M I C IN OIL PRODUCTION AT OFFSHORE PLATFORMS

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ABSTRACT

An overview on the results of monitoring and control programs to assess microbiologically influenced corrosion (MIC) and biofouling in different offshore platforms for oil production is presented. The effects of biocide treatments on sessile and planktonic bacterial populations and their correlation with corrosion of structural materials are studied through monitoring schemes based on laboratory and field measurements. A new versatile multipurpose sample device is used to collect biofilm and corrosion samples. Results obtained strongly emphasize the relevant role of biodeterioration processes on metal attack. The importance of an adequate interpretation of the interrelationship between inorganic and biological variables to select effective chemical treatments is highlighted.

KEYWORDS

microorganisms, MIC, biofouling, biofilms, waterflood systems, SRB, biocide, biodeterioration processes, water injection.

1. INTRODUCTION

The expansion of land and off-shore oil extraction activities, during the last two decades, has focused increased attention on the monitoring and control of one of the most significant problems encountered in waterflood systems: corrosion related to microbial growth and biofouling of the internal parts of the injection lines /1-3/. These problems have often been related to the presence of sulphate-reducing bacteria (SRB), generally accompanied by diverse types of slime forming bacteria (*Pseudomonas sp.*, *Bacillus sp.*, etc.) and iron oxidizing microorganisms. It has been reported /4/ that levels as high as 10^5 cells/cm^2 can colonize structural materials within a period of only two weeks.

Among the several factors influencing MIC and biofouling in waterflood systems, the most relevant are /5/: i) operational characteristics of the injection water (velocity, temperature, depth of pumping); ii) physico-chemical characteristics (chemical composition, pH, oxygen concentration, dissolved solids, etc.), and iii) ability of the biocide in use to gain access to the sessile population within the bacterial biofilms.

It was recently emphasized /6,7/ that an effective corrosion and scale inhibition treatment does not necessarily guarantee the good performance of an injection line, if MIC and biofouling are not kept under control.

The goal of this article is to review different problems related to several types of injection water systems studied in the last decade by the authors in the South Atlantic and the North Sea. The article will be illustrated with some practical cases of monitoring programs for MIC and biofouling implemented to select effective chemical treatment strategies.

2. SOME FEATURES OF MIC AND BIOFOULING INTERACTIONS IN SEAWATER

It is now widely accepted that metals immersed in a biologically active liquid medium like seawater undergo a sequence of biological and inorganic changes that result in an important modification of the metal/solution interface. The first stage of the biological sequence is the development of a thin film (approximately 20 to 80 μm thick) on the metal surface. This film, formed by inorganic ions and high molecular weight organic compounds, is able to change the electrostatic charge and wettability of the metal surface /8/. In a second stage, bacterial colonization, facilitated by the conditioning film, leads to the initiation of a biofilm, mainly formed by water, bacterial cells and extracellular polymeric substances (EPS) of a polysaccharidic nature. When compared with the EPS, bacterial cells represent only a small mass of the biofilm, where nearly 90% is water /9/. This complex interface structure drastically changes the conventional electrochemical concept of the metal/solution interface used to interpret inorganic corrosion. New concentration gradients are now present as well as important changes in the type of ions, pH values, oxygen levels and redox conditions that will modify the behavior of the metal surface and the characteristics of their corrosion products.

The sequence of inorganic changes related to corrosion and the formation of corrosion products occurs simultaneously with biofilm formation, although in the opposite direction. Whereas biological processes are essentially deposition processes directed from the bulk towards the surface, corrosion is oriented from the metal surface to the solution. Metal dissolution then leads to a progressive accumulation of corrosion products of dissimilar nature and structure that generally induce the passivation of the metal surface in that medium /10/.

As a consequence of this complex sequence of biological and inorganic processes, an entirely new "biologically conditioned" metal/solution interface is produced where a reciprocal conditioning between passive layers and biofilms directs the corrosion behavior of the metal surface. The monitoring strategies and countermeasures for avoiding biofouling and the deleterious effects of MIC must necessarily take into account the interactions between biological and inorganic processes, if reliable results are to be expected.

3. SOME CONSIDERATIONS ABOUT THE EFFECTS OF MIC AND BIOFOULING ON OFFSHORE STRUCTURES AND PROCESSES

Most of the circumstances in which organisms influence corrosion in the marine environment have been experienced by the offshore oil and gas production industry. The problems are similar to those of any onshore plant where hydrocarbons and water are present, but with the additional factor of seawater which is highly corrosive by itself, as well as being biologically active /11/.

