ISSN No:-2456-2165

The Effect of Norust 720 and CH1377A Inhibitors on N80 Steel Corroded by Bacterial Corrosion

Nourelhouda DEKHILI[1]
Department of Mechanics
University of Biskra
Algeria

Abstract:- This article discusses the effects of inhibitors used in the treatment of bacterial corrosion in the oil industry in southern Algeria on N80 steel corroded by Sulphate-Reducing Bacteria. These bacteria were found in the wells of water and oil. 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 in the formation of deposits on the inner surface of pipes which lead to the risk of clogging, In this work, we studied the effect of Sulphate-Reducing Bacteria on the surface of N80 steel samples and the NORUST 720 and CH1377A inhibitors on the surface of samples already corroded by the bacteria.

Keywords:- *Bacterial Corrosion, Sulphate-Reducing Bacteria, Inhibitor, Steel N 80.*

I. 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 [1,2]. 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 [3,4]. 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 [4-7]. 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 [8-10].

A corrosion inhibitor is a chemical compound, which added to low concentration in the Environment corrosive, slows down or stops the corrosion process of a metal placed in contact with this environment. Such a definition cannot be perfect; it avoids however to consider as inhibitors of the additives which, while responding 'has the second condition (decrease the speed of corrosion), do not fulfill the first (for example, the adjustment of the PH by the addition of basic or acid does not constitute a means of inhibition within the meaning of the definition). Conversely, some compounds that should be excluded in any rigor by the definition, can however be considered as of the Inhibitors.

Finally, the meaning given by this definition to the term prohibited inhibitor that the inhibition of the corrosion is interpreted in a sense too semantics as the slowdown, by whatever means, of the corrosion process of a metal (Example of the incorporation of an element of alloy in a metal: the Chrome is not an inhibitor of the iron when it enters in the composition of a stainless steel) [11].

The purpose of this work is the effect of bacteria on N80 steel and find out the effectiveness of the inhibitor in removing deposits resulting from the phenomenon of bacterial corrosion, so we have prepared a culture environment adapted for living bacteria. First, we place the N80 steel samples in this environment. Then, we add water extracted with petroleum which contains Sulphate-Reducing Bacteria, we leave the samples in the incubator. After 60 days, we inject the inhibitor NORUST 720 and CH1377A .Finally, we follow the deposits formed on the sample surface by SEM (Scanning Electronic Microscope) and EDX (Energy Dispersive X-ray spectrometry) machines, in order to determine the elements contribute in the formation of this deposit. This paper contains new results concerning the role of bacteria in corrosion by the formation of Sulfur (S) which forms the FeS deposits that cause blockage of oil pipes using in the southern Algeria and effectiveness of the inhibitor in the elimination on deposit resulting from bacterial corrosion.

The rest of this paper is organized as follows: Section 2 provides the needed materials and methods. Section 3 presents our results with discussions, and Section 4 concludes the paper.

ISSN No:-2456-2165

II. MATERIALS AND METHODS

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 Table1.

Component	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

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

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

Sample number	Description of situation
Sample 1	A steel N80 in a contaminated environment by SRB after 90 days at 37°C.
Sample 2	Steel N80 corroded by the SRB during 60 days and injected by CH1377A and has been left more 30 days at 37 °C.
Sample 3	Steel N80 corroded by the SRB during 60 days and injected by NORUST and has been left more 30 days at 37 °C.

Table 2:- Description of the Samples

While, Table 3 gives the different amounts of 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 environment	1L

Table 3:- The Chemical Composition of the Culture Environment of Bacteria

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 60 days. And after 60 days of incubation, we added two types of inhibitors used against the problems caused by the SRB and left it another 30 days in the incubator at 37°C.

III. RESULTS AND DISCUSSIONS

A. *Measurement of pH*

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

Environment	pH (before incubation)	pH (after incubation)
Environment of sample 1	7.10	8.54
Environment of sample 2	7.10	8.83
Environment of sample 3	7.10	8.94

Table 4:- pH in the Environment of the Samples

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 [12].

