CORROSION OF X-70 CARBON STEEL PIPELINE SUBJECT TO SULFATE REDUCING BACTERIA

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ABSTRACT
Carbon steels are commonly used as structural materials of piping systems in oil and gas industry because of their lower cost and wider availability despite their relatively lower corrosion resistance. This work investigates the preferable growth media for Sulfate Reducing Bacteria to proliferate rapidly and the effect of Microbiologically Influenced Corrosion activity towards carbon steel API 5L X-70 line pipe. Present research work highlighted that the preferred growth medium for ATCC 7757 and BARAM is Modified Baar’s and Postgate C for Sg. Ular types of SRB. In addition, the corrosion rate was calculated using data based on metal weight loss experiment. The result confirmed that the corrosion rate in biotic (presence of Sulfate Reducing Bacteria) environment is much higher compared to abiotic environment (absence of Sulfate Reducing Bacteria). The pitting morphology that developed with time due to SRB activity was characterized with Field Emission Scanning Electron Microscopy and Energy dispersive spectroscopy. It shows high peak of Sulfur (S) and Iron (Fe) present after exposure to biotic compared to the abiotic sample. Field Emission Scanning Electron Microscopy coupled with Energy Dispersive Spectroscopy results show that corrosion activity due to Sulfate Reducing Bacteria will form biofilm and iron sulfide layer on the metal surface. Future research should emphasize using local strain bacteria rather than microorganisms from culture collection sample to represent the activity and the effect or impact of microorganisms from the actual site.

Keywords: microbiologically influenced corrosion, sulfate reducing bacteria, API 5L X-70 carbon steel, corrosion rate.

1. INTRODUCTION
Pipeline can be defined as all parts of physical facilities through which products move in transportation, or transmission and gathering lines which transport products from production facilities to onshore locations, and storage equipment of the closed-pipe type. Pipelines could be found onshore (above the ground or buried) and offshore. For decades, pipelines have been reported as the safest and most effective way to transport highly pressurized products including crude oil and pressurized gas around the world [1]. Carbon steel API 5L pipeline is often used by local pipeline designers due to its strength, making carbon steel the material of choice in the construction industry [2]. The grade designations are taken from API Spec 5L Specification for Line Pipe. Grade designation A and B are the standard grade whereas the stronger grades have the designation X followed by the specified minimum yield strength of the pipe steel. This indicates that, the higher yield and tensile strength, the better grade and pipeline material. However, steel pipeline structure either buried or exposed to marine environment is vulnerable to corrosion problems such as Microbiologically Influenced Corrosion (MIC).

A great variety of microorganisms are associated with initiating and accelerating the corrosion process. MIC is the degradation of materials, usually metal, due to the activity of microorganisms. It is also known as biocorrosion and this form of corrosion mostly takes place underneath biofilms, which consist of colonies of microorganisms attached to a surface [3]. Microorganisms do not introduce a new or unique corrosion mechanism but rather accelerate existing chemical or electrochemical corrosion kinetics. An active biofilm or consortia can alter the electrochemistry at the biofilm and metal surface thus influencing cathodic and anodic reactions leading to MIC. Sulfate Reducing Bacteria (SRB) is the predominant groups of microorganisms responsible for the MIC [4-5]. SRB are facultative anaerobes living in oxygen free environments utilizing sulfate as a terminal electron acceptor to produce hydrogen sulfide (H₂S) as a metabolic byproduct. Stackebrandt et al., (1997) had summarized the classification of subgroups of SRB. However, each genus may contain different species of bacteria and may have its own characteristics of shape, size, capability of utilizing different substrates and other optimum performance parameters like temperature, pressure and pH [6]. They can grow in a pH range from at least 4.0 to 9.5 and tolerate pressure up to 500 atm [7]. SRB groups mostly can survive in temperatures ranging between 25 to 60 °C [7, 8, 9]. Different types of microorganisms probably have different growth reaction and impact towards the environment. The objective of this research work is to determine the preferable growth media for three different types of SRB to proliferate actively and the effect of SRB activity on corrosion of low carbon steel (API 5L X-70) pipeline. The biofilm and corrosion morphology was examined using Field Emission Scanning Electron Microscopy (FESEM) coupled with Energy Dispersive X-ray Spectroscopy (EDS).
2. MATERIALS AND METHODOLOGY

2.1 Microorganisms and medium

Three types of SRB were used in this research works. The SRB were obtained from American Type Culture Collection (ATCC), crude oil samples from an oil terminal tank located in East Malaysia and soil sample near the natural gas transmission line in Peninsular Malaysia later known as ATCC 7757, BARAM and Sg. Ular respectively. All types of SRB were cultivated in two different growth media for sulfate reducers such as Modified Baar’s medium (ATCC medium 1249) and Postgate C medium. The chemical composition for Modified Baar’s medium and Postgate C medium was tabulated and shown in Tables 1 and 2. All chemical ingredients were prepared based on 1000 mL of distilled water.

