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Study the formation of the deposit resulting from the sulfate-reducing bacteria on the steel surface of oil pipe N80

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ABSTRACT

This article examines the components of formed deposits on the surface of the petroleum pipes by Sulfate-Reducing Bacteria in the region of Hassi Messaoud (south of Algeria). These bacteria were found in the wells of water and oil. *However, we find the problem of bacterial corrosion in the circuits of production and injection when petroleum is extracted. This bacterial corrosion occurs when petroleum which contains water touched the pipes for well long enough to be able to start corrosion. This problem results to the formation of deposits on the inner surface of pipes which lead to the risk of clogging. In this work, we study the deposit resulting from bacterial corrosion on the surface of N80 steel samples and we have identified the most important components of the deposits resulting from the phenomenon of bacterial corrosion.*

Keywords: *Corrosion, Bacterial Corrosion, Sulfate-Reducing Bacteria (SRB), Steel N80.*

1. Introduction

The oil industry is an important driving force of the Algerian economy. But there are a number of problems, in particular bacterial corrosion. The Corrosion can be defined as a phenomenon of degradation of materials whose annual cost represents between 3 and 5% of GNP (Gross National Product) of an industrialized country (Marconnet et al., 2005 ; Maluckov & Biljana, 2012). Whereas, bacterial corrosion brings together all the phenomena of corrosion or the bacteria act directly, or through their metabolism, creating the favorable conditions for its establishment (Chantereau & Bouffard, 1977 ; Videla & Herrera, 2005). That's why we'll talk about the main bacterial types associated with this deterioration which are Sulphate-Reducing Bacteria or SRB. They are anaerobes capable of synthesizing and accumulating large quantities of sulphates in their natural habitat. Indeed, in a low oxygen environment and contains sulphate, SRB contribute to the mineralization of the organic material by reduction of sulphate (Videla & Herrera, 2005; Enning & Garrelfs, 2014). Microorganisms can be considered as formidable catalysts of a phenomenon of electrochemical nature (corrosion). Among these microorganisms, bacteria are feared for their extraordinary enzymatic potential that allows them to grow in very complex environments and to adhere to various surfaces, including metallic materials 8 (Santegoeds et al., 1998; Busscher et al., 2006).

The purpose of this paper was to study the deposit resulting from bacterial corrosion on the surface of N80 steel samples and determine the elements contribute in the formation of this deposit. In this work, we have prepared a culture environment adapted for living bacteria. First, we place the N80 steel samples in this environment. Then, we added a natural water extracted with petroleum which contains sulphate-reducing bacteria, then placed all the samples in the incubator at temperature of 37 °C for a different time period (30, 60 and 90 days) for observe the clearly formed deposits and to determine the most important components of the deposits.

This paper contains new results concerning the role of bacteria in corrosion by the formation of Sulfur (S) which forms the FeS (Ferrous Sulfide or Iron Sulfide) deposits that cause blockage of oil pipes using in the region of Hassi Messaoud (southern Algeria). The rest of this paper is organized as follows: next section provides the needed materials and methods. However, last section presents our results with discussions, and we conclude the paper by the conclusion.

2. Experimental materiel and techniques

This study was conducted on samples of oil pipe that carry crude oil during the extraction (steel N 80) that having a high resistance to the pressure. Also, it can be used during the process of drilling of oil wells and can withstand the wall of a well after the completion of the latter, in order to ensure a normal operation in all the wells. The surface of the samples is rectifies, degreases and dried, whose chemical composition (%) represent in the Table 1.

Table 1. The chemical composition of the base metal (weight %)

Componen	Weight (%)
C (Carbon)	0.24
Si (Silicon)	0.22
Mn (Manganese)	1.19
P (Phosphorus)	0.013
S (Sulfur)	0.004
Cr (Chromium)	0.036
Mo (Molybdenum)	0.021
Ni (Nickel)	0.028
Nb (Niobium)	0.006
V (Vanadium)	0.017
Ti (Titanium)	0.011
Cu (Copper)	0.019

On the other hand, Table 2 represents a description about the situation of each sample of our experimentations.

