

# THE SELECTION OF ADEQUATE METHODS FOR THE STRUCTURAL STUDY OF THE CORROSION PRODUCTS

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**abstract:** The present work is treating principal aspects of metal corrosion regarding the most important of the techniques used in the experimental studies. Examples of electrochemical, microscopic and spectroscopic methods are given.

**Keywords:** corrosion products, green rust, atmospheric corrosion.

## Introduction

The problems related to corrosion are present in all the domains of the national economy: machine building, naval and port building, chemistry, petrochemistry, metallurgy, semi-finished production, water and gas alimentary systems, energy production systems, transport, etc. [1]. The economic consequences of corrosion affect technology, too. A great deal of the development of new technology is held back by corrosion problems because the materials are required to withstand, with many cases simultaneously, higher temperatures, higher pressures and more highly corrosion environments [2].

Millions of dollars are lost each year because of corrosion. Much of this loss is due to the corrosion of iron and steel, although many other metals may corrode as well [2].

The study approaches of the metallic corrosion phenomena are represented due to the physical-chemical processes that may occur, by different and divers techniques. The large number of work on these topics pulled out the necessity of establishing of some qualitative and/or quantitative proceedings appropriate as either for lab conditions as for industrial media. The standardization of metal susceptibility investigation methods in different corrosion conditions and of the corrosion degree for the various metal groups facilitates, in a small part, the researches in the corrosion area [3].

## Theoretical

The applied methods for the corrosion study must fulfill the conditions of a firm control of different factors characterizing the corrosion process. The real work conditions must be fulfilled, too. The result of the metal corrosion due to a chemical medium is, usually, represented by a weight loss together with changes in the mechanical, structural or physical-chemical properties of the metal/alloy [3].

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Selecting of a corrosion products analysis technique is depending of some parameters as: corrosion process rate, corrosive attack type and the nature of the corrosion products. In Table 1 are listed some of the methods applied in the corrosion studies.

**Table 1. A simplified classification of the used experimental methods**

Corrosion process rate	Corrosive attack type and characterization of corrosion products	Nature of corrosion products
Gravimetric methods	Macroscopic method: - visual examination	Spectroscopic methods (IR, FTIR*, Raman, Mossbauer spectroscopy)
Electrochemical methods	Microscopic methods: - optics - electronics (SEM, TEM, STEM, AFM, STM)*	Diffraction methods: X-ray diffraction (XRD), electron diffraction (ED), etc.

\* see acronyms explanation in text

Corrosion rates of metals/alloys in aqueous medium can be determined using electrochemical corrosion testing equipment with the help of computerized automatic polarization system.

Direct current linear polarization (DCLP), alternative current electrochemical impedance spectroscopy (ACEIS) and corrosion potential measurements are use to investigate the corrosion of metals/alloys under cyclic wet and dry conditions. Electrochemical impedance spectroscopy and DC linear polarization measure the corrosion rate of the metals under the thin electrolyte layer [4].

To validate the corrosion rate determinations, measuring of weight losses is generally used.

#### **Electrochemical Corrosion Tests**

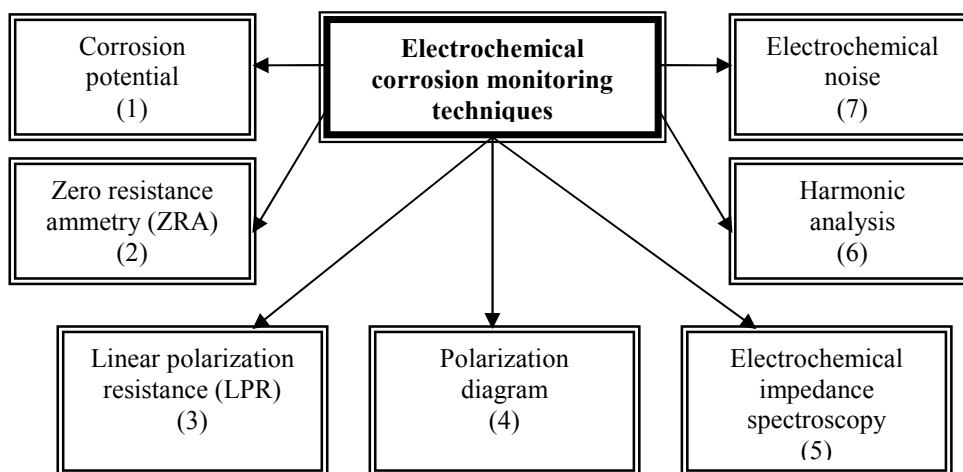
Electrochemical corrosion tests rely on electrochemical theory and electrochemical corrosion measurements to characterize corrosion damage and, where possible, estimate corrosion rates. Fundamentally, two types of electrochemical measurements can be made:

