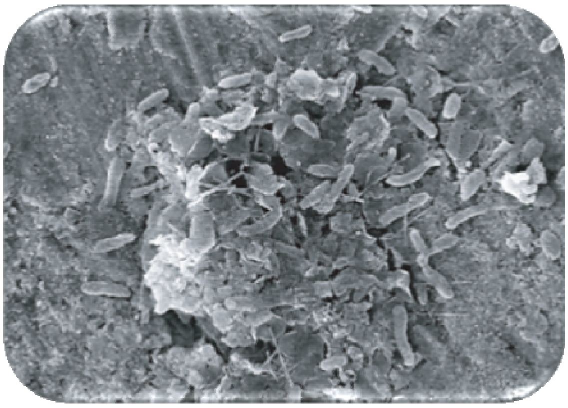
Biocorrosion



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Code TVA FR 70 345 010 557 00048 – BNP Paribas Compans Caffarelli Toulouse 30004/01570/00023040601/84

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I) Introduction

When we are walking around the sea or into a harbor, we use to see boats or iron pieces covered by rust. This phenomenon is called corrosion. It can happen also for a pipe which is buried in the ground. In this report, we will talk about corrosion because of water and especially seawater. The biocorrosion isn't a different way to have rust but the impact that bacteria have on the metal. It's also named MIC for Microbiologically Influenced Corrosion.

Studies about biocorrosion started in the 60s. The importance of the biocorrosion can be realized thanks to these data[1]: in France, 27 billion Euros are spent each year to repair what corrosion has destroyed. The biocorrosion is responsible of 5 to 10 per cent of this cost which means around 5 billion Euros per year. For the naval industry, it represents a big budget and that's why studies are more important to date.

In this report, first we will describe corrosion and biofilms. This knowledge permits to work on this question: *Do bacteria have positive or negative actions on marine corrosion?*

We will see two hypotheses and then solutions which exist to prevent biocorrosion.

II) Corrosion

The corrosion is the interaction that exists between the metal and the environment which is the sea in this case. The corrosion deteriorates the metal and creates holes in it. The system breaks when the corrosion is very important. For example, a pipe transporting petroleum mustn't be corroded. The marine corrosion is an electrochemical reaction between the anode and the cathode, depending on oxygen. When the metal is immersed into the water, we speak about electrode. The anodic reaction is an oxidation: $Fe \rightarrow Fe^{2+} + 2e^-$. Whereas the cathodic reaction is a reduction:

- Without oxygen: $2\ H_2O + 2e^- \rightarrow 2\ OH^- + H_2$
- With oxygen: $O_2 + 2\ H_2O + 4e^- \rightarrow 4\ OH^-$

[1] <www.biocorys.utc.fr>

Each reaction has an electrode potential: E_a and E_c. Before corrosion, both anodic and cathodic reactions are at equilibrium. The marine corrosion starts when E_c is higher than E_a and a new potential is generated: E_{corr} (corrosion potential).

The iron that forms the metal is modified and the rust appears:

- Anaerobic conditions: $2\ H_2O + Fe \rightarrow Fe\ (OH)_2 + H_2$
- Aerobic conditions: $4\ Fe\ (OH)_2 + O_2 + 2\ H_2O \rightarrow 4\ Fe\ (OH)_3$

We saw that water and oxygen are essential for corrosion and it's the same for bacteria growth.

