Demystifying MIC Mechanisms

Tingyue Gu and Dake Xu
Department of Chemical and Biomolecular Engineering
Stocker 159, Ohio University
Athens, Ohio 45701
Phone: 740-593-1499; Fax: 740-593-0873
gu@ohio.edu

ABSTRACT

Microbiologically Influenced Corrosion (MIC) is becoming increasingly important, especially to the oil and gas industry as more and more reservoirs are soured due to increased practice of water flooding and pipelines are aging (some even beyond their anticipated life expectancies). Despite the fact that MIC research has been going on for several decades, there is much confusion in the MIC literature regarding the fundamental mechanisms in MIC. This has greatly hindered the development of reliable prediction and new mitigation methods. A new MIC theory entitled Biocatalytic Cathodic Sulfate Reduction (BCSR) theory was presented in NACE/2009. It sheds some lights on MIC mechanisms. This work demonstrates how the theory together with bioenergetics, electrochemical kinetics, and mass transfer can be used to explain various mysteries in MIC. Some experimental data and model simulation results for MIC due to sulfate reducing bacteria (SRB) and acid producing bacteria (APB) are used in the explanations.

Keywords: MIC, Model, Mechanism, SRB, APB, Sulfate reduction, Proton reduction, Acid reduction
INTRODUCTION

Microbiologically Influenced Corrosion (MIC) causes billions of dollars in damages each year to the oil and gas industry as well as water utility and other industries.$^1$ It is becoming more important nowadays due to increased water flooding practice (that could introduce bacteria and nutrients to a system) to increase well pressures.

Many researchers have attempted to explain MIC mechanisms in different ways. The prevailing mechanism is the so-called classic Cathodic Depolarization Theory (CDT) for MIC due to Sulfate Reducing Bacteria (SRB) initiated by von Wolzogen Kuhr and Vlugt vander in 1934.$^2$ This theory was adopted by numerous publications on MIC.$^1,3,4,5$ It uses the following reactions to explain SRB corrosion.

\[
\begin{align*}
\text{Anodic reaction (iron dissolution)} & : 4\text{Fe} \rightarrow 4\text{Fe}^{2+} + 8e^- \\
\text{Dissociation of water} & : 8\text{H}_2\text{O} \rightarrow 8\text{H}^+ + 8\text{OH}^- \\
\text{Cathodic reaction} & : 8\text{H}^+ + 8e^- \rightarrow 8\text{H}_{\text{ads}} \\
\text{Cathodic depolarization by hydrogenase} & : 8\text{H}_{\text{ads}} (\rightarrow 4\text{H}_2) \rightarrow 8\text{H}^+ + 8e^- \\
\text{Sulfate reduction by SRB} & : \text{SO}_{4}^{2-} + 8\text{H}^+ + 8e^- \rightarrow \text{S}^2- + 4\text{H}_2\text{O} \\
\text{Corrosion product formation} & : \text{Fe}^{2+} + \text{S}^2- \rightarrow \text{FeS} \\
\text{Corrosion product formation} & : 3\text{Fe}^{2+} + 6\text{OH}^- \rightarrow 3\text{Fe(OH)}_2 \\
\text{Overall reaction} & : 4\text{Fe} + \text{SO}_{4}^{2-} + 4\text{H}_2\text{O} \rightarrow 3\text{Fe(OH)}_2 + \text{FeS} + 2\text{OH}^- \\
\end{align*}
\]

Cathodic reaction (Reaction 3) produces H atoms that adsorb onto the cathode causing the so-called "cathodic polarization." This stops the corrosion process unless \(\text{H}_{\text{ads}}\) is removed using one or both of the following reactions.

\[
\begin{align*}
\text{Chemical desorption} & : 2\text{H}_{\text{ads}} \rightarrow \text{H}_2 \\
\text{Electrochemical desorption} & : \text{H}_{\text{ads}} + \text{H}^+ + e^- \rightarrow \text{H}_2 \\
\end{align*}
\]

Both desorption processes are said to be rate-limiting. High activation energies are required. SRB’s hydrogenase enzyme converts \(\text{H}_{\text{ads}}\) to \(\text{H}_2\) and then \(\text{H}^+\), thus causes cathodic depolarization. This enzyme is a protein that catalyzes the conversion by lowering the activation energy.$^6$ CDT assumes multiple reactions that are difficult to implement in a mechanistic model. The critical role of an SRB biofilm as a surface-active catalyst is overlooked, making it difficult to explain many MIC phenomena.

