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METALLIC MATERIALS TO CONTROL CORROSION IN OIL&GAS INDUSTRY

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Abstract

The aim of this work is to analyze corrosion phenomena, their detection and their prevention, referring particularly to Oil & Gas applications. In the first part, I will explain how corrosion works and which are the different corrosion mechanisms. Subsequently, I will focus the attention on sour conditions, sweet conditions and risks due to hydrogen formation. Subsequently, I will present which kind of steels are usually employed in these environments and which are the main countermeasures employed in Oil&Gas industry.

Then, principal solutions are illustrated, like employment of CRA (Corrosion Resistant Alloy), use of coating and corrosion inhibitors.

Finally, I will illustrate possible developments of technology and new solutions currently under testing.

Compendio

Lo scopo di questo elaborato è di offrire una descrizione dei diversi fenomeni corrosivi nel loro insieme, nonché dell'individuazione dei loro effetti e della necessaria prevenzione, con particolare riferimento a quei meccanismi tipici dell'industria Oil&Gas.

Nella prima parte saranno appunto presentati i differenti fenomeni corrosivi analizzati dal punto di vista delle cause, degli effetti e dei meccanismi chimico-fisici che li contraddistinguono.

Successivamente, l'attenzione verrà concentrata sui meccanismi corrosivi tipici nell'industria Oil&Gas, cioè di quegli ambienti caratterizzati dalla presenza di solfuri ("sour") e/o CO_2 ("sweet") e sugli effetti dell'idrogeno all'interno dei materiali.

Quindi, verranno illustrate le principali soluzioni attualmente adottate, come l'uso di CRA, di rivestimenti e di inibitori di corrosione.

Per finire, sarà dato uno sguardo ai possibili sviluppi futuri e alle strade che già si stanno percorrendo per migliorare le esistenti tecnologie.

1 INTRODUCTION

1.1 *What is corrosion?*

The term “corrosion” means a continuous degradation process of a material, due to electrochemical reactions on material's surface, leading to a worsening of material's properties; a lot of different materials may be affected by corrosion, but we will focus our attention on metallic corrosion [1].

Another possible definition is “the destruction or deterioration of a material by reaction with the environment or as the tendency of a metallic material to return to its original state, as it is found in nature” [2].

Anyway, let's take a look at possible classifications of corrosion mechanisms.

First, we have to define dry corrosion and wet corrosion.

1.2 *Types of corrosion*

1.2.1 Dry corrosion (High-temperature corrosion)

Dry corrosion is a definition that comprehends all corrosion mechanisms that occur at high temperatures, in environments containing oxygen, sulfur or other compounds capable of oxidize the considered material.

This mechanism may take place in gas turbines, diesel engines, furnaces,...

the characteristic temperature range of dry corrosion is between 400°C and 1300°C. The presence of oxygen leads to oxidation on the metal surface forming an oxide scale, while other substances like sulfur or sodium form salts with low melting point that tend to react with the metal.

To predict effects of dry corrosion, we have to consider thermodynamic conditions and kinetics of the reactions involved.

Thermodynamic conditions determine if the reactions develop spontaneously at considered temperatures, while kinetics determine the velocity at which they take place.

At high temperatures, decay processes comprehend:

- thinning due to non-protective scale formation;
- corrosion by molten salts;
- erosion-corrosion;

- localized attacks at grain boundaries;
- embrittlement.

1.2.1.1 Thermodynamic conditions

High-temperature corrosion works in accordance with kinetics of chemical reactions in the gas phase. Thermodynamic conditions and solid-phase diffusion processes in the oxide scale formation are therefore important.

All metals oxidize spontaneously in presence of oxygen, except for gold and platinum.

Anyway, if oxide growth kinetics are slow, we may use metals for a long time, also at high temperatures.

In air and at room temperature, metals develop a protective layer, few nanometers thick, that prevents further metal oxidation. Rising temperature, layer thickness increases, leading to mechanical detachment on many metals.

Thermodynamically, oxidation of a metal occurs only if the partial pressure of oxygen at operating conditions is greater than the dissociation pressure of the metal, calculated using Ellingham diagram.

1.2.1.2 Kinetics

Formation process of oxide layer may be analyzed like an electrochemical mechanism, having the following oxidation reaction:

$$M + \frac{1}{2}O_2 \;\text{«}\; MO$$

that can be divided into:

$$M \;\text{«}\; M^{2+} + 2e^-$$
$$\frac{1}{2}O_2 + 2e^- \;\text{«}\; O^{2-}$$

Metal oxidation (anodic) takes place at the metal/oxide interface, while oxygen reduction (cathodic) takes place at oxide/gas interface.

Electrons migrate from anode to cathode; metal ions migrate from cathode to anode or O^{2-} move to cathode or both happen.

Differences in diffusion rates determine where film will grow and if it will happen. If metal ions diffuse faster than oxygen ions, the film grows at oxide/gas interface, in the other case at metal/oxide interface.

Kinetics determine also “quality” of the oxide film and its ability to protect metal after formation.

Different steps have to be considered analyzing scale oxide formation: oxygen adsorption at the surface of the metal, nucleation of the oxide and increasing in film thickness.

Let's first consider second step, nucleation, and then, if it is an effective protective layer, let's treat first step.

Nucleation of the oxide is favored at high energy sites, like surface defects: so it's influenced by surface finishing, temperature and partial pressure of oxygen. Once the film has formed over the whole surface, its growth occurs through solid state diffusion processes within the scale.

An oxide may be protective or not: to determine this ability exists a criterion, called Pilling-Bedworth ratio. The Pilling-Bedworth criterion is defined as the ratio of the volume of the oxide to that of the metal which has produced it. The oxide results protective only for values between 1 and 2,5. Below 1, oxide is not protective because it is insufficient to cover the metal; over 2,5 it is not protective because tends to detach from metal surface owing to residual stresses, originated during growth. In case of no protection, metal will be continuously exposed to aggressive environment and so we can consider corrosion rate as a constant term. Then, metal thickness decreases as follows:

$$x = C_1 \times t$$

where C_1 is a constant of the metal and t is time.

In case of protective oxide layer, growth rate is proportional to slowest diffusion mechanism, modeled by Fick's law:

$$J_{ions} = - D \times \frac{dc}{dx}$$

Assuming a constant concentration gradient, loss of thickness follows an expression like this:

$$x = \sqrt{(C_2 \times t + C_3)}$$

where t is time and C_2 and C_3 are metal constants.

Growth is parabolic.

As is known, D is depending on temperature as follows:

$$D = D_0 \times e^{(-\frac{Q}{RT})}$$

where D_0 is standard diffusion coefficient, Q is activation energy, T is temperature and R is gas constant.

Consequently, growth rate of an oxide, controlled by diffusion mechanism, presents an Arrhenius pattern according to temperature.

Some common metals oxides, such as Al, Be, Zn and Cr ones, present growth kinetics of logarithmic type:

$$x = C_1 \times \ln\left(C_5 \times t + 1\right)$$

where t is time and C_4 and C_5 are constants of the metal. There are different reasons for this behavior, maybe complex. Shortly, Al and Be behave in this way because of flow electrons mobility; Zn and Cr have low ions' diffusion rate; furthermore Al and Cr have an oxide's crystalline structure coherent with that of the underlying metal and is therefore extremely adherent and protective. Considering oxide formation from the semiconductors' point of view, we may separate them between n-type oxides and p-type oxides. This separation determines where film grows: p-type ones grow at the oxide-gas interface, n-type ones grow at the metal-oxides interface.

