Journal of Environmental Science and Technology

ISSN 1994-7887

science alert

ANSInet
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Journal of Environmental Science and Technology 7 (4): 209-217, 2014
ISSN 1994-7887 / DOI: 10.3923/jest.2014.209.217

Effect of pH and Temperature on Corrosion of Steel Subject to Sulphate-reducing Bacteria

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ABSTRACT

Growth of Sulphate-Reducing Bacteria (SRB) depends on the metabolic activity of the microbe which is greatly influenced by environmental factors. The environmental factors such as pH and temperature may affect the microbial activity which contributes to the metal loss phenomenon due to corrosion process. The study focuses on identifying the optimum value of pH and temperature that is most suitable for the constant growth of SRB which may lead to severe corrosion on carbon steel API 5L X70. Carbon steel coupons of size 20×10 mm were exposed to the ATCC 7757 modified Baar's medium broth number 1249 at 37°C for the period of 30 days. Initially, a group of anaerobic vial samples were cultured in the medium with constant temperature and pH values ranging from 5.5-9.5. The carbon steel coupons were retrieved after 30 days of incubation to determine the amount of weight loss. Among the range of pH value, the optimum value of weight loss was recorded at pH 9.5. This optimum pH was then tested on the range of temperature varies between 5 and 60°C. The calculation of weight loss and corrosion rate showed that the temperature of 37°C is the most favourable environment for the growth of bacteria with severe influence on the corrosion rate.

Key words: Sulfate-reducing bacteria, corrosion, pH, temperature, carbon steel

INTRODUCTION

Microbiologically Influenced Bacteria (MIC) or microbial corrosion is the deterioration of metals as a result of metabolic activity of microorganisms which leads to the pipeline failure. In anaerobic condition, of which bacteria grow in the absence of oxygen, sulfate-reducing bacteria was regarded as the most troublesome group which able to initiate and speed up corrosion process on metal in various form of metal loss. (Fonseca *et al*., 1997; Angell and Urbanic, 2000; Antony *et al*., 2007; Zhang *et al*., 2011; Stipanicev *et al*., 2013). When microorganisms attached on the material's surface, they grow and reproduce as a biofilm. The product of SRB biofilm then increases the corrosivity of the steel (Javaherdashti, 2007; Raman *et al*., 2008; Zhang *et al*., 2011).

In comparison to the aerobic respiration, anaerobic microorganisms used the organic or inorganic compounds as the terminal electron acceptor. SRB is the obligate anaerobic bacteria which make SO_4^{2-} reduced into H_2S to obtain energy (Javaherdashti, 2007; Zhang *et al*., 2011). Therefore, the concentration of H_2S produced by SBR is ultimately essential towards the microbial

activity (Lee *et al*., 1995; Zhang *et al*., 2011; Marchal *et al*., 2001). Other than corrosive products, favorable environment condition is also important towards metabolic activity of the microbe (Marchal *et al*., 2001; Javaherdashti, 2009). Yuzwa (1991) stated that pH value, temperature, redox potential and concentration of salts are some of the environment factors that may significantly influence the SRB growth.

The value of pH is one of the vital parameters that influence the cell adhesion of microorganism (Sheng *et al*., 2007). In marine environment, pH might be changing over period of time. Previous study showed that when in contact with medium, microorganism may motile and capable of migrating to more favourable condition (Pope, 1986; Javaherdashti, 2007). Javaherdashti (1999) stated that SRB can grow within pH range from 5-10. However, they are capable of raising the low pH environment thereby accelerating corrosion (Melchers and Wells, 2006).

Temperature also has a disproportionate role in controlling bacterial growth. Heterotropic microbes may differently respond to different level of temperature (Kirchman *et al*., 2005). Most SRB prefer temperature 20-30°C for growth, but they can survive up to 60°C (Zhang *et al*., 2011). This fact causes a great concern among pipeline operators since the temperature inside the operating transmission pipeline carrying crude oil and gas is close to 60°C.

