Full Paper

ECO-FRIENDLY INHIBITORS FOR EROSION-CORROSION MITIGATION OF API-X65 STEEL IN CO2 ENVIRONMENT

O.O. Ige
Department of Materials Science and Engineering, Obafemi Awolowo University, Nigeria.
ige4usa@yahoo.com

M.D. Shittu
Department of Materials Science and Engineering, Obafemi Awolowo University, Nigeria.

K.M. Oluwasegun
Department of Materials Science and Engineering, Obafemi Awolowo University, Nigeria.

O.E. Olorunniwo
Department of Materials Science and Engineering, Obafemi Awolowo University, Nigeria.

L.E. Umoru
Department of Materials Science and Engineering, Obafemi Awolowo University, Nigeria.

ABSTRACT

The study of chemical mitigation of erosion-corrosion of API-X65 Steel in a multiphase system containing brine, CO_2 gas, and sand at different shear stresses with two eco-friendly inhibitors are reported. The inhibitors investigated are a commercial grade synthetic product and a natural inhibitor (*Aloe vera*). The mass loss, linear polarization, and scanning electron microscopy techniques were investigated. The results obtained show that both inhibitors maybe useful in oil and gas industry, the synthetic inhibitor have quantifiable advantage over the natural inhibitor. From the results obtained these inhibitors are expected to have credible technical performance and as such reduce considerably the adverse effects on health, safety, and environmental factors associated with inhibition in oil and gas industries.

Keywords: *Erosion-corrosion, Inhibitors, Multiphase system, Steel, Rotating cylinder electrode, and scanning electron microscopy*.

1. INTRODUCTION

The importance of corrosion inhibitors in the oil and gas industry is well established and cannot be underestimated. Corrosion inhibitors are known to prevent discharge of oil and gas through leakages to the environment (Obesekesere *et al.*, 2002). They also play a significant role in internal corrosion control associated with oil and gas production and transportation (Taj *et al.*, 2006). Due to rapid depletion and huge exploitation, future oil and gas productions are expected to occur more in remote areas. This will lead to increasing challenges relating to asset management, which includes; sand presence in production fluids and the shift towards deeper wells. All these may result in difficulties in maintaining the integrity of pipes and process equipment (Wang *et al.*, 2005).

In particular, there have been extensive studies of chemical inhibition of erosion-corrosion. Some of these studies have concluded that corrosion inhibitors are effective in controlling erosion corrosion mechanisms. The attention has been focussed on mechanisms of inhibition, inhibition efficiency, and material degradation phenomena, among others (McLaury *et al.*, 1995; Schmitt, 2001; Ramachandra *et al.*, 2005 and Wang *et al.*, 2005). Research efforts have also been deployed to study the effectiveness of inhibitors in the presence of erosive flows and at different shear stresses (Neville and Wang, 2009).

However, in the majority of these studies related to chemical mitigation of CO_2 corrosion, the focus has been more on superior performance with little or no emphasis on the health, safety, and environmental factors (Chen and Chen, 2002).

However national government of various countries have invoked tighter and stringent conditions due to more severe environmental constraints. Hence several attempts have been made to develop the chemistry that is considered green in nature (Obeyesekere *et al.*, 2000; Killars and Finley, 2001; Chen and Chen, 2002).

There is little previous work that investigated the performance of eco-friendly inhibitors in the erosion-corrosion control. Therefore, the aim of this work is to examine the behaviour of mild steel in the presence of a synthetic "green" chemistry based system and a natural product as corrosion inhibitors in a multiphase system containing brine, CO_2 gas, and sand at different shear stresses. The data obtained are compared for their performance in order to determine the effectiveness of the inhibitors as candidates for inhibition in oil and gas industry.

2. MATERIALS AND METHODS

2.1. Materials

The steel used in this study is as-received API 5L X65 carbon steel with Vickers hardness of 240 HV. The samples were cylindrical shaped with dimensions of 12 mm by 8 mm. The microstructure and chemical composition are as shown in Figure 1 and Table 1, respectively.

2.2. Media and Inhibitors

Table 2 shows the chemistry of the process solutions was prepared according to the work of Hu *et al.* (2011). Two different corrosion inhibitors were studied. They are referred to as Aloe vera and inhibitor NA. The Aloe vera represents a natural inhibitor with green chemistry while the inhibitor NA is a commercially available, high shear eco-friendly CO_2 – based inhibitor.

