Chapter 1

Microbiologically influenced corrosion
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1.1 Corrosion

Corrosion is simply defined as the destruction of materials under chemical or electrochemical action by the surrounding environment [1]. Metallic corrosion is defined as the tendency of the metals to go to their original ore state. Corrosion entails the conversion of a metal from the atomic to ionic state, with the loss of one or more electrons. The anodic reaction produces positively charged metal ions and free electrons in accordance with the reaction.

\[
M^0 \rightarrow M^+ + ne^- \quad \ldots \quad (1)
\]

For e.g. \( Fe^0 \rightarrow Fe^{2+} + 2e^- \quad \ldots \quad (2) \)

Greene and Fontana [2] stated that the term 'Corrosion' includes the reaction of metals, glasses, ionic solids, polymeric solids and composites with environments that include liquids, gases and non-aqueous electrolytes. Corrosion is regarded as the cancer of metals that arises from the thermodynamic instability [3]. The dry cell consists of zinc metal, a carbon rod and an electrolyte consisting of ammonium chloride etc., when we use the dry cell by short circuiting the positive carbon electrode and zinc negative electrode electric current is obtained. When electric current flows through the cell, the zinc dissolves (corrodes) with the formation of zinc ions, which goes into solution with the release of free electrons [4].

It is necessary to devote more attention to metallic corrosion now -a-days than earlier, due to the increased use of metals in all fields of
technology. The use of rare and expensive metals for special applications such as atomic energy requires special precautions for preservation. A more corrosive environment is due to the increasing pollution of air and water. Mild steel is widely used in most of the chemical industries due to its low cost and easy availability for fabrication of various vessels, tanks, pipes etc. Since mild steel suffers from severe corrosion in aggressive environments, it needs to be protected by appropriate technique.

1.2 Forms of Corrosion

Fontana [5] categorized eight major forms of corrosion mainly based on appearance. Dillon [6] considered Fontana's basic forms of corrosion and divided them into three groups, based on their ease of identification. The three categories used were:

I. Readily identifiable by ordinary visual examination:
   - Uniform corrosion
   - Pitting corrosion
   - Crevice corrosion
   - Galvanic corrosion

II. May require supplementary means of examination
   - Erosion corrosion
   - Cavitation corrosion
   - Fretting corrosion
   - Intergranular corrosion.

III. Verification is usually required by microscopy and other chemical and electrochemical methods:
- Exfoliation
- Dealloying (selective leaching)
- Stress corrosion cracking
- Corrosion fatigue
- Microbial corrosion.

However, the corrosion of metals and alloys almost never follows a single law nor is governed by a single mode. Even the simplest situation can lead to the corrosion of a material by a combination of modes driven by intertwined mechanisms.

1.2.1 Uniform corrosion

Uniform corrosion is characterized by corrosive attack proceeding evenly over the entire surface area, or a large fraction of the total area. General thinning takes place until failure. On the basis of tonnage wasted, this is the most important form of corrosion. However, uniform corrosion is relatively easily measured and predicted, making disastrous failures relatively rare. In many cases, it is objectionable only from an appearance standpoint. As corrosion occurs uniformly over the entire surface of the metallic component, it can be practically controlled by cathodic protection, use of coatings or paints, or simply by specifying a corrosion allowance.

1.2.2 Pitting corrosion

Pitting corrosion is a localized form of corrosion by which cavities or ‘holes’ are produced in the material. Pitting is considered to be more dangerous than uniform corrosion damage, because it is more difficult to detect, predict and design against corrosion as products often cover the pits.
A small, narrow pit with minimal overall metal loss can lead to the failure of an entire engineering system. Pitting corrosion, which for example is almost common denominator of all types of localized corrosion attack, may assume different shapes. Pitting is initiated by localized chemical or mechanical damage to the protective oxide film. Water chemistry factors, which can cause breakdown of a passive film are acidity, low dissolved oxygen concentration and high concentration of chloride, and localized damage or poor application of a protective coating which also cause pitting corrosion. Besides, non-metallic inclusions also cause pitting. Pitting corrosion can produce pit with their mouth open (uncovered) or covered with a semi permeable membrane of corrosion products. Pits can be either hemispherical or cup shaped.

1.2.3 Crevice corrosion

Crevice corrosion is a localized form of corrosion usually associated with a stagnant solution on the micro-environmental level. Such stagnant microenvironments tend to occur in crevices (shielded areas) such as those formed under gaskets, washers, insulation material, fastener heads, surface deposits, disbonded coatings, threads, cap joints and clamps. Crevice corrosion is initiated by changes in local chemistry within the crevice such as, depletion of inhibitor in the crevice, depletion of oxygen in the crevice, a shift to acidic conditions in the crevice, build up of aggressive ionic species like chloride in the crevice.

1.2.4 Galvanic corrosion

Galvanic corrosion refers to corrosion damage induced when two dissimilar materials are coupled in a corrosive electrolyte. It occurs when two
or more dissimilar metals are brought into electrical contact under aqueous medium such as water. When a galvanic couple forms, one of the metals in the couple becomes the anode and corrodes faster than it would all by itself. While the other becomes the cathode and corrodes slower than it would alone. The driving force for corrosion is potential difference between the different materials. In the later part of the eighteenth century Luigi Galvani discovered the bimetallic driving force in a series of experiments with the exposed muscles and nerves of a frog that contracted when connected to a bimetallic conductor. Sir Humphry Davy and Michael Faraday in the early part of nineteenth century, also engineered the principle into the useful protection of metallic structures. In a bimetallic couple, the loss of noble material will become the anode of the corrosion cell and tend to corrode at an accelerated rate, compared to an uncoupled condition. The more noble material will act as a cathode in the corrosion cell. Galvanic corrosion can be one of the most common forms of corrosion and one of the most destructive.

