

Mechanisms of Microbiologically Influenced Corrosion: A Review

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Abstract: The main problem of biogenic is the production of H₂S in the oil industry that can lead to corrosion and reservoir souring. Collection of bacteria called sulfate-reducing bacteria (SRB) is always the responsible of problems such as reservoir souring, equipment and pipeline failures. The corrosion mechanism understanding of SRB is unavoidable. In this study, various mechanisms proposed for SRB induced corrosion are investigated.

Key words: Sulfate-reducing bacteria (SRB) • Corrosion mechanism, H₂S • Microbiologically influenced corrosion (MIC)

INTRODUCTION

The role of microorganisms on the metals corrosion has been known since early 1900s [1-2]. Microbiologically influenced corrosion (MIC) is a big concern in the oil and gas industry. MIC pitting attacks tend to result in reservoir souring, equipment and pipeline failures that are of great problems in oil field. Collection of bacteria called sulfate-reducing bacteria (SRB) is always the responsible of these problems [3-5].

SRB are nonpathogenic and anaerobic bacteria, but SRB can act as a catalyst in the reduction reaction of sulfate to sulfide [6]. It means they are able to make severe corrosion of metals in a water system by producing enzymes, which can accelerate the reduction of sulphate compounds to H₂S [7-8]. However, to occur this reduction, three components namely SRB, sulphates, free electrons as an external energy source must be present and the water temperature must be less than approximately 65°C [9]. Mild steel, Stainless steel and carbon steel are the most commonly exploited materials in the petroleum realm which are known to undergo from MIC.

To investigate SRB induced corrosion, understanding of its mechanism is necessary. Various different mechanisms have been proposed since 1934. Some of the mostly known mechanisms are presented in this study.

Cathodic Depolarization by Hydrogenise (1934): Von Wolzogen Kuehr and Van der Vlugt in 1934 [1] proposed mechanism of corrosion induced by SRB which is a depolarization through oxidation of the cathodic hydrogen as formulated in the cathodic depolarization theory. When metal expose to water, it becomes polarized by losing positive metal ions (anodic reaction). The free electrons reduce water-derived protons (cathodic reaction) in the absence of oxygen, to produce hydrogen that inhabits on the metal surface that will establish a dynamic equilibrium. Sulfate-reducing bacteria are expected to consume the formed hydrogen (according to reaction 4 indicated in Table (1), thus oxidation of Fe happens [10-11]. This mechanism increased the anodic metal dissolution and consequently FeS and Fe(OH)₂ as corrosion products are formed [12].

Table 1: Cathodic depolarization mechanism of metal corrosion by SRB.

Anodic reaction (1)	$4\text{Fe} \rightarrow 4\text{Fe}^{2+} + 8\text{e}^-$
Water dissociation (2)	$8\text{H}_2\text{O} \rightarrow 8\text{H}^+ + 8\text{OH}^-$
Cathodic reaction (3)	$8\text{H}^+ + 8\text{e}^- \rightarrow 8\text{H} + 4\text{H}_2$
Hydrogen oxidation (4)	$\text{SO}_4^{2-} + 4\text{H}_2 \rightarrow \text{H}_2\text{S} + 2\text{H}_2\text{O} + 2\text{OH}^-$
Precipitation (5)	$\text{Fe}^{2+} + \text{H}_2\text{S} \rightarrow \text{FeS} + 2\text{H}^+$
Precipitation (6)	$3\text{Fe}^{2+} + 6\text{OH}^- \rightarrow 3\text{Fe}(\text{OH})_2$
Total Reaction:	$4\text{Fe} + \text{SO}_4^{2-} + 4\text{H}_2\text{O} \rightarrow \text{FeS} + 3\text{Fe}(\text{OH})_2 + 2\text{OH}^-$

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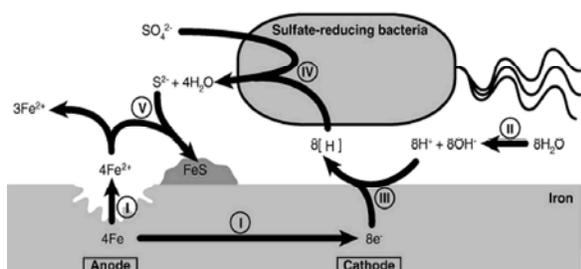
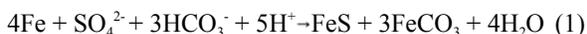


Fig. 1: Scheme of iron corrosion by SRB based on reactions as suggested by the cathodic depolarization theory [13]. I, iron dissolution; II, water dissociation; III, proton reduction; IV, bacterial sulfate reduction and V, sulfide precipitation.