B. Analysis of the samples surfaces by 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 (X65, 500X and X1000).

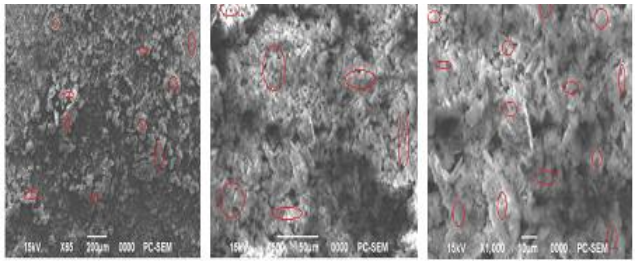

Fig 1:- SEM micrographs of experimental steel of the surface of the sample1 incubated in a contaminated environment by SRB at 37 ° C for 90 days.

The images of the surface of the sample 1 clearly show the existence of a stable adherent deposit in the form of colonies Such as shown in the picture with different magnifications and indicated in red.

Clearly, the images (Figures 1) 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 [13].

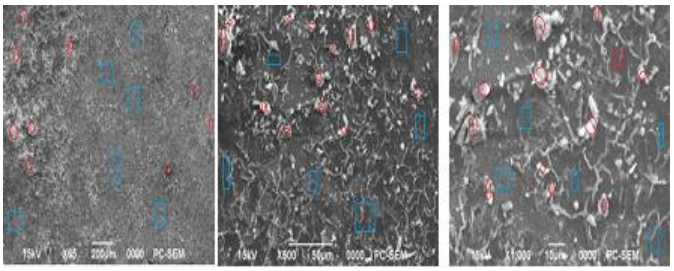

Fig 2:- SEM micrographs of experimental steel of the surface of the sample 2.

The images from the surface of Sample 2 clearly show the removal of much of a colony deposit on the surface of the sample, as shown in blue and the presence of some of the depots indicated in red.

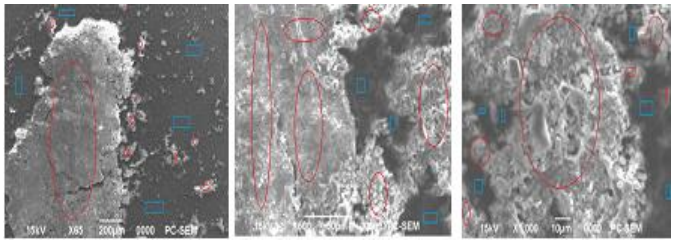

Fig 3:- SEM micrographs of experimental steel of the surface of the sample 3

The images of the surface of the sample 3 clearly shows the elimination of a deposit in the form of colonies referred to as blue and the appearance of deposit in the form of the layer Such as shown in red color.

C. Analysis of the samples surfaces 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.

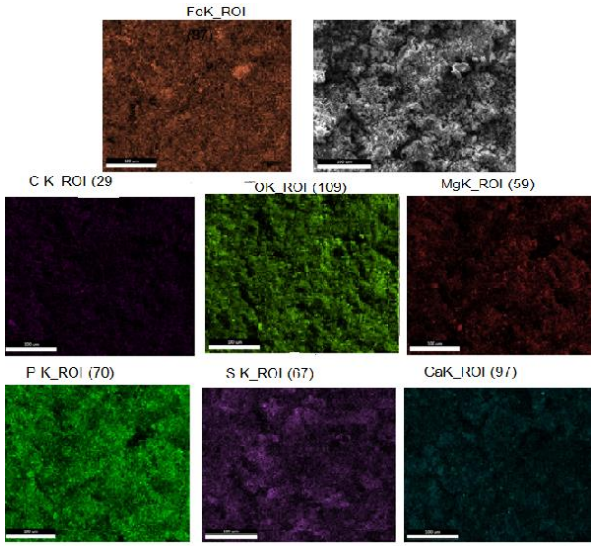

Fig 4:- Mapping-chemistry of the surface of the sample in a contaminated environment by SRB after 90 days of incubation at 37°C .

The most collected elements of the Mapping-chemistry on the deposit formed on the surface of the sample 1: Oxygen (O), Iron (Fe), Carbon (C), Magnesium (Mg), Phosphorus (P) and Sulfur (S).