The significance of environmental parameters toward SRB growth is still being investigated and more quantitative information is needed to improve the modelling of corrosion subject to MIC (Okabe *et al*., 1994; Marchal *et al*., 2001; Noor *et al*., 2011). The goal of this study is to describe quantitatively the effect of parameter pH and temperature on SRB growth (*Desulfovibrio vulgaris*) and how these optimum parameters can influence the corrosion process on carbon steel API 5L Grade X70 coupons.

MATERIALS AND METHODS

Bacterial strain and culture media: This study was performed using *Desulfovibrio vulgaris* ATCC 7757, obtained from the American Type Culture Collection, grown in modified Baar's medium (#1249 broth medium). Table 1 shows the composition of the medium.

All of the components were refilter-sterilized through a 0.45 μm membrane. The medium was then sparged with nitrogen gas for approximately 1 h to remove oxygen from it prior to autoclave at 121°C for 15 min. Component IV was not autoclaved since it is heat sensitive. Therefore, 0.1 mL of this solution was added to 5 mL of medium prior to inoculation.

Table 1: Composition of modified Baar's medium

Components	Chemicals and compositions	Values
1	$MgSO_4$ (g)	2.0
	Sodium citeate (g)	5.0
	$CaSO_4$ (g)	1.0
	NH_4Cl (g)	1.0
	Distilled water (mL)	400.0
2	K_2HPO_4 (g)	0.5
	Distilled water (mL)	200.0
3	Sodium lactate (g)	3.5
	Yeast extract (g)	1.0
	Distilled water (mL)	400.0
4	$Fe(NH_4)_2(SO_4)_2$ (mL)	0.1

Test material: The carbon steel coupon samples used in this study were cut from the original API 5L X70 pipes to a smaller size of 20×10 mm to fit into the anaerobic vials. All coupons were polished with sand papers (SiC paper) grade 60, 320, 600 and 800 followed by ethanol degreasing. Clean coupons were then dried, weighted and the total surface area of each coupon was recorded before utilised in the experiment.

Experimental procedures

pH: The experiments were carried out in anaerobic environment. A total of 18 steel coupons were placed in the same medium at pH values ranging from 5.5-9.5. They were placed into 9 anaerobic vials with 2 steel coupons per vials followed by oxygen purging with filtered nitrogen to ensure the anaerobic condition. Afterward the prepared medium was sterilized for 20 min at pressure of 1.2×10^4 Mpa. After the medium is cooled, 2 mL of ferrous ammonium sulfate $Fe(NH_4)_2(SO_4)_2$ was sterilized with 0.2 μm filter.

The experiment was carried out in anaerobic vials with temperature of 37°C. Oxygen free nitrogen was again used to remove oxygen in the solution. An amount of 2 mL of two-day old *Desulfovibrio vulgaris* stock culture was inoculated in each vial. The carbon steel coupon was exposed in inoxigenated MIC environment for 30 days with repeated observation every five days to avoid the occurrence of any unexpected problem.

Figure 1 shows the anaerobic vials containing steel coupons in medium with *Desulfovibrio desulfuricans* at day-30. All coupons were retrieved at day-30 and cleaned before weighted. The weight of W_a represents the weight of carbon steel coupon after being exposed to medium with the presence of SRB for 30 days.

Temperature: The experiments were safeguarded in anaerobic environment throughout the period of experiment. A total of 64 steel coupons were placed in the same medium adjusted at pH of 9.5 (optimum pH which obtained from experiment in previous section). They were placed into 32 anaerobic vials with 2 steel coupons per vial. The next process is similar to the aforementioned procedure in previous section. The carbon steel coupons were exposed in inoxigenated MIC environment at different temperature set at 5, 20, 37 and 60°C for a total of 30 days. Unlike retrieval method in this section, the coupon from each vial was retrieved on day 7, 14,

