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## PITTING DEPTH PREDICTION CAUSED BY SRB USING EMPIRICAL EQUATION

*Microbiologically influenced corrosion (MIC) is a serious problem in the oil and gas industry. The most common microorganism responsible for MIC is sulfate-reducing bacteria (SRB) which produces detrimental sulfide ions into the environment. Currently, there are some prediction models that develop to predict corrosion rate caused by SRB. However, among the models, the prediction is limited to predict the general corrosion rate, whereas, SRB caused localized corrosion. Thus, the objective of this work is to predict the pitting depth caused by SRB using available empirical equation. The study showed that the pitting depth increased with the increasing of sulfide concentration. In contrast, the pitting depth decreased with increasing sulfite concentration. The decreasing of pitting depth is related to the inhibitive FeS film formed, while the increasing of pitting depth is caused by the decreasing of the film thickness in the presence of sulfite.*

**Keywords:** Sulfate-reducing bacteria (SRB), prediction, empirical equation, pitting depth.

### 1. INTRODUCTION

Microbiologically influenced corrosion (MIC) is the deterioration of material caused or accelerated by the presence of bacteria and other microorganisms and their metabolic activities. MIC was reported to account for 20% of the damage caused by corrosion [1]. In oil and gas industry, the overall loss caused by MIC could be over US\$ 100 million per annum [2]. Sulfate-reducing bacteria (SRB) has been the most commonly studied group because of their detrimental effects and can exist in a variety of industrial environments. The failure caused by MIC could occur after the hydro testing test, whereby the hydro testing fluid is leaving in a pipeline system for many months [3]. The presence of bacteria in the fluid is the source of the MIC. It could initiate or accelerate MIC once the appropriate environments e.g. temperature, pH and nutrient are met [4]. Other examples of failure due to SRB were given by Abedi *et al.* and Tiller [5, 6].

Due to the nature of MIC which involves the activities and metabolism of microbes, the main challenge faced by the engineer is in the understanding of the corrosion mechanism related to the effect of metabolic products. A clearer understanding of the corrosion process leads to a better corrosion prediction and prevention of MIC. Previously, many theories had been proposed to explain the MIC mechanism such as cathodic depolarization theory (CDT).

The CDT was proposed by von Wolzogen Kuhr and van der Vlugt in 1923 [7]. According to the CDT, SRB accelerates corrosion of iron due to the removal of atomic hydrogen by the bacterial enzyme hydrogenase. The removed hydrogen reacts with sulfide produced by the SRB, forming H<sub>2</sub>S gas which is known to be toxic and corrosive. However, the CDT receives many criticisms such as by Dominique [8]. The main reason is that it does not capture other effects of SRB metabolic products that might contribute to the corrosion kinetics and mechanism.

Therefore, some studies have been conducted to investigate the behavior of abiotic sulfide representing SRB corrosion. In 1992, Newman *et al.* [9] conducted an experiment using abiotic sulfide on the corrosion of mild steel simulating the corrosion caused by SRB. The results showed that the corrosion rates obtained by abiotic sulfide and SRB experiments had a striking similarity. However, one difference was related to the possible massive

deposition of FeS as observed when SRB grew in the culture containing  $\text{Fe}^{2+}$ ; whereas in the abiotic experiment, FeS could only be formed as a result of corrosion.

Recently in 2007, Kuang *et al.* [10] also showed that the electrochemical behavior of SRB experiment had consistent results with the electrochemical behavior of abiotic sulfide. They concluded that the electrochemical corrosion behavior of carbon steel was dependent on the concentration of sulfide generated by the SRB metabolism and is hardly related to the biological activity of SRB and the SRB itself. Sherar *et al.* [11] concluded that the abiotic sulfide experiment is sufficient enough to develop a prediction of steel corrosion rate. However, this simplistic approach does not account for the heterogeneity that exists in the bacterial system.

In 2013, Fatah *et al.* [12] conducted the study on the effect of abiotic sulfide in a simulated solution containing metabolic product species. They concluded that the corrosion rate of X52 steel increased with the addition of 50 ppm sulfide. However, the corrosion rate decreased with the addition of 200 and 400 ppm sulfide. The increase of corrosion rate is due to the increase of cathodic reaction in the presence of sulfide. Whilst, the corrosion protection was related to FeS film formed, typically pyrrhotite and greigite.

