Characterisation of the anticorrosion and antiscale performances of production chemicals in a multiphase oil-water-gas system

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ABSTRACT

Aim: This study was aimed to characterize the anticorrosion and antiscale performances of production chemicals (corrosion inhibitor and scale inhibitor) used in the crude oil expedition line of an oil and gas facility which typically represents a multiphase oil-water-gas system.

Method and Materials: The residual amine and antiscale concentrations of produced water from crude oil obtained from an oil and gas installation representing a multiphase oil-water-gas system were analysed using a HACH Atomic Absorption Spectrometer (AAS). The corrosion inhibitor used consist primarily of imidazoline while the scale inhibitor is made up of poly phosphocarboxylic acid.

Results: Results of the produced water obtained from the Medium Pressure (MP) Separator showed that the residual amine at corrosion inhibitor concentrations of 15.0 – 20.0 mg/l were within Environmental Guideline and Standards for Petroleum Industries in Nigeria (EGASPIN) specification of 5.0 – 10 mg/l. Results of the produced water obtained from the Low Pressure (LP) Separator shows that the residual antiscale at scale inhibitor concentrations of 10.0 – 15.0 mg/l were within EGASPIN acceptable limit of 5.0 – 10.0 mg/l..

Conclusion: It was concluded that concentrations of the residual amine and antiscale of the produced water obtained from crude oil samples provide useful information on the effectiveness of corrosion inhibitors and scale inhibitors respectively.

Keywords: Scale, carbonate, mud, sludge, sand.

Introduction

The formation of various forms of scales as well as corrosion are processed of great concern in oil and gas industry. Oil and gas production involve transportation of large quantities of hydrocarbon fluids, water, carbon dioxide, hydrogen sulphide, which can trigger scaling and corrosion tendencies simultaneously (Touir et al., 2009). Scale formation and corrosion impact on oil and gas facilities through blockage of production equipment, destruction and collapse of metallic surfaces leading to hydrocarbon leakages as well as loss of capacity for temperature conservation and exchange. Scales are sparingly soluble inorganic materials formed in different locations of oil and gas installations with capacity to decrease the diameter of expedition lines resulting in subsequent choking of the production from reservoir (Martinod et al., 2008).

The disturbance of the solution equilibrium of water by pressure and temperature changes, dissolved gases or/and incompatibility between mixing waters results in scale formation. The scales frequently encountered in the oil and gas industry includes sulphates of (barium, strontium, calcium), hydroxides/oxides of (iron, magnesium), carbonates of (calcium, magnesium, iron) and sulphides of iron (Sun et al., 2009).

Corrosion is the deterioration and loss of a material and its critical properties due to chemical, electrochemical and other reactions of the exposed material surface with the surrounding environment. The different types of corrosion experienced in the oil and gas industry includes sweet corrosion, sour corrosion, crevice corrosion, erosion corrosion and microbiologically induced corrosion. Sweet corrosion occurs when CO_2 dissolves in water to form carbonic acid thereby creating an electrochemical reaction between the metal and the acidic contacting aqueous phase which is seen as corrosion in real life (Mohamed

and Oyekola, 2020; Lehtola et al., 2001). Sweet corrosion is affected by temperature, pH, aqueous stream composition, fluid flow rate, presence of non-aqueous phases and metal properties, it is the most common form of corrosion experienced in oil and gas installations. Sour corrosion is caused by the reaction between hydrogen sulphide (H_2S) and moisture resulting in the formation of weak acids, iron sulphides and hydrogen ions which are corrosion products. Crevice corrosion is a localized corrosion caused by concentration differences of corrosion products over a metal surface along the narrow crevices in the metal and the stagnated fluid. This type of corrosion is promoted by dissolved oxygen in production fluids (Popoola et al., 2013). Erosion corrosion occurs where there is a high turbulence flow regime and it is affected by density and morphology of solids present in fluid, it is often overlooked or attributed to wear. Microbiologically induced corrosion is basically caused by bacterial activities. Waste products from bacteria such as CO_2, H_2S and organic acids corrode pipes by increasing the toxicity of the flowing fluid in the pipeline (Ren et al., 2005). Scale and corrosion can be prevented, reduced or delayed with the use of specific concentrations of scale and corrosion inhibitors. Scale inhibitors or antiscalants can be classified as organic or inorganic compounds (Jordan et al., 2003). The inorganic scale inhibitors include condensed phosphate such as poly metaphosphates or phosphate salts while the organic scale inhibitors include poly acrylic acid, poly phosphinocarboxylic acid, sulfonated polymers and phosphonates (Martinod et al., 2008). Phosphonates are effective at high temperatures while sulfonated polymers are more effective at low temperatures. The molecular structure of poly phosphinocarboxylic is shown in figure 1. The exact mechanism of scale inhibitors are not completely understood however scale inhibitors possess large molecules that can adsorb unto the scale crystal surface just as they start to form and then envelop the microcrystals thereby hindering further growth (Ketrane et al., 2009).