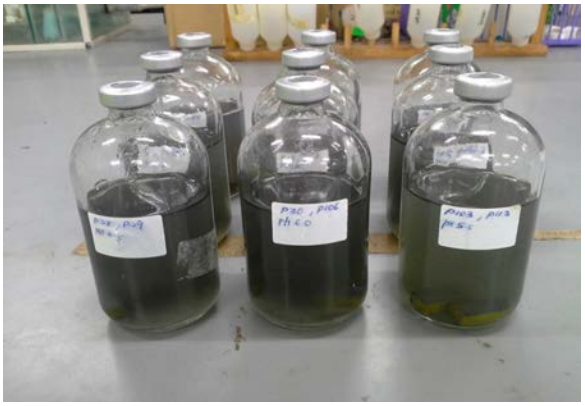

Fig. 1: Anaerobic vials with steel coupons and *Desulfovibrio desulfuricans* at day of retrieving

21 and 30. This is meant to observe the stage-by-stage progress of corrosion based on metal loss over time as well as to ensure the consistency of the weight loss and corrosion rate results.

Weight loss measurement: All coupons were retrieved and cleaned according to ASTM standards and weighted after drying process. The difference between the initial and final weight was reported as weight loss. Values of weight loss and corrosion rate measurement were determined by applying the following Eq. 1, 2:

$$\text{Weight loss (\%)} = (W_i - W_a) \times 100 \quad (1)$$

where, W_i is the initial weight before corrosion (g), W_a is the weight after corrosion (g):

$$\text{Corrorion rate (mm year}^{-1}) = \frac{K \times W}{A \times T \times D} \quad (2)$$

Where:

K = Constant (8.76×10^4)
T = Time of exposure (year)
A = Surface area exposed (mm^2)
W = Mass loss (g) and D is the density (g cm^{-3})

RESULTS AND DISCUSSION

pH: The results of weight loss and corrosion rate of carbon steel are shown in Table 2 and Fig. 2. Previous study showed that pH values above 7.2 may reduce the adhesion of corrosion products, therefore enhances the corrosion growth (Mor *et al.*, 1974; Ilhan-Sungur *et al.*, 2007). Values of C_R indicate the corrosion rate experienced by the steel coupon with the presence of SRB activity after 30 days of exposure. The results may suggest the optimum pH which can highly influences the C_R due to the H_2S produced by the microbial activity.

Figure 2 and 3 present the graph of weight loss over pH and corrosion rate over pH, respectively. The results show that the favourable pH for bacterial growth is in alkaline medium with pH of 9.5. As the pH increases from 5.5 to 7.0, corrosion rate starts to decrease before gradually gain the momentum of growth beyond pH 7.0 and reaching the maximum rate at pH of 9.5. The pattern clearly shows that the metal loss rate is low in the region of pH that is approaching neutral level of pH 7. It seems that SRB can highly influence corrosion process when the medium is considered highly alkaline or highly acidic.

Table 2: Average weight loss and corrosion rate of carbon steel coupon after 30 days of exposure to SRB at different range of pH

pH value	Weight loss (W %)	Corrosion rate (C_R mm $year^{-1}$)
5.5	1.97	0.01310
6.0	1.26	0.00851
6.5	0.98	0.00675
7.0	1.78	0.01200
7.5	1.10	0.00752
8.0	1.42	0.00935
8.5	1.64	0.01140
9.0	1.96	0.01310
9.5	2.09	0.01400

