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Biofilms: an approach in different industrial systems <u>*Patricia Guiamet</u>^{a,b}, Sandra Gómez de Saravia^{a,c}

Abstract

Abiotic corrosion processes probably influence the rate, extent and distribution of colonizing microbial species, as well as the chemical compositions and physical properties of resulting biofilms. The major groups of microorganisms most frequently implicated in corrosion processes are as follows: iron and sulphur–oxidizing bacteria, anaerobic sulphate-reducing bacteria, the fungus *Hormoconis resinae*. Practical cases can identify a number of situations where failure by corrosion of fouling is due to the interaction of microorganisms with industrial materials and systems. The cases presented show that the phenomenon is common to a great variety of material environmental conditions and locations through the world and that there is extensive concern about the problem. The aim of this work is to show the results about biocorrosion in different industrial systems: three plants of extraction and secondary oil and steel plants. It presents a comprehensive analysis and interpretation of the problem of corrosion present in the deposits using information obtained from microbiological and physicochemical fields in order to propose strategies for diagnosis, evaluation of solutions in laboratory and field

Keywords: Biofilms, Hormoconis resinae, sulphate-reducing bacteria

Introduction

The first mention of corrosion involving microorganisms were made in the early twentieth century, however, was in the 80's it was recognized worldwide that the microbiologically induced corrosion (MIC) creates serious problems in the oil industry, accounting for this among 50 to 90% of localized corrosion and 30% of the total cost that corrosion causes in this industry (1, 2). MIC problems are associated among other things, mainly to the presence of sulphate-reducing bacteria (SRB), which has generated substantial investments in the microbiological control of water injection, the persistence of localized corrosion and biofouling in lines distribution of water to oil production (3, 4). The presence of operational problems for poor performance of responsible operators in these facilities, may favour the development of MIC, which leads among other things, the replacement pipe failure, pressure loss in pipes, unplanned plant shutdowns for replacement and maintenance of pipes, etc. (3, 5). The cases presented show that the phenomenon is common to a great variety of material environmental conditions and locations through the world and that there is extensive concern

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about the different problem. The aim of this work is to show the results about biocorrosion on industrial systems located in Argentina. The strain of different bacteria *Pseudomonas* sp., acid producing bacteria, SRB and *Hormoconis resinae* were isolated from the plants. These microorganisms are directly related to their capacity of biofilm formation and aggressive conditions created at the fixation points that are the main causes of the localized biocorrosion of the metal (6).

It presents a comprehensive analysis and interpretation of the problem of corrosion present in the deposits using information obtained from microbiological and physicochemical fields in order to propose strategies for diagnosis, evaluation of solutions in laboratory and field. Several items in common are described, which are the clue to demonstrate the influence of the microorganisms on the biocorrosion process. In spite of the numerous variations it is evident that similar cases can occur with different materials in different environments or systems.

System 1: Pipes and tanks of steel rolling mill emulsion of a metalworking plants in Buenos Aires, Argentine.

The samples were two emulsions, E1, light and almost liquid and oxygenated and E2, heavy and almost black colored of muddy aspect, and a third sample from filters, they were sent to the laboratory to be subsequently processed.

Microbiological studies: The growth of heterotrophic mesophilic bacteria, acid producing bacteria, sulphate reducing bacteria (SRB), reducing sulphite bacteria, iron bacteria, Pseudomonas sp. fungi and yeasts were investigated (7).

Microscopic observations: All the samples were observed with JSM6360LV scanning electron microscope (SEM) and with Olympus BX51 optic microscope. To preserve the biological specimens, for the observation in the SEM, samples were fixed with a solution of glutaraldehyde at 2% in phosphate buffer, washed in distilled water and dried on gradual series of acetone up to 100% and by the critical point technique (7).

In Table 1 and Figure 1 it can be seen the microbial counts obtained of different samples.

SAMPLE	Acid producing bacteria	Sulphate reducing bacteria (SRB)	Iron oxidizing bacteria	Fungi and yeasts
E1	1000-10000	1-10	1-10	50
E2	100-1000	10-100	10-100	(-)

Table 1 - Microbial counts (mo/mL)

(-) growth was not observed.

