The Characterization of Some Steel Corrosion Products by FT-IR Spectroscopy**

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The present work is a continuation of our precedent studies [1, 2] as an attempt to characterize the corrosion products formed on the carbon steel (OL 37) exposed to natural and artificial environments, both having high relative humidity and chloride content. Samples of steel sheets of 200 . 100 . 2 mm dimension were prepared using abrasive blasting with specific requirements. As natural and artificial environment, a marine experiment site, respectively a salt spray test with specific exposure conditions, were used. Iron oxyhydroxides and oxides are typical constituents of rust, generated by the corrosion of steel surface in contact with aqueous phase [3, 4]. The phase composition of the rust depends on the physic-chemical factors from the environment such as: type of steel, time of exposure, electrolyte composition, pH and temperature [5, 6]. The composition and structure of carbon steel corrosion products for the two situations (accelerated lab and real conditions) were studied comparatively using an adequate FT-IR spectroscopy method and KBr pellets technique. The FT-IR spectrometer operates with OPUS program.

Keywords: rust, steel, atmospheric corrosion, FT-IR spectra

Nowadays in the most domains of the national economy such as buildings, water and gas supply systems, energy supply systems, transports, chemistry and petrochemistry, technological equipment, bridges, the metal structures are used. The economical and technological consequences of the metal wastages by corrosion are significant [5]. The published data show enormous financial losses due to the deterioration of metals, both for the individual units and for the national economy as a whole [5, 7].

The anticorrosive protection of the metallic buildings sitted in aggressive environments depends on the used metal type, the protection system, the mechanical stress and the environment [7]. The effective control of the corrosion must be based on the understanding of formation and transformation mechanisms of corrosion products and also the evaluation of their protection ability [8, 9]. Depending on their properties (compactivity, adherence, etc.) it is possible to establish the necessity of an adequate protection system, the minimum degree of cleaning of the surface for the application of anticorrosive protection system and the possibility for treatment of the incipient corrosion products with inhibitors.

Iron oxyhydroxides and oxides are typical constituents of rust, generated by the corrosion of steel surface in contact with aqueous phase. The phase composition of the rust depends on the physico-chemical factors of the corrosion process such as: electrolyte composition, *p*H, time of exposure, the environment, type of steel and temperature [3, 5]. The large number of works on these topics stressed out the necessity of establishing some qualitative and/or quantitative appropriate proceedings for both lab and industrial media conditions. The standardization of metal susceptibility investigation methods in different corrosion conditions and of the corrosion degree for the various steel types facilitates, in a small part, the researches in the corrosion area [2].

Because of the diverse metallic corrosion phenomena and also the different physico-chemical processes, there are a lot of techniques that enable the study of the corrosion products. Therefore, along the years several techniques for study were used: X-ray difractometry, electronic microscopy, electrochemical studies (electrochemical impedance spectroscopy), Mossbauer, Raman and FT-IR spectroscopy [4, 10-13].

Selecting of a corrosion products analysis technique depends of some parameters such as: the corrosion process rate, the corrosive attack type and the nature of the corrosion products [2].

Experimental part

The present work is an attempt to characterize the corrosion products formed on carbon steel (OL 37) exposed to natural and artificial environments, both having high relative humidity and chloride content using the technique of Fourier transform infrared spectroscopy (FT-IR).

As natural and artificial environment, a marine experiment site at Constanta (natural conditions), respectively a salt spray test (laboratory conditions) both belonging to INCERC (The National Building Research Institute), were used. We chose these conditions because the atmospheric corrosion cause the most losses for all the domains, especially for building industry; also ion chlorine (Cl^-) has an important influence to corrosion phenomena and to rust morphology.

The exposure conditions were:

- for the salt spray test: relative humidity more than 90%, temperature 35 ± 2^0C, sodium chloride (NaCl) concentration 5%, spray angle 45^0, according to SR EN ISO 9227:2007 [14].
- for the marine site at Constanta: 50 m away from coast and 7 m altitude in open area.

Both for the salt spray test and the marine site, samples of sheets of 200 . 100 . 2 mm dimension were prepared using abrasive blasting with specific requirements (S_a 2½). Abrasive blasting represents the process of preparing and cleaning a metallic surface by an abrasive jet material such as grit, corundum and sand.

The exposure time of steel sheets was for the salt spray test three months and for the natural conditions two years. The corrosion products formed and developed in time were sampled by brushing and stored after under lab conditions (about 23°C and 60% relative humidity).

