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INTRODUCTION

Scope

'Rust' is the most common effect of a corrosion process. A corrosion could be define as a deteoriation of material either by mechanical, thermal, chemical, electrochemical, microbiological, electrical, or even radiation. Corrosion could be implied not just only on Metallic materials. Almost all of materials are not immune from being corroded. The modules provide a comprehensive explanation about each factor which influence corrosion process.

It is important for an engineer to acknowledge the basic information of corrosion. At the beginning stage of the module, engineer will presented by an introduction phase where all of the adjective covered as in general terms. An introduction chapter consists of: Scope and General Design Considerations. General Design Considerations will divided into sub-chapter which arranged by any topics following: Causes of Corrosion, Corrosion on Science and Engineering, Importance of Corrosion, Risk Management, Material Selection for Corrosion Resistance, and The Influence of People.

Since it is imply not only on many industrial application, but also on everydaily around human activities, knowledge about corrosion is important, especially for an engineer. Lack of knowledge for corrosion could lead to a severe accident which caused many losses and disadvantage. Corrosion had also been proven as a silent danger by many incident experiences. Thus, At the second stage of the modul, it will explain about corrosion in-depth. The explanation of second stage composed from three major part: (I) Corrosion, (II), Corrosion control, and (III) Managing Corrosion.

Finally, all of the information about corrosion that gathered will lead an engineer to the way of how an engineer manage the corrosion itself. The last part of the module will cover the managing corrosion topics which sub-parted into 4 general ways, involving: An inspection, Maintenance, Monitoring, and Corrosion Management.

General Design Considerations

Causes of Corrosion

As in general, all materials or products, plants, constructions and buildings made of such materials are subject to physical wear during use. Thus, an overview of different kinds of wear caused by mechanical, thermal, chemical, electrochemical, microbiological, electrical, and radiation-related impacts represents in Figure 1.

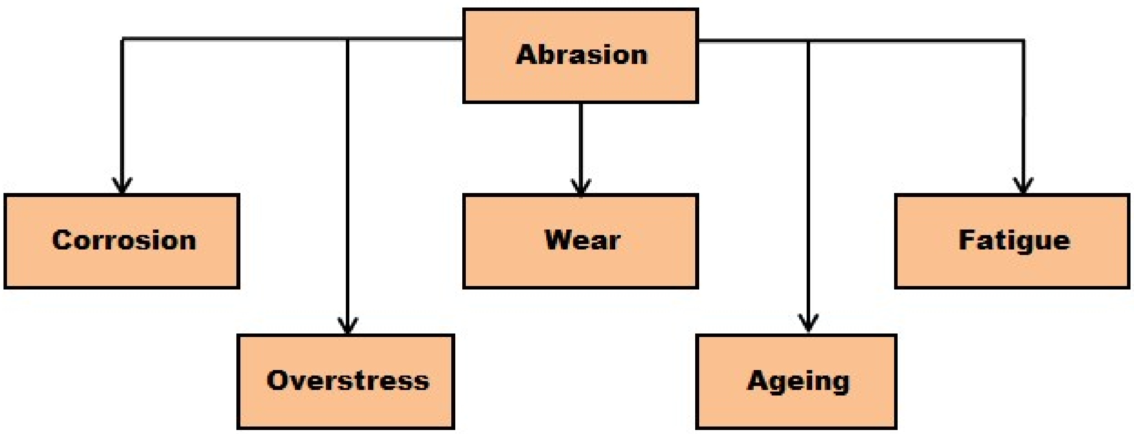
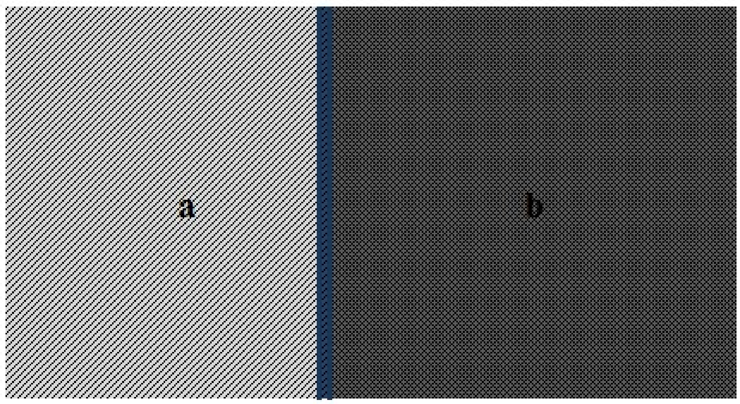


Figure 1. Types of wear of materials.

