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INVESTIGATION OF THE PROCESS PARAMETERS IMPLICATED FOR BIOCORROSION CONTROL IN OIL INDUSTRIES.

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ABSTRACT

Interaction with the corrosion products to prevent natural film forming characteristics on the corroding metals that would inhibit further corrosion was studied. Four treatments were used for the study to compare the biofilm clusters on steel coupons treated with the chemicals presently used by the petroleum industries to control corrosion. Process parameters considered were weight loss of the respective steel coupons treated and the bacterial growth on the corroding substrate The treatment used for this study are formaldehyde, polyamine, diamine and biguanide. Steel coupons used for the experiment is rectangular AMS mild steel coupons with dimension of 1.27cm x 7.62cm x 0.16cm and weighs 49.60g. The coupons were placed in the experimental pipes. The coupons were degreased with ethanol and rinsed with acetone before insertion. The pipes were run in a circulation mode for one day (1 day) under anaerobic condition and then inoculated. MATLAB computational software was used for the determining the rate of metal removal using the conventional weight loss equation. Results revealed that the weight loss in the coupon treated with biagunides is 0.9g during the period under study which can be assumed negligible compared to the losses in encountered in other coupons subjected to the rest of the treatment with trendline equation of $y = -3exp\text{-}13x^5 + 6exp\text{-}13x^4 - 3exp\text{-}07x^3 + 7exp\text{-}05x^2 + 0.004x + 0.122$*. Equations generated for the bacteria activities was observed to have polynomial functions in all the chemicals used for the control though of various degrees.*

Keywords: Biocorossion, Crude oil, Transmission pipes, Control mechanism , Industries

INTRODUCTION

In the petroleum sector, chemical inhibitors are extensively used to prevent corrosion in production fluids. This method for downhole corrosion control is however constrained by the dependability of chemical injection valves and mandrels. However, protecting topside machinery and these transmission lines is feasible using inhibitors. Several factors such as capital cost, environmental implications and efficacy of the inhibitors must be taken into account when selecting whether to utilize corrosion resistance alloys or carbon steel with corrosion inhibitors (Al-Abbas et al,2011).

The hardware for control, injection, and distribution, corrosion monitoring systems, storage weight, and space are all included in the capital expenditures. Chemicals, maintenance, monitoring, labor, additional selection programs, and technical support are all included in the running costs. Seawater corrosion is prevented with cathodic protection. To get the required performance from coating, the surface must be properly prepared. In regions where the coating has been damaged, cathodic protection is also utilized with coating to offer further protection (Kent,2004). According to research, between 20 and 30 percent of corrosion deposits are caused by microorganisms. The operations of petroleum pipelines are impacted by these creatures' actions in terms of reliability, safety, and integrity. The organism causes issues in every operation steps from production lines to transmission pipes, refineries, storage facilities, and even the fuel tanks and fuel filters of end-user vehicles. This organism that causes pipeline corrosion slows down production, lowers product quality, creates health risks in contaminated areas through leakage, and adds significantly to the cost of operating the oil industry (Chung et al, 2000).

Bacterial biofilms are intricate colonies of bacteria adhering to surfaces and kept together by self-made polymer matrices mostly made of polysaccharides, secreted proteins, and extracellular DNAs. Surface characteristics that have a significant impact on bacterial attachment and biofilm growth include surface roughness, oxide coating, chemical composition, and polarizations. The pipe's