Fatah *et al.* [13] also develop an empirical equation to predict SRB corrosion based on the effect of SRB metabolic products using abiotic chemistry approach. The curve obtained from LPR data were then fitted by using multiple non-linear regression model. Statistical analyses showed that the equation developed has a 95 % level of confidence. Comparison of the empirical equation with general corrosion rate obtained from open literature showed good agreement result. However, since the typical corrosion resulted by SRB is not only in the general form but also in pitting form, it is important to see the empirical equation performance to predict pitting depth.

Therefore, the objective of the study is to predict the pitting depth by using the empirical equation and compared the result with pitting depth found in the experiment and in the field.

## 2. METHODOLOGY

The empirical equation used is based on Fatah's *et al.* [14] study on the effect of SRB metabolic species. They showed that the corrosion rate of X52 steel is influenced by three dominant metabolic species resulted by SRB, i.e. sulfide, sulfite, and lactate.

$$\log CR = 0.685 + 0.163 \log[\text{sulphite}] - 0.444 \log[\text{sulphide}] - 0.0711 \log[\text{lactate}] \quad (1)$$

Where,  $CR$  is corrosion rate (mm/yr),  $[\text{Sulphite}]$  is sulphite concentration (ppm by weight),  $[\text{Sulphide}]$  is sulphide concentration (ppm by weight) and  $[\text{Lactate}]$  is lactate concentration (ppm by weight).

The above equation was used to predict the general corrosion rate which then converted to pitting depth. The calculation was conducted at 200 ppm lactate with various sulfide and sulfite concentrations (10, 50, 200 and 400 ppm).

The following assumptions were made for calculated pitting depth:

1. The pit form is assumed in the cylindrical and hemispherical form [15, 16].
2. For cylindrical form, the pitting diameter is assumed to equal to 160  $\mu\text{m}$ . The diameter assumption was based on pitting diameter found in the SRB experiments [17].

The pitting depth equivalent is derived from the following equation [18]:

$$Cr(\text{mm./ yr}) = \frac{87.6xW}{DxAxT} \quad (2)$$

For the mass loss

$$W(\text{mg}) = \frac{CrxDxAxT}{87.6} \quad (3)$$

$$W(g) = \frac{CrxDxAxT}{87600} \quad (4)$$

Where,

W = weight loss (mg)

D = metal density (g/cm<sup>3</sup>)

A = area of sample (cm<sup>2</sup>)

T = exposure time (hours)

Cr = corrosion rate (mm/yr)

The total metal loss is equal to the volume of the pit, therefore:

$$D(g/cm^3) = \frac{W}{V} \quad (5)$$

$$V(cm^3) = \frac{W}{D} = \frac{1}{87600} CrxAxT \quad (6)$$

For cylindrical geometry, the volume is  $V = \frac{1}{4}\pi d^2 h$

Thus, the pit depth is

$$h(cm) = \frac{4xCrxAxT}{87600x\pi d^2} \quad (7)$$

Where d is pitting diameter in cm.

$$h(\mu m) = \frac{4xCrxAxT}{8.76x\pi d^2} \quad (8)$$

For hemispherical geometry, the volume is  $V = \frac{2}{3}\pi r^3$

Since the hemisphere depth is equal to its radius, therefore, the pitting depth is

$$r = \sqrt[3]{\frac{3V}{2\pi}} \quad (9)$$

For the comparison purpose, a minimum value of 75 (μm) and a maximum value of 790 (μm) pitting depth is used. These data are taken based on the pitting depth found in the real SRB experiment [19] and in the wastewater environment [20].

### 3. RESULTS

#### 3.1. Pitting depth prediction

The prediction pitting depth of carbon steel ( $\mu\text{m}$ ) in various sulfite and sulfide concentrations for the cylindrical and hemispherical form is shown in Table 1 and Table 2, respectively.

**Table 1:** Pitting depth ( $\mu\text{m}$ ) of carbon steel (in cylindrical form) in various sulfite and sulfide concentrations.