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Crt. no.	Name	Formula	The predict environment for formation	System of crystallization	Elementary lattice constants (Å)	Observations
1.	Hematite	$\alpha - Fe_2O_3$	- water - soil	Trigonal	a = 5,04 c = 13,77	
2.	Maghemite	$\gamma - Fe_2O_3$	- soil	Cubic	a = 7,32	Observed only in soil rust by IR spectroscopy
3.	Magnetite	Fe_3O_4	- air - soil	Cubic	a = 8,35	
4.	Wustite	FeO	- soil	Cubic	a = 4,29	
5.	Goethite	α – FeOOH	- air - water - soil	Rhombic	a = 6,45 b = 10,02 c = 3,04	Most stable and compact modification of FeOOH
6.	Akaganeite	β – FeOOH	- water - saline	Tetragonal	a = 10,81 c = 3,02	
7.	Lepidocrocite	γ – FeOOH	- air - water - soil	Rhombic	a = 3,88 b = 12,54 c = 3,07	
8.	Crystallite	δ – FeOOH	- air	Hexagonal	a = 2,94 c = 4,58	
9.	Ferrous hydroxide	$Fe(OH)_2$	- air - water	Trigonal	a = 3,26 c = 4,60	Its formation is characteristic to basic media

Table 1
THE STRUCTURAL CHARACTERISTICS OF THE CRYSTALLINE IRON CORROSION PRODUCTS

The FT-IR spectra were carried out on Vertex 70 – Brucker spectrometer with spectral resolution better than 0.5 cm^{-1}, wave number accuracy better than 0,01 cm^{-1} and photometric accuracy better than 0.1%T at room temperature. The FT-IR spectrometer operated with OPUS program. Specimens were pressed into a spectroscopic pure KBr matrix (with 300:1 ratio).

Results and discussions

The structural characterization of the crystalline iron corrosion products is presented in the table 1 [1, 15].

When planning the research experiments we have studied the possibility to compare the corrosion products formed on carbon steel (OL 37) in laboratory and natural conditions.

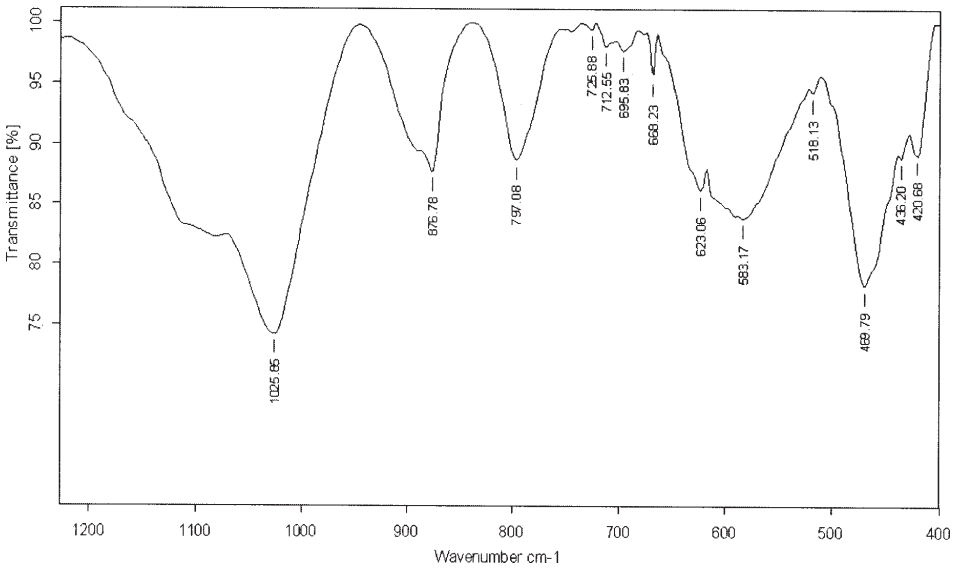

Fig. 1. FT-IR spectrum of the rust formed on carbon steel (OL 37) exposed to accelerated lab conditions (3 months time of exposure)