1. Applying external current to generate electrochemical data away from the free corrosion potential. These tests generally explore the relationship between electrochemical potential and current.
2. Electrochemical measurements at the free corrosion potential, without the application of an external current

#### **Electrochemical Techniques**

Electrochemical techniques rely on electrochemical corrosion theory and the measurement of electrochemical potentials and/or currents to monitor corrosion damage. The electrochemical potential is fundamentally related to thermodynamics of corrosion reactions, while currents are related to reaction kinetics (rate of corrosion). The relationship between electrochemical potential and current is important in several electrochemical

corrosion monitoring techniques. These range from simple to highly complex techniques and include the following (as in figure 1):



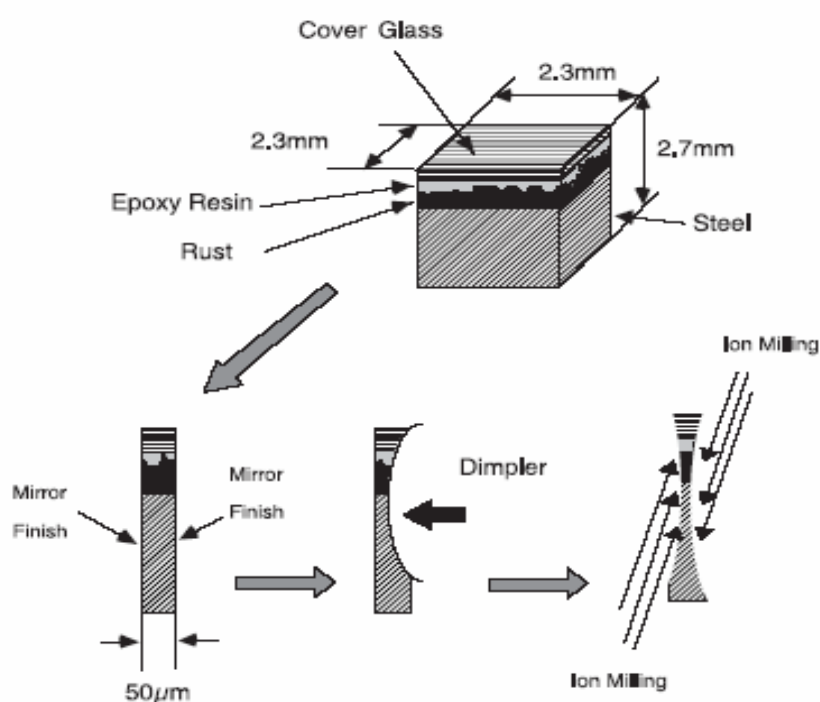
*Fig. 1. Classification of electrochemical corrosion monitoring techniques in order of increasing complexity*

**Electron microscopy** studies, e.g. scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM) and scanning tunnelling microscopy (STM) are used for characterization of corrosion products leading to identification of the cause of corrosion and for the determination of thickness and nature of the surface layers and coating and also for identification of the nature of fracture, identification of extraneous elements, etc. For instance, TEM and ED are used to determine the components of rust and in-depth distribution of rusts on steels exposed to atmosphere [5].

TEM analysis requires a special preparation of specimens using ion-milling method. It means that specimens for TEM are prepared as follows: a cross-section of resin-embedded specimen is sliced as thin as possible, and both sides of cross-sections of rust layer are polished down to 50  $\mu\text{m}$  thick with SiC paper, followed by rinsing in distilled water and methanol. Then the thick specimen is mechanically polished, followed by ion-milling from both sides. During milling specimens are cooled by liquid nitrogen. In Fig. 2 the process of TEM specimen preparation is shown [5].