The Aloe vera leaves were sliced open at the edges and the gel was squeezed out, sieved in order to obtain a clear concentrated semi-liquid. No water was added. The liquid is viscous, colourless, transparent, consists of water (98.5%), and polysaccharides (0.3%) (WHO, 1999). The polysaccharide composition was analysed by gas

-

Table 1: Chemical or elemental compositions of API 5L X65 carbon steel

Element	C	Si	Mn	P	S	Cr	Mo	Ni	Ti	Fe
Wt (%)	0.10	0.18	1.21	0.009	0.003	0.10	0.16	0.07	<0.01	Balance

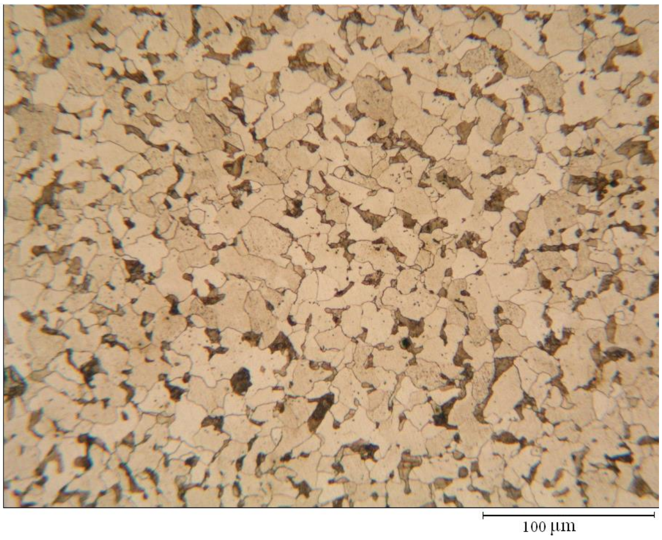


Figure 1: Optical microscope image of API 5L X65 carbon steel after being polished and etched in 2% nital solution for 10 seconds (dark background = pearlite and lighter background = ferrite)

Table 2: Composition of brine used in flow-induced corrosion and erosion-corrosion tests

Preparation	(mg/L)
NaCl (sodium chloride)	24090
KCl (potassium chloride)	706
$CaCl_2 \cdot 2H_2O$ (calcium chloride di-hydrate)	1387
$MgCl_2$ (magnesium chloride)	4360
$BaCl_2 \cdot 2H_2O$ (barium chloride di-hydrate)	16
$SrCl_2 \cdot 6H_2O$ (strontium chloride hexa-hydrate)	33
Na_2SO_4 (sodium sulphate)	3522
$NaHCO_3$ (sodium bicarbonate)	304

liquid chromatography and it reveals pectins, hemicellulose, glucomannan, acemannan, and mannose derivatives. It also contains amino acids, lipids, sterols, tannins and enzymes (WHO, 1999). The chemical preparation for inhibitor NA was based on a combination of ethandiol, ethoxylated imidazolines, carboxylic acid salts, and thioalcohol. The inhibitors were tested at concentrations of 0, 25, 50, 75, and 100 ppm (Table 3).

Table 3: Experimental matrix for rotating cylinder electrode (RCE)

Parameters	Conditions
Material	API 5L X65 in as-received condition
Temperature (°C)	50
CO_2 partial pressure (Bar)	1
Rotating cylinder speed (rpm)	1000, 3000, and 5000
Inhibitor	Aloe vera and G
Inhibitor concentrations (ppm)	0, 25, 50, 75, and 100
Stirrer speed (rpm)	750
Sand concentrations (mg/L)	0 and 500
Exposure duration (hours)	4

The inhibition efficiency was calculated using the following formula:

$$\text{Inhibition Efficiency} = \frac{(CRNI - CRWI)}{CRNI} X\,100 \qquad (1)$$

where CR_{WI} and CR_{NI} are the experimental corrosion rates with and without inhibition, respectively.

2.3. In-situ Corrosion Measurements

The erosion-corrosion tests were carried out using a rotating cylinder electrode (RCE) arrangement as shown in Figure 2. The RCE experiments were conducted in line with the work of Wang *et al.* (2005). The experimental matrix for the tests is as presented in Table 3. The hydrodynamic parameters of the RCE in terms of the Reynolds number R_e (Dalayan *et al.*, 1995) and wall shear stress (τ_ω) (Gabe and Walsh, 1983) used in this study are presented in Table 4. The tests were conducted with 500 mg/L of sand and the average diameter of the round silica sand used in these studies was 250 μm. The shape and size distribution are as illustrated in Figures 3a and 3b. The in-situ corrosion rate for the RCE was determined by using linear polarization resistance (LPR) technique according to the work of Hu *et al.* (2011). Also the specimens were weighed prior to exposure and after the tests to determine the total weight loss of each specimen using an analytical balance with the accuracy of 0.0001 g.

