

Corrosion. Types. Prevention

Corrosión. Tipos. Prevención



 Francisco Martínez-Pérez*

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¹Universidad Tecnológica de La Habana-CUJAE, Centro de Estudios de Ingeniería de Mantenimiento, Marianao, La Habana, Cuba.

ABSTRACT: Corrosion is defined as the degradation of materials as a consequence of electrochemical attack. In general, it could be understood as the general tendency of materials to search for its most stable form or the one with the least internal energy. The velocity of corrosion will depend on temperature, on the characteristics of the fluid in contact with and on the properties of the material. Nonmetallic materials also suffer corrosion by different mechanisms. In the present work, corrosion processes in metals, ceramic materials and polymers are characterized. Different types of corrosion, based in modern form of its classification, are explained and, in each case, the main ways of occurrence are updated. The acting forms for prevention are also explained, including information on cathode prevention. Finally, the economic and social consequences due to corrosion are shown.

Keywords: Material, Electrochemical Attack, Intern Energy, Properties of the Metals.

RESUMEN: La corrosión se define como el deterioro de un material a consecuencia de un ataque electroquímico por su entorno. De manera más general, puede entenderse como la tendencia general que tienen los materiales a buscar su forma más estable o de menor energía interna. Siempre que la corrosión esté originada por una reacción electroquímica, la velocidad a la que tiene lugar dependerá en alguna medida de la temperatura, de las características del fluido en contacto con el metal y de las propiedades de los metales en cuestión. Otros materiales no metálicos también sufren corrosión mediante otros mecanismos. En el presente trabajo se caracteriza el proceso corrosivo tanto en metales como en cerámicos y materiales poliméricos. Se explican los diferentes tipos de corrosión basado en las tendencias modernas de su clasificación; en cada caso se actualizan las vías principales de ocurrencia. Se explican las formas actuantes para su prevención. Se incluye información sobre la prevención catódica. Finalmente se destacan las consecuencias económicas y sociales de este proceso.

Palabras clave: material, ataque electroquímico, energía interna, propiedades de los metales.

INTRODUCTION

Corrosion is defined as deterioration of materials as a consequence of electrochemical attack by the environment. In a general form, it could be understood as the general tendency of materials to reach its most stable form or the one with less free energy. Always, when corrosion is due to a chemical reaction (oxidation), the velocity at which it takes place will depend, in some way, on temperature, salinity of the contact fluid with metal and on the material properties. Other nonmetallic materials also suffer corrosion but by other mechanisms (Martínez, 2016).

On chemical reaction (ox reduction) three factors will act:

- Manufactured element
- Environment
- Water

On electrochemical reaction, the most known factors are chemical reaction of metals caused by air, as rust of iron and steels or the formation of green film on cooper and its alloys (bronze, brass).

Corrosion is a wider phenomenon that affects all materials (metals, ceramics, polymers) and all environments (aquatic, atmosphere, high temperatures, etc.). It is an important industrial problem as it can cause accidents (element fractures) and it represents an important cost, as it is calculated that, every few seconds, 5 tons of steels all over the world are dissolved. It is invisible in each element but, multiplied by the steel quantities in the world, it represents an important number (García, 2011; 2012).

Corrosion is a field of materials science that includes knowledge of chemistry and physics (physic-chemistry).

*Author for correspondence: Dr.C. Francisco Martínez Pérez, e-mail: fmartinezperez2013@gmail.com

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Corrosion is due to a massive electric flux generated by the chemical differences between implied elements. Corrosion is an electrochemical phenomenon that occurs when a flow of electrons is established due to a potential difference between one point and other. When from a chemical species electrons migrate to other species, the species that donates electrons is named anode (oxidation occur) and the chemical species that receives them is called cathode (occur reduction).

An electrochemical differential must exist as a condition for this reaction. If one parts is separated, it is called half-electrochemical part and if both half parts are unified, an electrochemical part is formed. Each half part is associated to a potential of reduction, which was known as oxidation potential long ago. The metal or chemical species that exhibits a more positive reduction potential will proceed as a reduction and, vice verse, the one that exhibits a more negative reduction potential will proceed as an oxidation (Callister, 2000; Callister & Rethwisch, 2018; 2019; Callister Jr & Rethwisch, 2020). In Figure 1, the reduction potential of different metals elements are shown.