surface abnormalities during manufacture may be responsible for the original surface roughness. There has been debate over the impact of surface roughness on the bacterial attachment process. Some publications claimed that surfaces with higher levels of roughness result in more bacterial colonization and adherence, while others claimed that the converse is true. (Korber et al, 1997).
Microorganism attachment is negatively impacted by surface coverings like oxides and corrosion products, and one of the research topics for bacteria adhesion is how they affect metal oxides. During the corrosion process, several oxides, such as Fe_2O_3 and Cr_2O_3, can form on a surface. The majority of these oxides are well known for being interested in bacterial adhesion and offering secure attachment sites. The positively charged surface that the metal oxides create can greatly enhance the amount of bacteria that are deposited on the surface (Li and Began, 2004).
Numerous bacteria that fall within the general categories of aerobic and anaerobic bacteria have been linked to the corrosion of oil transmission pipes. While anaerobic bacteria do not require oxygen to survive, aerobic bacteria can only exist in the presence of oxygen. Although facultative bacteria can thrive in anaerobic environments, they prefer aerobic environments. Sulphate reducing bacteria (SRB) and metal-reducing bacteria are anaerobic bacteria involved in the corrosive process brought on by microorganisms, whereas metal-oxidizing bacteria and facultative aerobes are aerobic bacteria. They affect both the pipeline's internal and external surfaces.
Globally significant research is continuously conducted in an effort to create new and more potent inhibitors for microbial contamination on oil pipelines. For instance, Western Europe spends more than 500 million dollars on this every year. (Neale,2003).
The oil and gas sectors currently use the traditional methods to prevent bacterial growth from spreading across their facilities. To counteract microbial contamination, this study uses both organic and inorganic compounds such as formaldehyde, diamine, polyamine, biguanides and benzyl trimethyl ammonium chlorides.
As a result of numerous treatments administered by the petroleum industries to combat corrosion effectively and efficiently, this research is centered on the determination of the most effective treatment by considering the resistance offered by the bacteria to the various treatments in terms of bacteria growth and the rate of metal loss of the steel pipelines. Plots obtained using the surface response analysis will help to create a detailed insight of the interaction between the process parameters and generate mathematical model that accurately predict the variables in the corrosion medium.

1.1 CORROSION RATE

The degree at which a portion of a metal is removed from its parent material in a particular environment is known as the corrosion rate. It can also be described as the rate of thickness loss due to corrosion over a given period of time usually in a year. The type and state of the metal in question, as well as the environmental factors, all affect how quickly it deteriorates. To determine the corrosion rate of any given metal, a variety of data must be gathered. These include the decrease in weight of the metal during the period, metal densities, original total area of the surface and the length of time it took for the corrosion process.
The corrosion rate or the rate of metal removal as a consequence of chemical action is an important corrosion parameter. It is expressed as the corrosion rate (CR) or the thickness loss of material per unit of time.

$$CR = \frac{K(\Delta W)}{AT\rho} \quad (1)$$

Where:
W is the weight loss in grams (g)
T is the exposure time in hours (hrs)
ρ is the density of the steel coupon(g/cm^3)=7.86 g/cm^3
A is the exposed surface area of coupon in (cm^2)
K= constant for unit conversion = 8.76×10^4 = 87,600

For the purpose of this study, the constant of penetration used is expressedin millimeter per year (mm/yr)

If the rate expressed by the aforementioned function is used to compare corrosion rates calculated over short periods of time with rates calculated over longer periods, the rate expressed by the function may differ. This is because of the short time periods' susceptibility to varying environmental changes from season to season as well as day to day.

With this technique, a weighed test metal or alloy is exposed to a certain environment for a predetermined period of time. Once the corrosion products have been thoroughly removed, the weight of the metal that has been lost to corrosion is then calculated.

MATERIALS AND METHODS

- Material Sourcing

  Samples of oil and water mixture, corrosion products were collected from buried oil pipeline during maintenance known as Nembe-Brass trunkline in Bayelsa State. Samples were collected in 1000ml sterilized anaerobic serum bottles and were taken to Model Laboratory and Research Center, Agbor for further analysis. Four chemicals chosen for this study are Formaldehyde, Diamines, Polyamines and Biguanides which are currently being used by the petroleum industries.

Methodology

An extracting solution for enzymes was placed in a vial with the sample. A clean vial was placed in an anaerobic chamber with the solution after 15 minutes of contact. After turning on a gas generator, the hydrogen produced reacted with the oxygen in the chamber to eliminate it. The excess hydrogen is then oxidized by the enzyme, which also simultaneously decreases the indicator dye in the solution. The other experiment was the bacteria culture test using prepared agar medium as properly outlined in the work of Iweriolor and Ugochukwu,(2014). The Chemicals were injected in the four anaerobic pipes ranging from 5mg/l to 580mg/l at weekly intervals for thirteen months. The test coupons were washed, dried and weighed before putting it back for another concentration. The bacteria growth was determined by the viable count CFU methods, each sample was diluted with a phosphate buffer and counted with a dilution factor of 1:1000 and the number of colonies.