Until recently, there has been no mathematical mechanistic model for MIC pitting prediction due to a lack of understanding of complicated MIC mechanisms. In fact, many people questioned whether it would ever become possible. A breakthrough came when Gu et al.$^7$ introduced an electrochemical kinetics and bass transfer based mechanistic model using a new biocatalytic cathodic sulfate reduction (BCSR) theory. The model was solved numerically and implemented in an MIC software program. It assumes that a corrosive SRB (sulfate-reducing bacteria) biofilm is present on an iron surface causing the following reactions to go forward due to biocatalysis.

\[
\begin{align*}
\text{Anodic:} & \quad 4\text{Fe} \rightarrow 4\text{Fe}^{2+} + 8e^- \quad \text{(Iron dissolution)} \\
\text{Cathodic:} & \quad \text{SO}_{4}^{2-} + 8\text{H}^+ + 8e^- \rightarrow \text{HS}^- + \text{OH}^- + 3\text{H}_2\text{O} \quad \text{(BCSR)}
\end{align*}
\]
Reaction 11 reflects the half reaction of sulfate reduction from sulfate to sulfide. Some species were added solely to balance the charges and elements in order to be consistent with other reactions in this work. One should not interpret Reaction 11 strictly as converting proton to hydroxide because the actual sulfate reduction in SRB is coupled with other biochemical reactions.

The BCSR model has been extended to include acidic pH and organic acids at the pit bottom. SRB metabolites contribute to a low local pH. Acid producing bacteria (APB) also produce corrosive organic acids and contribute to the local low pH. In addition to the BCSR reaction (Reaction 11), proton and acid reductions can also couple with iron dissolution to cause additional corrosion:

\[2H^+ + 2e^- \rightarrow H_2 \quad \text{(Proton reduction)} \]  \hspace{1cm} (12)
\[2HAc + 2e^- \rightarrow 2Ac^- + H_2 \quad \text{(Free acetic acid reduction)} \]  \hspace{1cm} (13)

Free undisassociated organic acids are represented by free acetic acid in the BCSR model that considers both charge transfer resistance and mass transfer resistance. The Butler-Volmer equation is used to describe charge transfer for both anodic and cathodic reactions. Mass transfer resistance and charge transfer resistance are combined using the classical electrochemical kinetics. The transient model equations are solved numerically. A software program has been created for mechanistic MIC prediction based on the BCSR theory combined with proton reduction and acid reduction. The model yields pit growth, pitting rate, mass transfer resistance to charge transfer resistance ratio, contributions from BCSR, proton reduction and free acetic acid reduction, simulated sweeps, etc.

The BCSR model emphasizes the biocatalytic role of an SRB biofilm that moves the cathodic BCSR reaction forward. It is supported by SRB physiology and biochemistry of sulfate reduction at the molecular level discovered by evolutionary biologists, biochemists and other scientists. This work uses the BCSR theory to explain several long-standing myths in MIC.

**EXPERIMENTAL CONDITIONS**

The BCSR theory indicates a bottleneck in MIC due to SRB. To resolve the bottleneck, a special chemical (US patent application pending) was added as an MIC “promoter” into 100ml anaerobic vials containing SRB and carbon steel coupons. This MIC promoter is not corrosive by itself. After a week of SRB growth, coupons were examined using SEM and IFM (Infinite Focus Microscopy). *Desulfovibrio desulfuricans* ATCC7757 was used to represent SRB in this work. Table 1 shows the medium composition and Table 2 lists test conditions. Liquid medium was deoxygenated using nitrogen sparging. To study the pits on a carbon steel coupon, the coupon surface was cleaned using an acid solution before SEM and IFM.

**RESULTS AND DISCUSSION**

Although MIC has been established as a research field for many decades and hundreds of papers have been published by numerous research groups, there are quite a few long-standing myths or issues that have yet received satisfactory explanations.
(1) Why do sessile SRB cells attack steel anyway?

