# Sustainable Corrosion Inhibitors from Natural Sources

# Sustainable Corrosion Inhibitors from Natural Sources:

## *Structures, Properties and Applications*

By

Abderrahim Benmoussat

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# PREAMBLE

The research interests of Professor Abderrahim Benmoussat are in the field of functional materials, biomaterials, green technology, environment, and corrosion engineering. In this manuscript, we have developed some anti-corrosion solutions research in order to use environmentally friendly compounds without harming the natural environment. It is one of the major prerogatives of this manuscript to replace chemical products which, despite their anti-corrosion characteristics, are polluting and contribute to the degradation of the natural ecosystem.

Corrosion affects many industrial structures, particularly metallic materials such as steel structure, which are alloys based on iron and carbon due to their good mechanical and physico-chemical properties and their low cost, are widely used in various industries such as hydrocarbons and various constructions. Carbon steels or aluminum alloys are used as industrial structures materials such as hydrocarbon pipelines or automotive cooling systems due to their properties. These materials are sensitive to natural corrosion phenomena when they are in contact with an aggressive environment such as wet soils or cooling circuits.

Various synthetic chemical compounds, organic or inorganic, are used as inhibitors or coating having a good anti-corrosion action but are toxic dangerous for humans and not compatible with the natural environment, which has prompted many researchers over the past decade to become interested in inhibitors from natural sources for several reasons: ecological constraints, which require the search for new "green" formulations that can replace toxic compounds, and the need to offer biodegradable, ecological acceptability, renewable nature and water-soluble inhibitors

The natural reserve of plant extracts, rich in families of natural compounds, having in their structures varieties of heteroatom, heterocyclic and electrons, can constitute an appreciable source for the development of natural, ecological inhibitors and coatings anticorrosion environmentally friendly and available.

# INTRODUCTION

As defined by most authors, corrosion designates a type of material properties alteration caused by an electrochemical or chemical interaction with the corrosive environment. It depends on a large number of factors that intervene not separately, but in a more or less complex relationship. It is an irreversible interfacial reaction of the material with its environment which results in the material loss or dissolution into the material of an environment component.These factors involved in the corrosion process can intervene from the material such as its composition, atomic structure, microscopic and macroscopic, heterogeneities, properties, distributions of anodic and cathodic surfaces or from the environment such as chemical nature and concentration of reactants, atmospheric agents, aqueous medium,microorganisms, temperatures, the constraints imposed on it, flow rate (in the case of a fluid)or from the material/environment interface such as kinetics of oxidation-reduction reactions, nature of corrosion products, growth or dissolution of corrosion deposit.Corrosion phenomena can affect all kinds of materials such as metals, ceramics, and polymers in aqueous medium, atmosphere, and high temperatures.

Polymer degradation is a chemical change in a polymeric material that usually results in undesirable changes in the in-use properties of the material. Usually, degradation results in the loss or deterioration of useful properties of the material. However, in the case of biodegradation or degradation by biological activity, polymers may change into environmentally acceptable substances with desirable properties.

Corrosion affects many industrial structures, particularly metallic materials such as steel structures, which are alloys based on iron and carbon due to their good mechanical and physico-chemical properties and their low cost, are widely used in various industries such as hydrocarbons, and various constructions...Carbon steels or aluminum alloys are used as industrial structures materials such as hydrocarbon pipelines or automotive cooling systems due to their properties. These materials are sensitive to natural corrosion phenomena when they are in contact with an aggressive environment such as wet soils or cooling circuits by often complex mechanisms to turn over in a stable oxide. Their surface according to the exposure duration can be covered by a phase’s mixture film. The characteristics of the structure are modified. It is a form of alarming degradation in industry.

The corrosion problems cause the industry to suffer enormous economic losses resulting from direct and indirect costs which are sometimes difficult to assess, such as the increase in the maintenance of altered structures, loss of production time, and replacement of damaged parts.

Corrosion and protection studies have been developed in recent years to serve industrial anti-corrosion action much more and to find adequate methods of protection, which defines the economic importance of corrosion, which has become an extremely versatile field where one can confront the most advanced results of fundamental research and the experience acquired by industrial practice. This does not preclude studies of corrosion from relying permanently on the most recent developments of scientific knowledge.

The anticorrosion protection includes a range of treatments such as:

- Protection by surface treatments;
- Electrochemical protections;
- Protection by inhibitors;

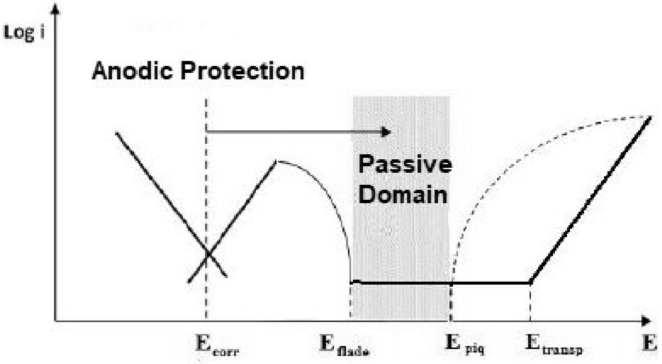
The protection by surface treatments is carried out by covering a film of protective coatings constituting a barrier between the corrosive environment and the material to be protected. They can be organic such as paints or metallic such as chrome plating and others offer technological advantages, economic and environmental. There are two types of metallic coatings: cathodic coatings where the protective metal is nobler than the metal to be protected. This is the case, for example, of a nickel or copper coating on steel and anodic coatings where the protective metal is less noble than the metal to be protected. This is the case of the process of galvanizing (zinc coating).

The electrochemical protection generally takes place by passing an electric current. It can be cathodic or anodic. This method is mainly used to protect heavy steel structures, such as chemical facilities, steel structures reinforced concrete, offshore oil rigs, and buried pipelines. Cathodic protection consists of imposing on the material to be protected a sufficiently low potential so that the rate of corrosion becomes negligible. It can be carried out by a sacrificial anode forming an electrochemical cell with the metal to be protected which acts as a cathode. These anodes must satisfy certain protection conditions. They are based on zinc, aluminium, or magnesium. Cathodic protection can be affected by an impressed current and the use of a rectifier. Its principle consists of connecting the material to be protected to the negative pole of a DC voltage generator, the positive pole being connected to an electrode sacrificial or inert, placed in the same electrolytic medium. The voltage is fixed at a value such that the potential of the metal to be protected corresponds to its immunity range.