Iron and Iron Alloys

Pure iron, with a low carbon content or low ally content has low resistance to oxidation and to corrosion and, in general, it requires the application of protective films or cathode protection to increase the resistance to corrosion even if the conditions are not severe. However, low-carbon steel is passive in the presence of alkaline solutions with high pH. Low-alloy steel corrodes on saline solutions with chloride content.

Alloy steels with Cr, formed the so called ferrite steels, as its structure is of ferrite; they are employed on petroleum and gas industries and some chemical industries. Austenitic steels, with Cr- Ni, of austenitic structure, depending on their composition, that has diverse forms, are employed on chemical and marine atmospheres, as well as on valves and pump shafts. Some of them are resistant in food and electrical industries, in heat interchange and turbines blades. (Martínez, 2009; 2016).

Cooper and Cooper Alloys

Cooper alloys have low tendency to corrosion. Strong acids attack cooper alloys what could be reduced with additions of elements such as antimony. Commercial pure cooper (99%) has excellent anticorrosive conditions in soils. Brass, mixture of cooper and zinc, until 40% of zinc, suffers an important reduction compared to pure cooper. Bronzes, more resistant to corrosion, are cooper alloys with nickel content and the addition of other elements such as Si and Mn. They are employed on food and

➤ serie fem estándar

Tabla 18.1 La serie fem estándar

Reacción del electrodo	Potencial de electrodo estándar, V ⁰ (V)
$\text{Au}^{3+} + 3e^- \rightarrow \text{Au}$	+1.420
$\text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O}$	+1.229
$\text{Pt}^{2+} + 2e^- \rightarrow \text{Pt}$	+1.2
$\text{Ag}^+ + e^- \rightarrow \text{Ag}$	+0.800
$\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+}$	+0.771
$\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4(\text{OH}^-)$	+0.401
$\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$	+0.340
$2\text{H}^+ + 2e^- \rightarrow \text{H}_2$	0.000
$\text{Pb}^{2+} + 2e^- \rightarrow \text{Pb}$	-0.126
$\text{Sn}^{2+} + 2e^- \rightarrow \text{Sn}$	-0.136
$\text{Ni}^{2+} + 2e^- \rightarrow \text{Ni}$	-0.250
$\text{Co}^{2+} + 2e^- \rightarrow \text{Co}$	-0.277
$\text{Cd}^{2+} + 2e^- \rightarrow \text{Cd}$	-0.403
$\text{Fe}^{2+} + 2e^- \rightarrow \text{Fe}$	-0.440
$\text{Cr}^{3+} + 3e^- \rightarrow \text{Cr}$	-0.744
$\text{Zn}^{2+} + 2e^- \rightarrow \text{Zn}$	-0.763
$\text{Al}^{3+} + 3e^- \rightarrow \text{Al}$	-1.662
$\text{Mg}^{2+} + 2e^- \rightarrow \text{Mg}$	-2.363
$\text{Na}^+ + e^- \rightarrow \text{Na}$	-2.714
$\text{K}^+ + e^- \rightarrow \text{K}$	-2.924

Inactividad creciente (catódicos) ↑
↓ Actividad creciente (anódicos)

FIGURE 1. Reduction potential of different metallic elements.

chemical industries, on marine conditions and kitchen elements (Askeland, 1998; Askeland et al., 2017).

Aluminum and its Alloys

Aluminum alloys owe their resistance to ambient attack to the rapid formation of an oxide film. They are very employed on houses (doors and windows), in kitchen and on chemical industry. Under neutral pH condition, aluminum alloys may suffer attack by the presence of chlorides or pure chloride. Some alloy elements added to aluminum alloys (Zn, Cu, Mg, Mn) affect in an important way the corrosion resistance of these alloys.

Ceramic Materials

Ceramic materials have a wide and diverse application in the world. This is due to the wide form of structures and properties that are obtained from the different chemical compositions and obtaining processes. They have application in electric and electronic industries, in metallurgical processes, in chemical industry and in the processing of glasses. In general, they have great resistance to corrosion.

Corrosion of these materials occurred by a simple chemical dissolution and no by electrochemical process as in metals. Refractory materials must resist not only high temperatures but also scoria attack, smelted glasses and salts by long periods (Askeland, 1998; Askeland et al., 2017).

