of hydrate formation and CO2 corrosion of the internal walls of the pipeline. Proberezhny et al. [3] stated that corrosion of natural gas pipeline can be attributed to H₂S and CO₂ which are constituents of the gas that is transported and by the formed hydrate in the pipeline. Abbas et al. [4] in their study on neural network modeling of high pressure CO2 corrosion in pipeline steel evaluated the severity of CO₂ pipeline corrosion in economic terms. They stated that CO₂ corrosion is so huge that its cost implications in relation to the production and manufacturing sector of the U.S economy was \$34.4 billion in the year 2014. They reported that the gas industry share of this amount was up to 50%. Studies in understanding the interplay between hydrate formation and CO₂ corrosion by researchers have been carried out. Zunzhao et al. [5] deployed a natural gas hydrate loop device to measure the corrosion rate of CO₂ in the presence of hydrate on X80 steel, Obanijesua et al. [6] developed a model to predict CO2 corrosion rate of natural gas pipeline in the presence of hydrate, their obtained results show that the corrosion rate of CO₂ was higher than the gas liquid equilibrium.

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Studies [7,8] on CO₂ corrosion prediction using model by researchers has shown the availability CO₂ prediction models. Nesic et al. [9] listed the three general groups of models used for CO2 corrosion prediction as: mechanistic, semiempirical and empirical while Kahyarian et al. [10] grouped CO₂ corrosion prediction models into empirical/semi-empirical, elementary mechanistic and comprehensive mechanistic with the mechanistic been more complex to handle, though affording user greater insight into major variables moving the entire corrosion process [11]. Recent studies [4,12] have shown the growing interest in the use of Neural Network (NN) modeling for the prediction of CO₂ corrosion. Hatami et al. [13] reported that the use of least square support vector machine (LSSVM) for the prediction of CO2 corrosion has yielded good result. They further maintained that out of the three kernel functions (linear, polynomial and Gaussian) compared, the Gaussian function was the best in predicting CO2 corrosion. Different approach is used by CO2 corrosion prediction models in predicting the effect of protective film on CO₂ corrosion and in predicting the effect of oil wetting on CO₂ corrosion [14].

 CO_2 corrosion prediction is also affected by environmental factors, based on this De Ward et al. [15] advocated the use of correction factor for CO_2 corrosion under different environmental settings. Bernandus et al. [16] while making a strong case for the need for a sound knowledge of the governing processes of CO_2 corrosion parameters, asserted that model accuracy is less important than the knowledge of the major corrosive parameters governing the CO_2 corrosion mechanism.

One very reliable model used in CO_2 corrosion prediction is the NORSOK M-506, a standard which is an empirical model used by the Norwegian oil and gas industry capable of matching large volume of laboratory data. The NORSOK M-506 is built to consider the effect that protective film has on CO_2 corrosion mechanism at higher temperature and high P^H more than many other prediction models. This model is well reputed for giving a good representation of the maximum corrosion rate in a CO_2 corrosion controlled system [7,8,17].

2. METHODOLOGY

2.1. Programming used

The programming used in this study includes Matlab software, Excel spreadsheet application and Unisim design software which is an interactive process modeling software that enables engineers to create steady and dynamic state models for plant and process systems

2.2. Method

2.3. Hydrate Formation Simulation

The process simulation for fluid flow with the intent of investigating the hydrate formation

potential of the natural gas was done using Unisim R380, a Honeywell's hydrate prediction software. The fluid was modeled as Peng Robinson property package. The operating conditions for the simulation were: temperature of 5° C and pressure of 60 bar. The composition of the natural gas stream is as represented in Table 1.

Components	Mole composition (%)
C ₁	74.805
C ₂	5.633
C ₃	4.264
nC4	2.411
1C4	1.651
nC₅	3.21
1C ₅	2.104
C ₆	1.712
C ₇	0.867
C ₈	0.652
C ₉	0.321
C0 ₂	1.978
N ₂	0.294
H ₂ 0	0.098
	100.00

Table 1. Mole composition of natural gas

2.4. CO₂ Corrosion Simulation

Hydrate prone natural gas from one of the offshore fields in Niger Delta Nigeria was simulated for possible corrosion effect on pipeline using the NORSOK M-506 model. At different temperatures, CO_2 fugacity, P^H and wall shear stress possible state of corrosion was analyzed. The model used for the analysis is derived from research program at the Institute of Energy Technology in Norway. The corrosion rate equation for various temperatures (5°C - 160°C) range used for the prediction is given according to Eqs. (1-3).

