UNIVERSITY POLITEHNICA OF BUCHAREST

THE FACULTY OF MATERIAL SCIENCE AND ENGINEERING

PhD THESIS

SUMMARY

EVALUATION AND CONTROL OF MICROBIOLOGICALLY INFLUENCED CORROSION IN OIL INDUSTRY USING A BIOFILM SAMPLING DEVICE

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This PhD thesis consists in evaluating the microbiologically influenced corrosion (MIC) of pipelines in oil industry, by microbiological, metallurgical and chemical techniques, integrating the results to demonstrate the presence of bacterial activity and their effects on the metal and, respectively, controlling this type of corrosion with specific methods to each location where the phenomenon has been identified.

Microbiological activity is internationally recognized as a significant contributor to corrosion problems and this is valid for Romanian oilfields too, where features of this phenomenon have been identified.

MIC, a very important subject in the oil industry from an economic and environmental point of view, has been the subject of extensive studies in the recent decades and several models have been proposed to explain the mechanisms of this corrosion type [1].

MIC is a form of corrosion caused by living microorganisms, such as bacteria, algae or fungi, often associated with the presence of organic substances in the form of tubercules [2]. Although it is well known that chemical and microbial mechanisms contribute to corrosion, the exact contribution of microbial activity to general corrosion of pipelines cannot be estimated. It has been estimated that 40% of the internal corrosion of pipelines in the oil industry can be attributed to MIC, but data from practical applications in the natural environment are needed to confirm or recast this estimation [3].

Investigation of microbial species found in pipelines transporting petroleum compounds has traditionally been based on laboratory cultivation of bacterial species obtained from pipelines [4]. Laboratory culture media cannot reflect the real environmental conditions in the pipelines and microbiologists have recognized that the most of microbial species cannot be grown in the laboratory [5]. A thorough knowledge of the causes of MIC is required, but efficient methods of detection and prevention are not sufficiently developed. It is well known that microorganisms are one of the main cause of corrosion of metal pipelines, but despite decades of study, it is not yet known for sure how many species of microorganisms contribute to corrosion, how their presence to be detected before corrosion appearance or how to rapidly evaluate the efficiency of biocides [6].

MIC is an interdisciplinary subject and, therefore, diagnosing and evaluating it require knowledge of metallurgy, chemistry and microbiology. Investigation on this corrosion type must be integrated with microbiological results to distinguish MIC from other corrosion mechanisms.

Sessile bacteria (in the form of biofilm) are the most important microbiological component of oilfield ecology, from corrosion point of view. Analyzes based only on planktonic microorganisms are limited for MIC diagnosis [7].

In Romanian reservoirs, it has been conducted until now microbiological analyzes only on bacteria present in water in planktonic form, which had provided limited results for MIC diagnosis and evaluation. Therefore, in order identify the connection between microbial activity and their effect on metal surface and, respectively, to confirm this corrosion type, in addition to planktonic bacteria analysis, it is necessary to determine the type and number of sessile bacteria, together with the metallurgical aspects.

Current OMV Petrom oifields situation, respectively identification of corrosion problems of pipelines caused by microbiological activity, led to the decision to design and manufacture an unique device, which allows the accumulation of biofilm, in order to assess and confirm MIC thoroughly, specific for OMV Petrom reservoirs.

The biofilm sampling device, designed and manufactured in ICPT Câmpina, allows the evaluation of microbiological activity by accumulation of the biofilm on metal surface and indicates the corrosive attack severity.

The general objective of the PhD thesis was the confirmation of MIC in specific locations of the oilfield, through a complex assessment, which involves the analysis of sessile bacteria, along with metallurgical aspects and chemical analysis, and the implementation of effective control methods.

The thesis is structured in 15 chapters, of which 7 chapters form the bibliographic research and 8 chapters represent the original contributions.

Chapter 1 contains general information about MIC. Chapter 2 presents the microorganisms that cause this type of corrosion. Chapter 3 describes the steps in biofilm development on the metal surface and the environmental factors that influence it. Chapter 4 presents the best known mechanisms of MIC. The effects of MIC on the metal equipment are presented in Chapter 5. Chapter 6 consists of techniques for analyzing and diagnosing MIC. The last chapter of the bibliographic research describes the control methods of this corrosion type.

The original contributions begin with the research strategy, indicating the objectives.

Chapter 8 presents the materials, research methods and experimental program. This chapter describes the biofilm sampling device, the methods for characterization of metal coupons and deposit, the microbiological analysis and the corrosion monitoring methodology. Also, the chapter includes the experimental program of the research carried out within this PhD thesis.

Chapter 9 contains the design of the biofilm sampling device, as well as the standards used.

Chapter 10 consists in the characterization of metal coupons, before exposure in flow, in which are presented the results of the visual examination and the dimensional measurements, the surface roughness, respectively the chemical, metallographic analysis and the microscopic examination.

Chapter 11 represents the characterization of the deposit, by chemical analysis of the injection wastewater, morphology, determination of the elemental composition, microbiological analysis and microscopic examination.

Chapter 12 consists in the microbiological analysis of the biofilm from 3 chosen locations, by serial dilution method, being presented the analysis method and the results of each monitoring campaign.

Chapter 13 presents the surface morphologies of the metal coupons samples from the 3 chosen locations, identified by microscopic examination using digital microscope, obtaining two-dimensional and three-dimensional images of the corrosive attack.

Chapter 14 presents the chemical analysis of the fluid from the 3 locations of interest and the last chapter of the original contributions consists in the results of corrosion monitoring using corrosion coupons.

The final part of the thesis presents the conclusions and future directions of research and development, as well as the references.

The original results were partially highlighted by ISI publications, the patent application for the device, as well as presentation at conferences.

Corrosion is the main cause of pipeline failures in the oil industry, but quantifying the operating and maintenance costs associated, in general, with corrosion and, in particular, with MIC, cannot be accurately achieved and generates controversy.

Ferrous materials are corroded not only by physico-chemical reactions, but also by the metabolic activity of microorganisms [3]. MIC is an electrochemical process resulting from the activity of microorganisms that react with the metal surface, causing corrosion, or influencing other corrosion processes of metallic materials [2].