Polymers

Polymeric materials also suffer attack in contact with the environment. For this, degradation is the term used instead of corrosion, as the process is different. Polymeric degradation is a physical chemical process that has a great adverse course. They degrade by swelling and dissolution. The rupture of their covalent links occurs by the action of thermal energy, by chemical reaction and by radiation effect. Many polymers, by the presence of solutes as gasoline,

absorb molecules of solute that are inserted in the polymer molecules, separating, dilating and swelling them. This process will be greater as the structure of the solute and the polymer are more similar. Temperature also influences on it. Polymers have more resistance to corrosion than metals in the presence of acids and basic solutions [5].

DEVELOPMENT

Types of Corrosion. Prevention

The conducting force of corrosion process, as in the majority of metallurgical processes, is the diminishing of the free energy of the system, to reach a more stable structure (Tomashov, 1965; 1971). There are different forms to classify the corrosion types. One of the most common forms is shown in Figure 2, (Jones, 1992; Ashby & Jones, 2011; Jones & Ashby, 2012)..

Uniform attack on great areas of a metallic surface is the most common form of corrosion and it can be humid or dry, electrochemical or chemical; it will be necessary to select construction materials and a form of their protection to control it (like paints). Uniform corrosion is the easiest one to be measured and unexpected failures could be avoided by simple regular inspection.

Homogeneous corrosion occurs when the material wears in equal form, getting thinner progressively, like Zn in dilute sulfuric acid solution and Cu and its alloys in aqueous environment. It is very easy to prevent and to control it. It is a typical form of metals oxidation at high temperatures, requires of high activation energy and occurs in less magnitude at room temperature (Domínguez et al., 1987).

Heterogeneous corrosion is the widest spread, is very dangerous and difficult to control and is characterized by anode and cathode zones. It is more intense in some places (Domínguez et al., 1987).

Different factors contribute to corrosives processes. In Table 1, some of them are shown.

TABLE 1. Factors that contribute to corrosive processes

Factors that affect Corrosives Processes	
1.	Stress concentration
2.	Rapid change in section
3.	Different materials union
4.	Different phases in the same material
5.	Bad surface quality
6.	Deposition places
7.	Not enough air in some places
8.	Unions with stress concentration
9.	Turbulence
10.	Environment
11.	Bad selection of materials
12.	Bad maintenance

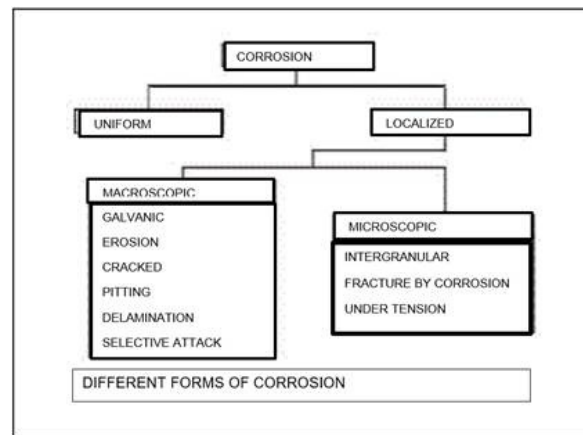


FIGURE 2. Form of classification of corrosion (uniform or localized).

Analyses of Different Types of Corrosion and Their Prevention

Galvanic Corrosion

Galvanic corrosion takes place when two different metals in contact or connected by an electrical conductor are exposed to a conducting solution. In this case, there is a difference in the electrical potential between the two metals and it behaves like a directory force for the establishment of electrical flow through the corrosive agent. In this case, the electrical flow corrodes one of the metals of the pair formed. This type of corrosion will occur by concentration cells. It occurs due to difference of potential on structures, due to difference of concentration of metallic ions or because of the presence of an oxidizing media).

The greater the potential difference between metals, the greater the probability of galvanic corrosion. This type of corrosion only causes the degradation of one metal; the other one does not suffer damage. The corroded metal is named active metal; the other one is called noble metal.

Galvanic corrosion will be recognized by the increase of the attack on the metals junction. It will be controlled by the use of isolation or limiting the use of metal unions when a great potential difference appears on the medium where they work. Other preventive method is to avoid the formation of huge areas of active and noble metals. The most important method is not selecting different materials for the same equipment or if it were necessary, it would be advisable to select metals with close electrical potential, to interpolate isolating materials or cover the active metal to an optimum distance.

It is also recommended to avoid the presence of holes or slots, to avoid threats unions in different metals, to add substances that consume oxygen such as sodium hyposulphite or hydrazine and to employ paints in fluids to avoid death zones that are places that could form deposits of corrosion products. In

Figure 3, galvanic corrosion is shown (Schweitzer, 2010).