Anodic protection applies to passive metals, whose potential for corrosion is in the active range.

$$E_{corr}<E_{pass} \tag{1}$$

Where $E_{corr}$ is the corrosion potential and $E_{pass}$is the passivation potential. The passivation is initially caused by a relatively intense current (about 5A/m²) using a current generator, then we maintain this passivation by a lower current (<1 A/m²). This method is used for very corrosive environments, which cathodic protection requires intensities that are too high. In this case, an anodic polarization makes it possible to move the potential in the passive domain. Maintaining anodic protection requires only low current density.



**Fig,1** Principle of anodic protection of a passively metal: displacement of the potential in the passive domain corresponding to Eflade<. E <Epiq (Where Eflade is the Flade potential, Etransp is the transpassivation potential and Epiq is the pitting potential).

The anticorrosion treatment by inhibitors comes from the corrosive medium by adding small quantities of the inhibitory formulation as a mixture of molecules or isolated molecules to retards corrosion without significantly modifying the concentration of any corrosive agent contained in the aggressive environment. As defined by the national association of corrosion engineers (NACE) “an inhibitor is a substance that retards corrosion when it is added to a low-concentration environment” [NAC 65]. An inhibitor must have some fundamental properties such as stability, compatibility, no toxicity, do not modify other species, and must be accessible and inexpensive substances. It may be else by an intervention from the middle through the use of inhibitors to increase the lifetime of metals, especially in acidic media. These constitute an original means of combating corrosion. Mechanisms and principles of action of corrosion inhibitors are related to the corrosion system. An inhibitor can act as a barrier between the metal and the corrosive medium and this can be pre-existing: the layer of oxide or hydroxide already formed and, in this case, the mechanisms most often involve adsorption and surface blocking processes. The mode of action can also be kinetic; the inhibitor can then slow down the rate of the cathodic reaction or the anodic reaction or act simultaneously on both,

Inhibition can also result from the formation of an insoluble compound that clogs sensitive areas and the rate of corrosion then decreases with time. The inhibitory effectiveness is essentially attributed to the presence in the structures of polar functions, heteroatom (S, O, N, etc.), heterocyclic and/or n electrons, considered to be responsible for the adsorption process of these inhibitors leading to the blocking of the active corrosion sites on the metal surface.Inhibitory effectiveness is related to several parameters such as chemical stability at operating temperatures and reduction in corrosion rate without affecting the physicochemical properties of the base material, solubility and dispersion in the medium, effectiveness at low concentration, standards of non-toxicity, and non-expensive. This efficiency depends mainly on the concentration of the inhibitor and the temperature for a focus of inhibitor given the range in the potential of the passivation stages increases with the increase in temperature and the inhibitory effect follows an adsorption isotherm.

Various synthetic chemical compounds, organic or inorganic, are used as inhibitors having good anti-corrosion action but are toxic and dangerous for humans and not compatible with the natural environment, which has prompted many researchers over the past decade to become interested in inhibitors from natural sources for several reasons: ecological constraints, which require the search for a new "green" formulations that can replace toxic compounds, and the need to offer biodegradable, ecological acceptability,renewable nature, and water-soluble inhibitors. The natural reserve of plant extracts, rich in families of natural compounds, having in their structures varieties of heteroatom, heterocyclic, and electrons, can constitute an appreciable source for the development of natural, ecological, environment-friendly inhibitors, and harmless and available.

In this perspective, many studies have prospected, in particular, a variety of plant extracts in terms of their effectiveness in inhibiting the corrosion of different metals. For this, we turn to plant extracts (leaves, flowers, roots). Extracts are easy to obtain, are not expensive, and always contain more than one organic product, so corrosion inhibition is improved by the synergistic effect such as oil or plant extracts. The authors [1] report that the number of publications (patents included) increased from 1920 to 2018 following an exponential tendency (figure 2). Energy valorization by biomass of green waste is another form of extension of green applications from the perspective of the circular economy.

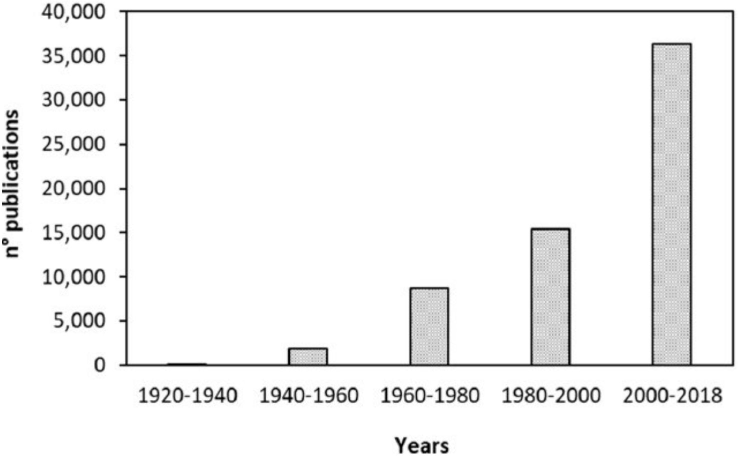


**Fig. 2** Number of publications per 20-year –range from 1920 to 2018 (Stefania Marzoti, and all. Molecules 2019, 24,48, DOI: 103390/molecules 24010048).

Corrosion inhibitors from natural sources can be classified according to their corrosion-inhibiting powers and their impact on the environment [2]. Green inhibitors based on oils or essential oils constitute a first group such as pennyroyal oil (mentha pulegium, essential oil and oil of artemisia, jojoba oil, clove oil, fennel essential oil (Foeniculum Vulgare), where the inhibitory effectiveness varies from 80 to 100 %% for Jojoba oil.

Plant extracts constitute the second group such as extracts of leaves gossipiumhirsutum L., kalmegh (Andrographis paniculata), henna (Lawsonia inermis), olivier (Olea europaea L., Aloe vera, Jasminum nudiflorum, Citrus aurantiifolia, or extracts of root Zallouh (Ferula harmonis), or ocimum sanctum, aegle marmelos, solanum trilobatum, artemisia pallens (Asteraceae), khillah (Ammi visnaga), coconut water nucifera L., ground coffee, oxandraasbeckii (alkaloids).

