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FACULTY OF MATERIALS SCIENCE AND ENGINEERING
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THESIS

SUMMARY

EXPERTISE IN THE FIELD OF ECOSOCIOTECHNOLOGICAL DEGRADATION OF METALLIC MATERIALS

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CONTENT

EXPERTISE IN THE FIELD OF ECOSOCIOTECHNOLOGICAL DEGRADATION OF METALLIC MATERIALS

ABSTRACT

In his doctoral thesis, the author defines and researches the degradation of materials as an integrated process in the interactions between different events or phenomena occurring within or between the Natural Ecological systems, the Social System and the Technological System, taking into account the following premises:

- the correlation between the integration of material degradation and the quality parameters of the environment, knowing that the Natural Ecological System is the most important system;
- degradation of materials causes losses in all phases of the life cycle;
- the losses that affect the performance of the three systems are represented by the secondary materials (waste and residues).

The mechanisms of the main causes that produce damage or destruction for 13 particular cases existing in the industrial environment with an effect on the durability of the materials have been identified, being identified the following types of degradations produced by corrosion:

- 3 cases of degradation caused by corrosion in points;
- 3 cases of degradation caused by corrosion under stress / cracking;
- 1 case of degradation caused by galvanic corrosion;
- 2 cases of degradation caused by deposits formed by corrosion products;
- 1 case of degradation produced by excessive hardening by plastic deformation;
- 1 case of degradation caused by atmospheric corrosion and mechanical fatigue;
- 2 cases of degradation caused by oxidative corrosion.

Chapter I: GENERAL CONSIDERATIONS ON THE INTEGRATION OF THE MATERIALS DEGRADATION PROCESS INTO THE GLOBAL ECOSOCIOTECHNOLOGICAL EVENT SCENE

1.1. Introduction

In order to address the integration of the materials degradation process in the megasystem represented by the global sphere of eco-sociotechnological events, it is necessary to analyse a series of concepts, terms and definitions that will allow us to understand how the megasystem in which metallic materials go through the successive stages of their life cycle, from natural resources to final degradation, is structured.

The transition from the Information Society (IS) to the Knowledge Society (KS) has imposed, at the level of the megasystem (MS) made up of the natural-ecological system (NES), the social system (SES), the economic system (ES) and the technological system (TS), the need for sustainable development (SDD) determined by intra- and inter-system interconnections and interactions, as shown in Figure 1.1.

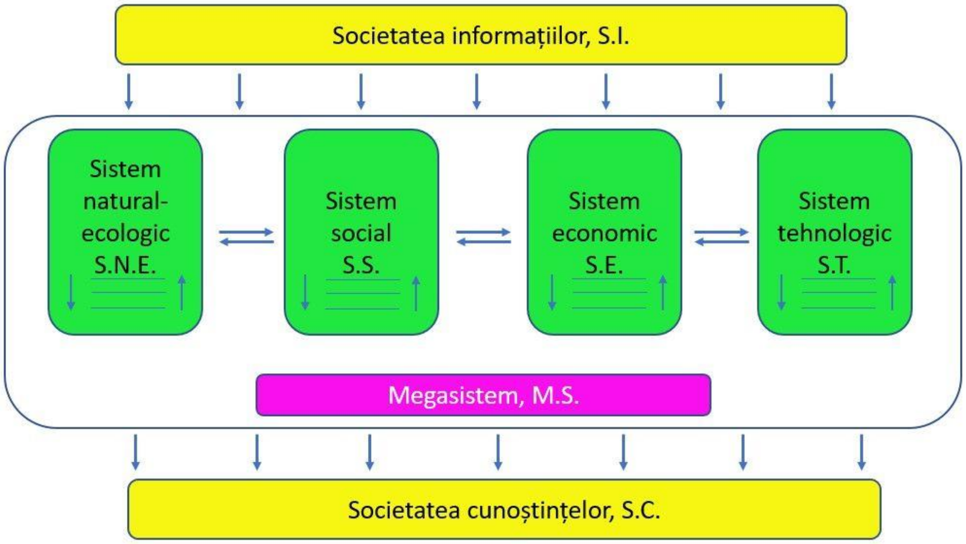
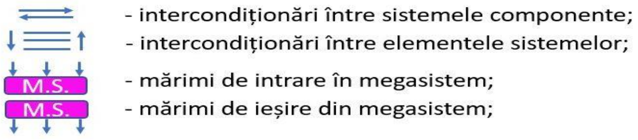


Figure 1. 1 The megasystem and its component systems



In turn, resulting from the synergy of two models of development (sustainable - S and durable - D), sustainable development requires two requirements to be met:

- ensuring sustainability, when it becomes necessary to control the consumption of natural resources (N.R.) in the upstream area of the technological system. It can be mentioned that for the technological system extensive consumption (Cet) is specific, due to technological rigours.

These should not be confused with excessive consumption (Cec) due to subjective reasons.

- For sustainability, pollution (P) due to activities in the two systems: the technological system and the social system, is of major importance.

1.2. Metal material and its life cycle

Material is the substance which, through a technological process, generates goods of social utility. The product is the object (body) which, through a technological process, acquires social utility. For example, the case of a steelworks where steel is the material and sheet is the product.

The life cycle (l.c.) of the material means the totality of the stages (phases) that the material goes through during its processing in the three systems [27, 28].

The main phases specific to the life cycle of a metallic material are shown in Fig. 1.3.

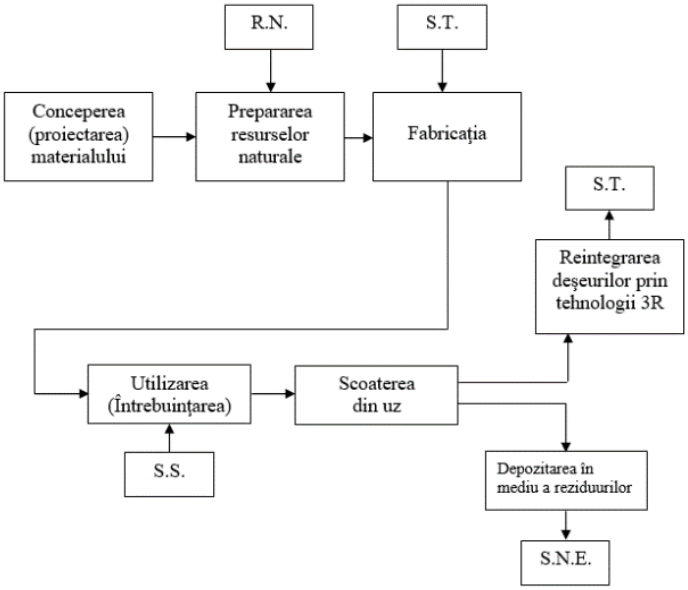


Figure 1. 3. Life cycle stages/phases of a metallic material

Conclusions

Disuse due to the action of various destructive agents mainly concerns corrosion of materials. However, it is clear that the actual situations are diversified and need to be systematised into three areas:

- material degradation, which refers to the substance (matter) used in technological processes to obtain social utility;

- product degradation, which refers to the object delivered to the beneficiary for use and which is finally taken out of use due to destruction;

- degradation of equipment (plant, aggregate) which is a set of products (specified as parts, devices, mechanisms, connecting elements) and which perform various social functions.

Chapter II: THE CURRENT STATE OF KNOWLEDGE OF MATERIAL DEGRADATION

2.1. Corrosion in the primary phases of materials manufacture

In almost all the literature, the impairment of the functional integrability of the material (alteration of the quality characteristics of the product throughout the life cycle) is not investigated as a complex inter- and intra-system degradation process (S.N.E.S.S.T.), but as a corrosion process. As corrosion is an important (even the most important) case of degradation, in the following, we will mainly refer to the corrosion of metallic materials investigated in recent surveys.

The study of the current state of knowledge on degradation was carried out on the basis of methodological recommendations specific to this situation. They are briefly presented below.

Qualitative analysis - the study of phenomena in relation to their effects on the composition, structure and properties of materials.

Quantitative analysis - quantitative determinations by evaluation, measurement, quantification.

Analysis must be complemented by synthesis. This involves comparing the results obtained by analysis and specifying the links between them. Analysis and synthesis can be based on documentation, information and modelling [50-55].

2.2. Civil and industrial systems subject to corrosion processes

Corrosion of steel elements in building facade systems is one of the most important examples of material degradation processes.

Corrosion of steel requires the simultaneous existence of moisture and oxygen. Common atmospheric factors that can lead to steel corrosion (Fig. 2.3) include temperature, humidity, rain, wind speed and solar radiation [77].

Figure 2.3. Corrosion of steel anchor plate embedded in precast concrete wall [71].

2.3. Behaviour of steel railway structures exposed to corrosive atmospheric environments

The problem of corrosion damage to steel structures and technological equipment is by far the most urgent worldwide.

Steel elements are affected by atmospheric and climatic factors, transported chemical goods, mineral raw materials and fertilisers, fuel and other aggressive products. Corrosion of metal on railways leads to a decrease in the load-bearing capacity of structures, causes failure of electrical equipment, water, heat and braking system, contamination of transported food products, and leads to failure and accidents of technological equipment, environmental pollution and ultimately huge economic losses [113, 114, 115].

The most serious atmospheric corrosion of railway structures is present on track elements, catenary system and bridge structures. The most common examples of corrosion damage to such structures are shown in Fig. 2.5.

Metallurgical and structural factors also have a significant impact on the nature of atmospheric corrosion of steel railway structures. These include in particular the composition and content of alloying parent elements, the method of processing the steel, its microstructure, the stress state, the presence (integrity) of a protective coating, cyclic loads from passing trains and other factors favouring the corrosion process (Fig. 2.6).

Figure 2. 5. Typical examples of corrosion defects in different parts of cast iron and steel railway structures exposed to the atmosphere: (a-d) supports, beams and bridge elements; (e-g) channel components; (h) catenary and (i) track elements [116].

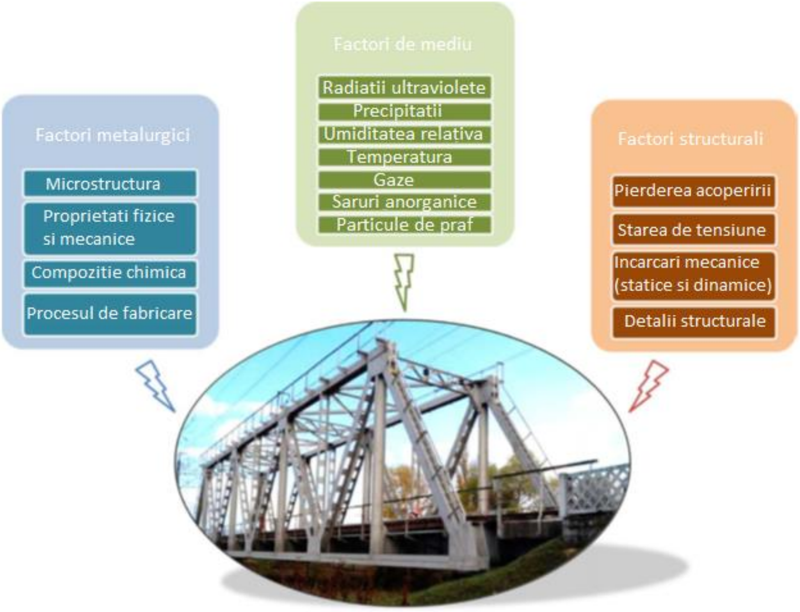


Figure 2. 6. Factors affecting corrosion of steel railway structures [116].

2.4. Economiser damage in an energy boiler

Gas turbines are used for power generation and waste heat from the gas turbine system is used to generate steam in recovery boilers.

Various causes of failure found in boiler tubes are stress corrosion cracking [126], creep at elevated temperatures [127, 128, 129], erosion corrosion [130].

The crack was detected on the tube located close to the sight glass door (Fig. 2.8). The inner side of the tube appears to have a brown layer with deposits (Fig. 2.9a) and the outer surface appears to be affected by uneven corrosion (Fig. 2.8b). Adjacent to the perforation there appear to be ridges with shallow indentations. The actual metal temperature of the defective tube was measured by attached thermocouple. The average temperature during the 7100 hours of boiler operation (excluding start-up and shut-down) before the fault occurred was found to be approx. 140°. The random elbow at the economizer bank was sectioned for visual inspection (Fig. 2.9b).

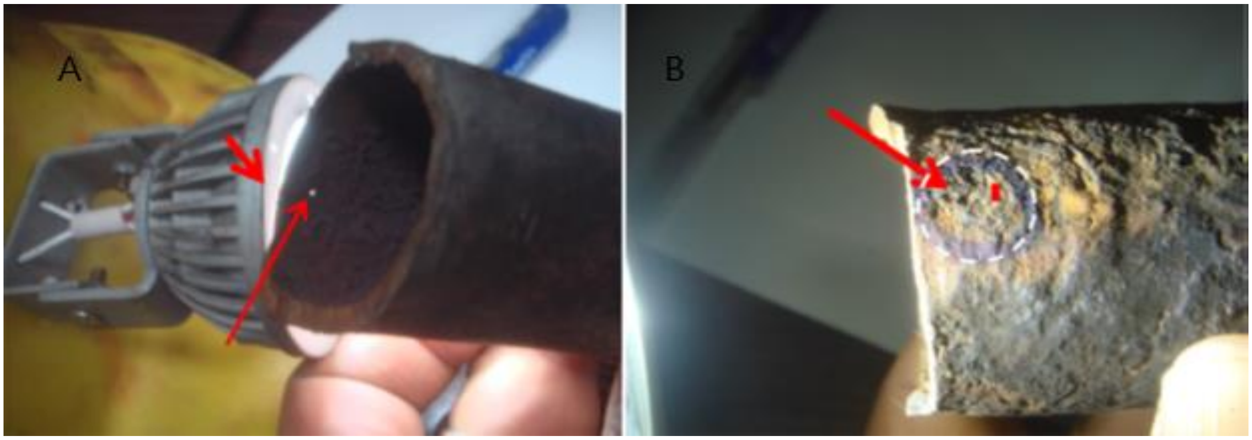


Figure 2. 8 Defective tube a) view from inside - water circuit; b) view from outside - flue gas contact, after light removal of deposits [132].

