Evaluating Microbiologically Influenced Corrosion

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Introduction

MICROBIOLOGICAL CORROSION, more accurately termed microbiologically influenced corrosion (MIC), is not fundamentally different from other types of aqueous electrochemical corrosion; it is simply that the chemical or physical conditions giving rise to the aggressive environment are produced by microorganisms as by-products of their energy-obtaining metabolism. This may involve the production of an aggressive chemical agent such as hydrogen sulfide (H$_2$S) or acidity. Microorganisms may also consume chemical species that are important in corrosion reactions (e.g., oxygen or nitrite inhibitors). Alternatively, their physical presence may form a slime or poultice, which leads to differential aeration cell attack or crevice corrosion. They may also break down the desirable physical properties of lubricating oils or protective coatings (Ref 1, 2, 3). Microorganisms can therefore be viewed as catalytic entities, effectuating chemical reactions that would otherwise be negligible because of their high activation energy.

Microorganisms, including the corrosion-inducing microorganisms, are present almost everywhere in soils, freshwater, seawater, and air. Therefore, the mere detection of microorganisms in an environment does not necessarily indicate a corrosion problem. What is important is the number of microorganisms of the relevant types.

The salient characteristics of microorganisms from the engineer's viewpoint are that they are small, ubiquitous, potentially very rapid growing, and subject to certain common restraints, such as temperature, pH, and nutrient availability. A problem exists only when conditions become favorable for a specific microbial population to explode, giving rise to thousands or even millions of cells per gram of environmental material. Even then, most microorganisms are harmless from the standpoint of the corrosion engineer; therefore, it is important that the microbiological assessment is type-specific.

The purpose of this article is to address the issue of how an engineer might go about assessing the risk of MIC in an industrial situation. It is not the author's intent to describe in detail the mechanisms of microbiologically mediated corrosion nor to address remedial measures. The role of microorganisms in the corrosion of metals was the subject of a number of classic review articles in the 1970s and 1980s (Ref 4, 5, 6, 7). For more detailed recent reviews of the subject, the reader is referred to the article “Microbiologically Influenced Corrosion” in this Volume and the articles cited under the Selected References at the end of this article. However, it is useful to begin with some limited background information about MIC.

References cited in this section


Most *Desulfovibrio* will only grow in the pH range 5 to 10 and the temperature range 5 to 45 °C (40 to 115 °F), up to a pressure limit of approximately 50 MPa (500 atm) (Ref 8). Some less common groups of SRB have the ability to grow at elevated temperatures up to at least 70 °C (160 °F). Reference 9 cites two cases of corrosion by thermophilic SRB activity: one case being in a tank of hot molasses at a sugar refinery, the second being a transformer tank buried in London clay, where the temperature was 60 to 80 °C (140 to 175 °F) for long periods.

Systems that are susceptible to the effects of MIC by SRB include oil fields (due to use of contaminated drilling mud and injection water), low-velocity lines and storage tanks, aircraft jet fuel tanks and lines, hydrotest waters, cooling waters, and wastewaters. The petroleum-production industry has been particularly plagued by the activities of SRB, because it handles large volumes of deaerated water. These waters can become very sour with H$_2$S if infection with SRB occurs. The situation in the oil industry is the subject of a useful, practical review by NACE International (Ref 10). The phenomenon of unexpected increase in H$_2$S levels in produced fluids from petroleum reservoirs (reservoir souring) has been observed over a period of many years in different areas of the world (Ref 11, 12, 13, 14, 15, 16). Most workers in the field have directed attention to the activities of the SRB, and considerable money has been invested in biocide treatment programs for water injection, with the principal aim of killing or controlling this group of microorganisms (Ref 8).