Nevertheless, all materials which exposed by an environmental effects could impair and destroy their usefulness. Most of the damage in the case of metals is caused by corrosion. The reactions between material and its environment are mainly electrochemical.

Electrochemically, a metal surface is the active state (the anode) in which metal tends to corrode or is being corrode. Whilst the metal passive is in the cathodic state, the state of metal when its behavior is resists corrosion than its position in the emf series would predict. However, a corrosive reaction with the environment could be brought by an erosion of protective coatings (erosive corrosion).

The types of material changes brought about by corrosion are manifold. Since corrosion reactions usually occurred on metal surface, they are termed interfacial processes and could be represented by a phase diagram (Figure 2).



c

Figure 2. Corrosion as phase interface reaction (a: Metal, b: Liquid, Solid, gaseous medium, c: Phase boundary)

A distinction is made between the metal phase, the liquid, gaseous, or solid medium and the phase boundary. The corrosion process takes place at the metal – medium phase boundary and is therefore a heterogeneous reaction in which the structure and condition of the reaction surface play a significant role. The corrosion which usually confined to the metal surface often called the 'general corrosion'.

There are several terms which usually used on the corrosion such as:

- Corrosion system
  A system consisting of one or several metals and such parts of the environment that impact corrosion.

- Corrosion phenomenon.
  Modification in any part of the corrosion system caused by corrosion.

- Corrosion damage.
  Corrosion phenomenon casting the impairment of the metal function, of the environment or of the technical system in which they form a part.

- Corrosion failure.
  Corrosion damage characterized by the complete loss of operational capability of the technical system.

- Corrosion resistance.
  Ability of a metal to maintain operational capability in a given corrosion system.

Major corrosion phenomena could be indicated by several physical form, involving:

- Uniform surface attack.
  A form of corrosion where the metal material is almost uniformly removed from the surface. This form is also the basis for the calculation of the mass loss (g/m2) or the determination of the corrosion rate (μm/y).

- Shallow pit formation.
  A form of corrosion with irregular surface attack performing pits with diameters much larger than their depth.

- Pitting.
  A form of corrosion with crater-shaped or surface-excavating pits or pits resembling pin pricks. The depth of the pitting spots usually exceeds their diameter.

Therefore, it is very difficult to seek a differentiation between shallow pit formation and pitting.

Corrosion is an electrochemical process that involves the passage of electrical currents on a micro or macro scale. The change from the metallic to the combined form achieve by an ‘anodic’ reaction:

$$M \rightarrow M^{+} + e^{-}$$
$$\text{Metal} \rightarrow \text{Soluble salt} + \text{Electron}$$

Electrochemical reaction could be defined as the result of electrical energy passing from negative area to a positive area through an electrolyte medium. The positive and negative electrode areas interchange and shift from one place to another place during the corrosion reaction proceeds.

Therefore, metallic corrosion is essentially an electrochemical process. Four components are necessary to set up an electrochemical cell such as:

- Anode.
  Which the corroding electrode.

- Cathode.
  Which the passive ones, non-corroding electrode.

- The conducting medium (electrolyte).
  The corroding fluid.

- Completion of the electrical circuit.

Cathodic areas can arise in many ways:

- Dissimilar metals.
- Corrosion products.
- Inclusions in the metal, such as slag.
- Less well-aerated areas.
- Areas of differential concentration.
- Differentially strained areas.