Effectively,SRB use as electron acceptors compounds derived from the oxidation of Sulfur such as: Sulphate (SO_4^{-2}), Sulphites (SO_3^{-2}), Thiosulfates ($S_2O_4^{-2}$), andelemental Sulfur (S°). These compounds are reduced entirely to Sulfide [14].The basic metabolic reaction of these bacteria is the reaction of the Sulfate ion. More precisely, the Sulphate is produced entirely to Sulphideas follows [15]:

ISSN No:-2456-2165

$SO_4^{-2} + 8H^+ \rightarrow S^- + 4H_2O$ (1)

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

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

Subsequently, the sulphide ions will react at the level of the anode with ferrous ions and iron ions are formed [16].

$S^- + Fe^{++} \rightarrow \text{FeS}$ (3)

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

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

$3Fe^{++} + 6OH^- \rightarrow 3\text{Fe}OH_2$ (4)

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

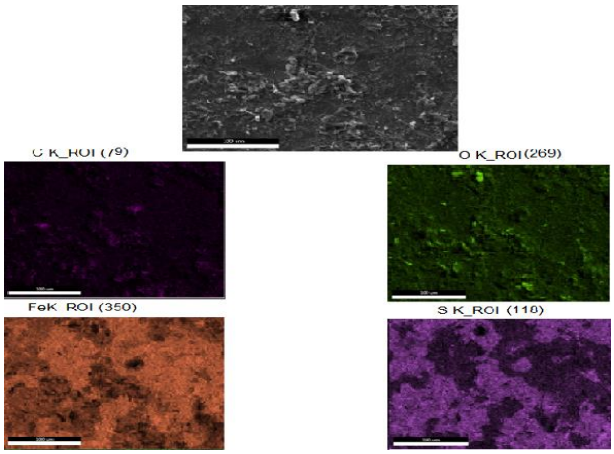

Fig 5:- Mapping-chemistry of the surface of the sample 2.

The observation of the mapping-chemistry images of the surface of samples shows that the high presence of Oxygen (O), with respect to the percentage of Sulfur (S).

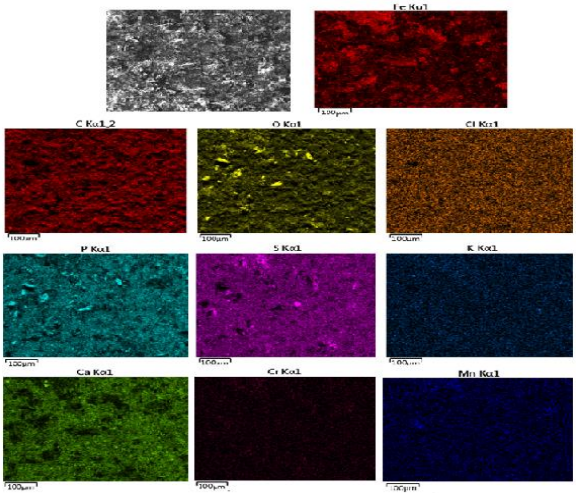

Fig 6:- Mapping-chemistry of the surface of the sample 3.

The observation of the map-chemistry images of the sample surface shows that the high presence of Oxygen (O), Iron (Fe), with respect to the percentage of Carbon (C), Phosphorus (P) and Sulfur (S) and chrome (Cr) .

IV. CONCLUSION

The present work is a contribution to understanding of the phenomenon of bacterial corrosion through the follow of Effect of bacteria on the surface of the steel N80. For confirmed the activation of bacteria, we measure the pH of environment and we observe the deposit on the surface of the sample using the SEM and the EDX machines. By this way, we conclude the following results.

For the sample 1: We found pH of environment increases means that the bacteria (SRB) are active.

Sample 2 and 3. We found that, the pH is high but not as the sample 1, this means that the bacteria were active and have stopped their activity because of the inhibitor that we have added after 60 days.

The images 1 (corresponding to the sample 1) clearly shows the existence of a deposit stable in colony form. This sample contains a bacterial activity to through deposits on the sample surface. By against, the analysis of the images 2 and 3 (corresponding to the sample 2 and 3) clearly shows the elimination of a deposit in form of colonies on the sample surface, but there is a layer of deposit smooth.

