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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<sub>2</sub> 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<sub>2</sub> 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 CO<sub>2</sub> mole percent shows a decrease in corrosion rate with an increase in  $P^H$ , and an increase with increase in CO<sub>2</sub> mole percent. Furthermore, the obtained results highlight a rise as high as 5.7 mm/year at a 3 mole percent CO<sub>2</sub>. 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<sub>2</sub>S, CO<sub>2</sub> and mercaptans if present.*

**Keywords:** CO<sub>2</sub> corrosion, model, simulation, hydrate, MATLAB

### 1. INTRODUCTION

Currently there are global quest 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 deployment of exploration and exploitation technologies and the building of massive infrastructure for gas processing, treatment and transportation.

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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 gas is faced with the flow assurance problem of hydrate formation and CO<sub>2</sub> corrosion of the internal walls of the pipeline. Proberezhny et al. [3] stated that corrosion of natural gas pipeline can be attributed to H<sub>2</sub>S and CO<sub>2</sub> 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 CO<sub>2</sub> corrosion in pipeline steel evaluated the severity of CO<sub>2</sub> pipeline corrosion in economic terms. They stated that CO<sub>2</sub> 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 CO<sub>2</sub> corrosion by researchers have been carried out. Zunzhao et al. [5] deployed a natural gas hydrate loop device to measure the corrosion rate of CO<sub>2</sub> in the presence of hydrate on X80 steel, Obanijesua et al. [6] developed a model to predict CO<sub>2</sub> corrosion rate of natural gas pipeline in the presence of hydrate, their obtained results show that the corrosion rate of CO<sub>2</sub> was higher than the gas liquid equilibrium.

Studies [7,8] on CO<sub>2</sub> corrosion prediction using model by researchers has shown the availability CO<sub>2</sub> prediction models. Nesic et al. [9] listed the three general groups of models used for CO<sub>2</sub> corrosion prediction as: mechanistic, semi-empirical and empirical while Kahyarian et al. [10] grouped CO<sub>2</sub> 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 CO<sub>2</sub> corrosion. Hatami et al. [13] reported that the use of least square support vector machine (LSSVM) for the prediction of CO<sub>2</sub> 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 CO<sub>2</sub> corrosion. Different approach is used by CO<sub>2</sub> corrosion prediction models in predicting the effect of protective film on CO<sub>2</sub> corrosion and in predicting the effect of oil wetting on CO<sub>2</sub> corrosion [14].

CO<sub>2</sub> corrosion prediction is also affected by environmental factors, based on this De Ward et al. [15] advocated the use of correction factor for CO<sub>2</sub> 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<sub>2</sub> corrosion parameters, asserted that model accuracy is less important than the knowledge of the major corrosive parameters governing the CO<sub>2</sub> corrosion mechanism.

One very reliable model used in CO<sub>2</sub> 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<sub>2</sub> corrosion mechanism at higher temperature and high P<sup>H</sup> more than many other prediction models. This model is well reputed for giving a good representation of the maximum

corrosion rate in a CO<sub>2</sub> 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.

Table 1. Mole composition of natural gas

Components	Mole composition (%)
C <sub>1</sub>	74.805
C <sub>2</sub>	5.633
C <sub>3</sub>	4.264
nC <sub>4</sub>	2.411
1C <sub>4</sub>	1.651
nC <sub>5</sub>	3.21
1C <sub>5</sub>	2.104
C <sub>6</sub>	1.712
C <sub>7</sub>	0.867
C <sub>8</sub>	0.652
C <sub>9</sub>	0.321
CO <sub>2</sub>	1.978
N <sub>2</sub>	0.294
H <sub>2</sub> O	0.098
	100.00

#### 2.4. CO<sub>2</sub> 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<sub>2</sub> fugacity, P<sup>H</sup> 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°C

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

For T = 15°C

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

For: 20°C T 150°C

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

Where  $Cr_{CO_2}$  is CO<sub>2</sub> corrosion rate, mm/year,  $K_T$  is constant dependent on operating temperature,  $S$  is wall shear stress in Pa,  $F_{CO_2}$  is CO<sub>2</sub> 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).

$$F_{CO_2} = a \times P_{CO_2} \quad (4)$$

Where:  $a$  is fugacity co-efficient and  $P_{CO_2}$  is the partial pressure of CO<sub>2</sub> which is represented as shown on Eq.(5).

