Lecture 28

Mechanisms and Models for SRB Corrosion

Keywords: Anaerobic Corrosion, Hydrogenase, Biogenic Sulfides, Depolarization

Microbiological characteristics of several sulfate reducing bacteria were illustrated in lecture 27.

Role of SRB in metallic corrosion can be understood by

a) \( \text{H}_2\text{S} \) generation
b) Creation of oxygen concentration cells
c) Formation of insoluble metal sulfides
d) Cathodic depolarization

A well known mechanism involving SRB involves generation of several corrosion cells by their attachment and subsequent interaction and metabolism. Many hydrocarbons encountered in oil and gas exploration and mining sustain SRB through nutrient supply. Cathodic hydrogen (as a common corrosion reactant) generated at metal surfaces (as in pipes) promote SRB growth. Hydrogenase-positive SRB are implicated in hydrogen utilization which is used for bacterial reduction of sulfate. The bacteria thus scavenge away cathodically-generated hydrogen leading to **cathodic depolarisation** promoting anodic corrosion. A model for SRB attachment on steel surfaces resulting in subsequent hydrogen depolarization is shown in Fig. 28.1.

![Fig. 28.1 Model showing surface anchoring of SRB cells and cathodic depolarization.](image-url)
Proposed reactions include

Anode \[ \text{Fe} = \text{Fe}^{++} + 2e \]

Cathode \[ 2\text{H}^{+} + 2e = \text{H}_2 \]

Depolarization \[ \text{SO}_4^{-} + 8\text{H} = \text{S}^{-} + 4 \text{H}_2\text{O} \]

Interaction with iron \[ \text{Fe}^{++} + \text{S}^{-} = \text{FeS} \]
\[ \text{Fe}^{++} + 2\text{OH}^{-} = \text{Fe(OH)}_2 \]

Overall reaction can be stated as
\[ 4 \text{Fe} + \text{SO}_4^{-} + 4\text{H}_2\text{O} = 3 \text{Fe(OH)}_2 + \text{FeS} + 2\text{OH}^{-} \]

The following aspects need be stressed to explain promotion of metallic corrosion in the presence of SRB.

a) Necessity of hydrogenase enzyme as a catalyst in hydrogen utilization.

b) Bacterial generation of \( \text{H}_2\text{S} \) (\( \text{HS}^{-} \)) and formation of \( \text{FeS (MeS)} \) as a reaction product.

c) Depolarization through cathodic hydrogen removal.

d) Role of iron (and or metallic) sulfide.

Possibility of galvanic cell formation between steel (Fe) and the iron sulfide which serves as cathode indeed promotes corrosion. The presence of bacteria can be seen as a biocatalyst promoting the electrochemical reactions as illustrated in Fig. 28.2.

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Fig. 28.2 Model showing galvanic interaction between Fe and FeS in the presence of SRB cells.
Metal corrosion rate is proportional to iron sulfide content in the environment.

Many other factors can also influence metallic corrosion in the presence of SRB.

a) Anodic depolarization.
b) Formation of volatile phosphorus compound.
c) Presence of iron-binding biopolymers.
d) Sulfide-induced stress corrosion cracking.
e) H$_2$ induced stress corrosion and cracking.

The basic idea of cathodic depolarization theory is the removal of hydrogen from the cathodic regions by the bacterial hydrogenase, coupled with sulfate reduction to sulfide. Severe corrosion of steels in water-logged clay soils can be attributed to this type of MIC. Ferrous sulfide and hydroxides are corrosion products. In fact, SRB uses the adsorbed hydrogen in sulfate reduction, increasing the anodic corrosion rate by allowing the cathodic reaction to proceed faster. Such a microbial reaction bypasses the recombination of adsorbed hydrogen atoms, which requires higher activation energy. Another suggestion regarding cathodic polarization in the presence of SRB is attributed to bacterially generated H$_2$S.

Cathodic reaction such as \[ \text{H}_2\text{S} + e = \text{HS}^- + \frac{1}{2} \text{H}_2 \] can occur.

Effect of precipitated iron sulfide need also be stressed. The depolarizing effect of ferrous sulfide on hydrogen evolution was also confirmed.

In metals and alloys exhibiting active-passive behavior, breakdown of passivity by the metabolic products of SRB can occur promoting pitting corrosion. (Eg:- Stainless steels).

Properties of biogenic sulfides generated by SRB and chemical sulfides need be compared. SRB metabolites containing thiosulfates and polythionates are corrosive to steel. Added presence of chlorides as in sea water would further aggravate the corrosion process.
MIC in anoxic environments in the presence of SRB need thus be understood in the light of various combinations of parameters such as:

a) Biogenic sulfides – nature of protective film on metal surface.
b) Depending on pH, poorly protective sulfide films could form.
c) Breaking down of passivity by SRB metabolites.
d) Cathodic depolarization – hydrogenase activity or iron sulfide precipitation.