It is important to consider diffusion through defects for different kind of oxides, to value how much protective they are. For example, diffusion through defects becomes relevant at high temperatures for Cr and Al oxides, while is important at low temperatures for Ni.

We may have different oxides for the same metal. In this case, the oxide composition is a sequence of layer, characterized by different stoichiometric ratios between O^{2-} and metal atoms. The order of these layers and them composition depends on:

- purity of the metal;

- composition of the gas;
- impurities of gas;
- pressure;
- temperature;
- flow rate of the gas;
- orientation of crystal lattice;
- surface finish of metal.

in case of alloys instead of metals as oxidized species, a more complex situation arises.
Since we have different metals forming the alloy, we will have different oxides forming the oxide layer, the composition of which will depend on stoichiometric ratio of the alloy but also on other factors, for example different diffusion coefficients of metal atoms.
Assuming an alloy of two metals, A and B, oxides AO and BO may be completely miscible, completely immiscible or partially miscible. If one of the two metals prevails, we will have a doping situation.
To have a protective oxide scale we choose to introduce metals that form stable oxide layers that adhere to the alloy surface. [3]

1.2.2 Wet corrosion

Wet corrosion defines all the processes that take place in presence of a low-temperature aggressive solution, in contact with the metal.
This solution may be aggressive because acid or because containing oxygen. This two situations may be schematized as follows:

$$metal + oxygen + water \text{ « } corrosion\ products$$

$$iron + acid\ solutions \text{ « } metal\ ions + hydrogen$$

they are both based on an electrochemical mechanism involving metal electrons. Every reaction is composed by two different processes: metal oxidation at the anode and oxygen reduction or hydrogen reduction (or both) at the cathode. First one produces electrons that migrate to cathode, where they are consumed by anodic reaction.

The two processes must proceed at the same velocity, in order to maintain electroneutrality.

Let's try to represent these processes.

Starting with the anodic one, an oxidation reaction takes place, so:

$$M \;\text{«}\; M^{z+} + ze^-$$

where M is a generic metal, z is the valence, M^{z+} is the metal ion that passes into solution, z is the valence.

We may also have the tendency to form hydroxide by metal oxidation, then:

$$M + zH_2O \;\text{«}\; M(OH)_z + zH^+ + ze^-$$

in this case, also water is directly involved into the reaction and ionic hydrogen develops.

About cathodic processes, they are more limited in number.

In case of corrosion by acid solutions, we have hydrogen reduction:

$$2H^+ + 2e^- \;\text{«}\; H_2$$

in natural environments, most frequent situation is corrosion by oxygenated water, so oxygen reduction will take place; in case of neutral/basic environment:

$$O_2 + H_2O + 4e^- \;\text{«}\; 4OH^-$$

while in case of acid environment:

$$O_2 + 4H^+ + 4e^- \;\text{«}\; 2H_2O$$

the oxygen appearing in the two reactions is molecular oxygen dissolved in water.

Wet corrosion is an electrochemical process, so it is possible to analyze it using Faraday's laws, establishing a relationship between masses and circulation electrical current:

$$\Delta m = e_{ech} q = q_{chem} / F$$

where q is the charge circulated, e_{ech} is the electrochemical equivalent, e_{chem} is the chemical equivalent and F is Faraday's constant.

Relationship between corrosion rate as mass loss and the current exchanged by metal is:

$$V_{corr} = V_{corr,m} / \gamma = \frac{\Delta m}{\gamma A t} = \frac{e_{ech} q}{\gamma A t} = \frac{e_{ech} i_a}{\gamma}$$

where i_a is the anodic current.

1 mA/m^2 of anodic current corresponds to 1 μm/year.

1.2.2.1 Thermodynamic and kinetics

Obviously, corrosion will start spontaneously only if it is thermodynamically favored: this means that associated ΔG must be negative.

Considering the already known reactions:

$$M + \left(\frac{z}{a}\right) A \leftrightarrow M^{z+} + \left(\frac{z}{a}\right) A^{a-}$$

$$M \leftrightarrow M^{z+} + ze^{-} \quad (anode)$$

$$\left(\frac{z}{a}\right) A + ze^{-} \leftrightarrow \left(\frac{z}{a}\right) A^{a-} \quad (cathode)$$

we may calculate free Gibbs energy *ΔG* as:

$$\Delta G = -zF\Delta E$$

where *ΔE* is equivalent to the electromotive force of the reaction considered, *z* and *F* are valence and Faraday's constant.

Because of *ΔG* must be negative, *ΔE* must be positive to have spontaneous reactions.

Defining, from literature:

$$\Delta G = \Delta G^0 + RT \ln\left(\frac{\Pi_{prod}}{\Pi_{react}}\right)$$

$$E^{\frac{mz^+}{M}} = E^0 + \left(\frac{RT}{zF}\right)\ln\left(\frac{\left[M^{z^+}\right]}{[M]}\right)$$

we obtain Nernst's law. Equivalently:

$$E^{\frac{A}{A^-}} = E^0 - \left(\frac{RT}{zF}\right)\ln\left(\frac{\left[A^{a^-}\right]}{[A]}\right)$$

so, because of ΔE must be positive:

$$\Delta E = E_c - E_a$$

$$E_c - E_a > 0$$

$$E_c > E_a$$

This means than, to have spontaneous corrosion reaction, we must have cathodic potential greater than anodic one. In other words, potential of the cathodic reaction is more noble than potential of the anodic one.

Considering now only anodic reaction, thermodynamically condition to proceed is when its potential is more noble than the equilibrium potential, indicated by E_{eq}, and defined as follows:

$$E_{eq} = E^0 + \left(\frac{RT}{zF}\right)\ln\left[M^{z^+}\right]$$

where E^o is standard potential of the metal and $\left[M^{z^+}\right]$ the concentration of its ions in the electrolyte, in contact with surface.

Everything said so far is a necessary but not sufficient condition to have corrosion: kinetic factors may influence the system, avoiding corrosion, even if thermodynamically permitted.

Four processes take place at the same time: anodic process, cathodic process, current flow in environment and current flow in metal.

These steps are characterized by currents: I_a, I_c, I_m, I_{env}. The corrosion rate is determined by the slowest of the four partial processes, then we have:

$$I_a = I_c = I_m = I_{env} = I_{corr}$$

Usually, electrical resistance of the metal is very low, so current flowing in the metal is not a slow process. To reduce corrosion rate we have to work on other three steps.

For example, presence of passivation will reduce I_a (anodic process), the intervention of overpotential will reduce I_c (cathodic process): the first case is known as anodic control, the second as cathodic control.

To analyze these situations, it is opportune to use Evans diagram: the two axes show the potential E and the current density ($\log j$). The diagram shows characteristic curves of the anodic and cathodic reactions, experimentally obtained starting from the reaction's equilibrium potential. As the current increases, in an anodic or cathodic direction, the reaction potential shifts from the equilibrium potential by a value known as the overpotential, η, which represents the dissipative term expanded as the reaction proceeds and which increases with reaction velocity on a logarithmic pattern. Anodic reaction is characterized by positive overpotential, negative for cathodic one.

Corrosion potential (E_{corr}) can be directly measured representing characteristic curves of anodic and cathodic processes are drawn on the same graph: the point where the two curves meet identifies corrosion conditions.