1.2.5 Erosion corrosion

Corrosion of metal or alloy can be accelerated when there is an abrasive removal of the protective oxide layer. It is the increase in the rate of attack of a metal because of relative movement between a corrosive medium and the metal surface. Generally, this is removed from the surface either in the form of dissolved ions or in the form of solid corrosion products, which are mechanically swept from the metal surface.
1.2.6 Cavitation corrosion

Cavitation occurs when a fluid's operational pressure drops below its vapour pressure causing gas pockets and bubbles to form and collapse. This can occur in what can be a rather explosive and dramatic fashion. In fact, this can actually produce steam at the suction of a pump in a matter of minute. The locations where this is most likely to occur such as the suction of a pump, at the discharge of a valve or regulator, at the geometry-affected flow areas such as pipe elbows and expansions.

1.2.7 Fretting corrosion

Fretting corrosion refers to corrosion damage at the asperities of contact surfaces. This damage is induced under load and in the presence of repeated relative surface motion, as induced for e.g. by vibration. Pits or grooves and oxide debris characteristics are the typical example of fretting damage, typically found in machinery, bolted assemblies and ball or roller bearings.

1.2.8 Intergranular corrosion

The microstructure of metals and alloys is made up of grains, separated by grain boundaries, intergranular corrosion is localized attack along the grain boundaries, or immediately adjacent to grain boundaries, while the bulk of the grains remain largely unaffected. This form of corrosion is usually associated with chemical segregation effects or specific phases precipitated on the grain boundaries. Such precipitation can produce zones of reduced corrosion resistance in the immediate vicinity. The attack is usually related to the segregation of specific elements or the formation of a compound.
in the boundary. Corrosion then occurs by preferential attack on the grain boundary phase, or in a zone adjacent to it that has lost an element necessary for adequate corrosion resistance thus making the grain boundary zone anodic relative to the remainder of the surface. The attack usually progresses along a narrow path along the grain boundary. In any case the mechanical properties of the structure will be seriously affected.

1.2.9 Exfoliation corrosion

Exfoliation corrosion is a particular form of intergranular corrosion associated with high strength aluminium alloys. Alloys that have been extruded or otherwise worked heavily, with a microstructure of elongated, flattened grains are particularly prone to this damage.

1.2.10 Dealloying

Dealloying or selective leaching refers to the selective removal of one element from an alloy by corrosion processes. A common example is the dezincification of unstabilized brass, whereby a weakened, porous copper structure is produced. The selective removal of zinc can proceed in an uniform manner or on a localized scale. It is difficult to rationalize dezincification in terms of preferential zinc dissolution out of the brass lattice structure, rather, it is believed that brass dissolves with zinc remaining in solution and copper replating out of the solution.

1.2.11 Stress corrosion cracking

Stress corrosion cracking (SCC) is the cracking induced from the combined influence of tensile stress and a corrosive medium. The impact of SCC on a material usually falls between dry cracking and the fatigue...
threshold of that material. The required tensile stresses may be in the form of directly applied stresses or in the form of residual stresses. One of the most important forms of stress corrosion that concerns the nuclear industry is chloride stress corrosion.

1.2.12 Corrosion fatigue

Corrosion fatigue is the cracking as a result of the combined action of an alternating stress and corrosive environment. The fatigue process is thought to cause receptive or the protective passive film, upon which corrosion is accelerated. The introduction of a corrosive environment often eliminates the normal 'fatigue' limit of a ferrous alloy thereby creating a finite life regardless of stress level.

1.2.13 Microbial Corrosion

Microorganisms, inhabitants of all natural environments, influence corrosion phenomenon either directly by accelerating the electrochemical reactions or indirectly by virtue of their metabolic products. However, microbiologically induced corrosion (MIC) is not a new form of corrosion, but provides a new path way to an already existing process[7].

Microbes can induce corrosion by creating differential aeration/concentration cells [8], changing pH [9], depleting oxygen [10], utilizing cathodic hydrogen [11] or by producing hydrogen [12], removing atoms from metals [13], oxidizing [14], or reducing corrosion inhibitors [15], setting up of galvanic cells [16], disturbing or feeding upon protective organic coatings [17] and by their metabolic products [18].
In MIC research, the organisms mainly implicated and primarily studied are the sulphate reducing bacteria (SRB), which are distinguished by their sulfate reduction capacity [19]. The other important groups involved are sulphate-oxidizing bacteria belong to genus *Thiobacillus* sp [20] that are concerned with the oxidation of elemental sulphur and other sulphur compounds as well as the oxidation of iron.

In spite of the initial unawareness that existed about MIC, seriousness of this menace is slowly being recognized throughout the world during the past few decades, which is well evinced by the ever increasing case histories [21]. MIC is accused for failures in cooling waters [22], industrial process plants [23], underground sub-tanks [24], oil storages [25], alcohol industries [26], culvert pipes [27], nuclear power stations [28], ocean going tankers [29], off-shore concrete storage cells [30], heat exchangers [31] etc.