The fourth group is based on the metal/solution interface mechanisms which define the types of adoption either physisorption or chemisorption. The first type constitutes physical adsorption with the formation of weak bonds (dispersion forces of Vander Waals, London, polar forces, and hydrogen bonds) while the second type generates the formation of more stable chemical bonds by the pooling of electrons between the inhibitor molecule and the surface of the metal. The adsorption process can be influenced by various factors such as the nature and charge of the metal, the chemical structure of the inhibitor molecule, and the type of aggressive electrolyte.

Different parameters can be evaluated when studying corrosion such as the corrosion rate, the corrosion kinetics, the corrosion type, the products formed on the surface of metals, and the impact of degradation products. There are two main types of general study used to assess corrosion, namely the corrosion rate and the surface analysis including its elementary components related to corrosion.

Different physicochemical methods are used for corrosion and anticorrosion protection characterization such as optical microscopy, electron microscopy, electron microscopy coupled with energy dispersive spectroscopy, x-ray techniques, thermogravimetric analysis (TGA), gravimetry , which is an old method of direct measurement, stationary electrochemical methods (polarization curves) and transient electrochemical methods, including electrochemical impedance measurements.The non-destructive ultrasonic method is widely used to detect and characterize internal defects, but also to measure residual thicknesses resulting from corrosive phenomena. Generating ultrasonic waves in the material causes the propagation of coherent waves that propagate into the steel to detect different types of defects. This method has many advantages allowing it to be used in the industrial context as an intelligent tool [3].

# CHAPTER I

# NATURAL CORROSION PHENOMENA

## 1 Introduction

According to (ISO 8044) [5], corrosion can be defined as a set of interactions between a metal and its environment leading to changes in the properties of the metal resulting in significant weathering of the function of the metal. Corrosion affects most industrial sectors where metals are exposed to the action of solutions that act as corrosive agents such as in the refining of crude oil. According to "The national association of corrosion engineers" NACE (ISO standard 15156) [6], corrosion is the deterioration of a material, usually metallic, that results from a reaction with its environment. That is to say a gaseous environment (oxygen air), a liquid environment (water), an environment of constraints, or even a biological environment (bacteria settling in industrial nozzles - chemical or petrochemical - or extraction petroleum).

It is an unwanted destruction of materials structures and properties such as metals, ceramics, polymers, and concrete… under the action of corrosive environments such as atmospheric agents, chemical reagents, or soil solutions for buried structures such as steel pipelines. It is an irreversible interfacial reaction of the material with its environment which results in a loss of material or dissolution of environmental components Corrosion phenomena like any other phenomenon obey laws of thermodynamics where the metal tends to return to its original state more stable forms in which it exists in nature. This comes from the fact that, except noble metals (gold, platinum) which are found in their native state, the majority of metals are found on earth in the mineral state of oxides, sulfides, sulfates, carbonates, and silicates where the metals are found in a form of ores such as bauxite for aluminum, hematite for iron, chalcopyrite for copper, rutile for titanium.

Carbon steels are used in several industrial structures such as the hydrocarbon industry in many structures in the refining installations and the buried pipelines where transport is carried out. The main corrosion problems in industries that will develop in this part affect the buried steel pipes by soil and the corrosion by heat transfer fluids in the cooling circuits of engines which affect aluminum alloys in the automotive industry.

The factors involved in the corrosion process can intervene either on the material by the chemical composition, the atomic structure, microscopic and macroscopic heterogeneities, properties, distributions of anodic and cathodic surfaces, either on the environment by chemical nature, concentration of reactants, pressure, temperature, flow rate (in the case of a fluid), either on the metal/environment interface by kinetics of oxidation-reduction reactions, nature of corrosion products, growth or dissolution of the protective layer.

Corrosion is a physicochemical reaction between a material and its environment (aqueous or gaseous) which can manifest either in the form of dry corrosion which appears in the gaseous environments either in wet corrosion form of an electrochemical nature characterized by the appearance of an electric current and a movement of electrons within the metal. At the metal-solution interface, two chemical reactions simultaneously took place:

- An anodic reaction of dissolution of the metal in the form of $M^{n+}$ ions released in the aqueous phase;
- A reduction reaction in which the electrons coming from the ionization of metal atoms are neutralized;

The sum of the two electrochemical half-reactions (anodic, cathodic) gives the subsequent corrosion reaction.

Another form of biochemical corrosion may occur by the action of microorganisms and by the chemical action encountered in buried structures of pipelines.

Corrosion phenomena depend on several factors which can be classified according to the following groups:

- Attack modes: reagent concentration, oxygen content, pH of the medium; temperature, pressure, addition of inhibitors;
- Metallurgical factors: composition of the alloy, impurities, production processes, thermal or mechanical treatments;
- Conditions of use: surface condition, assemblies, shape, stresses, addition of inhibitors;
- Service life: aging, temperature, solicitations;

Carbon steels are used in several industrial structures such as the hydrocarbon industry in refining installations and the buried pipelines where transport is carried out and corrosion problems occur. In this part, we will develop the main corrosion problems in industries such as soil corrosion which affects the buried steel pipes in the oil industry, and the corrosion by heat transfer fluids in the cooling circuits of engines which affect aluminium alloys, in the automotive industry.

## 2 Carbon steel corrosion in soil

The growing increase in energy demand over the past fifty years particularly in hydrocarbons (gas and oil) requires more and more construction of new lines of pipelines because of their reliability and their low cost for the routing of large quantities over long distances estimated at thousands of kilometers. Pipelines regardless of their onshore or offshore type are exposed to the damage risk either by external or environmental interference or internal interference which results in a loss of metal by electrochemical and chemical type phenomena.