Handling an experimental work related to microorganisms requires careful precaution to avoid contamination. Therefore, in this research work all equipment were sterilized in an autoclave and the experimental works were performed in laminar flow chamber. To prepare the Modified Baar’s media, all ingredients except for Ammonium Iron (II) Sulfate Hexahydrate (Fe(NH4)2(SO4)2) were mixed together with distilled water. The pH of the medium was adjusted to desired pH using buffer solutions (NaOH, 1M and HCL, 1M) before sterilized in an autoclave at 121˚C for 20 minutes. The media was then purged with oxygen free nitrogen gas for approximately 1 hour to remove oxygen gas and to create anaerobic medium before being transferred to the vials. Since Fe(NH4)2(SO4)2 is heat sensitive, it does not undergo sterilization in autoclave and was added during purging nitrogen gas into medium. To prepare the Postgate C media, chemical composition tabulated in Table-2 was mixed thoroughly with distilled water and then were sterilized. Then, the growth media were transferred and 2 ml of SRB seed (ATCC 7757, BARAM and Sg. Ular) were injected into the anaerobic vials. Then the samples were incubated in an incubator for 28 days at desired temperatures.

2.2 Corrosion specimen preparation

The coupons were cut from an actual segment of API 5L X-70 carbon steel pipes. Quantitative chemical composition of carbon steel API 5L X-70 was analyzed using Glow Discharge Spectrometer (GDS) and the composition of the carbon steel coupon is as follows: 97.093% Fe, 0.078% C, 1.67% Mn, 0.15% Ni, 0.012% P, 0.3% Si, 0.023% Cu, 0.275% Cr, 0.11% Ti, and 0.002% S [11]. The coupons were machined to a size of 20 mm x 10 mm x 5 mm in order to fit the vial openings. The test carbon steel coupons were thoroughly polished with 100 grit silicon carbide (Si-C) paper and dried with acetone (99.5% purity) to remove all forms of dirt, grease and small particles of Si-C on the coupons surface. Then the cleaned and dried coupons were coated with heavy duty protective coatings (Zinc Chromate Primer, Nippon Paint) leaving only the top surface exposed for corrosion testing. The coated coupons were let to dry overnight. Prior to experimental work, the exposed surface area of coupons was polished with series of Silicon carbide (SiC) papergrade (100, 600 and 800) followed by acetone (99.5% purity) degreasing. Initial weight of carbon steel coupons and coupon numbering was systematically recorded.

Table-1. Chemical composition for modified Baar’s media.

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnesium Sulfate.7H2O (g L⁻¹)</td>
<td>4.096</td>
</tr>
<tr>
<td>Sodium Citrate.2H2O (g L⁻³)</td>
<td>5.700</td>
</tr>
<tr>
<td>Calcium Sulphate (g L⁻³)</td>
<td>1.000</td>
</tr>
<tr>
<td>Ammonium Chloride (g L⁻³)</td>
<td>1.000</td>
</tr>
<tr>
<td>Yeast Extract (g L⁻¹)</td>
<td>1.000</td>
</tr>
<tr>
<td>Potassium Phosphate (g L⁻¹)</td>
<td>0.500</td>
</tr>
<tr>
<td>Sodium Lactate (mL)</td>
<td>4.500</td>
</tr>
<tr>
<td>Ammonium iron (II) Sulfate Hexahydrate (mL)</td>
<td>5.000</td>
</tr>
</tbody>
</table>

*Ammonium iron (II) Sulfate Hexahydrate should not undergo sterilization.
2.3 Turbidimetric measurements

To monitor SRB growth, turbidity method is an alternative practice to enumerate SRB [12]. A spectrophotometer DR 6000 (HACH, US) was used to determine the optical density (OD) of the assigned broth culture at 600 nm wavelength in this research work. The medium was diluted once before the turbidity measurement was taken at selected period (duplicate for each sample).

