

## **Effects of Mass Transfer and Flow Conditions on SRB Corrosion of Mild Steel**

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### **ABSTRACT**

Microbiologically Influenced Corrosion (MIC) is a growing problem in the oil and gas industry resulting in huge financial losses. Sulfate Reducing Bacteria (SRB) are often the culprits although many other microorganisms can also be directly or indirectly involved. From the bioprocess engineering angle, mass transfer and flow conditions are very important in SRB biofilm formation and MIC corrosion rates. Experiments were carried out in a 2-liter electrochemical glass cell bioreactor with a carbon steel rotating cylinder coupon. ATCC 7757 strain of *Desulfovibrio desulfuricans* was used in this work with the ATCC 1249 medium. Experimental data indicated that mild agitations with a low linear velocity at increased cell growth and MIC corrosion compared to stagnant conditions, because mass transfer was facilitated. However, a high linear velocity exhibited inhibition of cell growth and MIC corrosion. The results have implications in predicting and controlling MIC in pipeline flow systems.

Keywords: Sulfate reducing bacteria, microbiologically influenced corrosion, mass transfer, *Desulfovibrio desulfuricans*

## INTRODUCTION

In 2002, the U.S. Federal Highway Administration released a landmark study on the direct costs of metallic corrosion in nearly all U.S. industries. The study conducted by C. C. Technologies reported that the total estimated direct cost of corrosion in the U.S. amounts to \$276 billion per year or approximately 3.1% of the gross domestic product of the U.S. Flemming<sup>2</sup> in a separate review attributed 20% of overall corrosion cost to Microbiologically Influenced Corrosion (MIC). At this percentage or even a much lower one, the cost of MIC is staggering. MIC is a growing problem in the oil and gas industry. Millions and Millions of dollars are spent each year on MIC mitigation. Many bacteria have been found to be involved in MIC<sup>3,4</sup> either directly or indirectly. Sulfate reducing bacteria (SRB) are the most common culprits. They are anaerobic bacteria that reduce sulfate to sulfide. This results in souring due to H<sub>2</sub>S production and sometimes FeS precipitation due to FeS supersaturation in a fluid.

By secreting sticky polymers known as exopolymers, some microbial cells are able to aggregate and adhere to a solid surface to form biofilms<sup>5,6</sup>. Under the biofilms, pitting attacks can occur. Mass transfer plays an important role in cell growth and MIC. Biofilms act like a mass transfer barrier. Nutrients, metabolites and corrosion products are transported across the biofilms. It is well known in bioprocess engineering that improved mass transfer enhances the growth of both suspended cells and immobilized cells<sup>7</sup>. Stagnant fluid offers the lowest mass transfer rates because convective mass transfer does not exist without fluid flow. However, cell adhesion and biofilm formation may benefit from the absence of shear. At the other end, a fast moving fluid generates turbulence that provides enhanced mass transfer, but the accompanying high shear stress may prove to be harmful to the cells and may lead to the prevention of cell adhesion and thus biofilm formation. A sufficiently high shear stress may even detach an established biofilm<sup>8,9</sup>. It was reported in biofouling studies that biofilm thickness increased with a higher nutrient concentration when fluid shear was held constant<sup>10</sup> but it decreased with fluid shear when the substrate-loading rate was kept constant<sup>11</sup>. Apparently, mild fluid flow offers the most favorable environment for cell adhesion and sessile growth and it likely yields the highest MIC corrosion rate.

Currently, MIC mitigation depends mostly on biocide and biostats. Increasingly restrictive environmental regulations put growing pressure on the uses of these chemicals. Costs are subsequently increasing. In recently years, some nonbiocidal approaches started to emerge, such as adding nitrate to promote the growth of nitrate reducers that deplete the nutrients needed for SRB growth<sup>12,13</sup>. This work studied the effects of mass transfer and fluid flow conditions on the MIC of carbon steel. High fluid shear was investigated for its potential to inhibit cell growth and MIC.

## EXPERIMENTAL PROCEDURE

The ATCC 7757 strain of *Desulfovibrio desulfuricans* was used in this work. It is a common SRB strain found in mud, soils and marine sediments. Table 1 shows the composition of the ATCC 1249 medium with reduced ferrous ion concentration used for cell growth. Ferrous ammonium sulfate in the medium is heat sensitive. It was filter sterilized and then mixed with an autoclaved solution of other nutrients. Ferrous ion addition to the medium leads to FeS precipitation and FeS film formation on the coupon during the experiments. They may complicate experimental results. However, without it experiments would last much longer. A 2-liter electrochemical glass cell bioreactor was set up for the experiments. The glass cell had a rotating shaft in the center. Its tip was fitted with a C1018 coupon that served as a working electrode. The cylindrical coupon had an outer diameter of 1.20 cm and an exposed surface area of 5.40 cm<sup>2</sup>. The bioreactor was equipped with a Gamry potentiostat, a platinum counter