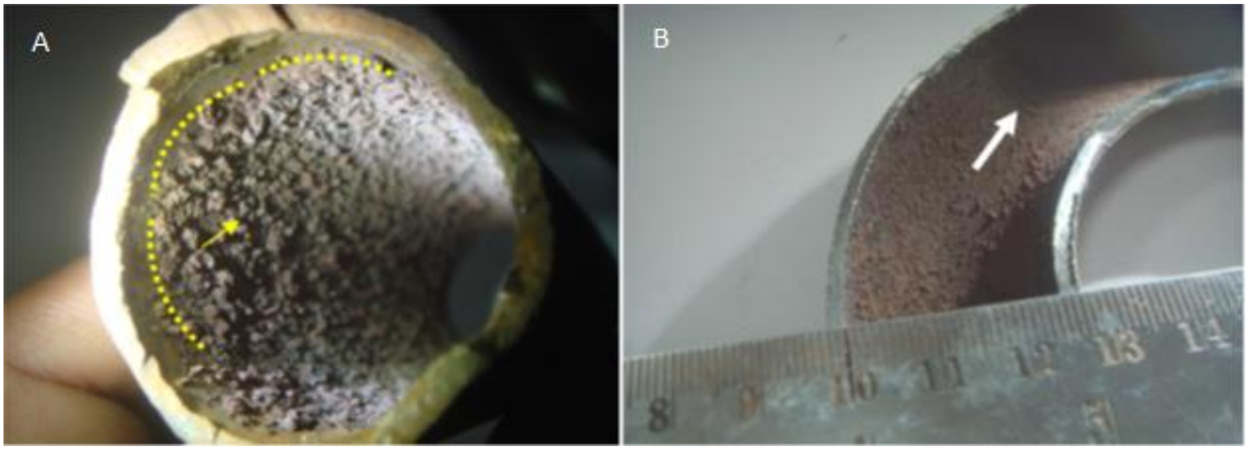


Figure 2. 9.a) Appearance of surface near crack; b) Appearance of elbow - no defect observed [132].

The presence of silica particles on the outside led to the formation of grooves, increasing the lateral corrosion rate on the grooved marks.

2.5. Degradation of construction equipment due to material quality

2.5.1. Stylet breakage from the arm placing device on a forklift truck

The styli failed during the construction of a building while the wet concrete mix was being poured high through a pipe using an arm placer. Fig. 2.16A shows the location of the failure on the arm where the stud was installed. The broken stud is shown in Fig. 2.16B.

The failed stud was collected for investigation to find the root cause of the failure. The shiny granular flat surface of the fracture (Fig. 2.17) indicates the brittle mode of fracture. The fracture was initiated from a lubrication hole (Fig. 2.17B). Visual observation (Fig. 2.17A) shows that the pin was hollow cylindrical in shape, with an inside diameter of 40 and an outside diameter of 90 mm.

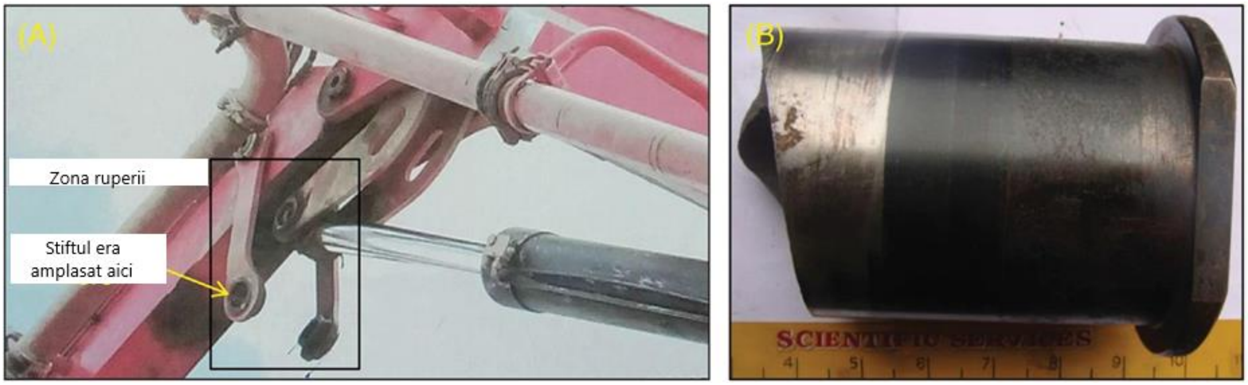


Figure 2. 16. (A) Location of the arm pin failure at the arm setter, (B) defective arm pin [137].

Figure 2.17. (A) Fracture surface of the arm pin, (B) initiation of chevron marks from the lubrication port indicating a brittle fracture, and (C) radial marks suggesting brittle fracture of the arm pin [137]

Structural analysis suggests that the pin fractured due to its low impact strength from improper heat treatment.

Conclusions

- Different types of corrosion can occur in facades depending on the environment.

- At an operating temperature below 150 °C, sulphur present in the flue gas reacts with the moisture in the heated boiler surface to form dilute sulphuric acid. This is the main cause of the failure.

- Fuel containing sulphur is a major factor in premature boiler tube damage. In addition, corrosion on the water circulation area, if properly treated, is greatly reduced.

- Corrosion negatively influences the sustainable and durable material function of metallic materials.

- Inclusions, in the vast majority of the cases analysed, negatively influence the quality of steel and are thus a very important degrading factor of metallic materials.

Chapter III: METHODOLOGY OF EXPERIMENTAL RESEARCH, APPARATUS USED, MATERIALS AND EQUIPMENT THAT WERE EXPERIMENTED

3.1. Aim and objectives of the experimental research

The purpose of the experimental research refers to:

- evaluation of current research results in the literature on material degradation;

- to identify the causes leading to premature degradation and decommissioning of industrial equipment operating at high temperature and pressure;

- Establish correlations between the operating regime of industrial equipment and its remaining safe lifetime.

The main objective of the PhD thesis is to create the premises for the foundation and development of mechanisms for the degradation of metallic materials in thermo-energetic and thermo-chemical equipment.

To this end, it is argued on scientific grounds that the degradation of materials represents:

- the result of interactions in areas of convergence between the natural-ecological system (N.E.S.), the social system (S.S.) and the technological system (T.S.);

- an event with inter-systemic implications of the eco-socio-technological type;

- a process of sustainable anti-development;

- generator of secondary materials (waste and residues);

- a determining factor in the growth of natural resource consumption.

3.2. Methodology and experimental research design

The research methodology was based on the current state of research in the field of metal degradation. The following types of degradation were analysed:

a) Corrosion degradation;

b) Degradation due to mechanical stresses during operation;

The research plan foresaw the following steps:

a) Justification of the need to address this research topic, focusing on the behaviour of materials in industrial equipment;

b) Definition of the specific objectives of the processes of expertise of metallic materials as component parts of industrial equipment

c) To establish the contributions made to the development and improvement of mechanical-metallurgical expertise.

3.3. Experimental research and equipment used

The experimental investigations are summarised in Figure 3.2 and include tests, analyses and characterisations carried out to determine the causes of material degradation of industrial equipment and their removal from industrial processes. The materials were subjected to a complex preparation programme for mechanical testing (tensile, hardness, impact strength) and then structurally characterised by optical and electron microscopy to determine their physico-mechanical and structural properties.

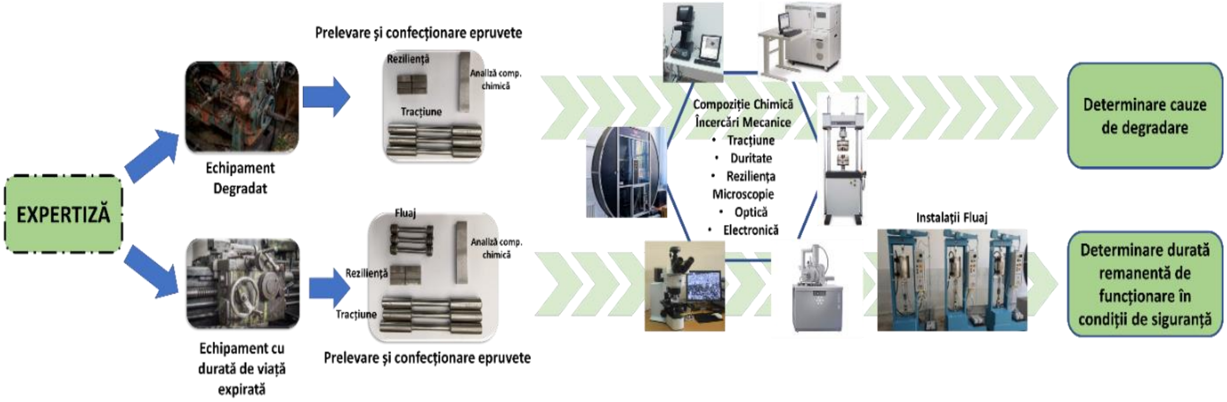


Figure 3. 2. Stages of the plan for carrying out a mechanical-metallurgical survey

To carry out the research, physico-mechanical analyses were carried out on 12 pieces of industrial equipment in order to determine the causes of their degradation and disuse, as shown in Table 3.1.

Table 3.1. Summary of the assessments carried out

Case No	Summary of degradation produced	Materials involved	Analyses carried out	Possible causes of degradation
A	- gas transmission pipelines; - shut-off valves;	- metal materials (steel and cast iron);	- microstructural analysis -	- oxidative corrosion; - technological operating conditions.
B	- radiant zone of a vertical cylindrical furnace	- alloy steel x10 CrNiNb 18.9	chemical composition analyses; - microstructural analyses	- general corrosion; - spot corrosion; - stress corrosion cracking.
C	- lower heat exchanger shell	- steel plate R 510.3b	- microscopic analysis	- stress corrosion cracking; - general corrosion.
D	- heat exchanger cracked pipe	- seamless high temperature steel pipe, SA - 106	- chemical composition analysis; - Microscopic analysis	- Exceedance of critical mechanical strength limits during operation.
E	- working fluid transport pipe in the presence of sulphur and chlorine compounds	- steel made SA - 106 A; - seamless pipe for high temperatures	- chemical composition analysis; - microstructural analyses	- general and spot corrosion; - galvanic corrosion.
F	- pipes and samples with deposits from heat exchangers	- steel made for boiler and vessel pipes	- microscopic analyses	- general corrosion; - point corrosion; - disposition of corrosion products
G	- cracking and degradation of railway rails	- OS 90A steel for railway rails	- chemical composition analyses; - macroscopic analyses	- exceeding of permissible values for contact fatigue strength; - corrosive action of natural environmental factors.
H	- heating furnace radiation coil pipe	- SA 335 steel - P9 grades	- chemical composition analyses; - macroscopic analyses; - Microscopic analysis	- Exceedance of permissible values for resistance to thermo-mechanical fatigue
I	- FVP column top cooler plates	- 316L stainless steel	- chemical analysis; - microscopic analysis	- corrosion at points; - mechanical hardening of steel plate.
J	- spring breakage for inlet and outlet valves of a compressor	- stainless steel X750	- macroscopic analysis of breakage surfaces	- exceeding of permissible values for mechanical twisting and bending strengths;
K	- corrosion of heat exchanger tubing	- P265 GH steel	- chemical composition analysis; - microstructural analysis	- stress corrosion generated by hydrogen sulphide.
L	- steam boiler screen	- carbon steel for tubes, brand OLT 45	tubes - chemical composition analysis; - microstructural analysis	- oxidative corrosion caused by prolonged maintenance at high temperatures

To carry out the tests summarised in table. 3.1 it was necessary to carry out a large number of chemical analyses, macro and microstructural analyses (tab. 3.2).

Table 3. 2 Evaluation of the number of analyses carried out in the framework of the material degassing tests

Case study analyses	Number of chemical	Number of macrostructural analyses	Number of microstructural analyses
A	-	4	4
B	1	1	4
C	-	1	-
D	1	2	1
E	4	1	4
F	-	6	-
G	6	6	-
H	2	2	4
I	1	6	-
J	-	3	-
K	1	1	1
L	4	1	-
Total	20	34	18

On the basis of the expert appraisals of the degradation of the metal materials used, it was possible to classify the main causes of damage or degradation.

3.4. Industrial materials and equipment assessed

The investigations carried out aimed at assessing the degraded material, which is made up of separate components, as well as equipment made up of components made up of different materials.

Conclusions

The materials and equipment analysed were selected from among the numerous surveys carried out at the ECOMET Centre. The following aspects were taken into account for the expertise:

- knowledge of the operating conditions provided by the beneficiaries: oil industry; power stations; transport; thermal equipment, etc.

- analysis of the influences exerted by various destructive agents and how they contributed to the development of the material degradation process;

- expertise on equipment in which degraded components were assembled by various technological solutions: welding, soldering, riveting, etc.

All the case studies presented included, as working steps:

- establishing the criteria for material selection: based on chemical composition, properties, recommendations for use, etc;

- identification of the environmental factors at work and the effects of the influences exerted;

- explaining the possible causes that contributed to the degradation of the material, or product, being tested.