For T = 5^oC

$$Cr_{CO_2} = K_T \times F_{CO_2}^{0.36} \times f(P^H)_T$$
 (1)

For $T = 15^{\circ}C$

$$Cr_{CO_2} = K_T \times F_{CO_2}^{0.36} \times \left(\frac{S}{19}\right)^{0.146+0.0324(F_{CO_2})} \times f(P^H)_T$$
(2)

For: 20°C T 150°C

$$Cr_{CO_2} = K_T \times F_{CO_2}^{0.62.} \mathbf{x}$$
$$\mathbf{x} \left(\frac{s}{19}\right)^{0.146+0.0324 \log(F_{CO_2})} f(P^H)_T$$
(3)

Where Cr_{CO_2} is CO_2 corrosion rate, mm/year, K_T is constant dependent on operating temperature, S is wall shear stress in Pa, F_{CO_2} is CO_2 fugacity in Mpa and $f(P^H)_T$ is the complex function of P^H and temperature. The fugacity factor is used in

place of partial pressure because, the natural gas does not exist in ideal condition, and is calculated according to Eq. (4).

$$F_{CO_2} = a \times P_{CO_2} \tag{4}$$

Where: a is fugacity co-efficient and P_{CO_2} is the partial pressure of CO₂ which is represented as shown on Eq.(5).

$$P_{CO_2} = \frac{mol \% of \ corrosion \ in \ the \ gaseous \ phase}{100} \times P \tag{5}$$

The fugacity coefficient 'a' is evaluated according to Eqs. (6-7) respectively.

$$a = 10^{P(0.0031 - \frac{1.4}{T})} for P \le 250 \ bar \tag{6}$$

$$a = 10^{250(0.0031 - \frac{1.4}{T})} for P > 250 \ bar \tag{7}$$

The wall shear stress S is evaluated according to Eq. (8).

$$S = 0.5 \times f \times \rho_m \times U_m^2 \tag{8}$$

Where *f* is the friction factor at the pipe wall, ρ_m is the density of the fluid mixture in $\binom{kg}{m^3}$ and U_m is the velocity of the fluid mixture in $\binom{m}{m}$ The friction factor is evaluated according to Eq.(9).

$$f = 0.001375 \left[1 + \left(20000 \frac{\kappa}{D} 10^6 \frac{\mu_m}{\rho_m U_m D} \right)^{0.33} \right]$$
(9)

Where *K* is the pipe roughness in inches, *D* is the pipe diameter in mm and μ_m is the viscosity of fluid mixtures in *Ns/m*².

Matlab 2014b software was used for the prediction of the corrosion rate of the pipeline due to hydrates formation. Scripts were written for solving the corrosion rate equation and performing iterations. With the Matlab software, executable scripts were run on command windows graphical user interface (GUI).

3. RESULTS AND DISCUSSION

The results on the study carried out using Unisim software and NORSOK-506 standard

model to investigate hydrate formation and its influence on natural gas pipeline is presented.

3.1. Hydrate Formation

The result of the hydrate formation simulation of the natural gas using Unisim Design R380 software shows that free water was found in the gas sample, and that both type I and type II hydrate will form. This is illustrated in Figure 1; the window showing the highlights under the design menu of the hydrate simulation program. At operating temperatures of 5°C, the performance utility of the software which gives discrete details, as shown in Figure 2 indicates that hydrate will form at 10.92 bar, and that at operating pressure of 60 bar, hydrate will form at 17.03°C. Figure 3 shows the phase envelope utility for the natural gas stream. In line with the presented result from Figure 1 and Figure 2, which suggests that both type I and type II hydrate will be formed at the operating conditions of 5°C and 60 bar.