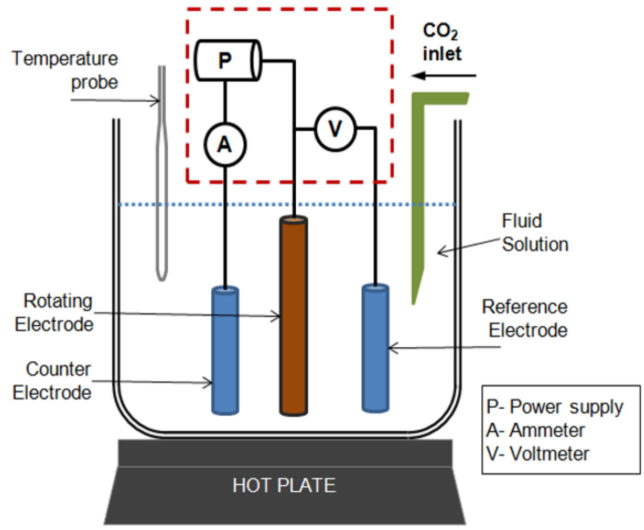


Figure 2: The set-up of the rotating cylinder electrode (RCE)

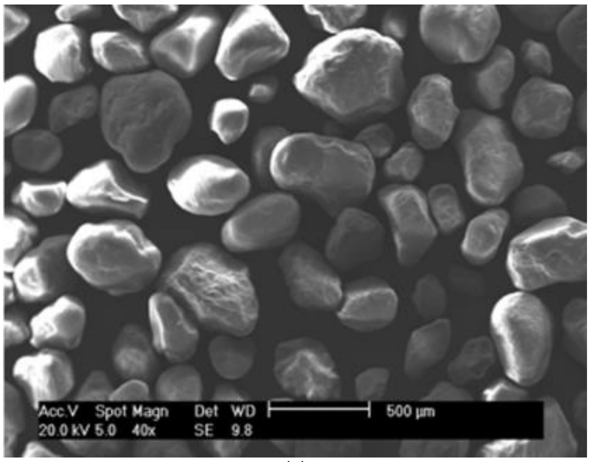
2.4. Scanning Electron Microscopy (SEM)

The possible mechanisms of degradation was investigated by SEM and the analysis revealed the extent and nature of the mechanical and electrochemical damage in the absence and presence of inhibitors (Figures 10a, b, and c).

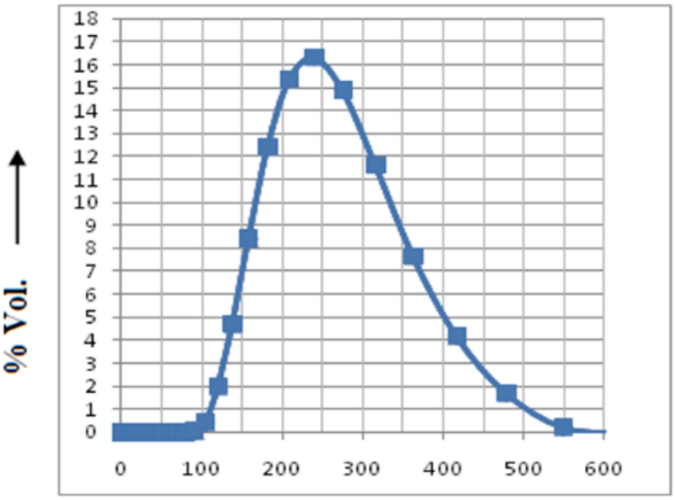
3. RESULTS

3.1. Erosion-corrosion Mass Loss

A typical illustration of the total mass loss obtained for the steel samples subjected to different flow velocities is shown in Figure 4. There is a sharp reduction in the material degradation rates when *Aloe vera* inhibitor is added to the system at a lower velocity regime (1000 rpm) leading to almost 50% reduction in the thickness loss. Further decrease was observed when the synthetic inhibitor is added to the solution. However, a remarkable decrease in the material loss was observed when the inhibitors were added at a higher velocity (5000 rpm). Although the percentage reduction decreases as the velocity increases, the commercial inhibitor used still exhibits better performance than the *Aloe vera* with about 50% reduction in corrosion rate compared to about 33% in the case of *Aloe vera*. It was observed that the corrosion rate increases as the flow velocity increases for uninhibited and inhibited solutions.



(a)



(b)

Figure 3: (a) Sand particles' shape and sizes from SEM and (b) Sand particles' size distribution from sieve analysis.