RESULTS AND DISCUSSION

Bacteria Growth Result

After 3 hours contact of the solution in the, the development of a blue colour was noticed anaerobic chamber in the presence of activated gas generator. The intensity of the color is proportional to the rate of hydrogen uptake which confirmed the activities of hydrogenase by the micro-organism.

Table 1: Bacteria Growth

Week	Concentration (mg/l)	Formaldehyde	Polyamine	Diamine	Biaguanide
1st	5	10^6	10^5	10^6	10^2
2nd	30	10^5	10^5	10^5	10^2
3rd	80	10^4	10^5	10^5	10^2
4th	130	10^4	10^3	10^5	10^2
5th	180	10^4	10^3	10^4	10^2
6th	230	10^3	10^3	10^4	10^2

7th	280	10^3	10^3	10^4	-
8th	330	10^3	10^3	10^3	-
9th	380	10^2	10^3	10^3	-
10th	430	10^2	10^2	10^3	-
11th	480	10^2	10^2	10^3	-
12th	530	10^2	10^2	10^2	-
13th	580	10^2	10^2	10^2	-

It can be observed generally from Table 1 that the bacteria growth reduces as the concentration and experimental time increases. On a specific note, biaguanide show no bacteria growth above the 6th week and concentration of 230mg/l. The result above shows the effectiveness of biguanides in curbing bacteria growth even at a very low concentration. Comparatively, it can be seen that the chemicals at their respective capabilities can inhibit the proliferation of the bacteria which is likely to cause an enhanced environment that favors their growth.

Corrosion Rate of the Biocides

Using the equation 1.1, the corrosion rate of each coupons used had a cuboids geometric shape and are of equal size, hence the exposed surface area (A) of each of them is given thus:

A = 2(LB+LW+BW) = 2(7.62 x 0.16) + (7.62 x 1.27) + (0.16 x 1.27) (1.2)

A = 22.2cm^2

Where:

L is length of the coupon

B is the breadth of the coupon

W is the width of the coupon

Similarly, ρ = 7.86g/cm^2 since it is a mild steel.

A sample of calculation of the corrosion rate of the first coupon exposed to formaldehyde for the first week which has 168 hours is as follows:

$$CR = \frac{K(\Delta W)}{AT\rho} = \frac{87600x0.02}{22.2x168x7.86} = 0.0598 \text{ mm/year}$$

The results of the corrosion rate for the entire 13 weeks of the experimental duration for the various biocides are tabulated in Table 2. On the average, the corrosion penetration rate was less in the sample treated with biguanides. This has once again proved that amongst all the chemical used for this study, biaguanide is the most efficient in inhibiting corrosion penetration rate (0.2226mm/year) as against formadehyde (1.5171mm/year), polyamine(1.3332) and diamine(1.5654mm/year).

Table 2: Corrosion Rate

week	Concentration(mg/l)	Formaldehyde	Polyamine	Diamine	Biguanide

1st	5	0.0598	1.1953	0.2988	0.0896
2nd	30	1.3149	1.3447	0.7471	0.0598
3rd	80	2.8588	2.6895	0.8965	0.0996
4th	130	2.6521	2.1665	2.8389	0.0896
5th	180	2.1516	2.1516	2.2711	0.4184
6th	230	1.7930	1.8926	1.8976	0.3686
7th	280	1.6222	1.8357	2.7322	0.3159
8th	330	1.4232	2.a0171	2.3906	0.2764
9th	380	1.2684	1.8461	2.2246	0.2490
10th	430	1.9125	1.6705	2.0022	0.2241
11th	480	1.7386	1.5756	1.8473	0.2173
12th	530	1.6187	1.4443	1.6959	0.2092
13th	580	1.5171	1.3332	1.5654	0.2758
	Average	1.6870	1.7818	1.8006	0.2226

