ABUAD Journal of Engineering Research and Development (AJERD)
ISSN (online): 2645-2685; ISSN (print): 2756-6811

Volume 8, Issue 1,113-121

Corrosion Mitigation with Chemical Injection in Welded Carbon Steel Pipe for Offshore Water Treatment Plant

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Date Submitted: 19/06/2024
Date Accepted: 06/02/2025
Date Published: 08/02/2025

Abstract: *In Floating, Production, Storage, and Offloading (FPSO) vessels, the steel pipes used for water treatment plants are susceptible to corrosion from dissolved oxygen and bacteria in seawater. Chemicals such as oxygen scavengers and biocides are used to combat this. However, using oxygen scavengers can lead to bacterial growth, which can cause a reduction in pipe diameter, increased water pressure, and potential leaks, particularly in the welded sections. Biocides are used to address bacterial growth. In this study, steel coupons were welded with a low-hydrogen electrode, and water from the Lagos lagoon was used to replicate seawater composition. The study employed two different media, agitated and non-agitated, to investigate the effect of water flow dynamics on corrosion rate. Chemical injections did not effectively mitigate corrosion in the tested conditions but sometimes increased it. The results revealed that general corrosion was observed in the samples when no chemical was injected into the system, with an average 0 mm/yr corrosion rate. The agitation of the media led to increased corrosion rates. For biocide injection, the rate increased from 1 mm/y to 2 mm/yr, while in oxygen scavenger solution, the rate increased from an average of 4 mm/yr to 8 mm/yr. Analysis of the cultured seawater parameters showed variations in salinity, total dissolved solids, oxidation-reduction potential, pH, temperature, specific gravity, and conductivity across different media. The pH of the solution generally increased with time, while the addition of an oxygen scavenger reduced the pH value from approx. 6.5 to 6.2. Agitation of the media and chemical injection increased the conductivity of the solution. Biocide introduction lowered the redox potential, while oxygen scavenger made the redox potential unstable. X-ray diffraction analysis of the steel surface exposed to the seawater indicated the presence of various compounds, suggesting ongoing corrosion processes and the existence of organic and inorganic contaminants. This research has the potential to significantly impact offshore water treatment, providing valuable insights into the challenges and potential solutions for corrosion mitigation in this critical area.*

Keywords: *Corrosion rate, Biofilm, Biocide, Oxygen scavenger, Offshore*

1. INTRODUCTION

FPSOs are usually deployed offshore to produce, store, and offload hydrocarbon resources [1]. They have production separators, storage tanks, offloading systems, and water treatment plants. [2]. The water treatment plant within an FPSO processes seawater to meet stringent quality requirements for cooling, injection, equipment cleaning, and other operational needs [2, 3]. However, the composition of the seawater makes it corrosive, thereby degrading the steel pipes used in constructing the water treatment plant [4, 5].

Corrosion is an electrochemical process that causes the deterioration and degradation of materials, particularly metals, through chemical reactions with their environment, leading to the decline of structural integrity and functional properties [6]. Several corrosion types are encountered in welded steel pipes. Olson et al. identified general corrosion, pitting corrosion, galvanic corrosion, stress corrosion cracking, hydrogen-assisted cracking, and microbial-influenced corrosion as mainly being present in weldments [7]. Pavlovic gave an overview of the causes, types, and preventive measures to mitigate corrosion. He stated that changing chemical composition, residual stress from welds, discontinuity like weld joints, poor design, and poor welding practices are the major causes of corrosion and that appropriate welding practices could help minimize corrosion in welds [8].

Corrosion of the pipes used in water treatment plants usually affects the operation of the FPSO. According to literature reports, the welded sections of a pipe are more susceptible to corrosion [4, 9]. This is primarily because the welding process introduces factors that affect corrosion resistance, such as heat-affected zones, residual stresses, and changes in microstructure. These create areas of higher vulnerability to corrosion in the welded regions, leading to plant shutdowns, resource waste, product loss or contamination, decreased efficiency, costly maintenance, etc [3].