Evans diagram are of semilogarithmic type, with current density represented on logarithmic scale to make characteristics linear. Then:

$$\Delta E = E_{corr} - E_{eq}$$

where E_{corr} is higher than equilibrium potential of the metal but lower than equilibrium potential of cathodic process. [4]

Let's talk shortly about overpotentials.

What is an overpotential?

“In electrochemistry, overpotential is the potential difference between a half-reaction's thermodynamically determined reduction potential and the potential at which the redox event is experimentally observed.” [5]

Referring to corrosion, we may have two kind of overpotential: activation overpotential and concentration overpotential.

Activation overpotential is associated to reactions where a charge transfer takes place: it coincides with the activation energy of the reaction.

“Activation overpotential is the energy lost due to the slowness of electrochemical reactions at the anode and the cathode electrodes. Activation overpotential is a measure of the activity of electrodes. It represents the overpotential required for electrochemical reaction—the current density (typically small) at which the overpotential is measured.” [6]

“The concentration polarization is associated to electrochemical reactions controlled by ions diffusion in the electrolyte. This kind of polarization can be explained considering hydrogen ions diffusion towards metal surface, to form molecular hydrogen, through the following cathodic reaction:

$$2H^{+} + 2e^{-} \rightarrow H_2$$

In this case, hydrogen ions concentration is low and the rate of reduction reaction of them at the metal surface is controlled by diffusion towards the surface.

Every variation of system conditions increasing diffusion velocity of ions in the electrolyte, decrease polarization effects and increase reaction rate. For example, the agitation of the electrolyte reduces concentration gradient of positive ions and increases reaction rate. Rising temperature, we determine an enhancement of diffusion velocity of ions and then a gain in diffusion rate.

Total electrode polarization in an electrochemical reaction is equal to the sum of activation overpotential effects and concentration overpotential effects. Activation overpotential is usually the controlling factoring low rate reactions, while concentration overpotential is usually the controlling factor in high rate reactions. When overpotential is almost localized at the anode, we say that corrosion rate is under anodic control; when it is localized at the cathode, we talk about cathodic control.” [7]

So, activation energy is the energy required to move an electron from an electrode to the other.

Then, it is possible to define a current, associated with this overpotential: this is a current density, defined by Butler-Volmer equation:

$$i = i_0 \cdot \left(e^{\frac{(1-\beta) zF\eta}{RT}} - e^{\frac{-\beta zF\eta}{RT}} \right)$$

where η is the overpotential given by

$$\eta = \left| E - E_{eq} \right|$$

i_0 is the exchange current density, β is the symmetry factor between the anodic and the cathodic branches, F is Faraday's constant and z the equivalence of the reaction. This equation “says” that a current is established only If activation energy is exceeded.

For high overpotentials, Butler-Volmer equation is substituted by Tafel one:

$$\eta = a \pm b \cdot \log I$$

with + for anodic process and – for cathodic one; a and b are positive constants, a depending on i_0, b is Tafel slope.

Empirically, it has been noticed that anodic and cathodic characteristics are symmetrical.

As far as the values of the overpotentials are concerned, three classes of behavior have been identified, depending on the atomic and crystalline properties of metals:

inert metals, characterized by overpotentials above 100 mV, even at low current densities. They are high melting point – metals: Fe, Co, Ni, Cr, Mo, Ti,...

normal metals, characterized by low overpotentials, below 10 mv, even at high current densities. They are low melting point – metals: Cd, Hg, Sn, Pb, Mg, Al, Zn, …

intermediate metals, with intermediate characteristics, between inert and normal metals.

There is a correlation between overpotential and melting point of metal, extending to mechanical properties: normal metals, for example, tends to have low hardness and mechanical resistance.

Variation of overpotential with current density is linear for normal metals, whilst varies following Tafel's law in other cases.

Iron, carbon and low alloy steels are commonly presents in natural environments under so-called active condition, that is anodic reaction resistance very low or null. Then, the anodic process cannot reduce corrosion rate.

So, a lot of different metals cover themselves with an oxide protective layer that avoid further corrosion: this mechanism is called passivation. A practical example is stainless steel.

In passivation condition, they act as noble metals.

Electrochemically, in active materials, anodic characteristic is a straight line with slight slope; in passive one, it is as represented in the following diagram [8]:

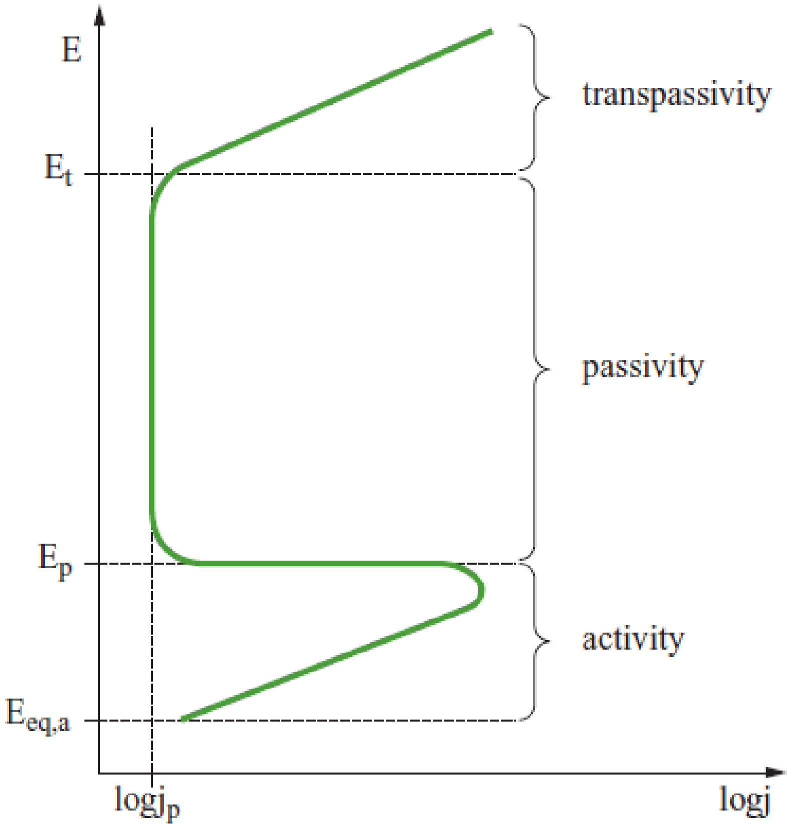


Figure 1: Diagram of potential-logarithmic of the current density of a metal with active-passive behaviour. Ep: passivation potential; Et: transpassivity potential; jp: passivity current density.

1.3 Corrosion mechanisms

1.3.1 Generalized corrosion

Generalized corrosion affects entire surface of a metal or a large part of it; it may be uniform or non-uniform: in uniform case, the corrosion rate (the rate of mass loss per unit of surface area exposed to the aggressive environment over the time) is almost the same everywhere; it is not true in the other case.

Generalized corrosion indicates also the large coincidence of anodic and cathodic areas.

Knowing environmental conditions and metal properties, we may generally predict corrosion rate, especially in uniform conditions.[9]

1.3.2 Localized corrosion

Localized corrosion occurs when the anodic and cathodic reactions take place on different surfaces, affecting only a limited part of the surface exposed to the environment.

Because of separation of areas, a galvanic current circulates from anode to cathode. Circulation of a current may have different causes, depending on environmental and metal conditions.