The types of bacteria considered to have the greatest impact on MIC are sulfate-reducing bacteria (SRB), sulfur-oxidizing bacteria (SOB), iron-oxidizing/reducing bacteria (IB), manganese-oxidizing bacteria and bacteria producing organic acids or extracellular polymeric substances [30]. In the anaerobic areas of carbon steel, SRB is likely to dominate, being the main cause of MIC [4].

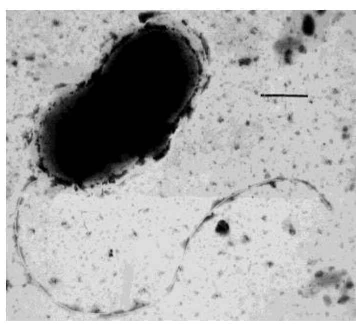

Fig.1 *Desulfovibrio vulgaris*, the most studied species of SRB [8]

Sulfate-reducing bacteria are a group of anaerobic bacteria that reduce sulfur compounds, such as sulfate, sulfite, thiosulfate and free sulfur to sulfide [9]. Although SRB are often considered strictly anaerobic, some genera tolerate oxygen [10] and, at low concentration of dissolved oxygen, some SRB are able to breathe with Fe^{3+} or even oxygen, with hydrogen acting as an electron donor [11].

SRB are the best known and studied bacteria involved in the MIC of copper and nickel alloys, cast iron, carbon steels, stainless steels and low alloy steels [12]. They are found in oil and natural gas production, transmission and storage facilities and are the most likely cause of corrosion of metal equipment [13]. The characteristics of the SRB attack on steel are the formation of black films of iron sulfide on the surface and pitting corrosion [14].

In order to investigate MIC, mainly SRB-influenced corrosion, it is necessary to understand its mechanism, explained by the cathodic depolarization theory.

When the metal is exposed to water, in the anodic reaction, it becomes polarized by the loss of positive ions. In the cathodic reaction, free electrons reduce water-derived protons to produce free hydrogen. SRB are expected to consume the formed hydrogen and there is the reduction of sulfate (SO_4^{2-}) to sulfide (H_2S). At the anode, only a quarter of the dissolved Fe^{2+} reacts with H_2S to form FeS. In the presence of CO_2 and bicarbonate, the rest of Fe^{2+} precipitates as $FeCO_3$. In the absence of bicarbonate, soluble $Fe(OH)_2$ is formed [15].

MIC is a type of localized corrosion that results from the activity of microorganisms in the form of pitting corrosion, crevasse corrosion or corrosion under deposit [16]. MIC is mainly characterized by localized terraced pitting [17].

Fig.2 Terraced pitting specific of MIC

Diagnosing corrosion as MIC is an interdisciplinary process that includes microbiological, metallurgical and chemical analyzes. The investigations consist in identifying the microorganisms that cause MIC in the fluid environment or associated with corrosion products, the appropriate morphology of the corrosive attack and, respectively, the chemistry of the corrosion products formed by microorganisms.

For many years, the main method of identifying corrosion caused by microorganisms has been the determination in the fluid environment of specific groups of bacteria (planktonic bacteria) or bacteria associated with corrosion products (sessile bacteria). In general, the method consists in growing microorganisms in a liquid or solid medium, extracting and quantifying a certain constituent, demonstrating and measuring cellular activity and demonstrating a spatial relationship between microbial cells and corrosion products by microscopic techniques [18].

Many aspects regarding the development, composition and distribution of the biofilm, respectively the spatial relations between the substrate and the corrosion products are identified with the help of scanning electron microscopy (SEM) [19].

MIC is usually observed in the form of pitting under deposits or tubercules, with the role in protecting microorganisms from the external environment. Corrosive attack is often characterized by cup-shaped and terraced pitting or underground cavities in carbon steel [2]. Moreover, the pitting can act as an initiator of stress corrosion cracking (SCC), because the "root" of the pitting causes the applied stress to multiply, resulting in much greater efforts than the tensile strength, thus causing damage to the metal [20].

One of the classic concepts for preventing the harmful effects of MIC in an industrial system is "keeping the system clean." Although it is a very difficult task in practice, several control methods (physical, chemical or biological) can be used [21].

The most common chemical method for controlling microorganisms in industrial water systems is the use of biocides. These can be either oxidizing or non-oxidizing chemicals. Chlorine, ozone and bromine are three types of oxidizing biocides for industrial use. Non-oxidizing biocides are more effective than oxidizing ones for controlling algae, fungi and bacteria, because they persist longer and are pH independent [21].

The biological method, called biocompetitive exclusion, consists of injecting nitrate, which stimulates the growth of competitive bacteria (nitrate-reducing bacteria, NRB) in water systems to inhibit the development of SRB [22].

Using NRB to control MIC may be an attractive option for industry because it is an environmentally friendly technique that can replace biocides. In this technique, nitrate is converted to nitrogen, which is an inert chemical compound [23].

These 2 control methods were implemented in the PhD thesis.

Thus, the final goal of the thesis was to evaluate the MIC of pipelines in the oil industry, through microbiological, metallurgical and chemical techniques, integrating the results to demonstrate the effect of bacterial activity on metal surface and control this type of corrosion, by implementing specific methods in each location where the phenomenon has been identified.

In this context, the general objective of the thesis was to confirm MIC in 3 locations of oilfield, through a complex assessment, which involves the analysis of bacteria in sessile form, along with metallurgical aspects and chemical analysis and the application of effective control strategies, such as biocide and nitrate treatment.

To achieve the purpose of this research, it appeared the need to design and manufacture an unique device, which allows the evaluation of microbiological activity by biofilm accumulating on the metal surface and indicates the severity of the corrosive attack.

In the PhD thesis, the following specific objectives were taken into account:

- the design and manufacture of the biofilm sampling device, in compliance with the safety requirements in operation;
- the installation of the biofilm sampling device in locations of interest for MIC evaluation;
- the use of metal coupons samples with similar metallurgy as one of the pipeline to reproduce the effects of MIC;
- the analysis of the deposit accumulated on the metal surface of coupons, in order to confirm the presence of bacterial activity;
- the microbiological analysis of the biofilm, by the serial dilution method, to determine the type and number of bacteria associated with MIC;
- the microscopic examination of metal samples, using a digital microscope, to identify different surface morphologies, including the localized corrosive attack, in the form of terraced pitting and shallow pitting, specific to MIC;

- the analysis of the fluids circulating through the pipelines, in order to know the environment in which MIC appears;
- the corrosion monitoring using corrosion coupons, in order to determine the aggressiveness of the environment in the chosen locations;
- the correlation and integration of results for diagnosing and confirming the presence of MIC.