2.4 Corrosion rate using weight loss method

All coupons were retrieved from the anaerobic vials on weekly basis up to day 28 (day 7, 14, 21 and 28) and Clarke’s solution was used to remove the corrosion product deposited on the exposed surface of coupon as shown in Figure 1. The Clarke’s solution was prepared using 1000 ml of hydrochloric acid (HCl, sp gr 1.19), 20 g of antimony trioxide and 50 g of stannous chloride as mentioned in ASTM G1-03 [13]. The corrosion rate was calculated based on the weight loss method calculated from the following Equation (1) [14];

\[
W = W_o - W_a
\]

(1)

where \( W_o \) is the initial weight of coupon (g) and \( W_a \) is the final weight of coupon (g). Additionally, by substituting Equation (1) into Equation (2), corrosion rate (Cr) of steel coupon can be determined [13, 15].

\[
\text{Corrosion rate (Cr)} = \frac{W}{A \times T \times D}
\]

(2)

where; \( k \) (in mm/year) is 8.76 x 10^4, \( W \) is the weight loss (g), \( A \) is the area (cm²), \( T \) is the time exposure (hours) and \( D \) is the density of steel coupon (7.86 g/cm³).

2.5 Sulfate reducing bacteria preferable growth media

The SRB sample was prepared as mentioned earlier in Section 2.1. The pH of the growth media was set up to its optimum pH 7.5 (Sg. Ular) [16] and 8.5 (ATCC 7757 and BARAM) [17], then the SRB sample was incubated in an incubator at temperature of 37°C for a week (7 days). The growth of SRB (ATCC 7757, BARAM and Sg. Ular) was enumerated using turbidity method as mentioned in Section 2.3 based on daily basis (day-1 to day-7) and the data were recorded systematically.

2.6 Weight loss upon sulfate reducing bacteria activity

Carbon steel coupon sample and the growth media was prepared as mentioned earlier in Sections 2.1 and 2.2. Each SRB was inoculated based on the most preferable media to growth and proliferate actively. The growth media was altered at optimum pH and were incubated at temperature of 37°C for 28 day. There are two types of exposure environment which included abiotic (absence of SRB) and biotic (presence of SRB). The carbon steel coupon were retrieved based on weekly basis.

Table-2. Composition of postgate C media [10].

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium Sulfate (g L⁻¹)</td>
<td>4.500</td>
</tr>
<tr>
<td>Ammonium Chloride (g L⁻¹)</td>
<td>1.000</td>
</tr>
<tr>
<td>Potassium Dihydrogen Phosphate (g L⁻¹)</td>
<td>0.500</td>
</tr>
<tr>
<td>Calcium Chloride.6H₂O (g L⁻¹)</td>
<td>0.060</td>
</tr>
<tr>
<td>Magnesium Sulfate.7H₂O (g L⁻¹)</td>
<td>0.060</td>
</tr>
<tr>
<td>Sodium Citrate.2H₂O (g L⁻¹)</td>
<td>0.300</td>
</tr>
<tr>
<td>Iron(II) Sulfate.7H₂O (g L⁻¹)</td>
<td>0.004</td>
</tr>
<tr>
<td>Yeast Extract (g L⁻¹)</td>
<td>1.000</td>
</tr>
<tr>
<td>Sodium Lactate (mL)</td>
<td>4.500</td>
</tr>
</tbody>
</table>

Figure-1. Cleaning process of coupon sample using Clarke’s solution.
(day 7, 14, 21 and 28) and the coupon was cleaned and recorded according to method that mentioned in Section 2.4 in order to calculate the corrosion rate.

2.7 FESEM Observation

Field Emission Scanning Electron Microscopy (FESEM) coupled with Energy Dispersive X-ray Spectroscopy (EDS) model Supra 35VP was used in present research work to observe the biofilm and corrosion surface of the carbon steel API 5L X-70 exposed to SRB activity. To observe the steel coupon with SRB biofilm, the coupon was immersed in preferred growth medium with presence of SRB (ATCC 7757, BARAM and Sg. Ular) and left incubated for 21 days. The coupon was retrieved on day-21 and the bacterial cells on the coupon surface were fixed in 4% (wt) Glutaraldehyde for 4 hours. Subsequently the cells were gradually rinsed with a series of ethanol solutions (25%, 50%, 75% and 100% purities) to dehydrate the biofilm for 5-10 minutes each [18]. In order to be observed with a FESEM, objects are first made conductive to current. This is done by coating them with an extremely thin layer (1.5-3.0 nm) of gold or gold palladium [19].