A corrosion inhibitor is a chemical compound that decreases the corrosion rate of a material typically a metal or an alloy. The chemical interrupts the chemical reaction causing corrosion by interacting with the metal surface or the environmental gases causing erosion (Kamal and Sethuraman, 2012). Corrosion inhibitors used in oil and gas production contains organic amines such as imidazoline compound as shown in figure 2. Compounds such as thiourea, alkynes and inorganic salts can also serve as corrosion inhibitors (Nesic, 2007). Scale inhibitor and corrosion inhibitor are production chemicals used in oil field operations to prevent scale and corrosion activities. Sweet corrosion and scale formation are both highly dependent on gas composition and water chemistry, while scales are basically formed in the aqueous phase, corrosion can be formed in both aqueous and gaseous phases (Touir et al., 2009). The selection of the appropriate concentration of scale and corrosion inhibitors suitable for specific oil and gas installation is highly dependent on the values of the key performance indicators of each process. The anticorrosion performance of corrosion inhibitor in gas expedition lines (gaseous phase) is determined by the corrosion rates of the produced water from the gas using a bubble test experiment while the anticorrosion and antiscale performances of corrosion inhibitor and scale inhibitor in a multiphase oil-water-gas system (aqueous phase) can be obtained by determining the residual amine and residual antiscale concentrations of the produced water respectively (Jordan et al., 2003). The aim of this study is to characterize the anticorrosion and antiscale performances of production chemicals (corrosion inhibitor and scale inhibitor) used in the crude oil expedition line of an oil and gas facility which typically represents a multiphase oil-water-gas system. Results obtained from this study will not only unveil the anticorrosion and antiscale performances of the production chemicals but will also give an insight on the degree of corrosion and scales prevalent in the installation which is also critical for chemical optimization.

Materials and Methods
A 1-liter volume of produced water sample was obtained from the water outlet of the medium pressure (MP) separator and low pressure (LP) separator respectively with a thoroughly clean glass bottle free from oil and other impurities. Sampling bottles were cleaned with alcohol and dried properly. The crude oil well which represents a multiphase oil/water and gas system is the source of the produced water obtained from these sampling points. The sampling point was adequately flushed for about 10 minutes before

obtaining samples. Sampling points were at a reasonable distance away from the corrosion inhibitor and scale inhibitor injection points to prevent interferences of high chemical concentration with the results obtained from analyses. Produced water samples from the MP separator were analysed at various concentrations of corrosion inhibitor injected into the MP manofold to determine the residual amine concentrations respectively while that from the LP separator were analysed at various scale inhibitor concentrations injected into the LP manifold to determine the residual antiscale concentrations respectively. The pH at various chemical concentrations were determined using a well calibrated pH meter. Samples were totally free from crude oil and analyses were carried out not more than 24 hours after sampling.

Residual Amine Analyses of Produced Water from Crude Oil

Produced water obtained from the sampling point was poured into a separating funnel to isolate any oil interferences. A 100 ml of the produced water sample obtained from the separating funnel was acidified with 2 drops of dilute hydrochloric acid (HCl), 4 ml of residual amine buffer and 2 ml of methyl orange indicator and shaken vigorously. The mixture was extracted with 100 ml Trichloroethylene to obtain the organic extract and the water layer drained into another separating funnel. A 50 ml dilute HCl and 2-3 drops methyl orange were added to the drained water layer and shaken vigorously to completely extract any remaining organic layer. The water layer contained in a cuvette was inserted in the HACH Atomic Absorption Spectrometer (AAS) to zero the equipment. A 10 ml of the organic layer contained in a cuvette was then inserted into the same equipment to obtain the residual amine (Hilfiker et al., 2008)

