X-RAY DIFFRACTION AS NON-DESTRUCTIVE CHARACTERIZATION METHOD OF DIFFERENT MATERIALS FROM CANDU NPP SECONDARY CIRCUIT

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Abstract

The occurrence of microbiological corrosion in some auxiliary systems in the secondary circuit from CANDU NPP is caused by many factors, the most important referring to: the construction material (carbon steel), the existence of the microbiological load in the raw water and the existence of areas with flow slow or stagnant that allow the attachment of microorganisms and the development of biofilms. To eliminate the appearance of microbiological corrosion on carbon steel pipes, it was proposed to replace them with pipes made of other commercial materials, currently on the market. For this purpose, studies were carried out to evaluate the behavior in the presence of microbiological culture media on the following plastic materials: polyvinyl chloride (PVC), polypropylene (PP) and polyethylene (PE). The test media were the following: oxidizing bacteria of iron, sulfate-reducing bacteria and heterotrophic bacteria. The long-term tests were carried out in microbiological culture media previously identified in the raw water. After 600 days of immersion, the samples were removed from the test medium, dried naturally and analyzed by optical microscopy and X-ray diffraction (areas with more consistent deposits).

Keywords: *Microbiologically influenced corrosion, Carbon steel pipe, X-ray diffraction analyses*

Introduction

Microbiologically induced corrosion (MIC) is a type of corrosion resulting from the presence and activity of microorganisms, including bacteria and fungi.

The raw water from some cooling systems contains a lot of microorganisms which can promote corrosion because the water is often untreated or minimally treated against microbial load. This microbial species can attach to inner side of the pipes and interact in complex ways to form biofilms and produce an environment at the biofilm / metal interface that is radically different from that of the bulk medium in terms of pH, dissolved oxygen, organic and inorganic species.

This way, microbiologically influenced corrosion appears, which is the label generally applied to corrosion involving the action of bacteria on metal surfaces. It is established that the most aggressive microbial corrosion takes place in the presence of microbial consortia in which many physiological types of bacteria, including metal-oxidizing bacteria, sulfate-reducing bacteria (SRB), acid-producing bacteria (APB) and metal-reducing bacteria (MRB) interact in complex ways within the structure of biofilms [1].

The appearance of failure caused by microorganisms inside of a carbon steel pipe from the auxiliary system of a NPP secondary circuit is presented in Fig.1 [2].

Carbon steel (SA 106 gr. B) is one of the most used materials for the pipes in water transport systems from the CANDU Nuclear Power Plant (NPP) secondary circuit. In raw water environments this material is susceptible to microbiological corrosion, a phenomenon with, major implications in the degradation of the carbon steel pipes.

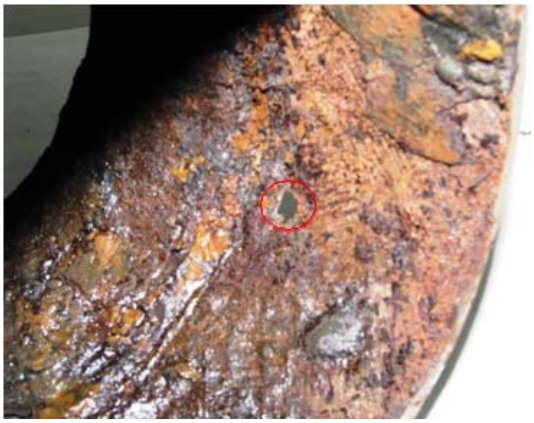


Fig. 1. Aspect of inside failure pipe, [2]

Outside the pipes, most types of microbiologically induced corrosion lead to detachements of the paint with which the pipe was covered. The potential for this type of corrosion in buried pipelines is determined by the availability of nutrients, water and electron acceptors.

Inside the pipes through which the raw water flows, water stagnation represents the main factor (mentioned in the specialized reports) responsible for the occurrence of microbiologically influenced corrosion.