The chemical composition of The deposit formed on the samples surface (before treatment) confirms the presence of: oxygen, iron, sulfur and with low concentration of the other elements. The chemical composition of The deposit (after treatment) appears reduction in the sulfur, with respect to the oxygen and iron.

Through, these results which we obtained from studying the phenomenon of bacterial corrosion on steel N80 for oil pipes, we find that the bacterial corrosion is divided into two main phases; oxidation of iron in the water, and the role of bacteria in the dismantling of the Sulphate to sulfur. In the two phases, we find bacterial corrosion resulting in the iron oxide (Fe(OH)2) and sulfur iron(FeS) that we see in the form of deposits on the surface of the samples .We also find the effectiveness of the NORUST 720 and CH1377A inhibitors in the elimination of the deposit formed by the bacteria is not large, although effective in protecting the steel before exposure to bacterial corrosion.

REFERENCES

[1]. C.Marconnet, C. Dagbert, M. Roy, and D. Féron. "Comportement d'aciers inoxydables en eaux naturelles." Matériaux & Techniques 93 (2005): s-83.
[2]. Maluckov, S. Biljana "Corrosion of steels induced by microorganisms." Metallurgical and Materials Engineering 18, no. 3 (2012): 223-232.

[3]. Chantereau, Jean, and Anne-Marie Bouffard. Corrosion bactérienne-bactéries de la corrosion. 1977.
[4]. [4] Videla, A.Héctor, and Liz K. Herrera. "Microbiologically influenced corrosion: looking to the future." International microbiology 8, no. 3 (2005): 169.
[5]. Karr, A.Elizabeth, W. Matthew Sattley, Deborah O. Jung, Michael T. Madigan, and Laurie A. Achenbach. "Remarkable diversity of phototrophic purple bacteria in a permanently frozen Antarctic lake." Appl. Environ. Microbiol. 69, no. 8 (2003): 4910-4914.
[6]. R. A.King, , and J. D. A. Miller. "Corrosion by the sulphate-reducing bacteria." Nature 233, no. 5320 (1971): 491.
[7]. Enning, Dennis, and Julia Garrelfs. "Corrosion of iron by sulfate-reducing bacteria: new views of an old problem." Appl. Environ. Microbiol. 80, no. 4 (2014): 1226-1236.
[8]. Santegoeds, M.Cecilia, G.Timothy Ferdelman, Gerard Muyzer, and Dirk de Beer. "Structural and functional dynamics of sulfate-reducing populations in bacterial biofilms." Appl. Environ. Microbiol. 64, no. 10 (1998): 3731-3739.
[9]. Davey, Mary Ellen, and A.George O'toole. "Microbial biofilms: from ecology to molecular genetics." Microbiol. Mol. Biol. Rev. 64, no. 4 (2000): 847-867.
[10]. J.Busscher, Henk, and C. Henny van der Mei. "Microbial adhesion in flow displacement systems." Clinical microbiology reviews 19, no. 1 (2006): 127-141.
[11]. P.Bommersbash, Evolution des propriétés d'un film inhibiteur de corrosion sous l'influence de la température et des conditions hydrodynamiques caractérisation par techniques électrochimiques, INSA Lyon, Décembre 2005.
[12]. Normand, Bernard. Prévention et lutte contre la corrosion: Une approche scientifique et technique. PPUR presses polytechniques, 2004.
[13]. E.Dennis, and G.Julia, Corrosion of Iron by Sulfate-Reducing Bacteria: New Views of an Old Problem. JOURNAL ARTICLE 2014 Feb 15. Applied and Environmental Microbiology. 1226-1236 VI-80, (2014).
[14]. De Beer, Dirk, Paul Stoodley, Frank Roe, and Zbigniew Lewandowski. "Effects of biofilmstructures on oxygendistributionand mass transport." Biotechnology and bioengineering 43, no. 11 (1994): 1131-1138.
[15]. Marty, Danielle, J. C. Bertrand, and P. Caumette. "Les métabolismes bactériens dans les systèmes sédimentaires marins." Microorganismes dans les écosystèmes océaniques. Masson, Paris, France(1989): 101-151.
[16]. SA. DEGRÉMONT, "Mémento technique de l'eau, édition du cinquantenaire, 9édition." LAVOISIER (Éditeur), Paris, France, tomes 1 (1989).