The MIC control was performed in 2 locations, simultaneously with the monitoring program within the PhD thesis, by treatment with nitrate, respectively biocides, its efficiency being presented in the conclusions of the thesis.

Information about wells operating conditions, pipeline characteristics, fluid characteristics, other than chemical constituents, were collected and analyzed as an important part of the complex MIC assessment process, but cannot be disclosed according to OMV Petrom confidentiality agreement.

The biofilm sampling device, hereinafter referred to as the device, designed and manufactured in ICPT Câmpina, allows the evaluation of microbiological activity by biofilm accumulation on the metal surface and indicates the severity of the corrosive attack, therefore, appropriate methods of MIC control can be recommended.

Fig.3 The device installed in location no.1

The device can be installed on any pipeline where microbial activity has been identified. It accumulates several components of the oilfield system, such as the biofilm containing sessile bacteria, the fluid flowing through the pipeline and corrosion products.

Laboratory tests of the biofilm and other components of the technological flow accumulated in the device allow the recommendation of effective methods to prevent or decrease MIC.

The importance of the device is given by the facts it allows assessment of microbiological activity by biofilm accumulation, it is sealed and prevents air contamination, reproduces exactly the natural conditions of bacteria attachment on metal surface and allows transportation of collected fluid and biofilm to the laboratory, maintaining the same natural environmental conditions (pressure, gas content, fluid and biofilm composition and so on).

The main part of the device is the special stud with the metal coupons on which biofilm accumulates. The coupons are mounted in a teflon protection, manufactured in two parts, which can be unfold in order to take out the coupons without biofilm contamination. 15 metal coupons are exposed internally into the device, located in “12”, “3”, “6”, and “9 o’clock” positions on the circumference of the device, to compare bacterial growth.

Fig.4 The special stud

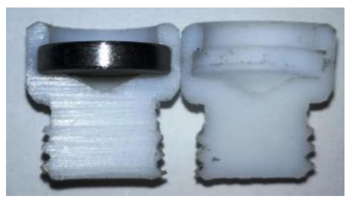

Fig.5 The metal coupon in teflon protection

The metal coupons can be made of any type of steel, can have a specific chemical composition and roughness, thus reproducing the effects of MIC on any type of metallic equipment from oil industry.

MIC monitoring program was implemented in 3 locations:

- location no.1, on a biphasic fluid transportation pipeline;
- location no.2, on a injection wastewater pipeline;
- location no.3, on a injection wastewater pipeline.

These locations were considered suitable for MIC evaluation due to microbiological analysis background which revealed planktonic bacteria presence in the fluids and identification of corrosion problems on metallic equipment suspected to be caused by microbiological activity.

Investigations were performed for structural characterization of the metal coupons, before exposing them in flow, such as visual examination and dimensional measurements, surface roughness with the digital roughness meter. The chemical composition of the metal was determined by spectrochemical method, according to ASTM E350-12. The metallographic examination of the surface was performed using an OLYMPUS SZX stereomicroscope, equipped with QuickMicroPhoto 2.2 software.

The characteristics of the metal surface were examined using the Keyence digital microscope and the Philips scanning electron microscope (SEM).

Fig.6 Keyence digital microscope

Chemical analyzes, SEM analysis and energy dispersive X-ray spectroscopy (EDS), used to obtain compositional information on deposits, as well as the identification of elemental composition of metal, were used to characterize the deposit.

Chemical analysis of injection wastewater was performed by specific analysis methods, as pH analysis according to 4500-H+B, conductivity determination according to 2510 B, determination of suspended solids content according to STAS 6953/81, determination of total alkalinity according to SR EN ISO 9963/2002, determination of sulfide content according to SR 7510/97, determination of selected elements by inductively coupled plasma optical emission spectroscopy (ICP-OES) according to SR EN ISO 11885/2009, determination of dissolved anions by liquid phase chromatography according to SR EN ISO 10304-1:2009, determination of carbonate alkalinity according to SR EN ISO 9963/2002 and determination of bacteria number according to AWWA 2012.

The microbiological analysis was performed by the serial dilution method on specific media whose salinity was brought to a level similar to the samples. Incubation was done at room temperature (22-24ºC) for a period of approx. 14 days. The serial dilution method is a statistical method by which serial dilutions are made until, theoretically, no bacteria are found in the last dilution. The estimated bacterial population is obtained from a statistical table [24].

For microbiological analyzes in water, it is mentioned that, in the case of SRB, the presence of a single bacterium is a potential problem, because they are bacteria attached to the substrate, and the working method detects only planktonic bacteria. However, the maximum allowed values are up to 10^2 / cm^2 for SRB, APB, aerobic and anaerobic bacteria [25].

The preparation, installation and analysis of the corrosion monitoring coupons were performed according to OMV Petrom internal methodology, which corresponds to NACE RP0775 [26].

The MIC monitoring program using the biofilm sampling device was implemented in 3 oilfield locations considered suitable for the evaluation and control of MIC.

The metal coupons used had a similar metallurgy to that of the pipeline to reproduce the effects of MIC on the pipeline. The chemical composition, surface roughness and microstructure of the metal corresponded to a non-alloy carbon steel used in pipeline manufacturing.

The chemical composition of the metal was determined by the spectrochemical method [27]. The chemical composition of the metal corresponded to a non-alloy carbon steel, type AISI 1035. The metallographic examination of the surface showed non-metallic oxide inclusions according to ASTM E45 [28] and homogeneous structure of ferrite and perlite, specific to carbon steel. The characteristics of the metal surface were examined using a digital microscope and SEM, to observe and compare the changes that will occur after the corrosive attack.