1.3 Economic losses due to MIC

It may seem surprising to look at the percentage of contribution of MIC towards total corrosion failures. Although the total cost of Microbial corrosion is difficult to ascertain, some estimates of losses due to MIC per annum are always available and are as presented in Table -1.
Table -1. Economic losses due to microbiologically influenced corrosion of metals

<table>
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<th>Source</th>
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<td>National Bureau of Standards, USA [32]</td>
<td>167 billion dollars</td>
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<tr>
<td>National Corrosion Service, UK [157]</td>
<td>10% of corrosion problems</td>
</tr>
<tr>
<td>United Kingdom [33]</td>
<td>250-1000 million dollars</td>
</tr>
<tr>
<td>France [34]</td>
<td>1.5 billion dollars</td>
</tr>
<tr>
<td>Australia [35]</td>
<td>2.5 million dollars</td>
</tr>
<tr>
<td>New Zealand [35]</td>
<td>5 million dollars</td>
</tr>
<tr>
<td>United Kingdom [36]</td>
<td>1000 million dollars</td>
</tr>
<tr>
<td>USA [15]</td>
<td>500-200 million dollars</td>
</tr>
<tr>
<td>Buried pipelines – UK [37]</td>
<td>20 million pounds</td>
</tr>
<tr>
<td>Cooling towers – UK [38]</td>
<td>300 million pounds</td>
</tr>
<tr>
<td>United Kingdom [39]</td>
<td>300-500 million pounds</td>
</tr>
</tbody>
</table>

1.4 Microorganisms associated with MIC

Microorganisms are thought to be primarily responsible for many metallic corrosion failures and are classified by metabolic groups as follows:

Those microbes using inorganic material as a carbon source is called autotroph and those using organic material as a carbon source called heterotroph. Microorganisms, which use chemical as an energy source, are called as chemotroph and those using light as an energy source are called phototroph. Microbes those using inorganic compounds as electron donor are called as lithotroph and organic compounds as an electron donor are called as organotroph. Most of the microorganisms associated with MIC come under the group chemotrophs refer to those get their energy from a chemical source rather than a light source. They are as follows:

- Sulphate reducing bacteria (SRB)
- Sulphur oxidizing bacteria (SOB)
- Iron oxidizing/depositing bacteria (IB)
- Manganese oxidizing / depositing bacteria (MnB)
1.4.1 Sulphate Reducing Bacteria

Sulphate reducing bacteria require strictly anaerobic conditions for their growth. Dissimilatory sulfate reduction is always associated with a respiratory chemiosmotic type of energy conservation. Several species of sulfate reducing bacteria obligatorily depend on sulfate or another sulfur compound as electron acceptor. Generally curved rods (ranging from Vibrio, spirilloid, semi lunar straight or coccoid) however morphology is influenced by age and environment. Motile by means of polar flagellum, non-pathogenic, gram negative and non-endospore forming bacteria with 3 cytochromes and desulfovibridine.

Chemo-organotrophs, which obtain energy by anaerobic respiration of sulfates or other reducible sulfur compounds to $\text{H}_2\text{S}$. Lactate, pyruvate and malate are oxidized to acetate and $\text{CO}_2$. Hydrogenase are usually present in obligatory anaerobes. They occur in soil, brackish and marine waters, especially in high numbers in polluted environments. In soils particularly in anaerobic water logged soils, the population density is high. Fresh water strains readily adapt to seawater and vice versa. Laboratory growth occurs in sulfate rich media.

The production of hydrogen sulfide in aquatic systems was recognized as a biologically mediated reduction of sulfate. Beijerinck’s [40] demonstrated microbial sulfide production resulted in the first isolation of a sulfate reducing bacterium, a strict anaerobe that may be called *Spirillum desulfuricans*. Van Delden [41] was the first to grow sulfate-reducing bacteria on lactate. Ruben schik [42] observed utilization of acetate and butyrate by sulfate reducers.
Baar's [43] demonstrated an organism called *Vibrio desulfuricans* which oxidized lactate or ethanol to acetic acid, another type *V. subentschikii* used in addition to acetate, propionate, butyrate and other compounds that were completely oxidized to CO₂.

1.4.1.1 Biochemistry of SRB

Principal insights into the biochemistry of sulfate-reducing bacteria, especially of the intermediates of sulfur metabolism, were achieved in the 1950s and 1960s [44-51]. All the sulfate reducers were classified based on phenotypic characters; important criteria were nutrition and morphology. Indeed, in many instances, similar morphological types also resembled each other nutritionally and biochemical characteristics corresponded to nutrition and morphology.

Later Guanine and cytosine (GC) content of the DNA has been used as a taxonomic marker. In many genera, however GC values cover a wide range. Large scale comparisons of genetic relationship at various taxonomic levels were first rendered possible by studying 16s rRNA sequences. Systematic sequencing of 16s rRNA from various mesophilic sulfate reducing bacteria confirmed the results obtained by the earlier method of oligonucleotide cataloguing and revealed further genetic groups [52-53]. They coincided to a high degree with the genera established by phenotypic characteristics, especially nutrition. Distribution of the capacity for dissimilarity sulfate reduction within the phylogenic tree of living organism is shown in Fig.1.
In culture of sulphate reducing bacteria, sulfide appears usually as the sole final product. All steps of sulfate reduction to sulfide occur in the cytoplasm, sulfate has to be passed across the cytoplasmic membrane. The transport of sulfate was studied in *D. desulfuricans*, *Desulfobulbus propionicus* and *Desulfococcus multivorans* grown at a limiting sulfate concentrations [54-56]. Sulfate uptake was low at external concentrations. The sequential reduction of sulfate to sulfide is shown in Fig. -2.
Many sulphate reducing bacteria can use molecular hydrogen as electron donor and can thus be considered as facultative chemolithotrophs. During this model of energy conservation, cell material may be synthesized from acetate and CO₂.

