

MODERN THEORETICAL AND PRACTICAL PROTECTION METHODS OF METALLIC STRUCTURES AGAINST THE EFFECTS OF CORROSION

Gh.C.Ionescu ^a, G.L.Ionescu ^{a*}, Gabriela Elena Badea ^b, Liana Marin ^c

^a University of Oradea, Faculty of Construction, Cadastre and Architecture, Department of Constructions, Oradea, Bihor, Romania; E-mails: gheionescu@gmail.com, * lucian.ionescu1985@yahoo.com

^b University of Oradea, Faculty of Informatics and Sciences, Oradea, Bihor, Romania; E-mail: gbadea@uoradea.ro

^c Linde GmbH, Germany; E-mail: liana.marin@linde.com

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ABSTRACT:

The problems of corrosion and anti-corrosion protection are currently an important area for preventing economic losses and combating environmental pollution. Corrosion-related problems are present in all economic fields, including machine construction, shipbuilding and port construction, chemistry and petrochemicals, metallurgy, water and gas supply systems, energy production systems, transports, etc. Corrosion is a complex process that depends on many factors, related to the variety of technical metal materials and technological environments. This paper can be considered a mini-review that contains some general theoretical aspects related to the corrosion of metals and some case studies from the specialized literature of the last five years, in the field of various technical and industrial constructions based on metal structures.

1. INTRODUCTION

Corrosion means the deterioration or transformation of metallic materials under the action of the surrounding environment. The visible effect of corrosion, in the case of iron and ferrous alloys, for example, is the appearance of "rust" consisting of hydrated iron oxides; although non-ferrous metals also corrode, the effect is not always noticed because the corrosion products are not coloured or soluble. Practically corrosion includes both deliberate and profitable transformations and spontaneous and unwanted deterioration (Varga, 2019).

The damaging effect of corrosion is supported by estimates of the damage caused, which converge towards 10-15% of the world production of metals direct losses. However, the real damages are much higher because to the direct losses must be added the indirect losses determined by loss of production, loss of capacity, contamination of products, especially in the chemical, pharmaceutical and food industry, as well as the loss of health or life, through the explosion or unforeseen damage to chemical equipment or transportation - planes, trains, cars and many others (Badea, 2022a).

The rapid dissolution of iron, in dilute solutions of nitric acid, represents a destructive transformation. If the concentration of nitric acid exceeds 65%, the reaction takes place only in the first moments, after which practically the dissolution of iron ceases, due to the formation of an adherent, thin film, invisible to the

naked eye, of iron oxide (Fe_2O_3). Magnesium, zinc, or aluminium are deliberately sacrificed during the cathodic protection of steel constructions. Corrosion reactions are not always detrimental to the metal. The use of many common metals (Al, Zn, Fe, Pb, Cr, Ni, stainless steels) and less common (Ti, Nb, Ta) - reactive metals in certain environments, is possible due to the formation of a reaction product film (film passive), which acts as a barrier between the reactants, significantly reducing the corrosion rate (Badea, 2022a), (Pandey, 2023).

Corrosion systems work on the principle of self-driven systems, i.e., spontaneously, with the difference that the electrical energy resulting from the corrosion process cannot be captured and is lost in the form of heat in the surrounding environment.

2. THE EXPERIMENTAL METHODS

The main electrochemical methods used for rapid corrosion rate measurements, applied to homogeneous corrosion systems, are extrapolation of Tafel slopes (Stern method); polarization resistance method (Stern-Geary method); electrochemical impedance spectroscopy (EIS). Other investigation methods can be added to these, such as optical methods, electron microscopy or atomic force microscopy (AFM), gravimetric measurements or chronopotentiometry.

3. RESULTS AND DISCUSSION

3.1 Theoretical Aspects of Metal Corrosion

3.1.1. The Thermodynamics of Corrosion: They define abbreviations and acronyms the first time they are used in the text, even after they have been defined in the abstract. Do not use abbreviations in the title or heads unless they are unavoidable. Any fundamental approach to the phenomenon of corrosion must consider three factors: the metal, the metal/environment interface, and the environment.