Figure 3 which represents the phase envelope utility for the analysed natural gas stream affirms the possibilities of hydrate formation in the pipeline. From Figure 3, the red line, blue line, yellow line and green line represents bubble point curve, dew point curve, critical point and hydrate formation line respectively. The phase envelope utility for the analysed natural gas stream shows that hydrate will not form if the natural gas pipeline conveying this gas is operated in the conditions of temperature and pressure to the right-hand side (RHS) of the hydrate formation line. But the result from Figure 3 indicates that hydrate formation line falls within the hydrate formation envelope, hence the prevalence of high threat of hydrate formation in the pipeline. Consequently, the need for hydrate inhibitors for reliable transportation of this gas through pipeline.



Figure 1. Hydrate formation utility for natural gas stream



Figure 2. Hydrate formation utility performance for natural gas stream

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3.2. CO₂ Corrosion

The results of the simulation carried out on natural gas well stream to determine the CO_2 corrosion on pipeline and the relationship between corrosion rate and temperature and P^H, corrosion rate-temperature for varying CO_2 mole percent and P^H values are shown in Figures 4 to 7 respectively. The result as obtained from Figure 4 shows that CO_2 corrosion increased with increasing temperature and peaked at 78°C thereafter, a dip in corrosion rate occurred.







Figure 5. Effect of P^H on CO₂ corrosion rate on natural gas pipeline

The result from Figure 5 clearly indicates that inverse. The CO_2 corrosion rate decreases with the relationship between corrosion rate and P^H is increase in pH value. The corrosion rate-

temperature relationship for varying CO_2 mole percent as obtained from Figure 6 shows that CO_2 corrosion increased in magnitude as the mole percent of CO_2 increases. The obtained result from the corrosion rate-temperature relationship for varying P^H values as represented in Figure 7 shows that the higher the P^H values the lesser the rate of corrosion on the pipeline.



Figure 6. Effect of temperature on CO₂ corrosion rate for varying CO₂ mole percent on natural gas pipeline



Figure 7. Effect of temperature on CO₂ corrosion rate for varying P^H values on natural gas pipeline

The CO₂ corrosion rate increased with increasing temperature and peaked at 78°C after which follows a dip in rate of corrosion as symbolized in Figure 4. This obtained result compares to that of studies by Niklasson et al. [18] and Krishnan et al. [19]. This can be explained using the concept of the formation of protective film on the pipeline. The film reduces the number of sites open for corrosion attack and also forms a compact ferrous carbonate barrier on the metal surface that is not easily moved. From Figure 5, it is evident that the relationship between corrosion rate and P^{H} is inverse. The corrosion rate decreases with increase in P^H values. This can be explained by the fact that at lower P^H , the natural gas stream becomes more acidic and the more acidic the natural gas stream, the more its corroding power. On the other hand, the higher the P^{H} of the natural gas stream, the more alkaline and less corrosive the fluid becomes. It is however

worthy of note that the impact of P^{H} on the CO_2 corrosion rate is dependent on the type of materials used in the construction of the pipe. Some materials are acid soluble (they are easily dissolved in acid solution) hence they are easily affected by corrosion. While others like noble metals are not affected by CO_2 corrosion because they do not dissolve in acid solutions. The result from Figure 6 shows an increase in size in corrosion rate with an increase in mole percent CO_2 .

The CO_2 corrosion rate rose as high as 5.7mm/yr at 3mole percent of CO_2 . This can simply be explained by the fact that the tendency of carbonic acid which is a corroding species to cause corrosion is higher at higher CO_2 concentrations. It is explicit from Figure 6 that 3mole percent CO_2 of the natural gas stream induced more corrosion on the natural gas pipeline internal wall than the 1mole and 2mole percent CO_2 composition. A 3mole

percent CO₂ induced 49%,53% and 102.5% more corrosion on the natural gas pipeline than the 1mole percent CO₂ for temperature of 5°C, 15°C and 20°C. This values and trend portray a bad omen for the affected natural gas pipeline. From Figure 7 it is crystal clear that the corrosion rate decreases with increase in P^H values. The fluid that has the highest P^H (5.5) value had the least corrosion effect while that with the least P^H (3.5) value has the most corrosion effect. The P^H of natural gas stream affects CO₂ corrosion as P^H controls the rate of dissolution of iron into solution. High P^H equates to high alkalinity which leads to a decreased iron carbonate solubility and scale formation.