Fig. 1 shows iron corrosion mechanism that is based on CDT. In real condition, SRB are attached to metal surface, but for convenience, the bacterial cells are shown separately. At the cathodic site, reducing agents designated as [H] from the iron flow to the bacteria and are used for reduction of sulfate (SO_4^{2-}) to sulfide (H_2S). At the anodic site, only one fourth of the dissolved Fe^{2+} reacts stoichiometrically with H_2S to form FeS [13]. In the presence of CO_2 and bicarbonate, as common in marine environments, the remaining Fe^{2+} precipitates as FeCO_3 ; in the absence of bicarbonate, the more soluble $\text{Fe}(\text{OH})_2$ is formed [14]. The total reaction of corrosion is as follows:



Iverson showed that this theory is valid for SRB corrosion of other metals such as aluminum alloys. He presented direct documentation for the cathodic depolarization theory via benzyl viologen (an electron acceptor) and a cell suspension of a hydrogenase-positive SRB [15]. Experimental results with *Desulfovibrio* species for supporting the cathodic depolarization theory have demonstrated frequently that they use H_2 very effectively [16]. Also Cypionka and Dilling in 1986 illustrated that the hydrogenase-negative *Desulfotomaculum orientis* could not depolarize the cathode, whereas hydrogenase-positive *Desulfovibrio vulgaris* could [17]. The current density at a given electrode potential in the presence of *Desulfovibrio vulgaris* cells was always higher than in their absence [16]. Booth and Tiller in 1968 utilized electrochemical techniques to investigate cathodic depolarization of steel with cell suspensions of different SRB [18].

Da Silva *et al.* demonstrated a new mechanism of cathodic depolarization. They explained the improvement of the charges exchanged must relate to a cathodic depolarization that happens by using a direct electron transfer from stainless steel to hydrogenase [19]. It was demonstrated that the corrosion rate with added FeS was significantly higher than without FeS. This result provide proof for the influence of FeS in cathodic depolarization [18]. Cord-Ruwisch and Widdel (1986) also revealed oxidation of cathodic hydrogen with sulfate in different growing cultures of hydrogenase-positive *Desulfovibrio* species. They demonstrated that the process took place only when lactate as an organic electron donor was present. It was believed that a simultaneous consumption of H_2 and the organic substrate occurred [20].

The corrosion rate was reported to depend largely on the total activity of hydrogenase within the biofilm rather on the bacterial population size [21]. The biofilms with SRB in pipelines with intense corrosion had lower cell numbers but much higher total hydrogenase activity [22]. In contrast, biofilm including SRB in a non-corroding pipeline had higher cell densities but low hydrogenase activity and showed a low corrosion rate. Often, hydrogenase genes have been subject to investigations with the goal to monitor corrosion under field conditions [22]. However, the primers used for the polymerase chain reaction (PCR) amplification or the probes applied to detect hydrogenase genes in situ covered merely *Desulfovibrio* species [22-23]. Thus, such approaches cannot yield a complete picture of SRB associated with corroding iron *in situ*.

FeS formed by SRB activity is feasible in terms of thermodynamically aspect. These corrosion products can speed up corrosion considering on the environmental and physicochemical conditions of the FeS film. Formation of FeS on metal surface can induce a local decrease in pH that enhances the breakdown of passive film, which can lead activation of corrosion cells between the steel surface as anode and the FeS as cathode [24]. Several important factors are not considered in the classical depolarization theory mention as following:

(a) The effects of sulfide, bisulfide and hydrogen sulfide produced from the sulfate reduction on the anodic reaction; (b) The effect of hydrogen sulfide on the cathodic reaction; (c) the effect of elemental sulfur from the biotic or abiotic oxidation of sulfur; (d) Fluctuations in the environmental conditions between anaerobic and aerobic conditions; (e) the production of other corrosive metabolites [10].

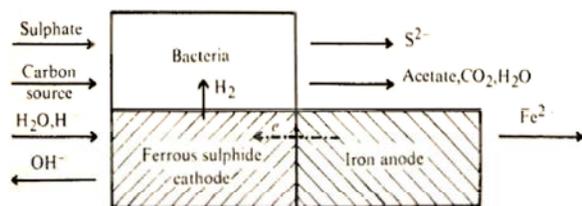


Fig. 2: King's proposed mechanism of corrosion by the sulfate reducing bacteria [25]

Iron Sulfides (King's Mechanism) (1971): King and Miller proposed that the solid FeS formed on the metal surface played the role of absorber of molecular hydrogen then iron sulphide can be reproduced [25]. In this situation where the area covered by iron sulfide becomes cathode, while biofilm area behaves as anode and the corrosion rate of metal will remain in high level [25-27]. An increase of Fe^{2+} concentration in the solution leads to the crack-up of the protective Mackinawite film, when the film was ruptured, the corrosion rate is accelerated in terms of the Fe^{2+} concentration [28]. Figure 2 schematically illustrates this proposed mechanism. It seems that after sufficient formation of FeS for starting a galvanic cell between FeS and Fe, no sulfide film are formed while a high rate corrosion rate was recorded by galvanic corrosion [25].