Chapter IV: CONTRIBUTIONS TO MATERIALS DEGRADATION IN ECOSOCIOTECHNOLOGICAL COORDINATIONS

4.1. General aspects of material degradation

As it studies the transformations undergone by materials (one of the fundamental vectors of development) in all phases of the life cycle, starting with conception (design), through manufacturing and use and ending with the reintegration of waste through 3R technologies, on the one hand, or the polluting disposal of residues, on the other, Materials Engineering has become one of the most complex scientific branches.

Materials Degradation Engineering is the scientific branch and academic discipline that studies the eco-socio-technological role of degradation in achieving sustainability and durability of the natural ecological system interacting with the social system and the technological system.

Materials Degradation Engineering functions as an integrator in a unified and coherent whole for three fields:

- Technological degradation (pending S.T.), a field that addresses the qualitative alteration of materials in the manufacturing phase of the life cycle;

- social degradation (depending on the S.S.), an area that aims to affect the standard of living through degradation; in this case, a specific situation must also be investigated, represented by the moral degradation of materials, which in some particular areas is known as obsolescence [42].

- environmental degradation;

The importance of assessing the life cycle duration of the material Dc.v. [life cycle years, a.c.v.] becomes obligatory because it characterises the intensity of degradation processes in the phases of the life cycle, especially in the use phase.

Remaining life, (RLV), is a life cycle assessment tool to predict the subperiod of use until the end of which the product is to be declared a secondary material [27].

For the predictive graphical determination of Vr , the material is creep tested in a specialised laboratory, which determines the endurance strength Rtr/n.o (t = temperature, n.o = number of test hours determined by extrapolation for the steel used). This is usually R540r/20000.

The methodological essence is to compare the variation in time of R540r/20000 with the reference stress (constant stress), Rref, established on the basis of the actual stress, Ref. The relations are used:

$$R_{ref} = R_{ef} + \Delta R \qquad (4.6)$$

$$R_{ef} = \frac{p_c(d - g_p)}{2g_p}, \quad [\mathrm{N/mm}^2]\,, \tag{4.7}$$

Where: d - pipe diameter; gp - wall thickness; R - safety size (10-20 N/mm2).

In the graph shown in Figure 5.2, the value Vr is at the intersection of the two curves.

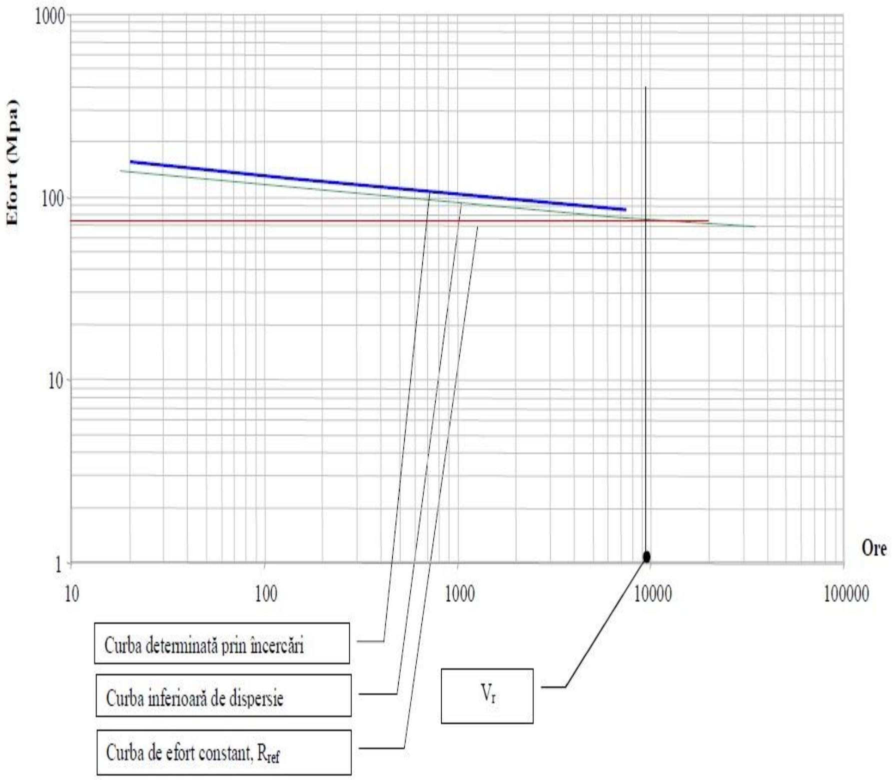


Figure 4. 2 Graphical method for determining Vr [27].

Conclusions

Materials degradation engineering is the science that studies the role of antidegradation with the aim of determining the sustainability and durability of the natural ecological system, interacting with the social system and the technological system;

Degradation is the consequence of complex interaction processes between materials and destructive factors composing destructive environments;

Life-cycle assessment makes it possible to determine, by prediction, the material's remaining/remaining life (Rv), i.e. the subperiod of use until the end of which the product is declared a secondary material, recoverable as waste;

Chapter V: CONTRIBUTIONS TO THE DEVELOPMENT OF DEGRADATION EXPERTISE PROCEDURES FOR METALS, PRODUCTS AND EQUIPMENT

5.1. Technical expertise of degradation of metallic materials. Corrosion classification criteria

The technical assessment of degradation of metallic materials refers to:

- Investigation of the causes of generation of defects leading to disuse;

- investigation of the mechanisms of material destruction in interaction with the destructive factors (agents) existing in the three systems (N.E.S, S.S, S.T);

- definition of the specific resistance to degradation for each type of process;

- transfer of the knowledge acquired to the beneficiaries, materialised in recommendations and technological standards for reducing degradation;

- the preparation on a scientific basis of an engineering guide (guideline) that can be used to identify and assess degradation processes;

Further, the experimental methodology used to carry out the expert assessments is systematised according to causes, mechanisms, effects and consequences.

According to the life cycle stage of the materials/products in which corrosion occurs, the following types of corrosion can be identified (Fig. 5.1):

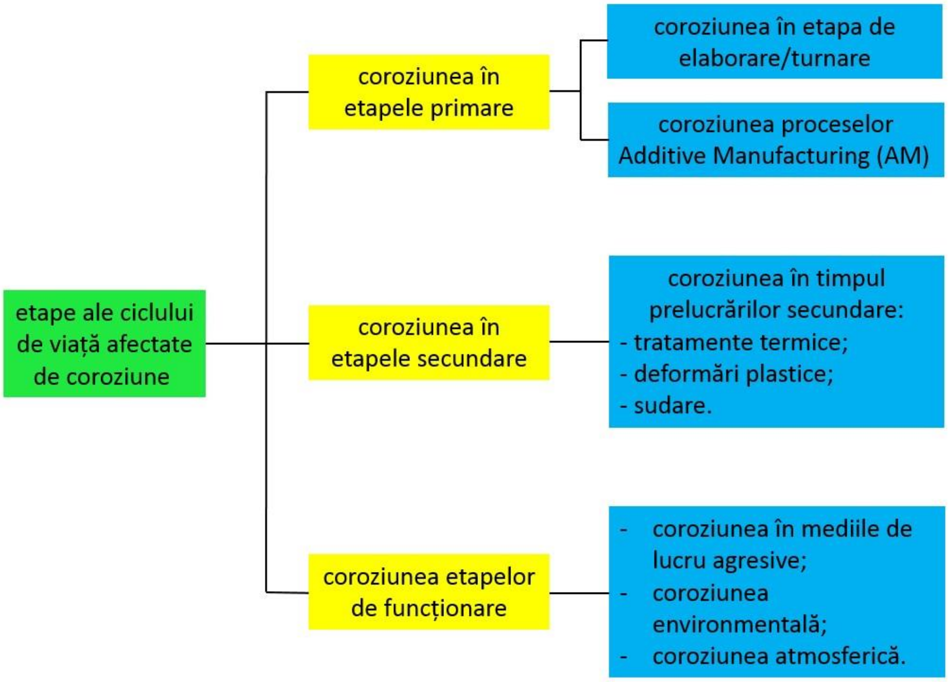


Figure 5. 1 Life cycle stages when corrosion of materials/products can occur

5.2. Operational assessment of material degradation caused by corrosion phenomena

Operational expertise on the degradation processes of metallic materials refers to the way in which the specific steps are carried out to identify the causes that have generated and developed the various forms of corrosion. Analysis of the numerous cases of expertise reveals the complexity of corrosion processes, which is often the result of the simultaneous action of multiple factors that will determine specific forms of manifestation.

5.2.1. Material degradation due to segregation corrosion - case F

Segregation (agglomeration) of elements or compounds in certain portions of the corroded zone (e.g. near or within the intercrystalline crack) generates chemical and structural non-uniformities that accelerate the corrosive effect of the destructive agent. This type of corrosion has been called segregation/aggregation corrosion.

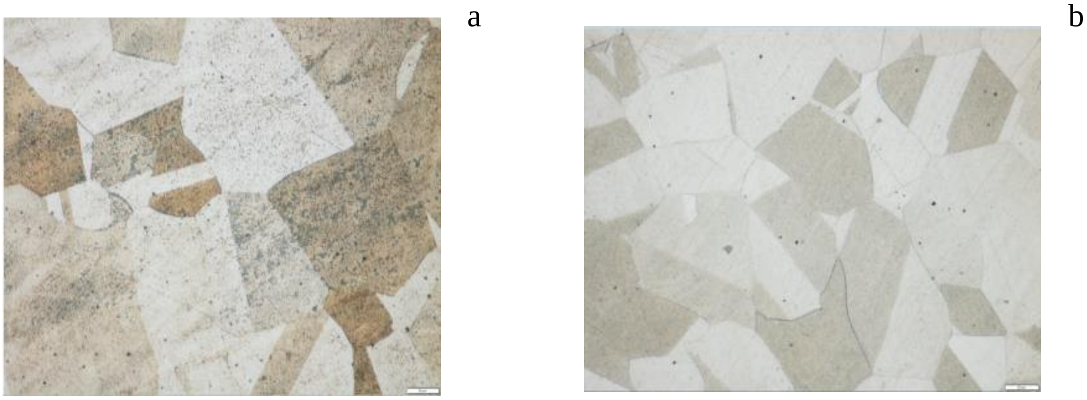
Experiments illustrating the real possibility of such a phenomenon occurring are represented by the case F of heat exchangers.

The chemical compositions of the metallic materials of the four samples, taken from the pipe wall according to SR EN 10216-5, were analysed. The analyses were performed on the LECO optical emission spectrometer, model GDS 500 A, at the UPB-ECOMET laboratories.

Analyses performed on the pipe samples do not confirm that the material meets the required recommendation for chromium content. The values determined on the samples were 15.8 ÷ 16.1 % Cr, compared to the minimum 17 % Cr - prescribed value.

Microstructural analysis.

Metallographic analyses were carried out at UPB - ECOMET, on the Olympus metallographic optical microscope, model BX51M. In Fig. 5.4 show the microstructures of the analysed *samples.*



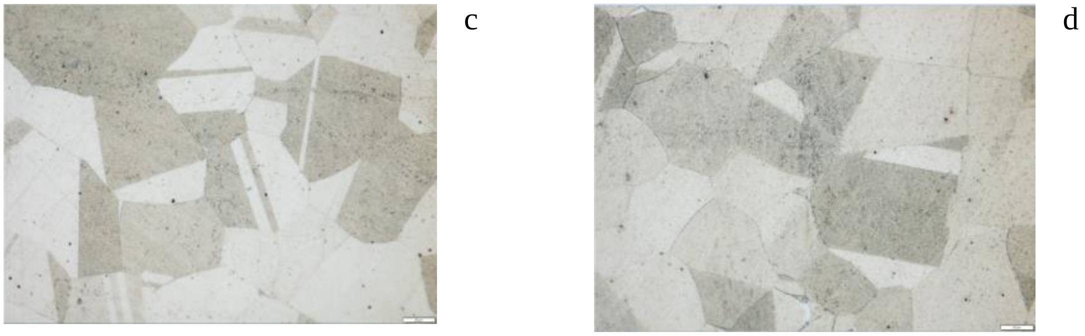


Figure 5. 4 Microstructures of samples from the 120 S1H heat exchanger tubes. (chemical attack with Marble reagent; magnification ×500) a) shingle space 2; b) shingle space 4; c) shingle space 7; d) shingle space 9

The microstructure of the pipe material consists of polyhedral austenite crystals. At magnification ×500, plastic deformation macules are observed in the austenite grains. According to SR EN 10216-5, the pipes are delivered in heat-treated condition by annealing at 10500C, followed by rapid cooling in water or air. The appearance of the microstructure confirms that the pipes have been delivered in the hot finished condition as stated in the supplier's quality certificate.

5.2.2. Material degradation due to corrosion caused by deposition of adherent substances - cases F and L

Macroscopic analysis

The adherent layers deposited on the pipe walls had a compact shape, fig. 5.5...fig. 5.8. The marking of the samples was done according to the positions of the spaces between the shims and the numbering was done starting from the entry connection into the space of the technological product.

Figure 5. 5 Deposition of adherent substances on the pipe bundle of exchanger 120 S1H - general appearance

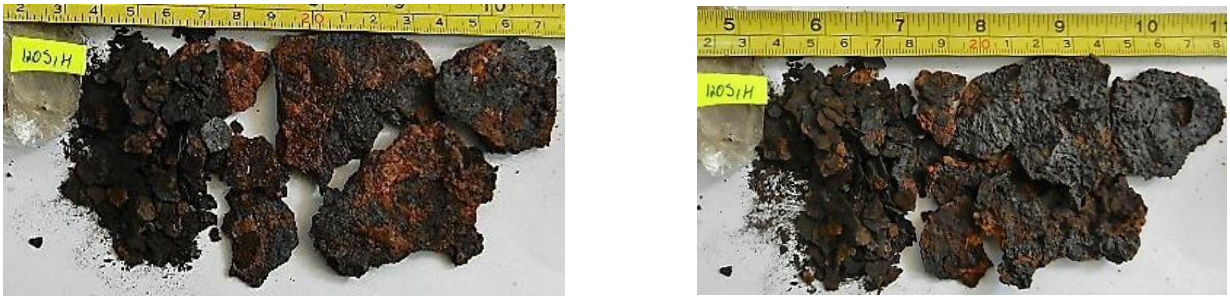


Figure 5. 6. Deposits in the zone of the shim 6. a) face 1 - front; b) face 2 - rear

Figure 5.7 Deposits in the shear zone 7.a) face 1 - front; b) face 2 - rear

Figure 5. 8 Depositions in the chicanery area 8

Chemical analysis of deposits

The deposit samples were prepared separately by homogenization and compaction. Chemical analysis was performed on the BRUKER X-ray fluorescence spectrometer - model S8 Tiger. The values obtained are shown in the table. 5.2.