FIGURE 3. Galvanic corrosion.

Pitting Corrosion

Pitting corrosion has a form of little holes on a surface that is almost not attacked and pitting may have different forms. The pitting form is responsible of its development, which means that a pitting may be consider as slot formed by itself. Holes, in general, are of little diameter and deep, that may be isolated or joint on rough surfaces on pipes or equipment. It is the most spread form of corrosion in the Caribbean countries.

Pitting corrosion is developed by the presence of aggressive anions or chloride ions. Aggression tends to vary logarithmically with chloride concentration. On this process, when perforation tends to develop, created conditions are so, that perforation tends to continue. The growing of the process also depends on metal composition. This process is more frequent on heat interchangers, pipes and on the bottom of tanks with remnants of cleansing products.

The causes of the appearance of this type of corrosion are the following according to (Denny A. Jones, 1996):

- Presence of metallic inclusions or different alloy phases with different electrical potential.
- Corrosion deposition that difficult oxygen access, that provoke the apparition of concentration cells.
- Rupture of passive places by the appearance of halogen anions Cl^- , Br^- , I^- and ClO^- , ClO_4^- . Among them, Cl^- is the most dangerous. This type of corrosion is more common in passive metals (iron, low-alloy steels, alloy steels, Al and its alloys).

The measures for the prevention of this type of corrosion are:

- Adequate selection for the metals to be used.
- Not to employ passive metals in media with the presence of chloride ions, halogens or seawater.
- Use Cu or cooper alloys such as Monel metal or Cu-Ni.

Pitting corrosion can be appreciated in [Figure 4](#).



FIGURE 4. Pitting corrosion.

Intregranular or Intercrystalline Corrosion

To understand this type of attack, it is necessary to consider that when a metal in foundry is put on a mold, its solidification begin with the formation of random nucleus. Each nucleon grows in an atomic random regular arrange to form what is so called grain or crystal. The atomic arrange and the space between the grains are the same in all crystals of a given metal; nevertheless, due to the random, the atomic plane of atoms close to the grains do not present good coherence and the space between them, with some disorder, is named “grain limit”.

Corrosion generally takes place because the corrosive agent attacks, with preference, the grain limits or a zone near them. These zones have lost a necessary element to poses an adequate corrosion resistance. This phenomena is sensitive to heat; that is why it is a byproduct of heat treatments such as welding or the stress relieving and it may be solved by other heat treatments or by the use of a modified alloy (Cary, 1988; 1989; 2004; Cooke, 2003; Palencia, 2011). The most common case is the corrosion of alloy steels no stabilized.

The measures to prevent this type of corrosion is to establish the maximum homogeneity of the materials utilized. This could be obtained in alloy steels stabilized with Ti or Mo, treated at temperatures in the range of 950-1050°C, cooled in water; also using steels with low carbon content. An example of intergranular corrosion is shown in [Figure 5](#).



FIGURE 5. Intergranular corrosion

Corrosion by Exfoliation or Selective Dissolution

Corrosion by exfoliation is a subsurface corrosion that begins on a clean surface and spread under it and differs from pitting in this aspect: that is laminar. Complete layers of the material are corrode and the attack is known for the scaly formation.

At the end of the attack the appearance is like cards as if some of them in aluminum alloys had been extracted. This mechanism is well known in aluminum alloys and it is stopped by proper alloys and heat treatments.

Selective dissolution corrosion happens when one of the alloy elements is removed. The best-known example is the elimination of zinc on cooper-zinc alloys, what is known as dezincification. This phenomenon produce a porous metal with very low mechanical properties and the prevention is done by producing alloys with no tendency to this process.

Exfoliation is only prevented by a correct selection of the alloy and its heat treatment. On dezincification it is necessary to consider:

- The environment aggression, the no presence of oxygen and the use of cathode protection.
- The use of Cu-Zn alloys where zinc is 15-20 %.
- The addition of low quantities of Sn, As, Sb and P.

In [Figure 6](#), it is possible to appreciate an example of exfoliation.

Corrosion with the Influence of Mechanical Factors

Corrosion due to Erosion

This corrosion occurs when the movement of the corrosive environment over the metallic surface increases the attack velocity due to the mechanical wear. This type of corrosion is called corrosion by erosion.