The corrosion challenge within the water treatment plant of an FPSO is exacerbated by dissolved oxygen and gases in seawater [10, 11]. Chemical agents like oxygen scavengers and biocides are commonly employed to mitigate this problem

[1, 12]. While oxygen scavengers effectively absorb dissolved oxygen, they inadvertently foster the growth of bacteria within the pipes. This bacterial proliferation reduces pipe diameter, resulting in heightened water pressure and potential leaks or ruptures, especially at welded sections [5]. Adding biocides to control bacterial growth does not adequately halt corrosion progression. Seawater's high chloride content accelerates corrosion reactions by dissolving the protective oxide layer on the metal surface and forming complex metal ions. This makes seawater a good electrolytic conductor [10]. It has been reported that using these chemicals may result in incompatibility issues, which render them ineffective in meeting their objectives [13]. Biocide and oxygen scavengers decrease biocides' effectiveness in removing bacteria in the system [14].

This accelerated corrosion appears in various forms within the treatment plant of an FPSO, each possessing different characteristics and mechanisms. Pitting corrosion is observed due to the formation of localized pits or cavities on metal surfaces, leading to rapid deterioration [4]. Corrosion can also occur within crevices or gaps, while galvanic corrosion could arise when dissimilar metals in contact undergo accelerated deterioration. A particularly concerning form of corrosion is Microbiologically Influenced Corrosion (MIC), wherein bacterial growth and biofilm formation on metal surfaces accelerate localized corrosion [15-17]. Larson et al. identified microbial action as a significant contributor to corrosion in metal alloys exposed to the following environmental conditions: seawater, hydrocarbon fuels, chemicals, soils, etc. [15] In a review by Little et al., microbial-induced corrosion was shown to be a significant problem, but a holistic approach to solving the problem is yet to be proposed [16]. Nicoletti et al. evaluated microbial corrosion under nitrate and nitrite breakthrough conditions in two FPSOs. The results showed that nitrite breakthrough conditions increased pitting density and that general corrosion rates were highest when no nitrate or nitrite was introduced [17]. All these types of corrosion collectively pose a substantial threat to the integrity of the water treatment infrastructure. Not many studies have been done on using varying compositions of the electrode and base metal and on the agitation of the media while the experiment is ongoing. The aim of this research is to investigate how using oxygen scavengers, biocides, and agitation of the medium affects the corrosion rate of welded sections of the water treatment plant in an FPSO.

2. METHODOLOGY

A stainless-steel bar with a composition similar to that used in constructing water treatment plants was procured from a steel market at Onipanu, Lagos [18]. The compositional analysis of the steel bar revealed the elemental concentrations, as shown in Table 1. Table 1 also shows the elemental composition of the low hydrogen electrode obtained from Owode Onirin market, Lagos.

Table 1: Elemental composition of the stainless steel and Electrode

	Element Concentration (%)							
	Fe	**Cr**	**Ni**	**Mn**	**Si**	**C**	**P**	**S**
Stainless Steel Electrode	71.31	18.16	8.77	1.3	0.32	0.13	0.0045	0.0031
Low hydrogen Electrode	99.01	0	0	0.41	0.36	0.21	0.006	0.004

2.1 Sample Preparation:

The carbon steel bar was machined to have a (75 x 2.5 x 10) mm dimension and, with a milling machine, was chamfered in the middle at 45^o, as shown in Figure 1a. Five pairs of samples were produced and welded using a low hydrogen electrode (gauge length: THJ422). The coupons were Butt-welded with an electric arc welding machine. A stable current of 120 A and voltage of 220 V were applied, and the welding speed was 1 mm/s. The picture of the welded samples is shown in Figure 1b.

(a) (b)

Figure 1: (a) Chamfered Steel bar (Butt joint) and (b) Welded Steel Bar (220V, 120A)

Water from the lagoon at the University of Lagos was collected and distributed into labelled containers representing five different corrosion media. 90 g of NaCl was added to 20 litres of lagoon water and thoroughly stirred to simulate the seawater conditions at the FPSO environment [19]. The containers with the seawater are shown in Figure 2.

Figure 2: Buckets containing seawater from the University of Lagos Lagoon

The oxygen scavenger and biocide were sourced from Port Harcourt, Rivers State, Nigeria. The oxygen scavenger's constituent is Ammonium bisulphate, while the biocide's constituent is Tetrakis hydroxymethyl phosphonium sulphate (THPS). The concentrations used align with typical usage in offshore water treatment plants. The reagents were injected into the designated buckets containing seawater and suspended steel coupons. Five different media were formulated for the experiment:

i. Non-agitated medium containing neither oxygen scavenger nor biocide
ii. Non-agitated medium containing 62 ml of oxygen scavenger.
iii. Non-agitated medium containing 62 ml of biocide.
iv. Agitated medium containing 62 ml of Oxygen Scavenger.
v. Agitated medium containing 62 ml of biocide.