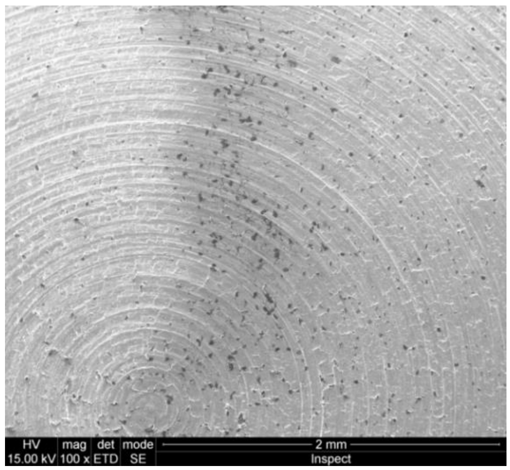

Fig. 7 SEM image of metal surface, 100X

The evaluation of MIC was performed by analyzing the deposit accumulated on the surface of metal coupons to confirm the presence of bacterial activity, microbiological analysis of biofilm to determine the type and number of bacteria, microscopic examination of metal coupons to identify the specific surface morphology, analysis of the circulated fluids for the knowledge of the environment in which MIC occurs, as well as corrosion monitoring with corrosion coupons in order to determine the aggressiveness of the environment of the chosen locations.

The control of MIC was performed simultaneously with the monitoring program, by treatment with nitrate and, respectively, biocides, in 2 locations. The interpretation and integration of the results led to the treatment optimization and recommendations for future directions.

The experimental program performed within the present PhD thesis is shown in figure 8.

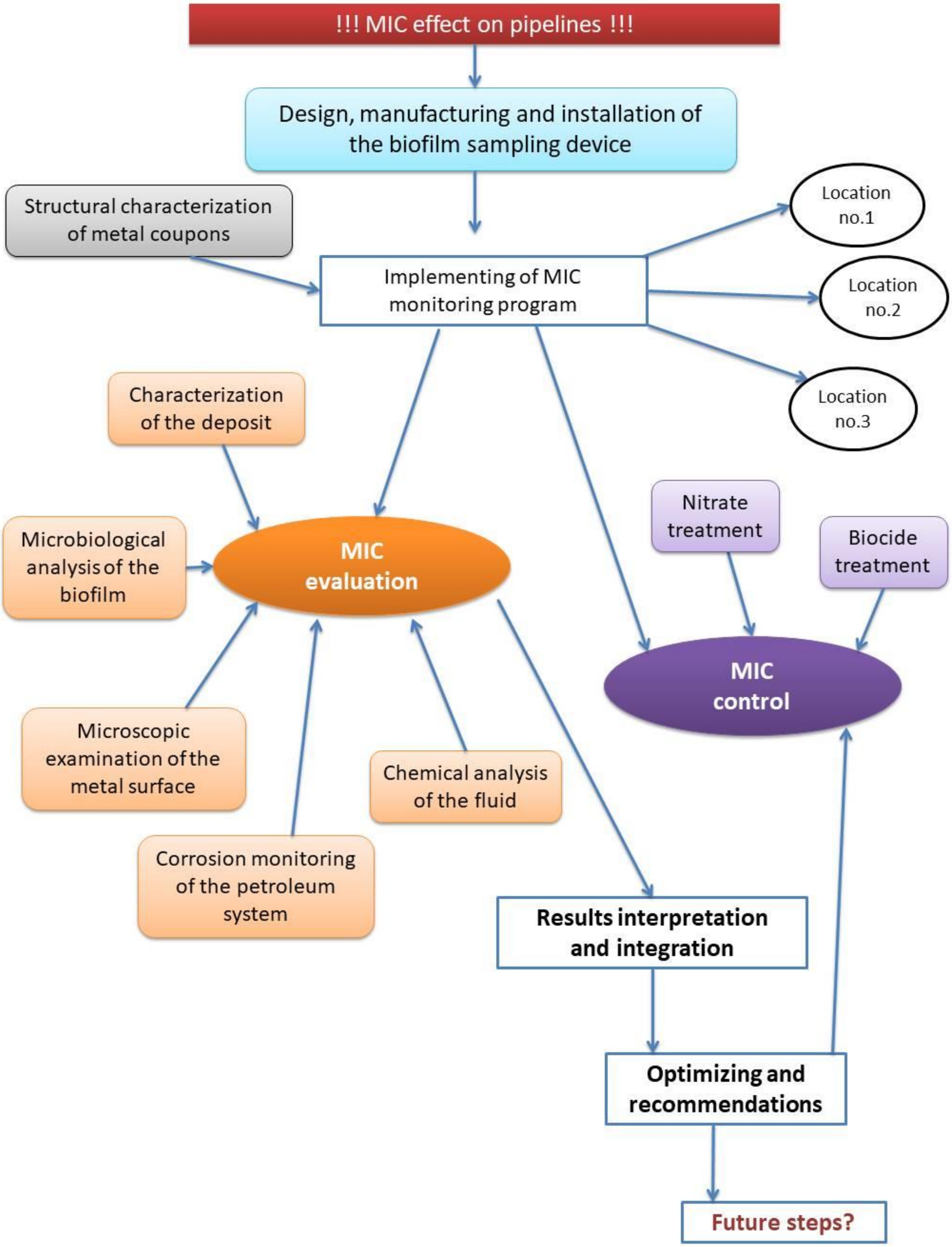

Fig.8 The experimental program of the research carried out within the present PhD thesis

In the first monitoring campaign, the accumulated deposit on the surface of metal coupons was analyzed to demonstrate the presence of microorganisms in the form of biofilms responsible for MIC. The analysis was performed only for the deposit sampled from location no.2, the results being relevant for the other locations.

The deposit is an accumulation of transported or corroded substances inside of a pipeline [29]. The deposits encountered in injection water pipelines include carbonates, sulphates, phosphates of alkaline earth metals, silica, corrosion products, microorganisms and suspension particles [2]. Usually, the deposits create favorable conditions for MIC appearance [29].

The deposit analysis indicated bacterial activity, confirmed by the analysis of injection wastewater. The characterization of the injection wastewater indicated the presence of indicators for bacterial activity. H_2S content is the most important indicator of microbial activity in an oil system. Organic acids, propionic and acetic, are by-products of microbial metabolism. Planktonic populations of SRB and APB were identified. Also, the acidic pH indicated the presence of bacterial activity in the water.

The morphology and the elemental composition of the deposit were characteristic of scale deposit, containing inorganic particles, especially salt crystals, in different hydration phases. Due to the large amount of salts, the microbiological mass could not be differentiated, except for the deposit taken from the "12 o'clock" position, where bacteria-like forms may have been identified.