There are more than 100 known elements, approximately 80 are metals, each with different physical, mechanical, and chemical properties. Although all can corrode in a given situation, each corrodes differently and probably in a different manner. Moreover, almost half of these metals have been alloyed, forming over 40,000 alloys. In addition to the great diversity of the chemical compositions of metal-based materials, the effects of the heterogeneities associated with a metal or alloy must be considered, such as: atomic (structural) heterogeneities and micro and macroscopic heterogeneities, which will determine the detailed mechanism of the corrosion process.

The environments, in contact with which metals are used, are of great variety, involving both natural environments: the atmosphere (rural, urban, industrial, marine, tropical, etc.); water (drinking, river, sea, mine, etc.); soil (sand, peat, clay, loess, etc.) as well as artificial media: aqueous solutions (acid, alkaline, salt solutions); organic substances and solutions, gases and vapours, metals and molten salts (Badea, 2022a).

The formation and growth of a reaction product film at the metal/medium interface will influence the ionization and dissolution of the metal, the reduction of the non-metal, adsorption.

Most of the metal corrosion processes take place according to an electrochemical mechanism. The only exceptions are the processes of damage to metals under the action of physical or mechanical factors, improperly called corrosion processes. The electrochemical mechanism of metal corrosion emerges from the definition of corrosion as a heterogeneous redox reaction, consisting of the oxidation of the metal and the reduction of the oxidant, which involves the exchange of electrical charges between the metal and the environment, according to equations (1) and (2):



The electrons (ze) released in the anodic reaction are accepted by an oxidant from the environment, for example oxygen or hydrogen ion, which are reduced in the cathodic reaction of the corrosion process:

Depending on the "location" of the partial reactions, three mechanisms of electrochemical corrosion are distinguished: homogeneous corrosion, in which anodes and cathodes cannot be distinguished experimentally, heterogeneous corrosion, in which certain areas of the metal, which can be distinguished experimentally, works predominantly anodic or cathodic. Due to the operation of local corrosion piles, the most widespread causes of uneven and localized corrosion of metallic materials; film corrosion characterizes corrosion systems in which the metal surface is covered with a film of adherent reaction product, oxide, or salt (Badea, 2022a).

For most metals in atmospheric conditions, the metal state is thermodynamically unstable. The tendency of metals to pass into an ionic state (corrosion) differs greatly from one metal to another and can be energetically characterized by the variation of the free enthalpy ΔG , which accompanies the process. An electrochemical process takes place spontaneously, if the free enthalpy variation acquires negative values, i.e.:

$$\Delta G = -zFE < 0 \quad (3)$$

In which:

$$E = \varepsilon_c - \varepsilon_a \quad (4)$$

and represents the electromotive force of the pile, the difference of cathodic and anodic potentials, ε , in which the anodic and cathodic reaction of the corrosion process is carried out reversibly. Substituting the value of E in the equation above, and setting the condition $\Delta G < 0$, we obtain the thermodynamic condition of corrosion that is met when corrosion occurs.

$$\varepsilon_a < \varepsilon_c \quad (5)$$

A metal corrodes electrochemically when its reversible potential, ε_a , is more electronegative than ε_c , the reversible potential of an oxidizing agent in solution.

The stability of the metal and its various oxidation products are generally dependent on pH and potential. The graphic representation of the balance between metal, ion, and oxide, in potential-pH diagrams, under isothermal conditions, constitutes the so-called Pourbaix diagrams or thermodynamic stability diagrams (Fig.1). They provide thermodynamic data on the corrosion phenomenon. Thus, the diagram is divided into three domains: - the corrosion domain (C) - the iron corrodes, - the immunity domain (I) - the iron is thermodynamically stable, - the passivity domain (P) - where ionization of the metal is thermodynamically possible but is kinetically inhibited by the corrosion products -oxides, hydroxides, formed on its surface, making the metal resistant to corrosion.

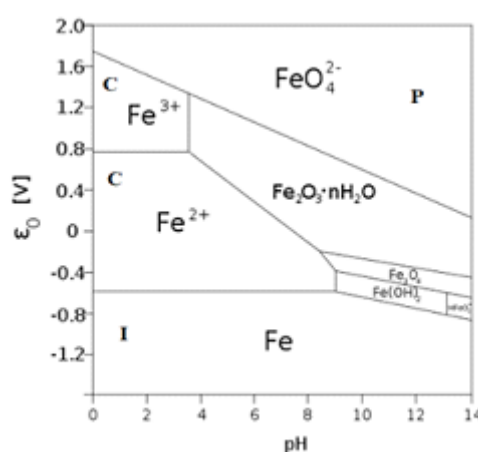


Fig.1. Potential-pH thermodynamic equilibrium diagram of the Fe/H₂O system, under standard conditions (T= 298K, p=1 atm)

3.1.2. Corrosion Kinetics: In practice, the evaluation from the thermodynamic point of view is not sufficient for the evaluation of corrosion processes. Corrosion is the result of the

simultaneous development and at the same speed, expressed by current density, $i=I/S$, of the two partial electrochemical reactions: ionization of the metal and reduction of the oxidant (depolarizer) from the environment-equations (1) and (2).