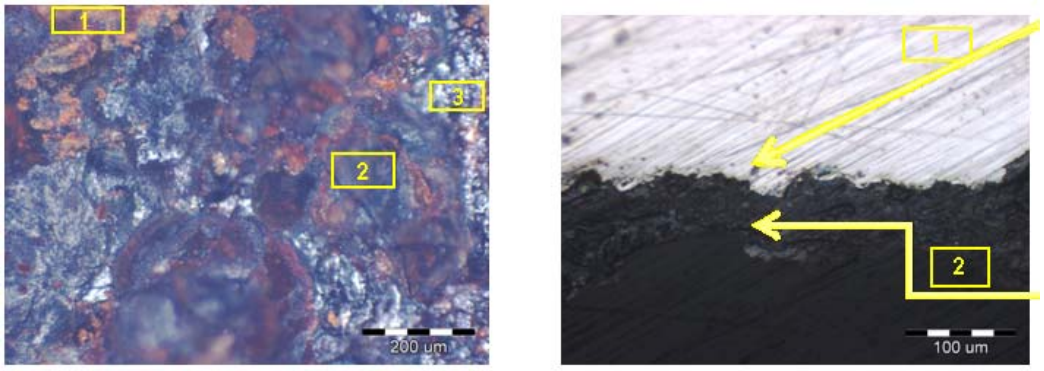
The metallographic analysis of some carbon steel pipe internal areas, emphasizes the deposits of corrosion products with different colors (Fig. 2a), [2]:
- zone 1 - brown as a result of heterotrofe aerobe and iron - oxidizing bacteria;
- zone 2 - black as a result of sulphate-reducing bacteria.

Also, uncovered areas of pipe (such as the zone 3) are observed, because microorganisms do not develop uniform biofilms on metal surfaces. By analyzing the cross-section (Fig. 2b) the ollowing aspects were observed:
- the non-uniform corrosion of the steel - arrow 1
- the bulky deposits with different thicknesses (ranging from 34 μm to 151 μm) - arrow 2.

The main obiective of this work was to evaluate the resistance to microbiologically influenced corrosion of some plastic commercial materials, in order to replace carbon steel pipes used for raw water in a CANDU NPP.

The following materials were tested:
- polyvinyl chloride (PVC);
- polypropylene (PP);
- polyethylene (PE).

The test media were the following:
- iron- oxidizing bacteria;
- sulfate-reducing;
- heterotrophic aerobic bacteria.



a) b)

Fig. 2. Optical micrograph of some areas from the corroded carbon steel pipe

Experimental works

X-ray diffraction analysis

The identification and characterization of corrosion products from different parts of secondary circuit give information which can be used to control and mitigate the corrosion process in the NPP CANDU secondary circuit.

X-Ray analyze is an nondestructive method of analysis useful for qualitative and semiquantitative identification of different corrosion material. It can provide information about phase composition. Also, XRD can distinguish between different modification of phases that have the same chemical formula.

The common technique used in the X-ray diffraction analysis does not allow thin film analysis due to the fact that the intensity of the reflected beam from the analyzed layer is very small (the analyzed volume is very small) compared with the intensity of the background or of the diffraction peaks corresponding to the substrate.

The most common used focusing configuration is the Bragg-Brentano geometry (or θ-2θ geometry), presented in Fig. 3a, [3]. In this geometry, the receiving slit and the X-Ray source must be placed on the diffractometer circle, having the center exactly on the sample. The modern diffractometers allow the use the θ-θ geometry, when the X-ray source and the detector move simultaneously over the angular range θ. In the case of common XRD techniques a monochromatic divergent beam is used. In the case of very thin deposits, the Grazing Incidence X-ray Diffraction (GIXRD) method is used (Fig. 3b).

Diffraction at small angles (Grazing Incidence X-Ray Diffraction-GIXRD) was developed by Marr, Eisenberger and Cho in 1979 to analyze thin films deposited on a substrate [4]. In this case, the incident angle is fixed at a very small value (typically between 0.3° and 3°) and does not change during the analysis. Therefore, the X-ray tube remains fixed and only the detector is rotated with a 2θ angle. In this way, can be obtained the X-ray beam path increasing in the thin film and hence an increased intensity of the diffracted beam by the thin layer. The penetration depth normal to the surface is proportional to the sinus of the angle of incidence [5], as long as this is larger than the critical angle (the angle of total external reflection). To be able to use the GIXRD, both the incident beam and the diffracted beam must be plane parallel (not divergent). This is possible using either narrow slits or Göbel mirrors in the incident beam path, in combination with a plane parallel collimator in the diffracted beam path. The collimator allows only quasi-parallel beam to reach the detector.

The analyses were performed using a PanAlytical X'Pert Pro MPD diffractometer for GIXRD. It was used a CuKα radiation (λKα1=1.5418Å), a divergence slit of 1/80 and a 10mm mask for the incident beam, and a plan parallel collimator of 0.270 with a Ni large filter (to minimize β radiation) for the diffracted beam, respectively. The angle of incidence was selected for each sample, function of oxide layer, and varied between 2° and 5°.

