# THE EFFECT OF $FeSO_4$ CONTAINING SOLUTION ON MICROBIOLOGICAL INFLUENCED CORROSION BY DESULFOVIBRIO BACULATUS BACTERIA ON API 5L X65 STEEL

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## Abstract

Microbiological Influenced Corrosion (MIC) is a common cause of metallic failure and currently known as one of the important case in pipeline failure. Sulfate Reducing Bacteria (SRB) is a bacteria that frequently caused corrosion in steel surface by creating pits.

In this research, the corrosion test was done by using one species of SRB which is Desulfovibrio Baculatus. The water that contains bacteria growth medium (API Sulfate Broth) is used as a media for API 5L X65 steel corrosion test. Sulfate for the growing of SRB was added in the solution for 8.56, 17.12, 42.8 and 85.64 ppm, and the immersion test was carried out for 1, 7, 14 and 21 days. The source of sulfate is $FeSO_4.7H_2O$, and this compound was also considered as a source of Iron (II).

The result shows that the weight loss increased at 7 to14 days of immersion time with immersion period as well as the increase of $FeSO_4$ content. But, it decrease after 14 days of immersion that represents a maximum weight loss attained at this moment. Morphologic observation revealed that the corrosion product consists of Iron Oxide and biological deposits that formed at the beginning of corrosion test, and after that, the formation of Iron Sulfide occurred were associated with the increase of corrosion rate.

So, the increase of $FeSO_4$ content as the SRB nutrition in the solution, gives a strong influence in the increasing of corrosion rate and formation of an unstable corrosion product.

**Keywords**: Desulfovibrio baculatus, FeSO4 Content, Immersion, MIC, SRB

## Introduction

Microbiological Influenced Corrosion (MIC) is a corrosion phenomenon that was caused by bacteria activity at metallic surface. This type of corrosion, become severe especially between pH 4 to 9 and at temperature between 10˚C to 50˚C, and it became more aggressive in a stagnant condition.

In MIC, Sulfate Reducing Bacteria (SRB) is a microorganism that was known of causing many failures especially in pipelines. This bacterium is remaining active at higher temperature of $100^oC$ and high pressure between 2500-4500 psi [1]. These bacteria corrode steel with formation of tubercle and create a corrosion cell below the tubercle [2] which creates pits.

Many microorganisms as bacteria, algae, fungi stay and growth at the metal surface and form a biofilm [2]. This film creates certain surface condition which increases the possibility of the occurrence of corrosion. In this condition, microorganism modify the variable of media or environment conditions as pH, corrosion rate, concentration etc. Hence the metal-electrolite interface condition will be affected by the present of biofilm and promote an acceleration of corrosion.

API 5L X65 steel is currently used in oil and gas industry for pipelines materials. Its character is adequate for pipelines operation condition, even though it suffers from a corrosion failure and it was reported in Canada that 20% of pipeline failure caused by MIC.

SRB is the bacteria that reduce sulfate to sulfide in its metabolism process [1, 2, 3]. This process is accompanied by oxidation of iron to $Fe^{2+}$ and with $S^{2-}$ form an iron sulfide. The complete reactions are as follows [2]:

| | | |
|---|---|---|
| $4Fe \rightarrow 4Fe^{2+} + 8e^-$ | anodic reaction | (1) |
| $8H_2O \rightarrow 8H^+ + 8OH^-$ | water dissociation | (2) |
| $8H^+ + 8e^- \rightarrow 8H$ | cathodic reaction | (3) |
| $SO_4^{2-} + 8H \xrightarrow{SRB} S^{2-} + 4H_2O$ | cathodic depolarization | (4) |
| $Fe^{2+} + S^{2-} \rightarrow FeS$ | corrosion product | (5) |
| $3Fe^{2+} + 6OH^- \rightarrow 3Fe(OH)_2$ | corrosion product | (6) |

The variation of concentration of sulfate in the media and time of exposure, and surface morphology will be studied in this corrosion test of API 5L X65 steel.