Residual Antiscale Analyses of Produced Water from Crude Oil

A 25 ml of the produced water sample after adequate separation in a separating funnel was introduced into a 25 ml cuvette of a HACH Atomic Absorption Spectrometer (AAS). A sachet of potassium permanganate (KMnO4) powder pillow was introduced into the cuvette and shaken until a homogenous solution was obtained. The Ultraviolet (UV) lamp was plugged to the power source and inserted into the solution. The set up was covered to achieve a dark room and allowed

to react for 15 minutes, then the set up was uncovered and the power source of the UV lamp put off. Two sachets of phosver-3-phosphate powder pillows were then added to the solution, shaken to achieve a homogenous solution, and allowed to react for 3 minutes. The solution was inserted into a HACH AAS spectrometer to obtain the residual antiscale of the sample. The HACH AAS Spectrometer was zeroed with produced water free from powder pillows obtained from the same sampling point before analyzing the residual antiscale of the sample (ASTM D4628, 2004).
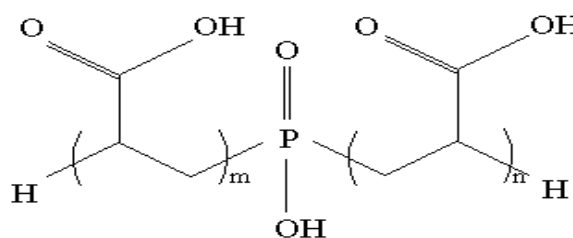
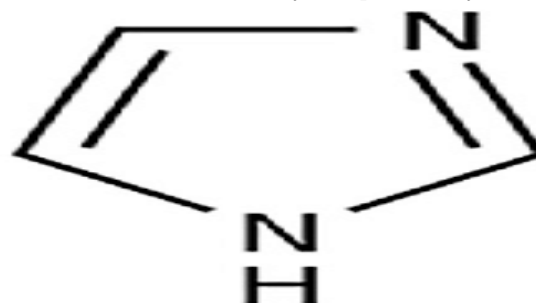

Fig 1: Molecular Structure of Poly Phosphocarboxylic acid

Fig 2: Chemical Structure of Imidazoline (Corrosion Inhibitor)

Results and Discussion

Residual amine of produced water from water outlet of MP separator (Table 1), residual antiscale of produced water from water outlet of LP separator (Table 2), plot of residual amine against corrosion inhibitor concentration (Fig 3) and plot of residual anti scale against scale inhibitor concentration (Fig 4) were recorded .

Produced water from crude oil is one of primary sources of corrosion in oil and gas installations. The residual amine and residual antiscale concentrations obtained from produced water in crude samples are key performance indicators that helps in ascertaining the degree of corrosion and scale formation in the petroleum industry, they are also required in ascertaining the optimal concentration of corrosion inhibitors and scale inhibitors suitable within a multiphase oil-water-gas system.

Table 1: residual amine of produced water from water outlet of MP separator

Corrosion Inhibitor Concentration (mg/l)	Residual Amine (mg/l)	pH
5.00	0.80	6.50
10.00	3.20	7.00
15.00	6.50	8.50
20.00	9.80	9.40
25.00	12.60	10.50

Table 2: Residual antiscale of produced water from water outlet of LP separator

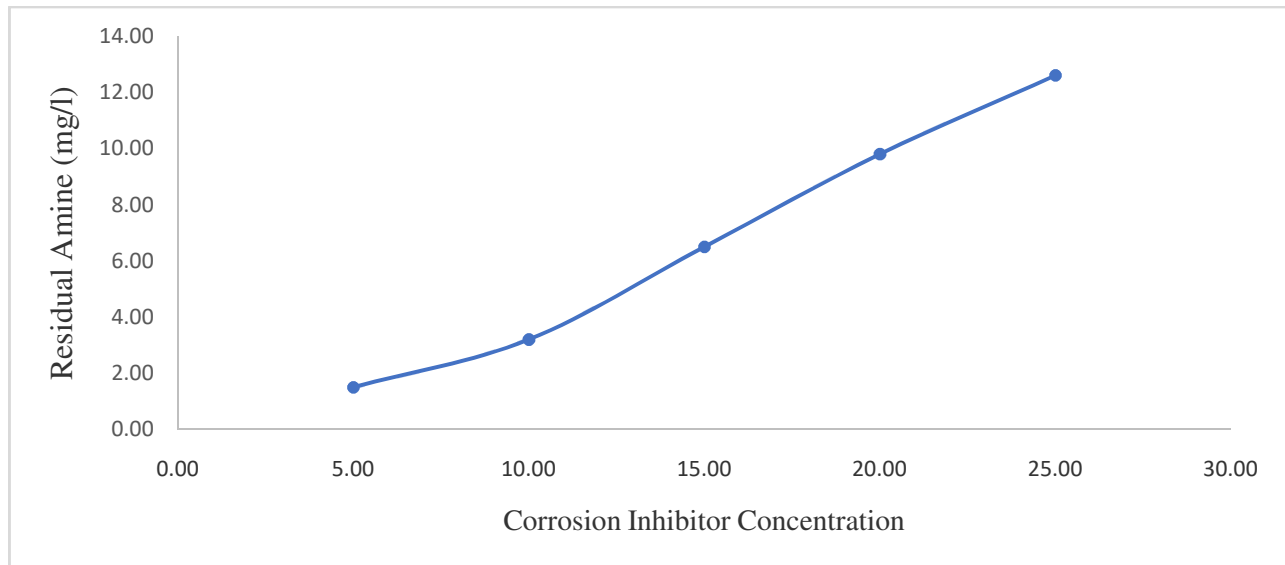| Scale Inhibitor Concentration (mg/l)	Residual Antiscale (mg/l)	pH
5.00	2.60	5.50
10.00	6.80	4.80
15.00	10.60	4.20
20.00	14.80	3.60
25.00	18.50	2.80