High Score Plus software and Data Base ICDD MP+ were used for identification the iron oxides on the samples and to estimate the amount of each compound in the crud.

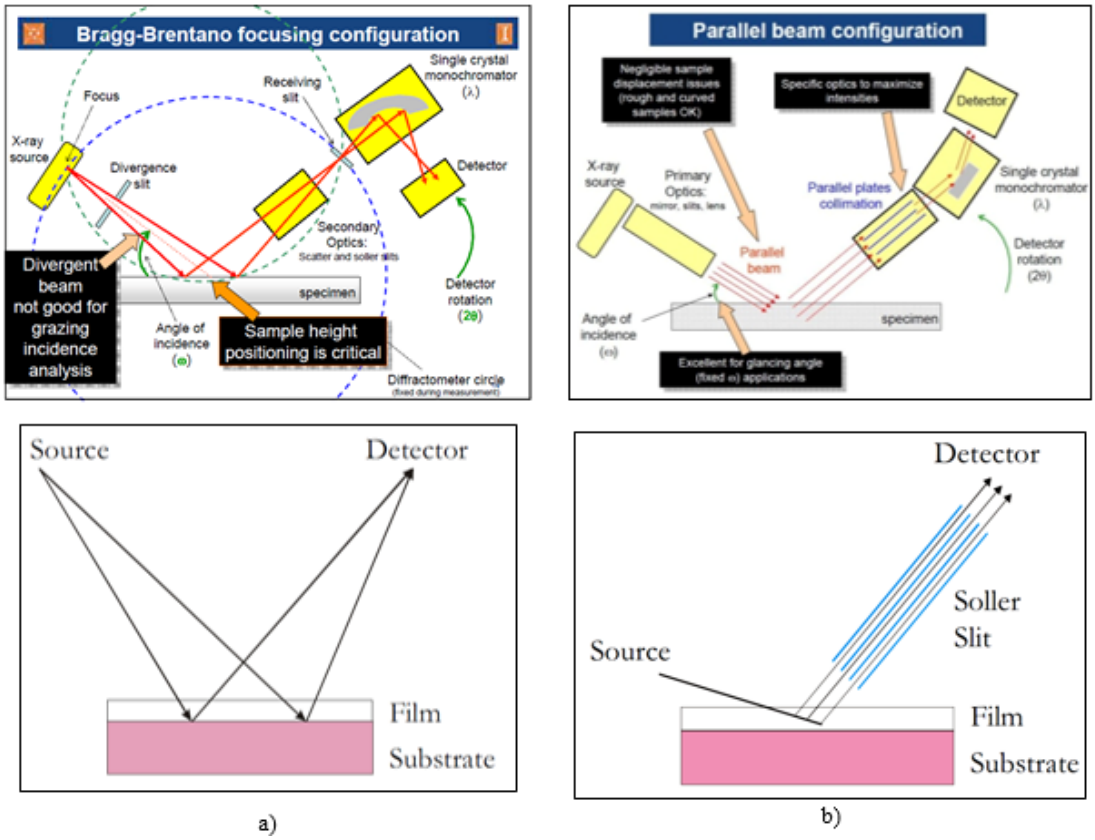


Fig.3. The difference between Bragg-Brentano focusing configuration (a) and parallel beam configuration used in the GIXRD geometry (b) [3]

X-ray diffraction analysis of the corrosion products developed on the carbon steel pipe

In the brown zone (zone 1) from Fig. 2a), the identified corrosion products were as follows: Fe_2O_3 - 63%, Fe_3O_4 - 3%, FeO(OH) - 18%, $FeO_{0.990}$ S - 4% and FeS - 14%.

No.	Visible	Ref. Code	Compound Name	Chemical Formula	Display Color	Crystal System	SemiQuant [%]
1	☑	00-039-1346	Iron Oxide	Fe2 O3	Red	Cubic	63
2	☑	03-065-3107	Iron Oxide	Fe3 O4	Lime	Cubic	3
3	☑	01-079-5975	Iron Sulfide	Fe0.990 S	Blue	Hexagonal	4
4	☑	01-078-8774	Iron Oxide Hydro..	Fe O (O H)	Maroon	Orthorhombic	18
5	☑	01-071-4468	Iron Sulfide	Fe S	Fuchsia	Hexagonal	6
6	☑	04-008-7840	Iron Sulfide	Fe S	Yellow	Orthorhombic	8

Fig.4. Chemical composition of the brown zone in Fig. 2 of heterotrofe aerobe and iron-oxidizing bacteria

In Fig. 5 are presented the corrosion products identified in the black zone (zone 2) from Fig. 2a), namely: Fe_2O_3 - 43%, FeS - 28%, FeO(OH) - 20%, and Fe_3O_4 - 10%.