Fig.2 shows the simplified corrosion diagram of a homogeneous metal in an acid solution (Badea, 2022a). On the pure metal immersed in an acid solution, a mixed potential, ϵ_{cor} , is established, constant in time, at which the oxidation of the metal and the reduction of the oxidant (depolarizer) occur at the same rate. Expressed by the equality between the anodic current density, i_a , and cathodic current density, i_c , and which represents the corrosion current density, i_{cor} :

$$i_{cor} = i_a = |i_c| \text{ module} \quad (6)$$

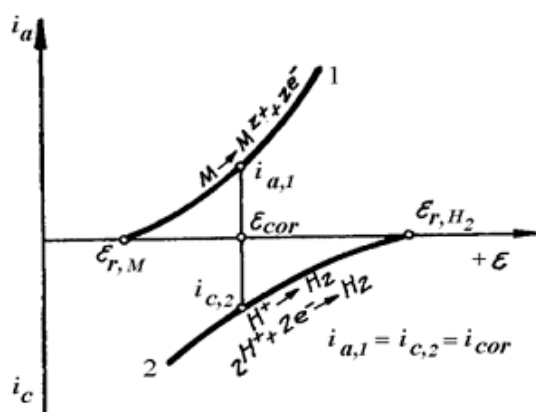


Fig.2. Simplified corrosion diagram of the metal/acid solution system: 1 - the anodic polarization curve of the metal, 2 - the cathodic polarization curve of H^+ ions

3.2 Practical Aspects of Metal Structure Corrosion

In this chapter, various aspects of the corrosion of metals or metal structures from different industrial constructions will be presented, as they can be found in the specialized literature in the last five years. These cases come to emphasize the diversity of corrosion factors and conditions and to draw attention to the fact that for each case there is a specific solution, the result of corrosion studies and anti-corrosion protection.

In the past five years, a multitude of books, reviews, and research articles have come to highlight the fact that metals, more so than other materials, are the foundation of any construction (Pandey, 2023), (Varga, 2019). Additionally, the process of discovering the appropriate material that can withstand a particular metal structure for an extended period is an essential component of engineering. Concrete, steel, brick, wood, glass, and other materials are just some of the diverse types of building components that are typically used in construction projects.

When designing a building or structure, the planning staffs is responsible for deter-mining which kinds of materials will be the most appropriate given the design and the in-tended use of the structure. The primary construction material that is used in most commercial and industrial buildings is either structural steel or aluminium and reinforced concrete (Heidenreich, 2019). These materials are used most frequently. The impact of

corrosion on some steel that are used in prestressed concrete is discussed to gain an understanding of the reasons for corrosion of bar as well as its affect on bond strength and the structural performance of normal and prestressed concrete (Bhagwat, 2022). The purpose was to understand the state of the art and to present the reasons for corrosion of bar. One of the most important aspects of building new transportation infrastructure is the construction of bridges. Main research progress in China and other countries identifies important aspects to take into consideration. These include the following: bridge structure, concrete bridge and high-performance materials, steel bridges, analysis theories, bridge disaster prevention and mitigation, monitoring and detection of steel bridge, and durability of the concrete bridge under the complex environmental conditions. Also displayed were emerging technologies for bridges, such as bridge assessment and reinforcement, as well as intelligent construction for safe and efficient operation (Zhao, 2022). One of the most significant variables that reduce the longevity of bridge structures is the deterioration of traditional mechanical expansion joints in simply supported spans. To gain a deeper comprehension of the structural behaviour of proposed FRP-reinforced ECC link slabs in bridge decks, a number of ECC link slabs in full-scale bridge decks were built and subjected to monotonic cyclic loadings in a sequence of tests. The results of these tests were analysed. The functionality of the link slab was dependent on the weight as well as the development of cracks (Zhang, 2023a).