Table 5. 2 Chemical elements present in the deposits on the heat exchanger tube bundle

Element	**Z**	**Concentration/Analysis method**	**Element**	**Z**	**Concentration/Analysis method**
Fe	26	54,72% XRF 1	Se	34	0,02% XRF 1
S	16	24,97% XRF 1	Ni	28	0,01% XRF 1
Cl	17	0,25% XRF 1	Nb	41	0,01% XRF 1

Mn	25	0,17% XRF 1	Cr	24	0,01% XRF 1
Si	14	0,13% XRF 1	Br	35	0,01% XRF 1
Ca	20	0,04% XRF 1	Cu	29	97 PPM XRF 1

The dark-coloured crusts represent iron oxide particles (concentration approx. 55% Fe) fallen from the mantle wall. The corrosion products have high concentrations of sulphur (ca. 25% S) and chlorine (ca. 0.25% Cl).

In case F, the segregation degradation of the steels involved in the construction of the heat exchanger pipes was manifested by corrosion produced by zonal accumulations of adherent substances of organic nature.

5.2.3. Degradation of materials by the formation of layered deposits, case C case D

Layered deposits represent the spatial arrangement on the surface of the base material of the products resulting from destructive corrosion processes.

Deposits result from interactions between the base material and H, S, Cl-based compounds present in the process fluids.

Case C refers to deposits identified on the surfaces of a heat exchanger in a hydrofinishing plant (Fig. 5.9). The process fluid contains sulphur compounds.

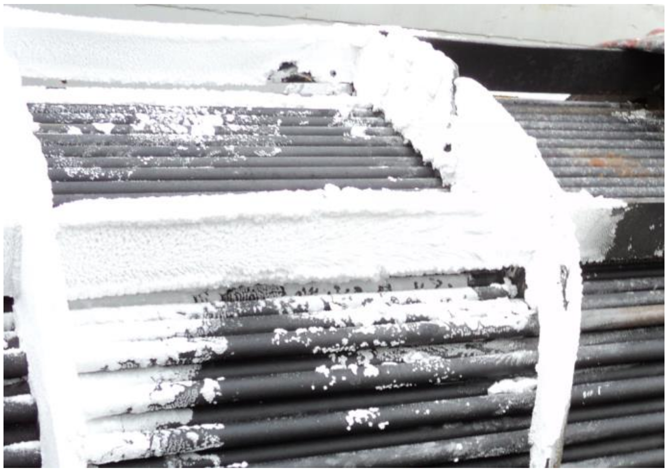


Figure 5. 9 Macroscopic appearance of deposits formed on heat exchanger elements.

Macroscopic analysis

The macroscopic analyses were carried out after cleaning of the inner surfaces of the shell and shell casing, as well as the thermally influenced areas of the welded joints. An aggressive corrosion process was found, fig. 5.10.

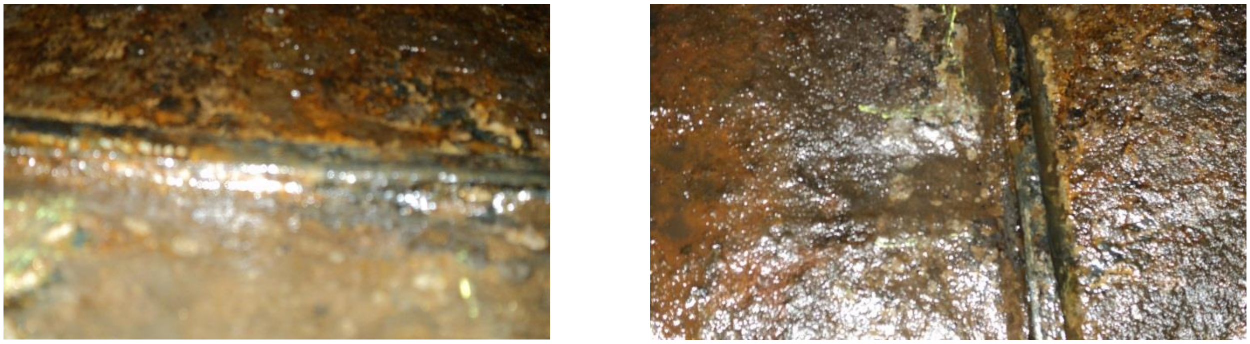


Figure 5. 10 Macroscopic aspects of the inner surface of the central shell of heat exchanger 120 S1D after removal of the light-coloured deposit

Macroscopic analysis of the investigated surfaces revealed the presence of an aggressive corrosion process.

Microscopic analysis

The optical microscopic analysis carried out on surfaces not treated with chemical reagents is shown in Fig. 5.11.

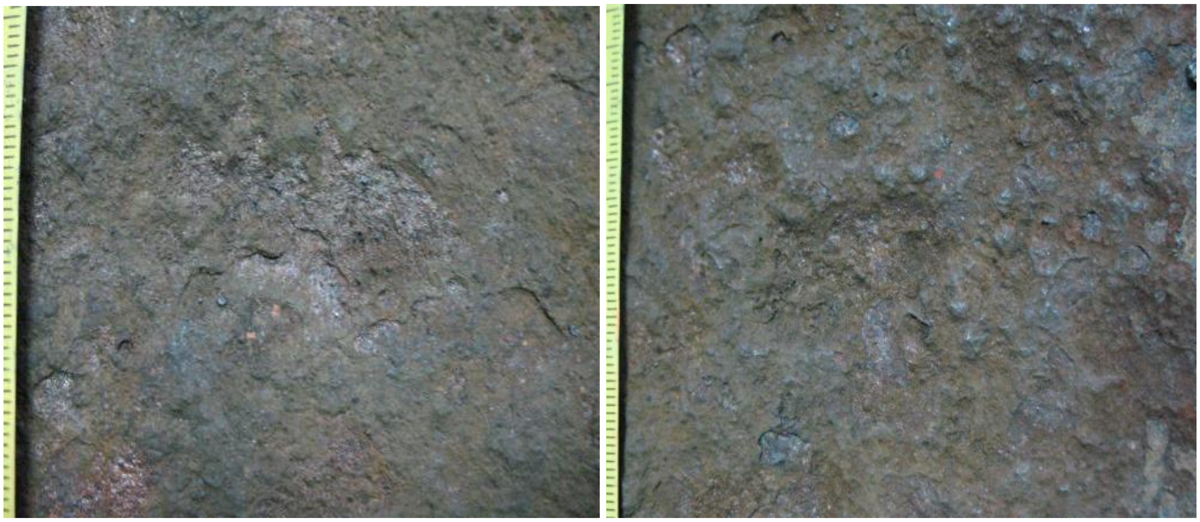


Figure 5. 11 Details of the inner surface of the heat exchanger shell wall 120 S1D

The images shown confirm the existence of corrosion process due to deposits that are totally or partially detached from the metal shell wall and are carried away by the technological working fluid.

Investigations have shown that the layer detached from the inner wall of the shell did not play a self-passivating role, but favoured the cracking of the metal substrate (fig. 5.12).

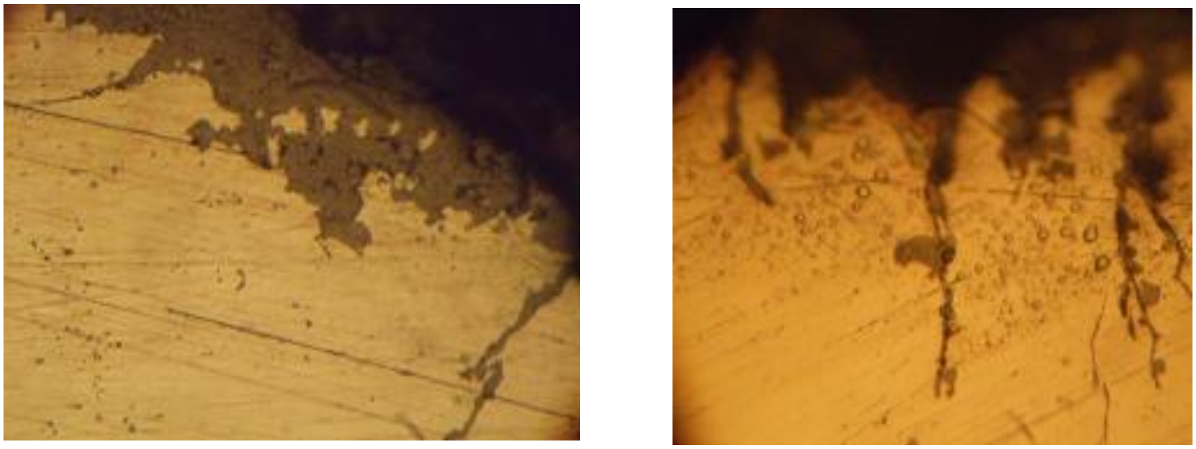


Figure 5. 12 Cracking of the metal material under the layer with sulphur and chlorine-based salt deposits

In case D, reference was made to the analysis of the degradation of metal components of a heat exchanger/heater in an oil plant where the temperature and fluid pressure in the injection zone created conditions for the condensation of chemical compounds based on sulphur, nitrogen and chlorine deposited as salts (NH4HS and NH4Cl) from the process fluid. The deposits could form particularly dangerous crusts due to the risk of development of acidic solutions at the interface with the metal, with a strong corrosive effect.

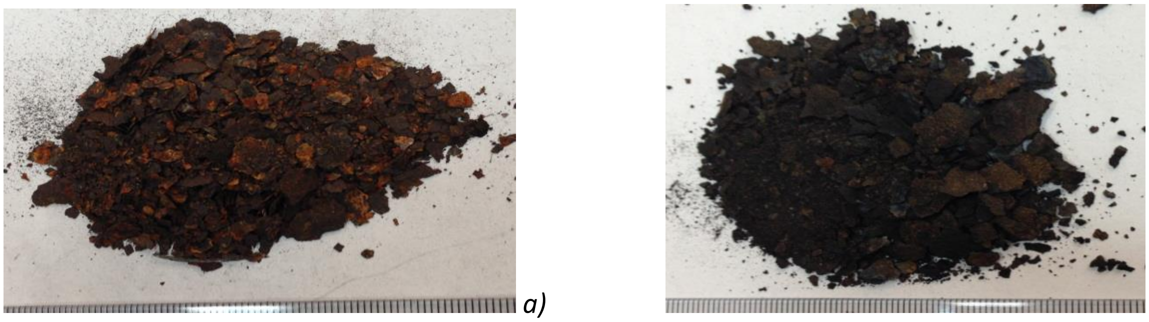
5.2.4. Barnacle corrosion degradation - case E

Barnacle corrosion is the result of the synergistic action of sulphur-based and chlorine-based chemical compounds in the presence of water. The risks of this corrosion are increased by the values of the technological working parameters: $p \geq 60$ bar and $T =$ min. 100o C. Through the corrosion reactions that occur, complex chemical compounds will be formed and deposited on the inner walls of metal pipes intended for the transport of working fluids.

Experimentation carried out on the GH-120-201-150-60 C1 pipeline of the gasoline hydrofinery (see Chapter IV) revealed barnacle corrosion.

Macroscopic analysis

The macroscopic appearance of the corrosion products extracted from inside the pipeline is shown in Fig. 5.15.



a) *b)*

Figure 5. 15 Samples of corrosion deposits extracted from inside the GH-120-201 pipeline. a) reddish coloured deposits, taken from the DN100/DN150 reduction area; b) dark coloured deposits, taken from the DN100 elbow area.

Chemical analysis

Chemical analysis by X-ray fluorescence revealed the compositions shown in the table. 5.6.

Table 5. 6 Chemical compositions of the deposits extracted from inside the GH-120-201 pipeline

Nr. crt.	Element	Conținut, [%]	
		Deposits of red colour	Deposits of dark colour
1	Fe	58,58	56,84
2	S	9,71	24,25
3	Cr	9,00	0,84
4	Mo	1,24	0,35
5	Cl	1,22	0,41
6	Si	0,82	0,26
7	Al	0,31	0,11
8	Mn	0,20	0,10
9	Ni	0,19	0,10
10	Cu	0,11	0,17
11	Ca	0,08	0,04
12	W	0,08	0,09
13	Rh	0,02	-
14	As	0,01	71 ppm
15	V	0,01	-
16	Co	-	0,07
17	Zn	80 ppm	-

It is found that all the deposits extracted have a high content of iron element which comes from the composition of steel for transport pipes. The reddish deposits contain a lot of sulphur and chromium (more than 9%), but they also have a considerable amount of chlorine (more than 1%). High contents of sulphur (over 24%) and chlorine (over 0.41%) are also found in dark deposits.

5.2.5. Degradation of materials by concentrated corrosion (pitting) - cases F and D

Case F refers to corrosion deposits on heat exchanger pipes at an oil refinery. The two surfaces, outer and inner, of the samples taken from different pipes were tested at two distinct stages: before flushing and after flushing.