**X-ray diffraction (XRD)** represents the method of choice for the analysis of corrosion products, as it is the only analysis method that readily provides information about the phase-composition of solid materials. For instance, a mixture of  $\text{Fe}_3\text{O}_4$  (magnetite),  $\text{FeO}(\text{OH})$  (goethite) and  $\text{Fe}_5\text{O}_7(\text{OH})_x4\text{H}_2\text{O}$  (ferrihydrite) can be identified and quantified as such, while other analysis methods will only reveal that the corrosion product is Fe-based.

Furthermore, XRD can readily distinguish between different modifications of phases that have the same chemical formula. Goethite, lepidocrocite, feroxyhyte and akaganeite can be told apart, even though they all have the chemical formula  $\text{FeO}(\text{OH})$  [6].



**Fig. 2.** Schematic illustration of specimen preparation process for TEM observation.

The identification of phase compositions (as opposed to elemental compositions) is crucial for the understanding of corrosion processes [7]. Different phases build under different conditions and in different environments. Information about the chemical phases is not only helpful to explain the corrosion process, but can help to locate the origin of corrosion in a facility and, at the same time, provide solutions to the problem. For instance, the origin of corrosive scale material in the pipe system of a power plant can be narrowed down, if the corrosive material was identified by XRD as a phase that only builds above a certain temperature and at a specific pH. The process settings of the respective facility section can then be adjusted accordingly to suppress the buildup of the corrosive scale material.

Utilizing microprobe techniques ( $\mu\text{XRD}$  and  $\mu\text{PIXE}$  – Proton induced X-ray emission) it may be obtain local composition and structural information from different iron/steel constructions and its protective scale [7].

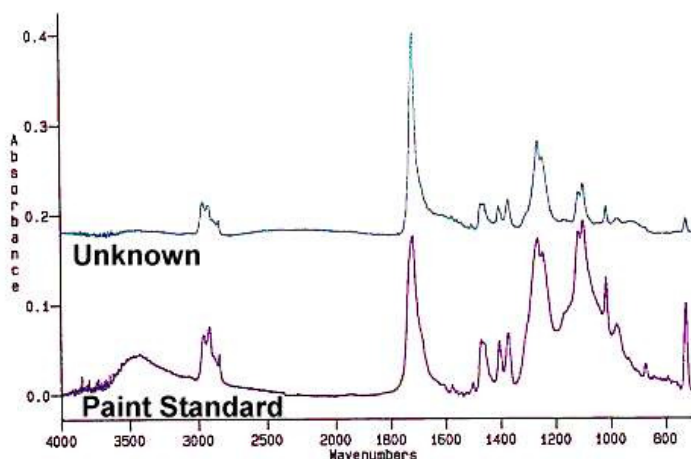
XRD and SEM analysis are used in order to identify the various elements that make up the layer of rust, which produced on steel exposed to different atmosphere [8].

**Fourier Transform Infrared Spectroscopy (FTIR)** is a powerful tool for identifying types of chemical bonds in a molecule by producing an infrared absorption spectrum that is like a molecular "fingerprint".

FTIR is most useful for identifying chemicals that are either organic or inorganic. It can be utilized to quantify some components of an unknown mixture. It can be applied to the analysis of solids, liquids, and gasses. The term Fourier Transform Infrared Spectroscopy (FTIR) refers to a recent development in the manner in which the data is collected and converted from an interference pattern to a spectrum. Today's computerized FTIR instruments make them faster and more sensitive than the older dispersive instruments.

Absorption bands in the range of 4000 - 1500 wave numbers are typically due to functional groups (e.g. -OH, C=O, N-H, CH<sub>3</sub>, etc.) [9]. The region between 1500 - 400 wave numbers is referred to as the fingerprint region [9]. Absorption bands in this region are generally due to intra-molecular phenomena, and are highly specific for each material [10]. The specificity of these bands allow computerized data searches to be performed against reference libraries to identify a material.

In Fig. 3 FTIR spectra for paint analysis is shown.



**Fig. 3.** FTIR spectra for paint analysis.

FTIR can be used to identify chemicals from spills, paints, polymers, coatings, drugs, and contaminants. FTIR is perhaps the most powerful tool for identifying types of chemical bonds (functional groups). The wavelength of light absorbed is characteristic of the chemical bond as can be seen in the annotated spectrum.