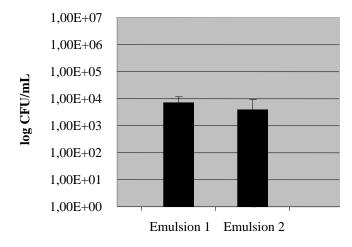


Figure 1 - Total heterotrophic mesophilic bacteria

It can be observed in photograph of optical microscope of the stain from the E1 and E2 samples (Figure 2) that allow examining and corroborating the development of microbial consortiums formed by *Hormoconis resinae*, yeasts and bacteria coming from the emulsions.

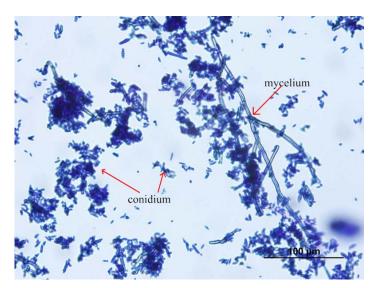


Figure 2 – Optic microscope photograph observed Hormoconis resinae (40X)

The growth of aerobic heterotrophic bacteria and facultative anaerobic ones (*Pseudomonas* sp. among them) generates a microenvironment encouraging the biofilm formation and the subsequent growth of oxidizing iron bacteria and yeasts. Yeast through their metabolic routes bring about pH decreases allowing the fungi development such as *Hormoconis resinae* isolated from these systems (Table 1) (8, 9). The pH decreases at acid values could be given by the activity of the *Hormoconis resinae* fungi (10)

Pseudomonas sp. is a microorganism able to growth at the expense of the synthetic oil in demineralised water at 4 % (of oil), to use the compounds present in these emulsions such as esters and emulsifiers (10, 11), to degrade them and to adhere to surfaces forming biofilms (12, 13). These biofilms originate zones of different oxygen gradients that accelerate the biocorrosion processes (12, 13).

The surface studies with optical microscopy on the filters allow to observe brilliant zones and the formation of ochre-orange-colored tubercles together with pits irregularly distributed on the surface (Figures 3 and 4). This was corroborated by the growth of viable microorganisms indicated in Table 1. These microorganisms are involved in the MIC processes (8, 9, 14).

It is important to remark that biocorrosion processes (10, 11) are clearly of electrochemical nature. In both systems studied the corrosion process was developed in the long term and was not controlled by workers.



Figure 3- Optic microscope photograph of the filter. Orange colored zones (indicated) and brilliant streaks can be observed (10X)



Figure 4- Photograph the zone attacked by pitting can be observed.

Besides this situation, promising conditions are generated for the growth of *Hormoconis resinae* that causes pH decrease. These also suggest biocorrosion risk.

The growth of *Pseudomonas* sp. could take place at the expense of the compounds present in the emulsion what could lead to its deterioration.

The low values of pH, the chloride and sulphate concentrations present in the plants could prove an inorganic corrosion risk at the different sampling solutions. It is necessary to set monitoring plans at long term by means of physicochemical and microbiological studies, with staff training, in order to avoid stopping the plant and replacing pieces. It means a potential risk of significant economic losses in the plant facilities.

System 2: Waterflood systems for secondary oil recovery

The 93 to the 95% of the production is water. Wells of this system are mature; it means that their oil production average 7%, the rest is water. They presented SRB with a concentration up to 100 times higher than the maximum value of 104, generating then H_2S .

The most important problem was connected with the use of a non oxidizing biocide (acrolein) because as soon as it was not injected in the plant, a blockage in the wells took place.

Hypochlorite and glutaraldehyde and later acrolein were used. It was started with two patching per week of 1100 ppm of acrolein, each of them during one hour. The basin where the water of the treatment plant passed through was modified and from that moment when passing through the basin the acrolein concentration decreases at the exit as it get mixed up with the whole water of the basin. Then, the biocide concentration was modified to one patching per week of 2200 ppm during four hours.

At the end of 2004 a dispersant plus biocide was used. The disincrustant caused the blockage of the wells and the consequent pipe bursting (Figure 5). Pressure increased so much that serious damages occurred in the system. Face to this situation the use of these chemical products was suspended and acrolein was used again. Probably an excessive dilution of the acrolein was used and this could have decreased its effectiveness. It is a system physically difficult to gain access to place a side stream with coupons. Some 15 m³/hr of fresh water from the Colorado River enter to the water treatment system into the washing tank. This could be a source of nutrients for the SRB.