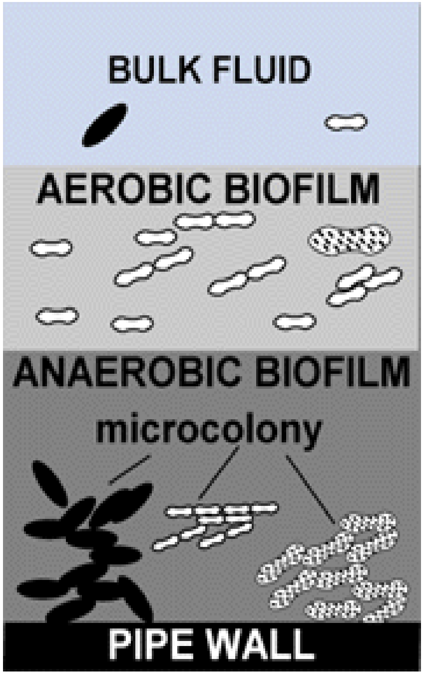
III) Bacteria and biofilms

Bacteria belong to the prokaryote micro-organisms: they don't have nucleus. It's possible to distinguish two kinds of bacteria: Gram-positive or Gram-negative. For Gram+ bacteria, the extracellular membrane is absent and the peptidoglycan is very important. In the structure of bacteria, there are flagella and pili which permit the fixation on the metal. Bacteria can be separated in two groups: aerobe if they need oxygen and anaerobe if they can live without oxygen. More specifically, we will talk about sulfate-reducing bacteria (SRB) for anaerobes bacteria. With their metabolism, bacteria secrete several macromolecules (proteins, nucleic acid, lipid…) called Extracellular Polymeric Substances (EPS). They use energy and change the environment around them.

Bacteria are hanging into the water or organized into a biofilm. A biofilm contains 25% of bacteria and 75% of EPS. Bacteria need several elements to live: these elements are going through the biofilm.

The development of the biofilm is in five steps:

1. Adhesion: Thanks to their pili and flagella, bacteria move into the water. They find a metal support and start a reversible adhesion.
2. Consolidation: If bacteria have everything to grow, the adhesion becomes irreversible.
3. Colonization: Bacteria are protected by their EPS, they can grow without problems.
4. Maturation: The biofilm is mature and acquires its 3D structure.
5. Sloughing: Some bacteria leave the biofilm to find a new one especially when there is a nutrient starvation in the environment.



The biofilm begins when an iron pipe is in contact with water for example. The biocorrosion appears because bacteria alter the environment locally and because a biofilm is heterogenic: there are aerobes and anaerobes bacteria and most of time aerobes bacteria are near the fluid and anaerobes bacteria are closed to the metal. Moreover, the biofilm has different thickness.

IV) Biocorrosion

Bacteria modify the interaction between the support and the environment. The biocorrosion is induced because of three elements: metal, solution and micro-organism.

A) Acceleration of corrosion

In the first assumption, bacteria enhance corrosion. It's the aerobe bacteria which start the reaction thanks to enzyme. Actually, these bacteria use the oxygen with glucose. The enzyme called glucose oxidase (GOD) transforms this element into gluconic acid and hydrogen peroxide: D-glucose + $O_2 \rightarrow$ D-gluconic acid + H_2O_2. This H_2O_2 increases the corrosion potential E_{corr} and thus the corrosion. The H_2O_2 can be reduced by catalase and peroxidase. So, the kinetic of the corrosion depends on all of these elements. The aerobes bacteria diminish the oxygen into the biofilm and it's better for anaerobes bacteria. The sulfate-reducing bacteria (SRB) reduce the sulfate into sulfur. The sulfur can be associated with iron (Fe) to create iron sulfide (FeS) or with hydrogen (H_2) to create hydrogen sulfide (H_2S). These elements accelerate the corrosion in places of the pipe and dig a pit. It's called SRB corrosion.

The biocorrosion has a special kinetic described in a model with 5 steps:

1. Step 0: When the metal gets into the water, bacteria colonize it and the biofilm begins. There are more aerobes bacteria than anaerobes.

2. Step 1: The metal is victim of an oxidation. Some products of corrosion appear. The kinetic is linear.
3. Step 2: The corroded part increases and there is less oxygen. The anaerobes bacteria have better conditions to live. The kinetic slows down.
4. Step 3: If the bacteria have enough nutrients, they grow and the corrosion continues.
5. Step 4: The system is balanced and the kinetic of corrosion is linear again.

The duration of the steps depends on the environment: nutrients, oxygen, bacteria…

Three main mechanisms have been described by scientists [6] and are studied still. They explain how biofilms interact with the metal and how they are responsible of biocorrosion.

In the first mechanism, scientists show that “biofilms create oxygen heterogeneities”. Actually, bacteria use oxygen but the biofilm is heterogenic. Consequently, the concentration of oxygen is heterogenic which induces potential differences: it’s the establishment of the corrosion. For the second mechanism, scientists explain that “biofilm matrix increases the mass transport resistance”. The EPS of the biofilm make the transport of chemical elements difficult. The conditions around the metal are affected in the same way as in the first mechanism: the resistance is different at various locations on the metal which modify the concentration of oxygen. There is also a lower pH: acid solutions are bad conditions for the iron. The third described mechanism is about “metabolic reactions in biofilm [which] generate corrosive substances”. The sulfate-reducing bacteria don’t need oxygen and create elements like H_2S and FeS thanks to their metabolism. But when these elements meet the oxygen of the water, new reactions transform them into elemental sulfur (S^0) which is known as a corrosive agent. All the reaction can start again and that comes full circle.