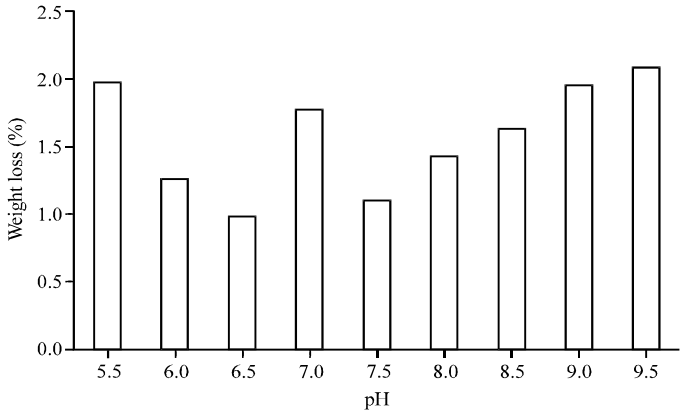

Fig. 2: Weight loss of carbon steel coupons over pH

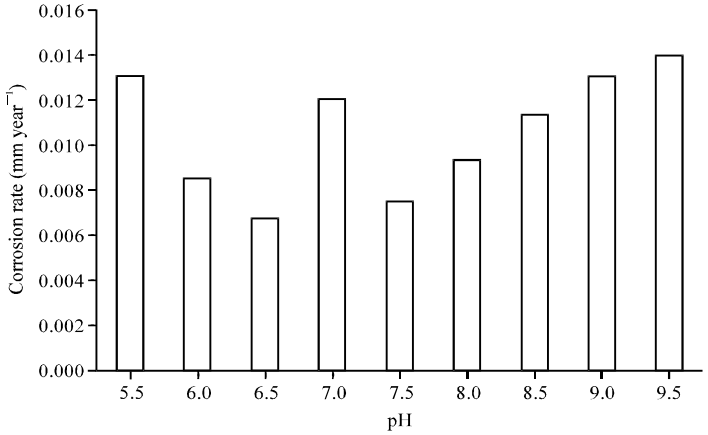

Fig. 3: Corrosion rate of carbon steel coupons over pH

In general terms, most species of *Desulfovibrio* grow best at the range of pH 5.5 to 9.0. Previous study reveals that the mechanism of acid corrosion in oxygenated environment indicates that most of the end-products of MIC are corrosive for carbon steel (Evan *et al*., 1973; Zhang *et al*., 2011). According to White and Gadd (1996), the amount of metal removed and the rise in pH both varied with the amount of sulphate reduction occurring. Cao *et al*. (2009) stated that at higher level of pH, the rate of H_2S dissolution is faster. Thus, corrosion rate of carbon steel will be higher as compared to lower pH level. The pH is essential as the alkaline environment assists in microbial activity by fasten the production of metabolic product H_2S which is essential for SRB corrosion.

Temperature: Table 3, Fig. 4 and 5 show the results of weight loss and corrosion rate of steel coupons exposed to SRB at different range of temperature. Previous study stated that bacteria can barely survive in high temperature environment since most of the bacteria normally grow at temperature below 60°C (Angell and Urbanic, 2000). However, at extremely low temperature, bacteria require more dissolved organic material to match the growth rate observed at higher temperature (Kirchman *et al*., 2005).

Figure 4 indicates that at 5 and 37°C, the pattern of metal loss is consistent over time. Nevertheless, results obtained from steel coupons, of which retrieved from medium with

Table 3: Average weight loss, weight loss rate and corrosion rate of the carbon steel coupon as a function of temperature

	Temperature							
	5°C				20°C			
	Days							
Parameters	7	14	21	30	7	14	21	30
Weight loss, W (%)	1.24	1.19	1.13	1.25	0.53	1.07	3.48	1.89
Weight loss rate (g mm^{-2})	6.3E-05	5.8E-05	5.6E-05	6.3E-05	2.6E-05	5.5E-05	1.8E-04	9.3E-05
Corrosion rate, C_R (mm year^{-1})	0.03680	0.01685	0.01081	0.00851	0.01522	0.01592	0.03503	0.01261
Parameters	37°C				60°C			
Weight loss, W (%)	1.81	2.06	2.04	1.43	1.12	2.76	1.36	1.64
Weight loss rate (g mm^{-2})	9.0E-05	1.0E-04	1.1E-04	7.2E-05	5.6E-05	1.4E-04	6.7E-05	9.3E-05
Corrosion rate, C_R (mm year^{-1})	0.05222	0.02942	0.02056	0.00969	0.03251	0.04013	0.01294	0.01265