Hydrogenase activities have been demonstrated in strains of the genera *Desulfovibrio* [57], *Desulfobulbus* [58-59], *Desulfobacter*, *Desulfobacterium*, *Desulfosarcina* [60], studies on their localization of *Desulfovibrio* hydrogenases revealed that hydrogenase is often a periplasmic enzyme. There is evidence for the presence of more than one hydrogenase enzyme in several strains [57]. The hydrogenases are subdivided into three groups, iron hydrogenases, nickel iron hydrogenases and nickel iron selenium hydrogenases.

The possible generation of a proton mobile force during the growth of *Desulfovibrio* on H₂ and sulfate enzymes and other compounds involved in sulfate reduction to hydrogen sulfide are shown in Fig -3.

![Fig-3. Components and factors involved in the reduction of sulfate to hydrogen sulfide](image-url)
Sulphate reducing bacteria are the important elements in the anaerobic scenario, by their nature and adaptation or tolerance to a variety of concentrating environmental condition like occurrence at below 500 meters depth oil wells [61] and at Marianas trench [25] tolerance over oxygen shocks [62-63]. These adaptations enabled this specialized group of bacteria maintaining their key vote in the scenario of cintrophic corrosion.

1.4.1.2 Cathodic depolarization by SRB

Gaines [64] was the first to exemplify that the involvement of bacteria might be the cause for the corrosion of steel and iron under anaerobic environments. However, a logical mechanism for the corrosion caused by sulfate reducers was first provided by the classical theory (Von Wolzogen Kuhr). The theory proposed the following sequence of events as the mechanism of anaerobic bacterial corrosion.

\[
\begin{align*}
4Fe & \rightarrow 4Fe^{2+} + 8e^- \\
(\text{Anodic reaction}) & \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad
\end{align*}
\]

Ph.D. Thesis
Kuhr et al. [11] claimed that cathode is depolarized by the metal oxidation of hydrogen by reducing bacteria for its characteristic sulfate reduction process. The proposal was supported by an earlier observation that SRB passes the enzyme hydrogenase that helps in the removal of hydrogen for the reduction of sulfate [65]. Later, data in support of this theory was obtained from Starkey and Tiller groups [66-72].

Starkey and Wight [66] reported underground corrosion of iron due to SRB in support of cathodic depolarization theory. Iverson [69] experimented with two physically separated mild steel electrodes but electrically connected with each other and exemplified the oxidation of cathodic hydrogen evidenced by the reduction of redox indicator. Cathodic depolarization due to hydrogenase activity by showing complete inactive performance was exhibited by hydrogenase negative Desulfatomaculum orientalis [69, 73-74].

The suggestion of classical theory is that the ratio of metal corroded is proportional to the sulfide produced (4:1), however, much different from this theory have been known [9, 75]. The quantitative importance of biogenic sulfide was well advocated by Hardy [76] who demonstrated the oxidation of cathodic hydrogen by a marine Desulfovibrio with the consequent depolarization of mild steel electrode. The typical schematic diagram for cathodic depolarization by SRB is shown in Fig. 4.
1.4.1.3 Anodic depolarization by SRB

Wanklyn and Spruit [77] while studying the potential excursions of iron in bacterial cultures, suggested a relationship between iron corroded and ferrous sulphide product obtained. They concluded that microbial corrosion by SRB was due to the stimulation of anodic dissolution of iron by sulfide produced. An increase in corrosion current was noted in culture media or soil extracts containing sulfide [78] which was further supported by the changes observed in the corrosion potential of submerged mild steel specimens [79]. Sasaki et al [80] summarized that the variations in electrode potential observed and polarization characteristics of steel could be explained by variations in H₂S concentration. However, initial changes in the potential of mild steel may be due to factors like microfouling rather than FeS production [81].

1.4.1.4 Effect of Biogenic sulphides

Sulfides have the tendency to adsorb on metal surfaces owing to their high molar polarization and can promote electron exchange reactions thereby
catalyze pitting and stress corrosion cracking problems (SCC), sulfide is characterized for its influence on localized attacks. Rostrom [82] established sulfides as one of the most effective anions in destroying iron passivity. Mara and Williams [83] while investigating the corrosivity of FeS on pure iron suggested that the biogenic sulfide minerals were less effective depolarizers. However King and Wakerley [84] reported that approximately 10mg of iron was corroded by 88mg of FeS added at pH 7.0. On the other hand, questions on the proposed protective nature of sulfide films was raised by several workers [85-86]. When the initial pH was between 6.5 and 8.8, mackinawite film formation was enhanced, but the optimum pH range in which more protective pyrrhotite and pyrite film formed generally outside this range. The non-protectiveness of mackinawite scale was attributed to the large number of defects in the crystalline structure and hence the resultant increased electronic conductivity which allows diffusion at the crystalline boundaries [85].

The role of bacteria in corrosion of steels has been the subject of numerous investigations and the availability of a number of excellent review articles on this topic shows steels are the widely studied metals as far as MIC is concerned. Moreover, the first suggestions that bacteria were involved in electrochemical corrosion were made on the observation of buried iron pipelines [64]. Specific reviews include those by Tiller, Iverson and Pope et al [9,87-89]. There has been an upsurge in the number of reports of various types of MIC involving iron and steel [89] and in the level of interest in this
topic shown by members especially the chemical process, petroleum and water treatment industries [90-93].

Effect of SRB and minimal iron/iron rich nutrient media on the weight loss of mild steel [94], role of corrosion by bacteriogenic sulfide [8] metabolic rates of SRB and corrosion rate [33] active pitting potentials due to sulfide produced by SRB [96] adsorption of SRB to the surface and maintenance of sulphide rich layer [97] are well documented. It should be mentioned here that a major part of studies on the MIC of mild steel was attributed to SRB or bacteriogenic sulfide alone.