Not all metals and their alloys react in a consistent manner when in contact with corrosive fluids. One of the common intermediate reactions of a metal surface is achieved with O_2. O_2 sometimes could be functioned as an electron acceptor and cause cathodic depolarization by removing the 'protective' film of H_2 from the cathodic area.

What usually seen by the engineer about corrosion process is that the process produces a new and less desirable material from the original metal and could result in a loss of function of the component or system. The corrosion product that commonly occurred is what it called 'rust' which forms on the surface of steel or other metal and somehow. The simple reaction that represent the change of the metal form should as follows:

$$\text{Steel} \rightarrow \text{Rust}$$

The term 'Rusting' applies to the corrosion of iron-based alloys with the formation of corrosion products consisting largely of hydrous ferric oxides. Nonferrous metals and alloys corrode, but do not rust.

For the major component of steel, Iron (Fe) at the surface of a component undergoes a number of simple changes. First,

$$Fe \rightarrow Fe^{n+} + n \text{ electrons}$$

The iron atom can lose some electrons and become a positively charged ion. This allows it to bond to other groups of atoms that are negatively charged. The engineer that wet steel rusts to give a variant of iron oxide so the other half of the reaction must involve water (H_2O) and Oxygen (O_2).

$$O_2 + 2H_2O + 4^{e-} \rightarrow 4OH^-$$

Or simplified as

$$2Fe + O_2 + 2H_2O \rightarrow 2Fe(OH)_2$$

$$\text{Iron + Water with } O_2 \text{ dissolved} \rightarrow \text{Iron Hydroxide}$$

Oxygen will dissolves quite readily in water, regarding to an excess, it will reacts with the iron hydroxide.

$$4Fe(OH)_2 + O_2 \rightarrow 2H_2O + 2Fe_2O_3.3H_2O$$

$$\text{Iron hydroxide + Oxygen} \rightarrow \text{Water + Hydrated iron oxide (brown rust)}$$

Not all corrosion is gradual and silent. Many example of serious incident are initiated because of corrosion of critical components, causing personal injury and death. Environmental damage is another danger, oil pipeline leaks, usually take many years to heal.

Corrosion on Science and Engineering

Since corrosion processes are mostly electrochemical, an understanding of electrochemistry is also important. The corrosion scientist studies corrosion mechanisms to improve such as:

- Background (causes) of corrosion.
- Ways to prevent or at least minimize damage caused by corrosion.

On the other hand, the corrosion engineer applies scientific knowledge to control corrosion process. In example: Using cathodic protection on large scale to prevent corrosion of buried pipelines. In addition, the corrosion scientist develops better criteria of cathodic protection. Both viewpoints from corrosion scientist and corrosion engineer will supplement each other in the diagnosis of corrosion damage and in the prescription of remedies.

Importance of Corrosion

It is important that engineers must getting the job done well and safely should take precedence over cost.

- Promote public safety.
- Preserve the environment.
- Decrease the cost of corrosion.

To decrease an economic impact of corrosion, the engineers must aim to reduce material losses as well as the accompanying economic losses, which result from the corrosion of piping, tanks, metal components of machines, ships, bridges, marine structures, and so on.

Economic losses could be classified as:

- Direct losses.
  This term including the costs of replacing corroded structures and machinery or their components such as:
    - Pipelines.
    - Condenser tubes.
    - Metal roofing.
    - Mufflers.
    - Labor cost.

  Direct losses will include the extra cost of using corrosion-resistant metals and alloys instead of carbon steel where the latter has adequate material properties but not sufficient corrosion resistance.

- Indirect losses.
  Indirect losses are difficult to assess, but some survey of typical losses of this kind compels the conclusion that they add several billion dollars to the direct losses already outlined. Some of examples for indirect losses are as follows:

- Shutdown.
- Loss of Product.
- Loss of Efficiency.
- Product Contaminant.
- Overdesign.

In direct losses are essential part of the economic tax imposed by corrosion, although it is difficult to arrive at a reasonable estimate of total losses.

Loss if metal by corrosion is a waste not only of the metal, but also of the energy, water, and also human effort that was used to produce and fabricate the metal structures in the first place. In addition, rebuilding corroded equipment requires further investment of all these resources (metal, water, energy and human).