It has long been understood that SRB cells do not “eat” iron\textsuperscript{10}. Ferrous ion is almost always available either as a supplied nutrient in lab tests or as a corrosion product in pipeline fluids. There is no need for SRB cells to obtain iron from steel from a nutritional point of view. There must be some kind of advantage for SRB to attack iron. Bioenergetics\textsuperscript{11} is a critically important theory in the studying microbial metabolism. It is also essential in explaining microbial behavior in MIC. Some SRB biofilms are known to be very dense\textsuperscript{12}. It may limit organic carbon (such as lactate) diffusion to the steel surface. On the other hand, sulfate tends to be more available because it is usually available at a higher concentration in the bulk phase thus providing a larger mass transfer driving force. In order to perform sulfate reduction at the steel surface, sessile SRB cells on the surface relies on the electrons donated by iron dissolution instead of those from organic carbon oxidation because the latter may not be available locally. The standard (reduction) potential of iron (-0.45V) is close to those of lactate (-0.43V) and formate (-0.43V), and significantly more negative than those of acetate (-0.29V), butyrate (-0.28V) and propionate (-0.28V). Thermodynamically speaking, iron oxidation is at least equally favored by SRB compared to the aforementioned common organic carbons. The redox reaction from the two half electrode reactions of BCSR (Reaction 1\textsuperscript{11}) and iron dissolution (Reaction 1) combined have a negative Gibbs free energy ($\Delta G^\circ \approx -200$ kJ/mol sulfate). This means the overall redox reaction is thermodynamically favorable (i.e., exergonic or energy producing). However, a thermodynamically favorable reaction does not necessarily proceed forward at an appreciable rate if the kinetics is too slow which is the case for sulfate reduction. This reaction must rely on the biocatalysis of the hydrogenase enzyme system in SRB\textsuperscript{13-15}.

Sessile SRB cells attack the steel to obtain electrons in the redox reaction that is bioenergetically beneficial in SRB metabolism. The energy generated by the redox reaction is useful when used as maintenance energy in the absence of organic carbon or when the supply of organic carbon is locally limited. Research is under way in our lab to prove this experimentally.

(2) What is the reason that planktonic SRB cell count usually does not correlate with MIC pitting?

It has been long observed in the lab and in the field that the presence of SRB in the liquid phase does not necessarily indicate MIC pitting\textsuperscript{16}. Even when there is MIC pitting, it appears that the planktonic cell count is not directly related to pit growth\textsuperscript{8}. In the BCSR theory, MIC pitting is due to the sessile SRB cells right on a steel surface (not those sessile SRB cells that are away from the surface)\textsuperscript{17}. These sessile cells are capable of accepting the electrons donated by the iron dissolution reaction. In the liquid medium, the electrons needed for sulfate reduction by planktonic SRB cells are provided by carbon source oxidation\textsuperscript{18}. The redox reaction can be explained by Reaction 14 using lactate as a representative carbon source.

$$\text{SO}_4^{2-} + 2\text{CH}_3\text{CHOHCOO}^- \rightarrow 2\text{CH}_3\text{COO}^- + 2\text{CO}_2 + \text{HS}^- + \text{OH}^- + \text{H}_2\text{O} \quad (14)$$

This redox reaction does not need additional electrons. In fact, electrons from iron dissolution on a steel surface cannot “swim” in the liquid medium to be absorbed by the planktonic cells in
the bulk fluid because it is a common knowledge to electrochemists that an aqueous medium is a very poor electron conductor.

If the corrosive chemicals produced by planktonic SRB such as hydrogen sulfide and organic acids contribute significantly to pitting underneath biofilms, the planktonic cell count would be a factor. However, such contribution may be limited because sessile cells are much denser than planktonic cells, thus possibly generating much more H$_2$S locally. Quantitative investigations are needed to resolve this controversy.

(3) Does a thicker SRB biofilm lead to more severe MIC pitting?