The relative importance of mechanical wear and corrosion is sometimes difficult to be established and it varies greatly depending on the concrete situation. The erosion mechanism, in general, is attributed to the removal of surface protective layers, such as oxide layers form by air or products of corrosion. The occurrence of erosion corrosion generally has the appearance of pitting not so deep on a smooth surface; the attack may present a directional distribution due to the movement of aggressive agent over the metal surface. This type of corrosion can be observed in [Figure 7](#).

Erosion corrosion develops in condition of high velocity, turbulence and shock. It is frequently observed on pumps, agitators and joints with direction change in pipelines. Liquids with hard solid particles in suspension may equally cause this damage.



FIGURE 6. Exfoliation corrosion in a water treatment plant.

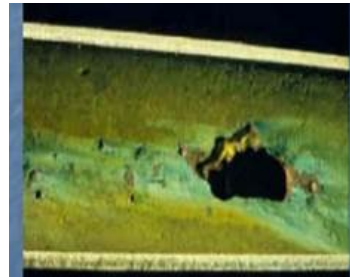


FIGURE 7. Erosion corrosion.

Surface is characterized by directional slots. Fail time are very short and preference is present on soft metals like cooper. They are produced by hot gases with high velocity and hard particles in suspension and by organic systems in movement. This type of corrosion may be avoided by design changes or by more resistant materials.

Corrosion by Wear (Fretting Corrosion)

Corrosion by wear (fretting corrosion) occurs when to metal pieces slid one over the other, causing mechanical wear to one or both pieces and the slid is the result of vibration. This type of corrosion may be attenuated using construction harder materials, by the use of lubrication or increasing vibration to a point that slid is impossible to happen.

Cavitation

It is an especial form of erosion-corrosion. This type of corrosion occurs by the condensation of vapor bubbles on a liquid near to metal surface. It is typical in pipelines, impelling propels and other surfaces where turbulence regimes and high velocity zones are present with low pressure. For carbon steel it happens for velocities $\geq 4,5$ m/s. Bubbles impact against surface and provoke noise and a hammering that destroy locally the surface.

Preventive methods to this type of corrosion are:

- To employ resistant alloys from mechanical point of view with strong adherent protective layers like Cr-Ni steel alloys, aluminum bronzes and Monel metal.
- Avoid the use of current foundry irons.
- Operate rotors and impellent to the maximum possible pressure charge to avoid bubbles formation.

- Avoid turbulence.
- Eliminate suspension solids.
- Employ passive substances such as chromates and dichromate and cathode protection.
- Cover surfaces with rubber, porcelain or special resins.

In [Figures 8](#) and [9](#), it is possible to observe the process development and its consequence.

Under Tension Corrosion

The joint action of a tension stress and a corrosive environment will result on fracture of metallic alloy. The majority of alloys are susceptible to this attack, but by fortune, the number of combination alloys-corrosive that cause this problem are relativity few. Nevertheless, this problem is one of the more serious metallurgical ones.

The efforts that cause fracture come from cold works, welding and heat treatment or others applied externally during the equipment work. Fracture may appear in intergranular or transgranular way that, in some cases, show ramification.

Some of the characteristics of under tension corrosion fracture are:

- A stress tension is required.
- Alloy's metallurgical conditions have great influence.
- Time of exposition is very important.

To avoid under stress corrosion it is necessary to resist the applied stress, relieve tensions by heat treatment or select a more resistant material.

In [Figure 10](#), an example of under stress corrosion can be observed.

Fatigue Corrosion

Corrosion by fatigue is a particular case of under stress corrosion fracture and it appears even with no corrosion environment, under the action of cyclic repetitive stresses. This type of failure is common on structures with continued vibration. It is increased, of course, in the presence of corrosive environments in such a way that the necessary stress to produce fatigue corrosion is reduced, in some cases, to the half of that necessary to produce the failure in dry air.

This corrosion takes place in metallic materials that support simultaneously the action of tension stresses in a specific corrosive environment. In this type of corrosion surfaces suffer less damage but in the interior of the material, scars in intergranular or transgranular form are formed. Its occurrence occurs when stresses are alternatives, and even if the applied stresses are less than the admissible ones. In this case, corrosion is intergranular with ramification. Its

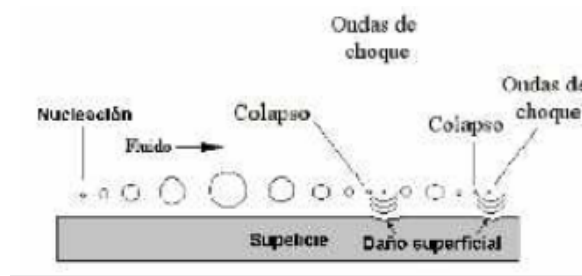


FIGURE 8. Cavitation process.