Results of the study proved that the estimated total annual direct costs of corrosion in the United States during the time of 1999 to 2001 are $276 billion and approximately equals to 3.1 % of the U.S Gross Domestic Product (GDP).

Safety is a critical considerations in the design of equipment. Corrosion could compromised the safety of operating equipment by causing failure such as catastrophic consequences. In the event of loss of health or life through explosion, unpredictable failure of chemical equipment, or wreckage of airplanes, trains, or automobiles through sudden failure by corrosion of critical parts, the indirect losses are still more difficult to assess.

Risk Management

Risk (R) could be described as the probability (P) of an occurrence multiplied by the consequences (C) or:

$$R = P \ x \ C$$

Since the risk of a corrosion-related failure equals the probability that such a failure will take place multiplied by the consequences of that failure. Consequence is typically measured in financial terms which is total cost of a corrosion failure, including the cost of replacement, clean-up, and repair, downtime, and so on.

Any type of failure that achieves with high consequence should be one that seldom occurs. Reversely, failures with low consequence could be tolerated more frequently. Figure 3 is illustrates an approach of risk management.

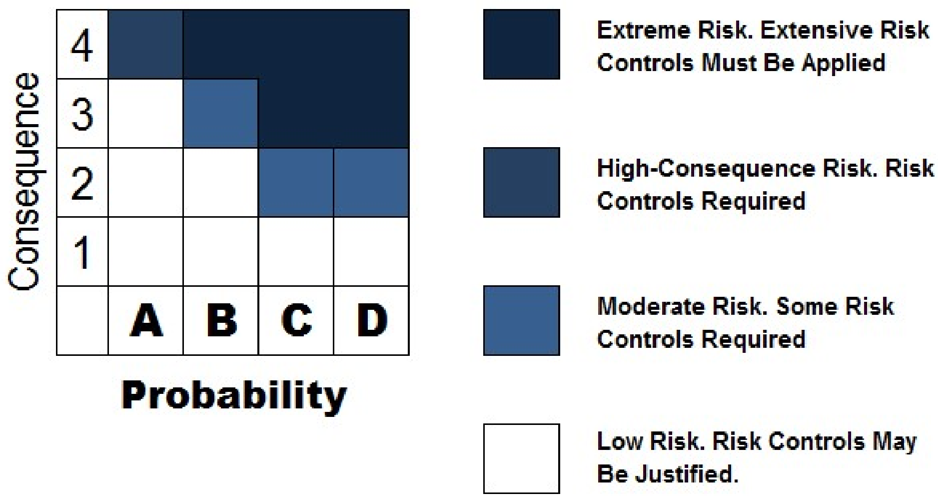


Figure 3. Simplified approach of risk management.

Managing risk is an important part of many engineering undertakings nowadays. Managing corrosion is an essential aspect of managing risk. First, management should be involved in the design stage, and then, after operation starts, maintenance must be carried out so that risk continues to be managed.

Engineering design should include corrosion control equipment, such as cathodic protection systems and coatings. Maintenance should be carried out so that corrosion is monitored and significant defects are repaired, so that risk is managed during the operational lifetime. Nonetheless, all decisions in engineering design must involve risks, but the successful engineering design is basically rely on minimizing the consequences of the risks itself.

Material Selection for Corrosion Resistance

In order to select the correct material of construction, the process environment to which the material will be exposed should be clearly defined. In addition to the main corrosive chemicals present, the following factors should be considered:

- Pressure.
- Temperature.
- Impurities.
- pH.
- Agitation.
- Stream velocity.
- Heat transfer rates.
- Amount of aeration.

The conditions that may arise during abnormal operation, such as at startup and shutdown, must be considered, in addition to normal, steady-state operation. More comprehensive data, covering most of the materials used in the construction of a process plant are given by Perry et al (1997), Lai (1990) and Scweizer (1998). The corrosion guides could be used for the preliminary screening of materials that are likely to be suitable, but the fact that pblished data indicate that a material is satisfactory cannot be taken as guarantee that it will be suitable for the process environment being considered.

