

## **MICROBIALY INFLUENCED CORROSION (MIC) –AN UP TO DATE OVERVIEW**

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### **Abstract**

Iron is a material which is sensitive to corrosion. This process has tremendous financial and safety implications for many industries. The annual direct cost of corrosion in 1996 in the United States of America was up to 276 billion dollars. Conservative estimates link at least 10% of these costs to MIC. Whereas iron corrosion in the presence of oxygen is predominantly an electrochemical process, iron corrosion in the absence of oxygen (in anoxic zones like sediments or inside of iron pipes) is largely biologically influenced. This anaerobic process is in most cases linked to the activity of sulfate-reducing bacteria (SRB). SRB gain their biochemical energy for growth by reducing sulfate to sulfide with natural electron donors that are oxidized to carbon dioxide (or acetate), a process also referred to as sulfate respiration. In addition, many SRB can also use molecular hydrogen or in some cases metallic iron.

Concrete or other cement based building materials are also susceptible to corrosion influenced by micro-organisms. Here, sulfides produced by SRB or sulfur (as a product caused by chemical oxidation) are oxidized by sulfur-oxidizing bacteria (SOB) to sulfuric acid. This process is called biogenic sulfuric acid corrosion. This paper will provide an overview about the mechanisms and the microorganisms involved in MIC, show some case studies and summarize the newest research developments in this field.

### **Introduction**

Under the term microorganisms algae, fungi (mould and yeast, not higher fungi), bacteria, and archaea are summarized. The last ones are somewhat similar to bacteria but resemble a different line of evolution.

The degradation of organic material by microorganisms is most important recycling process in nature and essential for all kind of element cycles. The major players here are fungi and bacteria. Microorganisms are also able to degrade inorganic materials. The reason for them to do this is that these inorganic materials can be oxidized and the electrons can be used by the bacteria to gain energy. This process is then coupled to carbon dioxide fixation for providing carbon for biomass formation. The process when bacteria are using only inorganic sources for energy formation and carbon fixation is called chemosynthesis (or more precise chemolithoautotrophy). Prominent examples are ore leaching, corrosion of iron, degradation of building materials, and alteration processes. In principle all these compounds are thermodynamically instable and the microorganisms use this instability for their own purpose. For a long time people thought that these processes were purely chemical mechanisms and were not linked to the activity of microorganisms but this view has changed.

A good example is the oxidation of iron. If oxygen is present, this oxidation is mainly of chemically origin. Together with water the oxygen will catalyze the oxidation by forming localized cathode and anode areas. In general, this process is very fast and microorganisms have no chance to compete with this chemical reaction. There are only a few reports where this process was triggered by certain bacteria which are capable to use metallic iron and ferrous iron as electron donor at a neutral pH value [1]. The oxidation of ferrous iron to ferric iron allow some specialized bacteria to obtain energy but only in habitats with an acidic pH like iron springs or ore deposits.

In the absence of oxygen the chemistry is completely different and the corrosion by microorganisms becomes dominant. This process is called “microbially influenced (or induced) corrosion” (MIC) and is catalyzed by anaerobic microorganisms. Therefore, MIC is predominantly linked to anoxic (oxygen-free) zones where these bacteria live. Oxygen is toxic for these bacteria or will at least allow no growth. A good example is the corrosion of steel piles shown on Fig. 1 which will corrode from the back and not from the water side. The pitting was caused by the activity of SRB and had drastic effects as can be seen by the hole.

Nevertheless, the term MIC includes also aerobic bacteria as can be seen in the example above.

## **Corrosion in the absence of oxygen**

### **MIC by sulfate-reducing bacteria**

A common feature of sulfate-reducing bacteria (SRB) is the ability to use sulfate as electron acceptor which is reduced to sulfide. This process can be called “sulfate-respiration”. Many sulfate-reducing bacteria can also grow by fermentation or use other electron acceptors like sulfite, thiosulfate, or tetrathionate which are also reduced to sulfide. Only a few of them can reduce sulfur to sulfide or reduce nitrate to ammonia. They are widespread in nature and primarily found in anoxic sediments or water [2]. SRB can use a large variety of electron donors and carbon sources going from simple organic compounds like organic alcohols, organic acids, fatty acids to more complex compounds like aromatic compounds, long chain fatty acids, alkanes

to polycyclic aromatic compounds or other oil related compounds. In addition, there are several SRB which can grow only on hydrogen and carbon dioxide [2]. Because of the ability to use compounds which are present in crude oil, they can cause souring and massive corrosion problems in oil industry [3]. Many SRB can live at higher temperature or live in alkaline or acidic habitats. Beside SRB also some archaea, e.g. *Archaeoglobus* spp. can also use sulfate as electron acceptor. These microorganisms can grow at elevated temperature (up to 90°C) and might cause problems at high temperature oil production sites.



Figure 1: Hole in steel pile caused by MIC from sulfate-reducing bacteria.

Beside SRB there are many other microorganisms which are anaerobic and produce sulfide. These are bacteria which mineralize sulfur-containing organic compounds like amino acids or thiophenes, sulfur-reducing bacteria, or bacteria which will reduce sulfite or thiosulfate to sulfide. These physiological properties are widespread among anaerobic bacteria, but they are not SRB. The focus of this paper will be on SRB.