3. RESULT AND DISCUSSIONS

3.1 Sulfate reducing bacteria growth in different media

As shown in Figure-1, the black layer presence onto the coupon surface show the existence of SRB metabolism activity in the environment which is similar found by past research [23]. Figures 2 to 4 illustrates the SRB (ATCC 7757, BARAM and Sg. Ular) growth curve in the two different growth media with optimum pH as mentioned in Section 2.5. The SRB samples were incubated at 37°C for 7 days. The SRB growth curve was obtained by measuring the turbidity of the SRB sample based on daily (day 1, 2, 3, 4, 5, 6, and 7) basis. As mentioned earlier in section 2.1, two types of common growth media (Modified Baar’s and Postgate C) were used in order to investigate the preferable media for different types of SRB (ATCC 7757, BARAM and Sg. Ular) to grow and proliferate actively. According to Maria et al. (1999), the growth media or sample will become turbid due to the presence and growth of SRB in the media [20]. The growth media will turn black in color as shown in Figure 5 and result in a pungent “rotten egg” smell. This is the evidence of SRB growth and its metabolism in the medium [10].

The results show that the growth rate based on turbidity measurement under optimum pH and temperature of 37°C for ATCC 7757 and BARAM in Modified Baar’s media is found to be higher than the growth rate in Postgate C media (refer to Figures 2 and 3). However, the isolated SRB from local site exhibits better growth in Postgate C media according to the turbidity of the medium which is much higher when compared to the growth in Modified Baar’s media as shown in Figure-4. Therefore, throughout the experimental work ATCC 7757 and BARAM was inoculated in Modified Baar’s media and Postgate C was used for isolated SRB Sg. Ular.

![Figure-2. Turbidity against day for ATCC 7757 in different growth media.](image-url)
3.2 Corrosion rate, Cr

The API 5L X-70 steel coupons were exposed to abiotic (Modified Baar’s or Postgate C media without SRB presence) and biotic (Modified Baar’s or Postgate C media with presence of SRB) sample up to 28 days and the metal weight loss as a result of exposure towards SRB activity were recorded systematically. The corrosion rate of the carbon steel coupons inoculated with and without SRB were calculated based on weight loss procedure [13, 14, 15] as stated in Section 2.4. Figure 6 illustrated the result of corrosion rate of carbon steel coupon exposed to abiotic (Modified Baar’s or Postgate C media) and biotic (presence of ATCC 7757 or BARAM or Sg. Ular) sample. The bar graph displays a pattern whereby the rate of corrosion in SRB sample was extremely high in the beginning of experiment for Sg. Ular (0.5639 mm/year), followed by ATCC 7757 (0.5058 mm/year) and BARAM (0.3209 mm/year) compared to abiotic Modified Baar’s (0.1791 mm/year) and abiotic Postgate C (0.0995 mm/year), respectively. The corrosion rate in all SRB sample was decreasing steadily from second retrieval onwards. However, after 672 hours of exposure the corrosion rate of the API 5L X-70 steel coupons in SRB samples is slightly increased. This might be due to the aggressive activity of SRB at early stage which influence the corrosion process and as time goes by probably the formation of corrosion product and biofilm attach onto the
steel coupon surface that might inhibit and sometimes may influence further corrosion. The maximum corrosion rate for Sg. Ular (0.5639 mm/year) was 82% higher compared to abiotic (Postgate C media) sample (0.0995 mm/year) followed by ATCC 7757 (0.5058 mm/year) of 65% and BARAM (0.3209 mm/year) of 44% higher compared to abiotic (Modified Baar’s media) sample (0.1791 mm/year). In addition, the result of corrosion rates on the API 5L X-70 steel coupon as shown in Figure-6 throughout incubation period indicates that none of the corrosion rates of the API 5L X-70 steel coupon exposed to the Modified Baar’s and Postgate C medium exceeded samples with SRB (ATCC 7757, BARAM and Sg. Ular). Results also confirmed that the presence of SRB in the environment will induce higher metal loss as compared to abiotic environment. The results are in line with the previous statement as the SRB may expedite rate of corrosion on the steel coupon. Apart from that, the corrosion rate on the API 5L X-70 steel coupons between the SRB samples is slightly different, where the result reflects that different types of SRB (ATCC 7757, BARAM and Sg. Ular) may have different corrosion impact towards metallic pipeline structure. Different SRB types or strain might have the same influence upon pH and temperature but the reaction of the microorganisms towards the corrosion process might not be the same.

3.3 Field emission scanning electron microscopy examination

Figure-7 shows a magnified image for the surface of API 5L X-70 carbon steel under FESEM after being polished using various grade of Si-C paper as described in Section 2.2. The microstructure of the steel coupon can be seen clearly at 1000 times magnification and the API 5L X-70 carbon steel surface is not yet disturbed by the microorganism’s activity or biofilm formation. The deposited chemical element of the steel surface was illustrated in Figure 8 which was obtained from the Energy Dispersive X-ray Spectroscopy (EDS). Based on the result, high peak of iron (Fe) and low peak of carbon (C) was observed.