The Influence of People

The effects of corrosion failures on the performance maintenance of materials would often be minimized if life monitoring and control of the environmental and human factors supplemented efficient designs. The concept which translate between variable inputs such as:

- People (p).
- Materials (m).
- Environments (e).

The concept will produce the simple basic fault tree as illustrate in Figure 4, where the consequences, or a corrosion failure can be represented by combining the three previous contributing elements. The top even probability (P_{sf}) could be evaluated with Boolean algebra which will leads to equation:

$$P_{sf} = P_m P_e Factor_p$$

Where:

P_m : Probability of failure caused by materials.

P_e : Probability of failure caused by environment.

F_p : Influence of people on the lifetime of a system.

The $Factor_p$ could be either inhibiting ($Factor_p < 1$) or aggravating ($Factor_p > 1$). The justification for including the people element as inhibit gate or conditional event in the corrosion three should be obvious.

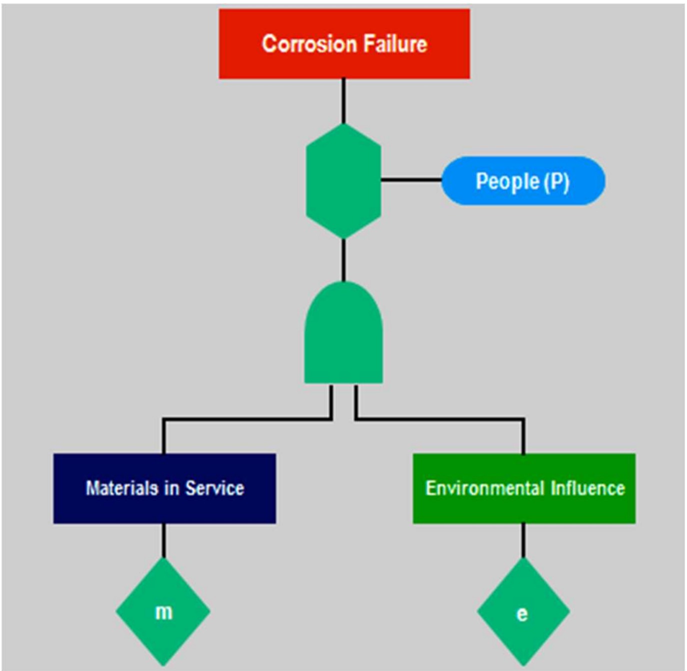


Figure 4. Basic fault tree of corrosion failure.

What might be defined as purely mechanical failures occur when Pm is high and P_e is low. Most well-designed engineering systems in which P_e is approximately 0 achieve good levels of reliability. The most successful systems are usually those in which the environmental influence is very and continues to be so throughout the service lifetime. It will conclude that when P_e becomes a significant influence on an increasing P_{sf}, then the accident of corrosion failures normally also increases.

Thus, minimizing P_{sf} only through design is difficult to achieve in practical application because of the number of ways in which P_m, P_e, and $Factor_p$ can vary during the system lifetime. However, the influence of people in a failure is extremely difficult to predict, being subject to the high variability level in human decision making.

Most-well designed engineering systems perform according to specification, largely because the interactions of people with these systems. Figure 5 shows the causes that responsible for failures investigated by a large process industry.