The unknown IR absorption spectrum is compared either with standard spectra in computer databases or a spectrum obtained from a known material to determine the identity of the material being analyzed [10]. Matches identify the polymer or other organic constituent(s) in the sample.

FTIR spectroscopy is also suitable for fundamental biofilm research, as well as for monitoring biofilm formation on surfaces, including reflecting surfaces like metals, which become especially corroded in the presence of natural waters in industrial service waters containing microorganisms [11].

It is a perfect tool to characterize and locate deterioration products and bacteria associated with corrosion occurring on metal coupons.

**Raman spectroscopy** allows the measurement of the wavelength and intensity of inelastically scattered light from molecules. The Raman scattered light occurs at wavelengths that are shifted from the incident light by the energies of molecular vibrations.

The mechanism of Raman scattering is different from that of infrared absorption, and Raman and IR spectra provide complementary information [10]. Typical applications are in structure determination, multi component qualitative analysis, and quantitative analysis. The Raman scattering transition moment is:

$$R = \langle X_i | a | X_j \rangle \quad (1)$$

where  $X_i$  and  $X_j$  are the initial and final states, respectively, and  $a$  is the polarizability of the molecule:

$$a = a_0 + (r-r_e)(da/dr) + \dots \text{higher terms} \quad (2)$$

where  $r$  is the distance between atoms and  $a_0$  is the polarizability at the equilibrium bond length,  $r_e$ .

Polarizability can be defined as the ease of which an electron cloud can be distorted by an external electric field. Since  $a_0$  is a constant and  $\langle X_i | X_j \rangle = 0$ , value of  $R$  simplifies to:

$$R = \langle X_i | (r-r_e)(da/dr) | X_j \rangle \quad (3)$$

The result is that there must be a change in polarizability during the vibration for that vibration to inelastically scatter radiation.

The polarizability depends on how tightly the electrons are bound to the nuclei. In the symmetric stretch the strength of electron binding is different between the minimum and maximum internuclear distances. Therefore the polarizability changes during the vibration and this vibrational mode scatters Raman light (the vibration is Raman active).

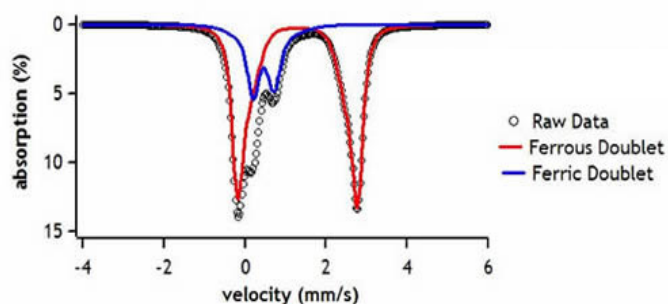
In the asymmetric stretch the electrons are more easily polarized in the bond that expands but are less easily polarized in the bond that compresses. There is no overall change in polarizability and the asymmetric stretch is Raman inactive.

Raman spectroscopy is an effective technique for in situ identification of the layered corrosion products and the detection of water films formed on metal surfaces [4]. A combination of Raman spectroscopy and electrochemical impedance spectroscopy can be used to monitor atmospheric corrosion [4].

**Mössbauer spectroscopy** is a versatile technique that can be used in many areas of science in order to obtain information [10]. It can give very precise information about the chemical, structural, magnetic and time-dependent properties of corrosion products.

One of the most suitable methods in analyzing and characterizing the steel corrosion products is the Mössbauer spectroscopy. Green rust is a corrosion product that is easily detected with this method. In Fig. 4 Mössbauer spectra of carbonate green rust is shown [12, 13].

Aspects on the necessary conditions of a corrosion investigation procedure may be obtained by consulting the standardized methods and techniques corrosion specific.



**Fig. 4** Mössbauer spectra for carbonate green rust

## Conclusions

Gravimetric and electrochemical methods are used to determine the metals/alloys corrosion rate and to characterize the corrosion damage.

Microscopy and spectroscopy studies are used for characterization and determination of thickness and nature of the corrosion products.

The choice of the most appropriate method for metal corrosion studying depends on the corrosion process, the ultimate goal and the place of the experiment.

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