Lee and Characklis in 1993 studied the impact of suspended FeS on the corrosion of mild steel in an anaerobic biofilm reactor where the Fe^{2+} concentration rose from 0 to 60 mg/L. When the increase of Fe^{2+} concentration reached 60 mg/L, FeS particles were able to penetrate through the protective iron sulfide film, consequently the protective film was ruptured. Intergranular corrosion were also detected on the metal surface by SEM imaging [29].

A Volatile Phosphorous Compound (1983): Iverson and Olson in 1983 demonstrated that a volatile material, a phosphorous compound was the responsible of corrosion event. They supposed that Sulfate reducers can accelerate corrosion through production of extremely corrosive phosphorous compounds such as phosphine (H_3P), which can lead to iron phosphide (Fe_2P) production [30-31]. The result shows that phosphorous compound was seen in yeast extract that seems to be a precursor to the corrosive phosphorous compound [32].

Anodic Depolarization (1984): Anodic depolarization by iron-reducing bacteria has been the subject of extensive investigation. According to Table 2, Corrosion of iron in

Table 2: Anodic depolarization mechanism of metal corrosion by SRB

Anodic reaction (1)	$4\text{Fe} \rightarrow 4\text{Fe}^{2+} + 8\text{e}^-$
Water dissociation (2)	$8\text{H}_2\text{O} \rightarrow 8\text{H}^+ + 8\text{OH}^-$
Cathodic reaction (3)	$8\text{H}^+ + 8\text{e}^- \rightarrow 8\text{H} + 4\text{H}_2$
Anodic depolarization (4)	$3\text{Fe}^{2+} + 6\text{OH}^- \rightarrow 3\text{Fe}(\text{OH})_2$
Hydrogen oxidation (5)	$\text{SO}_4^{2-} + 4\text{H}_2 \rightarrow \text{H}_2\text{S} + 2\text{H}_2\text{O} + 2\text{OH}^-$
Dissociation of hydrogen sulfide (6)	$\text{H}_2\text{S} \rightarrow \text{S}^{2-} + 2\text{H}^+$
Anodic depolarization (7)	$\text{Fe}^{2+} + \text{S}^{2-} \rightarrow \text{FeS}$
Total Reaction:	$4\text{Fe} + \text{SO}_4^{2-} + 4\text{H}_2\text{O} \rightarrow \text{FeS} + 3\text{Fe}(\text{OH})_2 + 2\text{OH}^-$

an aqueous anaerobic environment is an electrochemical event that electrons generated through anodic reaction of metal (reaction 1) and H^+ generated during dissociation of water (reaction 2). With combination of these two reactions molecular H_2 form (reaction 3). This process is called cathodic polarization that a layer of H_2 can protect metal. The main corrosion product is $\text{Fe}(\text{OH})_2$. When SRB come and reduce sulfate to sulfide by consumption of H_2 , reaction 5 will take place. Then dissociation of H_2S (reaction 6) increases the H^+ concentration in cathodic area, changing the kinetics of reaction 3. With anodic depolarization in reaction 7, a new corrosion product FeS forms [33-37].

Wang, H. and C.H. Liang demonstrated that SRB accelerates anodic active dissolution of 10CrMoAl steel in seawater through anodic depolarization process of sulfide. The S^{2-} ions from SRB activity reacts with Fe^{2+} ions to form FeS that will accelerate anodic active dissolution [38].

Fe-Binding Exopolymers (1995): Generally, biological deposits on any surface are called Biofilm and biofouling. In a better description, biofilms are a community of microbes and their extracellular polymer substance (EPS), usually polysaccharides. The protection of microbes is the main purpose of biofilm, although biofilm can trap nutrient for microbe growing. Many review articles are conducted on the influence of biofilm in different industries such as drinking water system [39], dairy and food [9] and oil field industries [5].