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

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

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

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

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

$$S = 0.5 \times f \times \rho_m \times U_m^2 \quad (8)$$

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

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

Where  $K$  is the pipe roughness in inches,  $D$  is the pipe diameter in mm and  $\mu_m$  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.

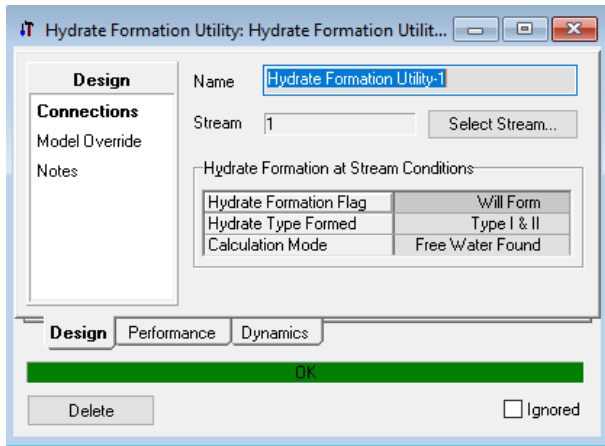


Figure 1. Hydrate formation utility for natural gas stream

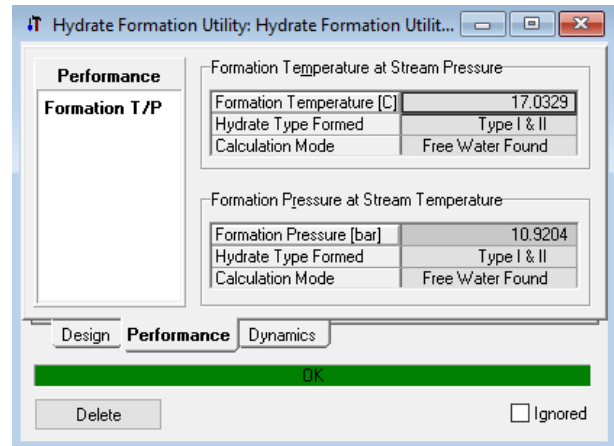


Figure 2. Hydrate formation utility performance for natural gas stream

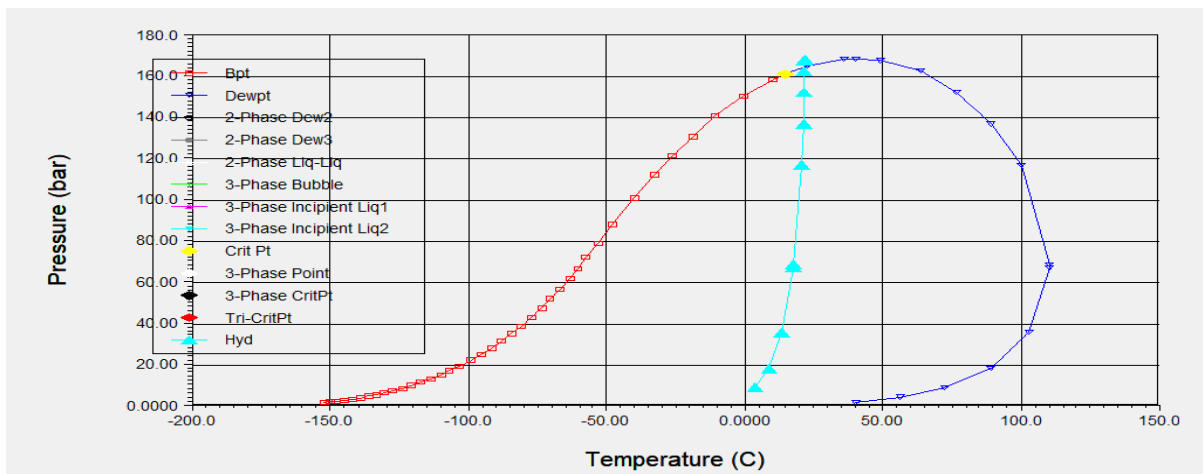


Figure 3. Phase envelope utility for the natural gas stream

### 3.2. CO<sub>2</sub> Corrosion

The results of the simulation carried out on natural gas well stream to determine the CO<sub>2</sub> corrosion on pipeline and the relationship between corrosion rate and temperature and P<sup>H</sup>, corrosion rate-temperature for varying CO<sub>2</sub> mole percent and

P<sup>H</sup> values are shown in Figures 4 to 7 respectively. The result as obtained from Figure 4 shows that CO<sub>2</sub> corrosion increased with increasing temperature and peaked at 78°C thereafter, a dip in corrosion rate occurred.