Studies on the shape defects, mechanical characteristics, and corrosion resistivity of steel/aluminium double-layered blanks that were generated through the flexible roll-forming process were carried out (Woo, 2020). The formation of fatigue cracks, which are caused by corrosion holes in a variety of metal structures, ultimately results in a reduction in fatigue life. Experimentation and numerical analysis are used to investigate the impacts of primary and secondary pits on the failure mechanism and the stress concentration factor (Li, 2020). A steel surface was investigated in saline spray environment to find a random field model for corrosion depth. The distribution of corrosion depth was found to be characterized by a random field model of a cosine trigonometric function, using an element analysis method (Deliang, 2021).

In another study (Zhang, 2020b), researchers investigated the impacts that corrosion and different levels of prestressing force had on the flexural capacity, failure modes, and interfacial stress of steel beams that had been strengthened by carbon fibber reinforced polymer (CFRP). Grids for the transportation of water in cities are extremely complicated systems that must contend with the issue of maximizing energy efficiency.

In heterogeneous systems, corrosion is caused by various physical and chemical irregularities, such as the chemical composition of water and soil, the character of the metal, or the technological parameters pressure and temperature. Monitoring the specific conditions in any environment, but particularly in a water urban grid, necessitates the use of automation, management, and sensors in some form or another (Simo, 2022).

Studies of statistical data analysis or the number of failures represents the basis for a model of reliability and evaluation to limit or eradicate the corrosion phenomena and to increase the energy efficiency of the water urban pipelines (Ionescu, 2019). Studies of statistical data analysis or the number of failures represents the basis for a model of reliability and evaluation.

Corrosion inhibitors, which can come in the form of amino acids, pharmaceuticals, various minerals and plant products, and even rare earth elements, could be used to prevent general and local corrosion, such as pitting. This could be accomplished by preventing pitting. The issue of selecting the appropriate criteria for corrosion inhibitors is one that is essential (Arya, 2022). For this reason, protecting the metal surface of steel requires strategies that are non-toxic, cost-effective, and environmentally friendly. The electrochemical impedance spectroscopy methodology was used to investigate the anticorrosion coating performance of chitosan on carbon steel in chloride solutions (Maior, 2022).

It is necessary for the welded hollow spherical joints (WHSJ) to corrode, which poses a potential risk to the structural integrity. To determine the failure pressure of corroded WHSJ using finite element analyses, some authors (Chen, 2021a) conduct an evaluation of the precision of quality inspection procedures that are typically used by spatial grid structures. (FEA). The findings have the potential to serve as a basis for the prediction and assessment of the residual bearing capacity of space grid structures using WHSJ. Corrosion issues are caused by chloride ions in all equipment that comes into contact with seawater. When it comes to the piping and other pieces of equipment used in the oil and gas business, a significant number of marine and offshore structures make use of various kinds of stainless steel (Patel, 2023). Some austenitic steels were investigated for pitting susceptibility in seawater immersion test, in order to determine if they are suitable as marine offshore structure materials. These tests are carried out in an environment containing chloride ions (Cl^-), which are well known as initiators of pitting corrosion by destroying the passive layer (Patel, 2023). Experiments using potentiostatic steady state voltammetry and electrochemical impedance spectroscopy were carried out to investigate the effectiveness of employing stainless steel in an electrolysis cell as working electrodes for the purpose of extracting hydrogen from seawater (Badea, 2009b), (Cojocaru, 2009), (Hora, 2022), (Badea, 2022c). On the kinetics parameters, such as exchange current density and charge transfer coefficient, the impact of temperature (Badea, 2009b) and pH (Cojocaru, 2009) was evaluated. Corrosion of rebar brought on by chloride exposure is the primary source of damage in reinforced concrete structures (RCS). In addition to this, the impact that concrete's electrical resistance has on macrocell currents in solution and in concrete, as well as the limiting effect of the cathode/anode surface (Cs/As) ratio, was investigated (Lliso-Ferrando, 2023). The rate of corrosion drops below a critical level when the temperature is increased, provided that the steel strands in the reactive powder concrete are present. The pH meter, ion chromatography, mercury intrusion porosimetry (MIP), and electrochemical methods were utilized throughout the course of the experiments (Yang, 2020).