No.	Visible	Ref. Code	Compound Name	Chemical Formula	Displa..	Crystal System	SemiQuant [%]
1	☑	04-014-8087	Iron Sulfide	Fe S		Hexagonal	18
2	☑	04-003-4471	Iron Sulfide	Fe0.985 S		Hexagonal	10
3	☑	04-015-8201	Iron Oxide Hydro..	Fe O (O H)		Orthorhombic	20
4	☑	01-076-8881	Iron Oxide	Fe2 O3		Orthorhombic	43
5	☑	01-080-6404	Iron Oxide	Fe3 O4		Cubic	10

Fig.5. Chemical composition of black zone in Fig.2 as a result of sulphate-reducing bacteria

The important information provided by X-ray diffraction analysis is to highlight the deposition of corrosion products specific to both aerobe (iron –oxidizing bacteria) and anaerobe bacteria (sulphate-reducing bacteria). This demonstrates that in normal conditions, specific biofilms are relatively rare, most of them being composed of a mixture of microorganisms, as is mentioned in the literature data, too [1].

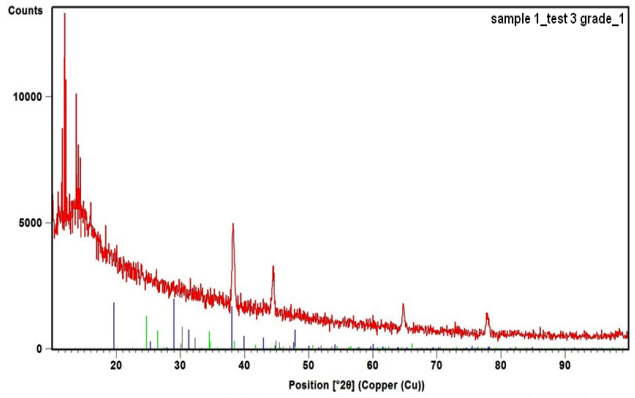
Due the susceptibility to the MIC of the carbon steel pipes, the problem of replacing carbon steel with other types of materials was raised. Plastic commercial materials such as polyvinyl chloride, polypropylene, polyethylene, were tested in microbial media (iron –oxidizing bacteria and sulphate-reducing bacteria).

X-ray diffraction analysis of the compounds identified on plastic materials

After 600 days of immersion in microbiological cultures, it was found that consistent deposits were formed only on certain samples (PVC in iron oxidizing bacteria and PE in sulfate reducing bacteria).

The formed deposits were removed from the surface of the plastic samples and analyzed by X-ray diffraction to identify the compounds.

Fig. 6 shows the spectrum and semi-quantitative analysis of the compounds from the deposits developed on the polyvinyl chloride (PVC) samples exposed in the environment with iron-oxidizing bacteria. Compounds from the culture medium specific to this type of bacteria such as calcium chloride, magnesium sulfate, sodium nitrate were especially highlighted.

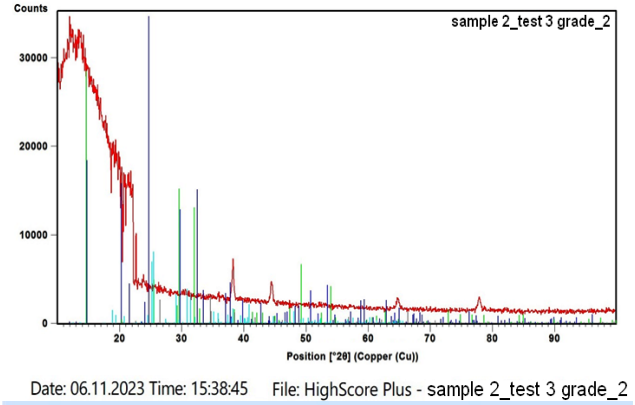


No.	Visi..	Ref. Code	Compoun...	Chemical F...	Sc..	Scale...	RIR	Dis...	Qual...	Su...	Crystal ...	Semi...	Databa..
1	☑	04-012-6045	Calcium C...	Ca Cl2	9	0.149	2.080		I;NAT	Ino...	Tetrago...	46	PLU2023
2	☑	04-015-4049	Magnesiu...	Mg (S O4)	7	0.097	2.010		I;ALT	For...	Orthor...	31	PLU2023
3	☑	04-009-2322	Sodium Ni...	Na (N O2)	11	0.065	1.770		S;NA...	Cer...	Orthor...	23	PLU2023