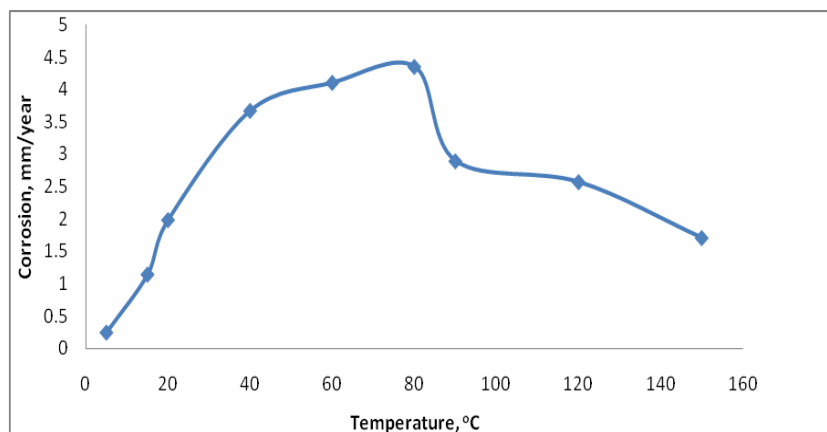


Figure 4. Effect of temperature on CO<sub>2</sub> corrosion rate on natural gas pipeline

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

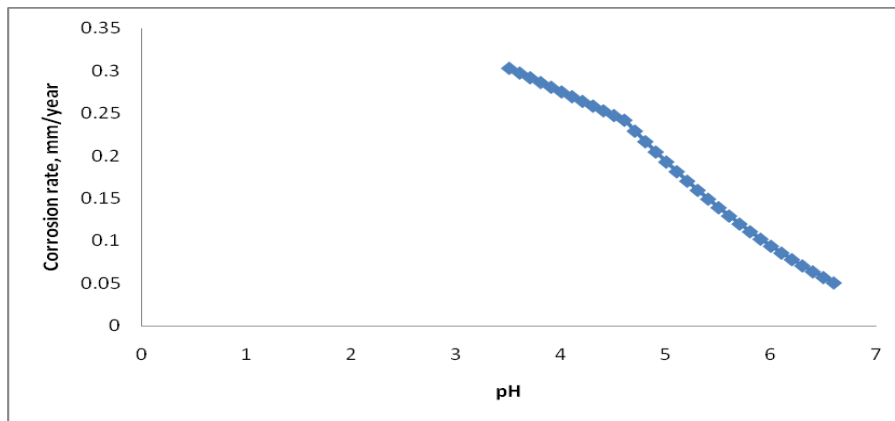


Figure 5. Effect of  $P^H$  on  $CO_2$  corrosion rate on natural gas pipeline

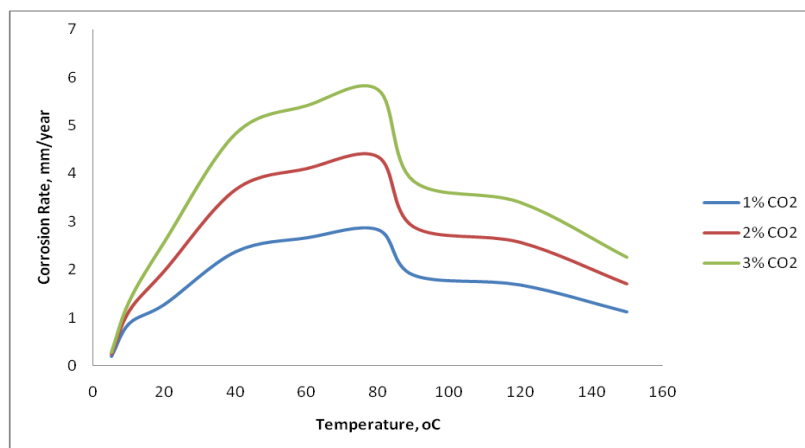


Figure 6. Effect of temperature on  $CO_2$  corrosion rate for varying  $CO_2$  mole percent on natural gas pipeline