SULPHITE CONCENTRATIONS (PPM)	SULPHIDE CONCENTRATIONS (PPM)			
	10	50	200	400
10	845	427	233	173
50	1095	553	302	224
200	1377	695	380	282
400	1542	778	425	316

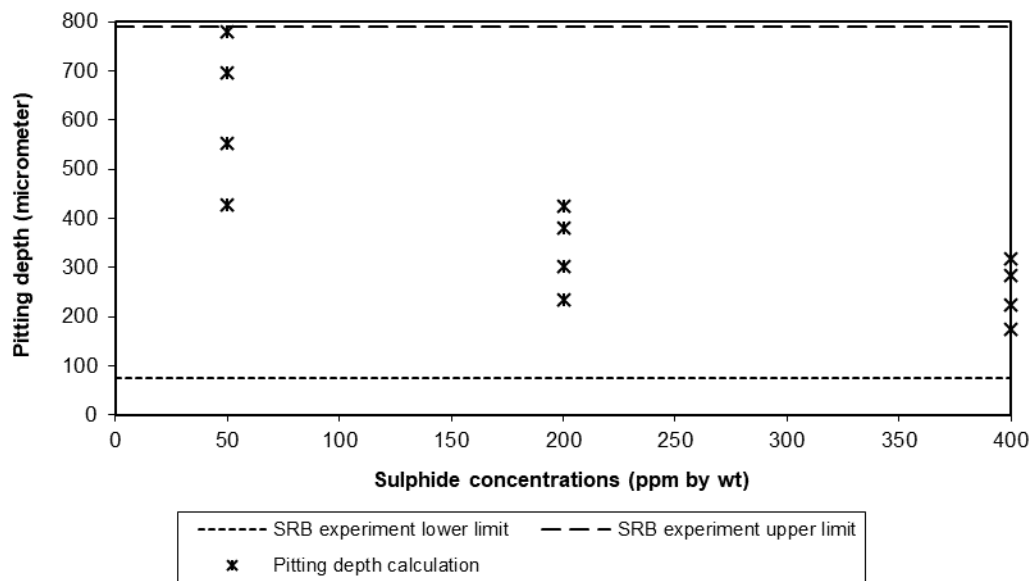
**Table 2:** Pitting depth ( $\mu\text{m}$ ) (in hemispherical form) in various sulfite and sulfide concentrations.

SULPHITE CONCENTRATIONS (PPM)	SULPHIDE CONCENTRATIONS (PPM)			
	10	50	200	400
10	200	160	130	118
50	219	174	142	129
200	236	188	153	139
400	245	195	159	144

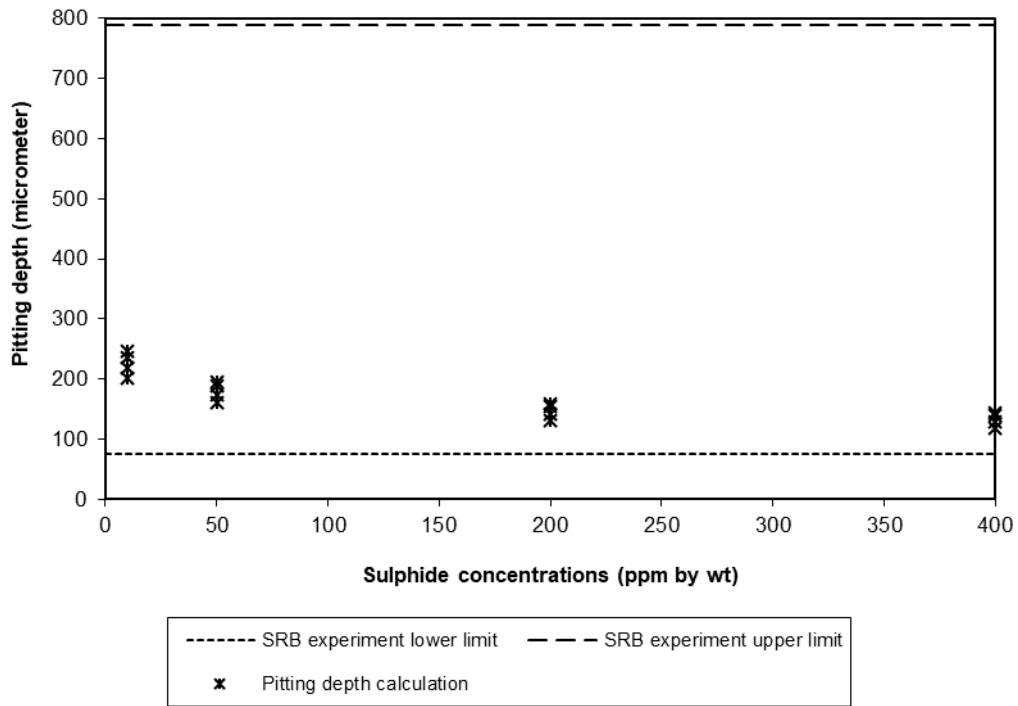
From Table 1 & 2, it is observed that with the addition of sulfide concentrations, there is decreasing in the pitting depth. In contrast, there is increasing of pitting depth with the addition of sulfite concentrations.