1.3.2.1 Bimetallic corrosion

Sometimes, localized corrosion takes place because of coupling of different materials. If these materials have got different nobility, they are both conductive and they are exposed to an aggressive environment, we've got bimetallic corrosion on the less noble material. The corrosion rate of the less noble metal undergoes an acceleration which depends on the ratio of the area of the more noble metal (cathodic area) to that of the less noble metal which is corroded (anodic area). As a consequence of galvanic coupling, we may have an hydrogen release, leading to hydrogen embrittlement.

In resistive environments the attack is localized and restricted to the areas where the two metals are close to one another; by contrast, in environments with high conductivity, such as sea water, attack is more widespread and affects surfaces distant from one another.

The corrosion rate due to galvanic contact is given by the general expression

$$corrosion\ rate = j_{cat} \times \left(1 \big/ S_c S_a \right)$$

where j_{cat} is the velocity of the cathodic process, and S_a and S_c are the anodic and cathodic areas respectively. In water, the velocity of the cathodic

process is the limit current density of oxygen diffusion, j_l.

A possible solution is apply coating on the cathodic area or cathodic protection.[10]

1.3.2.2 Pitting

Pitting is a localized attack, characterized by pits or cavities; it affects only small portions of materials, but it's very penetrating. This mechanisms is common on materials with an active/passive behavior, like stainless steels, copper and aluminum.

The initiation stage consists in rupture of passivity film by specific substances present in the environment (Cl^- for example). Initiation is characterized by a threshold value of aggressive substance concentration, it's favored by turbulence and high temperature.

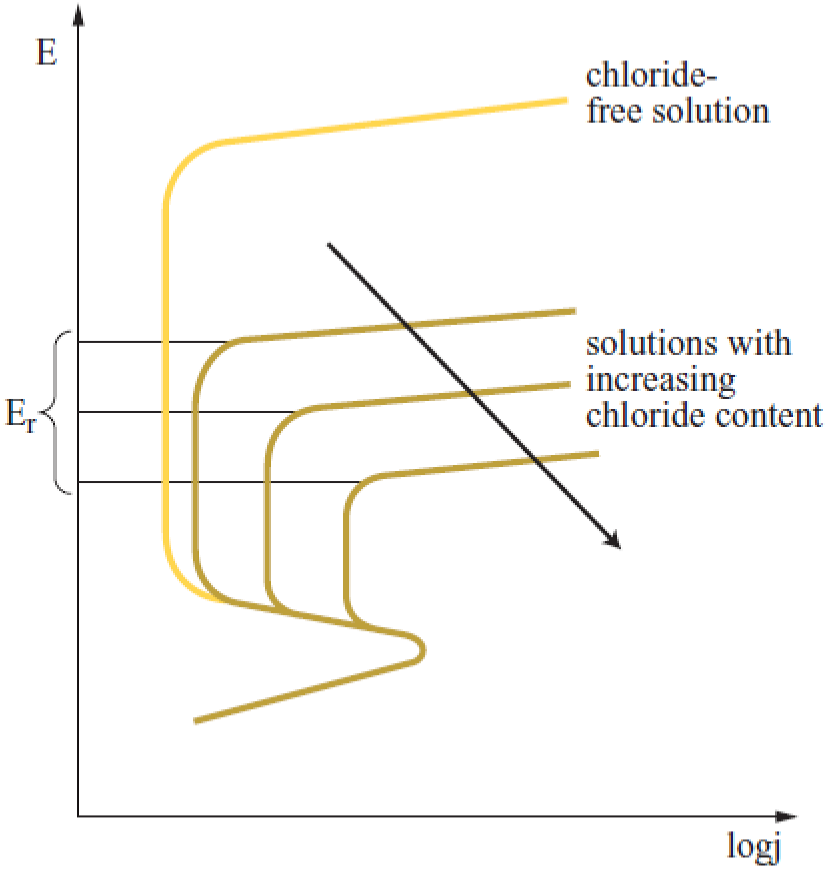


Figure 2: Active-passive behaviour of a stainless steels in an aqueous solution, with and without chloride ions

During propagation, we have a current established between anodic areas (cavities) and cathodic areas (where passivation survived).

Corrosion rate is in the order of mm/year, because of untoward ratio between anodic and cathodic areas.

Propagation is characterized by an autocatalytic mechanism: solution in pits becomes more and more aggressive because of an hydrolysis reaction:

$$M^{z^+} + zH_2O \text{ « } M(OH)_z + zH^+$$

Due to this reaction, pH decrease below 2 and we have an increase in Cl- concentration.

Prevention of pitting is usually possible only during the initiation stage; it consists in a correct choice of operating materials, based on PREN:

$$PREN = Cr\% + 3.3(Mo\% + 0.5W\%) + 16N\%$$

Contrariwise, cathodic protection is operating both during initiation and propagation stage.[11]

1.3.2.3 Crevice corrosion

Crevices represent an aggravating factor for the corrosion of a metal; they usually measure less than a μm, so they are very small and often not detectable to the naked eye.

Crevices favor corrosion through different mechanisms; for example, for metals in an active state (low alloy steels in water or soils), the reduced oxygen supply inside the crevice creates a differential aeration cell, with the anodic area located inside the crevice, where the oxygen supply is low or absent, and the cathodic area outside the crevice, where oxygen supply is high.

Corrosion rate is equal to the product of the limit current density of oxygen diffusion on the cathodic area and the ratio of the cathodic area to the anodic area under a deposit.

Crevice corrosion mechanism in stainless steel in a solution containing chloride ions is quite different. There are two stages: initiation and propagation. During initiation phase, composition of the solution within the crevice changes until passivity is destroyed by consumption of all the oxygen present in the crevice by the passivity current and, subsequently, by the establishment of a galvanic current which, as in the case of pitting, gives rise to the propagation stage, the accumulation of chlorides and the decrease in pH.

Prevention is based on elimination of environmental dishomogeneities and secondarily the use of coatings and the application of the cathodic protection, in case of deposit of active materials. In case of stainless steels, solutions without crevices must be adopted during the design stage; in case of joints, it is preferable to use full penetration welds rather than superimposition or flanges. Anyway, cathodic protection is effective during both stages.[12]

1.3.2.4 Intergranular corrosion

This kind of corrosion is characterized by localized attack at the grain boundaries, due to the presence of precipitates. Grain boundaries is a preferential site for processes involving segregation and precipitation of compounds(i.e. carbides, sulphides, intermetallic compounds,...). All alloys in which precipitates are present at the grain boundaries are vulnerable to intergranular corrosion, particularly stainless steels and nickel-based alloys.

We may describe this mechanism considering it on AISI 304 (18%Cr – 8%Ni): this steel is supplied in this form as annealed, obtained with a solution heat treatment which involves bringing the steel to a temperature of 1050 °C o solubilize the chromium carbides, followed by rapid cooling to prevent their precipitation; if then the steel is brought to critical temperature range 600-850 °C, chromium carbides precipitate at the grain boundaries, lowering the chromium content to below 12% in the zones adjacent to the grain boundaries themselves; these zones lose their stainless properties and undergo galvanic corrosion (cathodic areas are grains). Corrosion rate is usually very high because of unfavorable ratio of anodic to cathodic areas.

Protection is based mainly on prevention of carbides precipitation, repeating heat treatment on the welded piece; if this is not possible, we may lower C content under 0,03% or add titanium or niobium, stabilizing steels.