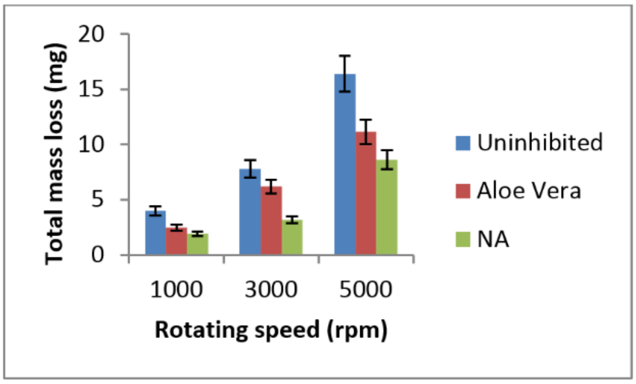


Figure 4: Comparison of total mass loss (mg) as a function of the rotating speed (rpm) and 50oC for uninhibited and 100 ppm of the inhibitors

3.2. In-situ Erosion-corrosion Analysis

The electrochemical measurements of the in-situ corrosion samples subjected to erosion-corrosion were carried out. The linear polarization resistance plot of the solutions when uninhibited and inhibited with *Aloe vera* and inhibitor NA is presented in Figure 5. The result shows that there is little change in the polarization resistance (R_p) for uninhibited solutions at different velocities. The data show that the R_p increases as the flow velocity increases with the highest rate obtained for the synthetic commercial inhibitor. Meanwhile at all velocity regimes the R_p decreases with the introduction of Aloe vera and further reduction occurs in solution inhibited with NA. The reduction becomes significant as the flow velocity increases.

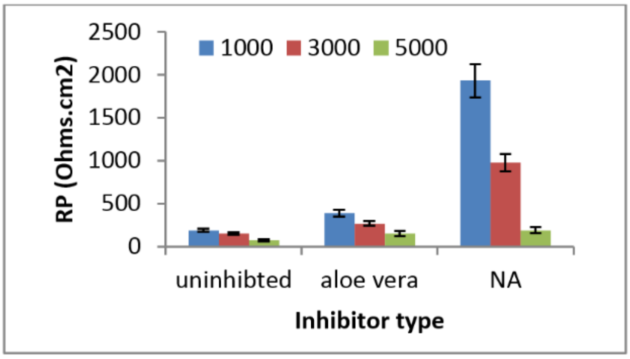
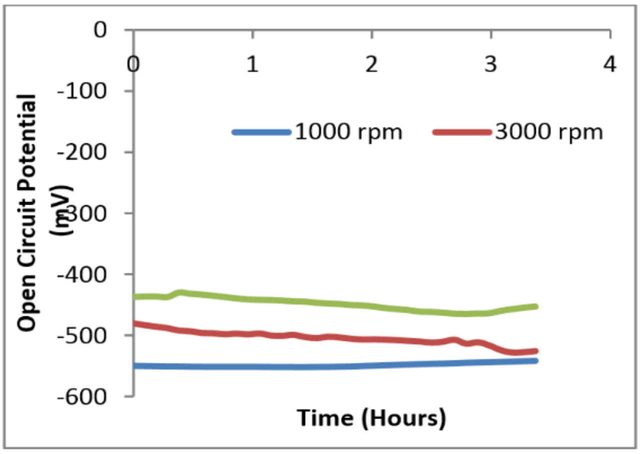
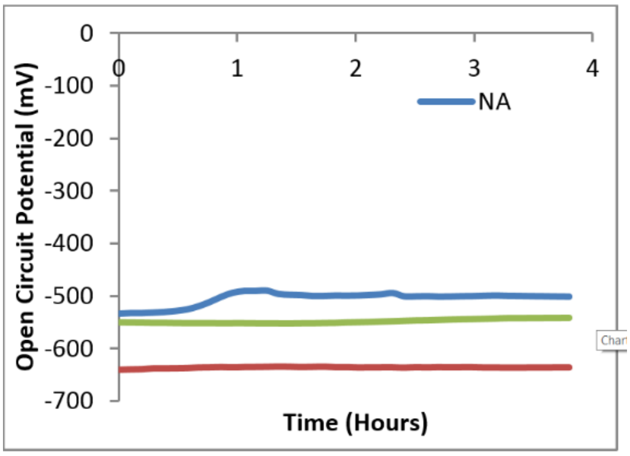


Figure 5: The Rp values from linear polarization at different rotating speeds and 50oC for the various inhibitors

Figure 6 shows the behaviour of the samples with and without inhibitors with respect to the open circuit potential (OCP). The results as presented are representative of a triplicate set of tests. In the uninhibited solution at different velocities, the OCP shifts to the positive direction as the velocity increases (Figure 6a). There is also a large shift towards the positive region as Aloe vera is introduced and a deeper shift is noticed as inhibitor NA is added (Figure 6b). This behaviour is representative of the characteristics of the inhibitors at different velocities.