1.4.1.5 Recent research in SRB:

Little et al [98] demonstrated that in a sterile, continuously aerated medium, pits were initiated and repassivated, while in the absence of aeration, pits were initiated and propagated. Pit propagation was also observed in continuously aerated medium inoculated with a heterotrophic bacterium, originally isolated from a corrosion tubercle formed on a steel pipe in a fresh water environment. Autoradiography of bacteria following uptake of $^{14}$C-acetate into cellular material in combination with scanning vibrating electrode (SVE) activity. Pre-labeled bacteria also preferentially attached to corrosion products over the anodic sites. Confocal laser microscopic studies revealed that attraction to anodic sites did not depend on bacterial viability and was not specific for iron as a substratum. The results suggest that bacteria may preferentially attach to the corrosion products formed over corrosion pits. The biofilms over these anodic sites may create stagnant conditions within corrosion pits that result in pit propagation.
Videla [99] has suggested that the growth of SRB in marine environments causes significant modifications of many physicochemical parameters at the steel/seawater interface, including local changes in pH and redox potential values, variations in anion and cation concentrations and alteration of the composition and structure of corrosion products. Complex chemical and biological reactions and equilibria are also markedly altered during bacterial proliferation. These effects, which are absent in abiotic media, often lead to significant changes in the corrosion behaviour of steel. The complicated nature of the local environment at the steel/seawater interface is enhanced in the presence of microorganisms and their extra polymeric substances (EPS). As a consequence of biofilm heterogeneity, areas with different ion concentrations are formed and the development of corrosion product layers of dissimilar protective characteristics occurs.

Hamilton [100] has proposed the MIC in the context of metal microstructures. The essential redox character of the electrochemical reactions of corrosion metal loss is stressed and parallels are drawn with the redox reactions of microbial cellular energetics. An electron transfer hypothesis is proposed which both rationalises our present understanding of the mechanisms involved, and provides a theoretical framework for the design and interpretation of microbial corrosion. Biezma [101] describes the role of microstructural features on microbiologically influenced corrosion process. It is found that the integral hydrogen content of steel is dependent on the corrosion rate and quantity of bacterial cells in the corrosive medium. The integral hydrogen content of the steel subsurface layers was less in
specimens, corroded in aqueous salt medium containing sulfate-reducing bacteria if organic substances with inhibitive action were noticed [102].

Martins et al [103] have evaluated the effect of soluble iron and media composition on the growth and metabolism of sulfate-reducing bacteria (SRB) from the Desulfovibrio genus: D. gigas, D. vulgaris, D. desulfuricans, D. alaskensis and D. indonensis, Cultures of D. gigas were grown in Postgate C, lactate/sulfate and in VMN (semidefined medium) media. The other strains were grown in VMN. All the strains were studied in the presence or absence of iron. Bacterial growth kinetics were affected by iron concentrations and culture media compositions.

Jeffrey & Melchers [104] reported that, the bacteria and microbiological consortia play an important role in the corrosion of steel in marine environments. The SEM, EDS and XRD observations tend to confirm that the metamorphosis of iron to forms of iron oxide and then to iron-sulphur compounds for steel under marine corrosion condition. The images show what appear to be new details of the involvement of bacteria in the transformations. Little et al [105] reported the relationship between marine bacteria and localized corrosion. They suggested that the ferric corrosion products produced by well-established artificial crevices in 304 stainless steel in abiotic seawater were allowed to accumulate before addition of marine bacteria. Environmental scanning electron microscopy demonstrated that large numbers of bacteria were associated with corrosion products after brief exposures. Bacteria did not alter the distribution or composition of corrosion products. Mora et al [106] identified that the protein is responsible for bacterial...
adhesion to metal structures. Two proteins of permanent adhesion were
detected (one at 50 kDa and the other one at 25 kDa). Both are OMP that
promote adhesion from the bacterial cells to the metallic surface.

Rao et al [107] describes the biofilm formation indifferent aquatic
systems. Their result suggests that thickness of biofilms increased from 52 to
128 μm in the photic environment and from 17 to 30 μm in the aphotic
environment during 24-120 h of exposure. Biofilm biomass, chlorophyll and
other biochemical constituents were higher under illuminated conditions.
Diatom numbers, as could be expected, were higher on the photic panels. In
the estuarine biofilm, thickness, turbidity and biomass showed similar trends
of temporal distribution. The biofilm nutrient levels were 100-1000 times
higher than those in the ambient water. In the fresh water, biofilm nutrients
concentration factors were consistently higher in aphotic than in photic
conditions. Diatom numbers and hexose sugar content of the biofilm showed
very good correlation (r=0.97 and p=0.0001). Anaerobic bacteria such as
nitrate and sulfate reducers were observed within 24 h of biofilm formation.
Denitrification phenomena were observed up to 96 h of biofilm growth.

Sreekumari et al.[108] reported that the influence of microstructure on
bacterial adhesion, it revealed that coupons with different microstructure
showed differences in the area of adhesion in spite of uniform surface
condition. The heat-affected zone showed maximum number of attached
bacterial cells with the base metal showing the least. This suggests that the
bacterial adhesion to metals is influenced by microstructure, segregation of
elements on the metal surface in and surface roughness. The variation role of
SRB in media with different pH values and the effects of these variations of bacteria on the corrosion of carbon steel have been studied. They present that the activities of acid-resistance bacteria and alkali-resistance bacteria are compared to those of SRB. The acid-resistance bacteria live in-groups and the body of SRB presents roundness with flagellum. Alkali-resistance bacteria are bacilli, and larger and longer than the original SRB. The distribution of sulfur in corrosion product is not uniform [109].