Macroscopic analysis

In the case of heat exchanger 120 S1, the risk of activation of the corrosion process is determined by the possibility of the formation of deposits of residues with a high water content, during the periods when the equipment is emptied for inspections or repairs, Fig. 5.18.

Figure 5. 18 Residue deposits on the inner surfaces of heat exchanger tubes.

These conditions allowed preferential installation of concentrated corrosion at the expense of crevice corrosion for which the internal stress condition is insignificant.

Chemical analysis

Chemical analyses performed by X-ray fluorescence allowed the determination of sulphur and chlorine contents in the compound layers deposited on the pipe walls, tab. 6.8.

Table 5. 8 Chemical composition of the residues formed

	S,[%]	**Cl,[%]**
Inner wall	9,37	2,28
Outer wall	13,15	0,14

Case D refers to the corrosion spot testing which can occur in two different situations:

- by the formation of a layer of residue, adherently deposited at the edge of the pipe wall;
- by the formation of a layer of residue, deposited without adhesion to the pipe wall.

Optical microscopy on surfaces unattached with chemical reagent revealed "pinches" of material on the walls of the investigated pipes, Fig. 5.19.

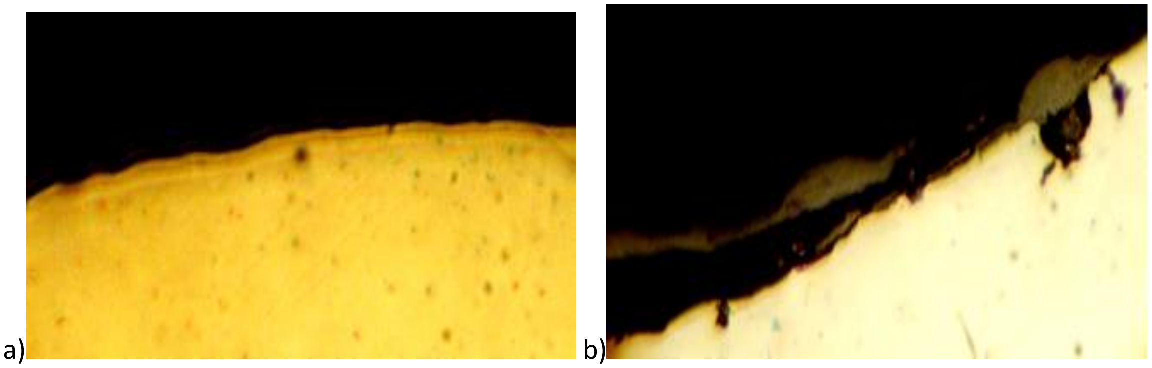


Figure 5. 19. Concentrated corrosion, or pitting corrosion, a) layer of residue with adhesion to the outer pipe wall edge; b) layer of residue without adhesion to the inner pipe wall edge

A more intense corrosive action is observed at the inner surface of the pipe where pitting is evidenced by the formation of more numerous and different sized "pinches" of material.

5.2.6. Degradation by intercrystalline cracking - cases F and K

The pipe bundles of heat exchangers 120S1 and 120H1, represent critical areas in terms of ensuring a safe lifetime. The technological environments with which these pipes are in contact are as follows:

- inside, the working medium is a mixture of petrol at approx. 15 bar - recovered from several process machines, hydrogen at 12.2 bar and condensate water - injected to entrain and/or dissolve any deposits or precipitates. The residues of this mixture contain sulphur and chlorine based compounds. In normal operation, the product temperature is 50...55 0C - inlet, 90...95 0C - outlet. As a process parameter, the flow rate of the formed mixture is of great importance;

- desulphurised gasoline from the reactor effluent is circulated externally at a temperature of 140...160 0C (inlet) and 110...120 0C (outlet) and a pressure of approx. 13 bar.

Chemical composition analyses

The chemical analyses carried out identified the composition of the reaction effluent: 1.12% H_2, 0.24% H_2S, 130 ppm NH_3 and 670 ppm water. In the water collected from the dome of vessel 120 V2, chlorine ions were identified in the proportion of 7.6...18 mg/l, sulphides 652...705 mg/l, ammonium nitrogen 260...288 mg/l and a pH index = 6.46...6.58.

Microstructural analyses carried out by optical microscopy on the cross-section of the walls of the pipes used revealed the development of a cracking phenomenon due to the corrosive action of the products formed. It is found that these products tend to adhere to the outer walls of the pipes in the form of black areas with corrosive action, or to be located inside the corrosion cracks formed. Microscopic aspects of corrosion cracks are shown in Fig. 5.20 and fig. 5.21.

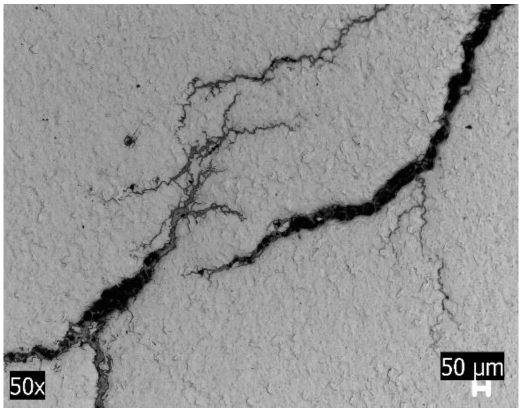


Figura 5. 1 Branched crack development

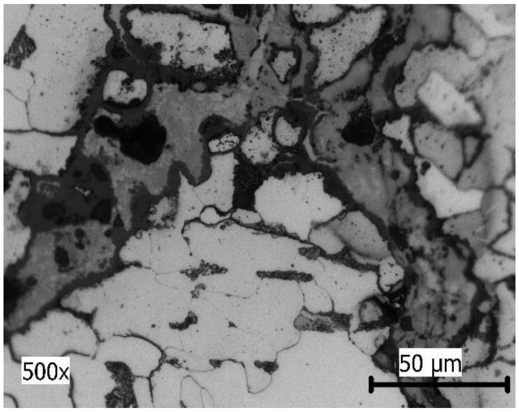


Figura 5. 2 Intercrystalline propagation of corrosion cracks formed and preferential location of corrosion products (black areas)

EDAX analysis of a micro-array in the crack zone demonstrated the homogeneity of the chemical composition of the localized corrosion products, Fig. 5.22.

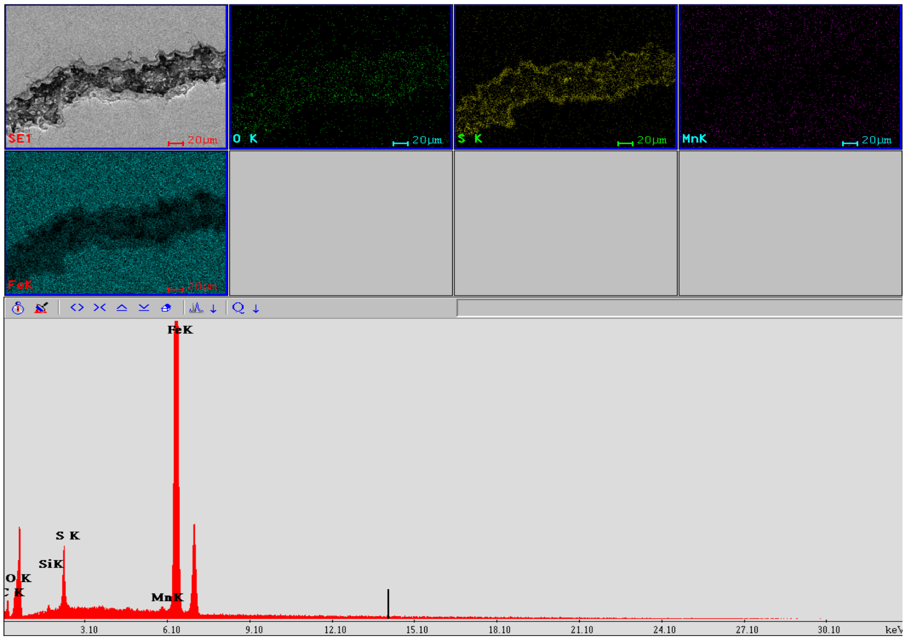


Figure 5. 22 Energy dispersive X-ray spectrum (EDAX) and homogeneous distribution of chemical elements in the microarray of the investigated crack (see Fig. 5.20)

The results of the analyses performed allow the following conclusions to be drawn:

- The formation of organic sulphur-based compounds is not exclusively endogenous. It is possible that they belong to the working environments used, being specific to the technological process. Knowing their origin will make it possible to identify the causes of their formation and establish ways of reducing the corrosion process;
- stress corrosion cracking is more intense in liquid media containing mixtures of water and small amounts of H2S;

The effect of pitting corrosion is the initiation of pitting corrosion which will trigger stress corrosion cracking, or cavern corrosion.

5.2.7. Transcrystalline cracking degradation of materials - case B

Stress corrosion cracking or corrosive cracking is that type of corrosion which can propagate intercrystalline or transcrystalline under mechanical stresses produced by the flow of the working fluid.

Case B refers to the degradation of stainless steel pipes in the construction of the heating zone of furnace 125H1 (HDV plant). The working parameters are: e = 75.2 bar and T = 450oC. The working medium is diesel and/or gas, with a high content of H2 and H2S.

Macroscopic analysis

Macroscopic examination of samples taken from the degraded pipes revealed the following:

- adherent layers of residues were deposited on the inner walls as a result of the corrosion process;

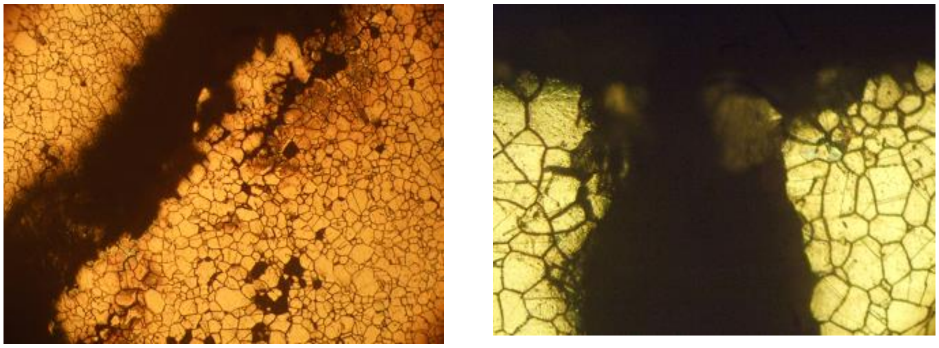
- the pipes were stressed by the action of a thermomechanical stress oriented in the axial direction;

- a corrosion crack was present on the inner wall of a pipe, oriented perpendicular to the longitudinal direction of the pipe (Fig. 5.23).

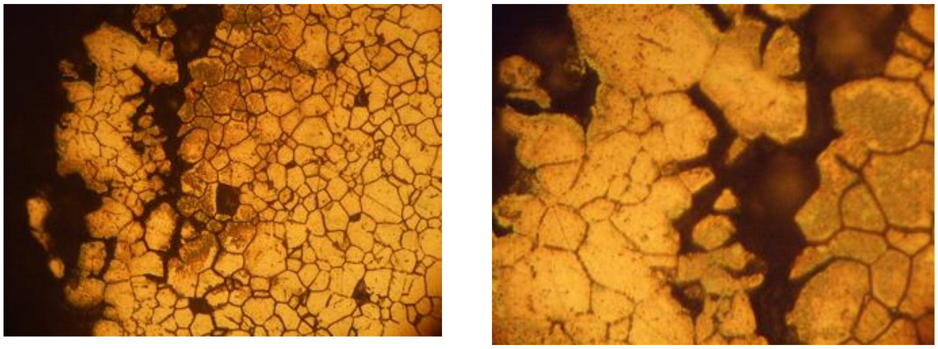
Figure 5.23 Macroscopic appearance of the surface of the cracked specimen (tube No. 51)

Optical microscopy analyses were carried out in two distinct areas of the pipe wall (Figure 5.24):

- near the inner surface of the pipe;
- near the outer surface of the pipe.



a) *b)*

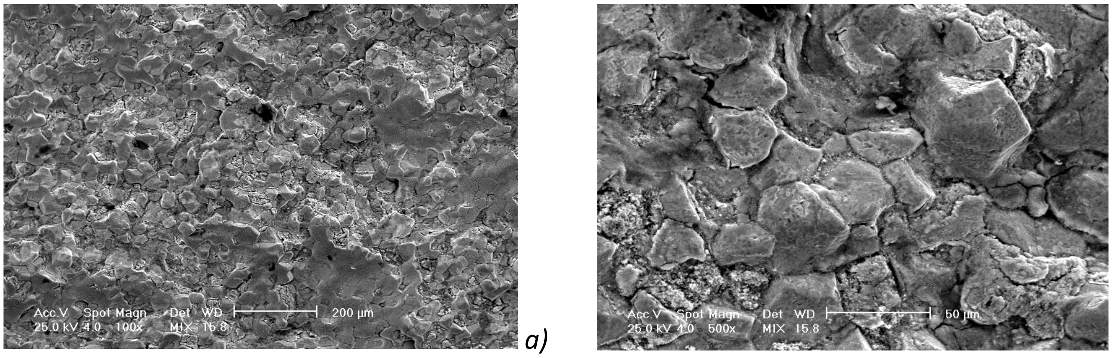


c) *d)*

Figure 5.24 Microscopic analysis of cracked areas. Electrolytic chemical attack with oxalic acid, 20% concentration a) crack towards inner surface, magnification ×100; b) crack towards inner surface, magnification ×200; c) crack towards outer surface, magnification ×200; d) crack towards outer surface, magnification ×500

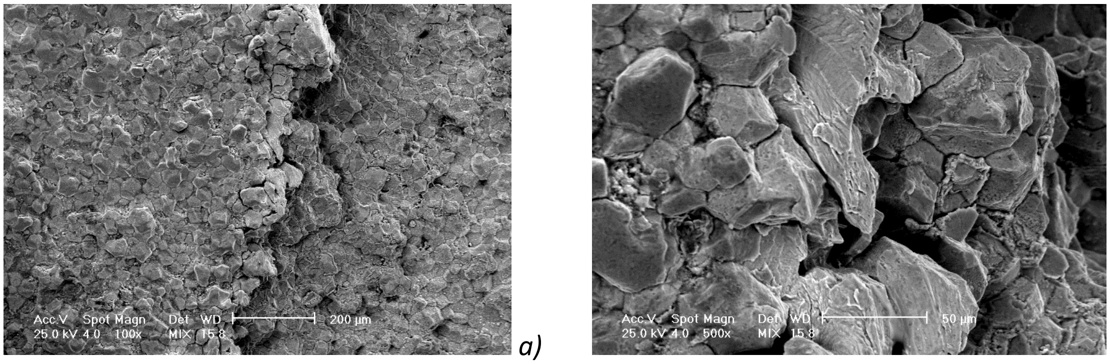
All cracks present are found to be trans-crystalline in character and oriented perpendicular to the pipe surfaces. It is possible that branches of secondary cracks may form from the main crack, which may be intercrystalline in character (Fig. 5.24-c and Fig. 5.24-d).