(a)



(b)

Figure 6: The effect of open circuit potentials (OCP) as a funtion of time at velocity of 1000 rpm (a) Uninhibited (b) 100 ppm

There were significant reductions in the erosion-corrosion rates as *Aloe vera* was added into the system at different velocities (Figure 7). The figure could be interpreted that there is an increase in the rates of degradation as the flow velocity increases for the uninhibited and inhibited solutions. However at each velocity regime there is considerable decrease in the erosion-corrosion rate with the addition of the inhibitors. At a flow velocity of 3000 rpm the erosion-corrosion rate is about 3 mm/yr, and about 0.5 mm/yr for samples inhibited with Aloe vera while it further reduced to about 0.15 mm/yr for inhibitor NA.

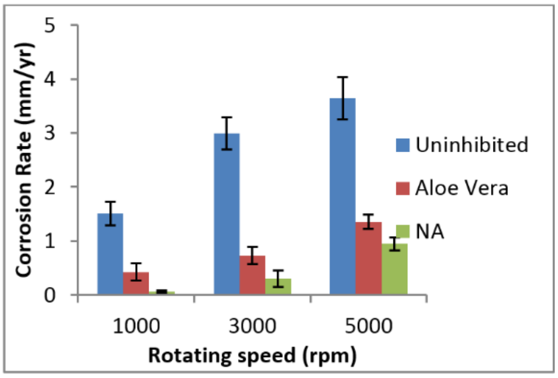
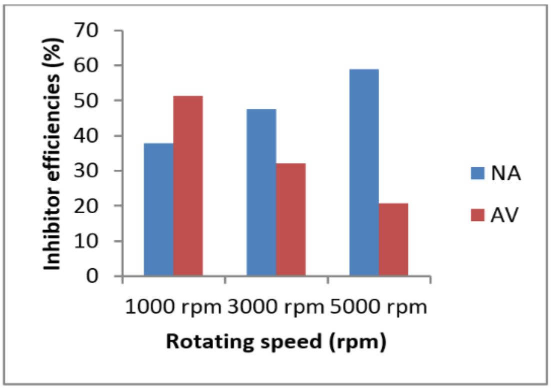


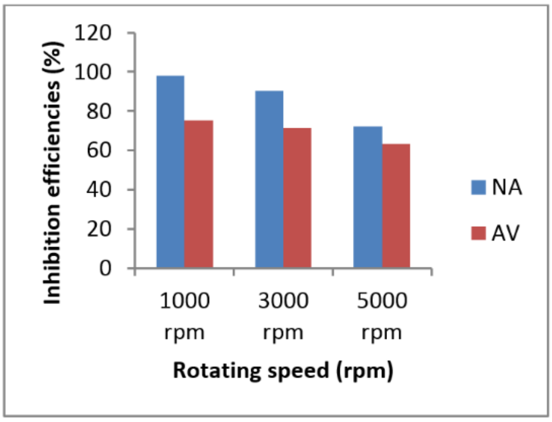
Figure 7: The in-situ corrosion rate of the samples at various rotating speed

3.3. Inhibition Efficiencies (IE%)

The inhibition efficiency is used to assess the performance of inhibitors and it is presented in Figure 8. Typically, the inhibition efficiency for total mass loss for *Aloe vera* decreases as the flow velocity increases. Interestingly the trend is reversed for inhibitor NA (Figure 8a). At lower flow regime the *Aloe vera* may offer better protection than the commercial inhibitor with a margin of about 15%.



(a)



(b)

Figure 8: The inhibition efficiency at various rotating speed as a function of the techniques (a) TML (b) Electrochemistry

However, with increase in the velocity, the reverse occurs with inhibitor NA offering better coverage. Generally, the highest inhibition efficiency for the system is observed at 5000 rpm for inhibitor NA with about 60% while the least efficiency occurs at the same velocity with about 21% efficiency for *Aloe vera*. Figure 8b shows the inhibition efficiency of the inhibitors during in-situ corrosion measurement. Broadly, inhibitor NA exhibited better performance at all velocities and the efficiency decreases as the velocity increases as against the observation that was obtained for the total mass loss. The *Aloe vera* behaves similarly with a relatively lower protection efficiency at 1000 rpm. The maximum coverage occurs at 1000 rpm for inhibitor NA which is around 98% and the lowest is for *Aloe vera* at 5000 rpm with about 60% efficiency.

3.4. Shear Stress Evaluation

The erosion-corrosion rates of the samples as a function of wall shear stress is shown in Figure 9. The shear stress values for RCE were determined according to Silverman and Walsh (1987):

$$\tau_w = 0.0791 Re^{-0.3} \rho r^2 \omega^2 \quad (2)$$

where, Re is the Reynolds Number, ρ is the solution density (g cm^{-3}), ω is the rotation rate (rad/sec), and r is the radius of the outer diameter (cm).