4. CONCLUSION

Based on the obtained results and discussions under hydrate formation and its influence on natural gas pipeline using simulation approach, there is higher probability of formation of both type I and type II hydrate at the conditions of 5°C and 60 bar. This above conclusion is in agreement with the principle of hydrate formation where decrease in temperature and increase in pressure favours hydrate formation. This study clearly indicates that the relationship between corrosion rate and P^{H} is inverse, as CO2 corrosion rate decreases with increase in P^H. It can therefore be confidently stated from this study that P^H is a parameter that critically affects the CO2 corrosion rate by influencing the rate of dissolution of iron into solution. The general result obtained shows that rate of corrosion increases with increase in temperature, increase in CO₂ mole percent of the natural gas stream and decreases with increase in P^H values with them all peaking at 78^oC before a dip from their respective trend.

From the results obtained in this study, it is concluded that the rise in corrosion rate as much as 5.7 mm/year at 3 mole percent CO_2 is worrisome. This study has successfully established in quantified term from the obtained results the increment in corrosion rate that equates to 49%, 53% and 102.5% for the temperature conditions of 5°C,15°C and 20°C when mole percent increase from 1 to 3. This is a true effects and reflections of the propensity of carbonic acid, a corroding species that remains higher at higher CO_2 concentration. This values and trend as obtained in this study portray a bad omen for the affected natural gas pipeline.

Nomenclature

- a Fugacity coefficient
- bar Unit of pressure measurement
- CO2 Carbon dioxide (carbon II oxide)
- Cr_{CO_2} CO₂ corrosion rate
- D Internal diameter of pipe (mm)

- f Friction factor
- F_{CO_2} CO₂ Fugacity
- $f(P^H)_T$ Complex function of P^H and temperature
- GUI Graphic user interface

H₂S - Hydrogen sulphide

- IFE Institute for energy technology
- K Kelvin (temperature scale)
- K Pipe roughness

 K_T - Operating temperature dependent constant MATLAB - Matrix laboratory

NORSOK-Norsk sokkels konkurranseposisjon

NORSOK M-506 - CO₂ corrosion prediction model NN - Neural network

- P_{CO_2} Partial pressure of CO₂
- P^H Hydrogen potential

RHS - Right hand side

- S Wall shear stress
- T Temperature
- U_m Velocity of fluid mixture

Unisim - Equation oriented simulation software package

 ρ_m - Mixture density

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IZVOD

FORMIRANJE HIDRATA I NJEGOV UTICAJ NA CEVOVOD PRIRODNOG GASA: SIMULACIONA STUDIJA

Ova studija je istovremeno proučavala dvostruki problem hidrata i korozije koji se javlja u gasovodu prirodnog gasa, utvrđujući njihovu međuzavisnost korišćenjem simulacionog pristupa. CO₂ korozija je simulirana korišćenjem standardnog modela NORSOK M-506 u matlab-u. Glavni faktori koji se razmatraju su odnos između brzine korozije i temperature, brzine korozije i PH, odnos korozije i temperature za različite molske procente CO₂ i PH vrednosti. Rezultat ove studije je pokazao da se i hidrati tipa I i tipa II mogu formirati pri radnim uslovima od 5°C i 60 bara. Dobijeni rezultat, takođe, pokazuje da se brzina korozije smanjuje i povećava sa povećanjem PH vrednosti i temperature do određene temperature od približno 78°C, a zatim pada u stopi korozije. Rezultat za odnos korozije temperatura za različite vrednosti PH i molskog procenta CO₂ pokazuje smanjenje brzine korozije sa povećanjem PH i povećanje sa povećanjem molskog procenta CO₂ t. Štaviše, dobijeni rezultati ističu porast od čak 5,7 mm/godišnje pri 3 mol procenta CO₂. Ova vrednost i trend predstavljaju loš znak za pogođeni cevovod. Ova studija preporučuje da prirodni gas koji se transportuje cevovodom treba zasladiti i preraditi kako bi se uklonili H2S, CO₂ i merkaptani ako su prisutni. **Ključne reči:** CO₂ korozija, model, simulacija, hidrat, MATLAB

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