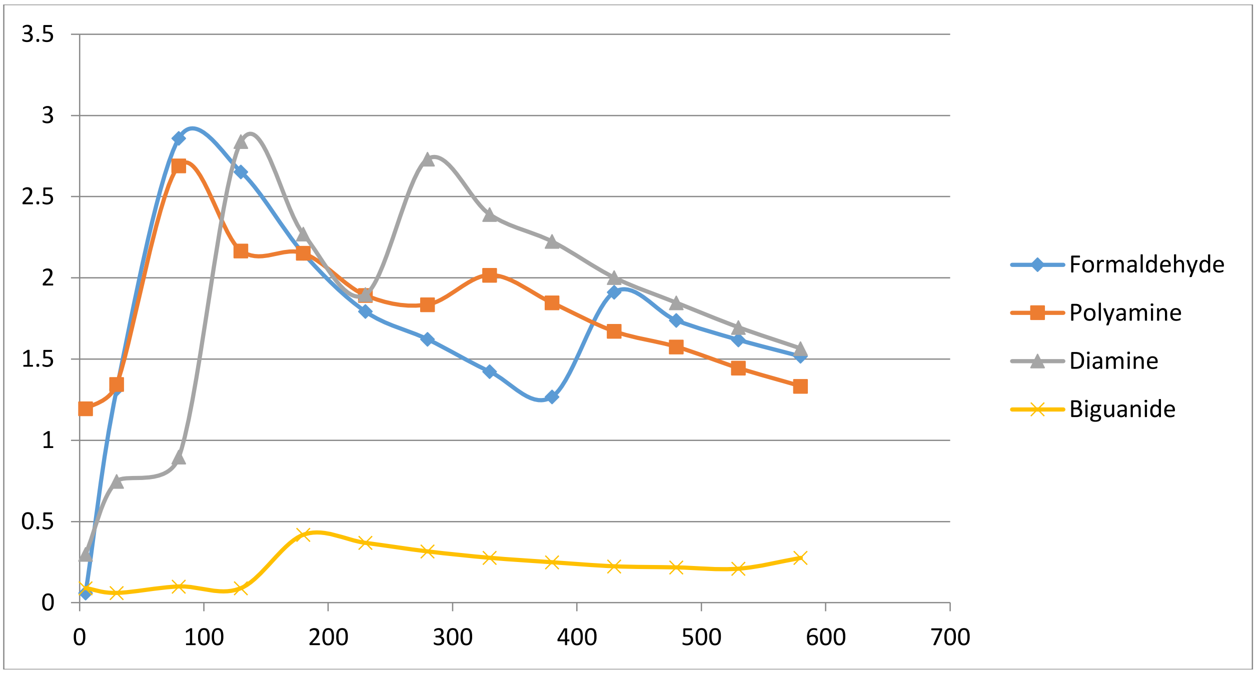

Fig. 1: corrosion rate against Concentration

Fig 1 showed the graphical representation of the rate of corrosion penetration , it was observed that as concentration of the chemicals used increases, there is a resulting decreases in corrosion rate on the metals even if it is not proportional.

Comparatively, one can conclude that the coupons treated with biguanides experiences little or no corrosion based on figure 1.

Table 3: Corrosion Rates Model Equations and Coefficient of Determination

Chemicals	Model equations	R^2
Biguanide	$-3exp{-13}x^5+6exp{-13}x^4 -3exp{-07}x^3+7exp{-05}x^2+0.004x+0.122$	0.809
Diamine	$-2exp{-0.5}x^2+0.012x+ 0.401$	0.718
Polyamine	$1exp{-12}x^5-2exp{-09}x^4+1exp{-06}x^3-0.000x^2+0.0038x+0.842$	0.814
Formaldehyde	$-7exp{-10}x^4+9exp{-07}x^3-0.0003x^2+0.057x-0.090$	0.912

Table 3 depicts the mathematical models generated which accurately predict the relationship between the variables in the process. For all the chemicals used for this study, the R^2 values are closer to unity. Biguanides is at 80%, Diamine is 71.8%, polyamine is 81.4% and lastly formaldehyde at a very high value of 91%. The implications is that The R^2 values for each of the chemicals indicates that a good measure that future outcomes are likely to be predicted well by the developed models.

CONCLUSION

This study has no doubt brought to limelight the activities and implications of bacteria in the deterioration of oil facilities and as such calls for a synergy between engineers and microbiologist for the purpose of combating this bactericidal activities.

From the study, it was seen that biguanide is the most efficient chemical to be used in comparison with other chemicals used in the course of this study for the control of microbial contamination. The concentration of biguanide required to terminate bacteria growth is as low as 280mg/l while bacteria growth was observed for other chemicals even with a concentration of 580mg/l.

The antimicrobial properties of other chemicals used were evident in the study but it's obvious that of biagunides is far higher in inhibiting the bacteria growth thereby preventing the corrosion of the steel coupons.

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