The biodeteriorating effects of organisms in the offshore platforms fall into three main interactive classes: i) fouling (due to the coverage and blockage of offshore structures and systems by both macro- and microorganisms); ii) souring (due to hydrogen sulfide production by microorganisms in air or water) and iii) corrosion (due to the influence of microorganisms on corrosion electrochemistry).

The different environments and the type of biological activity in each one of them are: i) the external surfaces exposed to seawater and marine fouling (ranging from bacteria to macroalgae of several meters long) and ii) the internal parts of plant and pipework that is mainly fouled by bacteria, and can be subdivided into the seawater handling and oil production facilities.

Among the external effects are those caused by living organisms covering the submerged surface of the platform, both in seawater and in the muds at the base of the structures. Thus, the four ways in which external effects may affect offshore structures can be summarized as: obscuring the substratum, enhancing corrosion, increasing hydrodynamic loading and enhancing corrosion fatigue. The internal effects are those encountered in the seawater handling system and in the oil production system itself. In this case, apart from the seawater filtration system, nearly all the problems arise from bacterial fouling on the surfaces of pipes and plant, causing blockage, decreasing heat exchange efficiency, enhancing corrosion and souring the oil or water with sulphur compounds. The major concern about microbial effects in oil and water systems is the enhancement of corrosion that can be due to both direct and indirect actions by microorganisms. These general concepts can be applied both to offshore or onshore waterflood oil production systems.

4. WATER INJECTION SYSTEMS STUDIED

The monitoring program for MIC and biofouling has been implemented in different waterflood systems using seawater and lake salty water as injection fluid /12/. The general operating characteristics of these systems and their flow sheets, with the corresponding sampling and monitoring points, are depicted in Figures 1 and 2.

5. FIELD AND LABORATORY MONITORING SCHEME

The monitoring program implemented in the South Atlantic oil production systems was primarily based on: i) water quality control; ii) sessile and planktonic bacterial counts; iii) scanning electron microscopy (SEM) observation of biofllms and sessile population; iv) field corrosion monitoring (corrosion coupons, electrical resistance and linear polarization probes); v) laboratory corrosion assessment (potentiodynamic polarization techniques and corrosion potential vs. time measurements); vi) optical and SEM observation of metallic corrosion (morphology and degree of attack); vii) biofilms and corrosion product analysis by energy dispersive X-ray analysis (EDXA).

The sampling devices were used in a side-stream or directly implanted in the line. In the former case, a new sampling device denominated RENAprobe™[(1)] (acronym for REusable Non-conventional Appliance) was used. It consists of a Teflon™[(2)] carrier rod (Figure 3), alternately drilled on opposite faces to accept 8 round metal coupons, each of 0.5 sq. cm surface area, mounted four on each face. Coupons were generally made of the same structure materials as the injection line (generally N-80 or SAE 1020 steels).

[(1)]Trade Mark of Aquatec Quimica, Sao Paulo, Brazil.
[(2)]Trade Mark of Dupont de Nemours, Beaumont, TX, USA