This concentration of the chemicals was chosen because it aligns with the concentration used industrially for such purposes [20]. The water in the vicinity of the FPSO has previously been characterised. A submersible pump (220V, 18W) operating at a flow rate of 820 L/hour agitated the solutions while the non-agitated media remained static constantly.

The experimental setup allowed for continuous observation and measurement of corrosion rates and mechanisms every 7 days. The weight loss method measured the corrosion rate in the steel coupons. The coupons were removed from the solution weekly and weighed with an analytical balance. Before weighing the samples, they are usually cleaned using distilled water and a soft cloth according to the global standard [21].

The corrosion rate was calculated assuming that uniform or general corrosion is prevalent. The weight loss method was used to calculate the corrosion rate using the formula in Equation 1:

$$R_{corr}\left({mm}/{year}\right) = 87.6 * \left(\frac{w}{DAT}\right) \tag{1}$$

Where w = weight loss in mg, D = density of the steel (g/cm^3), A = area of the sample (cm^2), T = exposure time of the steel (hours)

Additionally, the seawater was analysed to measure changes in pH, salinity, total dissolved solids, and the reducing-oxidizing environments. The measurement was made with an HQ40d Advanced Portable Meter.

The salinity was evaluated to determine the concentration of Cl^- in the water, which is empirically equal to 1.80655 × [Cl^-] [22].

The total dissolved solids in the solution, which is a measure of dissolved organic and inorganic contents in the solution, was calculated using the expression in Equation 2 [23].

$$\text{TDS (mg/L)} = ke * EC \tag{2}$$

Where EC is the electrical conductivity and ke is a correlation factor at a particular temperature and pressure

The pH of the aqueous solution was calculated based on the concentration of the hydronium ion in moles per litre.

$$pH = -\log [H_3O^+]. \tag{3}$$

The conductivity of the solution was calculated using the formula in Equation 4:

$$\text{Conductivity } (\kappa) = (1 / \text{Resistivity}) \tag{4}$$

The corrosion products obtained after the experiments were collected and analysed with X-ray diffraction to determine the phases present. The measurements were made with an X-ray diffractometer (PHILIPS Analytical X'Pert) operating continuously at a step size of 0.026^{o}. The generator settings are at 45 kV, 40 mA, with a start position of 5.0130^{o} and an end position of 89.9810^{o}.

3. RESULTS AND DISCUSSION

3.1 Salinity

A graph of the salinity in parts per thousand (ppt) of the solution as a function of the number of days is shown in Figure 3. In the first 20 days of the experiment, unstable salinity values were obtained. After this time, however, a more apparent trend was obtained. The non-agitated medium without chemical injection consistently had the lowest salinity levels (32-35 ppt). The non-agitated medium with chemical injection followed this.

The non-agitated solution containing biocide and oxygen scavenger had salinity levels between 40 and 45 ppt. This suggests that chemical injection alone does not effectively reduce salinity levels since additional ions and compounds are introduced, leading to increased salinity. The agitated media with chemical injection consistently had the highest salinity levels. This is because agitation enhances the dissolution of salts and minerals in the medium, elevating the overall salinity. The salinity levels of the solution with both agitation and chemical injection are between 45 and 53 ppt. This is much higher than the values obtained for mild steel (25-30 ppt) when only 3.5% of NaCl was added to the water [11].

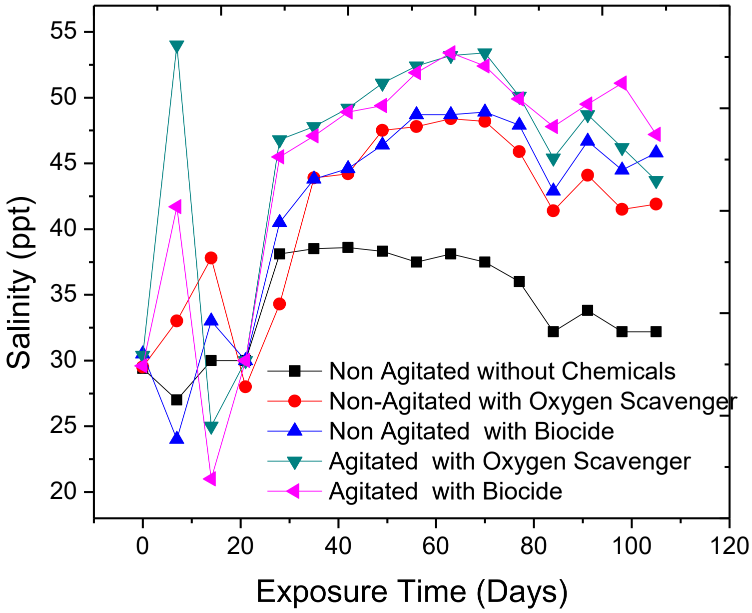

Figure 3: Salinity of the seawater as a function of exposure time in the different media