Extracellular polymeric substances (EPS) produced by SRB have the ability to accelerate corrosion by binding with metal ions [40-43]. SRB with EPS of different composition were shown to cause different corrosion rates. In EPS released by a relatively aggressive *Desulfovibrio* strain, uronic acid was detected [44-45]. Fang *et al.* in another study showed that the increased production of EPS in the presence of Cr^{3+} also accelerated the corrosion of mild steel in seawater [46]. Chan *et al.* in 2002 demonstrated that EPS alone is a metal corrosion

agent. They prepared two solution with 1% EPS and without EPS and the result showed that EPS enhanced corrosion [47]. It also supposed that EPS can trap metal ions leading to stimulation of the anodic reaction [48].

Videla in 2001 [49] presented four steps for biofilm formation on the metal surface as following:

- 1) Transportation of organic material to metal surface;
- 2) Transportation of microbial cells from bulk to surface,
- 3) Attachment of microbial cells;
- 4) Growth within the biofilm.

These mechanisms can modify the interface structure by biofilm accumulation that should be considered as the main reason of MIC [49-50].

Sulfide and Hydrogen -Induced Stress Corrosion Cracking (SCC) (1995): Undoubtedly, we can say SRB activity can enhance the corrosion-fatigue crack growth and hydrogen embrittlement [51-52]. The corrosion fatigue crack growth of the high strength steel notably accelerates by the biologically produced hydrogen sulphide in natural sea water [53].

Biologically active environment change with the activities of the bacteria and their interactions with other components of the environment such as interactions of bacteria and the metal, production of EPS, degradation by large fouling organisms. There are two different local environments surrounding the metal surface with and without bacteria, even with the same levels of sulphide. Furthermore, sour environments are specifically corrosive because of high levels of hydrogen accessible at the metal surface or in a crack because of sulfide activation at the cathode [26]. The influence of hydrogen can be modified by the presence of organic molecules on the metal surface and EPS matrix, which can describe the differences between crack tip effects (as measured by crack growth) and general embrittlement effects (as measured by hydrogen flux) [51]. The differences between abiotic and biotic solution including similar levels of corrosive compounds such as iron sulfides can be associated with to the presence of EPS and to the heterogeneities produce at the metal surface by the formation of a biofilm [26].

Domalicki *et al.* described that SRB can produce hydrogen sulphide at low and medium cathodic polarization. Hydrogen sulphides decrease pH near electrode electrolyte and inhibit the deposits formation and thus encourage the hydrogen charging and the plasticity loss. These effects are a function of studied steels. The same amount of hydrogen makes a less detrimental effect on the sorbite steel of increased

strength, but at similar cathodic polarization, this steel absorbs the highest amount of hydrogen and reveals the most pronounced degradation [53].

Sulfide (1998): Little *et al.* in 1998 investigated the role of biomineralization in microbiologically induced corrosion. They demonstrated biomineral dissolution reactions by metal-reducing bacteria remove oxide layers or force mineral replacement reactions that promote decomposition of metal. Biomineralization that results in mineral deposition on a metal surface can shift the corrosion potential in either a positive or a negative direction, depending on the nature of the mineral. Bioprecipitated sulfides move the corrosion potential in a negative, more active direction, resulting in accelerated corrosion of some metals and alloys. Iron oxide formation can begin a sequence of events that results in under deposit corrosion of susceptible metals [8, 54].

Three Stages Mechanism (Romero Mechanism) (2005): Recently, Romero proposed a mechanism for the SRB induced corrosion of iron. As it is clear from Figure 3, this mechanism is defined by three stages [55]. In the first stage (Table.3), the adsorption of bacterial cells and iron sulfide products were taken place. A micro galvanic corrosion cells form through iron sulfide products (Mackinawite and Pyrite) and the metallic surface that generated a hydrogen permeation peak [55-56].

There is equilibrium between bacterial and inorganics in second stage (Table.4). The metal was slightly ennobled in this stage by the development of a combination film of a more dense iron sulfide film and EPS [55-56]. Bacterial corrosion and film stabilization are two major occurrences at this stage. The third stage (Table.5) was controlled by a local pH decrease that caused by SRB activity on the steel in the presence of HS⁻. SRB reduce locally Pyrite to Mackinawite, which produce a severe, localized corrosive process configured into groups of deep, rounded holes, then subsequent detachment took place. It supposed that a galvanic corrosion generated between the anodic metal and the cathodic iron sulfide products, composed of Mackinawite, Pyrite, Esmitite, Marcasite, Greigite, Troilite and Pyrrhotite. In this more aggressive phase, there was no hydrogen permeation due to the barrier or anti-diffusive effect of the EPS. At this stage, the bacteria grow exponentially about 10⁸ UFC/cm² that can generate enough H₂S. So the corrosion accelerates without the absorption of atomic hydrogen [55-56]. Reactions could be occurring as shown in Table 5.