## Experimental Procedures

16 pieces of API 5L X65 steel with certain dimension were prepared for immersion corrosion test. Those samples were cut and ground with a 1000 mesh grinding paper.

**Table 1. Chemical Composition of API 5L X65 Steel**

| No | Elements | (wt-%) |
|---|---|---|
| 1. | Fe | Balance |
| 2. | C | 0.070 |
| 3. | Si | 0.276 |
| 4. | Mn | 1.050 |
| 5. | P | 0.050 |
| 6. | S | 0.009 |
| 7. | Cr | 0.108 |
| 8. | Mo | 0.164 |
| 9. | Ni | 0.287 |
| 10. | Al | 0.040 |
| 11. | Cu | 0.192 |
| 12. | Ti | 0.004 |
| 13. | V | 0.080 |

**Tabel 2. Mechanical Property of API 5L X65 Steel**

| Yield strength (Mpa) | Tensile strength (Mpa) |
|---|---|
| 445 | 519.9 |

Figure 1. Immersion of steel samples in the media

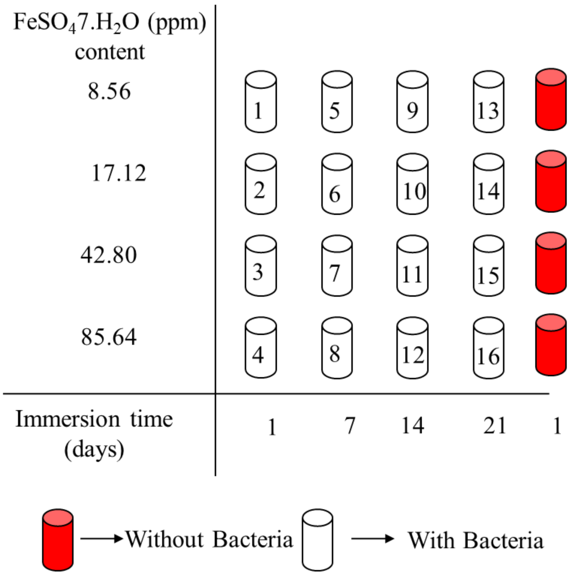


Figure 2. Experimental matrix

At the beginning, the chemical composition and the mechanical behavior of this steel were tested, and the result is reported in Table 1 and Table 2.

Desulfomircobium Baculatum or Desulfovibrio Baculatus as an SRB species was used in this experiment. A mixture of 1 g NaCl, 0.52 g sodium lactate, 0.1 g yeast extract, 0.02 g $MgSO_4.7H_2O$, 0.01 g ascorbic acid, 0.001 g $K_2HPO_4$ in 100 ml aquadest was used for the growing medium. After sterilization in the autoclave, the beaker glass containing bacteria were introduced to the medium for inoculation for 1 day.

An amount of 25ml bacteria medium was mixed with 250 ml water and added by 8.56, 17.12, 42.8 and 85.64 ppm $FeSO_4.7H_2O$ as a source of Sulfate, and the steel samples were immersed in this medium for 1, 7, 14 and 21 days as shown on Figure 1. For control and comparison, the medium without the bacteria was employed for the test.

## Discussion

On the sample surface a formation of black spot was observed this indicated the presence of bacteria colony or biological deposits and create a corrosion cell as shown at Figure 3. This phenomenon is called passive influence, and the concentration cell forms a variation of a conditions situation below the colony and at the bulk system [2, 3, 5]. These variation conditions are oxygen concentration, $Fe^{2+}$ dan $SO_4^{2-}$ content, slimes and excretion product content beneath the colony.