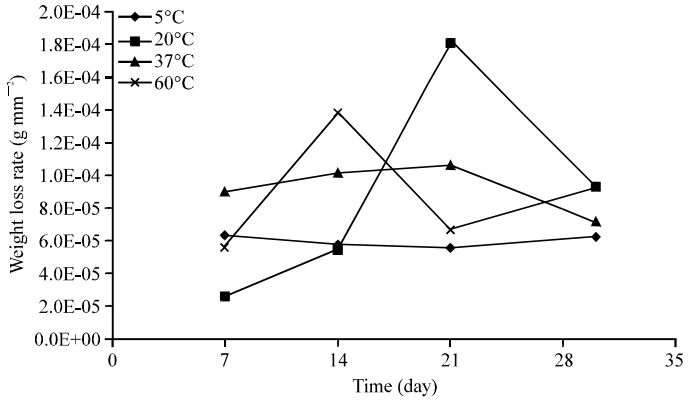

Fig. 4: Weight loss rate of carbon steel coupons over temperature

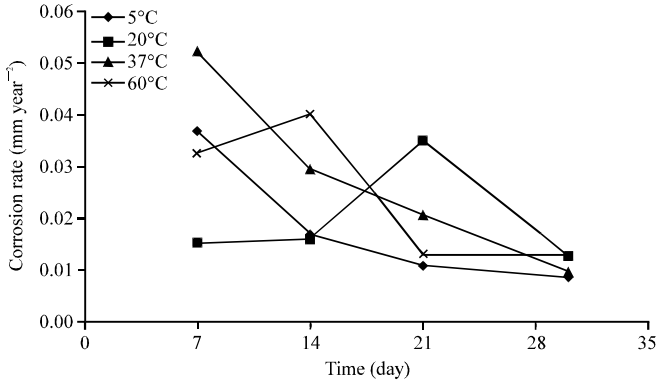

Fig. 5: Corrosion growth rate of carbon steel coupons over temperature

temperature of 20 and 60°C, suffer from anomalies based on the inconsistent pattern of metal loss. There is a sudden rise of metal loss on day-14 and day-21 for medium with temperature of 60 and 20°C, respectively. In fact, the metal loss decreases on the succeeding retrieval. These results may

be categorised as outliers provided that more evidence can be made available through statistical analysis (Noor *et al*., 2007). Throughout the experiment, careful measures have been taken to maintain the uniformity of steel coupons, medium and vials. This is of importance since each vial is not related physically whereby the retrieved coupon is not returned to the vials for the next retrieval. Instead, different steel coupons left for a longer period is used to connect the metal loss result. Therefore, the utilised methodology may rather prone to errors associated with the preparation of samples, coupons and bacteria.

Figure 5 shows the evidence that the highest corrosion rate was achieved when the coupons exposed to SRB for a period of 7 days at 37°C. Moreover, by observing the pattern of corrosion rate for all range of temperature, it is apparent that the highest corrosion rate was measured in the first seven days before the rate started to decrease. This reflects the power law pattern of corrosion growth. The formation of rust and the depletion of food supply in a medium has restrict the progress of corrosion, hence the decrease in metal loss volume. Optimum temperature is essential to support the microbial activity in producing the corrosive product which is H_2S. Unpleasant smell due to H_2S release and black precipitation of sulphides are the simplest way in determining the SRB growth (Yuzwa, 1991; Beech *et al*., 2000). At 20 and 60°C, the medium became too dark in the first 14-days before turning brighter to the end of the experiment. In contrast, medium at 37°C constantly turn darker until day-30. This is a sign of a constant production of H_2S from the microbial activity.

CONCLUSION

The outcome proposes that the microbial activity can reach its peak when the medium is very alkaline or very acidic. The range of pH that approaching neutral pH of 7 may not provide apposite environment for the growth of SRB to the extent that the microbial activity can speed up corrosion growth in a medium. Assisted by temperature of 37°C, the corrosion progress may become severe due to vigorous microbial activity. The results may suffer from hidden anomalies associated with the uniformity of coupons and bacteria preparation. As a suggestion, the experiment should be repeated to increase the number of results. Overall, the results indicate that the presence of SRB can be very harmful to steel when the environmental factors reach its optimum value. Serious measure of mitigation must be taken seriously to combat this problem since structure failure due to MIC has cost a staggering amount of money to pipeline industry.

ACKNOWLEDGMENT

This study was financially supported by Universiti Teknologi Malaysia (Grant No. GUP 03H49), the Ministry of Science and Technology of Malaysia, MOSTI (Grant No. ScienceFund 4S019) and the Ministry of Education of Malaysia, MOE (Grant No. ERGS 4L090).

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