Figures 9 to 14 shows the magnified FESEM image of SRB biofilm formation on API 5L X-70 steel with EDS spectrum upon SRB (ATCC 7757, BARAM and Sg. Ular) activity respectively. The biofilm microstructure and the attached ATCC 7757, BARAM and Sg. Ular cell onto the steel coupon surface can be observed clearly as shown in Figures 9, 11 and 13 respectively (SRB cell were indicated by the arrow). The deposited chemical element of the steel surface upon ATCC 7757, BARAM and Sg. Ular activity and metabolism was illustrated in Figures 10, 12 and 14 respectively which was obtained from the EDS. Based on the EDS spectrum, the analysis revealed significantly high Sulfur (S) and Iron (Fe) peaks in the environment with presence of SRB when compared to environment without presence of SRB. These results have proven that the presence of SRB will produce hydrogen sulfide (H₂S) through its metabolism and will react with Fe²⁺ [21]. Through the electrochemical reaction the iron sulfide (FeS) is probably then deposited onto the metal surface.

Figure-6. Corrosion rate of carbon steel after exposure towards SRB activity.

Figure-7. FESEM image of API 5L X-70 carbon steel surfaces at 1000x magnification.
Figure-8. EDS spectrum for API 5L X-70 carbon steel surfaces.

Figure-9. FESEM image of biofilm formation for ATCC 7757 at magnification 2500x.

Figure-10. EDS spectrum on the API 5L X-70 carbon steel surfaces exposed to ATCC 7757.
Figure-11. FESEM image of biofilm formation for BARAM at magnification 2500x.

Figure-12. EDS spectrum on the API 5L X-70 carbon steel surfaces exposed to BARAM.

Figure-13. FESEM image of biofilm formation for Sg. Ular at magnification 5000x.

Figure-14. EDS spectrum on the API 5L X-70 carbon steel surfaces exposed to Sg. Ular.
As the active SRB present in the environment can react with the metal and nutrients, it will have a catastrophic impact on the pipeline system if precautionary steps are not been taken to overcome MIC problem. Theoretically, SRB have the ability to modify the electrochemical process which induce higher corrosion rate and form pit corrosion. Pit corrosion is caused by the catastrophic thinning of pipeline thickness and pitting corrosion growth prediction could be influenced by many uncertainties that may cause inaccuracies in the outcome [22]. Figure 15 shows an example of pitting corrosion onto API 5L X-70 steel coupon after exposure to SRB activity. Thus, the findings prove and are in line with past research that SRB could have a catastrophic effect on pipeline system if not well maintained. In addition, different types of SRB (ATCC 7757, BARAM and Sg. Ular) could have different reactivity and impact towards metallic structure as presented in this research work.

4. CONCLUSIONS

The present study examined the preferable growth media for SRB from different origin and types to grow and proliferate actively. The preferable growth media for bacterial growth has been identified through bacteria enumeration using turbidity measurement. Results shows that, the preferable growth media for ATCC 7757 (standard cultured SRB) and BARAM (marine SRB) were Modified Baar’s Media and Postgate C media for Sg. Ular (isolate SRB from soil). Based on the preferable growth media, each type of SRB was cultured and the effect of MIC activity upon API 5L X-70 carbon steel coupons was investigated. The corrosion rate volume of API 5L X-70 steel coupons was successfully recorded by measuring the metal weight loss differences of steel coupons after being exposed to abiotic and biotic samples. The maximum corrosion rate in biotic environment; ATCC 7757, BARAM and Sg. Ular recorded at with 0.5058 mm/year, 0.3209 mm/year and 0.5639 mm/year respectively; was found higher compared to abiotic Modified Baar’s (0.1791 mm/year) and Postgate C (0.0995 mm/year) environment. Moreover, the research also revealed different kinds of microorganisms might have different response towards the environment and corrosion growth rate. Therefore present study suggests that future research should emphasize using local strain bacteria rather than microorganisms from standard culture collection sample to represent the activity and the effect of microorganisms from original site. Field Emission Scanning Electron Microscopy (FESEM) provides physical evidence of SRB existence and biofilm formation onto steel coupon surface. In addition, the Energy Dispersive X-ray Spectroscopy (EDS) spectrum provides important information of chemical elements that attached onto the surface such as the Sulphur (S), Iron (Fe) and Oxygen (O) elements which are likely corrosion and metabolic products of SRB activity.

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REFERENCES