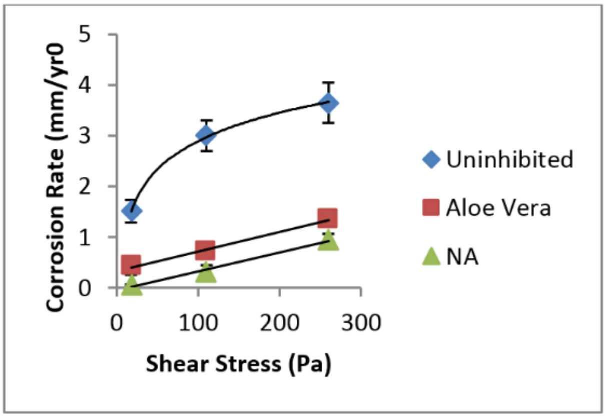
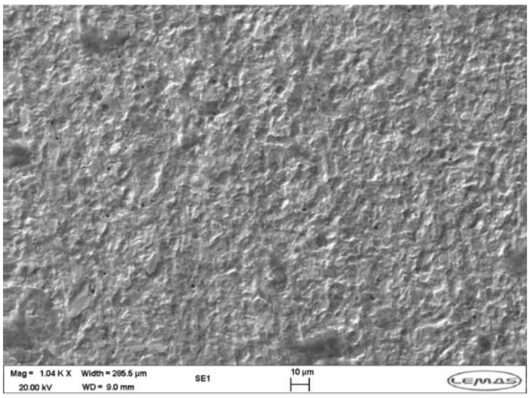


Figure 9: Shear stress vs Corrosion rate

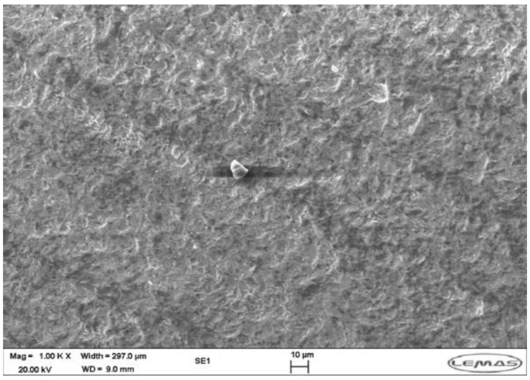
It is observed that the corrosion rates increases as the shear stress increases for both uninhibited and inhibited solutions. The trend of the uninhibited solution displays a logarithmic series while the inhibited solutions show linear relationship.

3.5. Surface Analysis

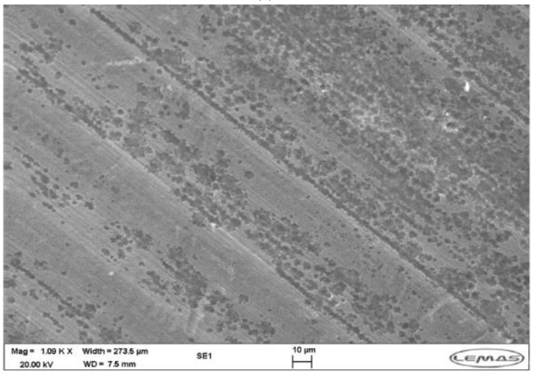
The morphologies of the specimens subjected to 5000 rpm rotating speed were observed by SEM, as shown in Figure 10. This figure illustrates the behaviour of the samples at different velocities and inhibitor concentrations. Figure 10a is for the uninhibited sample which is characterized by material dissolution and scanty localized attacks. Uniform corrosion is dominant and the surface is roughened-like due to minimal plastic deformation coupled with impact trails. Compared with *Aloe vera* inhibited samples (Figure 10b), relatively higher material dissolution is prevalent, while the ferrite is dissolved leaving cementite protrusions. Carbonate films are suspected and confirmed by elemental composition analysis by energy-dispersive x-ray spectroscopy (EDX). The inhibitor NA adsorbs easily on the samples surface and this confirmed the earlier results reported above (Figure 10c). The adsorptions may have led to a uniform microstructure which consists of an unalloyed iron matrix with a homogeneous distribution of fine cementite (carbide).



(a)



(b)



(c)

Figure 10: SEM micrograph of uninhibited and inhibited samples at 50 oC (a) uninhibited sample (b) 75 ppm Aloe vera (c) 75 ppm inhibitor NA

4. DISCUSSION OF RESULTS

4.1. Erosion-corrosion Mass Loss Assessment

From Figure 4 it could be inferred that the material loss increases with increase in the rotating speed (flow velocity). This is in agreement with earlier studies (Jiang *et al.*, 2005 ; Musa *et al.*, 2009). The presence of the inhibitors reduces the degradation tendency at all velocities. Inhibitor NA has the best coverage at all velocities and this can be attributed to the fact that it is a high shear formulated chemical package for CO_2 corrosion.