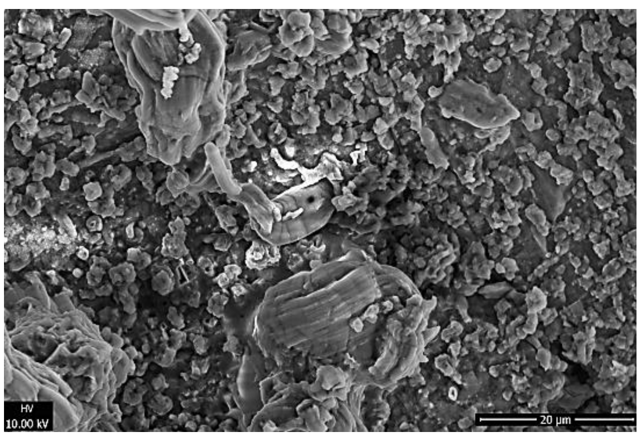

Fig.8 Scanning electron micrograph of the deposit from “12 o’clock” position, 5000X

The elemental composition of the deposit corresponds to scale type, containing high amount of salts, represented by Na and Cl compounds. Zn is naturally present in water and, therefore, in the hydrated deposit. Also, silica, oxides and carbonates are present, represented by Si, O and C. The corrosion products identified are Fe, Mn and Cr. As presence in the spectrum can classify the scale as calcium carbonate type.

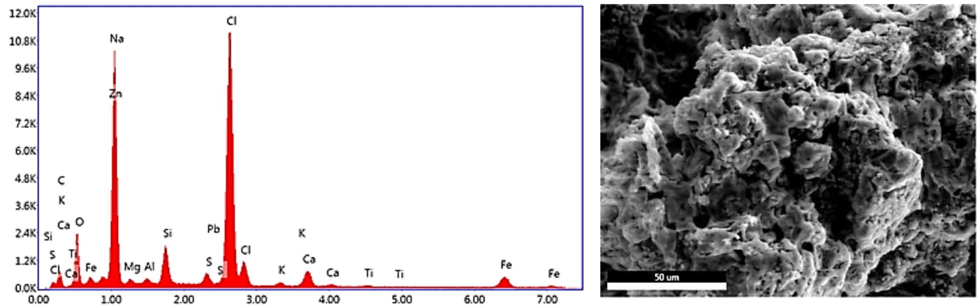

Fig.9 EDS spectrum of the deposit and SEM micrograph of sample from which spectrum was generated

Therefore, the deposit was microbiologically analyzed to confirm the presence of biofilm containing bacteria. The method used to grow the above mentioned bacteria was serial dilution. The bacteria number was calculated for each deposit sample, considering the exposed surface of the metal coupons of 63.62 mm^2.

The microbiological analysis revealed the presence of bacteria responsible for MIC and a diversity of bacterial communities in the biofilm samples from different positions on the circumference of the device. Also, in the deposit, forms of bacteria were distinguished using the optical microscope.

The confirmation of bacterial activity in the deposit allowed its analysis and treatment from a microbiological point of view, in order to implement MIC control methods (e.g biocide treatment) specific to this location.

For biofilm characterization, the bacteria number was classified as:

- high, over 10^5 / exposed area;
- moderate, between 10^2 and 10^5 / exposed area;
- low, below 10^2 / exposed area.

There was observed a diversity of bacteria populations in the biofilm for each position on the circumference of the device. Bacteria associated with MIC were identified in all biofilm samples.

The biofilm samples were microbiologically analyzed by the method of serial dilution, to determine the following types of bacteria associated with MIC:

- aerobic bacteria;
- anaerobic bacteria;
- sulfate-reducing bacteria (SRB);
- acid-producing bacteria (APB)
- iron-oxidizing bacteria (IOB);
- sulfur-oxidizing bacteria (SOB);
- nitrate-reducing bacteria (NRB).

An example of microbiological analysis of the biofilm is presented in Table 1. The microbiological analysis in monitoring campaign 1 indicated high number of anaerobic bacteria, APB and SRB, moderate number of sulfur-oxidizing bacteria and low number of iron-oxidizing bacteria. All values exceeded the acceptable limit. The "6 o'clock" and "9 o'clock" biofilm samples contained a higher bacterial population of APB and SRB than the "12 o'clock" and "3 o'clock" biofilm samples. No nitrate treatment was applied during this period.

Table 1 Microbiological analysis of the biofilm in monitoring campaign 1

Biofilm sample		**Bacteria number / exposed surface**				
		Anaerobic bacteria	**APB**	**SRB**	**IOB**	**SOB**
"12 o'clock"	1	10^7	10^7	10^3	<10	10^3
	2	10^7	10^2	10^3	10	10^3
	3	10^7	10^7	<10	10^2	10^3
"3 o'clock"	1	10^4	10^3	10^2	10^2	10^2
	2	10^3	10^4	10^2	10	10^2
	3	10^2	10^2	10^3	<10	10^3
"6 o'clock"	1	10^7	10^7	10^5	10^4	<10
	2	10^6	10^6	>10^7	<10	
	3	10^6	10^5	>10^7	<10	10^2
"9 o'clock"	1	10^4	10^2	>10^7	10	10^4
	2	10^7	10^7	>10^7	10	
	3	10^7	10^7	>10^7	10^4	10^3

In location no.1, nitrate treatment was applied, in predetermined concentrations, to reduce the number of SRB. The initial concentration of nitrate was 230 ppm, to produce a rapid development of NRB, followed by a lower concentration of 100 ppm after one month of treatment, for economic reasons.

In location no.2, biocide treatment was applied to reduce the number of bacteria responsible for MIC. The treatment consisted in alternative application of 2 biocides, so that the bacteria do not adapt to a single biocide, periodically, in a concentration of 50 ppm, established according to the water volume. Also, due to the tendency of scale formation on the surface of the pipelines, continuous treatment with scale inhibitor was applied, in a concentration of 5 ppm.

In location no. 3, no treatment was applied to observe the natural development of the biofilm inside the device.

The microscopic examination of the metal surface after flow exposure was performed using the digital microscope, obtaining two-dimensional and three-dimensional images of the corrosive attack. Metal coupons from each position on the circumference of the device were investigated to compare the development of the biofilm and its effect on metal surface. The corrosion morphology on the metal surface was different for each location.