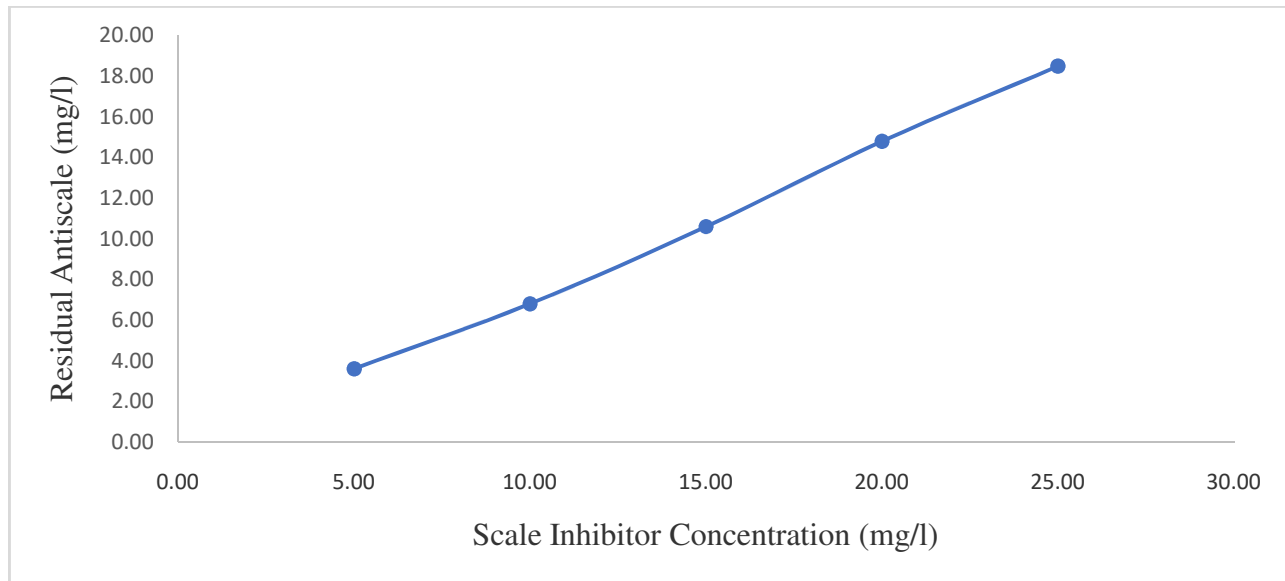Fig 3: Plot of Residual Amine against Corrosion inhibitor Concentration