Webster et al.[110] reported that the main factor controlling microbiologically induced corrosion (MIC) of copper has been identified as a decrease in pH, which in conjunction with the incorporation of bacterially produced extra cellular polymeric substances (EPS) in the copper oxide film, decrease the protective nature of the film. The biofilm (bacteria and EPS) is believed to have a secondary role to the nature of the oxide film in controlling the rate of corrosion. MIC was produced in Laboratory reactors containing the electrodes exposed to simulated potable water in the presence of biofilm composed by microorganisms isolated from a field site. In the presence of biofilm, small but significant reductions in pH occurred from an initial value of 7.5 to a value between 6.5 and 6.9. Using Electrochemical impedance spectroscopy (EIS), it was shown that the presence of a biofilm caused higher corrosion rates similar to those measured in inorganic tests at pH 6.8.

Moreno et al [111] documented the influence of microstructure on the microbial corrosion of stainless steel. Two species of SRB have been used in order to ascertain the influence of microstructure. The morphology of corrosion pits produced in both chloride and chloride plus sulphide-SRB
metabolites was inspected by optical scanning electron microscopy (SEM) complemented with energy dispersive X-ray (EDX) analysis. They showed different behaviour regarding corrosion resistance. Sensitized austenitic stainless steels were more affected by the presence of aggressive sulfides and the pitting potential (Ep) values were more cathodic than those of as received state. A corrosion enhancement is produced by the synergistic action of biogenic sulphides and chloride ions.

1.4.2 Sulphur oxidizing bacteria

Sulphur oxidizing bacteria are found in soils rich in sulfur, sulfur springs, acid mine water and marine resources. They are small rod shaped cells (0.5 x 1.0 – 4.0 μm) with some species mobile by means of polar flagella. They are gram negative and obligate aerobes. Energy is derived from the oxidation of reduced sulfur compounds including sulfides, elemental sulphur, thiosulfates, polythionates and sulfites and the final oxidation product is sulfate generally. Optimum temperature ranges from 28 to 30°C and pH between 2.0 to 3.5. Upper limit of growth is near pH 6.0 and lower limit usually near 0.5. However, a negative pH has also been reported by Sijderius [112].

1.4.2.1 Chemistry of sulphuric acid production

The chemistry of acid production by Thiobacilli has been discussed by various workers [7,113-114]. All the possible Thiobacilli induced sulphuric acid generation mechanisms reveal that many inorganic compounds are susceptible to Thiobacilli induced oxidation. In the biological pathway or oxidation, the various oxidative steps are mediated by specific enzymes with
coupling to an electron transport system, where oxygen is reduced to water as terminal reaction

\[
\frac{1}{2} \text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}
\]  

(10)

Various steps involved in the pathway of sulfide, elemental sulfur and sulfo-oxy anions oxidation are discussed [115]. Production of sulphur oxyanions as meta stable intermediates by *Thiobacilli* has no significant role to play in aerobic MIC due to their unstable nature in oxidative environments. However, Murphy et al [116] pleaded that some of the intermediates like, \( \text{S}_4\text{O}_6^{2-} \) may accumulate until the substrate is completely oxidized, but the ensuing oxidation leads to the formation of sulphuric acid. Tuovinen and his co-workers [117-118] claimed for the accumulation of sulfur as a result of *Thiobacilli* induced disproportion of \( \text{S}_2\text{O}_3^{2-} \) is a stress factor such as, inadequate toxic metal ions or excessive acidity is imposed on the bacteria. Although the factor like inadequate aeration plays a role in the disproportion of \( \text{S}_2\text{O}_3^{2-} \), some *Thiobacilli* were reported to oxidize sulfur compounds under anaerobic conditions. For instance, sulfur compounds can be oxidized by *T.denitrificans* and *T.thioparus* using nitrate or nitrite as an electron acceptor.

Bacteria can release aggressive metabolites, such as organic and inorganic acids and accumulation of acids leads to the deterioration metallic structure. The Effect of acid producing bacteria on metallic structure is shown in Fig-5 [119]. Under deposit corrosion occurs underneath these bacteria [120].
Tiller et al [119] gives the typical reaction for this sulphur oxidizing bacteria (SOB).

\[
\begin{align*}
\text{H}_2\text{S} + 2\text{O}_2 & \rightarrow \text{H}_2\text{SO}_4 \\
2\text{S} + 3\text{O}_2 + 2\text{H}_2\text{O} & \rightarrow 2\text{H}_2\text{SO}_4 \\
5\text{Na}_2\text{S}_2\text{O}_3 + 4\text{O}_2 + \text{H}_2\text{O} & \rightarrow 5\text{Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4 + 4\text{S}
\end{align*}
\]

(11)  
(12)  
(13)

Considerations on the physiology of *Thiobacillus sp* indicate that this organism may not be active in many soils. However, Parker et al [121-122] have described several species of *Thiobacillus* which will reduce soil pH to 6.0. Horvath [123] established much higher weight loss in the presence of *Thiobacilli* than in their absence, and observed a rapid fall in solution pH corresponding to a shift in redox potential of the metal in negative direction. The same work correlated the increased corrosion rate to the decreased pH. *T. ferroxidans* was regarded to be specifically associated with acid production in Pyrite deposits water main [124]. Pope et al [89] pointed out the mechanism of steel corrosion by *Thiobacilli* through \( \text{H}_2\text{SO}_4 \) production, where the local pH
around these organisms may be very low and the surrounding material may disintegrate quite rapidly.