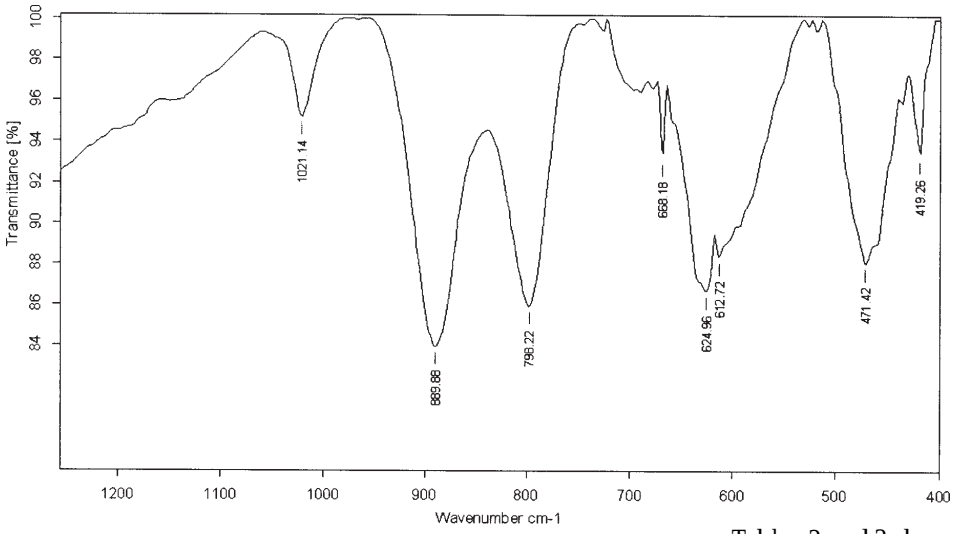

Fig. 2. FT-IR spectrum of the rust formed on carbon steel (OL 37) exposed to marine atmosphere environment conditions (2 years time of exposure)

Figures 1 and 2 show FT-IR spectra of the corrosion products formed on carbon steel exposed to lab conditions (fig. 1) and to natural environment (fig. 2).

Tables 2 and 3 show the composition of the rust formed on carbon steel exposed to lab conditions and to natural environment respectively (two replicates for each sample).

Table 2
OBSERVED FREQUENCIES IN FT-IR SPECTRA FOR SAMPLES EXPOSED TO LAB CONDITIONS

Crt. no.	Sample indicative	Frequence range (cm^{-1})	Intensity of signal	Attribution
1.	I.1 OL 37	1025,86	intense	γ – FeOOH
		876,78	medium	α – FeOOH
		797,08	medium	α – FeOOH
		725,88	very weak	Fe_2O_3
		712,15	very weak	Fe_2O_3
		695,83	very weak	α – FeOOH
		668,23	weak	α – FeOOH
		623,06	weak	γ – FeOOH
		583,17	medium	Fe_3O_4
		469,79	medium	δ-FeOOH
		436,20	very weak	Fe_3O_4
		420,68	weak	Fe_3O_4; γ-Fe_2O_3

2.	I.2 OL 37	1025,53	intense	γ – FeOOH
		876,20	medium	α – FeOOH
		797,36	medium	α – FeOOH
		729,05	very weak	Fe_2O_3
		701.52	very weak	Fe_2O_3
		692,12	very weak	α – FeOOH
		669,55	weak	α – FeOOH
		623,87	weak	γ – FeOOH
		583,45	medium	Fe_3O_4
		469,45	medium	δ-FeOOH
		432.42	very weak	Fe_3O_4
		419.23	weak	Fe_3O_4; γ-Fe_2O_3

Table 3
OBSERVED FREQUENCIES IN FT-IR SPECTRA FOR SAMPLES EXPOSED TO MARINE ATMOSPHERIC CONDITIONS

Crt. no.	Sample indicative	Frequence range (cm^{-1})	Intensity of signal	Attribution
1.	II.1 OL 37	1021,14	medium	γ – FeOOH
		889,88	intense	α – FeOOH
		798,22	intense	α – FeOOH
		668,18	weak	α – FeOOH
		624,96	intense	γ – FeOOH
		612,72	medium	α – FeOOH?
		471,42	intense	δ-FeOOH
		419,28	weak	Fe_3O_4; γ-Fe_2O_3
2.	II.2 OL 37	1021,14	medium	γ – FeOOH
		889,52	intense	α – FeOOH
		798,76	intense	α – FeOOH
		667,15	weak	α – FeOOH
		625,06	intense	γ – FeOOH
		612,14	medium	α – FeOOH?
		472,52	intense	δ-FeOOH
		420,15	weak	Fe_3O_4; γ-Fe_2O_3