Table 2. Description of the samples

Sample number	Description of situation
Sample 1	A steel N80 in a contaminated environment by SRB after 30 days at 37°C.
Sample 2	A steel N80 in a contaminated environment by SRB after 60 days at 37°C
Sample 3	A steel N80 in a contaminated environment by SRB after 90 days at 37°C.

While, Table 3 gives the different amounts of chemical composition of the culture environment of bacteria.

Table 3. The chemical composition of the culture environment of bacteria

The components	The quantity
Magnesium Sulfate $MgSO_4$, $7H_2O$	1.0g
Ammonium sulphate $(NH_4)2SO_4$	1.0g
Sodium citrate trisodium $Na_3C_6H_5O_7$, $2H_2O$	1.0g
DI-potassium Hydrogenophosphate K_2HPO_4	1.0g
Ascorbic acid	0.2g
Yeast extract	0.2g
Agar-agar	0.1g
Sodium Lactate	4.0ml
Distilled water for the manufacture of medium	1L

After the preparation of the culture environment, we measured the pH of the environment. Then, we have filled 9 ml of environment prepared in vials penicillin's, in order to add our metal samples defatted prior to acetone in these vials. We have plugged the vials to using capsules of rubber, capsuling then were blocked by the aluminum. After that, we have purged the vials with nitrogen to create the anaerobic environment and sterilize by autoclaving under wet pressure at 120°C for 50 minutes. Then, using a syringe, we collected 1 ml of water contains bacteria, and we eliminated the trapped air bubbles possibly in the syringe. Subsequently, we injected the contents of the latter through the capsule in the rubber stopper of the vial containing 9 ml of culture environment. Finally, we have labeled the vials. They have incubated in the incubator at 37°C for 30, 60 and 90 days.

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3. Results and discussion

The pH measurements

The pH measurements of environment samples before and after incubation were calculated. It is described in Table 4.

Table 4. pH in the environment of the samples

Environment	pH (before incubation)	pH (after incubation)
Environment of sample 1	**7.10**	8.54
Environment of sample 2	**7.10**	8.88
Environment of sample 3	**7.10**	9.01

The table 4 shows that pH of environments increases as incubation time increases, this environment is suitable for the multiplication of bacteria and the formation a biofilm (the biofilms have complex structures consisting of cells and clusters of bacteria, randomly distributed). This biofilm develops or can develop under extreme conditions of: temperature (12° C to 115° C), pH (0 to 13) and hydrostatic pressure (Normand, 2004).

Analysis of the surface of the samples by scanning electronic microscope (SEM)

The determination of the morphology of deposit that formed on the surface of the steel N80 has been carried out by scanning electron microscopy (see Figure 1). We have achieved for each sample an image with expansions of (500X).

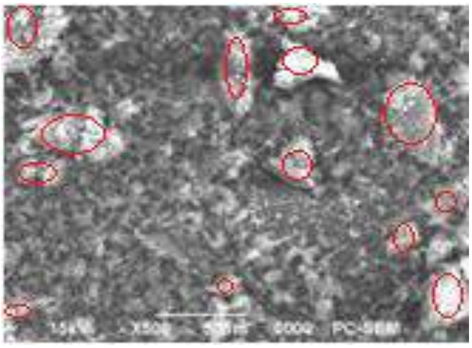

Figure 1. The image of the surface of the sample 1 by SEM at 37 ° C for 30 days of incubation

The formation of the deposit in the form of colonies on the surface of the sample was noted as specified in red in the image.