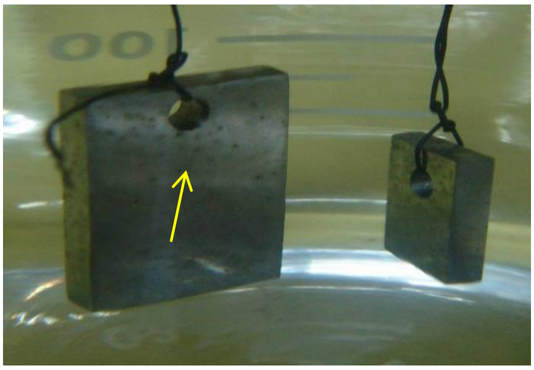

Figure 3. Black spot at the sample surfaces indicates the formation of biological deposit

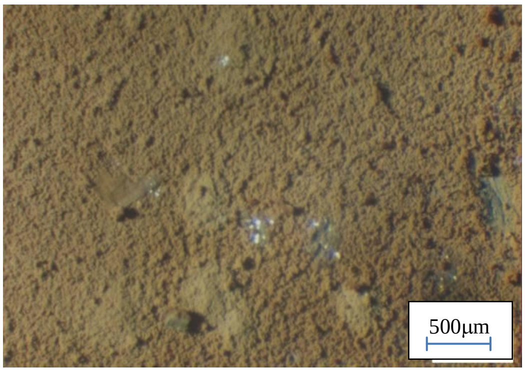


Figure 4. Corrosion products at sample surfaces after 3 weeks of immersion

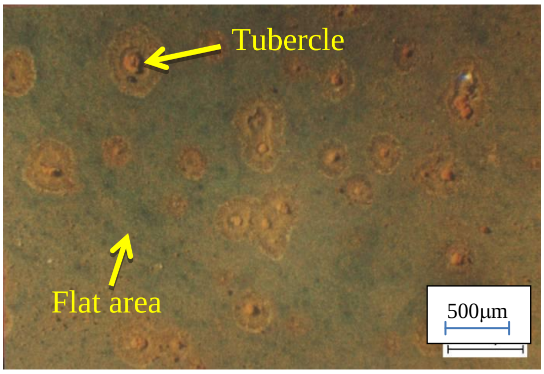


Figure 5. The presence of tubercle in spot forms that cover pits after the sample was taken from the solution

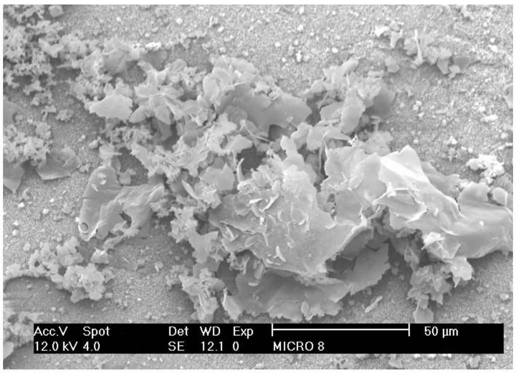


Figure 6. Morphology of plate like corrosion product (Sample 8)

From the sample morphology, the formation of corrosion product was developed in thickness and quantity following the immersion time. Sample that was immersed for 3 days has a surface covered by a thick corrosion product and biological deposit as shown by Figure 4, but it could be removed easily when the sample was taken from the solution with small agitation or vibration.

From surface observation, it could be observed from Figure 5, a corrosion product consists of Iron Hydroxide in spot forms or tubercles that covered the pits beneath. Around those spots, the biological deposits or biofilm is still covering the flat surface of the samples.

SEM observation, at sample 8 and 12 that were immersed for 1 and 7 days in 85.64 ppm sulfate concentration, showed an image of plate like corrosion product as shown by Figures 6 and 7. EDS examination result of those products in Figure 8 shows the present of sulfur and oxygen in those oxides which are iron (II) oxide and iron sulfide. Observation to the surface of the sample as shown on Figure 5, showed that there was a failure of biological deposits as shown by Figure 9. An examination was done to this area and its surrounding and the result is presented in Table 3.