The presence of goethite (α – FeOOH) is confirmed by the two typical IR bands at 876 cm^{-1} and 797 cm^{-1}, for lab conditions and 889 cm^{-1} and 798 cm^{-1} for marine atmospheric conditions. The bands at 668 cm^{-1} (table 2) and 612 cm^{-1} (table 3) may also be asigned to goethite. The presence of lepidocrocite (γ – FeOOH) is confirmed by its IR characteristic band at 1025 cm^{-1} and a suplimentary band at 623 cm^{-1} (table 2), 1021 cm^{-1} and a suplimentary band at 625 cm^{-1} (table 3). Magnetite was identified in the rust sampled from the steel sheets exposed to natural conditions with its characteristic band at 583 cm^{-1}. An additional band of magnetite at 419-420 cm^{-1} was observed. The band at 469 cm^{-1} for artificial conditions and 472 cm^{-1} for natural conditions respectively, corespond to crystallite (δ-FeOOH). The weak bands at 725 cm^{-1} and 712 cm^{-1} may be assigned to Fe_2O_3. There are no proves for akaganeite (β – FeOOH) presence. This denotes a fast evolution of

iron oxyhydroxides to more stable forms (goethite is the most stable form of iron oxyhydroxides).

The observed bands of the spectra have been compared with the characteristic frequencies of the corrosion products according to literature data [3, 16, 17].

Conclusions

In case of exposure to artificial atmosphere lepidocrocite is the predominant component while in the other case – marine atmosphere exposure – goethite is predominant, lepidocrocite being in a smaller proportion; so we can sustain that lepidocrocite is a precursor for goethite.

As a final conclusion it may be stated that there is a good correlation between evolutions of the corrosion products formed on carbon steel as well in accelerated lab conditions as in real (natural) conditions.

References

1.NEAGOE, C., CHIOSA, V., MANDRAVEL, C., Annals of University of Bucharest, (new serie), 1999, p. 59

2.SOARE, A., MANDRAVEL, C., Annals of University of Bucharest**,** (new serie), **I-II,** 2005, p 353

3.MUSIC, S., NOWIK, I., RISTIC, M., OREHOVEC, Z., POPOVIC S., Croatica Chemica Acta CCACAA, **77,** 2004, p.141

4.REFAIT, Ph., GÉHIN, A., ABDELMOULA, M., GÉNIN, J.M.R., Corrosion Science, **45,** 2003, p. 659

5.BADEA, T., POPA, M. V., NICOLA, M., Science and engineering of corrosion, Edited by Romanian Academy, Bucharest, 2002, p 231

6.TAKASAKI, S., YAMADA, Y., Corrosion Science, **49,** 2007**,** p. 240

7.PĂUNEL, M. A., Controlling corrosion of the overhead steel structures, 2002 (BREN Publishing House – Second revised edition).

8.RODRIGUEZ, S., SANTANA HERNÁNDEZ, F. J., GONZÁLEZ, J. E., Corrosion Science**, 44**, 2002 p. 2425

9.YAMASHITA, M., SHIMIDZU, T., KANISHI, H., MIZUKI, J., ULCHIDA, H., Corrosion Science, **45,** 2003, p. 381

10.VANDENBERGHE, R.E., DE GRAVE, E., LONG, G.J., GRANDJEAN, F., Mössbauer Spectroscopy Applied to Inorganic Chemistry, **3**, Plenum Pres, New York, 1989 p.59

11.LEGRAND, L., ABDELMOULA, M., GÉHIN, J. M. R.., CHAUSSE, A., GÉHIN, A., Electrochimica Acta, **46,** 2001, p. 1815

12.ASAMI, K., KIKUCHI, M., Corrosion Science **45,** 2003, p. 2671

13.DE FARIA, D. L. A., VENANCIO SILVA, S., DE OLIDEIRA, M. T., J. Raman Spectroscopy **28**, 1997, p. 873

14.SR EN ISO 9227:2007 „Corrosion tests in artificial atmospheres - Salt spray tests"

15.VAN OCTERON, K. A., Korrosionschutz durch Beschichtungstoffe, **2**, Spriger Verlog, Munchen-Wien, 1980, p. 42

16.SCHWERTMANN, U., CORNELL, R.M., Iron Oxides: Preparation and characterization, 2000, N.Y. Publishers Inc.

17.PACHECO, A.M.G., TEIXEIRA, M.G., Corrosion Journal, **25**, nr. 1, 1990, p. 57

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