On the other hand, in the first case we have inferior mechanical properties, in the second we may have “knifeline” attack.[13]

1.3.2.5 Selective corrosion

This kind of corrosion affects particularly metal alloys and involves the preferential dissolution of the less noble metal because of exposure to medium corrosive environments. The most important examples are: the dezincification of brass (copper-zinc alloys), where the zinc passes into solution and the copper remains as a metallic residue; the graphitization of cast iron (mainly affecting grey cast iron), in which the iron matrix undergoes selective corrosion with the formation of a more or less superficial residue layer of graphite.

The most common example is selective leaching of zinc from brass alloys containing more than 15% zinc (dezincification) in presence of oxygen and moisture, e.g. from brass taps in chlorine-containing water. It is believed that both copper and zinc gradually dissolved out simultaneously and copper precipitates back from the solution. The material remaining is a copper-rich sponge with poor mechanical properties, and color changed from yellow to red. Dezincification can be caused by water containing sulfur, carbon dioxide and oxygen. Stagnant or low velocity waters tend to promote dezincification. Graphitic corrosion is selective leaching of iron from grey cast iron, where iron gets removed and graphite grains remain intact. Affected surfaces develop a layer of graphite, rust, and metallurgical impurities that may inhibit further leaching. The effect can be substantially reduced by alloying the cast iron with nickel. Remedies involve using alloys not susceptible to grain boundary depletion, applying an heat treatment, modifying the environment (lowering oxygen content), using cathodic protection.[14]

1.3.2.6 Stress Corrosion Cracking (SCC)

Stress Corrosion Cracking is a definition that comprehends all phenomena involving formation and propagation of cracks in a metal subjected to the combined action of tensile (but not compressive) mechanical stresses and a corrosive environment.

We cannot describe a general scheme independently from specific combinations of materials and environment, but we may indicate some general features: there is a mechanical stress threshold; it mainly affects alloys; corrosion rate is high, but lower than that of cracks of purely mechanical nature. Tensile stresses may have both external and internal nature. Cracks may be individual or branched, intergranular or transgranular.

Anyway we may roughly divide this mechanism into:

- Dissolution mechanism: cracks propagate because of anodic dissolution of the tip;
- Embrittlement: cracks grow due to mechanical fracture of the zone near the crack tip.

Embrittlement need entry of atomic hydrogen, produced by cathodic reaction, into the crystal lattice of the metal, diffusion to the crack tip in strong plastic deformation state and subsequent interaction.

Instead, the first one is determined by anodic reaction of metal dissolution.[15]

1.3.2.7 SCC by Chlorides

Austenitic stainless steels (particularly 304 and 316) and austenitic-ferritic stainless steels are the most affected materials by SCC. Ferritic stainless steels with a Ni content below 4% are practically immune.

Some conditions are necessary to SCC to occur; one of this is a temperature above 60°C (at least: in fact, initiation temperature rises the lower the concentration of chlorides ions in solution); then, SCC needs a concentration of chlorides in solution above a certain threshold, at least 10 ppm, but depending on steel composition; obviously, also an applied stress is needed, higher than about 30% of the breaking load.

Austenitic stainless steels with high Ni content are less affected by SCC than 304 and 316 types.[16]

1.3.2.8 Hydrogen embrittlement

Hydrogen embrittlement is the process by which various metals, most importantly high-strength steel, become brittle and fracture following exposure to hydrogen. Hydrogen embrittlement is often the result of unintentional introduction of hydrogen into susceptible metals during forming or finishing operations and increases cracking in the material. This phenomenon was first described in 1875.

The hydrogen ion reduction reaction, which takes place in acid environments, involves a first stage with the formation of atomic hydrogen adsorbed onto the metallic surface. This atomic hydrogen may form a hydrogen molecule, or penetrate inside the metal’s crystal lattice if specific poisons are present on its surface which inhibit the formation of molecular hydrogen. These poisons include metal sulphides and hydrogen sulphide (H2S), often present in environments associated with hydrocarbons. The presence of H2S gives rise to the form of stress corrosion cracking due to hydrogen embrittlement known as sulphide stress cracking (SSC).

The steels susceptible to SSC are those with a high yield limit (breaking load above 700 MPa) whose microstructure is particularly sensitive to the effects of hydrogen. The ruptures are characterized by transgranular cracking.

The prevention of stress corrosion cracking takes place above all during the design phase by choosing materials which are not vulnerable in the environment specified, and by putting in place measures able to remove states of residual stress (for example, a heat extension treatment after the welding of joints). In some cases, recourse is made to environmental conditioning, for example by modifying the pH (this is the case with the treatment of drilling muds for oil wells with a pH above 10 when H2S is present). Cathodic protection is only effective for stress corrosion cracking with an anodic dissolution mechanism.

$$2H^+ + 2e^- \leftrightarrow H_2$$

$$H^+ + e^- \leftrightarrow H_{ads}$$
$$H_{ads} + H_{ads} \leftrightarrow H_2 \quad \textit{or} \quad \textit{penetration into the lattice}$$

[18]

1.3.2.9 Corrosion fatigue

Corrosion fatigue (CF) is a kind of corrosion generated by simultaneous presence of variable mechanical loads (fatigue stresses) and a common corrosion process (or a corrosive environment).

Aggressive environment is relevant only at low frequency variations in stress amplitude, because at high frequency mechanical effects become prevailing.

When CF is present, practical fatigue limit of steel elements may be reduced by up to 50%, comparing to fatigue limit in neutral environments (e.g. air); S-N curves for steels (intensity applied stress-number of cycles) become similar to that of non-ferrous materials.

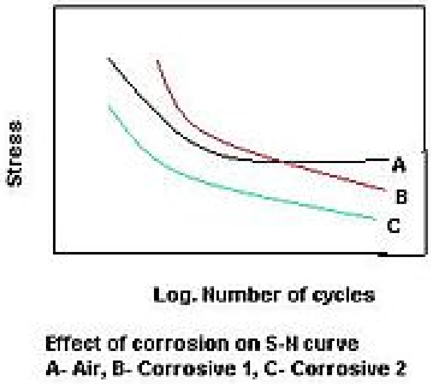


Figure 3: effect of corrosion on S-N diagram.

As you can see in the graph, curve A shows fatigue behavior of a material tested in air: you can notice a fatigue threshold, corresponding to the horizontal part of the curve. B and C, instead, represent fatigue behavior of the same material in two different corrosive environments. In B, fatigue threshold disappears and fatigue failure at high stress level is retarded; in C, the whole curve is down-shifted, again without a fatigue threshold. So, a corrosive environment causes a general worsening of mechanical properties and almost disappearance of fatigue limit.

Consequently, determine corrosion fatigue life of a workpiece becomes important in terms of safety and money. Generally, two different approaches may be adopted to do this: fatigue limit curves as a function of number of cycles and the fracture mechanics expressed by the crack growth velocity curves per cycle as a function of the ΔK variation of the stress intensity factor. Usually about 10 percent of life of workpieces is sufficient for crack nucleation, while 9 percent is involved in crack propagation: so, more attention is paid to crack propagation behavior during corrosion fatigue, especially to crack-propagation velocity measurements. Since fatigue crack grows in a stable way below critical stress-intensity factor for fracture (fracture toughness), the process is called sub-critical crack growth. This diagram shows typical fatigue crack-growth.