Carbon steel is commonly used in pipeline transportation of gases and liquids in most industrial applications due to having accepted employment properties such as maximum yield strength, toughness, weldability, corrosion resistance, and low cost. Pipeline steel consists of seamless and welded steel tubes according to its manufacturing methods. High-strength carbon steels are alloys made from a combination of iron and carbon. By varying the percentage of carbon, it is possible to produce stronger low-carbon steel. Other elements are added to improve its properties such as manganese with a maximum content of 1.65%, silicon and copper with a content not exceeding 0.60%, which can be laid in cold areas with high sulfur content or under the sea. Manganese is the only favorable element with a limited hardening effect pipeline steels have developed in recent years to obtain high-strength low-carbon micro-alloy steels called HSLA class (Strength Low Alloy Steels) with a ferrito-pearlitic or ferrito-bainitic microstructure. They are obtained by metallurgical diagrams of thermo-mechanical treatments by rolling at controlled temperature to refine the ferritic grain resulting in an increase in the elastic limit and the transition temperature. The refinement of ferritic grain size has been obtained by different mechanisms of hardening and precipitation based on the dislocation movement that increases elasticity limit and steel tenacity. Hall-Petch laws [4] have since been verified experimentally and explain the hardening induced by a reduction in the ferritic grain size.

$$\sigma_y = \sigma_i + K_y . d^{-1/2} \tag{2}$$

$\sigma_y$: Elasticity limit;
$\sigma_i$: Sum of hardening stresses based on the dislocation movement;
$K_y$: Constant expressing the grain size effect;
d: Size of ferritic grain;

Consequently, a fine microstructure makes it possible to reduce the ductile-brittle transition temperature to favor the ductile domain where the toughness is better. The Hall - Petch law makes it possible to link the cleavage stress to the grain size which leads to a reduction in the transition temperature by refining the ferritic grain.

Given the pipeline manufacturing process, the steel must have good weldability properties. These properties depend on the carbon content which should be low and on the equivalent concentration Ceq defined by relation 3. This explains the evolution of steels for tubes, observed over the last 40 years where the carbon content is 0.05%.

$$C_{eq} = C + \frac{Mn+Si}{6} + \frac{Ni+Cu}{15} + \frac{Cr+Mo+V}{5} \quad (3)$$

The steels commonly used in the manufacture of pipelines are defined according to two specifications 5L and 5L* corresponding respectively to normal qualities and high resistance qualities according to the API norm [American petroleum Institute] adopted by the oil industry throughout the world.

The mechanical parameters and chemical composition shall conform to specify tensile and yield strength test requirements and comply with acceptance criteria of flattening test and bend testing where no crack should occur in any part of the pipe and no opening should occur in the weld. The chemical composition is specified as the maximum limit of four elements, carbon, manganese, phosphorus, and sulphur were used for the welded tubes. Measured values were compared to values quoted in the test certificates. Values can vary significantly between pipes. These variations result in substantial differences in the defect performances of pipeline steel.

Buried steel pipelines whose depth varies between 0.6 and 1 m are protected from external risk by a thick coating applied on site containing bitumen binders or polymers and reinforced by a cathodic protection system (CP) which the potential is maintained to – 850 mV $Cu/CuSO_4$ to isolate the steel from the soil environment and to prevent any risk of corrosion.

Unfortunately, external surface defect problems have been developed under certain conditions generating corrosion pitting, cracking, or welding joint defects… The corrosion soil process involves many physicochemical parameters such as soil composition, soil resistivity, and steel chemical composition. It is a consequence of the electrochemical interaction between steel and soil environment to return an oxide state from thermodynamically more stable. The damage process involves many solicitation types such as electrochemical reactions, mechanical stresses, microbiological effects… It can be seen in its overall shape as a spontaneous reaction of electron exchange at the metal/environment interface. The design is usually based on the knowledge of the real or perceived initial state. However, this configuration evolves; there is generally an adding of new deformities due to the operation, but also to the loss of material located in the corroded areas.

Default risks such as external corrosion are preoccupying phenomena in the oil industry and research laboratories. They are the major threats that can reduce the structural integrity of the pipeline transmission system to find an adequate repair to allow rapid start-up and limit production downtime.

## Carbon pipeline steel failures

Carbon steels for buried pipelines intended for the transport of hydrocarbons that despite the double protection by coating and active cathodic protection by sacrificial anode or by imposed current method can present defective surfaces such as pitting corrosion cracking.... as a result of the interaction of the bare steel with the corrosive soil solution where the process involves many physicochemical parameters such as soil composition, soil resistivity and steel chemical composition. It is a consequence of electrochemical interaction between bare steel and soil environment to return an oxide state form thermodynamically more stable.

Pipelines regardless of their onshore or offshore type are exposed to the damage risk either by external or environmental interference or internal interference which results in a loss of metal by electrochemical and chemical type phenomena. The main corrosion-promoting factors are:

- Coating protection defects;
- The shortcomings of the cathodic protection system;
- The aggressiveness of the surrounding medium such as soil with low electrical resistivity or sea water;
- The aggressiveness of the fluid passing through the pipe;

Recent studies made by the (European Gas Pipeline Incident Group) [7], for 1060 cases of rupture in the pipelines, showed that 49.6% were caused by external attacks. The other causes of incidents are broken down into corrosion defects (15.3%), construction defects (16.5%), opening of valves by mistake (4.6%), landslides (7.3%), and others 6.7%.

To increase the profitability of this mode of transport, manufacturers have increased the service pressure as well as the diameter of the pipes. From 1910 to 2000, the diameter was multiplied by 4 and the transport pressure was multiplied by 60 [8] because of research work that allowed the improvement of the mechanical characteristics of pipeline steels by metallurgical mechanisms such as the thermo-mechanical treatments by rolling at controlled temperature to refine the ferritic grain resulting in an increase in the elastic limit and the transition temperature.

The operator's concern with pipeline networks is to ensure the maintenance of these networks to preserve the safety of populations as well as the impact that may have a major failure on the environmental aspect, particularly in the case of explosive gases. In addition, the economic and financial losses are considerable in terms of pipe replacement, public works, and losses operating. The prevention of ruptures is therefore a necessity and is carried out by inspection and analysis of the defect's harmfulness.

The presence of a defect in a pipeline such as corrosion pits, cracks, or deformation associated with the effect of internal pressure may cause a localized rupture leading to a leak and possibly an explosion.

Internal pipeline corrosion is caused by corrosive chemical compounds in the transported medium. Different media cause different corrosion factors. In the case of natural gas, it contains high concentrations of $H_2S$, $CO_2$, water content, and dust, which can lead to punctures and bursts. Internal pipeline corrosion is also related to the material and pipeline manufacturing process, as well as stresses favored by the activity of microorganisms such as the sulfate-reducing bacteria (BSR).