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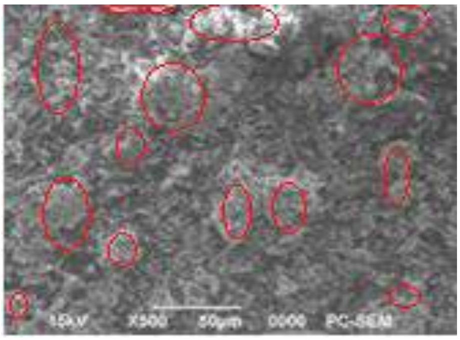

Figure 2. The image of the surface of the sample 2 by SEM at 37 ° C for 60 days of incubation

We observe an increase in the formation of the deposit in the form of colonies on the surface of the sample as specified in red in the image.

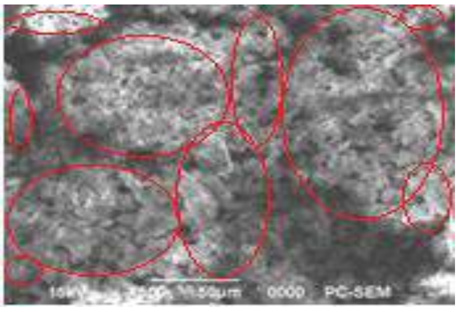

Figure 3. The image of the surface of the sample 3 by SEM at 37 ° C for 90 days of incubation

For sample 3, we observe that the deposit is formed densely in the form of colonies on the surface of the sample as indicated in red in the picture.

Clearly, the images (Figures 1, 2 and 3) of the surface samples show the existence of a stable adherent deposit in the form of colonies. Where, the amount of deposits on the sample surface is greatering whenever the incubation period for samples is longer. These samples contain active bacteria owing to deposits formed on the surface of samples in colonies.

To justify the presence of the deposit, we give the theory of cathodic depolarization (or VWK theory). The basis of this theory was originally formulated in 1934 by Von Wolzogen Kühr and Van Der Vlugt (De Beer et al., 1994). It postulates the microbiological consumption of hydrogen from the cathodic reaction by the following mechanism:

- Ionisation of water:

$$8\ H_2O\ \leftrightarrow 8\ H^{\mp} + 8OH^-$$

Equation 1

- Anodic corrosion of iron:

$$4Fe\ \leftrightarrow 4Fe^{2+} + 8e^-$$

Equation 2

- The formation of hydrogen at the cathode:

$$8H^+ + 8e^-\ \leftrightarrow 8H^{\circ}$$

Equation 3

- The absorption of hydrogen by bacteria:

$$SO_4^{2-} + 8H^{\circ} \xrightarrow{\text{Hydrogenase}} S^{2-} + 4H_2O$$

Equation 4

- Anodic secondary reactions:

$$Fe^{2+} + S^{2-} \rightarrow FeS$$

Equation 5

$$3Fe^{2+} + 6OH^- \rightarrow 3Fe(OH)_2$$

Equation 6

- Global reaction:

$$4Fe + SO_4^{2-} + 4H_2O \leftrightarrow FeS + 3Fe(OH)_2 + 2OH^-$$

Equation 7

Analysis of the surface of the samples by EDX

In order to know the chemical compositions of the layer are formed on the surface of the samples, we observed the samples by EDX (Energy Dispersive X-ray spectrometry). The maps were carried out for each sample to obtain a distribution of chemical elements with an allocation of color for each element detected (see Figure 4 to 6). Whenever the color is shiny, it means that the element is abundant; and in the case of the matte color, it means that the element exists in the form of traces.