3.2 Total Dissolved Solids

Total Dissolved Solids (TDS) measures the concentration of dissolved minerals, salts, and other inorganic matter in water. The higher the TDS level, the more dissolved solids are in the water. TDS is used to quantify both inorganic and organic compounds in different conditions. When the TDS value is less than 1500 ppm, the water is classified as fresh, and between 1500 ppm and 5000 is considered brackish, and above this quantity, it is classified as saltwater [22]. All the test media can be categorized as saline solutions based on the above.

The plot of total dissolved solids as a function of exposure time is shown in Figure 4. The TDS levels were consistently lower in the non-agitated medium without chemical injection than in the non-agitated medium with either oxygen scavenger or biocide injection. This suggests that chemical injection is not effective at reducing TDS levels. Also, the TDS levels are generally lower in the media with oxygen scavenger than in the media with biocide. This may be because oxygen scavengers react with dissolved oxygen to form gas, which then escapes from the water. At the same time, biocide increases TDS levels by killing bacteria that help to break down solids. The TDS levels in the agitated media are the highest because the solids' dissolution rate increases.

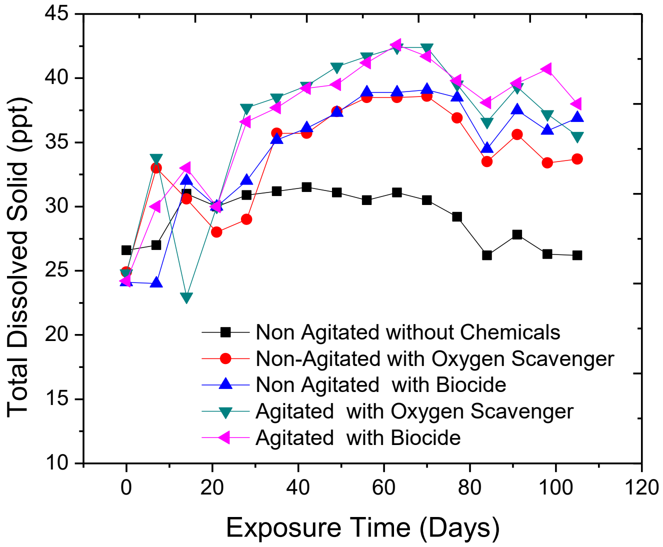

Figure 4: Total dissolved solids as a function of exposure time in the different media

3.3 Oxidation-Reduction Potential

The oxidation-reduction potential (ORP) data provides insights into the redox reactions in the different media used for corrosion mitigation. Figure 5 shows the ORP graph as a function of the number of days. The ORP values varied across the tested media, indicating differences in the redox potential and the presence of oxidizing or reducing agents. The media containing agitated and non-agitated oxygen scavengers showed a lot of instability in the obtained potential values.

This suggests that although the environment should oxidize, a highly reducing environment remains. For the other media, in the first 20 days, the environment was oxidizing (up to 200 mV), and afterward, there was a gradual reduction in the potential with each measurement. After 105 days of immersing the coupons in the seawater, the potential in the system has dropped to -150 mV. The agitation process slightly influenced the medium's availability and distribution of oxidizing or reducing agents, leading to varying ORP values.