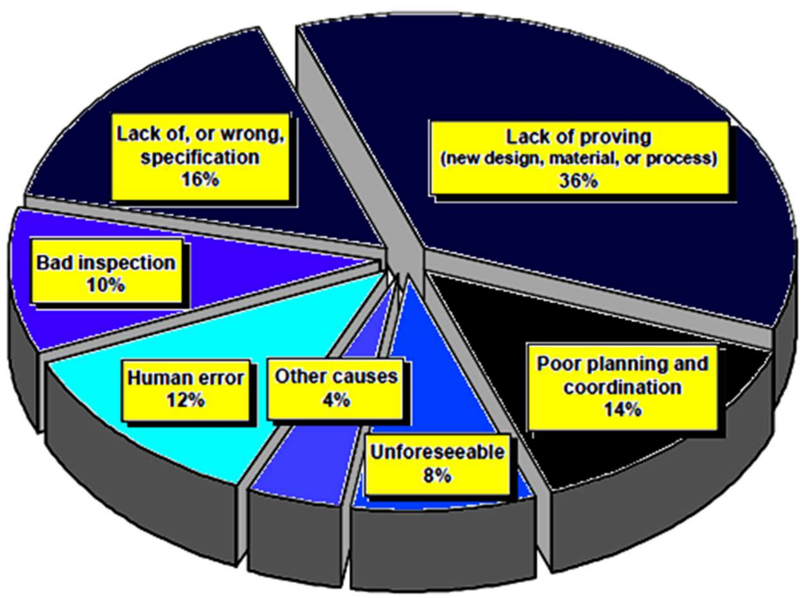


Figure 5. Causes that responsible for corrosion failures.

Meanwhile, Table 1 listed some example of historical landmarks of discoveries related to the understanding and management of corrosion. It can be expected that the main progress in corrosion prevention will be associated with the development of better information-processing strategies and production of more efficient monitoring tools in support of corrosion control programs.

Table 1. Example of Historical Landmark.

Date	Landmark	Source
1675	Mechanical original of corrosiveness and corrodibility	Boyle
1763	Bimetallic corrosion	HMS Alarm report
1819	Insight into electrochemical nature of corrosion	Thenard
1824	Cathodic protection of Cu by Zn or Fe	Sir Humphrey Davy
1834-1840	Relations between chemical action and generation of electric currents	Faraday
1908-1910	Compilation of corrosion rates in different media	Heyn, Bauer
1910	Inhibitive paint	Cushman, Gardner
1920-1923	Season-cracking of brass = intergranular corrosion	Moore, Beckinsale
1924	Galvanic corrosion	Whitman, Russell
1930-1931	Subscaling of "internal corrosion"	Smith
1931-1939	Quantitative electrochemical nature of corrosion	Evans
1938	Anodic and cathodic inhibitors	Chyzewski,Evans
1938	E-Ph thermodynamic diagrams	Pourbaix
1968	Electrochemical noise signature of corrosion	Iverson
1970	Study of corrosion processes with electro-chemical impedance spectroscopy (EIS)	Epelboin

DEFINITIONS

Active procedures – A Corrosion protection which will help to reduce or avoid corrosion by means of manipulation of the corrosion process, corrosion protection-related material selection, project engineering, design and manufacturing.

Aluminum – A silvery white, soft, ductile metal which have an atomic number of 13 and symbol Al.

Anode – A part which the corroding electrode.

Biological corrosion – Corrosion which established by living microorganisms as a result of their influence on anodic and cathodic reactions.

Brass – An alloy consists of Copper and Zinc.

Carbon Steel – Steel in which the main interstitial alloying constituent is carbon in the range of 0.12 – 2.0%.

Cast Iron – An alloys consists of iron, carbon and silicon.

Cathode - Which the passive ones, non-corroding electrode.

Cathodic Protection – Electrochemical Methods which is iconnecting an external anode to the metal to be protected and the passing of an electrical dc current so that all areas of the metal surface become cathodic and will not be corroded.

Cementation – A process which consists of tumbling the work in a mixture of metal powder and a flux at elevated temperatures, allowing the metal to diffuse into the base metal.

Copper – A ductile metal with very high thermal and electrical conductivity, have an atomic number of 29 and symbol Cu.

Corrosion - An electrochemical process that involves the passage of electrical currents on a micro or macro scale.

Corrosion damage - Corrosion phenomenon casting the impairment of the metal function, of the environment or of the technical system in which they form a part.

Corrosion failure - Corrosion damage characterized by the complete loss of operational capability of the technical system.

Corrosion phenomenon - Modification in any part of the corrosion system caused by corrosion.

Corrosion resistance - Ability of a metal to maintain operational capability in a given corrosion system.