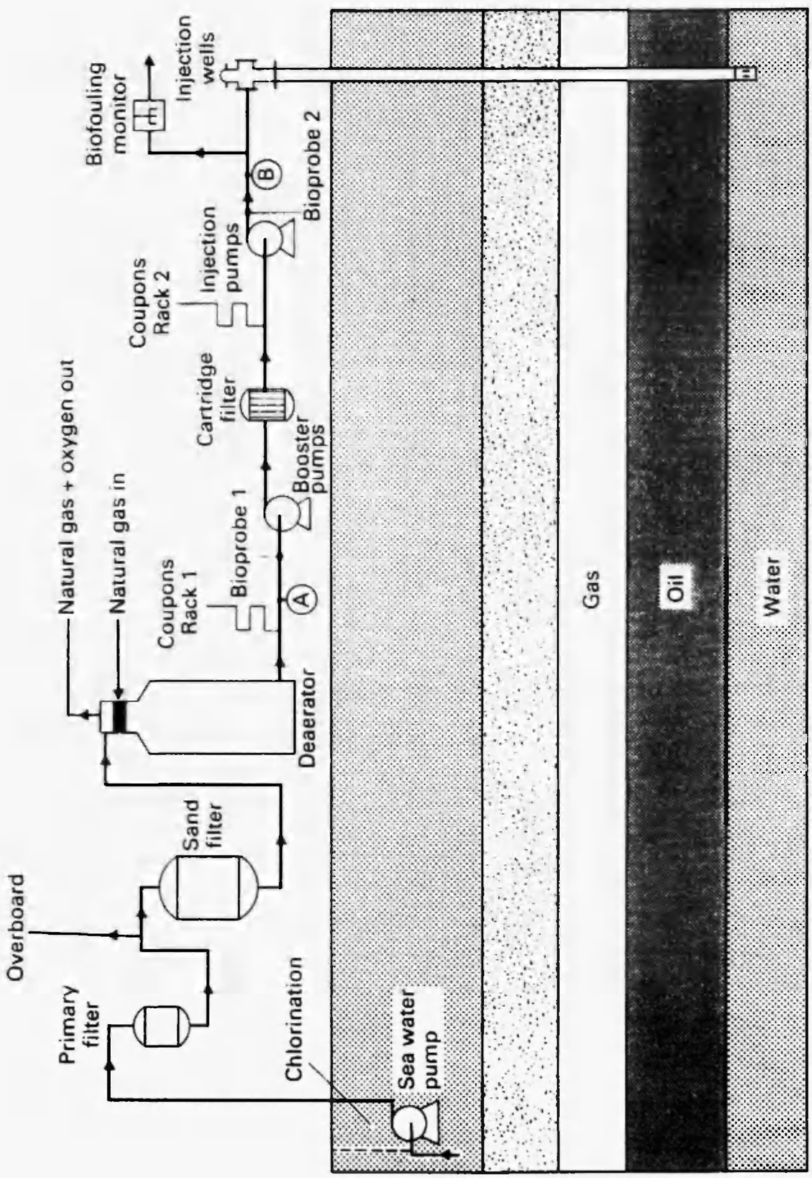

Fig. 1: Flow sheet of two similar offshore systems: 1) Location: Brazil. Water source: seawater; average temperature in the injection line: 27C; water velocity: 1,050 m^3/day. 2) Location: Brazil; water source: seawater; average temperature in the injection line: 34.5C; water velocity: 4,200 m^3/day. (With permission of NACE International, Houston, TX, USA, from reference 6.)

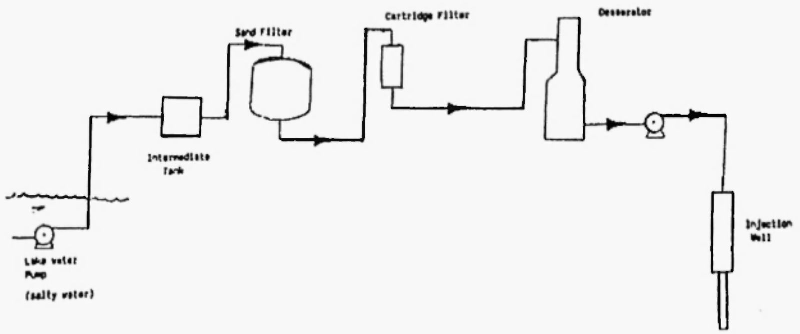

Fig. 2: Flow sheet of a lake salty water injection system. Location: Venezuela; water source: lake water (salty water); average temperature in the injection line: 36C; water velocity: 7,500 m^3/day.

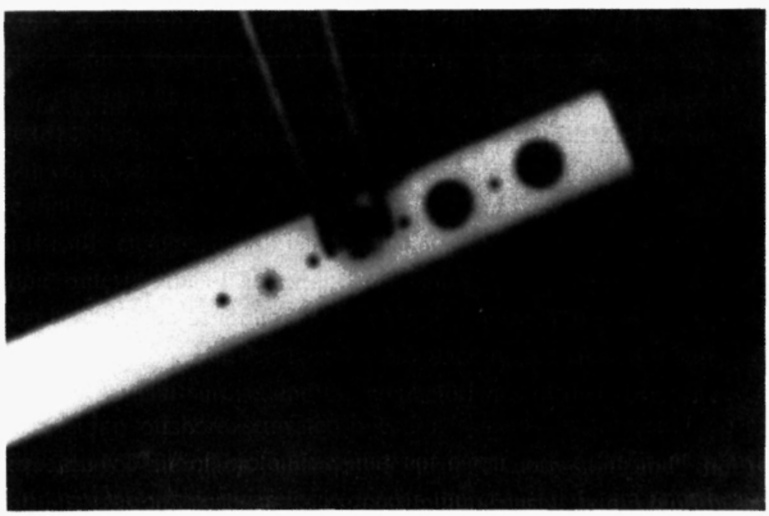

Fig. 3: Photograph of RENAprobe sampling device (with permission of ASTM, Philadelphia, PA, USA, from reference 12).