electrode and a saturated Calomel Ag/AgCl reference electrode that was connected to the glass cell via a Luggin capillary. Before each experimental run, the bioreactor was autoclaved. 1.8 to 2.0 liters of the sterilized medium was poured into the glass cell and then the medium was sparged with filtered nitrogen for 45 minutes to remove oxygen. After deoxygenation, the medium was inoculated with a fresh SRB culture that was about four days old. A small positive overhead pressure was maintained by feeding filtered nitrogen to the glass cell to prevent contamination during cell growth. To accelerate the experiments, the temperature of the medium in the glass cell was maintained at 37°C using a hotplate that was linked to a thermocouple inserted into the medium. The MIC corrosion rates were measured by the linear polarization resistance (LPR) method in addition to coupon weight loss measurements. Planktonic SRB cell numbers were counted under an optical microscope using a hemacytometer with serial dilutions. Each experimental run lasted five days.

## RESULTS AND DISCUSSION

Silverman<sup>14,15</sup> demonstrated that there are mathematical relationships between the coupon rotation speed in a glass cell and the linear velocity in pipe flow. The well-known Silverman correlations enabled the simulation of high linear velocities in pipe flow by using a glass cell.

In the glass cell experiments, the sterilized medium initially was light yellow in color and turbid as seen in Figure 1a. Figure 1b shows that after 2 days, the entire broth started to become black and became completely black in color in about two hours. This was due to the increased FeS production from the reduction of sulfate to sulfide by the SRB cells. After the FeS concentration reached supersaturation, black FeS particles precipitated and darkened the broth. Figure 2 shows that the LPR corrosion rate curves for the 0 rpm and 1000 rpm runs exhibited a peak at the time of FeS supersaturation on the end of Day 2. Surprisingly, the peak occurred at a much later time of around 72 hours after inoculation, corresponding to an extra delay of one day. Both LPR corrosion rates and weight loss corrosion rates in Figure 2 indicate that mild agitation at 1000 rpm yielded a higher corrosion rate than at 0 rpm. Further increasing the coupon rotation rate to 3000 rpm caused the corrosion rate to decrease.

Figure 3 shows the planktonic cell counts in the three glass cell experiments. It is obvious that 1000 rpm rotation rate gave faster initial cell growth. On Day 4 and afterwards, the cell counts were similar in all three runs. Although it is known that planktonic cell counts do not directly correlate with MIC corrosion rates, Figure 3 does show that coupon rotation rates had a significant effect on planktonic cell growth.

Figure 4 shows the pits on the cylindrical coupon surfaces left behind by MIC pitting attacks. The coupons were taken out at the end of Day 5 after each experimental run. Figure 4 shows that the 3000 rpm coupon had fewer but larger pits, corresponding to a larger weight loss compared to the 0 rpm coupon. The 2000 rpm coupon had far more and larger pits than the other two coupons. The pit images in Figure 4 qualitatively matched corrosion rates shown in Figure 2. It is reasonable to believe that at a high coupon rotation rate, the medium in the glass cell was agitated quite severely even though the smooth coupon could not match an impeller designed for efficient agitation. The shear at the coupon surface might have inhibited cell adhesion and the formation of a protective FeS film. This corresponds to using high linear velocity in pipe flow to inhibit biofilm buildup.

Obviously, more work needs to be done in this area especially on biofilm and FeS film quantification. It should also be noted that there is a significant centrifugal force on the rotating coupon in a glass cell with high rotation rate. This centrifugal force could repel cells away from the coupon

surface. Because this centrifugal force is absent in pipe flow, it is necessary to validate the data from glass cell experiments using a pipe flow system. A 4" ID MIC flow loop is currently being designed at Ohio University for this purpose. The flow loop will have a test section with different pipe diameters to achieve different linear velocities up to 9 m/s.

## CONCLUSIONS

This work showed that mild agitation facilitated initial planktonic cell growth and increased MIC corrosion of carbon steel probably because the cells benefited from enhanced nutrient distribution and mass transfer of corrosion products. This observation contradicted the conventional belief that a stagnant fluid was more prone to MIC attack than a moving fluid. Experimental results also showed that when the agitation rate became much higher, both initial planktonic cell growth and MIC rate experienced inhibition. This result demonstrated that fluid shear might be potentially used as a useful tool in MIC mitigation.