Fig. 6. X-ray diffraction results of the biofilm in the deposits formed on the polyvinyl chloride (PVC) samples by the iron –oxidizing bacteria

The spectrum and semi-quantitative analysis of the compounds formed on PE samples exposed in the environment with sulfate-reducing bacteria are presented in Fig. 7.

The results of this analysis highlight the fact that the sulfate-reducing bacteria attached themselves to the polyethylene surface and assimilated compounds from their culture medium (KH_2PO_4; $MgSO_4$, $Fe_2(SO_4)_3$, $CaSO_4$).



No.	Visi..	Ref. Code	Compoun...	Chemical For...	Sc...	Scal...	RIR	Displa...	Q...	S...	Crystal S...	SemiQua...	Databa...
1	☑	01-073-0148	Iron Sulfate	Fe2 (S O4)3	12	1.394	1.390		E S	C...	Hexagonal	66	PLU2023
2	☑	04-013-2161	Calcium S...	Ca (S O4)	11	0.821	3.500		L I;...	C...	Hexagonal	15	PLU2023
3	☑	04-002-8227	Magnesiu...	Mg (S O4)	7	0.107	1.230		(P;...	F...	Orthorh...	6	PLU2023
4	☑	04-020-5568	Hydrogen...	H2 K (P O4)	10	0.232	1.130		A S;...	In...	Monoclinic	13	PLU2023

Fig. 7. X-ray diffraction results of the biofilm in the deposits formed on the polyclorure (PE) samples by the sulfate-reducing bacteria

Visual and Metallographic analysis of the deposits on the plastic materials

As previously mentioned the plastic commercial materials such as polyvinyl chloride, polypropylene, polyethylene were tested in microbial media (iron –oxidizing bacteria and sulphate-reducing bacteria) and the samples were visually and metallographically analysed.

The appearance of the Polyvinyl chloride (PVC) samples after 600 days of immersion is shown in Fig. 8.

For the samples immersed in cultures of ferrobacteria and sulfate-reducing bacteria (Fig. 8b and c), the appearance of this films, unevenly distributed on the surface, is evident. In case of the samples from cultures of aerobic heterotrophic bacteria, no point deposits are observed (Fig. 8d).

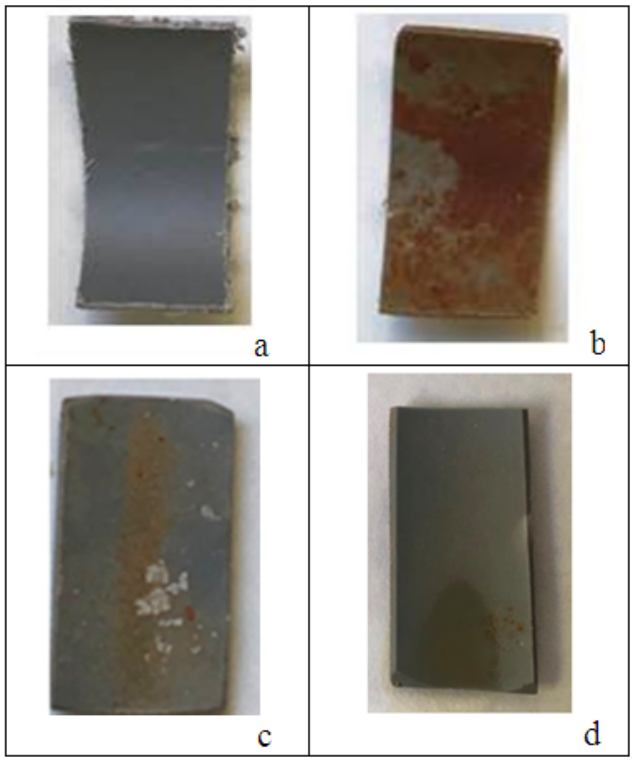


Fig. 8. Appearance of PVC samples immersed into different types of cultures: a) blank sample; b) iron-oxidazing bacteria; c) sulphate-reducing bacteria (SRB); d) aerobic heterotrophic bacteria

The microscopic appearance of the deposits (X200) developed on Polypropylene (PP) samples is shown in Fig. 9, highlighting unevenly deposited products in case of immersion into iron-oxidazing bacteria and sulphate-reducing bacteria (SRB).