Fractographic analyses (fig. 5.25,...fig. 5.29) were performed by SEM electron microscopy at the marked points (1,2,...5) on the surface of the sample taken from tube no. 51.



a) *b)*

Figure 5.25 Fractographic analysis of area 1 a) magnification ×100; b) magnification ×500



a) *b)*

Figure 5. 26 Fractographic analysis of zone 2 (a) magnification ×100; (b) magnification ×500

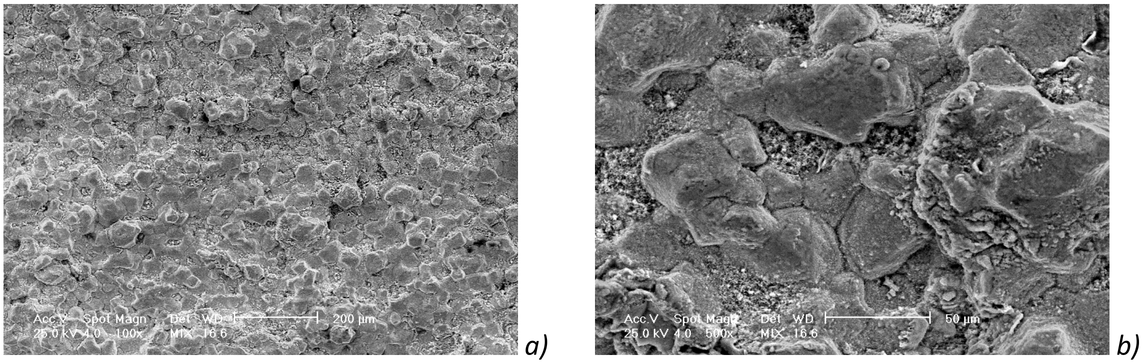


Figure 5. 27 Fractographic analysis of area 3 a) magnification power ×100; b) magnification power ×500

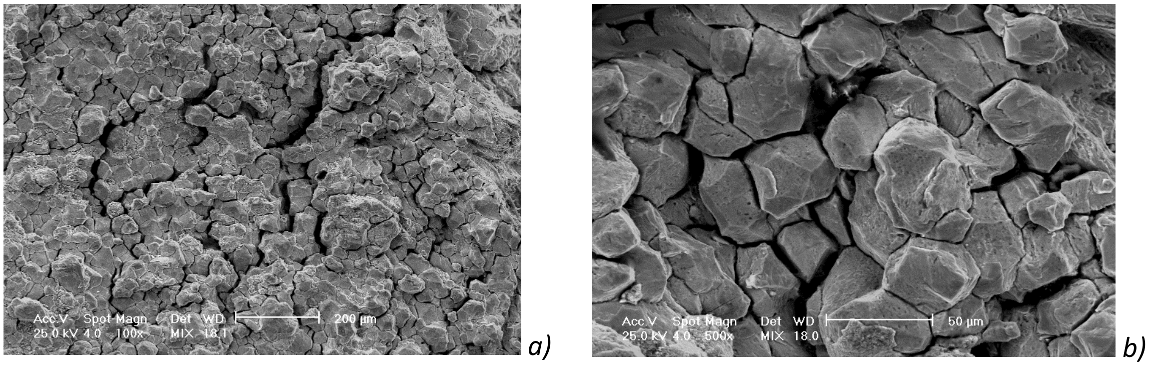


Figure 5. 28 Fractographic analysis of area 4 (a) magnification power ×100; (b) magnification power ×500

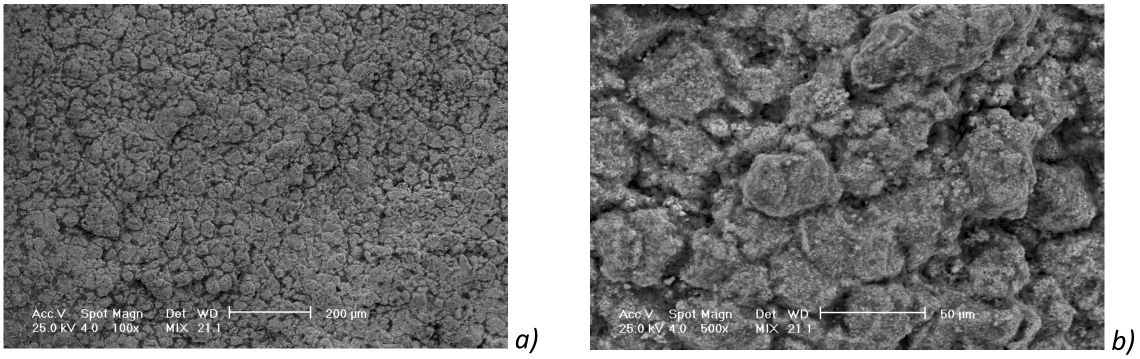


Figure 5. 29 Fractographic analysis of area 5 (a) magnification power ×100; (b) magnification power ×500

5.2.8. Material degradation by galvanic corrosion, case E

The corrosion sensitivity of materials can be a cause of degradation of steels in the thermally influenced zone of welded joints (the zone where the temperature reaches the critical sensitivity range). Degradation in this zone is more pronounced in thick plates than in thin plates.

Macroscopic analysis

Macroscopic analyses revealed:

- on the outside, the presence of large pores in the welded areas, probably developed from the initial cracks (fig. 6.30 and 6.31);

- on the inside, the surface of the pipes shows pronounced signs of general/extended corrosion and spot corrosion, including in the welded seam areas - fig. 5.30. The surface of the inner walls is covered with extensive dark deposits - fig. 5.31.

-

Figure 5. 30 Macroscopic appearance of the outer surfaces affected by the presence of pores due to corrosion (area of the DN 100/DN50 reduction made by welding - pipeline GH - 120-201)

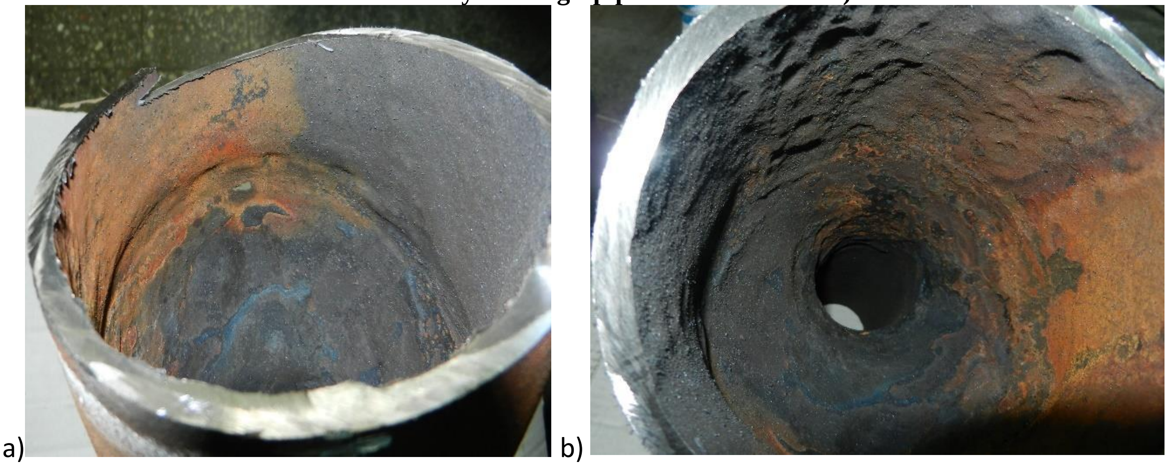
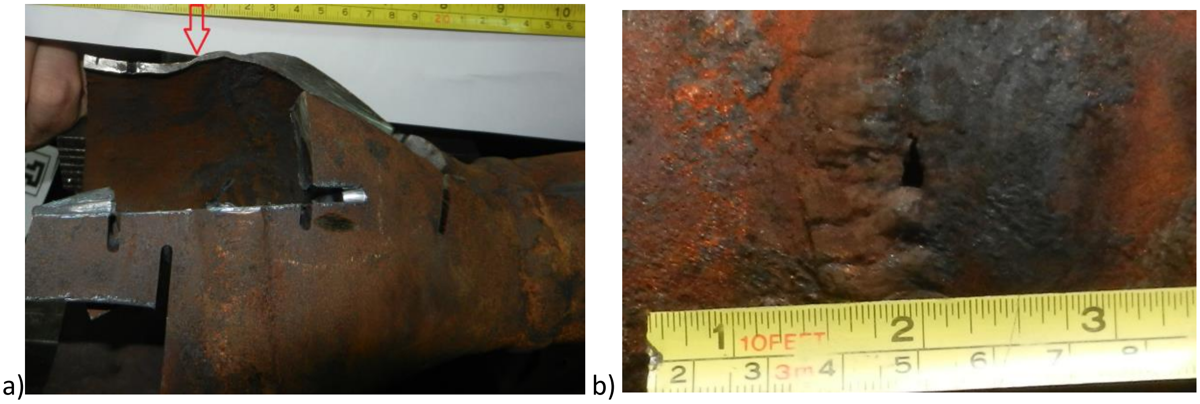


Figure 5. 31 Macroscopic appearance of the surfaces of the DN 100/DN 50 welded reduction body. a)- view from the direction of the small radius of curvature (inner surface of the curvature towards the DN50 pipe) b)- view from the direction of the large radius of curvature (outer surface of the curvature towards the DN100 pipe)

It can be seen that the wall penetration occurred in the area of the weld bead where the transition is made between the two pipes with different diameters and wall thicknesses, fig. 5.32.



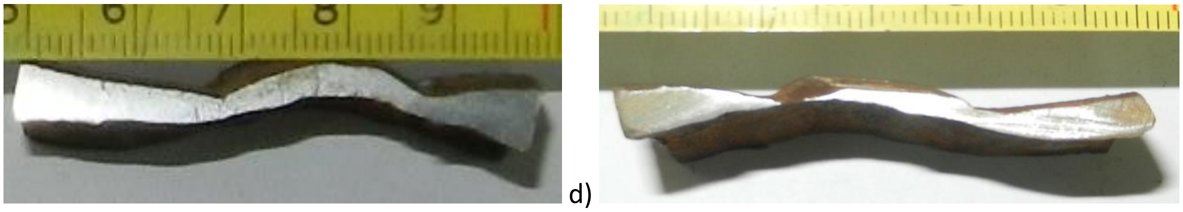

c) d)

Figure 5. 32 Macroscopic appearance of the welded joint area of the DN100/DN50 reduction and the DN100 elbow in the pore formation area. a) joint assembly after sampling; b) detail of the joint surface in the pore area; c) section in the pipe wall at 30 mm from the pore; d) section in the pipe wall at the pore formation site.

In order to check whether the base material in the welded joint area would withstand the mechanical tensile stresses due to the pressure of the working medium, the following was carried out:

- microstructural analysis of welded joints;
- determination of the mechanical strength properties, tab. 5.10;
- determination of the hardness of welded materials, tab. 5.11.

In Fig. 5.35 and fig. 5.36 show the results of the microstructural analyses carried out in the areas of weld B and weld D.