Corrosion system - A system consisting of one or several metals and such parts of the environment that impact corrosion.

Crevice corrosion - one of localized type of corrosion which usually exhibited within or adjacent to narrows gaps or openings formed by metal-to-metal or metal-to-nonmetal contact.

Dipping - Process which carried out by immersing the metal on which the coating is to be applied (usually steel) in a bath of the molten metal that is to constitute the coating.

Electrolomotive force (emf) - The tendency for a metal to corrode.

Electrolyte Corrosion – Corrosion which result of direct current from outside sources entering and then leaving a particular metallic structure by the way electrolyte.

Electroplating – A process which the substrate or base, the metal is made the cathode in an aqueous electrolyte from which the coating is deposited.

Erosion corrosion – A Corrosion that achieves from the movement of a corrodent over the surface of a metal. The movement is related to the mechanical wear.

Galvanic Corrosion - Galvanic corrosion is self-generated activity resulting from differences in energy levels or potentials which develop when metal is placed an electrolyte.

General Corrosion – The corrosion which usually confined to the metal surface.

Gibs Energy - the change in free energy of the metal and environment combintaion brough about by the corrosion.

Inhibitors - The substances which reduce or eliminate the aggressiveness of a corrosive medium and are either already contained in the corrosive medium or are specifically added to it.

Intergranular corrosion - localized form of corrosion which taking place at the grain boundaries of metal with a little or no attack on the grain boundaries.

Ion implantation - A process of producing thin surface alloy coatings by bombarding the metal with ions in vacuum.

Lead – A soft, malleable and heavy post-transition metal which have an atomic number of 82 and symbol of Pb.

Magnesium – An alkaline earth metal which have an atomic number of 12 and symbol Mg, becomes the eighth most-abundant element in the Earth's crust.

Nickel – A silvery-white lustrous metal with a slight golden tinge, have an atomic number of 28 and symbol Ni.

Passive Procedures – A Corrosion which is prevented or decelerated through the isolation of the metal material from the corrosive agent by protective layers application.

Pitting - A form of corrosion with crater-shaped or surface-excavating pits or pits resembling pin pricks. The depth of the pitting spots usually exceeds their diameter.

Risk - the probability of an occurrence multiplied by the consequences.

Rusting - the corrosion of iron-based alloys with the formation of corrosion products consisting largely of hydrous ferric oxides.

Selective leaching - the process when one element in a solid alloy is removed by corrosion.

Shallow pit formation - A form of corrosion with irregular surface attack performing pits with diameters much larger than their depth.

Spraying – A process which the metal coatings process goes by a gun is used that simultaneously melts and propels small droplets of metal onto the surface to be coated.

Stainless Steel – A steel alloy with a minimum of 10.5% chromium content.

NOMENCLATURE

R	: Risk
P	: Probability
C	: Consequences
p	: People
m	: Materials
e	: Environments
P_m	: Probability of failure caused by materials.
P_e	: Probability of failure caused by environment.
F_p	: Influence of people on the lifetime of a system.
E	: Driving force / Electrolocomotive force (Volts).
F	: Constant of Faraday (96,490 Coulumbs).
n	: Number of moles of electrons per mole of metal involved in the process.
G	: Gibs Energy
I	: The current (Ampere)
R	: The resistence (Ohms)
WL	: weight loss (kg)
D	: density (kg/m^3)
A	: area (m^2)
T	: time (second)
mpy	: mils per year
A_w	: water activity.
V_s	: vapor pressure of the solution.
P_w	: vapor pressure of pure water.
n	: Charge number (dimensionless).
i_{aM}	: partial anodic current density for metal dissolution.
A	: A constant.
exp	: The base of natural logarithms.
Q	: The activation energy required to begin corrosion process.
R	: The gas constant (8.314 J/K.mol).
T	: Absolute temperature (K).
$CR_{uninhibited}$	: Corrosion rate of the uninhibited system
$CR_{inhibited}$	: Corrosion rate of the inhibited system

SYMBOLS

η_R : The resistance polarization
σ : Standard deviation of potential.

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