Figure 5- Photograph the zone attacked can be observed

Solutions

It is necessary to replace acrolein by a safer biocide. A previous dose of disincrustant must be used before starting with other biocide. Once the suitable biocide is determined and after starting to apply it, a long-term monitoring program must be carried out. The aim of the treatment with biocides is to reduce as much as possible the H_2S in the wells. A decrease of the SRB counting must be reached. It is important that the test do not end abruptly, since once the results expected are obtained, the dose must fall up to a maintenance level.

Studies about the microbial charge of the Colorado River at the different seasons of the year were performed, incorporating a sampling protocol.

Bioremediation is applied to lower processes (for example, petroleum spills on soils or water). Here the system is very fast and there would not be enough time to do bioremediation. With wastes, it could be possible to carry out bioremediation of the petroleum by-products by activating nitrate reducing bacteria (NRB) and SRB in aerobic and anaerobic way

System 3: Waterflood systems for secondary oil recovery

There is a great environmental problem since there is no place to throw wastes removed from water. In the water treatment plant wastes are reinjected so the contamination reenters into the system generating a feedback system. Very high countings of SRB (10^{15} mo/ml) were obtained. In a liquid medium the maximum concentration expected is of 10^{10} mo/ml . (Figure 6). These high values observed in different systems are frequently due to staff dismissals caused by socioeconomic problems or to operators working without the suitable training.

When the Northern Plant is working and water is sent there to be processed, the microorganisms concentration decreases but when it is not, the concentration increases.

Tetrakishydroxymethyl phosphonium sulphate (THPS) was applied.

There are high H_2S concentrations of genetic and microbiological origin. The treatment of water to be reinjected is not very effective. There are too much solids.

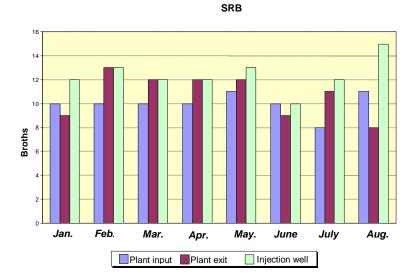


Figure 6 SRB countings

The well was closed. Sulphydric is generated by SRB. The system has a lot of genetic H_2S as water is not injected, only gas. There always was sulphydric in the wells.

There are three water treatment plants:

- o Plant of water collection: it treats the river water.
- Center Plant: it treats the saltwater for injection
- o Northern Plant: it treats the washing water (it does not work)

At the Center Plant quaternary salts and glutaraldehyde (GA) were injected together with alcohol. The GA is added at the both patchings per week, 200 ml/min during 4 hours. THSP was also used, 150 ppm-160 ppm, at two patchings per week.

Solutions

One of the solutions would be to carry out a pilot testing in the wells, a producer one and an injector one, in order to evaluate the biocompetence. The growth of nitrate reducing bacteria will be helped to stop the growth of the SRB and to reduce the sulphydric. Countings and microbiological studies must be performed. The concentration of H_2S diluted in water and gas, ions such as: nitrate, sulphate, phosphate, volatile fat acids, injection water salinity, etc., must be determined.

Another solution would be to run the Northern Plant and implement the waste recycling that provides a microbial charge to the system. This could decrease the SRB and H_2S concentrations. Lines cleaning and well interventions are also recommended.

Conclusions

Global solution proposal for problems of the systems 1, 2 and 3

It is expected to give a solution for the biofouling, biofilms and biocorrosion problems through the following global proposal: service of microbiological management of the systems and a set of consultancies and specific services. The general proposal is to collect, organize and display all the information related with microorganisms, as a tool for monitoring, controlling and preventing the bacteria and fungi presence in the systems.

The aim of the service: It will be to train the operators and responsible staff of the plants in order to decrease at the maximum mistakes when making decisions when unsuitable effects caused by the presence of microorganisms in the systems come out. It will be also possible to have a service and a methodological microbiological management of the systems.

Theoretical and practical courses on biofouling, biofilms and biocorrosion issues will be provided to the operators to acknowledge and train them on taking, preserving and transporting the samples.

A handbook of procedures for the operators will be creating on the management of the microbiological works to do in the field and at the laboratory.

Collecting qualitative-quantitative data of the reservoir, production installations and water injection will be carried out, as well as gathering and/or measuring of variables and parameters of interest necessary to characterize the systems.

Among other possibilities, it is proposed here to solve the problem by the use of the suitable biocides in their suitable proportion according to studies performed by authorized staff.

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