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TABLE 1  
COMPOSITION OF MODIFIED ATCC 1249 MEDIUM FOR SRB

<b>Component I</b>	MgSO <sub>4</sub>	2.0 g
	Sodium Citrate	5.0 g
	CaSO <sub>4</sub>	1.0 g
	NH <sub>4</sub> Cl	1.0 g
	Distilled Water	400 ml
<b>Component II</b>	K <sub>2</sub> HPO <sub>4</sub>	0.5 g
	Distilled Water	200 ml
<b>Component III</b>	Sodium Lactate	3.5 g
	Yeast Extract	1.0 g
	Distilled Water	400 ml
<b>Component IV</b>	Fe(NH <sub>4</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub>	0.127 g
	Distilled Water	50 ml

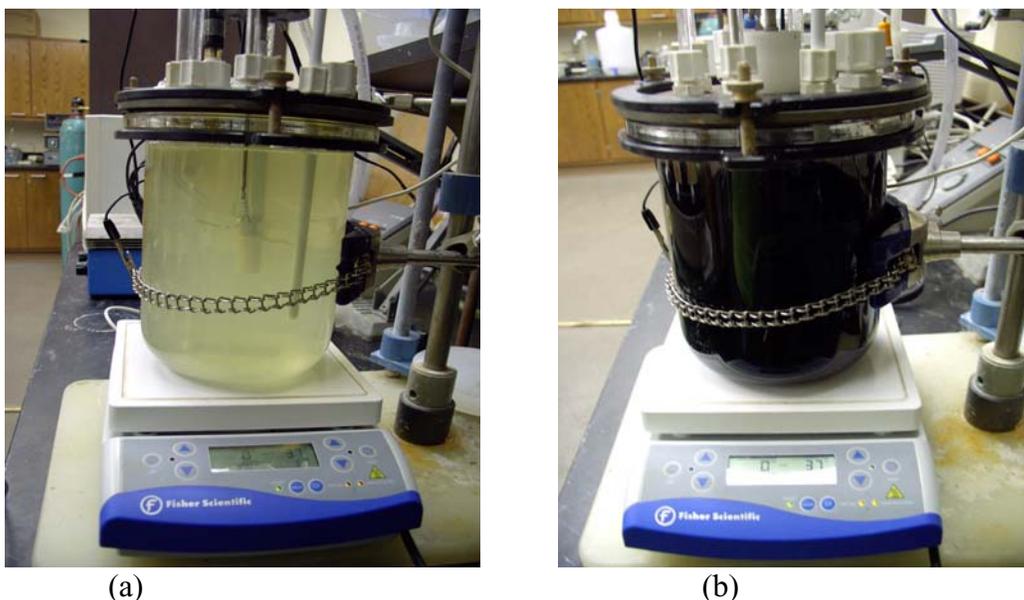


Figure 1. Electrochemical glass cell bioreactor images for the experimental run with 25 ppm  $\text{Fe}^{2+}$  at a rotation rate of 1000 rpm. (a) Picture taken on Day 1. The medium had a turbid light yellow color. (b) Picture taken on Day 3. The medium was completely dark in color due to  $\text{FeS}$  precipitation.