Metal losses due to external corrosion are caused by electrochemical and chemical interaction phenomena between pipeline steel and soil environment or by stray current corrosion from current that corrodes and damages metal pipes outside the design of the protection system for underground flow.

Corrosion of buried pipes can be caused by bacterial attack. Indeed, the metabolism of the development of certain bacteria causes the formation of chemical products that attack the metal.

We will develop as following the different types of corrosion that affect buried pipes such as:

- Electrochemical corrosion;
- Soil corrosion;
- Bacterial corrosion;

## Iron electrochemical corrosion

Electrochemical corrosion is responsible for 97% of industrial corrosion cases. The buried pipelines manifest this mechanism under certain conditions. It is the phenomenon in which metals return to their thermodynamically state more stable of oxide when they are in contact with atmospheric moisture or aqueous solutions such as buried structures.

Electrochemical reactions result from the establishment of local currents due to the existence of local batteries. The cathodic reduction and the anodic oxidation are located in two distinct zones. This creates a potential difference between these two areas. Reactions 4 and 5 are electrochemical reactions that take place at the interface between an electrode and electrolyte characteristics of the Metal/solution leading to oxidation-reduction corrosion reactions where the ions pass into the electrolyte, while the electrons remain in the ionic conductor, the metal. An electrolyte can be a gas or a solid, but it is most effective in a liquid form.

When an electronic conductor such as metal is in contact with an ionic conductor (electrolyte), it constitutes an electrode. On a macroscopic scale, these reactions take place simultaneously in the same place.

$$\text{Metal} \Leftrightarrow (\text{n M+, n e-})$$

$$(\text{M+})_{\text{metal}} \rightarrow (\text{M+})_{\text{solution}} \qquad (4)$$

$$\text{Or } (\text{n M+, n e-})_{\text{metal}} \rightarrow \text{n } (\text{M+})_{\text{solution}} + \text{n } (\text{e-})_{\text{metal}}$$

$$(\text{Ox+q})_{\text{solution}} + (\text{e-})_{\text{metal}} \rightarrow (\text{Red+ (q-1)})_{\text{solution}} \qquad (5)$$

It is established on both sides of the interface of electronic charges on the metal side and ionic charges on the one side potential difference called “electrode potential” “electrochemical potential” or “metal potential”.

Reactions 4 (anodic oxidation) and 5 (cathodic reduction) correspond to electric currents crossing the interface metal/solution”. These currents are called anodic and cathodic respectively. The consequence of these two reactions is the dissolution of the metal in the form of an ion. The charge flux densities (electrons in the metal, ions in the solution where there are no electrons) correspond to current density I, a ratio of current I to area S of the interface traversed. It is not directly measurable; only indirect measures (analysis of the solution, of the loss of thickness, etc.) make it possible to quantify the current density I. According to the general convention of electricity, the direction of the current is the direction of the movement of positive charges. The anode current of reaction 4 “leaves” the metal and the cathodic current of reaction 5 “enters” the metal.

The anodic oxidation reaction (4) may comprise the elementary steps schematized in figure 3. It is essentially:

- One or more charge transfer steps with the formation of adsorbed ions at the metal surface;
- A desorption step;
- Step(s) corresponding to a chemical reaction;
- Transport stage(s) of the formed products, from the metal-solution interface within the solution;

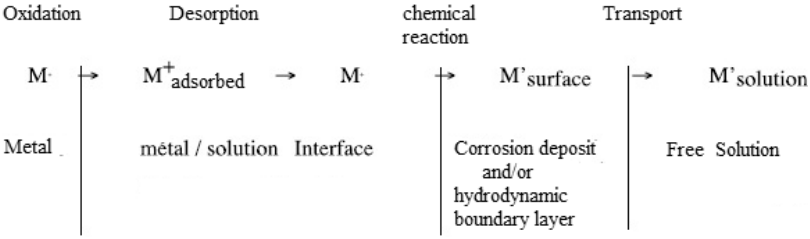


**Fig.1-3** The elementary steps schematized during the anodic oxidation reaction.

The cathodic reduction reaction (5) may include the elementary steps shown schematically in figure 4 it is essentially:

- A transport from within the solution to the metal-solution interface;
- Step corresponding to a chemical reaction;
- Absorption on the surface of the metal;
- One or more charge transfer with formation of species;
- Adsorbed on the metal surface;
- A desorption step;
- Chemical reaction;
- Transport of the products formed from the metal-solution interface to the breast of the solution, possibly coupled to other chemical reactions;

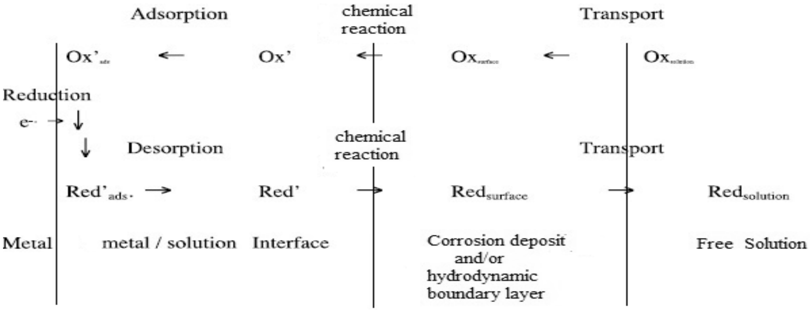


**Fig.1-4** The elementary steps schematized during the cathodic reduction reaction.

## Thermodynamic approach of iron corrosion

The corrosion electrochemical reaction at the electrolyte electrode interface is:

$$\nu_O \, Ox + ne^- \rightleftarrows \nu_R \, Red \qquad (6)$$

The equilibrium potential Eeq corresponding to the electrochemical equilibrium of the metal solution M/S interface, is equal to the thermodynamics equilibrium given by Nernst's law.

$$E_{eq} = E^0 + \frac{RT}{nF} \ln \frac{a_{ox}^{\nu ox}}{a_{Red}^{\nu red}} \qquad (7)$$

$a_{ox}$ and $a_{Red}$: Activity of oxidant and reducer;
$E^0$ : Standard potential of the working electrode, the metal;
n: Number of electrons;
R: Perfect gas constant (8.314 $J.mol^{-1}.K^{-1}$);
F: Faraday's constant (96485 C. $mol^{-1}$);
T: Absolute temperature;