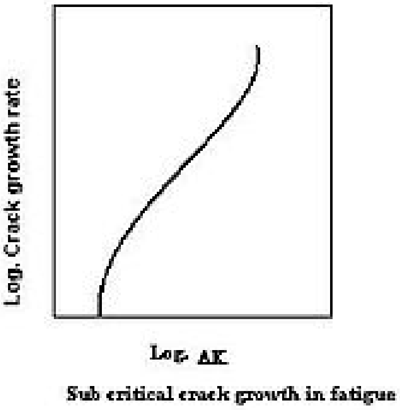


Figure 4: log-log plot of crack propagation velocity against applied stress intensity range.

In this log-log plot, the crack-propagation velocity is plotted against the applied stress-intensity range. Generally there is a threshold stress-intensity range, below which crack-propagation velocity is insignificant. Three stages may be visualized in this plot. Near the threshold, crack-propagation velocity increases with increasing stress-intensity range. In the second region, the curve is nearly linear and follows Paris' law; in the third region crack-propagation velocity increases rapidly, with the stress-intensity range leading to fracture at the fracture-toughness value. Crack propagation under corrosion fatigue may be classified as a) true corrosion fatigue, b) stress corrosion fatigue or c) a combination of true, stress and corrosion fatigue.

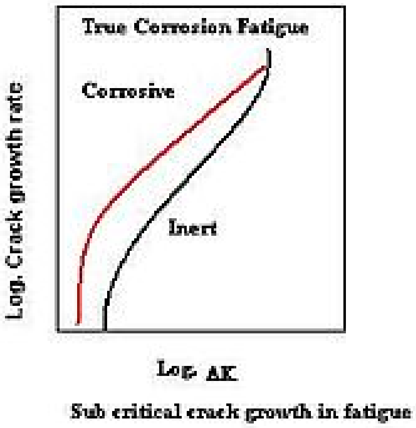


Figure 5: fatigue-crack-growth in true corrosion fatigue.

In true corrosion fatigue, the fatigue-crack-growth rate is enhanced by corrosion; this effect is seen in all three regions of the fatigue-crack growth-rate diagram. This diagram is a schematic of crack-growth rate under true corrosion fatigue; the curve shifts to a lower stress-intensity-factor range in the corrosive environment. The threshold is lower (and the crack-growth velocities higher) at all stress-intensity factors. Specimen fracture occurs when the stress-intensity-factor range is equal to the applicable threshold-stress-intensity factor for stress-corrosion cracking. When attempting to analyze the
effects of corrosion fatigue on crack growth in a particular, both corrosion type and fatigue load levels affect crack growth in varying degrees. Common types of corrosion include filiform, pitting, exfoliation, intergranular; each will affect crack growth in a particular material in a distinct way. For instance, pitting will often be the most damaging type of corrosion, degrading a material's performance (by increasing the crack-growth rate) more than any other kind of corrosion; even pits of the order of a material's grain size may substantially degrade a material. The degree to which corrosion affects crack-growth rates also depends on fatigue-load levels; for instance, corrosion can cause a greater increase in crack-growth rates at a low loads than it does at a high load.

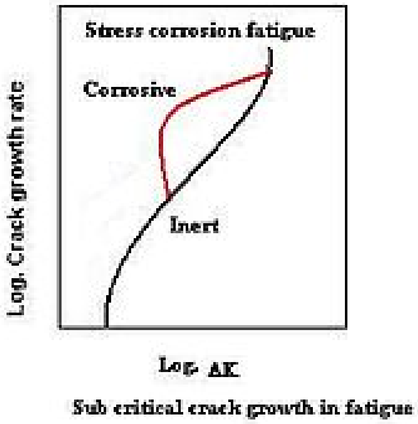


Figure 6: crack-growth behaviour under stress-corrosion fatigue.

In materials where the maximum applied-stress-intensity factor exceeds the stress-corrosion cracking-threshold value, stress corrosion adds to crack-growth velocity. This is shown in the schematic right here. In a corrosive environment, the crack grows due to cyclic loading at a lower stress-intensity range; above the threshold stress intensity for stress corrosion cracking, additional crack growth (the red line) occurs due to SCC. The lower stress-intensity regions are not affected, and the threshold stress-intensity range for fatigue-crack propagation is unchanged in the corrosive environment. In the most-general case, corrosion-fatigue crack growth may exhibit both of the above effects; crack-growth behavior is represented in the last diagram. [19]

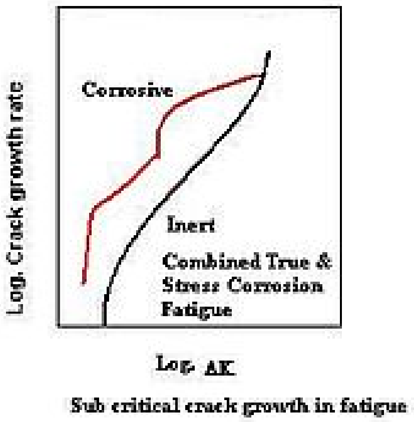


Figure 7: combined true-corrosion and stress-corrosion fatigue

1.3.2.10 Erosion corrosion

This type of corrosion takes place in presence of severe fluid dynamic conditions, often enhanced by presence of suspended solids, slurry, particles, all of them transported in fast flowing liquid or gas.

The synergy between corrosion and mechanical action of the fluid affects most metallic materials when given conditions of turbulence expressed by the critical erosion corrosion rate are exceeded: in oil industry this rate is calculate with this empirical formula:

$$u_e = \frac{C_m}{\sqrt{r_m}}$$

where u_e is the critical erosion corrosion rate (m/s), C_m is a constant depending on the metal and r_m is the density of the fluid under operating conditions (Mg/m^3).

C depends on characteristics of material, operating conditions and presence of inhibitors.

Rate of erosion increases in turbulent conditions and can result in leakages in tubes and pipes: turbulence may be caused by pitting or poor finishing.

Some useful precautions and remedies:

- Reduce the turbulence of the fluid in the tube by streamlining the piping.
- Control the velocity of the fluid to reduce high-flow velocities.
- Use corrosion-resistant materials.
- Use corrosion inhibitors and cathodic protection.
- Avoid sharp angles in the piping system, replacing them by gentler angles to avoid constrictions.
- Reduce the amount of oxygen dissolved in the fluid.
- Adjust the pH value of the fluid.
- Choose most adapt metal alloy. [20]

1.3.2.11 Microbiological corrosion

Microbiologically Induced Corrosion (MIC) takes place in water and soils and is caused by action of bacteria. This type of corrosion applies to non-metallic objects as well as metals. This bacteria may be both aerobic and anaerobic, so we have MIC quite independently from oxygen supply. This allows MIC to be present in a lot of different environments, at the bottom of the sea or under several meters of earth.

Aerobic bacteria act through reactions involving oxygen and creating acid conditions, but the most dangerous are anaerobic bacteria, that comprehend SRB (Sulphate Reducing Bacteria).

Environments where oxygen is absent are ideal, from an electrochemical point of view, to avoid corrosion processes, but they are also ideal to encourage growth of these bacteria; furthermore, SRB are extremely adaptable and resistant to extreme conditions. They are reported to resist to temperatures up to 80°C and pressures of 400 bar. Last but non least, they are inactive in aerobic environments, but anyway they survive, waiting for more favorable conditions.