The mechanism of SRB-mediated sulfide corrosion of ferrous metals has been well reviewed (Ref 17). It involves H$_2$S and FeS. Corrosion rates tend to be slow at first and then accelerate with time (Ref 18).
Attack by Sulfate-Reducing Bacteria

The most important group of bacteria associated with corrosion is the sulfate-reducing bacteria (SRB). Most reviewers have approached the subject of MIC from the viewpoint of the microbiologist and have emphasized the complexity and diversity of metabolic processes. In practice, the great majority of MIC failures are related to the activities of SRB. Sulfate-reducing bacteria are anaerobic (oxygen-free) bacteria that obtain their required carbon from organic nutrients and their energy from the reduction of sulfate ions to sulfide. Sulfate-reducing bacteria will only flourish and cause damage if they obtain sufficient sulfate. Sulfate is abundant in freshwaters, seawater, and soils. Sulfide appears as $\text{H}_2\text{S}$ (dissolved or gaseous), $\text{HS}^-$ ions, $\text{S}^{2-}$ ions, metal sulfides, or a combination of these, according to conditions. Sulfides are highly corrosive to many materials. In the case of iron and mild steel, the characteristic black iron sulfide (FeS) corrosion products liberate $\text{H}_2\text{S}$ on acid treatment, distinguishing them from black iron oxide (magnetite). The corrosion products are often loose and, when dislodged, exhibit pits lined with bright metal corresponding to areas of anodic dissolution.

Bacteria of this type can also use hydrogen by sulfate reduction:

$$4\text{H}_2 + \text{SO}_4^{2-} \rightarrow \text{S}^{2-} + 4\text{H}_2\text{O}$$

The most commonly encountered SRB type is known as *Desulfovibrio* (Fig. 1).
In natural conditions, SRB grow in association with other microorganisms and use a range of carboxylic acids and fatty acids, which are common by-products of other microorganisms. Biological slimes are commonly found in the water phases of industrial process plants (Fig. 2). A wide range of common bacteria (e.g., *Pseudomonas* and *Flavobacterium*) can secrete large amounts of organic material under both aerobic and oxygen-free (anaerobic) conditions. Conditions at the base of even thin slimes (biofilms) can be ideal for the growth of SRB, with high organic nutrient status, no oxygen, low redox potential, and protection from biocidal agents. Figure 3 illustrates the steps in biofilm formation. The SRB can thereby produce active sulfide corrosion even in systems where the bulk liquid phase has a low nutrient status, a high oxygen concentration, and will not support growth of anaerobic bacteria.
The muddy bottom of any relatively stagnant body of water with a high biological oxygen demand often supports massive growth of SRB, as may waterlogged soils. Any metallic installations buried or immersed in such environments can be expected to suffer badly from microbiological corrosion. The most serious economic problem is to pipelines, although sheet piles, hulls of ships, piers, and so on are frequently attacked. In some instances, cast iron pipes of 6.3 mm (0.25 in.) thickness have become perforated within 1 year under such conditions, while perforation in 3 years is common.

A large-scale study of many factors at 59 sites in the United Kingdom (Ref 19, 20) led to the suggestion that aggressive sites were characterized by soil resistivity of less than 20 Ω · m (2000 Ω · cm) or a mean redox potential more negative than +400 mV (on the hydrogen scale) at pH 7. Borderline cases were classified according to water content—those containing more than 20% water being deemed aggressive soils. Similarly, all soils with a mean soluble iron content of over 120 μg/g were found to be aggressive. A particularly corrosive situation is when H₂S diffuses upward into the aerated zone, where it becomes oxidized by air to sulfur (Ref 21).

There is a widespread belief that copper and its alloys are toxic to microorganisms and therefore are not susceptible to MIC. This notion is false. Copper alloys are much less toxic to bacteria than they are to macrofouling organisms, such as seaweed or shellfish, and suffer severe attack by sulfide if conditions allow the growth of SRB. A gun-metal impeller that was located in a polluted harbor (Fig. 4) failed in a matter of weeks after the pump was switched off, due to the growth of SRB in the stagnant pump. The component had previously given 2 years of trouble-free operation in aerated seawater.