The standard potential of the electrode is measured relative to a reference electrode called a standard hydrogen or calomel electrode.
Numerical expression of Nernst's law can obtained at room temperature (25°C),

$$E_{eq} = E^0 + \frac{0.059}{n} \log \frac{a_{ox}^{\nu ox}}{a_{Red}^{\nu red}} \qquad (8)$$

Electrochemical corrosion can take place at ordinary temperature; it is studied with the potential – pH diagram (thermodynamic) and current – potential i-E (kinetic) diagrams. The E = f (pH) diagram is obtained from the equilibrium equations for the oxidation-reduction reaction, taken from the Nernst equation. These diagrams make it possible to predict metallic corrosion reactions without intervening kinetic considerations. The potential depends on the pH of the solution leading to the formation of oxides in an aqueous medium involving $H^+$ ions

The thermodynamic possibility of corrosion of a given metal as a function of pH can be visualized by this diagram. The concentrations of metallic species resulting from corrosion phenomena are generally weak. In the case of iron corrosion, it is the oxide Fe $_2O_3$(s) that appears instead of Fe $(OH)_3$(s) hydroxide,FeO(s) not being stable at the ordinary temperature we obtain the potential-pH diagram (figure 5) which makes appear three areas:

- An area where metal is thermodynamically stable: this is the immunity zone;
- A zone where the metallic element considered predominates in the soluble form: this is the corrosion zone;
- A zone where the metallic element is considered to exist in the state of oxides or compounds insoluble: this is the passivation zone;

The oxide covers the metal with a very thin layer, which forms a screen between the metal and the solution. The different bounds correspond to the different equilibrium according to the different species of iron.

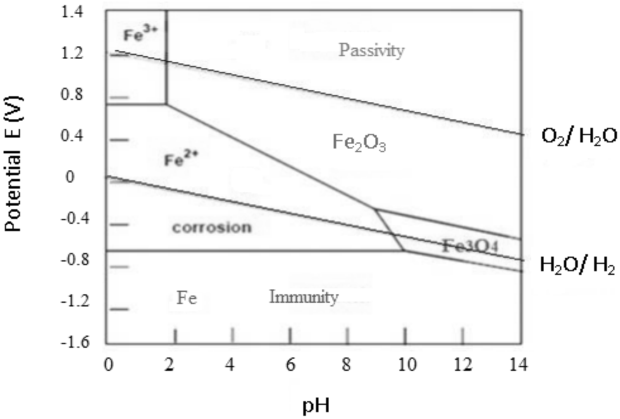


**Fig.1-5** potential-pH diagram of iron corrosion in $H_2O$ at room temperature (T = 25°C).

## Double-layer model

The interface between the two phases represents a very strong disturbance in the local distribution of their electrical charges. It is established on both sides of the interface, electronic on the side of the metal and ionic on the side of the solution. As a first approximation, the distribution of these electric charge densities of opposite sign can be considered asa double-layer model according to Helmholtz [8] in which the excess charge on the side of the electrolyte is distributed uniformly vis-à-vis that of the metal, at a distance $L_H$ from the interface (Figure 6). The interface behaves like a plane capacitor with capacitance $C_H$ which can be calculated according to the following relationship:

$$C_H = \frac{dq}{d\Delta E} = \frac{\varepsilon_{H2O}\varepsilon_0}{L_H} \tag{9}$$

Where:

$\Delta E$: the potential difference (V) across the terminals of the double layer ($\Delta E$ = Em - Es);

$L_H$: Thickness (m);

q: The charge density in the double layer ($C.m^{-2}$);

$\varepsilon H_2O$, ε0: the permittivity constant

$\varepsilon_{H2O}$ represents the dielectric constant of the adsorbed water;

$\varepsilon_0$ represents the permittivity constant($F.m^{-1}$);

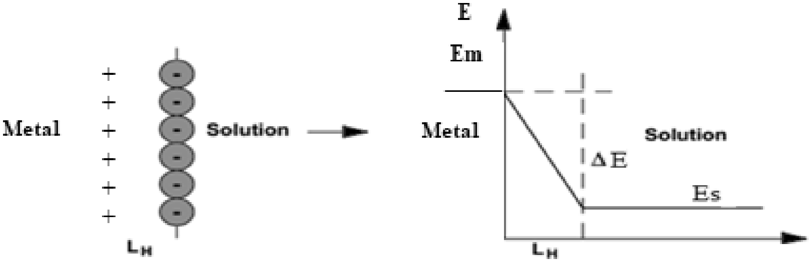


**Fig. 1-6** Charge distribution and the potential profile at the interface according the Helmholtz model.

The double layer capacity can in certain cases depend on the concentration of ions in the electrolyte which do not occupy a fixed position in a plane but according to a statistical distribution of Boltzmann in a zone located close to the surface of the metal defining a double diffuse layer or Gouy-

Chapman layer [8]. This behavior is observed for weakly concentrated solutions, resulting from the thermal agitation of the ions.

The double layer can result from the combination of the two previous models. The potential difference ΔE between the metal and the solution comprises two terms, due to a compact layer of the Helmholtz type, and the other, accounting for a diffuse layer of the Gouy-Chapman type. This is the Stern model [9]. The resulting double-layer capacitance contains two capacitors in series. Stern's model gives a good description of the metal-solution interface electrical behavior for many systems but does not give the influence of the chemical nature of the anions and the crystal orientation of the metal surface on the capacitance double layer.

Between the two "plates" of this capacitor there is a potential difference, usually called "electrode potential", "electrochemical potential" or "metal potential". The resulting electric field and the associated electrode potential influence the electric charge transfer between the metal and solution phases. These transfers modify the space charges and therefore the potential difference of the capacitor.

## Kinetic corrosion approach

Iron corrosion is characterized by the anodic oxidation reaction (4) and the cathodic reduction reaction (5). The speed of an electrochemical reaction corresponds to the transfer of a certain number of electrons at the metallic material/solution interface. It can therefore be directly evaluated theoretically from the measurement of the density and the kinetics of the cathodic and anodic reactions which generates the overall speed of the process to supply the surface with reaction products or return the soluble species to a homogeneous medium.