The sampling device is usually mounted in a conventional corrosion test rack. Two stations of corrosion racks, holding corrosion coupons and sampling devices, were generally used. One was located before the point of biocide addition to observe biofilms and corrosion attack on metal samples exposed to injection water without biocide or corrosion treatment, and the other one was located after biocide injection to assess the effects of the biocide in mitigating the causes of biodeterioration. After each exposure period (generally within 1 and 5 days), the couponholder was withdrawn and the coupons removed for examination. A typical distribution of probe coupons (per RENAprobe) was: one corrosion resistant coupon (generally of the AISI type 316 stainless steel) for biofilm observation by SEM; 2 coupons of the system structural material for sessile bacterial counts (in duplicate); 2 other coupons for SEM observation of biofilms/passive layers; 1 coupon for EDXA of biological and inorganic deposits; and 1 coupon for corrosion measurements at the laboratory. The use of one coupon of a corrosion resistant steel was adopted to avoid interference by the corrosion products with the observation of biofilms and sessile bacteria by SEM. The easy installation and low construction cost of the sampling device simplify the performance of duplicate tests when required.

For sessile bacterial counts, the entire couponholder was taken to the laboratory within a period of 12 h, in a closed receptacle filled with system water (Figure 4). Biofilms are later detached either by scraping with a sterile scalpel blade or by means of an ultrasonic device. Enumeration of SRB and other main groups of microorganisms (total aerobes, anaerobes and iron oxidizing bacteria) was made in liquid media by using the standard extinction dilution method. Dilutions are generally incubated for two weeks within the temperature range of the injection water. Reading for SRB viable counts is started after 24 h of inoculation and continued on a daily basis for two weeks.

SEM observation of biofilm and sessile bacteria requires fixation of samples with a glutaraldehyde solution in phosphate buffer, followed by gradual dehydration through a series of acetone dilutions, and critical point drying.

For observation of corrosion products the previous treatment of the samples is not required, and coupons may be metallized before microscope examination. However, when EDXA or electron microprobe analyses of corrosion products or biological deposits are planned, metallization with gold or gold/platinum must be avoided, to eliminate interference with elementary analyses.

Occasionally, a sampling line which had been directly implanted on the line (under pressure) was used.

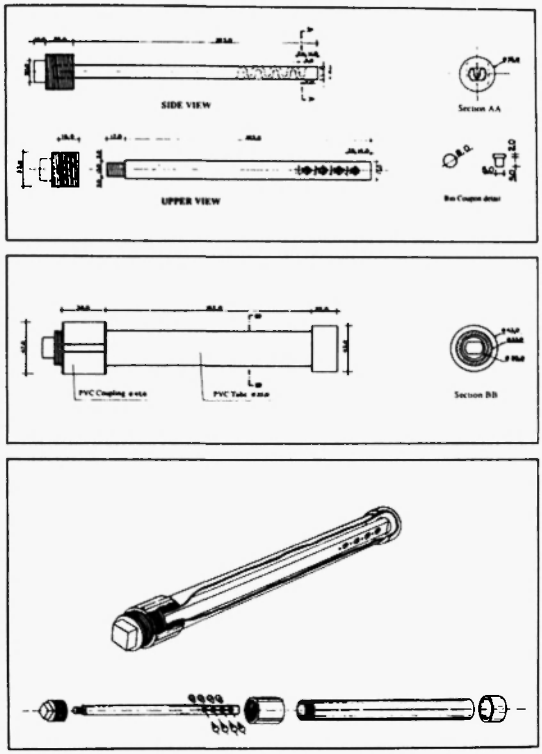

Fig. 4: Scheme of RENAprobe sampling device and carrier (with permission of ASTM, Philadelphia, PA, USA, from reference 12).

Corrosion data from the field (weight loss of corrosion coupons, corrosion resistance or linear polarization probe data) are generally correlated with results obtained in the laboratory through corrosion potential vs. time evolution, redox potential and potentiodynamic polarization measurements. The latter are generally used for the assessment of pitting corrosion, through breakdown (Eb) and repassivation (Er) potentials evaluation.