It is very challenging to construct tunnels through the high-content salt rock stratum because the stratum is exceedingly water-soluble, corrosive, and expansive. Additionally, the stratum has a high-water solubility. During construction, the China-Laos cross-border railway friendship tunnel, which travels through a high-content salt rock stratum, was subjected to exceptionally severe damage. Investigating the processes by which the salt rock stratum tunnels deteriorate over time is essential to assuring that the tunnel will continue to be useful for a very long time. In this study, a comprehensive method system was used to determine the mechanisms by which the tunnels are damaged in the high-content salt rock stratum. This

included on-site exploration, laboratory tests, and theoretical analysis (Zhou, 2021).

The knowledge gap has been filled by several studies that were directed toward numerous engineering fields. These studies examined the correlation between the prevention of corrosion and the rust removal process in a variety of steel structures (Gowri, 2021). These steel structures were made of mild steel, carbon steel, weathering steel, and stainless steel. It has been suggested that design and calculation methodologies for corrosion-resistant steel structures should be developed. To evaluate the tensile behaviour of a corroded specimen over the course of time, non-linear finite element methods (F.E.M.) are also conducted (Kim, 2022).

A goal-oriented planning activity for the creation of products, processes, and systems with intended functions through the use of specifications is an example of structural design. Structural design can refer to the design of materials used in construction or other structures used in civil engineering. In the field of civil engineering, the term "structural design" refers to the process of constructing buildings and infrastructures with primary qualities including safety, resilience, serviceability, and sustainability (Ming, 2022). A unified strength-durability design theory is suggested as an approach to the description and development of any civil infrastructure (Ming, 2022). This proposed theory takes an interdisciplinary and holistic approach to the problem, and it includes all processes that are directly involved in the life cycle of the infrastructure. The fields of civil engineering, industrial engineering, and mining engineering all make extensive use of wire ropes. When working with wire rope, protecting human life has always been a primary concern for everyone involved. Fretting behaviour is influenced by several parameters, including the material of the wire rope, its tensile strength, the lubrication, and coating material, as well as environmental variables such as the operating temperature and the presence of corrosive medium (Kumar, 2020).

In the field of metal corrosion, microorganism activity often encounters the weathering process. Steel and other building components face a significant obstacle in the form of MIC, which stands for "microbially induced corrosion". In the presence of phosphate, which is known to act as a corrosion inhibitor in metals, research conducted in Canada came to the conclusion that acidophilic heterotrophic microbes form a biofilm by outgrowing and covering acidophilic chemoautotrophs (Kalin-Seidenfaden, 2022). This led to the formation of the biofilm. Considering the need to reduce CO₂ emissions, it is essential to increase production of environmentally friendly cements, which should include alkali-activated materials (AAMs). AAMs are made by exposing precursors to an alkaline solution, which is a potentially corrosive environment. These precursors have large concentrations of aluminium, silica, and calcium. According to the findings of an analysis on AAMs, low-calcium AAMs demonstrate superior performance in terms of their ability to maintain their freshness and longevity (França, 2022).

Collaborations between businesses and educational institutions, as well as the exchange of information and expertise, provide an essential route to creativity. Using dual-layer networks, which are comprised of both organizations and subjects, it is possible to comprehend and manage corrosion, as well as any other problematic natural phenomenon. The feasibility of the methodology is illustrated by a case study that focuses on

university-industry collaborations in the information and communications technology sector (Chen, 2022b).

In order to avoid or limit the problems caused by corrosion, anti-corrosion protection is used, which can be achieved through the following methods: - choosing the construction material and its mechanical, thermal or chemical treatment; coatings with metal or non-metal protective layers; treatment of the aggressive environment: pH variation, removal of gases that intensify corrosion, use of corrosion inhibitors; electrochemical protection methods: anodic protection and cathodic protection. The complexity of corrosion processes makes it necessary in many cases to combine protection methods.

4. CONCLUSIONS

Due to the very numerous technological environments and the variety of metal based materials, each corrosion system presents a particular behaviour, in which laboratory and technological experience becomes a very important guide in solving corrosion problems.

The choice of the protection method is made taking into account the maximum efficiency, right from the design phase, therefore the choice of the metal material for a certain metal construction, which works in a specific environment, is practically the most important anti-corrosive measure, which can ensure the sustainability of the project on long term.

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