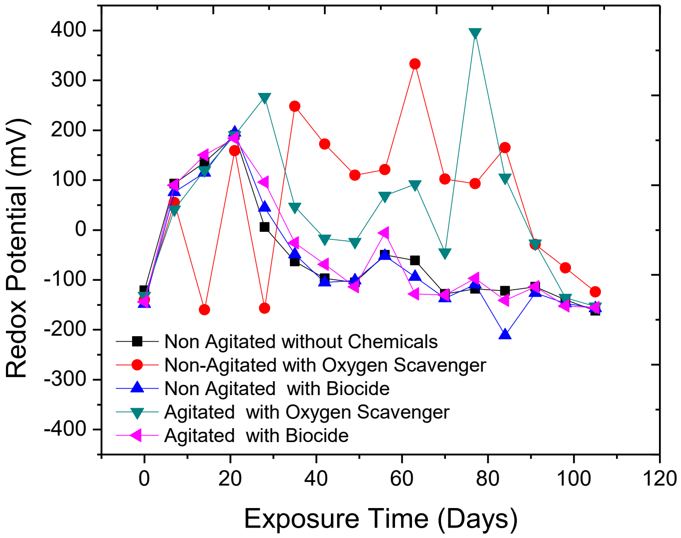

Figure 5: Oxidation-reduction potential as a function of exposure time in the different media

3.4 Solution pH

The graph of solution pH as a function of the number of days immersed is shown in Figure 6. In all the media analysed, the pH of the solution increased with an increasing number of days immersed. This increase in pH is often associated with the growing concentration of the OH- usually at the interface between the metal and the electrolyte [16]. The reactions that best explain the phenomenon are shown in equations 5 and 6 for different environments.

For aerated conditions: $2H_2O + O_2 + 4e^- \rightarrow 4OH^-$ (5)

For basic conditions: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ (6)

The medium without any chemical injection consistently exhibited the highest pH levels, rising from 6.05 to 6.55 at the end of the experiment. The agitation in the system had very little or no influence on the pH of the solution. Among the media with chemical additives, those containing biocide showed higher pH levels than those with oxygen scavengers, with values reaching 6.4. The media with oxygen scavenger consistently displayed the lowest pH levels, with 6.3 being the highest recorded value. This is similar to literature reports by [2].

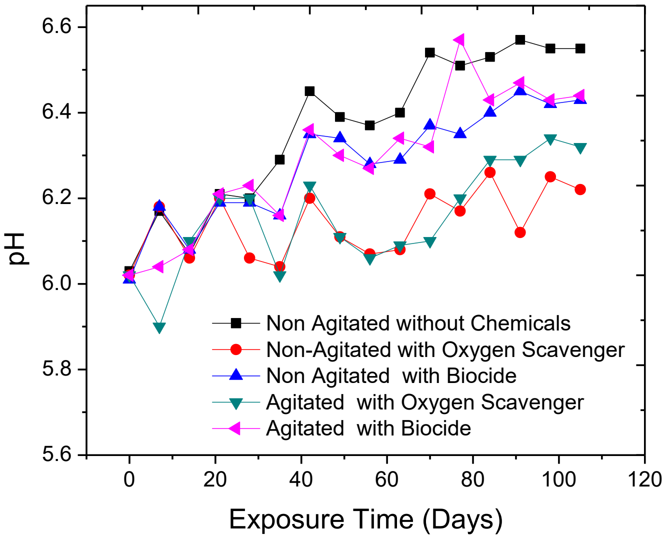

Figure 6: Graph of pH as a function of exposure time of the different media

3.5 Conductivity

The plot of conductivity of the solution as a function of exposure time is shown in Figure 7. Below the exposure time of 20 days, the conductivity values were not uniform. The higher the electrolyte conductivity, the easier it is for current flow and corrosion thereof [3]. The non-agitated medium with no chemical injection consistently displayed the lowest electrical conductivity levels. This suggests that the absence of chemical additives resulted in a lower concentration of dissolved salts and ions, contributing to a lower overall electronic conductivity. Among the media with chemical additives, those agitated had slightly higher conductivity values than those without agitation. Agitation promotes the dissolution and dispersion of conductive substances in the seawater, increasing electric conductivity. It is believed that the presence of biocide may have introduced additional ions into the solution, leading to a slightly elevated electric conductivity. Based on the paper, when 5% NaCl was added to the solution, the conductivity was ~70 µS/cm, while 3.5% NaCl addition resulted in 50 µS/cm [11]. Except for the sample containing no injections, whose conductivity is approximately 50 µS/cm, the other solutions had conductivity values between 75 and 80 µS/cm.