Some existing MIC models$^{19,20}$ relate the amount of sessile cells in an SRB biofilm to pit growth. The BCSR model has a very different view. In biofilm catalysis, it has widely known that a surface electrochemical reaction can only be catalyzed by the sessile cells that are directly or extremely close to the surface. In MIC due to sulfate reduction, this means that only these sessile cells are capable of BCSR and accept the electrons donated by iron dissolution. The other sessile cells in the bulk of the SRB biofilm cannot accept such electrons because a biofilm is a very poor electron conductor. Instead, these sessile cells carry out sulfate reduction by utilizing the electrons donated from organic carbon oxidation if the organic carbon diffuses to that biofilm depth. The ability to carry out BCSR relies on the surface SRB cell density and activities rather than the biofilm thickness. This means MIC pitting from BCSR does not benefit from a thicker SRB biofilm. In fact, a thicker biofilm presents a larger mass transfer barrier that may limit the nutrient flow to the steel surface thus reducing the SRB biocatalytic activity$^{21}$. It also limits the diffusional removal of corrosion products under the biofilm.

A thick biofilm can lead to more severe MIC pitting, if the MIC mechanisms include proton reduction (due to acidic pH), free organic acid reduction or reaction of other corrosive species such as H$_2$S because the local amounts of these corrosive species increase with the amount of sessile cells. This aspect should not be confused with BCSR.

(4) Does pigging always reduce MIC pitting threat?

Pigging is widely used to mitigate the threat of MIC in pipelines. The scrubbing of a pipe surface can remove biofilms effectively in most cases. However, in cases with deep pits, physical pigging alone may exacerbate MIC in some locations because it may expose sessile cells on a steel surface that was previously buried deep inside the pit. The sessile cells might be less active earlier due to the mass transfer limit on nutrients exerted by a thick layer of biofilm and debris. Removal of this layer may reinvigorate the biofilm because nutrient supply may now become more accessible after pigging. This is why the MIC group at Ohio University Corrosion Institute recommends biocide dosing during or right after pigging if a pipeline is suspected to have deep MIC pits already. This also applies to pipelines that have not been pigged for quite a few years when MIC pitting situation cannot be accessed because biofilms are notoriously difficult to detect.
(5) Why Laboratory MIC pitting rates cannot explain more severe MIC pitting in the field

Lab experiments conducted using pure SRB strains published by various research groups often indicate an MIC pitting rate around 1 mm/yr\textsuperscript{19} or lower. Much more aggressive MIC pitting has been indicated by field operators. There are several possible explanations.

(a) SRB cells grown on lactate or acetate may produce organic acids in the biofilm causing a high local concentration due to the fact the a biofilm has a much larger cell density compared to that in the liquid phase. A severe pitting case may involve a low local pH and relatively high local concentrations of free organic acids (secreted by APB and/or SRB). One academic MIC research group studied the local pH inside an SRB biofilm using a micro pH sensor\textsuperscript{22}. They detected very acidic pH in their SRB biofilm. This finding is extremely important and definitely deserves further in-depth investigations.

Figure 1 shows the importance of acidic pH and free organic acids on overall pit depth using computer simulation based on model presented above. The low pH due to dissociated organic acid leads to proton reduction while the undisassociated free organic acid can also be reduced directly. Effects of proton reduction and free organic acid reduction can be dominating at a sufficiently low pH (e.g., pH 4 in Figure 1) due to the presence of a significant amount of organic acids at the pit bottom (e.g., 35 ppm acetic acid in Figure 1). Figure 1 also shows that individually, BCSR and proton reduction have similar corrosion current densities for the given set of simulation parameters when each of them is present alone without other corrosive species. However, when BCSR, proton reduction and organic acid reduction are all present, BCSR contribution to the overall corrosion is completely negligible under the simulated conditions. Proton reduction and more importantly organic acid reduction dominate.

(b) The BCSR theory points to the possible existence of “MIC promoters.” Guided by this, our research group has successfully found a class of chemicals that can greatly accelerate BCSR leading to much more severe MIC pitting. Figures 2 and 3 shows the dramatic MIC pit depth increase when an MIC “promoter” was added to the test medium at a low concentration. In the culture medium used in this work, the “promoter” did not promote planktonic or sessile SRB growth in repeated experiments (data not shown). This exciting discovery may lead to a new aspect of MIC monitoring, and a non-biocidal mitigation method that may even allow us to live with corrosive microbes with much reduced MIC pitting when the promoter’s MIC acceleration effect is inhibited.