The corrosion speed is measured by the corrosion current intensity $\mathrm{I_{corr}}$ accordingto the following equation:

$$\mathrm{V_{corr}} = \frac{\mathrm{I}_{corr}}{\mathrm{n\,F\,S}} \tag{10}$$

Where:

S: metal surface;

$\mathrm{V_{corr}}$: Corrosion speed expressed by mol. m-$^2$. S-$^1$;

n: Number of electrons involved the stoichiometric coefficient of electrons in the electrode reaction;

F: Faraday's constant 96485 C. mol$^{-1}$;

The corrosion rate of a metal in a corrosive environment depends on both temperature and pH. The increase in temperature accelerates the corrosion phenomena. It decreases the domains of stability and accelerates reaction and transport kinetics. The susceptibility to corrosion is a function of the pH of the electrolyte. It increases with the decrease in the pH of the medium. The corrosion rate is expressed in loss of thickness per year in millimeters (mm/year) given by the following Faraday equation.

$$\mathrm{m} = \frac{A.I_{corr}.t}{\mathrm{n\,F}} \tag{11}$$

Where:

m: mass loss (gram);
$I_{corr}$ : corrosion current intensity (A);
$t$ : Time;
n: valence number of the metal (n = 2 for iron);
F: Faraday's constant 96485 C. mol$^{-1}$;
A: atomic number of metal (A = 55.85, for iron (g));

The corrosion speed is proportional to the corrosion current density which travels through the corroded metal. In consequence; the corrosion rate is all the greater as the surface area of the metallic conductor is low.

In practice, corrosion kinetics can be controlled by three main processes:

- Charge transfer;
- material transfer;
- Mixed transfer;

The charge transfer (figure 7) is verified when the reaction occurring at the interface does not lead to a significant change in the concentration of ''redox'' species in the electrolyte. The transfer of electrons across the metal-solution interface causes oxidation or reduction which obeys Faraday's law. Under certain conditions, at a given metal-solution interface, there may exist a potential domain where no charge transfer reactions take place because such reactions are thermodynamically impossible or kinetically disadvantaged. However, other processes such as adsorption or desorption may occur. These processes are called non-Faradic.

The Butter-Volmer relation applied to corrosion makes it possible to describe the behavior of the system according to the following equation:

$$\mathrm{I} = \mathrm{I_{corr}}\{\exp\left[\frac{2.3(\mathrm{E}-\mathrm{E_{corr}})}{\mathrm{b_a}}\right] - \exp\left[\frac{2.3(\mathrm{E}-\mathrm{E_{corr}})}{\mathrm{b_c}}\right]\} \tag{12}$$

Where:

$I_{corr}$: Corrosion current density;
$E_{corr}$: Corrosion potential;
$b_a b_c$: Tafel coefficients being parameters involving kinetic data;

This expression allowing to simply obtaining the value of the current of the system, is variable under certain conditions such as diffusion and the corrosion potential $E_{corr}$ is not too close to the reversible potential of each elementary reactions.

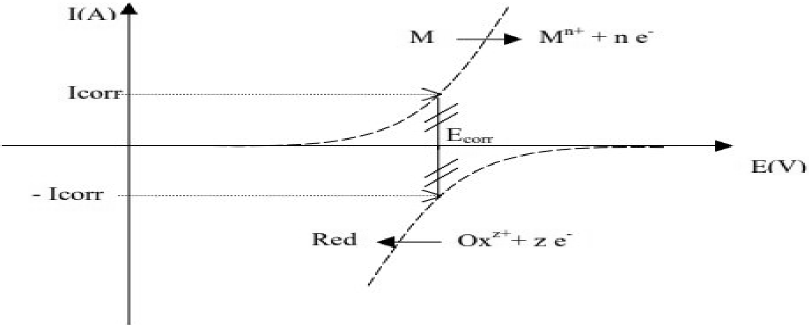


**Fig.1-7** Electrochemical corrosion reaction followed by a charge transfer process.

The phenomenon of follow-up by mass transfer processes is encountered particularly in aerated solution where the consumption of oxygen at the metal/electrolyte interface is not completely compensated by the flux of dissolved oxygen coming from the solution and the reaction is then limited by mass transfer.

The position of the “limit” diffusion level determines in this case, the value of the corrosion current $I_{corr}$ is directly proportional to the quantity of oxygen dissolved in the solution.

$$I_{corr} = I_{lim} = \frac{n\,F\,C_{O2}\,D_{02}}{\delta \text{ x } 10^{-3}} \quad (13)$$

Where:

$C_{O2}$: Dissolved oxygen concentration of the solution (mol/L);
$D_{O2}$: Diffusion coefficient ($cm^2/s$) ;
δ: Thickness of the diffusion layer (cm);
n: Number of electrons involved (stoichiometric coefficient of electrons in the electrode reaction);
F: Faraday’s constant 96485 C. $mol^{-1}$;

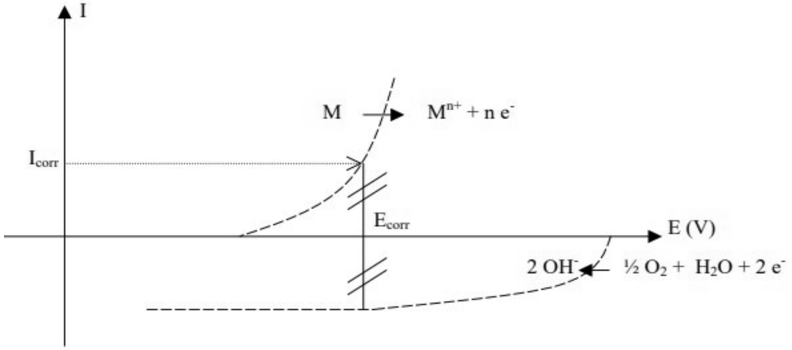


**Fig. 1-8** Electrochemical corrosion reaction followed by a material transfer process.

In the case of a mixed transfer, the response depends on several rate constants and the phenomena are much more complicated, as opposed to the case where a step in an electrochemical reaction controls the overall kinetics and for which the response of the system to the input signal depends preferentially on the rate constant of this step.