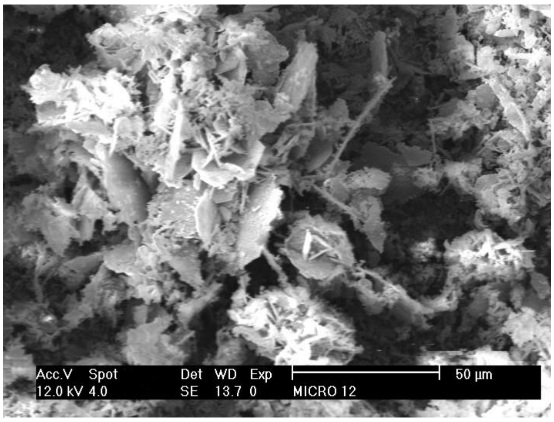


Figure 7. Morphology of plate like corrosion product (sample 12)

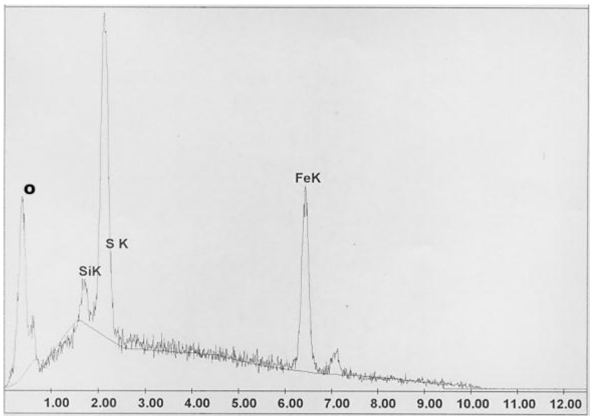


Figure 8. EDS observation on the plate like corrosion product

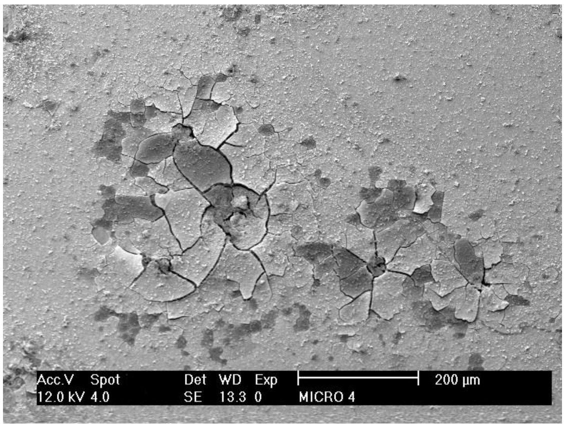


Figure 9. The failure of biofilm.

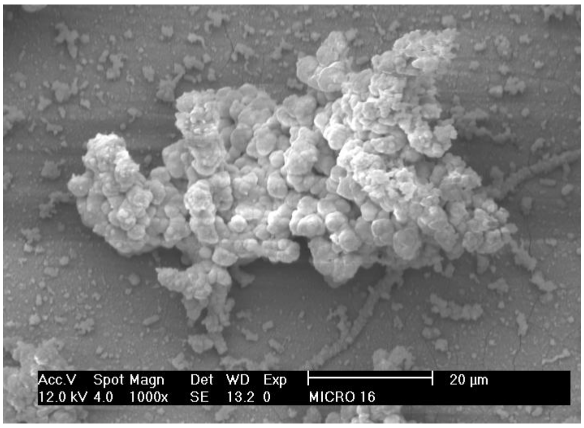


Figure 10. Globular hydroxide.

It was found that the failed area is rich of sulfur comparing to the unfailed area. It explain that the surface was covered by biofilm. There were two layers of corrosion products, the top layer consist of iron oxide and the bottom layer near the metal surface consists of iron sulfide. The failure on top layer failure cause the exposure of the bottom layer which rich in sulfur content. Later, it forms a hydrosulfide in association with humidity of the air [3].

**Table 3. Composition of the Fractured Biofilm and its Surrounding**

| Inside the failed area (Wt-%) | | Around the failed area (Wt-%) | |
|---|---|---|---|
| O | 2.52 | O | 1.14 |
| Si | 13.45 | Si | 17.87 |
| S | 0.76 | S | 4.57 |
| Fe | 83.28 | Fe | 76.42 |

Robert Jefrey and Robert E Merchers (2002) found a globular corrosion product at the surface of the samples after certain period of corrosion test. Analysis on this product shows that this globular corrosion product is iron hydroxide [6]. This type of hydroxide was found also at the sample no 16 (figure 2) that was immersed for 21 days as shown on Figure 10.