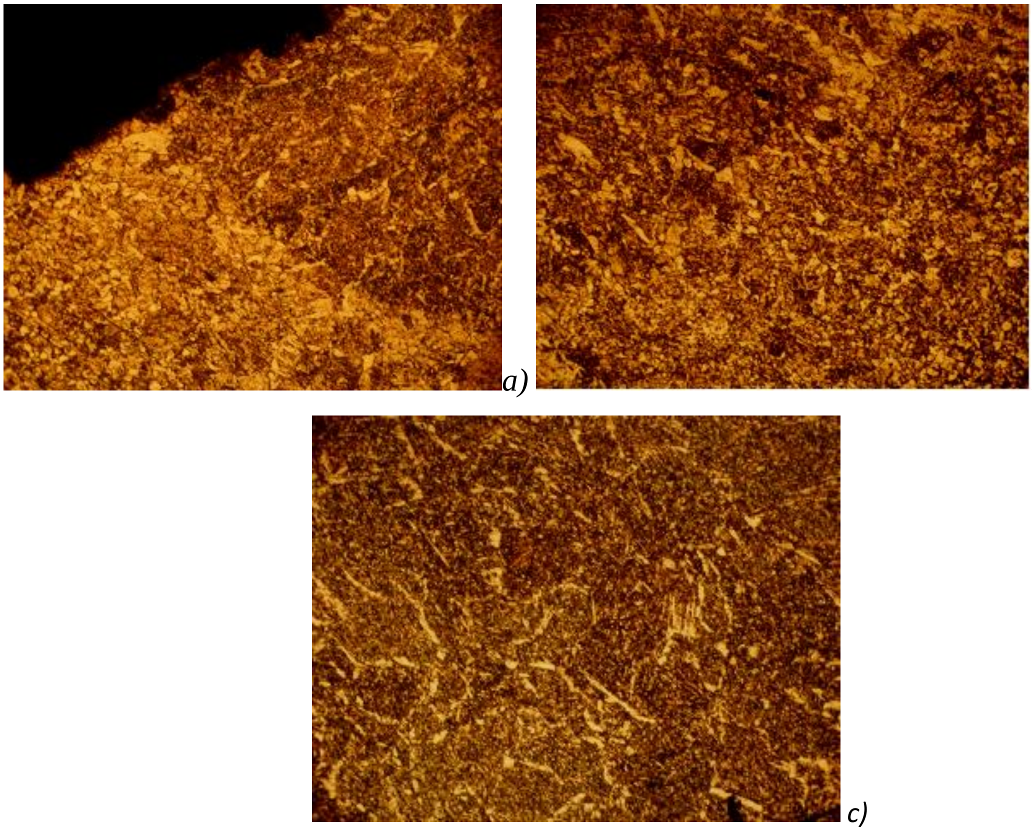

a) *b)*
c)

Figure 5. 35 Microstructures of the pipe steel in the areas of the weld joints between the DN50/DN100 reduction and the DN100 elbow (weld B). Thermal attack, × 100 a) thermally influenced zone (ZIT) towards DN50/DN100 reduction; b) thermally influenced zone (ZIT) towards DN100 elbow; c) weld bead zone: filler material (MA).

The material zones investigated included the pore formed by corrosion. In the ZIT zone towards the DN100/DN50 reduction (Fig. 5.35-a), a mixed bainite-sorbite-pheritic (B - S - Fα) structure is present. The same microstructure was also evident in the ZIT zone towards the DN100 bend (Fig. 5. 35-b). The weld bead zone (Fig. 5.35-c) is characterized by the formation of intermediate constituents, with acicular or filamentary appearance, due to the cooling rate and thermal gradient on the heat removal directions.

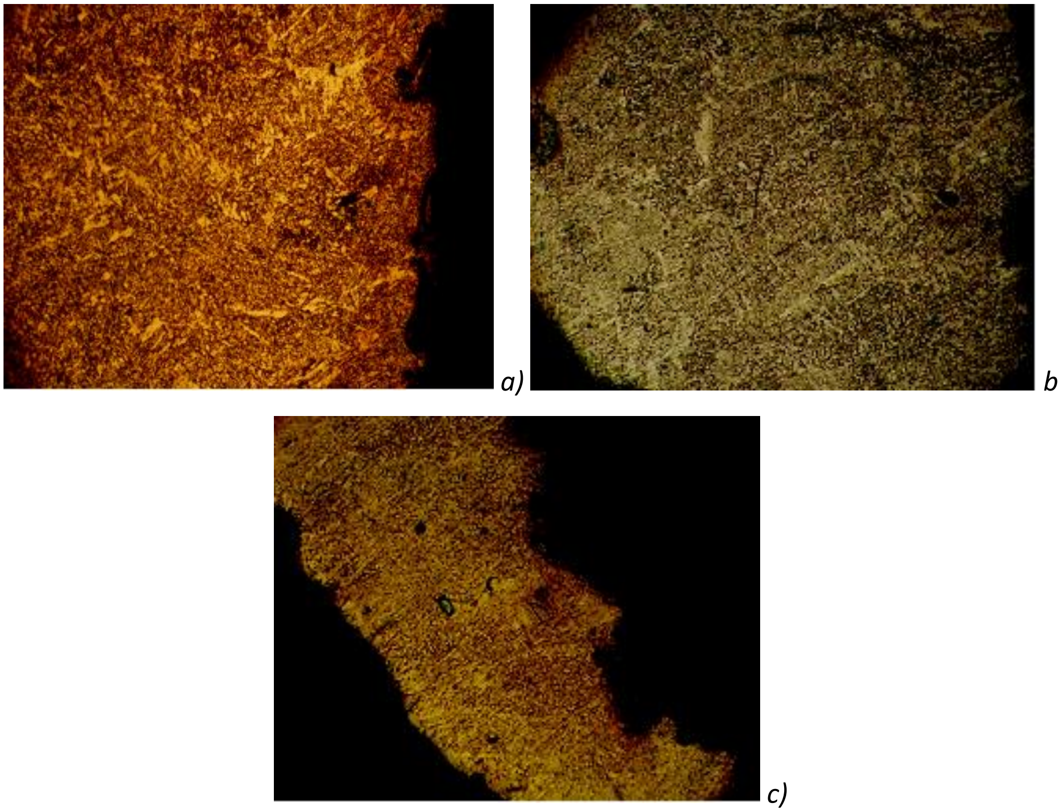


Figure 5.36 Microstructures of the welded joint between the DN100/DN150 reduction and the DN100 pipe (weld D) where an open pore has formed due to corrosion. Nital attack, ×100 a) edge of weld bead and presence of pore; b) weld seam thinned by corrosion; c) seam area thinned by corrosion until the pipe wall is pierced and the open pore is formed.

Processes of the general corrosion and spot corrosion type were amplified by the presence of the working fluid rich in H2 and Cl2 vapours. In the welded joint areas, made between materials with different galvanic potentials due to the specific chemical compositions of the pipe steel and the welding electrode material, conditions were created for the onset of localised galvanic corrosion.

5.3. Operational experiment on material degradation under mechanical stress

The operational experiment on material degradation under mechanical stress revealed that the state of internal stresses in the crystalline structure can cause the processes of crack germination and development. Maintaining these mechanical stresses for a longer period of time will create favourable conditions for the transformation of micro-cracks into macro-cracks, which may eventually lead to total material degradation.

5.3.1. Degradation by mechanical fatigue - case G

Case G shows material degradation under the action of a complex state of mechanical stress:

- contact mechanical fatigue
- contact wear.

The expertise referred to the behaviour of steel intended for the manufacture of rail track.

Macroscopic analysis

The macroscopic analyses were carried out on five samples taken from different samples of degraded rails (Fig. 5.39).

a)

b)

Figure 5. 39 Macroscopic appearance of degraded rail samples: a - sample C1; b - sample C23;

Fractographic analysis suggests a classical fatigue fracture produced under the cyclic action of contact pressure. In the upper part of the rail ("mushroom") several microcracks appear which, under alternating cyclic stresses, develop slowly and intermittently.

Microstructural analysis

Microstructural analyses were performed in two distinct situations:

- G1, on samples not treated with chemical reagent;
- G2, on chemically attacked samples.

Microstructural analyses on chemically attacked samples

In order to highlight the microstructure of the steels used in the construction of railway rails, specific chemical attack was performed: Nital, 2%.

Microstructural investigations were carried out on both the cross-section and the longitudinal section of the five samples. The metallographic samples were taken from the three specific areas of a railway track (see Fig. 5.37). Microstructural analyses were performed at different magnification powers (Fig. 5.45...Fig. 5.47).

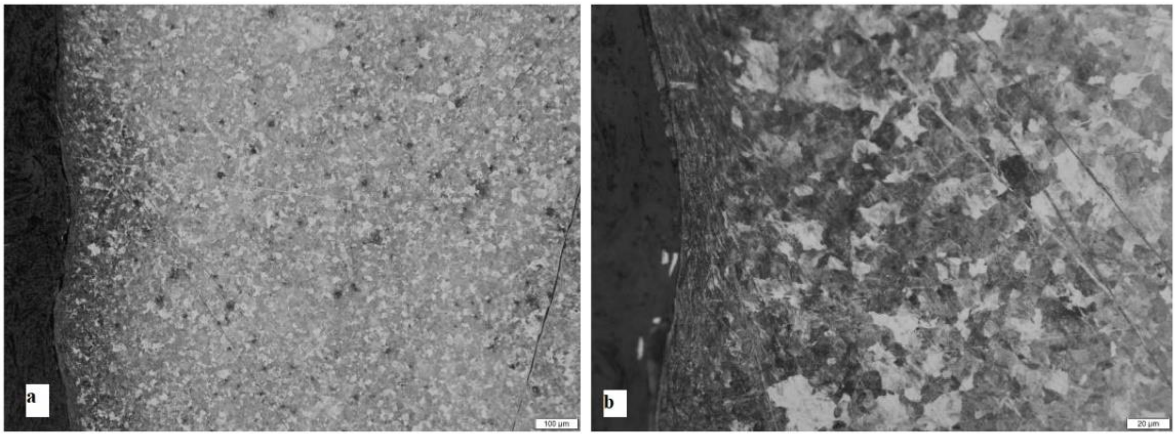


Figure 5. 45 Microstructures of the steel in the "mushroom" area of the rail - sample C32. 2% Nital attack. a) magnification power x 100; b) magnification power x 500

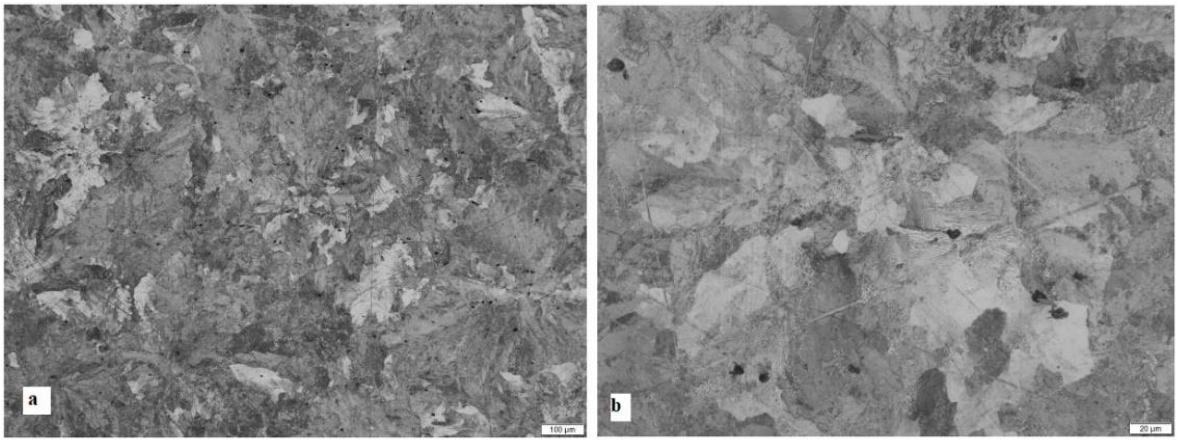


Figure 5. 46 Microstructures of the steel in the "heart" area of the rail - sample C32. Attack with Nital 2%. a) magnification power x 100; b) magnification power x 500

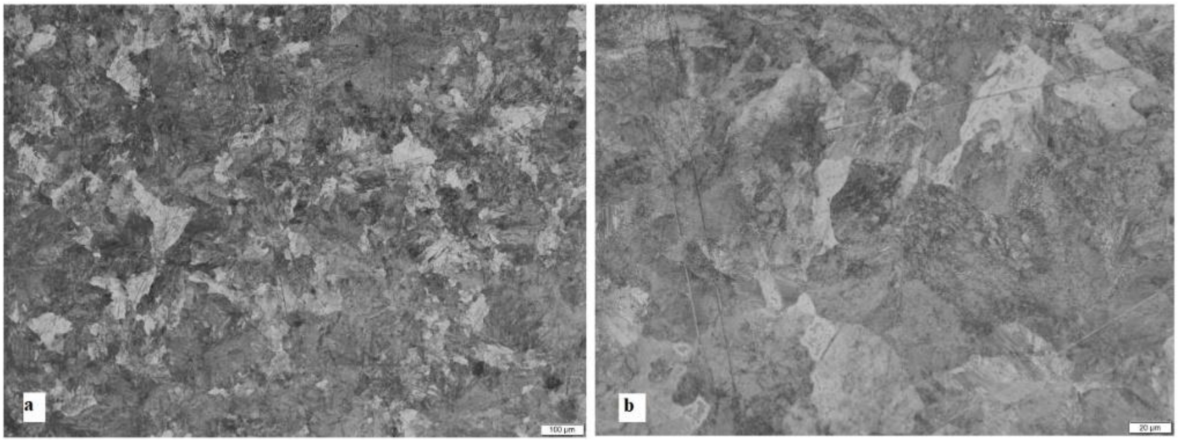


Figure 5. 47 Microstructures of the steel in the "sole" area of the rail - sample C32. Nital 2% attack: a) magnification power x 100; b) magnification power x 500

Microstructural analyses revealed the following:

- Mechanical fatigue contact stress triggered crack formation in critical sections of the "mushroom". The high number of stress cycles allowed propagation of cracks in the volume of metal material and development of newly formed surfaces until degradation by breakage of some portions of the rail profile;

- a remarkable contribution to the degradation mechanism of the rail material was made by the wear stress existing at the contact between the lateral surface of the wheel tread and the "mushroom" area of the rail.