SRB – influenced corrosion of steel is seen to be significantly influenced by the nature and structure of the sulfide films. Metal-biofilm-solution interface and parameters such as pH, ionic concentration, oxygen levels and exopolymeric substances control the surface corrosion products. Corrosion or protective nature of such product films may vary depending on the environment. Presence of aggressive anions such as chlorides could impact the corrosion rate.

SRB has been most troublesome among all organisms involved in MIC, especially in environments related to oil, gas and shipping industries. Considerable work has been focussed on the influence of SRB on mild steel and other iron-based alloys. Serious problems in petroleum industries include increased refining costs due to bacterial H₂S generation (oil souring). SRB growth in sea water injection systems leads to equipment damage besides contamination of oil and gas with viable cells and their reaction products. They are termed obligate anaerobes obtaining energy from oxidation of organics, using sulfate as external electron acceptor. Corrosion of steels is generally realized as a localized attack as pitting.

Many strains are capable of respiring oxygen with hydrogen serving as electron donor. General pH range of activity is from 5 to 10 within temperatures 5°C to 50°C. In industrial environments, SRB exhibit strong affinity for adhesion to available surfaces to develop often patchy biofilms. Such sessile SRB biofilm initiates localized pitting corrosion. Extracellular polymeric substances (EPS), entrapped particles, precipitates, adsorbed ions and organic molecules are present in SRB biofilms which are heterogeneous with thickness ranging from microns to centimeters.
Biofilm formation involves steps such as:

- Transport of organic matter to metal surface.
- Transport of planktonic cells to surface to become sessile cells.
- Attachment and growth of cells within biofilm.

A pictorial representation showing stages in the attachment of SRB cells on metal surfaces is given in Fig. 28.3.

![Fig. 28.3 Stages in metal surface attachment of SRB cells](image-url)
Hydrogenase and depolarization activity of some SRB are given below:

**Fresh water isolates**

- *Desulfovibrio vulgaris* ++ Depolarization
- *Desulfotomaculum orientis* - No depolarization

**Thermophiles**

- *Desulfotomaculum nigrificans* + Depolarization

**Halophiles**

- *Desulfovibrio desulfuricans* + Depolarization
- *Desulfovibrio spp* - No depolarization

Activity of SRB in soils and waters should be reflected in the measured rest potentials.

For example.

<table>
<thead>
<tr>
<th>Eh</th>
<th>Corrosivity</th>
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<tr>
<td>&lt; 100 mV</td>
<td>Severe</td>
</tr>
<tr>
<td>100 – 200 mV</td>
<td>Moderate</td>
</tr>
<tr>
<td>200 – 400 mV</td>
<td>Low</td>
</tr>
<tr>
<td>&gt;400 mV</td>
<td>Insignificant</td>
</tr>
</tbody>
</table>

Aggressive and nonaggressive soil sites can be classified in relation to soil resistivity, redox potentials, pH, water content and SRB cell counts. Similarly, soil types such as clayey, chalky, sandy and loamy can have a bearing on metallic corrosion. Water samples from fresh water and salty water environments can similarly be analyzed for the various parameters for corrosivity.

Recording of redox potentials of liquid samples can be useful to establish the presence and growth conditions for SRB. Any contamination of the system by SRB can be monitored through physicochemical and biochemical tests. Accumulation of
black iron sulfides and the emanation of $\text{H}_2\text{S}$ smell will invariably suggest SRB presence. SRB can be detected in solid and liquid samples using Starkey medium (in water or in presence of $\text{NaCl}$)

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Concentration (g/L)</th>
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<tr>
<td>Dipotassium hydrogen phosphate</td>
<td>0.5</td>
</tr>
<tr>
<td>Ammonium chloride</td>
<td>1.0</td>
</tr>
<tr>
<td>Sodium sulfate</td>
<td>1.0</td>
</tr>
<tr>
<td>Calcium Chloride</td>
<td>0.1</td>
</tr>
<tr>
<td>Magnesium sulfate</td>
<td>2.0</td>
</tr>
<tr>
<td>Sodium lactate (70%)</td>
<td>5.0</td>
</tr>
</tbody>
</table>

Addition of iron sulfate into the inoculated culture would result in black precipitate and evolution of $\text{H}_2\text{S}$.

SRB can usually be found in

a) Stagnant regions in flow lines.

b) Under sludge or in mud at bottom of pits.

c) Under the scales in low velocity flow lines, crude oil storages and water tanks.

d) Sand and gravel filters- sewerage lines.

e) Injection wells, oil-fields, oil-water interface

f) Buried pipe lines.

Hydrocarbon degrading SRB proliferates in oil and gas reservoirs. Anaerobic bacteria such as SRB can be found even in oxygenated environment and the existence of oxygen-resistant proteins in some species has been observed. Possible use of oxygen as terminal electron acceptor by SRB is also mentioned. Oxygen gradients in biofilm include anoxic zones rich in SRB.