The observation result for samples that were immersed for 1 to 7 days in the corrosion media, are shown on Figures 11 to 15. Without the presence of bacteria, there is no indication of corrosion at the surface, but in the same period using a media containing bacteria, the initiation of pits could be visibly seen as shown on Figure 12. Pits were formed below the tubercle. Tubercles are growing with the increase of the immersion time as presented by Figure 12 to Figure 15. The formation of pits follows the formation of tubercles.

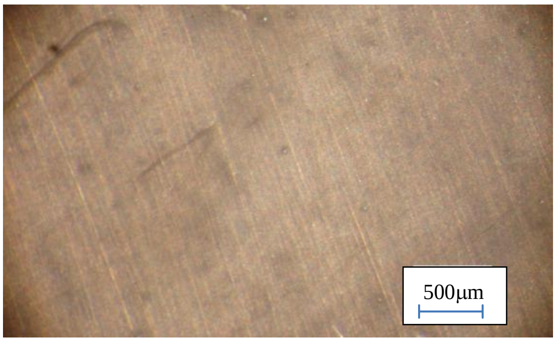


Figure 11. Sample surface after 1 day immersion in the media without bacteria


Figure 12. Sample surface after 1 day immersion in the media with bacteria

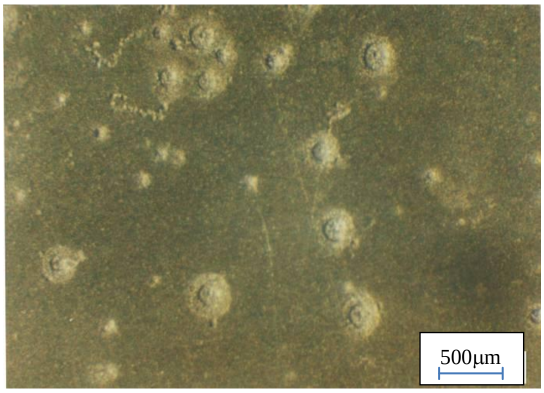


Figure 13. Sample surface after 14 days immersion in the media with bacteria

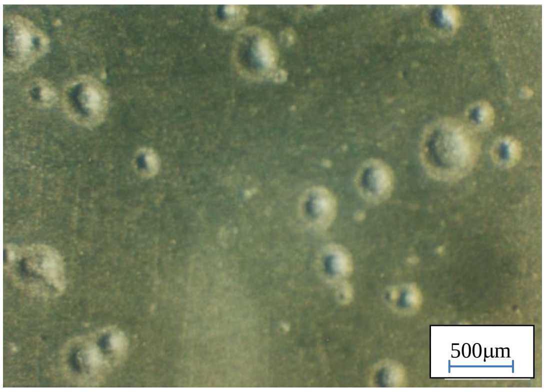


Figure 14. Sample surface after 21 days immersion in the media with bacteria

Figure 12 and 13 show some tubercles and around those tubercles it could be observed a clear area that was called Aureoles. The area where the Aureoles are found, is the area that was etched lightly and forme a new concentration cell where the formation of corrosion products become more effective [3]. At the higher velocity of fluid flow, the form of Aureole become elliptic in the direction of fluid flow.

The tubercles will growth with the increasing time. The excessive growth of the tubercles forms a specific corrosion product that was called as bull eye pattern [3] which is in general situated at the middle of aureoles.

It was known that the weight change will increase with immersion time (Figure 15). But, it was found from the corrosion test, rate of weight change which represent corrosion rate has a significant increase between 7 to 14 days. Beyond 14 days, the corrosion rate will be lowered and this was caused by the decrease of sulfate source that consumed by the bacteria activity.