A set of typical analyses and monitoring devices used for assessing MIC and biofouling in the injection water of one of these offshore systems is shown in Figure 5.

Monitoring field devices and analytical techniques (systems I and II)

SYSTEM	LOCALIZATION	FIELD DEVICES AND ANALYTICAL TECHNIQUES		EXPERIMENTAL MEASUREMENTS
I	1	COUPONS RACKS	1020 CARBON STEEL COUPONS	CORROSION RATES (mm/Y)
II	2			
I	A	FIELD TEST KITS "IN SITU" CHEMICAL ANALYSIS		OXYGEN (ppb)
II	B			HYDROGEN SULFIDE (ppm)
I	A	WATER ANALYSIS		pH/pALK/TOTAL ALK/ TOTAL HARDNESS Ca Mg/ CHLORIDE/SiO_2/SO_4/ TOTAL IRON (Fe)/ TOTAL DISSOLVED SOLIDS/ Ba/Sr
II	B			
I	1	BIOPROBE (N-80 AND CARBON STEEL COUPONS)		SCANNING ELECTRON MICROSCOPY (SEM) OBSERVATIONS
II	2			
II	–	BIOFOULING MONITOR (N-80 AND CARBON STEEL COUPONS)		MOST PROBABLE NUMBER OF COLONY-FORMER UNITS PER UNIT AREA (CFU/cm^2)
I	A	MICROBIOLOGICAL COUNTS OF PLANKTONIC SRB		MOST PROBABLE NUMBER OF COLONY-FORMER UNITS PER UNIT VOLUME (CFU/ml)
II	B			

Fig. 5: Monitoring devices and analytical techniques used in offshore systems (with permission of NACE International, Houston, TX, USA, from reference 6).

6. PRACTICAL CASES

6.1. Seawater Injection

Two Brazilian offshore seawater injection systems have been used in a detailed study /13/ of biofouling and corrosion under different seawater conditions. One system was located near the coast of Ceara (northeastern Brazil) and the other off the coast of the state of Rio de Janeiro, some 1300 miles to the south.

A monitoring program similar to that previously described, and different monitoring periods and equipment locations (Figure 5), were used to assess microfouling settlement and corrosion of two types of steel (N-80 and carbon steel). It was possible to study how the bacterial fouling interacted with increasing amounts of corrosion products with time. At both sites, weight loss measurements and corrosion probes were used: one was an on-line

Bioprobe™[3] under pressure, and the other a side stream biofouling monitor (Figure 1). SEM and EDXA analyses of biofouling and corrosion products were carried out on coupons removed from these systems and, in addition, polarization and open circuit measurements were made in the laboratory.

In a brief outline, the results of this monitoring program, used to assess the performance of two types of steel, before developing a biocide strategy, allowed the following conclusions to be drawn:

i) Both steels used in the injection systems showed a poor corrosion resistance in seawater;
ii) The initial high corrosion rates for both metals produces complex interactions between corrosion products and bacterial biofilms;
iii) SEM observation of the corrosion attack revealed that, while N-80 samples exposed to seawater for only five days showed many areas severely damaged by pitting and general corrosion, carbon steel samples revealed few areas of pitting attack.
iv) SEM observations also showed that operation conditions in one of the systems were more favorable to corrosion attack. In this case, considerable slime masses were encountered in several parts of the system, suggesting that biofouling deposits could be the cause of the increase in corrosion.
v) In all cases, the corrosive characteristics of the injection seawater were not enough to cause the degree and type of attack observed on metal surfaces.

6.2. Lake Salty Water Injection

The general characteristics of this waterflood system have been outlined in Figure 2. The main goal of this monitoring program was to use EDXA analyses and electron microprobe to detect the degree and type of attack due to MIC and biofouling, both already detected in the injection line. Thus, a complete study consisting of more than 30 EDXA analyses and 50 SEM observations was made.

The sample coupons for SEM observations were metallized with a gold/palladium coating by sputtering (cathodic metallization) and with carbon for EDXA to eliminate interference with elementary analyses. It was possible to

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[3] Trade Mark of PETROLITE Corporation, St Louis, MO, USA.

assess the coverage of metal coupons by bacterial biofilms (Figure 6), to observe microbial morphology and, after cleaning the deposits, to evaluate the degree and morphology of the metal attack (Figure 7). The observations and analyses made with different metallic coupons, located before and after the point of biocide addition, let us select the most efficient biocide treatment to preserve the system from biodeterioration effects. EDXA, performed on the inorganic deposits, allowed us to determine the elementary percentage composition of the corrosion products, its chemical identity and the alterations induced by each biocide treatment tested.