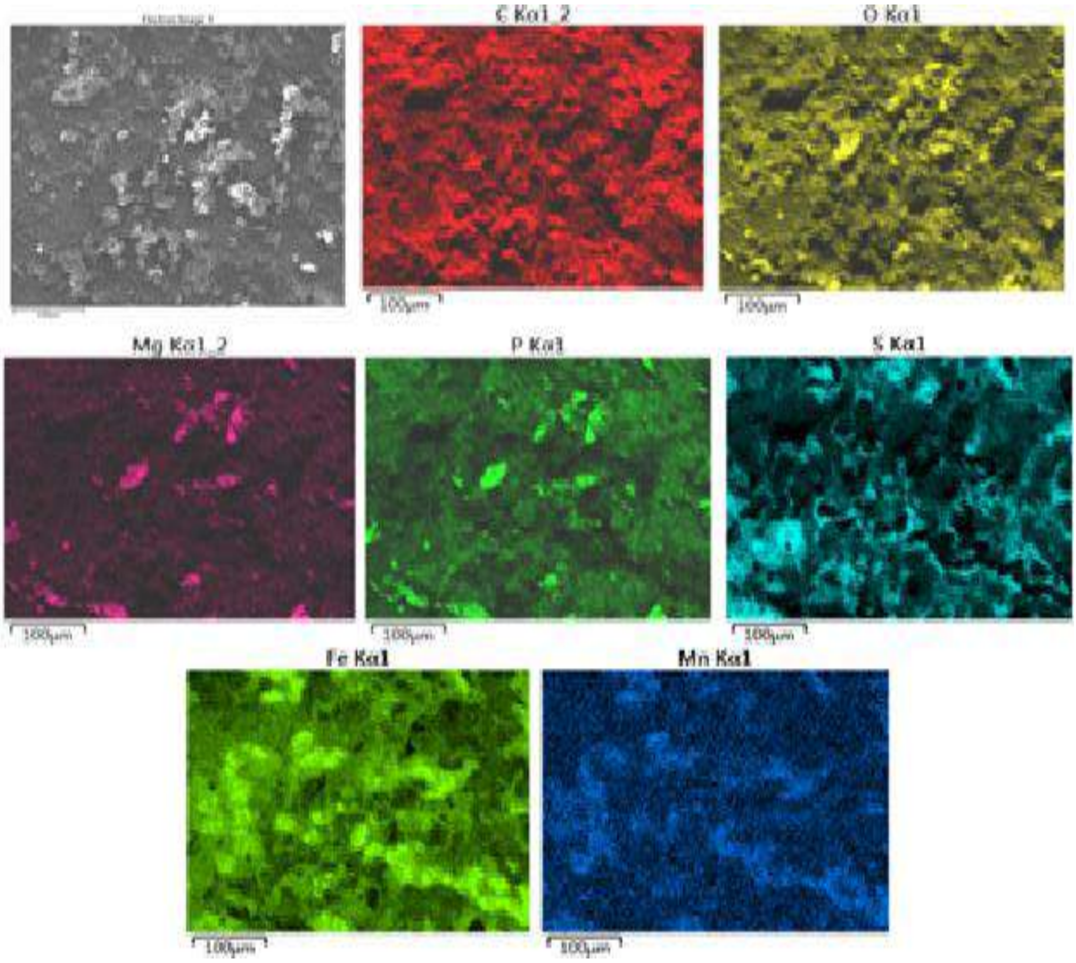

Figure 4. Mapping-chemistry of the surface of the sample 1 after 30 days of incubation at 37°C

We observe in figure (4) that the elements existed in the deposition layer are: **Oxygen (O), Iron (Fe), Carbon (C), Manganese (Mn), Magnesium (Mg), Phosphorus (P) and Sulfur (S).**