MIC has been noticed in jet fuel tanks: they live in the water-fuel interface of the water droplets, form dark black/brown/green, gel-like mats, and cause microbial corrosion to plastic and rubber parts of the aircraft fuel system by consuming them, and to the metal parts by the means of their acidic metabolic products. Microorganisms can affect negatively radioelement confinement in nuclear waste.

Corrosion rate may reach 1 mm/year.

Biggest difficulties come from SRB corrosion mechanism, that has not yet been fully clarified. By hypothesis, they are supposed to produce an enzyme, hydrogenase, that produces the hydrogen used by the sulphate reducing bacteria to reduce sulphate to sulphides; this is followed by cathodic depolarization due to the precipitation of iron sulphide; finally, anodic stimulation by the sulphide ion occurs with the passing into solution of the iron and the formation of occluded cells.

Aerobic or anaerobic conditions may be verified by a potential measurement, using a platinum electrode: at pH equal to 7, potentials lower than 0,1 V SHE indicate absence of oxygen, while potentials higher than 0,4 V SHE indicate oxygenated conditions.

The presence of bacteria, or more accurately the so-called biofilm, is responsible for triggering pitting corrosion on stainless steels in waters and especially in sea water. The cause of this behavior is associated with the nobilization of the cathodic processes caused by the biofilm, bringing the corrosion potential above steel’s pitting potential.

MIC can be prevented through periodic mechanical cleaning, chemical treatment using biocides, dry storage and total drainage. [21]

1.3.2.12 Stray/Alternating current corrosion

Stray current corrosion, also called electrolytic corrosion, is caused by electrical interference phenomena; stray current responsible for this corrosion are usually generated by DC distributor lines, railway systems, substations. We may have also a contribute from alternating currents, coming from different sources.

We may have also stray current corrosion as collateral effect of cathodic protection, on the same workpiece or on a near one; this may happens in case of wrong spatial layout of structures, for example, or for wrong sizing of protection plant.

Stray current corrosion is almost similar to galvanic corrosion; the main difference is that, in the second case, the current is internally generated, whilst in the first one comes from an external source.

Other aspects are quite similar between two phenomena, such as electrochemical reactions at metal interface and the electrolyte.

Obviously, anode is taken to be the metal that corrodes, cathode is placed where current flows.

Considering a buried metal structure, for example, the mechanism is as follows: current circulating in the earth uses the structure as an electricity conductor, causing corrosion attacks in areas where the current leaves the structure. Current entry zones are in conditions of cathodic protection and don't suffer any corrosion.

Exit zones are usually localized and corrosion rate may be very severe: 1 mA released by 1 cm^2 of metal surface leads to a loss of thickness of 10 mm/year.

There are various prevention methods to avoid or limit stray current corrosion, for example use of insulating coating, electrical sectioning of the structures, electrical drainage and equipotential connections.

About alternating current corrosion, it is also caused by electrical interference, but needs a very high density of the current exchanged between the metal and the earth, usually above 30 A/m^2, about five order of magnitude greater than in stray current case.

Alternating current corrosion takes place when structures run parallel to high voltage power lines and by dispersion into the earth from high speed railway lines.

This corrosion may be limited using insulating coatings, but, if we have a defect in the coating, corrosion rate will be very severe in it. For this reason, main countermeasure is correct positioning of the structure in the ground. [22]

2 CORROSION IN OIL&GAS PLANTS

2.1 Introduction

The total annual cost of corrosion in the Oil&Gas production industry is estimated to be higher than $1.3 billion (www.nace.org, 2008), $600 million only about surface pipeline and facility costs, more than $400 million in downhole tubing expenses and, finally, more than $300 million in capital expenditures related to corrosion.

So, act on this share to reduce corrosion costs may be effective: supposing to reduce to one half corrosion's costs, we will reduce of more than $150 million per year Oil&Gas costs, about the 15% of the whole expenditure. [23]

About this: “[...] Furthermore, according to the U.S. Department of Transportation office of pipeline safety, in the U.S.A. Internal corrosion caused approximately 15% of all reportable incidents affecting gas transmission pipelines overt the past several years leading to an average cost of $3 million annually in property damage, as well as several fatalities. The need to manage and mitigate corrosion damage has rapidly increased as materials are placed in more extreme environments and pushed beyond their original design life. [...]” [24].

It is widely recognized within the Oil&Gas industry that effective management of corrosion will contribute towards achieving the following benefits:

- increased plant availability;
- reduction in unplanned maintenance;
- reduction in deferment costs;
- reduction in leaks.

Corrosion attacks every component at every stage in the life of every Oil&Gas field, from a casing string to production platforms, from drilling to abandonment, corrosion is stronger and more worthy than all technologies we can try to oppose to it. [25]

In this work, we focus our attention on pipelines and fittings, analyzing corrosion mechanisms, with a brief overview on historical developments in this field and solution found to corrosion problems, especially about materials selection and alloys composition.

Pipelines are not the most expensive or complex part in an Oil&Gas plant or distribution net; we have got drilling systems, valves, pumps, etc... . on the other hand, they may extend for thousands kilometers and then weigh a lot on the sum of corrosion costs.

So a strategy to save money based on pipeline technologies is a strategy based on quantity of material involved, not on quality of the workpiece.

The presence, in Italy but also in the rest of the world, of a lot of industry working in this field and researching about new materials and technologies is a good proof of what I am saying is true, but corrosion never rests and, then, also research cannot do it.

A good example of what could happen underestimating corrosion danger is given by Prudhoe Bay's oil spill, occurred in 2006. Below an extract of Wikipedia article about the disaster:

“The Prudhoe Bay oil spill (2006 Alaskan oil spill) was an oil spill that was discovered on March 2, 2006 at a pipeline owned by BP Exploration, Alaska (BPXA) in western Prudhoe Bay, Alaska. Initial estimates of the five-day leak said that up to 267,000 US gallons (6,400 bbl) were spilled over 1.9 acres (7,700 m2), making it the largest oil spill on Alaska's north slope to date. Alaska's unified command ratified the volume of crude oil spilled as 212,252 US gallons (5,053.6 bbl) in March 2008.The spill originated from a 0.25-inch (0.64 cm) hole in a 34-inch (86 cm) diameter pipeline. The pipeline was decommissioned and later replaced with a 20-inch (51 cm) diameter pipeline with its own pipeline inspection gauge (pig) launch and recovery sites for easier inspection.

[...]

In November 2007, BPXA pled guilty to negligent discharge of oil, which prosecutors said was the result of BP's knowing neglect of corroding pipelines, a misdemeanor under the federal Clean Water Act, and was fined US$20 million. In July 2011, BPXA paid a $25 million civil penalty, the largest per-barrel penalty at that time for an oil spill, and agreed to take measures to significantly improve inspection and maintenance of its pipeline infrastructure on the North Slope to reduce the threat of additional oil spills. In November 2012, it was announced that the U.S. state of Alaska would collect $255 million related to BP Plc's pipeline leaks and a resulting shutdown in 2006. BP's share was $66 million since it would pay the award and then be reimbursed by partners, including Exxon Mobil Corp and ConocoPhillips, based on their proportionate share of ownership.

Red flags and warning signs had been raised about corrosion on several occasions both from within and outside the organization but had been ignored. The 1992 tests on the eastern line had indicated the presence of calcium in the line, but nothing was done about it. A company report in year 2005 said BP based its corrosion-fighting on a limited budget instead of needs.