(c) There are also other possible explanations for more severe MIC pitting such as CO\textsubscript{2} corrosion, and other types of corrosive microbes (e.g., iron oxidizing bacteria). In stainless steel corrosion involving seawater, MIC may form synergy with chloride attack leading to very aggressive pitting\textsuperscript{3}.

(6) Why can a biofilm suddenly become more aggressive?

Field operators indicated that they sometimes observe increased MIC pitting when there was seemingly no change in microbial population and nutrients. There are several possible reasons\textsuperscript{23}: (a) Planktonic cell counts are typically measured in the field, not sessile cell counts. It is possible that undetected aggressive biofilms have formed causing increased MIC pitting,
including APB joining the biofilm community on the steel surface. (b) The presence of the aforementioned “MIC promoter” emerged. Such a chemical compound is naturally occurring and its assay has yet to be applied to MIC detection. Its presence could be due to contribution from a non-corrosive microbe joining the biofilm community.

(7) Why a more negative voltage is needed in cathodic protection for MIC compared with non-MIC? Why do some cathodically protected iron surface have actually more sessile SRB cells?

These two questions have puzzled some people. Several published works in the literature\(^ {24,25}\) indicated that the criterion of -0.950 V (vs CSE) is not negative enough to protect carbon steel from MIC against pipelines in a wet clay soil or submerged in sea or brackish water. They even reported a surprising increase of sessile SRB cells on cathodically protects irons surfaces. This sessile SRB population increase in our view is probably due to the externally supplied electrons for the SRB to carry out BCSR when an impressed current is used. Another factor may be that SRB cell walls carry charges that are attracted to the surface. If there is a stoppage of the electron supply, the sessile SRB cells may turn to attacking iron to get electrons for BCSR. To assure a steady supply of externally supplied electrons, a continuous impressed current is desired. Due to the increased Ohmic resistance exerted by the biofilm, a more negative voltage (i.e., a larger driving force) is needed to deliver the current.

(8) Are sulfate and organic carbon both necessary for SRB to grow?

SRB can perform dissimilatory sulfate reduction\(^ {26}\) to harvest energy when this reduction is coupled with oxidation of a carbon source. SRB are a diverse and versatile category of microbes that are important to evolutionary microbiology. It is well known that they can utilize other oxidants such as CO\(_2\) to replace sulfate when sulfate is unavailable\(^ {9,27}\). The standard reduction potential of CO\(_2/\)CH\(_4\) is sufficiently less positive when coupled with iron oxidation as a redox couple. This means MIC pitting due to SRB utilizing CO\(_2\) is still bioenergetically beneficial for the sessile SRB cells on a steel surface. The energy harvested from such a redox reaction is useful as maintenance energy when an organic carbon source or sulfate is absent locally either due to diffusional limitation or a total lack in the bulk medium. When a very different nutrient is used, SRB need to produce different enzymes first in order to utilizing CO\(_2\) and this switch can take time. SRB utilization of CO\(_2\) is no longer dissimilatory. Some carbon atoms from CO\(_2\) will be incorporated into the cell mass\(^ 9\).

From a viewpoint of evolutionary microbiology, before the earth atmosphere became aerobic, acetate or lactate was not available in the ocean. When SRB first evolved, they lived an autotrophic life utilizing nonorganic molecules such as dissolved CO\(_2\) and H\(_2\) for carbon and energy\(^ {28}\). SRB eventually gained the ability to utilize more favorable or abundant carbon and energy sources such as volatile organic acids. SRB cells that are used in lab research and those identified in the field still possess the operons that can be switched on to produce enzymes needed for autotrophic growth\(^ {9,28}\).

Keep in mind that, other synergistic microbes may also live an autotrophic lifestyle and produce organic carbon to supply SRB. This means an organic carbon such as lactate or acetate may not be needed in the bulk fluid for heterotrophic SRB growth if the synergistic
microbes are in the biofilm community. CO₂ sequestration is a hot research topic right now. It is plausible that one may not completely rule out the possibility that a barophilic SRB of some sort may eventually appear in a supercritical CO₂ transportation pipeline.

(9) Can we attribute MIC due to SRB to biogenic H₂S corrosion?

