

## Application of modified langelier saturation index model to pipeline corrosion

J. I. Achebo

*Department of Production Engineering, University of Benin, Nigeria*

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### Abstract

The aim of the research presented in this paper was to apply the Langelier saturation index (Is) model to determine the cause of pipeline corrosion in the oil industry with reference to the production water from the reservoir. From the test, it was found that the Langelier saturation index model applied, gave a value of -4.44 at a pH of 4.20. The CO<sub>2</sub> level in the pipeline was found to be 0.55% and also the presence of sulphate reducing bacteria (SRB) was very low. These figures however show that although the water in the pipelines was given the standard treatment, the high CO<sub>2</sub> lead to the continuous occurrence of corrosion in the pipeline despite this treatment. Thus CO<sub>2</sub> content has to be reduced by the Dienthanolamine (DEA) unit application to safe levels of 0.1 – 0.3%

*Keywords:* Modified Langelier saturation index model; Pipeline corrosion; CO<sub>2</sub>; Production water; Sulphate reducing bacteria

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### 1. Introduction

The upstream sector of the Nigerian oil industry relies heavily on the use of pipelines to convey crude oil directly from reservoirs to other facilities, usually for refining, storage, or shipping. Pipeline corrosion could lead to leaks and on occasion major spills (Bang et al, 2002; Kiefner, 1994; Kiefner and Fischer, 1998). This is a significant problem; this study is aimed at addressing it.

Some researchers have observed that the major causes of pipe leakages are corrosion and wear due to abrasion (Schmitte and Nitsche, 2006; Edwards et al, 2000). Different methodologies have been developed to determine the corrosion behavior of transmission pipeline fluids using the finite element analysis, magnetic stray flux leakage measurement technique, developed computational and simulation methods, etc. (Bahr et al, 2000; Seleznev, 2005). In this study, the Saturation Index Model was applied to determine the cause of corrosion. This methodology is not new but the simplicity, ease of application and accuracy of prediction has motivated its use in this study with some modifications

### 2. Experimentals

Crude oil is a loose composition of oil, gas, sand and water. Pipeline corrosion is traceable to the mixture of its water content; known as production water and its gas content which form a corrosive environment as follows:  $H_2O + CO_2 = H_2CO_3$  (Acidic solution)

To determine the causes of the high corrosion rates of the internal surface of the pipe, water samples were collected from the separator tank by opening the valve controlling water. The production water contains Fe<sup>2+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, (cations) and SO<sub>4</sub><sup>2+</sup>, CO<sub>3</sub><sup>2+</sup>, NO<sup>-</sup>, HCO<sup>-</sup> (anions) which are constituent elements when in certain proportions are associated with corrosion. These constituent elements were determined by the use of a digital titrator and a laboratory spectrophotometer.

#### 2.1. Determination of Ca<sup>2+</sup>, Mg<sup>2+</sup>, Cl<sup>-</sup>, CO<sub>3</sub><sup>2+</sup>, HCO<sub>3</sub><sup>-</sup> Reagents

One calgon table indicator, pH 10 and 12 buffer solution, 0.02N EDTA solution, potassium dichromate solution, 0.1N silver nitrate solution, phenolphthalein indicator, hydrochloric acid, methyl orange indicator, carbonate ion solution and 10 cm<sup>3</sup> of production water.

#### Equipment

The digital titrator was used to determine the volume of the titrant.

#### Equation

The quantity of the ionic content of each constituent element was determined by

$$\frac{g}{dm^3} = \frac{\text{mol. wt.} \times N \times V_2}{V_1} \quad (1)$$

where, mol. wt = molecular weight in g/mol  
 N = normality of the titrant  
 $V_1$  = volume of the sample in  $cm^3$   
 $V_2$  = volume of titrant in  $cm^3$

### 2.2. Determination of $SO_4^{2-}$ , $NO_3^-$ , $Fe^{2+}$ reagents

Sulfa ver 4 sulphate reagent powder pillow, nitrate ver nitrate reagent powder pillow, dilute hydrochloric acid, concentrated nitric acid, ferro ver iron reagent powder pillow and 25 $cm^3$  of production water.

#### Equipment

Spectrophotometer was used to determine the quantity of each of the constituent elements as the results were displayed on the screen.