Monte et al. [125] examined the structural and morphological changes in marble samples undergoing microbial attack. In particular, the development of *T. thiooxidans* leads to an increase in total porosity and a change in pore distribution. Fungal growth leads to production of oxalic acid which, by forming oxalates, leads to exfoliation phenomena. Corrosion reactions between *T. ferrooxidans* and pure iron were studied, the results revealed that biocorrosion of iron differs from abiotic corrosion in that ferric iron is generated by bacterial metabolic activity [126].

Pesic and Storhok [127] analysed the reactions of metallic iron in several different aqueous solution systems: water, medium salt solution used for the growth of *T. ferrooxidans* ferric iron solution and solution containing *T. ferrooxidans*. Each system was studied under abiotic and biotic conditions in the presence of *T. ferrooxidans* and as a function of pH, particle size of iron powder, temperature, ferrous and ferric iron concentrations. It was found that metallic iron reacts with water differently than does with ferric iron in water. Surprisingly, *T. ferrooxidans* were non-functional in the dissolution of metallic iron. Also, the reactions of metallic iron with pure water were indistinguishable from the reactions with water containing medium salts for bacterial growth. The reactions with ferric iron were also independent of medium culture compounds. The mechanisms of metallic iron reactions with ferric ions are different from the mechanisms of metallic iron reactions with water. The microorganisms associated with various microbiologically
influenced corrosion is shown in Fig-6. It also gives information regarding the
effect of various substrates and their role in bacterial metabolic activities and
their relationships among the particular group.

![Diagram of various bacterial genera in association with its substrates and corrosion process]

Fig -6. Schematic diagram of various bacterial genera in association with its substrates and corrosion process

1.4.3 Iron Bacteria

The iron bacteria are a diverse group of bacteria that are able to
oxidize and/or deposit iron oxides extracellularly or, sometimes,
intracellularly. The role of bacteria on the reduction of iron in steel are shown
in Fig-7. Iron bacteria are chemolithotrophs deriving energy from the oxidation
of ferrous iron Fe(II) with the formation of ferric hydroxide Fe(III). Iron bacteria
are able to fix carbon dioxide by ripulose pentose phosphate cycle. Iron

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Reducing bacteria can modify the protective oxide film that forms over a mild steel surface causing the surface to depolarize [128].

Fig -7. Effect of iron bacteria in the reduction of iron in mild steel

1.4.3.1 Reduction

The redox cycling of iron plays a major role in the biogeochemical cycling of many elements in natural systems [129-130]. Within the reductive side of the iron redox cycle, dissimilatory microbial systematic reduction of Fe(III) oxides has an extremely broad range of influences on the aqueous solid phase geochemistry and behaviour of natural and contaminant compounds in non sulfidogenic subsurface sedimentary environments. The microbiology and environmental significance of bacterial Fe(II) oxide reduction have been extensively reviewed over the last ten years [131-139]. Facultative anaerobes of Pseudomonas sp. capable of using ferric ions and sulfide as terminal electron acceptors for anaerobic respiration, use low molecular weight compounds such as lactate as carbon source. Some of these bacteria
attached to mild steel coupons and removed a passive $\gamma$-Fe$_2$O$_3$ film and replaced it with a biofilm under which pits developed. The bacteria use ferric oxide as an alternate terminal electron acceptor. Uninoculated controls remained passive with the anodic current decreasing steadily with exposure. The cathodic reaction was polarized during these experiments under both inoculated and uninoculated conditions [140].

1.4.3.2 Oxidation

Iron oxidizing bacteria which oxidize ferrous ion to ferric ion, sometimes promote the corrosion of iron and stainless steel pipes in aerobic environments. Corrosion products composed of ferric hydroxides and other metal salts form tubercles which accumulate on the inner surface of the pipes. The area beneath the deposit becomes anaerobic due to the oxygen diffusion barrier created by the precipitate and the respiratory activities of the bacteria.

A wide spectrum of studies explored the possibility of using *Thiobacillus ferrooxidans*, the bacteria that oxidize iron from ferrous to ferric state in addition to the sulfur oxidation, to extract iron from coal [141-145] based on its ability to promote oxidative dissolution of FeS$_2$ in coal [146-147]. The mechanism of FeS$_2$ removal was proposed by Hoffman et al [148] as follows:

$$\text{FeS}_2 + \frac{7}{2} \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 2\text{H}^+ \quad \ldots (14)$$

$$\text{Fe}^{2+} + \frac{1}{4} \text{O}_2 + \text{H}^+ \rightarrow \text{Fe}^{3+} + \frac{1}{2}\text{H}_2\text{O} \quad \ldots (15)$$

$$\text{FeS}_2 + 14\text{Fe}^{3+} + 8\text{H}_2\text{O} \rightarrow 15\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+ \quad \ldots (16)$$

Equation 16, which is linearly dependent on equation 14 and 15, can be used to represent the overall reaction stoichiometry for kinetic purposes.
Equations 15 and 16 can be used to reflect the overall mechanistic sequences. Singer & Stumn [149] proposed that the equation 15 is catalyzed by \textit{T. ferrooxidans} through the results of their experimentations on pyrite dissolution in the presence and absence of \textit{T. ferrooxidans}. The oxidized iron will either oxidize sulfur compounds to form \( \text{H}_2\text{SO}_4 \) or induce anodic reaction directly.

The iron oxidation and precipitation in presence of filamentous bacteria are shown in Fig -8.

Fig – 8. Deposition of iron by various bacterial genera and its impact on corrosion of steel.