7. CONCLUSIONS

- Control of MIC and biofouling is essential to corrosion control within waterflood systems used in oil recovery operations. Proper monitoring of both biological processes requires careful evaluation of biological and electrochemical parameters which contribute to both phenomena.
- Many valuable analytical tools are available to identify the nature of the

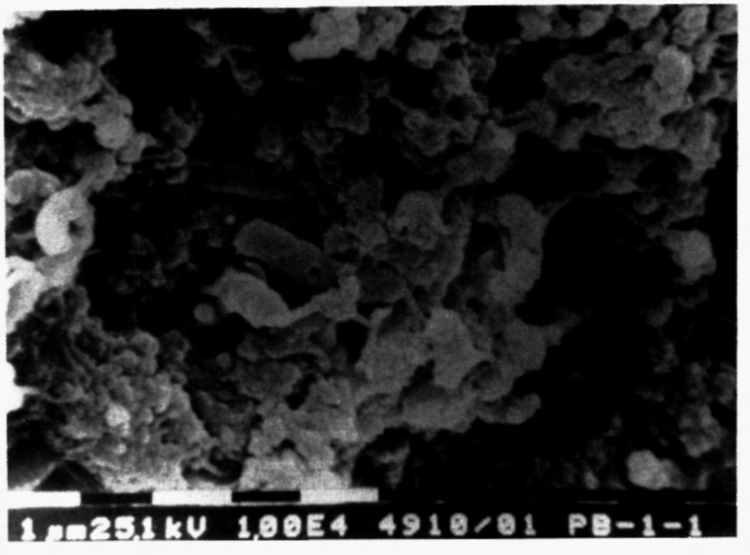

Fig. 6: SEM micrograph of bacterial biofilms, EPS and corrosion products on a carbon steel coupon exposed to lake salty water (magnification x 10,000).

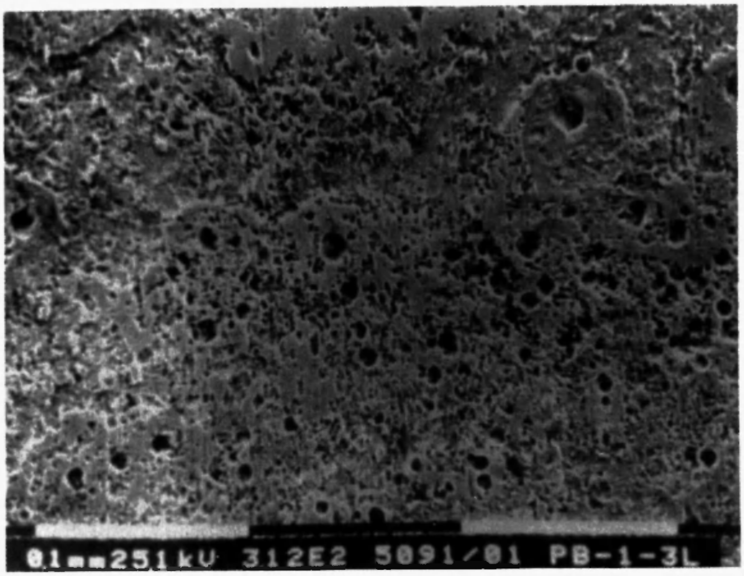

Fig. 7: SEM micrograph of the corrosive attack on a carbon steel coupon exposed to lake salty water, after removing inorganic and biological deposits (magnification x 312).

corrosion process, quantify corrosion rates and evaluate the results of control programs. The experience gained during the last decade, monitoring MIC and biofouling in different oil production systems located in the South Atlantic and the North Sea, is overviewed.

- A monitoring scheme, based on combinations of advanced laboratory analytical techniques (SEM, EDXA, electron microprobe), field and laboratory corrosion measurements and microbiological techniques was used jointly with an easy-to-use multipurpose sampling device (the RENAprobe) to evaluate the effectivity of biocide treatments for mitigating biodeterioration effects.
- In the practical cases reviewed, MIC and biofouling effects were the main causes of the severe localized attack observed on structural materials, even for the shortest periods of exposure.

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