### 2.3 $CO_2$ Analysis

Table 1:

The application of langelier saturation index model

Ions	ppm	mol. wt.	Conc(mol/g)	ionic strength, $\mu$	K	pH	pca	palc	Is
$HCO_3^-$	0.378	61	$6.2 \times 10^{-3}$	$\mu^1 = \frac{1}{2} [HCO_3^- + NO_3^-]$ $= \frac{1}{2} [6.20 \times 10^{-3} + 1.84 \times 10^{-4}]$ $= 3.19 \times 10^{-2}$	1.45	4.20	2.09	5.10	-4.44
$NO_3^-$	11.44	62	$1.84 \times 10^{-4}$						
$CO_3^{2-}$	0.08	60	$1.32 \times 10^{-3}$	$\mu^{11} = \frac{1}{2} [(CO_3^{2-})^4 + (SO_4^{2-})^4 + (Fe^{2+})^4 + (Ca^{2+})^4 + (Mg^{2+})^4]$ $= \frac{1}{2} [1.32 \times 10^{-2} + 1.01 \times 10^{-4} + 4.24 \times 10^{-6} + 8.17 \times 10^{-3} + 6.41 \times 10^{-2}]$ $= 3.2 \times 10^{-2}$					
$SO_4^{2-}$	9.68	96	$1.01 \times 10^{-4}$						
$Fe^{2+}$	0.24	56	$4.28 \times 10^{-6}$						
$Mg^{2+}$	0.15	24	$6.41 \times 10^{-3}$						
$Ca^{2+}$	0.33	40	$8.17 \times 10^{-3}$						

$$\mu = \mu^1 + \mu^{11} = 3.19 \times 10^{-3} + 3.20 \times 10^{-2} = 3.25 \times 10^{-2}$$

$\mu = \frac{1}{2} [M_j Z_j^2]$  where M = molarity and Z = ionic charge  
 Langelier Saturation Index, Is = pH - pca - palc - K

pca = concentration of calcium =  $-\log(Ca^{2+}) = 2.09$

palc = concentration of alkaline =  $-(\log HCO_3^- + \log CO_3^{2-}) = 5.10$

Temperature of the flowline = 44°C

K = the ionic activity at the temperature of the flowline  
 $= -\log(\mu_{total}) = 1.45$

### 3.2. Result interpretation

$0 > Is > 1$  shows that water is corrosive

#### Apparatus

Gas bladder,  $CO_2$  dragger tube, calibrated from 0.1% to 1.0% and Dragger pump.

#### Test result display

The amount of  $CO_2$  absorbed, which reveals itself in a deep blue coloration, was read off the  $CO_2$  dragger tube.

### 2.4 Sulphate reducing bacteria (SRB) analysis apparatus

Incubator, Test kits, syringes, mohr's salt, automated mixer, 2  $cm^3$  of production water

#### Test Incubation

The diluted test kits were put in the incubator at 37°C to develop

## 3. Results and discussion of results

### 3.1. Results

Table 1 shows the process of applying the modified Langelier Saturation Index Model to determine the corrosive behaviour of the fluid in the pipeline.

Is < -1 shows the possibility of forming calcium carbonate scales

Is: -1 and 0 indicates that production water is not aggressive and can not form scales. It also shows that the reservoir is well treated with inhibitors.

### 3.3. Discussion of result

The main objective of this study is to apply the langelier saturation index (Is) model to determine the causes of pipeline corrosion in the oil industry. To achieve this, the samples of production water were collected for laboratory investigation. The water in its production state contains  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Cl^-$ ,  $HCO_3^-$ ,  $CO_3^{2-}$ ,

$\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , and  $\text{Fe}^{2+}$ . From the investigation, it was found that the production water contains  $0.0327\text{g}/\text{dm}^3$  of  $\text{Ca}^{2+}$ ,  $0.156\text{g}/\text{dm}^3$  of  $\text{Mg}^{2+}$ ,  $13.67\text{mg}/\text{dm}^3$  of  $\text{Cl}^-$ ,  $0.378\text{g}/\text{dm}^3$  of  $\text{HCO}_3^-$ ,  $0.079\text{g}/\text{dm}^3$  of  $\text{CO}_3^{2-}$ ,  $11.44\text{mg}/\text{dm}^3$  of  $\text{SO}_4^{2-}$  and  $0.240\text{mg}/\text{dm}^3$  of  $\text{Fe}^{2+}$  respectively. When the langelier saturation index (Is) model was applied, Is was -4.44 at a pH value of 4.20.  $\text{CO}_2$  in the pipeline was found to be 0.55%.

#### 4. Conclusion

Saturation Index model has been successfully applied. The result shows that there is the possibility of the scales of calcium carbonate forming in the production water if not properly treated with the standard proportions of inhibitors and dispersants as specified by the company. The SRB investigation showed that the presence of small number of bacteria were considered too weak to cause any corrosion. It was found that the cause of corrosion was the corrosive environment caused by the high  $\text{CO}_2$  content in the pipeline. However, it is observed that the Dienthanolamine (DEA) unit; which is a borate buffer system used to neutralize the effect of  $\text{CO}_2$  by absorbing most of it and maintaining the pH of glycol in the 7 to 8 range, leaving a small quantity of less or equal to 0.3%, an acceptable level in the pipeline; has not been effective. This report was submitted to the affected Oil and Gas Company and their DEA Unit was upgraded to accommodate the required acceptable  $\text{CO}_2$  absorption capacity. As a result of this, since the

transmission pipelines were changed there has not been any reported incident of corrosion.

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