## Steel corrosion by soil

The physical and chemical properties of the soil and the electrochemical inhomogeneity of the metal material meet the conditions of electrochemical corrosion of buried pipelines, resulting in corrosion Soil is essentially a porous gelatinous capillary with three phase states: solid, liquid, and gas. Soil pores are filled with air and water. A certain amount of salt in the water gives the soil ionic conductivity... The characteristics of the soil are the risk indicators of external corrosion of the buried steel pipelines. It depends not only on its mineralogical character but on its moisture content, pH, chemical composition, resistivity, and aeration. Soil corrosivity is considered as the ability of the environment to produce and develop the corrosion phenomenon. The physical and chemical diversity of soils and the different physico-chemical parameters influencing the corrosivity of soils should be considered to better understand corrosion phenomena in these particularly complex environments. The study of T.R. Jack [10] carried out over several years concerning the pipelines of Canada described six scenarios that have been identified via the corrosion products:

- Aerobic corrosion (3% of cases): main corrosion products = oxides of Fe(III);
- Anaerobic corrosion (29%): main product = siderite $FeCO_3$;
- Biocorrosion in an anaerobic environment (SRB) (27%): corrosion products = siderite, amorphous FeS, mackinawite FeS, greigite $Fe_3S_4$;
- Aerobic corrosion then biocorrosion in an anaerobic environment (3%): Mackinawite, $FeS_2$ pyrite, $FeS_2$ marcasite, Fe(III) oxides;
- Anaerobic then aerobic corrosion (21%): $FeCO_3$ + Fe(III) oxides;
- Biocorrosion in anaerobic than aerobic environment (17%): goethite, lepidocrocite, elemental sulfur α-S8.

The main parameters influencing corrosion in soils are:

- Type of soil where clays such as montmorillonite promote corrosion;
- Soil granulometry;
- Soil resistivity and ions concentration where the soil corrosivity increases when the soil resistivity decreases;
- Water content;
- pH: the corrosion rate of steel $V_{corr}$ increases when the soil pH is less than 4;
- Redox potentialis often correlated with aeration;
- Bacterial activity;

### ➢ Soil granulometry

The granulometry or the size of the particles contained in the soils is an important parameter in the study of corrosivity. Indeed, it is this parameter that defines the texture of the soil on which the aeration and the rate of soil moisture will depend. In soils consisting of relatively coarse particles with a diameter greater than 2 mm such as gravel, stones … whose proportions of clay and silt are low; the circulation of gas or liquid is facilitated. Contrary, in soils rich in clay and silt, whose particles are finer than 2 mm such as sand 0.05 – 1 mm, silt 0.002 – 0.05 or Clay < 0.002, the aeration and the circulation of fluids will be slowed down. In the context of corrosion, the oxygen and the humidity level as well as the porosity are important parameters to explain the electrochemical behavior of the materials studied.

A graphical representation (Figure 9), proposed by the United States Department of Agriculture [11] in the form of a ternary diagram, makes it possible to better visualize the different soil compositions.

### ➢ Soil aeration

The aeration process in soils contributes to the oxidation of soil elements which then combine with the metal in the form of oxides, hydroxides, or salts. These compounds may be soluble and be evacuated from the initial anodic zone and leave the process of corrosion to continue or on the contrary accumulate and form an oxide which will have a barrier, thereby reducing the rate of corrosion of the structural metal. But if the film formed is rather porous and not continuous, the effect will then be more harmful, because we could then witness the appearance of localized corrosion phenomena.

The physical characteristics of the soil can also lead to the formation of differential aeration stacks on the surface of the metal. Indeed, the pores may have brought oxygen and electrolyte near the surface of the metal, then, by soil movements, the path that allowed this supply of active species may close. We then have an area confined, conducive to probable crevice corrosion.

The morphology of the soil evolves according to the weathering that takes place on the surface. This will be particularly the case for clay soil which will tend to swell during wet periods, and then retract during drier periods. However, when such a type of soil dries out, it cracks and forms channels that will allow subsequently a preferred path for oxygen and/or electrolyte to the surface of the metal.

The surface of the anodic and cathodic zones is also an important parameter in the assessment of a corrosion mechanism. Indeed, for a difference of given potential, if the anodic area is considerably larger than the surfacecathodic, the anodic current density and hence the corrosion rate will be low or even negligible. However, if the anode current due to the same potential difference is concentrated on a much smaller surface, the anodic current density will then be high, and degradation, even perforation of the material, will be fast.

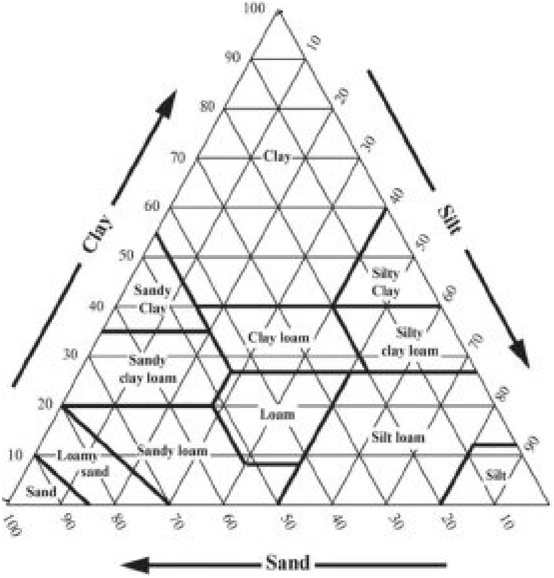


**Fig. 1-9** Ternary diagram of soil classification adopted by the United States Department of Agriculture [11]

Clay (<0,002 mm) - Sand (0,05 - 1 mm) - Silt (0,002 – 0,05mm).

### ➢ Soil electrolyte

Soil moisture allows the transport of ions between anodic and cathodic sites and promotes the corrosion process. These ions can come from the water or dissolved salts. The concentration of these species actively participates in the “electrical” configuration of the electrolyte particularly in terms of electrical conductivity, or in terms of resistivity to compare the corrosivity of soil. It is clearly shown that the more the soil is concentrated in these soluble species, the more it will be corrosive. It is possible to divide these species into two families: the basifying elements such as sodium, potassium, calcium, or even magnesium, and acidifying elements such as carbonates, bicarbonates, chlorides, nitrates, and sulfates. It is therefore possible to cross soils extremely acidic ($pH < 4.5$) to very strongly alkaline soils ($pH > 9.1$) [12]. The acidity of soil is also a parameter to be taken into account in the context of corrosion.

Electrical factors govern the distribution, size, and number of anode zones and cathodes as well as the importance of the current which circu-