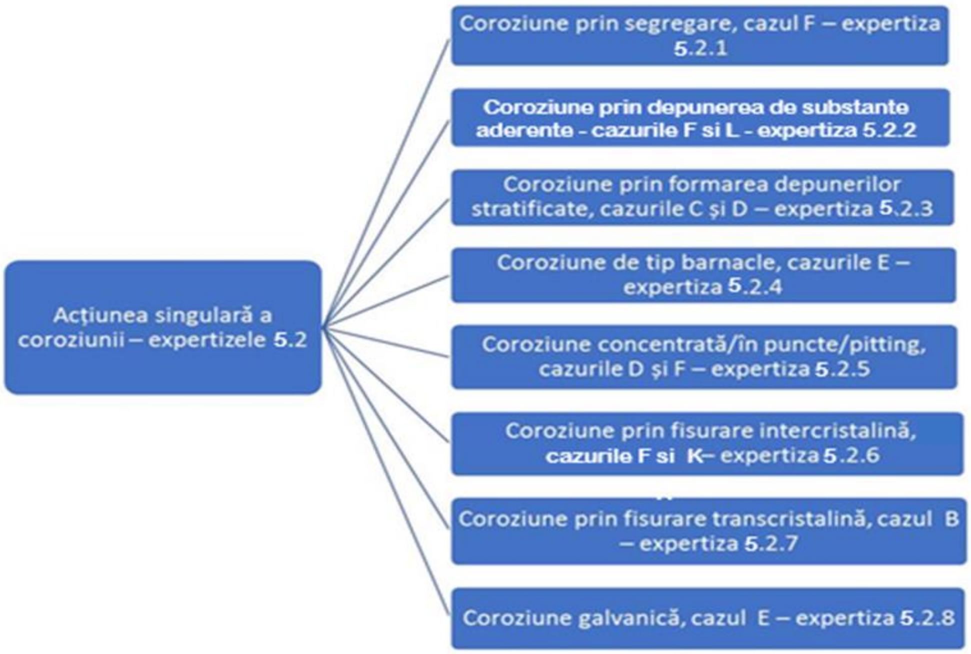
5.3.2. Exfoliation degradation - case H

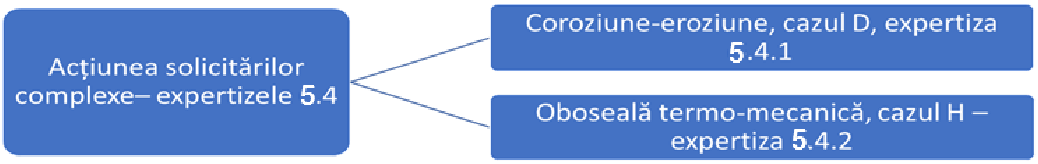
Exfoliation corrosion (lamellar corrosion, layer corrosion) is characteristic of those alloys which after cold plastic deformation (rolling, extrusion) show a fibrous structure, oriented in the direction of deformation and with inclusions oriented in the same direction. As a result of the textured structure, these alloys are susceptible to peeling. Corrosive attack advances along a number of crystalline planes, grouped in layer or sheet form, with the arrangement parallel to the plastic deformation direction. The corrosion products formed force the compactness of the layer/sheet and cause it to separate from the rest of the material. In some cases several separate films may result.

Conclusions

The operational experiments carried out aimed to identify the corrosion forms produced at the contact between metallic materials and working environments characterised by different chemical compositions.

The conclusions regarding the expertise on how degradation of materials occurs have addressed three possible causes:





The operational experiments carried out aimed to identify the forms of corrosion produced in contact between metallic materials and working environments characterised by different chemical compositions.

Chapter VI: GENERAL CONCLUSIONS, ORIGINAL CONTRIBUTIONS AND FUTURE DIRECTIONS

6.1 General conclusions

The studies carried out on the current state of research in the field of eco-socio-technological assessment of the degradation of metallic materials have enabled the following general conclusions to be drawn:

- In the current development of the human sphere it can be considered that it has the dimensions of a megasystem (M.S.) which will include three main components: the natural-ecological subsystem (N.E.S.), the social subsystem (S.S.) and the technological subsystem (T.S.).

- Material degradation is a complex process with consequences affecting all three subsystems, characterised by eco-socio-technological coordinates that are the subject of interdisciplinary concepts.

- Degradation of materials represents their transition from the ordered form (characterised by a minimum entropy) to the disordered form (characterised by an entropic increase) specific to the resulting residues. This evolution of the configurational entropy of the materials will result in entropisation of the environment (impact on N.E.S.).

- The decommissioning of equipment or installations will be the result of technological malfunctions, which may occur at any stage of their life cycle. Final decisions on the operation of machinery will adversely affect the subsystem (S.T.).

- Degradation can be generated in all phases of the material life cycle, so the following classification is possible: design degradation; manufacturing degradation; social degradation, with the component of moral degradation; environmental degradation; integration degradation, when applying 3R technologies.

- Experimentation requires high-level scientific knowledge, and also calls for ex-situ characterisation methods whereby the properties of materials are assessed under conditions outside their environment of use, so that a distinction can be made between a viable process and a viable technology.

- On a metallic material, the action of the corrosion process may be generalised over the whole surface, or it may be concentrated at points (on small and very small surfaces).

- Stress corrosion cracking is the result of the simultaneous action of two factors: the aggressive chemical composition of the technological fluid and the pressure with which it circulates inside the pipes.

- The further evolution of pitting corrosion is: pitting corrosion → stress corrosion cracking → cavern corrosion each stage contributing to the final degradation of the metallic material.

- Corrosion susceptibility can be a cause of degradation of steels with different chemical compositions that have been used in the welded assembly of pipe sections.

- When welding stainless steels, intercrystalline corrosion can be triggered in the weld bead area due to the high final cooling rate.

- In order to reduce the thermal stresses formed in the steels after welding processing, it will be necessary to apply a heat treatment capable of ensuring complete precipitation of chromium, titanium and niobium carbides.

- The action of corrosive factors occurs after clusters of crystalline, foil-like planes arranged parallel to the plastic deformation direction. The formation of several separate films is also possible. The accumulation of corrosion products will affect the compactness of the films, causing them to separate from the rest of the material.

- The velocity of fluid movement in the pipe will cause turbulence, accompanied by the formation of air bubbles. Repeated contact between the air bubbles and the metal wall will cause cracking of the metal wall, in successive stages, with the final effect of degradation of the pipe material.

- As a corollary of these general conclusions it can be stated that material degradation is an irreversible process that will increase the consumption of natural resources and will increase the level of environmental pollution. With these two consequences, material degradation is an anti-development process for the megasystem (M.S.) of the human sphere.

6.2. Original contributions

Original contributions are of a theoretical nature (Chapter IV), or of an applied nature (Chapter III and Chapter V).

The theoretical contributions made by the PhD thesis aim to promote new concepts that support the need for "Materials Degradation Engineering" to become a new component of the general science of "Materials Engineering".

To this end, current sustainable development strategies and policies are taken into account, as well as concepts capable of highlighting the eco-sociotechnological performance of materials. Obviously, new theoretical approaches to the degradation process of materials are presented by analysing the three components of the megasystem of the human sphere, as well as the phases of the life cycle of materials.

Methodological recommendations specific to the study of material degradation refer to the carrying out of analyses:

- qualitative, identifying the effects on the chemical composition, structure and properties of materials;
- Quantitative, allowing the assessment and measurement of the effects of degradation;

Different ways of classifying the types of degradation are presented: by phase of generation, by nature of the destructive agents, by nature of the degradation.

Two categories of destructive environments are identified:

- environmental/environmental environment, also called ex-situ, made up of environmental factors: air (atmosphere), water (hydrosphere), soil;
- the technological environment, also called in-situ, made up of technological factors, specific to installations and equipment, which act destructively on materials;

As an element of quantitative analysis, it has been proposed to assess the life cycle of the material (LCA), assessed in terms of life cycle years (LCA), in order to characterise the intensity of the degradation processes for each phase of the life cycle (especially in the use phase).

Life cycle assessment was defined by the notion of determination, (Dcv), which included: material or product manufacturing phase duration (Dfp), use duration (Du), end-of-life duration (Dsu) and secondary material reintegration duration (Drms).

Resistance to degradation was assessed by the resistance to eco-sociotechnological degradation (Rdest) and its components:

- Resistance to technological degradation (RdST), which takes into account the existence of technologically performing materials;
- Resistance to social degradation (RSD), which takes into account the existence of socio-materials;

- Resistance to environmental degradation (RoESD), which takes into account the existence of ecomaterials.

The applied contributions are represented by the numerous case studies/expertises analysed, all of which aim to identify the causes of material degradation through various techniques.

A comprehensive programme of assessment of the quality and current condition of components of industrial equipment has been carried out in order to determine the degradation mechanisms that have led to the depreciation of this equipment.

An investigation plan was developed through advanced characterisation of the structure and composition of the materials studied, the results obtained being validated by the accuracy and reproducibility of the analysis and characterisation equipment used at the ECOMET centre.

Work steps were developed to carry out the 12 technical expertises which included:

- establishment of material selection criteria (chemical composition, mechanical and technological properties, recommendations for use, etc);
- analysis of the state of demand during the operating period;
- identification of the environmental factors at work and the effects of the influences exerted;
- explanation of the possible causes that contributed to the degradation of the material, or the product, undergoing the assessment.

The mechanisms of the main causes of damage or destruction have been identified for 13 particular cases in the industrial environment with an effect on the durability of materials, and the following types of degradation caused by corrosion have been identified:

- 3 cases of degradation (F, D and I) produced by corrosion at points;
- 3 cases of degradation (B, F, K) caused by stress corrosion cracking;
- 1 degradation case (E) caused by galvanic corrosion;
- 2 cases of degradation (C and L) caused by corrosion product deposits;
- 1 case of degradation (J) caused by excessive plastic deformation shrinkage;
- 1 case of degradation (G) caused by atmospheric corrosion and mechanical fatigue;
- 2 cases of degradation (A and L) caused by oxidative corrosion.

It was established as a general conclusion, that in most of the case studies investigated, the main destructive agent identified was corrosion, in its many forms of manifestation: general, concentrated/point, stress/cracking, oxidising, galvanic, atmospheric, etc.

It was noted that in some surveys complex causes of degradation were involved, resulting from combinations of different forms of corrosion (B, E, F), or from different forms of corrosion combined with exceeding the values of the permissible mechanical strength (A, G, I). In most surveys a single cause of degradation was identified (D, E, H, J, K, L).

In order to identify as correctly as possible the causes of material degradation, the following were necessary:

- 20 chemical analyses, performed by different methods;
- 34 macrostructural analyses which required correct decisions at the sampling stage;
- 18 microstructural analyses carried out by optical microscopy, or electron microscopy.

The summary of the technical expertise carried out allowed a classification of the conditions that caused the degradation of the materials or equipment investigated:

- the singular action of corrosion, in its various forms: by segregation, deposition of adherent substances, formation of layered deposits, intercrystalline or transcrystalline cracking, etc;
- the action of mechanical stresses: mechanical fatigue, mechanical roughening, peeling, etc;
- combined action of destructive agents: by corrosion-erosion, thermo-mechanical fatigue, etc.

It has been found that corrosion can occur at any stage of the life cycle of metallic materials:

- in the primary stages of processing / casting, or additive manufacturing techniques;
- in the secondary stages of processing such as heat treatment, plastic deformation, welding, etc;
- in the operational stages, being caused by aggressive working environments, environmental or atmospheric corrosion.

The experimental research carried out has logically and gradually developed the case studies presented. They have followed the stages of expertise specific to the engineering of material degradation, an essential role having been played by the technical expertise of the causes that have caused the temporary or total disablement of the equipment/installations or of the structural elements of their structure, being analysed:

- the chemical compositions of the affected metal layers and the resulting corrosion products;
- structural changes produced by corrosion processes;
- the mechanical strength properties of metallic materials in various stages of degradation and the products resulting from corrosion processes;
- possibilities for limiting the consequences of the corrosion process;
- the technical solutions proposed for corrosion protection of materials, specific to each situation investigated.

The model of the mechanism of progressive formation and development of microcracks resulting from thermo-mechanical fatigue has been proposed on the basis of the microscopic analyses carried out, the model presented highlighting both the evolution of the cracking front and the generation of new surfaces formed that will produce the final degradation of the materials.

Some conditions of chemical composition, temperature and velocity of displacement have been established for the working fluids circulating through the tubing of the equipment under test and the effects of degradation produced on the metallic materials used. One effect repeatedly studied was the deposition, single or successive, of layers formed by sulphur, chlorine or nitrogen based salts (single or combined).

On the basis of the complex expert programme, the following characteristic aspects of the studied degradation phenomena were identified:

- regardless of their structure and chemical constitution the deposition of these structures contributed to the intensification of the corrosion process. The size of the metal surfaces covered by these chemical deposits will make the transition from concentrated/point corrosion to generalised/extended corrosion.
- In cases of degradation due to mechanical stress alone, it has been established that an important role is played by the type of technological processing (e.g. roughening) which can induce high internal stresses in the crystal lattice of materials.
- the application of plastic deformation processing operations (rolling, extrusion, etc.) to metallic materials used in corrosive environments will contribute to the onset of degradation such as peeling, lamellar corrosion, or layer corrosion.
- the increase in the complexity of the degradation process was specific to complex stresses such as corrosion-erosion or thermo-mechanical fatigue.

A pattern was established for the sequence of successive stages that will cause the final destruction of materials by corrosion-erosion.

The mechanism of microcrack development and crack front growth under thermo-mechanical fatigue stress was established and represented. All the models of degradation process development are intuitive in nature, their role being to establish the constitutive phases contributing to the final destruction of materials and the temporary or permanent decommissioning of equipment/facilities.

6.3. Directions for future scientific research

1. Continuation of the expertise of the destructive action of corrosion by participating in the expertise of new cases specific to the refining of petroleum products and power generation;

2. Study new forms of severe degradation of materials due to complex processes in which two or three degrading factors act simultaneously;
3. Identification of critical values of mechanical strength characteristics that allow the assessment of the stage of degradation of materials in order to prevent the occurrence of major technical events;
4. Analysis of the phenomenon of crack germination and development (conditions of formation and modes of propagation in metallic materials) in order to be able to assess their dimensional evolution, as well as the degree of degradation of the component elements and the structures of which they are part.

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