H₂S (sour) corrosion is a very active on-going research area. H₂S corrosion theories are still under development. The mechanistic modeling of conventional H₂S corrosion is still far less mature compared to CO₂ (sweet) corrosion. It is observed that in the low H₂S concentration range (0.05-75ppm) increasing H₂S concentration leads to more a severe H₂S attack²⁹. However, when the concentration further increases, sulfide films such as Mackinawite form on the steel surface and passivate the surface³⁰. In lab tests, biogenic H₂S generation is always observed through its rotten-egg smell in SRB cultivation using a sulfate-rich medium such as the Postgate’s medium. After biofilm removal, MIC pitting areas always show black sulfide films (often identified as Mackinawite³¹), most likely formed due to a high local concentration of H₂S under a biofilm. Some researchers believe that the sulfide film may be the dominating factor in MIC pitting³¹. It is important to further investigate whether biogenic Mackinawite can also slow down MIC pitting as in non-biotic H₂S corrosion experiments. Much more research needs to be done especially in finding out whether biogenic Mackinawite is more porous than abiotic Mackinawite and thus less protective against corrosion, and whether biogenic semi-conductive sulfide films form galvanic cells is the leading cause of MIC pitting due to SRB.

CONCLUSIONS

This work attempts to explain several long-standing MIC issues that have so far lacked satisfactory answers. Some of the views presented here are likely controversial or misunderstood. Other competing logical explanations may appear to be equally plausible. A thorough understanding of MIC mechanisms is a daunting task given the current state of the art in this field. A highly multidisciplinary approach utilizing knowledge in electrochemical kinetics, biochemistry, molecular biology, mass transfer, conventional corrosion theories and modeling is required. Information from evolutionary microbiology as related to SRB is also useful. Much more experimental work needs to be done to settle these long-standing issues.
### TABLE 1
Experimental conditions

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>SRB strain</td>
<td>Desulfovibrio desulfuricans (ATCC 7757)</td>
</tr>
<tr>
<td>Temperature</td>
<td>37ºC</td>
</tr>
<tr>
<td>Culture medium</td>
<td>ATCC 1249 medium</td>
</tr>
<tr>
<td>Initial pH</td>
<td>7.0 ± 0.1</td>
</tr>
<tr>
<td>Test duration</td>
<td>7 days</td>
</tr>
<tr>
<td>Material</td>
<td>C1018</td>
</tr>
</tbody>
</table>

### TABLE 2
Composition of modified ATCC 1249 medium for SRB

<table>
<thead>
<tr>
<th>Component I</th>
<th>MgSO₄</th>
<th>2.0 g</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sodium Citrate</td>
<td>5.0 g</td>
</tr>
<tr>
<td></td>
<td>CaSO₄</td>
<td>1.0 g</td>
</tr>
<tr>
<td></td>
<td>NH₄Cl</td>
<td>1.0 g</td>
</tr>
<tr>
<td></td>
<td>Distilled Water</td>
<td>400 ml</td>
</tr>
<tr>
<td>Component II</td>
<td>K₂HPO₄</td>
<td>0.5 g</td>
</tr>
<tr>
<td></td>
<td>Distilled Water</td>
<td>200 ml</td>
</tr>
<tr>
<td>Component III</td>
<td>Sodium Lactate</td>
<td>3.5 g</td>
</tr>
<tr>
<td></td>
<td>Yeast Extract</td>
<td>1.0 g</td>
</tr>
<tr>
<td></td>
<td>Distilled Water</td>
<td>400 ml</td>
</tr>
<tr>
<td>Component IV</td>
<td>Fe(NH₄)₂(SO₄)₂</td>
<td>0.25 g</td>
</tr>
<tr>
<td></td>
<td>Distilled Water</td>
<td>50 ml</td>
</tr>
</tbody>
</table>
FIGURE 1- Simulated effects of proton reduction, free acetic acid reduction and BCSR on overall MIC pit depth on day 365. (The pH at the pit bottom in carbon steel is maintained at pH 4 due to a local acetic concentration of 35 ppm)
FIGURE 2 - MIC pits with (top) and without (bottom) MIC promoter
FIGURE 3 - MIC pit depth comparison with (top) and without (bottom) promoter. (y-axis is pit depth in micron and x-axis pit position in micron.)
REFERENCES