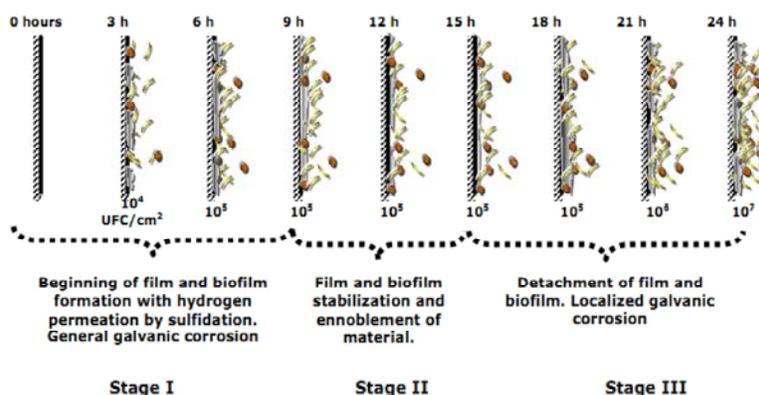


Fig. 3: Mechanism for the SRB induced corrosion of iron proposed by F. de Romero[56].

Table 3: The first stage reactions of Romero mechanism (3-9h)

$H_2S \rightarrow HS + H^+$	(1)
$Fe^{++} + HS \rightarrow FeS + H^+$	(2)
$FeS + HS \rightarrow FeS_2 + H^+ + 2e^-$	(3)
$3FeS + HS \rightarrow Fe_3S_4 + H^+ + 2e^-$	(4)
$2H^+ + 2e^- \rightarrow H_2$	(5)
$Fe \rightarrow Fe^{++} + 2e^-$	(galvanic) (6)
$Fe + HS \rightarrow FeS + H^+ + 2e^-$	(microbial) (7)

Table 4: The second stage reactions of Romero mechanism (9-15 h)

$FeS_2 (C) \rightarrow FeS_2 (O)$	(1)
$Fe_3S_4 (R) \rightarrow Fe_3S_4 (C)$	(2)
$Fe + HS \rightarrow FeS + H^+ + 2e^-$	(microbial) (3)
$2H^+ + 2e^- \rightarrow H_2$	(4)

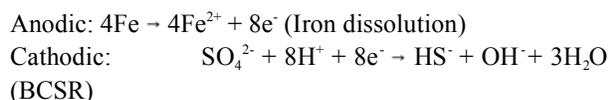
Table 5: The third stage reactions of Romero mechanism (>15 h)

$FeS_2 + H^+ + 2e^- \rightarrow FeS + HS^-$	(1)
$Fe \rightarrow Fe^{++} + 2e^-$	(galvanic) (2)
$Fe + HS \rightarrow FeS + H^+ + 2e^-$	(microbial) (3)
$H_2S + e^- \rightarrow \frac{1}{2}H_2$	(4)
$7FeS + HS^- \rightarrow Fe_7S_8 + H^+ + 2e^-$	(5)

Biocatalytic Cathodic Sulfate Reduction (BCSR) (2009):

In the BCSR theory, MIC takes place since the sulfate reduction at the cathode will consume the electrons released by iron dissolution at the anode with the help of biocatalyst and the interface of biofilm and the metal are a place for both anodic and cathodic sites [57-58].

It assumes that a corrosive SRB biofilm is formed on an iron surface causing the following reactions to go forward due to biocatalysis.



Cathodic reaction shows the half reaction of sulfate reduction from sulfate to sulfide due to biofilm catalysis. Some species were added solely to balance the charges

and elements in order to be consistent with other reactions. One should not interpret cathodic reaction strictly as converting proton to hydroxide because the actual sulfate reduction in SRB is coupled with other biochemical reactions. An increase in sessile SRB population may be observed due to externally supplied electrons in impressed current cathodic protection situation. 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. A more negative voltage (i.e., a larger driving force) is needed to deliver the current due to the increased ohmic resistance exerted by the biofilm [59].

CONCLUSION

Nowadays different methods are used to inhibit MIC. Understanding of microbial corrosion mechanism is one of primary tools to get better result in corrosion inhibition. We have considered many possible mechanisms that propose for SRB activity in steel-water interface. Depending on the environmental condition, one mechanism or a combination of several mechanisms can happen. Further studies must be done to find out how bacteria can grow and protect themselves from biocides and other inhibition methods.

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