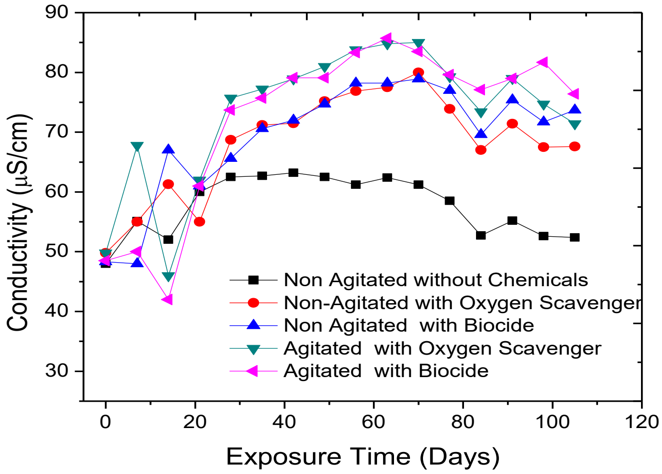

Figure 7: Conductivity as a function of Exposure time in different media

3.6 Corrosion Rate

Figure 8 shows the corrosion rate of the immersed stainless-steel coupons as a function of their exposure time. The media with oxygen scavengers had the highest corrosion rates of the entire media. When agitated, the corrosion rate initially increased to 10 mm/yr and gradually decreased to 6.2 mm/yr after 105 days. The medium without agitation gradually increased after 20 days from 0 mm/yr to 5 mm/yr after 105 days. The corrosion rate was higher in the agitated media than in the non-agitated media, most likely because the agitation exposes the metal to more turbulence. The solution that was not agitated and without chemicals exhibited the lowest corrosion rate. This is likely because available dissolved oxygen was consumed in a corrosion reaction in the first few days, while subsequent days only had minimal oxygen dissolved from the atmosphere, resulting in a lower corrosion rate. The non-agitated solution with Oxygen Scavenger showed increasing corrosivity over time. This is likely due to the increase in the concentration of oxygen scavengers and, as a result, a reduction in pH, making the water more acidic and corrosive. The non-agitated solution with Biocide showed a gradual increase in corrosivity over time. This is likely due to the increase in concentration of the biocide and, as a result, a slight reduction in pH, which makes the water more acidic and, hence, more corrosive. The pH reduction effect of the biocide is much less than that of the scavenger due to the hydrolyzing properties of the chemicals.

Agitation also increases the diffusion rate of oxygen and other corrosive species to the metal surface, which helps to accelerate the corrosion process. The corrosion rate was higher in the media with chemicals than in the media without chemicals. The solution agitated with the scavenger has a significantly low pH driven by the oxygen scavenger, and the agitation, which removes any protective scale, will result in markedly high corrosion rates.

The solution agitated with biocide has a relatively low pH, and the agitation that removes any protective scale will result in relatively high corrosion rates. However, the rates are lower than those caused by the scavenger.

The chemicals possibly reacted with the metal, especially the welded joints, to form corrosive compounds. For example, the biocide can react with the steel to form highly corrosive metal sulphides. Some possible reasons for increased corrosion in the agitated medium and in the media with chemicals are increased exposure to a corrosive environment, increased rate of diffusion of oxygen and other corrosive species, and the reaction of chemicals with metal [10].

Apart from the medium with an oxygen scavenger, whose corrosion rate increased with exposure time, the corrosion rates of other media decreased with exposure time. This is related to the formation of passive film on the surface of the steel, which acts as a protective layer. The high chloride ions, however, act to remove the cations on the anode, thereby increasing the corrosion rates [11].