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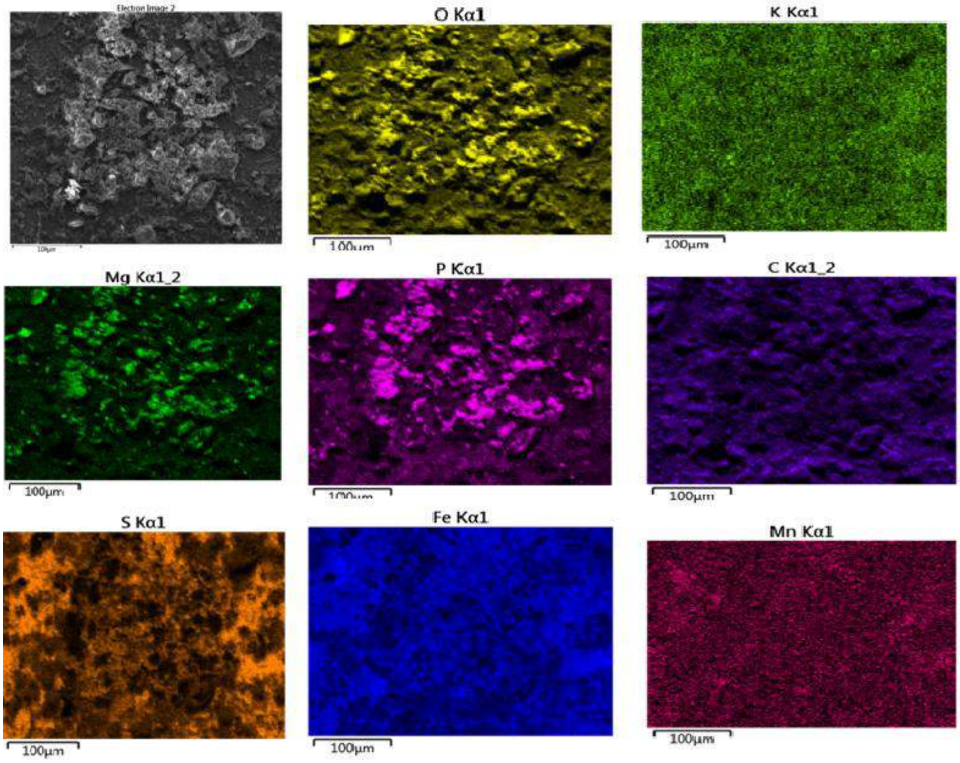

Figure 5. Mapping-chemistry of the surface of the sample 2 after 60 days of incubation at 37°C

We observe in Figure (5) that the elements existed in the deposition layer are: **Oxygen (O), Iron (Fe), Carbon (C), Magnesium (Mg), Phosphorus (P) and Sulfur (S).**