#### 3.2. Pitting depth comparison

Figure 1 shows the comparison of calculated pitting depth equivalent results with SRB experiment in the cylindrical geometry. For hemispherical geometry, the comparison is shown in Figure 2.



**Figure 1:** Comparison of pitting depth equivalent calculation with SRB experiments/field in cylindrical geometry.



**Figure 2:** Comparison of pitting depth equivalent calculation with SRB experiments/field in hemispherical geometry.

Both results (in cylindrical and hemispherical geometry) show that the pitting depth equivalent calculation is in the range of minimum and maximum pitting depth of SRB experiment/environment. However, it is observed that the pitting equivalent in cylindrical geometry shows more reasonable results than that of hemispherical geometry.

#### 4. DISCUSSION

In a solution containing sulfide, the decreasing of pitting depth is an indication of an inhibitive characteristic of H<sub>2</sub>S. Its inhibitive characteristic is related to the ferrous sulfide film, which is typically a thin mackinawite film [21, 22]. The mackinawite film could further transform into a more stable film, e.g. troilite, pyrrhotite, greigite, and pyrite [23]. Fatah *et al.* [12] confirmed the presence of FeS film i.e. pyrite, greigite and mackinawite in their study. Furthermore, Fatah *et al.* [12] also confirmed that there is increasing the FeS film thickness with the addition of sulfide concentrations.

According to Ma *et al.* [24, 25], a probable mechanism of the inhibitive effect of H<sub>2</sub>S could be described as follows:



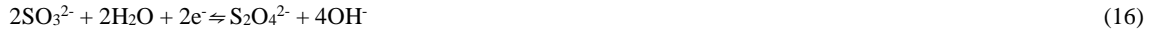
The species FeSH<sup>+</sup> may be incorporated directly into a growing layer of *mackinawite* via Eq. (5.6)



Or it may be hydrolyzed to yield Fe<sup>2+</sup> via Eq. (5.7)



Additionally, it is observed that the pitting depth increase with the addition of sulfite. According to Hemmingsen and Valand [26], sulfite ion can be oxidized to sulfate ions or reduced to hydrogen sulfide with the first partial reaction to form dithionite ion ( $\text{S}_2\text{O}_4^{2-}$ ). The reactions are shown below [26, 27]:



Furthermore, Fatah *et al.* [12] also confirmed that there is decreasing the FeS film thickness with the addition of sulfite concentrations.

In addition, the prediction in cylindrical geometry shows more reasonable result compare to hemispherical geometry. Because of its symmetrical geometry, the pitting depth in cylindrical is distributed equally along the geometry. While in hemispherical, as the geometry is not symmetrical, the depth is focus on the cone side. Thus, increasing the depth of pitting prediction.

## 5. CONCLUSION

The prediction of pitting depth shows that the pitting depth decreased with increasing sulfide concentrations. In contrast, the pitting depth increased with increasing sulfite concentrations. The decreasing of pitting depth in the presence of sulfide is related to the inhibitive characteristic and the thickness of the FeS formed. Meanwhile, the increasing of pitting depth in the presence of sulfite is due to the decreasing thickness of the film formed. Additionally, pitting equivalent in cylindrical geometry show more reasonable results than that of hemispherical. This is due to the equal distribution of the pitting depth along the cylindrical geometry.

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