FIGURE 9. Cavitation damage.



FIGURE 10. Under stress corrosion.

presence appears in carbon steels, on seawater and under the action of combustion products. It is also observed in propellers, steam boilers, pistons and wires.

The most effective preventive method in this corrosion is the cathode protection. Preventing intergranular corrosion, heating treatment to eliminate intern stresses and using inhibitors like hydrazine, sodium sulfite and phosphate solutions are also possible protecting methods. Other effective methods are the following:

- To diminish concentration of chloride ions.
- To utilize inhibitors such as sodium dichromate.
- To utilize cathode protection with zinc, cadmium or the use of protective layers.
- To reduce vibration and cyclic stresses.
- To generate compression stresses on surface by different methods.

In [Figure 11](#), an example of fatigue corrosion is shown.

Principles of Cathode Protection

Considering the electrochemical series of metals, a metal will have anodic character in respect to other one, if the first is over the second in the electrochemical series. That is, for example, iron will be anodic in respect to copper and cathode in respect to zinc. The anodic metal sacrifices in favor to cathode one; that is why this system is so called cathode protection by a sacrifice anode ([Domínguez et al., 1987](#)).

Nevertheless, majority of anodes are produced by foundry or gravitation, some of them are produced by continuous foundry or by extrusion. The foundry method produces the appearance and physical structure of anode and so does its commercialization and behavior. From the point of view of behavior, anodes have to be produced by foundry so as metal solidify without segregations and it should never have strange matter inclusions, blowing nor suction, because if it happens the anode tends to passive or to have physical disintegration. It should never develop passive substances or be obstructed with corrosion products or to obtain hydrogen over tension.

From the technical point of view, an anode should have a series of essential properties such as:

- To have a dissolution potential enough negative to polarize the structure (in iron -0,8 volts).
- To corrode uniformly.
- To have a high electrical performance in A/h kg.
- To be easily acquired and to have the possibility to be founded on different forms and sizes.
- To have a reasonable cost to obtain reasonable protection in amperes/year.

A.S.T.M. NORM B6-46 and USA specification Mil-A 18001 H defined anodes compositions for zinc, magnesium and aluminum alloys.

Social Economic Aspects of Corrosion

First estimation of corrosion costs agrees that they are approximately of 4 % of a country PBI ([Treseder, 1980; 2002](#)).

Corrosion is a phenomenon that can affect practically each material and when it is not controlled or prevented, it may reduce components, equipment and structure efficiency.

Economic losses of corrosion could be classified in direct or indirect ones. Direct losses are related with the necessary cost for structure, equipment, machinery or component repositions that will be unused by corrosion effects.



FIGURE 11. Fatigue corrosion.

Losses due to interruptions, product contamination and losses due to performance, product and over dimensioning can be considered as indirect ones.

It is estimated that the relation between direct and indirect expenses is about 1/6 or 1/10. Besides, it is estimated that 10 to 12% of steel world production is lost each year due to corrosion.

Social and Human Aspects

On this aspects the following could be considered:

- a. Security, so as violent failures may produce fires, explosions and liberation of toxic products and human life losses.
- b. Unhealthy conditions such as contaminations by the equipment corrosion products or products of corrosion itself.
- c. Exhaustion of natural resources such as metals and combustibles used in manufacture.
- d. Appearance, as corrode materials are unpleasant to see.

CONCLUSIONS

Corrosion is an electrochemical process that has as moving force, as in all metallurgical processes, to reach a diminishing of the free energy of the system.

All materials suffer corrosion process; only in polymers the process is named degradation as, in this case, it has a different occurrence mechanism.

There are diverse classification forms for corrosion, the most common describes uniform corrosion (homogenous) and localized corrosion (heterogeneous). In some cases of localized corrosion, mechanical factors influence. In all cases, prevention measures were presented in this revision.

Corrosion produces important social and economic consequences.

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Francisco Martínez Pérez, Dr.C., Profesor Titular, Centro de Estudios de Ingeniería de Mantenimiento, Universidad Tecnológica de La Habana-CUJAE, La Habana, Cuba, Tel.: 78335577, e-mail: fmartinezperez2013@gmail.com ORCID iD: <http://orcid.org/0000-0002-8947-7870>

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