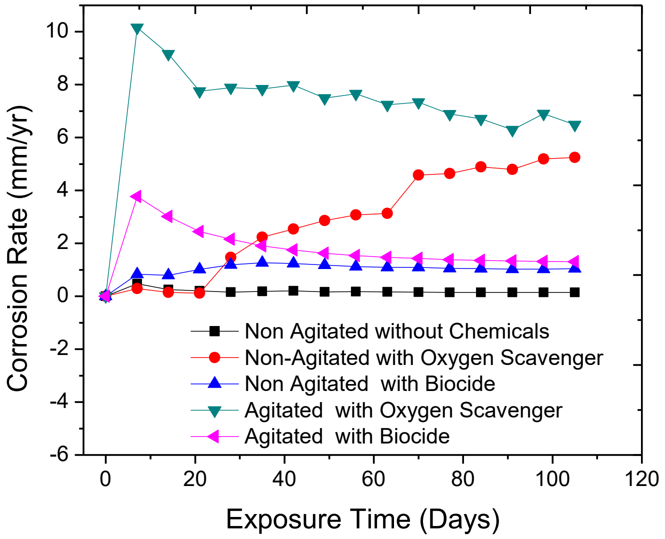

Figure 8: Corrosion rate as a function of exposure time in different media

3.7 X-ray Diffraction

The corrosion products from the steel surface were subjected to XRD analysis to determine the compounds present. The diffraction patterns for products injected with oxygen scavengers and biocides are shown in Figures 9a and 9b, respectively. For the oxygen scavenger, the diffraction data revealed the presence of hydrogen (H_2), fullerite (C_{60}), iron hydride (FeH), iron (Fe), and biphenyl ($C_{12}H_{10}$). The presence of hydrogen suggests a potential concern with hydrogen embrittlement, which can compromise the structural integrity of the steel. Fullerite, an allotrope of carbon, indicates the formation of carbonaceous deposits or contaminants on the steel surface. These deposits can impact the material's corrosion resistance and overall performance. Iron hydride (FeH) formation suggests an interaction between hydrogen and steel, potentially affecting its mechanical properties. As expected, iron (Fe) confirms the composition of carbon steel. The presence of biphenyl indicates the possibility of organic contaminants on the steel surface, which can influence corrosion processes.

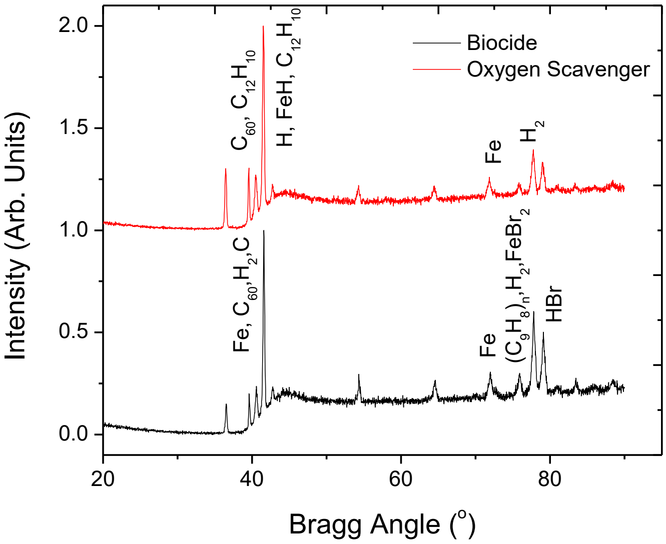

Figure 9: X-ray Diffraction patterns of the corrosion products from the steel surface immersed in cultured seawater containing oxygen scavenger and biocide.

The diffraction pattern of the corrosion products containing biocide reveals the presence of Fullerite (C_{60}), hydrogen (H_2), Polymethyl phenylacetylene (C_9H_8)n, bromoanthracene ($C_{14}H_9Br$), iron bromide ($FeBr_2$), and hydrogen bromide (HBr). These organic and inorganic compounds could interact with the steel surface, leading to corrosion.

4. CONCLUSION

This study examined the effectiveness of oxygen scavengers and biocides in reducing corrosion in the water treatment plant of FPSOs. Unfortunately, the results showed that chemical injections did not provide adequate corrosion protection for the carbon steel pipes. The solution's salinity and total dissolved solid value increased with chemical injection and solution agitation from 35 to 45 ppt and from approx. 27 ppt to approx. 35 ppt respectively. The redox reduction potential shows the solution is unstable with oxygen scavenger injection, while biocide and control samples led to negative potentials. The pH of the solution increased with increasing exposure time from approx. 6.0 to approx. 6.3. The injection. The conductivity of the solution also increased with injection of the chemicals from ~55 µS/cm to ~75 µS/cm. The corrosion rate of the carbon steel samples increased with oxygen scavenger up to ~5mm/yr. Additionally, X-ray diffraction analysis indicated the presence of various compounds on the steel surface, indicating that corrosion processes were ongoing. It is clear that relying solely on oxygen scavengers and biocides is insufficient to address the corrosion challenges posed by the dynamic seawater environment and the specific operating conditions of FPSOs._Therefore, the piping/equipment used for water treatment facilities should adopt corrosion-resistant materials (CRA) such as Glass Reinforced Epoxy, Nickel alloys, etc. Strategies to improve the result from the research, such as varying the concentration of biocide and oxygen scavenger being injected into the water stream, as well as the sequence of injection, can also be altered such that both chemicals are not introduced into the water stream at the same time may be explored.

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