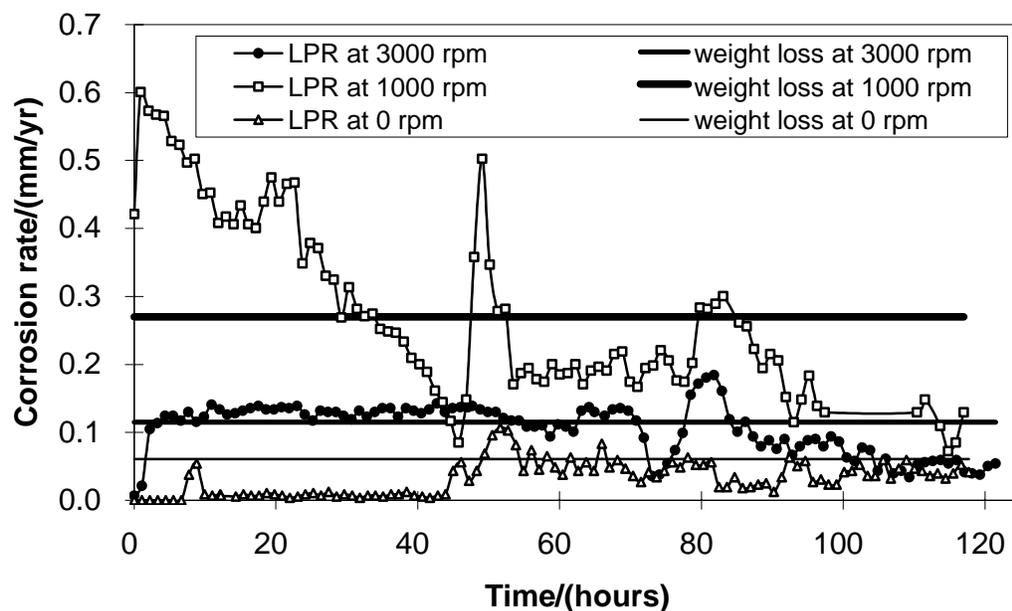


Figure 2. LPR and weight loss corrosion rates for the glass cell experiments at three different rotation rates. Initial cell counts were  $1.0 \times 10^5$  cells/ml (for 0 rpm),  $1.1 \times 10^5$  cells/ml (for 1000 rpm) and  $1.0 \times 10^5$  cells/ml (for 3000 rpm), respectively.

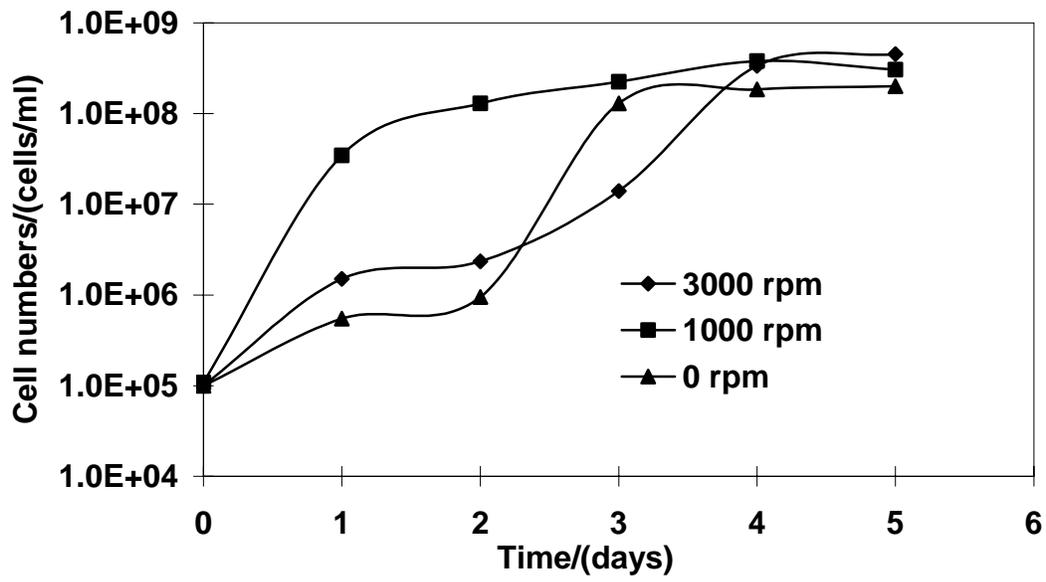


Figure 3. Planktonic cell number counts for the glass cell experiments.

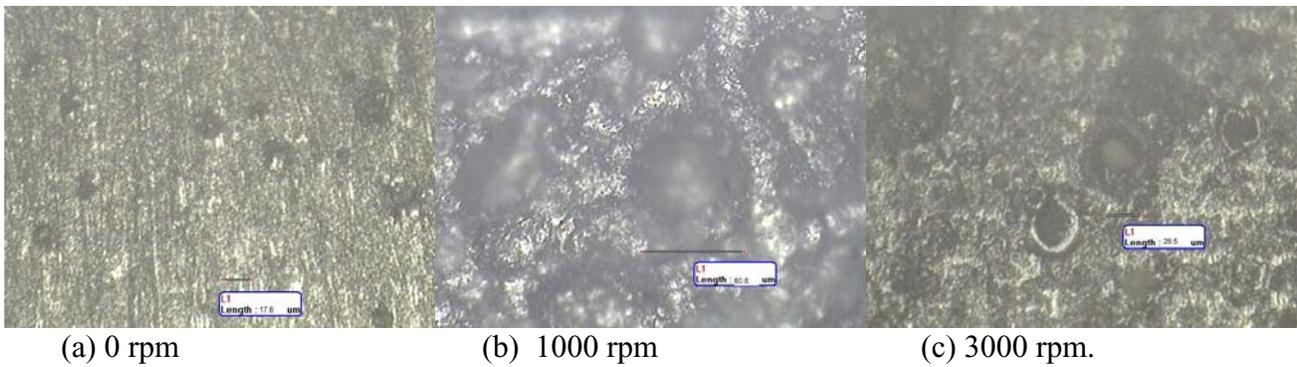


Figure 4. Pits on coupon surfaces after cleaning under microscope at 250X.