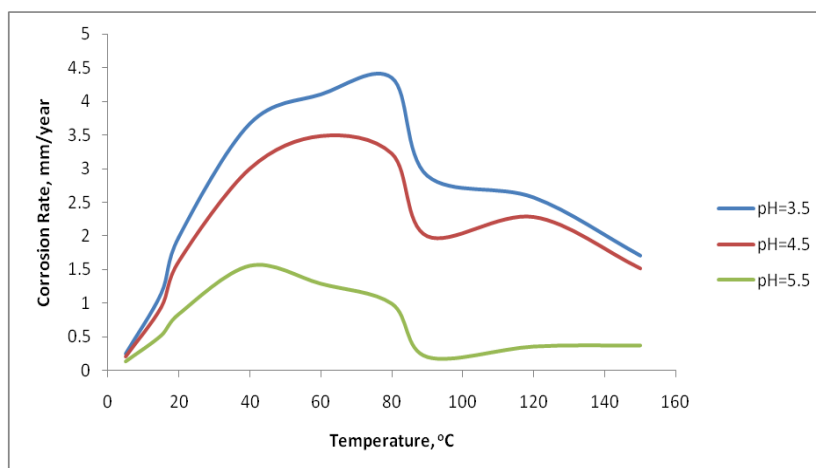


Figure 7. Effect of temperature on  $CO_2$  corrosion rate for varying  $P^H$  values on natural gas pipeline

The CO<sub>2</sub> 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<sup>H</sup> is inverse. The corrosion rate decreases with increase in P<sup>H</sup> values. This can be explained by the fact that at lower P<sup>H</sup>, 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<sup>H</sup> 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<sup>H</sup> on the CO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub>.

The CO<sub>2</sub> corrosion rate rose as high as 5.7mm/yr at 3mole percent of CO<sub>2</sub>. 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<sub>2</sub> concentrations. It is explicit from Figure 6 that 3mole percent CO<sub>2</sub> of the natural gas stream induced more corrosion on the natural gas pipeline internal wall than the 1mole and 2mole percent CO<sub>2</sub> composition. A 3mole percent CO<sub>2</sub> induced 49%,53% and 102.5% more corrosion on the natural gas pipeline than the 1mole percent CO<sub>2</sub> 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<sup>H</sup> values. The fluid that has the highest P<sup>H</sup> (5.5) value had the least corrosion effect while that with the least P<sup>H</sup> (3.5) value has the most corrosion effect. The P<sup>H</sup> of natural gas stream affects CO<sub>2</sub> corrosion as P<sup>H</sup> controls the rate of dissolution of iron into solution. High P<sup>H</sup> 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<sup>H</sup> is inverse, as CO<sub>2</sub> corrosion rate decreases with increase in P<sup>H</sup>. It can therefore be confidently stated from this study that P<sup>H</sup> is a parameter that critically affects the CO<sub>2</sub> 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 CO<sub>2</sub> mole percent of the natural gas stream and decreases with increase in P<sup>H</sup> values with them all peaking at 78°C 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<sub>2</sub> 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<sub>2</sub> 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
- CO<sub>2</sub> - Carbon dioxide (carbon II oxide)
- $Cr_{CO_2}$  - CO<sub>2</sub> corrosion rate
- D - Internal diameter of pipe (mm)
- $f$  - Friction factor
- $F_{CO_2}$  - CO<sub>2</sub> Fugacity
- $f(P^H)_T$  - Complex function of P<sup>H</sup> and temperature
- GUI - Graphic user interface
- H<sub>2</sub>S - 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 - CO<sub>2</sub> corrosion prediction model

NN - Neural network

$P_{CO_2}$  - Partial pressure of CO<sub>2</sub>

$P^H$  - Hydrogen potential

RHS - Right hand side

S - Wall shear stress

T - Temperature

$U_m$  - Velocity of fluid mixture

Unisim - Equation oriented simulation software package

$\rho_m$  - 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. CO<sub>2</sub> 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 procenete CO<sub>2</sub> 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 CO<sub>2</sub> pokazuje smanjenje brzine korozije sa povećanjem PH i povećanje sa povećanjem molskog procenta CO<sub>2</sub> t. Štaviše, dobijeni rezultati ističu porast od čak 5,7 mm/godišnje pri 3 mol procenta CO<sub>2</sub>. Ova vrednost i trend predstavljaju loš znak za pogođeni cevovod. Ova studija preporučuje da prirodni gas koji se transportuje cevovodom treba zasladi i preraditi kako bi se uklonili H<sub>2</sub>S, CO<sub>2</sub> i merkaptani ako su prisutni.

**Ključne reči:** CO<sub>2</sub> korozija, model, simulacija, hidrat, MATLAB

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