By microscopic examination of the metal coupons, different surface morphologies were identified, including the localized corrosive attack, in the form of terraced pitting and shallow pitting, specific to MIC.

In location no.1, MIC was observed on the surface of metal coupons in the following positions:

- "12 o'clock" and "6 o'clock", as localized shallow pitting, in monitoring campaign 2;
- "12 o'clock" and "9 o'clock", as localized shallow pitting, in monitoring campaign 3;
- "3 o'clock", as terraced pitting and, respectively, "12 o'clock" and "9 o'clock", as localized shallow pitting located, in monitoring campaign 5;
- in all positions, as terraced pitting, in monitoring campaign 6;
- "6 o'clock", as terraced pitting, in monitoring campaign 7.

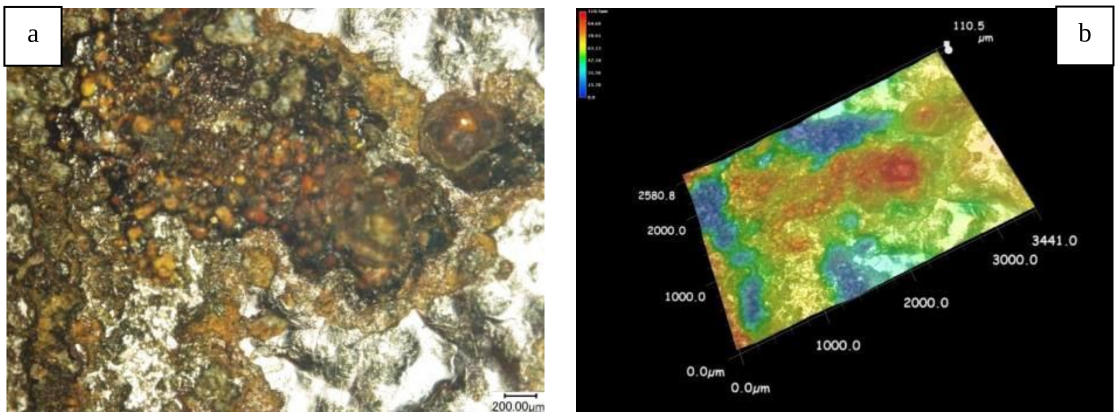

Fig.10 2D (a) and 3D (b) micrographs of the metal surface in "6 o'clock" position, monitoring campaign 7, 100X

The corrosion intensity was higher on the surface of metal coupons from "6 o'clock" position, where the predominant type of corrosion was general corrosion. The intensity of corrosion can be correlated with high bacteria number in biofilm samples.

The appearance of MIC on the metal surface was influenced by the exposure period. Metal coupons exposed for a longer period, of approx. 2 months, in monitoring campaigns 5, 6 and 7, showed a more severe MIC than those exposed for one month.

In location no.2, by microscopic examination of the metal coupons, different surface morphologies were identified, including the localized corrosive attack, in the form of terraced pitting and shallow pitting, specific to MIC.

MIC was observed on the surface of metal coupons in the following positions:

- "6 o'clock" and "9 o'clock", as terraced pitting, in monitoring campaign 2;
- "3 o'clock", as localized shallow pitting, in monitoring campaign 3;
- "12 o'clock" and "3 o'clock", as localized shallow pitting, in monitoring campaign 4.

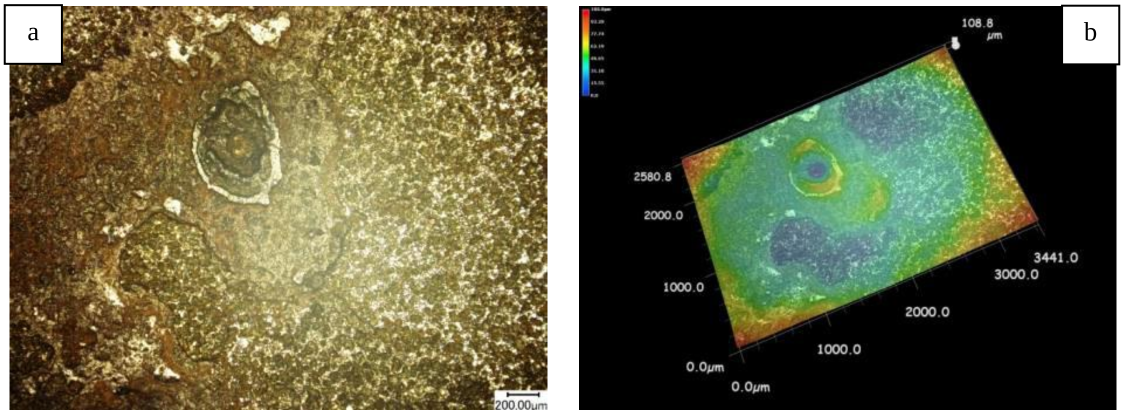

Fig.11 2D (a) and 3D (b) micrographs of the metal surface in "6 o'clock" position, monitoring campaign 2, 100X

In monitoring campaign 1, MIC was not identified on the surface of metal coupons, it randomly appeared in the following campaigns, for each position on the circumference of the device. This appearance could be influenced by variations of flow turbulence through pipelines, which entrain planktonic bacteria and allow the adhesion and development of the biofilm on the metal surface.

The intensity of corrosion was the lowest on the surface of metal coupons in "12 o'clock" position, correlated with low number of sulfate-reducing bacteria and acid-producing bacteria present in biofilm samples.

In location no.3, by microscopic examination of the metal coupons, different surface morphologies were identified, including the localized corrosive attack, in the form of terraced pitting and shallow pitting, specific to MIC.

MIC was observed on the surface of metal coupons in the following positions:

- “3 o’clock” and “9 o’clock”, as terraced pitting, respectively “12 o’clock”, as localized shallow pitting, in monitoring campaign 1;
- “12 o’clock” and “3 o’clock”, as terraced pitting, respectively “6 o’clock” and “9 o’clock”, as localized shallow pitting, in monitoring campaign 3.