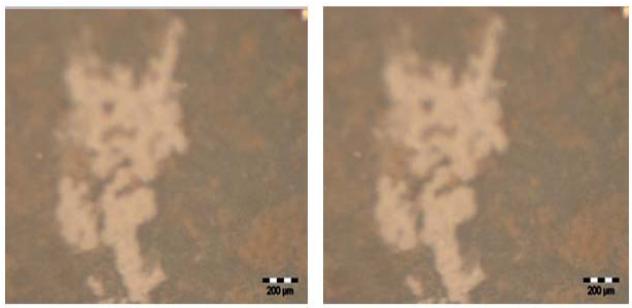


Fig. 9. The microscopic appearance of deposits on PVC samples in: a) iron-oxidazing bacteria; b) sulphate-reducing bacteria (SRB)

The appearance of the Polypropylene (PP) samples after 600 days of immersion of samples is shown in Fig. 10.

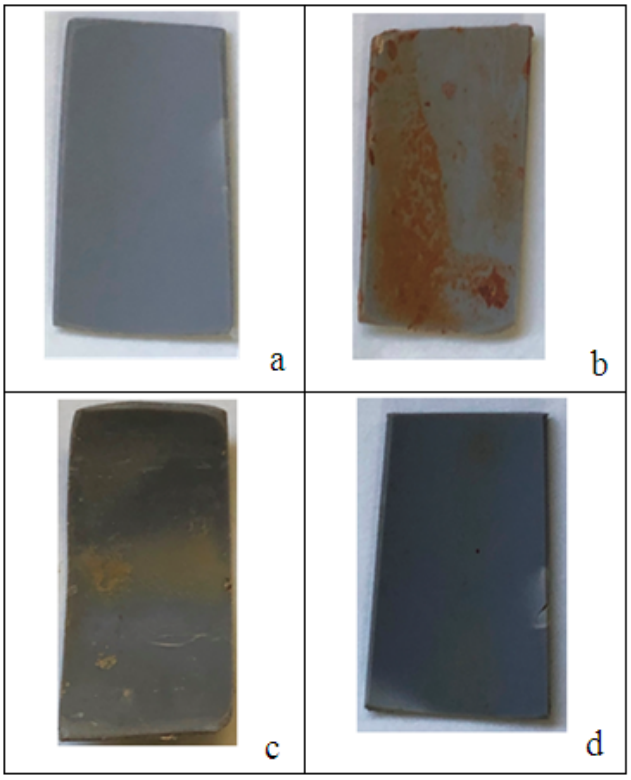


Fig. 10. Appearance of PP samples immersed into different types of cultures: a) blank sample; b) iron-oxidazing bacteria; c) sulphate-reducing bacteria (SRB); d) aerobic heterotrophic bacteria

The microscopic appearance of the deposits (X200) on the Polypropylene (PP) is shown in Fig. 11, highlighting unevenly deposited products.

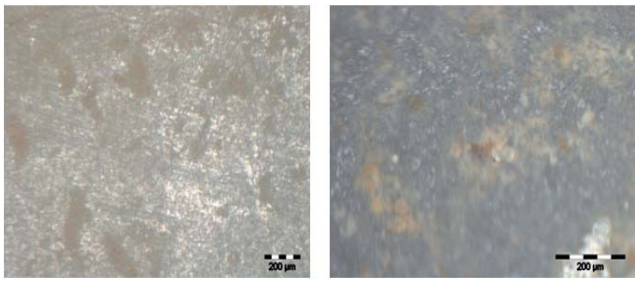


Fig. 11. Microscopic appearance of deposits on PP samples in: a) iron-oxidazing bacteria; b) sulphate-reducing bacteria (SRB)

In Fig. 12 total coverage of the Polyethylene (PE) samples exposed in sulphate-reducing bacteria SRB (Fig. 12 c), while in the environment of ferrobacteria there are small areas with deposits, and in the case of exposure to heterotrophic bacteria there are no deposits (Fig. 12 d).