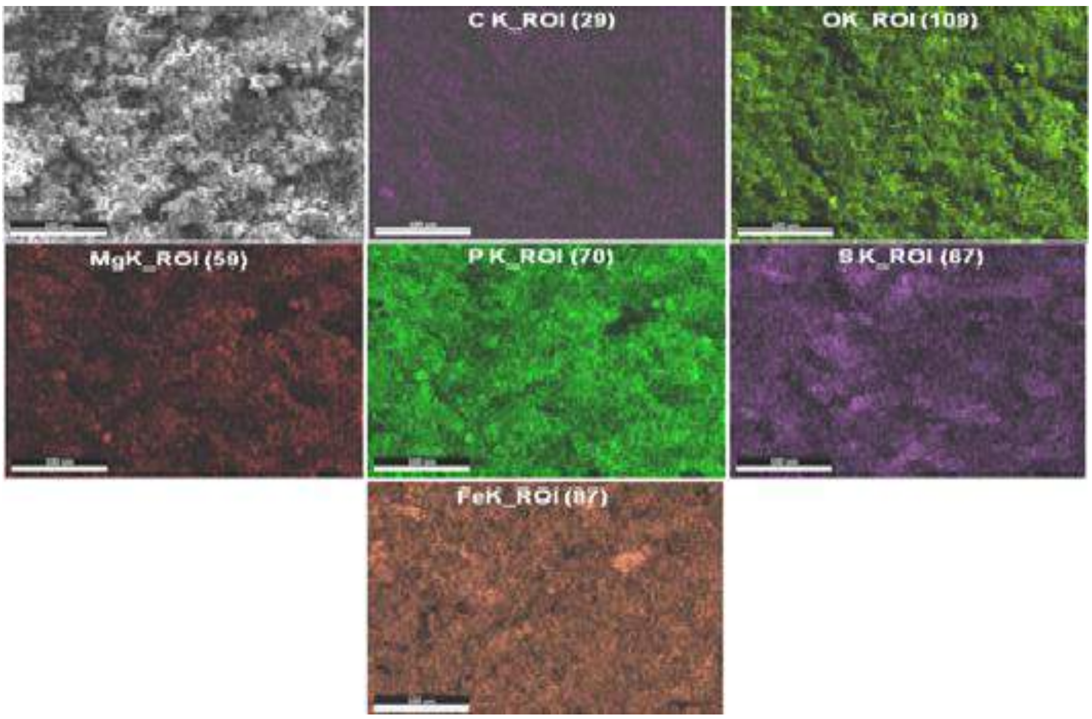

Figure 6. Mapping-chemistry of the surface of the sample 3 after 90 days of incubation at 37°C

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We observe in figure (6) that the elements existed in the deposition layer are: **Oxygen (O), Iron (Fe), Sulfur (S), Magnesium (Mg), Phosphorus (P) and Carbon (C).**

Through the results obtained by Mapping-Chemistry of our samples, we observe that the most important elements existed in the deposit layer are: Oxygen that appeared water ionization, Iron that appeared from iron oxidation, and the Sulfur that appeared from the conversion of Magnesium Sulfate and Ammonium Sulphate.

Effectively, SRB use as electron acceptors compounds derived from the oxidation of Sulfur such as: Sulphate (SO_4^{-2}), Sulphites (SO_3^{-2}), Thiosulfates ($S_2O_4^{-2}$), and elemental Sulfur (S°). These compounds are reduced entirely to Sulfide (Marty et al., 1989). The basic metabolic reaction of these bacteria is the reaction of the Sulfate ion. More precisely, the Sulphate is produced entirely to Sulphide as follows (DEGRÉMONT, 1989):

$$SO_4^{-2} + 8H^+ \rightarrow S^- + 4H_2O$$

Equation 8

In this reaction, Hydrogen is provided by organic materials such as alcohol, proteins, starch and hydrocarbons. The overall reaction is as follows:

$$4\text{Fe} + H_2O + SO_4^{-2} \rightarrow \text{FeS} + 3\text{Fe} + (OH)_2 + 2OH^-$$

Equation 9

Subsequently, the sulphide ions will react at the level of the anode with ferrous ions and iron ions are formed [15].

$$S^- + Fe^{++} \rightarrow \text{FeS}$$

Equation 10

However, other ferrous ions combine with the hydroxide ions to give the iron hydroxide:

$$Fe^{++} + 2OH^- \rightarrow \text{Fe}(OH)_2 \text{ and } 3Fe^{++} + 6OH^- \rightarrow 3\text{Fe}OH_2$$

Equation 12

Hence, the deposit formed on the surface of samples contains the iron oxide and iron Sulphide.

4. Conclusion

The present work is a contribution to understanding the phenomenon of bacterial corrosion by knowing the chemical constituents of deposits formed on the surface of the N80 steel. For confirmed the activation of bacterium, we measure the pH of environment and we study the deposit on the surface of the sample using the SEM and the EDX machines. We concluded the following results: The longer incubation period gives us a high pH. We found that deposit wide stable in the form of colonies on the surface. The most important chemical components involved in the composition of the deposits formed at the surface of the samples are the Oxygen, Sulfur, and Iron, low concentration for Magnesium, Carbon, and Potassium. Through these results which we obtained from studying the phenomenon of bacterial corrosion on steel N80 for oil pipes, we found that the bacterial corrosion is divided into two main phases; oxidation of iron in the water, and role of bacteria in the dismantling of the sulfate to sulfur. In the two phases, we find bacterial corrosion resulting in the iron oxide ($Fe(OH)_2$) and iron Sulphide (FeS) that we see in the form of deposits on the surface of the samples.

As future work, we plan to develop solutions to eliminate the problem of bacterial corrosion by extraction of organic biocides from plants and herbs widely available in Algeria and used as a solution for the eradication of this propblem.

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