Fig. 4 Copper alloy impeller failure due to sulfate-reducing bacteria in stagnant seawater

Cases of mysterious underdeposit or underfouling pitting corrosion of copper-nickel heat-exchanger tubes have been observed. Many of these failures are demonstrably due to biogenic sulfide produced by SRB. When copper alloys are electrically linked into a cathodic protection system, they tend to lose their antifouling properties and become susceptible to attack by SRB colonies underneath the consequent fouling mat if insufficient protective current is reaching the substrate surface to polarize it into the immunity zone. Silver suffers very severe attack by SRB in a similar way to copper.

Numerous examples of corrosion of stainless steel and higher active/passive alloys involving sulfide production by SRB have been published (Ref 22, 23). This phenomenon is best termed microbiologically assisted, chloride-induced pitting attack. Active/passive alloys are susceptible to localized pitting by chloride ions. Reduced sulfur compounds produced by SRB appear to bind to the metal surface and catalyze the initiation of this process at much lower chloride concentration and at lower temperatures than would otherwise be the case. Once a pit is established, the anodic reaction generates acidic conditions, accelerating the corrosion rate and causing flask-shaped cavities to form (Fig. 5). This is totally different from the shallow pitting attack of low-alloy materials exemplified in Fig. 6. The pits may be concealed beneath ferric hydroxide, and the process is often associated with copious amounts of brown-colored biological slime containing iron-oxidizing bacteria known as Gallionella. A typical example is shown in Fig. 7.
Fig. 5  Flask-shaped pit in an American Iron and Steel Institute (AISI) 304 (Unified Numbering System, or UNS, S30400) stainless steel pipe of 5 mm (0.2 in.) wall thickness

Fig. 6  Microbiologically influenced corrosion in a water pipe due to sulfate-reducing bacteria

Fig. 7  Slime formation by iron bacteria, *Gallionella*, in the pitted stainless steel pipe shown in Fig. 5
Bacterial metabolism is only involved in the pit initiation stage. Once the pit has formed and acidic chloride conditions develop within, the pit propagation process is the same as with any other case of chloride-induced pitting. Claims that MIC of stainless steels is characterized by a particular pit morphology, different from conventional chloride-induced pitting attack, should therefore be viewed with some skepticism.

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**Attack by Organisms Other Than SRB**
As already discussed, biological slimes are commonly found in the water phases of industrial process plants. A wide range of bacteria can secrete large amounts of organic material under both aerobic and anaerobic conditions.

Some components of slimes also use nitrogen-containing compounds as an energy source. They are involved in the cycling of nitrogen in the environment. Ammonia and amines are produced by microbial decomposition of organic matter under both aerobic and anaerobic conditions (ammonification). These compounds are oxidized to nitrite and nitrate by aerobic bacteria such as *Nitrosomonas* or *Nitrobacter* species. *Nitrobacter* is very efficient at destroying the corrosion-inhibition properties of nitrite-based corrosion inhibitors by oxidation, unless a biocidal agent is included in the formulation (Ref 24). The detrimental effects on brass of the release of ammonia at the surfaces of heat-exchanger tubes have also been highlighted (Ref 25).

The bacteria of the genus *Thiobacillus*, of which there are several types, belong to an unusual group of microorganisms called chemolithotrophs. These organisms obtain energy not by oxidation of organic compounds but by oxidation of inorganic sulfur compounds (including sulfides) to sulfuric acid. The organisms build up their cell material by fixation of carbon dioxide. The following interlinked reactions are performed by mixed cultures of *Thiobacilli* acting on elemental sulfur or sulfides (Ref 26):

\[
2\text{H}_2\text{S} + 2\text{O}_2 \rightarrow \text{H}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O} \\
5\text{S}_2\text{O}_3^{2-} + 4\text{O}_2 + 4\text{H}_2\text{O} \rightarrow 5\text{SO}_4^{2-} + \text{H}_2\text{SO}_4 + 4\text{S} \\
4\text{S} + 3\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{H}_2\text{SO}_4
\]