4.2. Electrochemical Analysis

The polarization resistance (R_p) are relatively stable over time at all velocities and this implies that the corrosion process is charge transfer controlled. The R_p decreases as the flow velocity increases which implies that there is an increase in the corrosion rate due to the increasing rate at which corrosion products are removed from corroded surfaces leading to greater attack on fresh metal surfaces (Figure 5). It has been reported that flow velocity increased the mass transport of electrolytes which may be beneficial in the presence of an inhibitor. However, this may lead to high shear stresses which will result in surface layer removal. This is harmful in the presence of an inhibitor (Jiang *et al*, 2005). The addition of sand may make surface layer removal to be the dominant mechanism because the sand will increase the kinetic energy of the impact on the metal surface. This will lead to an increase material dissolution.

It is observed that the open circuit potential (OCP) moves in the noble direction as the flow velocity increases as shown in Figure 6a. The Pourbaix diagram shows that iron dissolution will be prevalent and the anodic reaction will be the governing mechanism. The presence of inhibitors makes the OCP to move in the positive direction while the inhibitor NA shifts to the noble region, compared to that of *Aloe vera*. This implies that the inhibitors will suppress the anodic dissolution of the unalloyed iron from taking place. The anodic electrochemical reactions for low carbon steel corrosion in CO_2 – containing solution are as follows (Linter *et al.*, 2009):

$$Fe = Fe^{2+} + 2e^- \quad (3)$$

$$Fe + H_2CO_3 = FeCO_3 + 2H^+ + 2e^- \quad (4)$$

$$Fe + HCO_3^- = FeCO_3 + H^+ + 2e^- \quad (5)$$

$$Fe + CO_3^{2-} = FeCO_3 + 2e^- \quad (6)$$

The surface morphology reveals that equation (1) is predominant and may be the one that is suppressed by the inhibitors. The inhibitors being organic are regarded as adsorption or film forming inhibitors on metal surface even at high shear stress multiphase system and in the presence of sand particles (Nesic *et al.*, 1995; Neville and Wang, 2009).

Generally it is understood in CO_2 corrosion mechanism that mass transfer is important primarily at pH less than 5, when it will affect the limiting currents for H^+ reduction (Nesic *et al.*, 1995). The inhibitors are mainly anodic and are expected to block the anodic areas more effectively. Consequently, as coverage increases the ratio between anodic and cathodic areas increases, and so the corrosion rate on the uncovered zones rises. This may leads to unfavourable galvanic effects due to area ratios.

The corrosion rate increasing with shear stress as a power function for uninhibited solution which is according to the work of Effird (1993) while the inhibited solutions have linear relationship and is not in agreement with the earlier study.

4.3. Correlation of Mass Loss and Corrosion Resistance

As shown in Figure 8 the inhibition efficiency of the *Aloe vera* is observed to decrease as the flow velocities increases for both erosion-corrosion mass loss and in-situ corrosion measurements. This confirms earlier studies (Wang *et al.*, 2005; 2009). A significant result is that the inhibitor NA inhibition efficiency increases with flow velocity for erosion-corrosion mass loss which is contrary to what is obtained for in-situ corrosion measurement. It must be realised that this inhibitor is specially formulated for high shear CO_2 environment. It is believed that the inhibitors will be adsorbed and as such it can be deduced that inhibitor NA has good protection for the erosion parts (Wang *et al.*, 2005; 2009). Although it can be inferred that Aloe vera behaves positively in suppressing the corrosion aspect, it did not perform well in reducing the erosion of the samples.

4.4. Surface Analysis

The surface morphology revealed by SEM characterization showed that material dissolution and defects reduced with addition of the inhibitors. A less damaged surface was found in the case of inhibitor NA, which is in good agreement with the erosion-corrosion mass loss and in-situ corrosion results.

5. CONCLUSIONS

The results of this study have shown that increase in flow velocity for the erosion-corrosion samples caused a shift in corrosion potential towards positive directions. The inhibitors are anodic/mixed-type. The results show that inhibitor NA has better coverage for multiphase flow system in oil and gas industry. This study has shown that the chemistry of the inhibitors confer adequate inhibiting properties on the X65 steel in CO_2 environment by reducing damage in erosion-corrosion conditions.

ACKNOWLEDGEMENTS

The supervision and permission to use the facilities of iESTL, School of Mechanical Engineering, University of Leeds, UK by Prof A. Neville and Dr X. Hu are duely recognized. OOI will also like to thank the following organizations for their financial assistance: ETF, NIGERIA; NASENI, NIGERIA; Carnegie Corporation through OAU Linkages, NIGERIA and School of Mechanical Engineering, University of Leeds, UK.