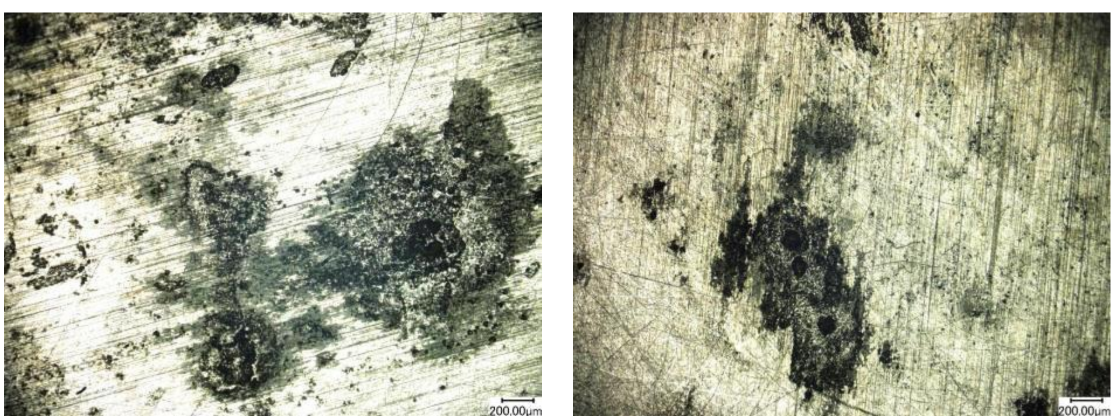

Fig.12 2D micrographs of the metal surface in "12 o'clock" position, monitoring campaign 3, 100X

MIC appearance on metal surface was influenced by the longer period of exposure, beeing observed very representative morphologies. Also, the intensity of MIC was determined by the lack of biocide treatment, the development of the biofilm not being influenced.

In addition to the microbiological analysis of the biofilm and the microscopic examination of the metal surface, the analysis of the fluids circulating through the pipelines in the 3 locations was performed, and the treatment with nitrate, respectively, biocide was implemented following the results.

Knowledge of the constituents of fluids, especially of water, circulating through pipelines and their properties is essential in the process of corrosion control and, respectively, MIC control in an oil environment.

The analysis of the fluids from the 3 locations was performed according to OMV Petrom internal methodology. Fluid samples were taken from the pipelines using sterile containers. The fluids were sampled from two sampling points, located downstream or upstream of the location where the device has been installed.

Fluid analysis revealed the presence of indicators of bacterial activity in all locations, such as H_2S content, the most important indicator of microbial activity in an oil system, organic acids, propionic and acetic, by-products of microbial metabolism and planktonic SRB and APB population.

Corrosion monitoring using corrosion coupons was implemented in the same locations where the device has been installed and it was performed during the same period.

According to NACE TM0212-2012, corrosion was classified according to corrosion rate as:

- low, below 0.025 mm / year;
- moderate, 0.025-0.12 mm / year;
- high, 0.13-0.25 mm / year;
- severe, over 0.25 mm / year [7].

In location no. 1, the corrosion type identified on the surface of corrosion coupons was, generally, severe corrosion, according to corrosion rate values. Also, the terraced pitting, respectively, localized shallow pitting morphologies, specific to MIC, was observed.

In location no.2, the corrosion type identified on the metal surface was severe and, respectively, moderate, according to corrosion rate values. Also, specific MIC morphology, as terraced pitting, was observed in monitoring campaign 4.

In location no.3, the corrosion type identified on the metal surface was moderate, respectively, high, according to corrosion rate values. The increase in corrosion rate values was caused by the lack of inhibitor treatment in this location. Terraced pitting, specific to MIC, was observed in all monitoring campaigns.

In conclusion, the correlation and interpretation of microbiological analyzes with metallurgical examination, together with chemical analysis and corrosion monitoring of the oil system, performed in this PhD thesis, demonstrated the effects of bacterial activity on metal surface and allowed an adequate and efficient assessment of MIC of pipelines, as well as the implementation and optimization of control methods.

The approach of the interdisciplinary subject of MIC could not have been possible without the biofilm sampling device implementation in the locations of interest, the biofilm representing the most important ecological component of the oil environment in terms of corrosion.

The uniqueness and novelty of the device consist in the evaluation of microbiological activity by the accumulation of the biofilm on the metal surface, where the severity of the corrosive attack can be observed.

The main characteristic of the device, namely, by its design, it does not allow the contamination of the biofilm and maintains the appropriate conditions for anaerobic bacteria growth, was exploited using metal coupons having similar metallurgy to the pipeline, thus reproducing the effects of MIC on pipelines in the oil industry.

Using the device, during the PhD thesis, investigations were performed on the 2 most important components in terms of MIC, sessile bacteria and corroded surface morphology. The research results demonstrated the efficiency and importance of device implementation in the process of MIC control.

The MIC monitoring program using the biofilm sampling device was implemented in 3 oilfield locations, considered adequate for the evaluation and control of MIC, thus location no.1, on a pipeline transporting biphasic fluid, location no.2, on an injection wastewater pipeline and, respectively, location no.3, on an injection wastewater pipeline.

These locations were considered suitable for the experimental program implementation due to microbiological analyzes background that showed the presence of planktonic bacteria in fluids and the identification of corrosion problems of metal equipment suspected to be caused by microbiological activity.

In location no.1, nitrate treatment led to a decrease in the bacterial population, especially of the target bacteria for which this type of treatment was applied, sulfate-reducing bacteria. The population of sulfate-reducing bacteria varied from high number in the first monitoring campaign, to moderate number in the last monitoring campaign. In monitoring campaign 6, the number of sulfate-reducing bacteria increased, which forced the increase of the applied nitrate concentration. Following the treatment optimization, the bacterial population decreased.

According to the method principle, the efficiency of nitrate treatment in location no.1 was demonstrated by decreasing the number of sulfate-reducing bacteria, simultaneously with the appearance and increasing the number of nitrate-reducing bacteria. The limited period of the treatment, the economic considerations, as well as the diversity of the oil environment determined the impossibility of decreasing the number of bacteria to zero.

The effects of bacterial activity on the metal surface are obvious in "6 o'clock" position on the circumference of the device. The high number of bacterial population is directly proportional to the intensity of the corrosive attack. Flow fluctuations and changes in the chemical composition of the fluid caused randomly occurrence of MIC in each position on the circumference of the device.

Also, the connection between bacteria number and MIC occurrence was observed in monitoring campaign 6. The growth of bacteria, mainly sulfate-reducing bacteria and acid-producing bacteria, influenced the appearance of MIC, in the characteristic form of terraced pitting and localized shallow pitting, on all 4 metal coupons examined.