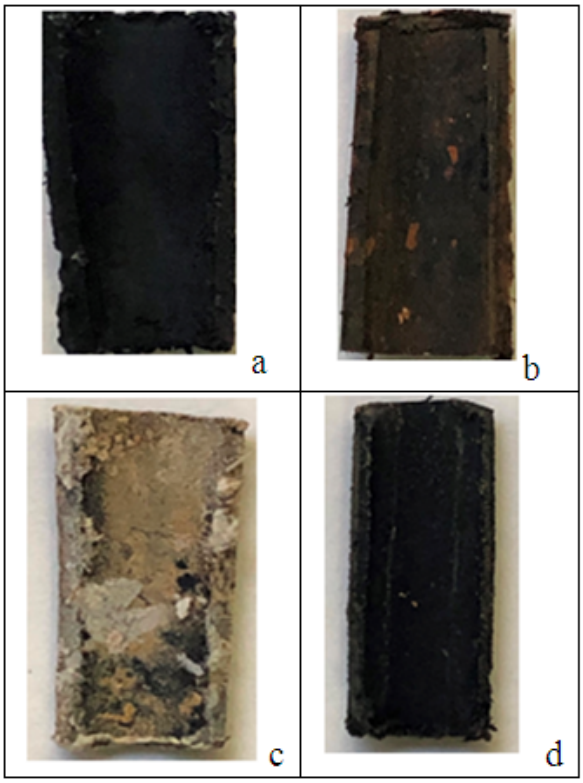


Fig. 12. Appearance of PE samples immersed into different types of cultures: a) blank sample; b) iron-oxidazing bacteria; c) sulphate-reducing bacteria (SRB); d) aerobic heterotrophic bacteria

The microscopic aspect of the PE sample in sulphate-reducing bacteria SRB (X200) is shown in Fig. 13 highlighting also unevenly deposited products.

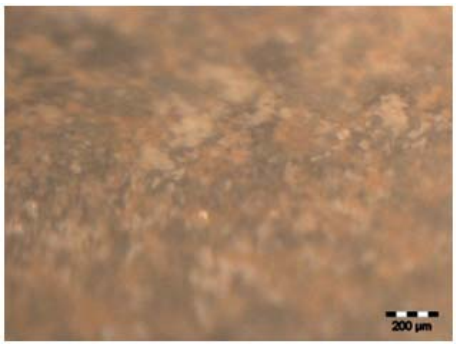


Fig. 13. Microscopic appearance of PE samples in sulphate-reducing bacteria SRB (x200)

Conclusions

X-Ray analyze was used as a nondestructive method for characterization of deposits developed in microbiological media on some plastic materials (polyvinil chloride -PVC, polypropylene -PP, polyethylene -PE).

Because these deposits were very thin, the Grazing Incidence X-ray Diffraction method was used.

After a testing period of 600 days, the following aspects were noted:

(C1) On the samples exposed to cultures of heterotrophic bacteria, some deposits ″in points″ were observed for the PVC samples, while on the surface of PP samples a slight coloration appeared. EP samples remained unchanged.

(C2) In presence of iron-oxidizing bacteria, appearance of thin films unevenly distributed on the surface (for PVC and PP samples) was highlighted, while in case of PE samples, several areas with deposits appear on a small surface.

XRD of some areas with more consistent deposits highlighted compounds from the culture medium of this type of bacteria such as calcium chloride, magnesium sulfate, sodium nitrate.

They were captured by the extracellular polysaccharide compounds resulting from the metabolism of iron-oxidizing bacteria during the exposure period in the microbiological environment.

(C3) In the cultures of sulfate-reducing bacteria, uneven deposits were observed in certain areas of the material (in case of PVC and PP samples), while the PE sample was completely covered by biofilm.

XRD analyses of this sample showed the presence of sulfate-reducing bacteria attached to the PE sample surface and assimilated compounds from the culture medium (KH_2PO_4; $CaSO_4$, $MgSO_4$). At the same time, the sulfates from the environment ($FeSO_4$x7H2O; Na_2S x 9H2O) were reduced to sulfides.

(C4) In all testing environments, the deposits developed are not adherent, and they can be removed by washing under a stream of water, after easy wiping, the surface of the samples remaining unaffected.

(C5) Demonstrating resistance to microbiologically influenced corrosion, the plastic materials tested can be used to replace areas in the carbon steel areas pipeline, susceptible to this type of corrosion.

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