Certain of the *Thiobacilli* will also leach metal sulfide ores according to the following reaction (Ref 27):

\[
4\text{FeS}_2 + 15\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{Fe}_2(\text{SO}_4)_3 + 2\text{H}_2\text{SO}_4
\]

The important points to note are that these bacteria require oxygen (the opposite of the situation with SRB) and a source of reduced sulfur. The end product is sulfuric acid; one species (*Thiobacillus thioxidans*) is said to remain active at pH 0.7, corresponding to more than 5% sulfuric acid (Ref 28).

Although fairly commonly encountered in nature, *Thiobacillus* proliferation only causes problems in a relatively few specialized industrial situations. One such condition can arise in sewage systems, in which sulfide concentration may be high, owing to the action of putrefactive bacteria, unless aeration is efficient. Suitable conditions can also arise locally in made-up ground into which industrial waste material sometimes finds its way. For this reason, sulfuric acid corrosion of underground pipelines is sporadic and unpredictable. Attack by sulfuric acid produced by sulfur-oxidizing bacteria such as *Thiobacillus* can be a severe problem in concrete sewers, mortar-lined ductile iron pipes, concrete manholes, and wastewater treatment plants and equipment (Fig. 8).

Figure 9 illustrates schematically the typical corrosion/deterioration of septic sewage systems in hot climates such as the Middle East. The problem starts with growth of anaerobic SRB in the sewage, producing H$_2$S. This gas migrates to the air space at the top of the line, where it is oxidized into sulfuric acid in the water droplets at the crown of the pipe by *Thiobacillus*. The corrosion problem is due to the combination of the bacterial action that results in dissolution of the alkaline mortar by the acid, followed by corrosion of the ductile iron.
A completely different type of organism from the various groups of bacteria are the fungi. The cells are much larger and grow in dense mats of material. Filamentous fungi are aerobic in nature and are involved in a wide range of biodeterioration problems. Timber, paper, fuel oils, cloth, and so on can be attacked by fungi. Fungal activity generates organic acids, leading to a low pH in the water and under the microbial mat. In addition to direct acid corrosion, oxygen concentration cells are set up between zones of metal covered with oxygen-depleted fungal mats and those areas where no fungi are present. This electrochemical cell drives the metal dissolution reaction beneath the fungal mat.

By far, the most troublesome fungus in engineering systems is a type commonly called *Cladosporium resinae*, although now reclassified as *Hormoconis resinae* (Fig. 10). *Hormoconis resinae* has the ability to thrive in the presence of kerosene and other hydrocarbons, which it uses as a carbon source for oxidation. It also produces spores, which can survive extremes of temperature, only to germinate when more moderate conditions prevail. *Hormoconis resinae* is a continuing problem in fuel storage tanks and in aluminum integral fuel tanks of aircraft (Ref 29).
Brown, slimy mats of *Hormoconis resinae* may cover large areas of aluminum alloy (Fig. 11), causing pitting, exfoliation, and intergranular attack due to organic acids produced by the microbes and the differential aeration cells. This type of problem is largely confined to tropical, humid locations and is particularly severe in short-haul aircraft and those that experience a lot of idle time, where condensation builds up.

The previously mentioned problem was unknown until the 1950s, when it became prevalent after the introduction of gas-turbine-engined aircraft, which use kerosene rather than gasoline as a fuel, and the adoption of integral or wet wing fuel tanks to replace the earlier rubberized fabric bay tanks (Ref 28). The problem of fungal growth in the fuel tanks of jet aircraft has generally diminished as the design of fuel tanks has improved to facilitate better drainage of condensed water and as biocides such as organoboranes have gained acceptance as fuel additives.

**References cited in this section**