The aggressiveness of the corrosive environment limited the effectiveness of nitrate treatment. Severe corrosion of the oilfield, identified by using corrosion coupons, cannot be controled and reduced by the treatment against bacterial activity only. Treatment with corrosion and scale inhibitors has not been the subject of this research!

In location no.2, biocide treatment was applied concomitantly with scale inhibitor treatment in order to reduce the high concentration of sulfate-reducing bacteria and acid-producing bacteria and, implicitly, the aggressiveness of MIC, and, respectively, to treat and prevent the scale deposits, which affect the pipeline integrity. The effectiveness of the treatment was demonstrated.

Thus, the population of sulfate-reducing bacteria decreased in the last monitoring campaign. Also, the acid-producing bacteria number present in the biofilm samples was low in the last monitoring campaign.

The appearance of MIC on the surface of metal coupons was closely related to the diversity of the bacterial population. In the case of lower bacterial activity, the effects of MIC were not identified by microscopic examination of the surface. After the increase in the bacteria number, in monitoring campaign 2, there was observed the occurrence of specific terraced pitting and localized shallow pitting.

The effectiveness of biocide treatment was also demonstrated by corrosion monitoring using corrosion coupons. There is a significant decrease in the corrosion rate after 6 months of treatment. The increase in the corrosion rate in campaign 4 was caused by a change in the concentration of suspended solids in the water flow and acidification at the well. Therefore, in order to control the aggressiveness of the environment, it is necessary to implement filtration and separation systems for suspension particles and, also, to apply corrosion inhibitor treatment, especially during acidification.

In order to prevent the growth of bacterial population and the associated problems, such as the appearance of MIC, respectively, the formation of iron sulfide, it is necessary to continue the alternative treatment with the 2 biocides and, possibly, to optimize the treatment concentration. It is also important to continue the treatment with scale inhibitor to prevent deposits inside the pipeline.

In location no.3, the effect of bacterial activity on the metal surface was "unaltered", no control method was applied, and it was the most interesting to observe.

This location was chosen for the research as a standard, to compare the natural development of the biofilm on the metal surface with the development influenced and inhibited by the treatments.

Even though the bacterial population maintained in low and moderate number of sulfate-reducing bacteria and acid-producing bacteria, the effects on the metal surface were the most spectacular of the three locations analyzed, being observed the specific pitting to MIC, especially in monitoring campaign 3.

The intensity of MIC on metal surface could be correlated with a higher exposure time, of 4 months, compared to one, respectively, two or three months, in the case of other locations.

An increase in corrosion rate of corrosion coupons was observed, which may demonstrate the importance of implementing an effective method of corrosion control in general, as well as the need to apply corrosion inhibitor treatment.

The final scope of this PhD thesis, the evaluation and control of MIC in oil industry pipelines, was achieved by defining the objectives, implementing monitoring strategies and using complex and modern techniques and methods of analysis.

Firstly, MIC monitoring was performed in 3 locations considered appropriate for the evaluation of this corrosion type, due to corrosion problems of metal equipment suspected of a microbiological cause.

Secondly, the presence of sessile bacteria in the form of biofilm in the deposit accumulated on the metal surface was initially confirmed. The morphology of the deposit obtained using scanning electron microscope (SEM), the elemental composition by energy dispersive X-ray spectroscopy (EDS), microbiological analysis by serial dilution method, as well as microscopic examination using the optical microscope were defining techniques to confirm bacterial activity of the deposit, which allowed its analysis and treatment from a microbiological point of view.

Thirdly, by serial dilution method, the bacteria responsible for MIC were identified in biofilm samples, mainly sulfate-reducing bacteria and acid-producing bacteria.

Also, using the digital microscope, the surface morphology of the metal coupons was examined and the corrosion type specific to MIC, terraced and localized shallow pitting, attributed to the bacterial activity, was observed.

In addition, for each monitoring campaign, chemical analysis of the fluid and injection wastewater was performed by characteristic chemical analyzes, as well as corrosion monitoring of the pipelines using corrosion coupons.

The correlation of the microbiological analysis with the morphology of the corroded surface, the fluid chemistry, as well as with the corrosion monitoring of the oilfield demonstrated the effects of the bacteria activity on the metal surface and allowed the evaluation of the efficiency of applied treatment and its optimization.

However, the management of MIC includes additional steps, which have not been the subject of this research. Significant investment of funds in the MIC management, covering all aspects of interest, is necessary to reduce the costs and consequences of this corrosion type. In a certain location, the cause of corrosion is not only microbiological activity, but also other factors. In order to be treated, it must firstly be differentiated from other types of corrosion, then a strategy to control all the factors that determine the corrosion of the metal system must be implemented.

The main costs associated with MIC control are:

- operating expenses (OPEX), which include pigging cleaning, biocide injection, monitoring activities and so on;
- capital expenses (CAPEX), which are related to the equipment needed for chemical injection, filters and so on.

If the diagnosis of MIC is not perfomened suitable for each location and if the other factors, such as the presence of aggressive gases, solids that cause its erosion, responsible for other types of corrosion, are not taken into account, the funds allocated to the control program are ineffectively spent.

The device implementation, the techniques and analyzes performed, as well as the application of control methods, performed in this PhD thesis, represent only a small part of the clear understanding of the unique behavior of MIC and of the complex control process in the oil industry.

During the research within the PhD thesis, some aspects were identified, new or current, that can be considered or improved.

As MIC does not only affect pipelines, I propose to expand the research of the effects of MIC on surface of other steel types, for example, steels used in the manufacture of sucker rods or tubing.

I also propose the implementation of the biofilm sampling device in production areas where three-phased fluid is transported.

Modern analysis techniques, such as electron microscopy and X-ray spectroscopy, must be used in every stage of MIC monitoring and evaluation.

Another indicator of corrosive attack severity on metal coupons is the corrosion rate, its calculation not being performed in this thesis, but which must be taken into account in the future.

Last but not least, the most interesting strategy for controlling MIC, found in the literature, is the application of ozone, with biocidal action on bacteria and very low toxicity to the environment. Thorough research is needed.

All these steps were analyzed, together with my colleagues from ICPT Câmpina, and will be carried out within an internal OMV Petrom project.

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