For example:

$$Fe^{2+} + HS^- \rightarrow FeS + H^+$$

Fe^{2+} comes from anodic reaction and HS^- is a metabolic product of SRB due to the enzyme hydrogenase. Then, there is a reaction between the water and the iron sulfide:

$$2H_2O + 4FeS + 3O_2 \rightarrow 4S^0 + 4FeO\,(OH)$$

The elemental sulfur is generated. It reacts with water to form hydrogen sulfide:

$$4\,S^0 + 4\,H_2O \rightarrow 3\,H_2S + H_2SO_4$$

$$2\,H_2S + 2e^- \rightarrow H_2 + 2\,HS^-$$

The environment becomes acid and enhances corrosion.

So, bacteria can accelerate the corrosion. Different reasons are possible and maybe others will be found in few years.

B) Inhibition of corrosion

The second hypothesis indicates that biofilms can inhibit corrosion. The most important explanation given by the scientists, is that the biofilm is protective against corrosive agents especially oxygen and that aerobe bacteria decrease the oxygen concentration. The best solution would be to find biofilms which secrete antimicrobials agents to reduce SRB and/or secrete corrosion inhibitors. But all the persons who are against this assumption remind that biofilms are heterogenic and uncontrollable. On the other hand, it can be interesting to understand these mechanisms to imagine solutions to stop biocorrosion.

V) Solutions

When we know the consequences due to biocorrosion, we realize that it's better to prevent this phenomenon. The principal idea is to keep the metal clean.

Different methods exist. First of all, the method can be a physical technique: cleaning the pipe with a sponge but the problem is that damages can be done and it will be worse. Then, a chemical method can be employed thanks to biocide treatments. There are two groups of biocides:

- Oxidizing: they go through the cellular membrane and kill the micro-organism. The most popular in industry is the chlorine but it must be used carefully because it has corrosive properties.
- Non-oxidizing: They inhibit some metabolic pathways of the bacteria. The glutaraldehyde is one example. These agents are more efficient than oxidizing biocides.

The problem is that biocides have an important toxicity towards the environment.

So, more and more restrictions are given by the minister. Moreover, bacteria can develop resistance against these biocides. Consequently, scientists are looking for natural mechanisms. For example, they try to use enzymes to avoid the biofilm adhesion on the metal.

Finally, another solution that works to inhibit biocorrosion is called cathodic protection. It's an electrochemical method that creates a battery. The cathode is the metal that must be protected. The oxidation of the anode is made into the protective system: the added anode is called sacrificial anode. It permits to diminish the corrosion potential E_{corr} to a protective potential E_{prot}. Actually, the purpose is to keep the iron from becoming stable. This technique gives electrons from the sacrificial anode (in aluminum for example) to the iron which is the structure that must be protected. It creates a layer of calcium and magnesium. This layer is protective and makes unfavourable conditions for bacteria especially SRB which cannot touch the iron. Thus, for the moment, the cathodic protection is the best solution to prevent biocorrosion and it can be associated with anti-fouling paints (for example on ship's hulls).

VI) Conclusion

The biocorrosion is a phenomenon that has to be considered today, especially by industrial. For most of scientists, bacteria have a negative action on marine corrosion because it accelerates it by inducing heterogeneities on the metal. But some studies demonstrate the positive impact as a protection against corrosion. Studies on biocorrosion increase nowadays. The problem is that scientists have to know different subjects such as electrochemistry, microbiology, chemistry, metallurgy, steel industry, corrosion engineering…

Mechanisms to fight against biocorrosion must be developed. The best way would be a natural process like enzymes to remove the biofilm. It can be associated with cathodic protection to prevent this formation. All the mechanisms must respect the environment.

To open up new horizons, it could be interesting to work on different kind of biofilms. They have negative impact on teeth and are responsible of nosocomial pathology. They are also a problem in the food-processing industry. On the other side, biofilms can be protective in the environment for several animals or in the intestine for human health.

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