Fig 4: Plot of residual anti scale against scale inhibitor concentration

Residual amine determination is required during corrosion inhibitor treatment while residual antiscale determination is required in scale inhibitor treatment (Touir et al., 2009). Corrosion inhibitor made up of primarily imidazoline compound was injected at various concentrations at the manifold of the MP Separator of an oil and gas installation while Scale inhibitor made up of primarily Poly phosphocarboxylic acid was injected at the LP manifold of the LP separator. The choice of different injection points within the installation is due to several factors for instance the MP separator is closer to the oil well than the LP separator and so has a longer distance with respect to the water network within the process as such more residence time for the corrosion inhibitor to function as opposed to the scale inhibitors which do not require as much residence time. Also, better separation is achieved at the LP separator which supports better scale formation hence the injection of the scale inhibitor at the LP manifold (Jordan et al., 2003; Sun et al., 2009). Results obtained from the residual amine determination were shown (Table 1). Amines provide appropriate protection against acidic corrosion caused by dissolved CO_2 which is prevalent in the petroleum industry however the concentration of residual amines within an oil and gas facility must be controlled within an acceptable range of 5.0 to 10.0 mg/l as stipulated by Environmental Guidelines and Standards for Petroleum Industries in Nigeria (EGASPIN). Residual amine concentration above the acceptable range will cause system deterioration and environmental hazard to the facility and the ecosystem (Mohamed and Oyetola, 2020). It was showed that the residual amine concentrations were below acceptable limits at corrosion inhibitor concentrations of ≤ 10.0 mg/l and was < 1.0 mg/l at a chemical concentration of 5.0 mg/l. Residual amines at chemical concentrations of 15-20 mg/l were within acceptable limits while values obtained at chemical concentration of > 20 mg/l were above acceptable limit. Table 2 shows that the residual antiscale concentration of the produced water obtained at the water outlet of the LP Separator were within acceptable limit of 5.0 to 10.0 mg/l based on EGASPIN specification at chemical (scale inhibitor) concentrations of 10.0 to 15.0 mg/l. Results obtained from Table 2 shows that chemical concentrations of 5.0 and 25.0 mg/l gave residual antiscale concentrations in the

produced water that were below and above acceptable limits respectively. Produced water with residual amines and antiscale concentrations below specification (< 5.0 mg/l) indicates that the water does not possess sustainable protection against corrosion and scale formation respectively and may require increased dosage. On the other hand, when these parameters (residual amine and antiscale) are above specification (> 10.0 mg/l), they indicate an over injection of the treatment chemicals which is not environmentally friendly and cost effective. Produced water with zero values for residual amine and antiscale indicates no protection at all which could be due to no chemical injection or extreme under injection unable to overcome the corrosive ions and scales prevalent within the process (EGASPIN, 2022). The most common ions responsible for corrosion in the petroleum industry (oil-wate-gas system) are the bicarbonate ions (HCO_3^-) produced from carbonic acid (H_2CO_3), while scales in oil and gas installations are primarily formed from magnesium and barium salts of carbonates and sulphates respectively (Touir, et al., 2009). Another factor that favors the optimal performance of corrosion inhibitor and scale inhibitor is the pH of the medium of operation. Corrosion inhibitors perform optimally with very good anticorrosion abilities at pH of 6.5 to 8.5. The performance of corrosion inhibitors reduces in acidic media (Goh et al., 2008). Results obtained from Table 1 shows that the higher the chemical concentration injected into the process the higher the pH of produced water from the crude. Results also show that the corrosion inhibitor will perform optimally at concentrations of ≤ 15.0 mg/l. The corrosion inhibition abilities of corrosion inhibitors at pH > 8.5 depends on other prevailing factors such as temperature, pressure, concentration of dissolved gases as well as the impact of the chemical composition of the corrosion inhibitor on these factors The influence of other factors on the anticorrosion abilities of the corrosion inhibitor are overridden when the chemical is injected in a strongly acidic medium (Churchill et al., 2000). From Table 2 it can be deduced that the higher the concentration of the scale inhibitor (poly phosphocarboxylic acid) the lower the pH of the produced water from the crude. Scale inhibitors function optimally at pH of 4.5 to 5.5. Strongly acidic medium < 4.5 will increase the corrosion tendencies of the water while higher pH values > 5.5 will reduce the antiscale efficiency of the

chemical in preventing and treating sulpnate and carbonate scales of barium and calcium ions. Results obtained (Table 2) showed that the scale inhibitor will be most effective at concentrations of 10 to 15 mg/l with respect to the pH of the medium (Ketrane et al., 2009). It was showed a plot of residual amine against the corrosion inhibitor concentration (Fig 3) while a plot of residual antiscale against the scale inhibitor concentration (Fig 4). Both plots a not too perfect straight-line graph which indicates a non-uniform variance between the parameters involved.

Conclusion

The concentrations of the residual amine and antiscale of the produced water obtained from crude oil samples provide useful information on the effectiveness of corrosion inhibitors and scale inhibitors respectively. The residual amine in produced water verifies the appropriate concentration of corrosion inhibitor suitable in the treatment of sweet corrosion arising from dissolved CO_2 in water while the residual antiscale validates the adequate concentration of scale inhibitor required in the treatment of sulphate and carbonate scales of barium and calcium ions respectively. Adequate knowledge of the residual amine and antiscale during corrosion and scale inhibitor treatment is critical in the preservation of the installation, environment, ecosystem as well as important in cost optimization. An in-depth knowledge of the pH of the medium is necessary as a guide because of the impact the chemicals have on the pH of the reference fluid (produced water) and the fact that the chemicals perform optimally at specific pH ranges.

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