However, it is important to consider that bacteria have the potential to concentrate metals on their cell walls though complexation by surface carboxylate and phosphate groups, and through production of extra cellular polysaccharides which have substantial metal-binding capacities [150-152]. These cell surface associated functional groups possess a negative charge at
circumneutral pH, with the result that they, much like hydroxyl groups on Fe (III) oxide surfaces, tend to sorbs cationic metals at circumneutral pH [153].

1.4.4 Manganese Oxidising Bacteria

Manganese oxidizing bacteria has the ability to catalyze the oxidation of divalent, soluble Mn(II) to insoluble manganese oxides of the general formula MnO. It resulted in the accumulation of conspicuous and easily detectable extra cellular deposits of insoluble brown-black manganese oxides. Many different organisms have the ability to catalyse manganese oxidation, including a diverse array of bacteria, fungi, algae and even eukaryotes [154-155]. Among the Prokaryotes, the ability to oxidize manganese is also quite widespread [156-158] included are members of many physicochemical and physiological groups of Cyanobacteria, a diverse heterotrophic rods, cocci, sheathed bacteria (Leptothrix), budding bacteria (Hypomicrobium) and Pseudomonas sp and still the controversial Metallogenium sp.

There is no evidence of any advantage that manganese oxidation confers on bacteria. The oxidation of Mn (II) to Mn(IV) is thermodynamically favoured under aerobic conditions with a negative free energy of approximately, 16 Kcal/mol [156, 159-160]. The aeration energy barrier can be overcome by raising the pH, or by the addition of manganese binding compounds. Manganese distribution and chemical specification is kinetically controlled, thus allowing for the inter convention of microbes and microbial products into system are shown in Fig.9.
The possible mechanism of Mn(II) oxidation by bacteria are broadly divided into two, i) indirect and ii) direct. In indirect methods, there are free radical or oxidants production of hydrogen peroxide, super oxide and hydroxy radical. Modification of redox environments by oxygen production, pH increase by the CO₂ consumption, acid consumption and release of ammonia production of organic chelators and Mn oxides. In direct methods, the Mn-binding components like proteins, glycocalyces, cell wall components and Mn-oxidising enzymes favours ferrous the Mn(II) oxidation process.

The manganese reduction has not received much attention and the available information is primarily from work done with *Schewanella putrefaciens* M-1 and *Bacillus sp.* Several substrates can serve as reductants.
The optimum temperature for manganese reduction is 30-35°C and the optimum pH is between 6-7 [162-163].

It has been found that the actively metabolizing manganese-oxidizing bacteria deposits MnO₂ creating anaerobic zone within it. These would favour the growth of sulfate reducers whose activity at low values of electrochemical potential might further stimulate the corrosion process initiated by the MnO₂. Oleson et al [164] reported that, the biomineralized manganese, deposited by the manganese oxidizing bacteria, L. discophora SP-6, grown on 316L stainless steel corrosion coupons under laboratory conditions, consisted of manganese dioxide, MnO₂. Natural biofilms grown under field conditions contained a wide variety of manganese minerals. Other not yet fully understood parameters, presumably of microbial nature, complicate the clear image of microbial manganese deposition we get from laboratory studies. Manganese dioxide, plated on stainless steel corrosion coupons, was reduced electrochemically to divalent manganese, Mn²⁺, obtaining two electrons from the metal substratum. Manganese oxyhydroxide, MnOOH, was determined as an intermediate product in this reaction. The presence of biomineralized manganese dioxide as a cathodic reactant may increase the corrosion rate and/or the probability of active corrosion. The manganese oxidizing bacteria, active in the process of manganese dioxide biomineralization, may hypothetically use the product of MnO₂ reduction, Mn²⁺, making the cycle perpetual.
Greene Madgwick [165] demonstrated microbial manganese oxidation at high Mn$^{2+}$ concentration in bacterial cultures and in presence of microalgae. They found that algae Chlamydomonas sp is an essential component of the reaction, a Pseudomonas sp was found to be the growth of sulfate reducers [163]. Unless the medium was supplemented with molybdenum, Acinetobacter calcoaceticans exhibited a very low amount of manganese reduction. In presence of nitrate in the medium inhibited the manganese reduction.

Based on one electron reduction of MnO$_2$ to MnOOH, 8.8$\mu$gcm$^2$ electron active MnO$_2$ was deposited during the 9day exposure. On the basis of their results, ennoblement was demonstrated that this process profoundly alters the electrochemical behavior of stainless steel and suggested the biomineralized MnO$_2$ may be responsible for widely observed pitting corrosion of microbiologically colonized stainless steel. Recently, the electrochemical behaviour of manganese depositors was explained by various researchers [166-169]. Cathodic and anodic polarization curves were explained along with manganese oxidizers. During cathodic polarization, the reduction peaks for iron and MnO$_2$ was routinely observed for the n-type stainless alloy, while they were consistently absent for the p-type.

1.5 Summary

This chapter mainly deals with the definition of corrosion followed by various forms of corrosion. Special emphasize is given to microbiologically influenced corrosion and the economic losses caused by MIC. The effect of various corrosion causing microorganisms such as sulphate reducing
bacteria, sulphur oxidizing bacteria, iron oxidizing bacteria/depositing bacteria and manganese oxidizing/depositing bacteria and their morphology, biochemistry of each microorganisms are discussed in detail. The mechanistic aspects of corrosion of metals caused by different microorganisms are also dealt with. The role of biogenic sulfides on the corrosion behaviour of various metals also discussed. Besides, some recent research in the area of microbiologically influenced corrosion and some open problems for further research have been also discussed in this chapter.