The corrosion of iron linked to SRB was first described by van Wolzgen Kuehr and van der Flugt in 1934 [4] who developed the model of cathodic depolarization. Similar to the process with oxygen and water a local cathode and anode develop on the iron surface. The reactions are shown in equation 1 to 6.

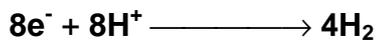
Dissolution of iron (equation 1):



Cleavage of water (equation 2):



Reduction of protons (equation 3):

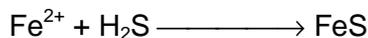


The hydrogen formed is taken up by the SRB and used for sulfate reduction to sulfide which will react with ferrous iron to form sulfide.

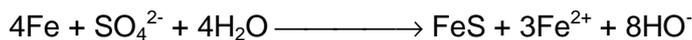
Reduction of sulfate (equation 4):



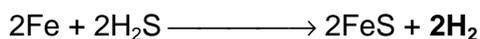
Formation of FeS (equation 5):



The overall reaction can be summarized as follows (equation 6):



This model is still used although there are many findings which cannot be explained by using it. The role of SRB is clearly an indirect effect, because they will use the hydrogen produced by a chemical reaction. In addition to the continuously depletion of hydrogen the SRB have another effect by producing sulfide. This compound has also an effect on the formation of hydrogen as can be seen by the following equations (7 to 9).



In 2004 Dinh and coworkers isolated the first anaerobic bacterium which was able to grow on iron as electron donor and carbon dioxide as carbon source [5]. It was a marine SRB which grew much slower on hydrogen than on iron and it required direct contact to the iron surface. At that time the authors already postulated a direct electron uptake from the iron. This was later confirmed by same group which also

found massive formation of conductive FeS and none conductive FeCO<sub>3</sub> on the metal surfaces [6; 7]; see also Fig. 1.

Today we now that there are two different mechanisms which can be distinguished for the corrosion by microorganisms [6; 7]. The first mechanism is called chemically influenced corrosion (CIC) and will follow the model of cathodic depolarization. The main trigger for this reaction is the formation of sulfide by the SRB. The hydrogen produced is taken up by the SRB. Many SRB would participate from the hydrogen but they are not the real corrosive ones [6]. The second mechanism is exclusively linked to certain SRB which are highly corrosive and can take up the electrons directly from the iron. This process is not only influenced but really induced by the SRB and can be called microbially induced corrosion (MIC). This direct uptake of electrons from the iron can only be achieved by a limited number of SRB strains although they are found all around the world.



Figure 2: Ferrous sulfide and carbonate precipitate on an iron plate corroded by sulfate-reducing bacteria.

### **MIC by methanogenic archaea**

Beside SRB also methanogenic archaea can use metallic iron as electron donor and can cause serious corrosion problems. The first methanogenic archaeon was isolated 2004 [5]. It grew on iron and carbon dioxide, which was used as carbon source for carbon fixation and as electron acceptor for methane formation according to the following equation 10:



Here the final product is not sulfide but carbonate. In contrast FeS the carbonate is not conductive and might hinder the corrosion after a certain level of deposit is formed. Nevertheless, this process is found to be prominent in storage tanks or oil production [8]

### **MIC by nitrate-reducing bacteria**

To prevent souring of oil many companies add nitrate to their injection water. Although there have no bacteria been isolated so far which can grow with iron, carbon dioxide and nitrate as electron acceptor, it is very likely that organisms exist or will adapt to such a metabolism. The nitrate would be either reduced to ammonia or to dinitrogen. In my opinion, ammonia formation would be more likely.

### **MIC by sulfur-oxidizing bacteria**

In contrast to all the other bacteria mentioned above these bacteria are aerobic ones and use oxygen as electron acceptor. They oxidize sulfide, elemental sulfur or other reduced sulfur compounds including metal sulfides to sulfuric acid. This process is named "biogenic sulfuric acid corrosion" and is very important for the deterioration of concrete as building material. The reduced sulfur compounds which are oxidized by this group of bacteria originate from the microbial activity of SRB. Their final product sulfide can then be oxidized chemically by oxygen to elemental sulfur. This reaction can also be catalyzed by bacteria. Sulfur is then further oxidized to sulfuric acid. A characteristic feature of most bacteria which catalyzed this oxidation is that they are very well adapted to acidic pH values and some of them tolerate even a pH below 1.

Important to mention is that the reduced sulfur compounds used as substrates are produced primarily by SRB. Other sources can be hydrothermal vents or gases from volcanoes. So the sulfuric acid formation can be regarded as a combined action of two groups of bacteria:

The SRB produce sulfide from sulfate and organic substrates (or hydrogen) in an anoxic zone. The sulfide will be released by the liquid as gas or stay in the liquid and enter oxic zones. There a chemical oxidation to sulfur might occur and a precipitate will be formed which will then be oxidized to sulfuric acid by sulfur-oxidizing bacteria (SOB).

The final result of this can then be the corrosive attack of sulfuric acid on all kind of materials which will have a dramatic effect. For example, in concrete the alkaline phases will be directly dissolved by the acid and in addition a new mineral will be formed as can be seen on Fig. 3. This new material called Ettringite ( $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$ ) has a larger volume and a massive formation of cracks will happen.



Figure 3: Biogenic sulfuric acid formation and the effects on a concrete cube.

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