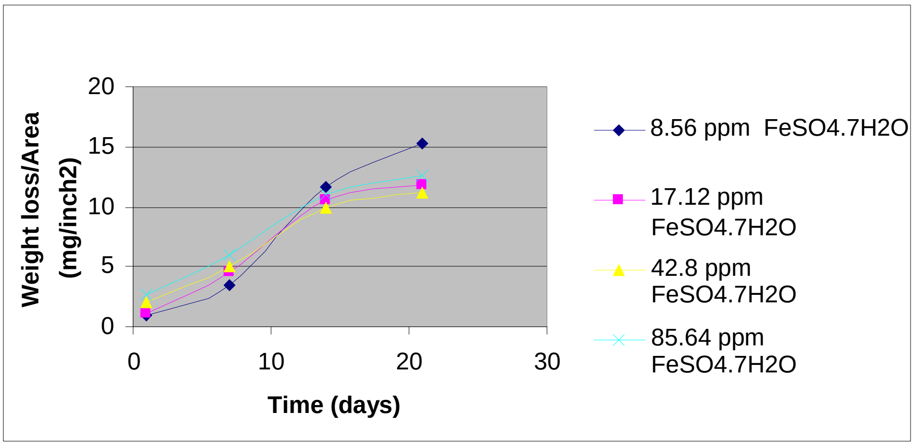


Figure 15. Influence of immersion time to weight loss/area

On the other hand, the corrosion rate was also relatively low at the beginning (1 to 7 days exposure time) due to the adaptation process of the bacteria from the aerobe to anaerobe condition.

The similar situation in general was observed for experiment in different $FeSO_4$ concentration. The corrosion rate was low at the beginning, increase after 7 days and decrease again over 14 days of immersion.

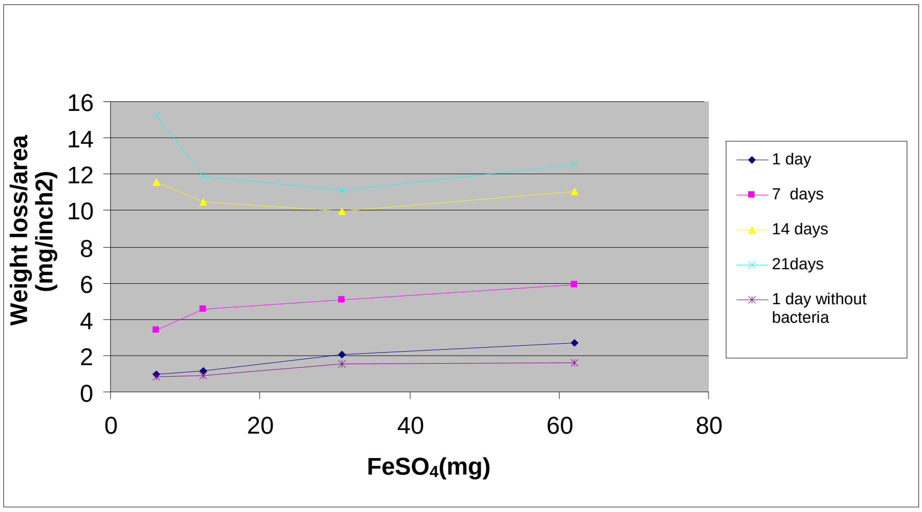


Figure 16. Influence of $FeSO_4$ to weight loss/area

From Figure 16, an important weight change for a long period of corrosion test. But it seems that is no important difference with the increase of $FeSO_4$.

However, the influence of bacteria is very clear. It creates a local corrosion in the form of pits, and this influence become higher with the increase of exposure time. In a specific condition the bacteria is capable to change the uniform corrosion to localized corrosion.

It must be noted that this experiment was done in stagnant condition and further test in a flowing media could be done for having an understanding on the effect of fluid velocity.

Due to the static condition, the presence of sulfate ions around tubercle is very low and pit penetration become less effective.

## Conclusions

The Desulfovibrio Baculatus is classified as SRB bacteria. It attacks the API 5L X65 Steel in a form of pitting as one of the MIC phenomena. The corrosion rate increase with the increasing of $FeSO_4$ content, but the bacteria behavior which can change in different situation and affect the corrosion rate model. It seems that a severe corrosion could be promoted by the formation of unstable corrosion product and it will decrease again when a stable corrosion product was formed.

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