REFERENCES

Chen, H.J., and Chen, Y. 'Environmentally friendly inhibitors for CO_2 corrosion', *CORROSION 2002*, NACE 02300, Houston, Texas, 2002.

Dalayan, E., Johar, T., Shadley, J.R. and Shirazi, S.A. 'Hydrodynamic correlations between pipe flow and rotating cylinder electrode (RCE) for oilfield corrosion – some insights', Houston, NACE International, CORROSION/95, paper no. 117, 1995.

Efird, K.D. Wright, E.J. Boros, J.A. and Hailey, T.G. 'Correlation of steel corrosion in pipe flow with jet impingement and rotating cylinder tests', *Corrosion*, 49 (12): 992-1003, 1993.

Gabe, D.R., and Walsh, F.C. 'The rotating cylinder electrode: A review of development', *Journal of applied electrochemistry*, 13 (1): 3-21, 1983.

Hu, X. Barker, R. Neville A. and Gnanavelu, A. 'Case study on erosion-corrosion degradation of pipework located on an offshore oil and gas facility', *Wear*, 271: 1295-1301, 2011.

Obeyekesere, N.N., Naraghi, A.R. and Zhou, S. 'Further advances of environmentally friendly corrosion inhibitors for CO_2 corrosion in North Sea oil fields' *CORROSION 2002*, Houston, Texas, NACE 02415, 2002.

Janine Killars, and Pat Finley. 'Move to environmentally acceptable products: How the OSPARCOM legislation affects the introduction of new products', *Symposium on oilfield chemistry*, SPE 65044, Houston, Texas, 2001.

Jiang, X. Zheng, Y.G. and Ke, W. 'Effect of flow velocity and entrained sand on inhibitor performances of two inhibitors for CO_2 corrosion of N80 steel in 3% NaCl solution', *Corrosion science*, 47: 2636-2658, 2005.

Linter, B.R. and Burstein, G.T. 'Reactions of pipeline steels in CO_2 solutions', *Corrosion science*, 41: 117-139, 1999.

McLaury, B.S., Shiraz, S.A., Shadley, J.R., and Rybick, E.F. 'Parameters affecting flow accelerated erosion and erosion-corrosion', NACE International, NACE 95120, 1995.

Musa, A.Y. Kadhum, A.H. Mohamad, A.B. Daud, A.R. Takriff, M.S. Kamarudin, S.K. and Muhamad, N. 'Stability of layer forming for corrosion inhibitor on mild steel surface under hydrodynamic conditions', *Int. J. Electrochem. Sci.* 4: 707-716, 2009.

Neville, A. and Wang, C. 'Erosion-corrosion mitigation by corrosion inhibitors – An assessment of mechanisms', *Wear*, 267: 195-203, 2009.

Neville, A. and Wang, C. 'Study of the effect of inhibitor on erosion-corrosion in CO_2-saturated condition with sand', *SPE projects, facilities and construction*, SPE 114081, 1-10, 2009

Nesic, S. Solvi, G.T. and Enerhaug, J. 'Comparison of the rotating cylinder and pipe flow test for flow-sensitive CO_2 corrosion', *Corrosion*, 51(10) : 773-787, 1995.

Obeyesekere, N., Narghi, A., Dharma Abayarathna, Prasad, R., Montgomeric, H. 'Environmentally friendly corrosion for CO_2 corrosion in north sea', Houston, Texas, NACE, *CORROSION 2000*, Paper 00020, 2000.

Ramachandran, S., Ahn, Y.S., Batrip, K.A., Jovancicevic, V., and Basset, J. 'Further advances in the development of erosion corrosion inhibitors', in: *CORROSION/2005*, NACE International, Houston, Texas, NACE 05292, 2005.

Schmitt, G. 'Drag reduction by corrosion inhibitors – A neglected option for mitigation of flow induced localized corrosion', *Materials and Corrosion*, 52 (5): 329-343, 2001.

Silverman, D.C. ' Rotating Cylinder Electrode – Geometry relationships for prediction of velocity – sensitive corrosion', *Corrosion*, Vol 44 (1: 42, 1987.

Taj, S. Papavinasam, S. and Revie, R.W. 'Development of green inhibitors for oil nd gas applications' *CORROSION 2006*, Houston, Texas, NACE 06656, 2006.

Wang, C., Neville, A., Ramachandran, S. and Jovancicevic, V. 'Alleviation of erosion-corrosion damage by liquid-sand impact through use of chemicals', *Wear*, 258, 649-658, 2005.

World Health Organizations. 'Aloe vera gel: in WHO monographs on selected medicinal plants' Volume 1, World Health Organization, Geneva, pp 43-49, 1999.