Employees had raised their concerns before the actual incident, which were ignored by BP management. In an e-mail to a company lawyer in June 2004, Marc Kovac, an official of the United Steelworkers union representing workers at the BP facility, forwarded a collection of his earlier complaints to management. One of these, dated February 28, 2003, concerned "corrosion monitoring staffing levels". It began, "The corrosion monitoring crew will soon be reduced to six staff down from eight." Initially BP denied that they took money-saving measures maintaining the pipeline. Robert Malone, the chairman of BP America, cited a report commissioned by BP which concluded that "budget increases alone would not have prevented the leak". He later admitted that there "was a concerted effort to manage the costs in response to the continuing decline in production at Prudhoe Bay". One of the reasons for the pipeline failure was an insufficient level of corrosion inhibitor, a liquid which resists corrosion of pipeline by the corroding liquid, which is water. John Dingell read from an internal BP email that said budgetary constraints would force the end of a program to inject corrosion inhibitor directly into the pipeline system. The process of injecting corrosion inhibitor directly into a pipeline, though costly, is much more effective than injecting in a process plant.

In the subsequent investigation, Carolyn Merritt, chief executive officer of the U.S. Chemical Safety and Hazard Investigation Board, told the committee that "virtually all" of the root causes of the problems at Prudhoe Bay had "strong echoes" of those that led to the 2005 explosion in Houston. These had included cost cutting and a failure to invest in the plant. The committee was also told that the spillage happened at a time when BP was making huge profits.

[…] “.

BP lost a lot of money for this disaster, in addition to incalculable environmental damage caused by dispersed oil. This is only an example of what underestimation of corrosion may lead to: it is at least a contributory in a lot of oil spills, from pipelines or platform.

2.2 Corrosion mechanism in Oil&Gas industry

Corrosion mechanisms in Oil&Gas plants and pipelines are almost related to the presence of water, wetting the corroding surface in a permanent or intermittent way.

So, corrosion strictly depends on the composition of the hydrocarbon phase and the operating conditions.

There is an empirical rule, useful to evaluate quantitatively how much dangerous a situation may be: water wetting occurs in vertical flows (i.e. in wells) when the percentage of the aqueous phase exceed 20% in volume, whereas in horizontal flows (i.e. pipelines) this percentage is lower than 1%. This happens because, according to difference densities, water tends to flow at the bottom of the pipe in horizontal transportation lines and this favors wetting by water phase. At the contrary, in vertical flows water is more dispersed and less in contact with walls of the pipe.

These percentages of water are not referred to total water content, but only to the free water phase, that is not emulsified in the hydrocarbon phase.

This water usually has got the same composition of formation water, so with high salinity, above 100g/L.

Furthermore, water wetting depends on temperature, pressure and presence of gas; the presence of gas is correlated with the bubble point pressure at the temperature considered: if the pressure is above the bubble point pressure, all the gas is dissolved in the liquid hydrocarbon phase.

Water wetting makes oxygen available to start corrosion processes involving it, but there are other mechanisms.

Water carries on also CO_2, that can cause severe corrosion; acids, used to reduce formation damage around the well or to remove scale, readily attacks metal; sands, mud and sludge flowing with oil and water may cause erosion-corrosion; presence of sulphides may lead to correlated corrosion mechanisms and the same for free hydrogen ions. [27]

Handling all these corrosion situations, with the added complications of high temperatures, pressures and stresses involved in drilling or production or distribution is very difficult and requires a careful choice of materials to employ and development and use of adequate countermeasures.

Even though it is almost impossible to prevent all these kind of corrosion at the same time, the most economical solution (and probably the only possible one) is to control corrosion rate, reducing one of the four processes seen in the chapter 1.2.2.1.

So, start analyzing in details how corrosion works in an Oil&Gas plant.

2.2.1 Corrosion by CO_2

The presence of CO_2 in the aqueous phase of hydrocarbons leads to the formation of carbonic acid which, even though it is a weak acids, is very aggressive on carbon steel. Corrosion rate of carbonic acid, for example, is ten times higher than corrosion rate in hydrochloric acid, that is a strong acid at the same pH. This happens because of different kinetics of the reaction of the hydrogen ion reduction and the subsequent release of molecular hydrogen; for carbonic acid, bicarbonate ion participates directly in the reduction and hydrogen release reaction.

Presence of CO_2 may activate different corrosion mechanisms, varying with temperature and partial pressure of carbon dioxide.

Below 80°C, CO_2 presence causes generalized corrosion, with a typical morphology called Mesa corrosion.

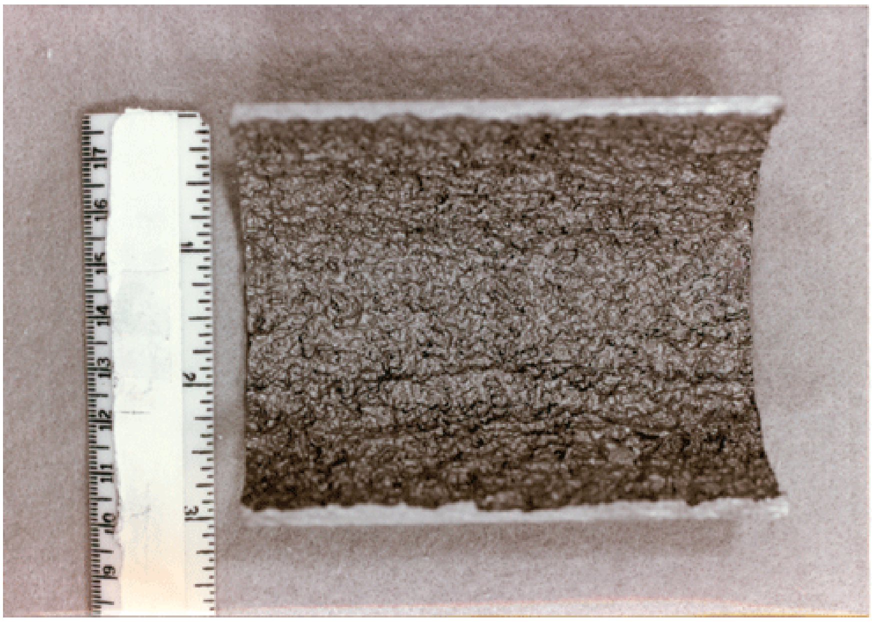


Figure 8: Mesa corrosion case (www.pipelinemaster.wordpress.com)

Rising the temperature (80°C – 120°C), we also have generalized corrosion but with formation of partially protective Fe and Ca carbonates, creating passivation conditions; this leads to a negligible corrosion rate for temperatures higher than 120°C.

So, briefly:

- $T < 60°C$, $p_{CO2} < 5$ bar : corrosion products are not protective;
- $60°C < T < 100°C$: corrosion products are partially protective;
- $T > 100°C$: corrosion products are protective.

Adding chromium to steel, we improve corrosion resistance by as much as 0,5% (especially to Mesa corrosion) at temperatures below 90°C.

In addition to temperature and CO_2 partial pressure, corrosion rate of carbon steel varies also depending on pH of the aqueous phase (linked to salinity and concentration of hydrogencarbonates).

Partial pressure is given by the product of the mole fraction of CO_2 in the separated gas phase and the working pressure in presence of gas in equilibrium with the liquid phases or the bubble point pressure if the gas is dissolved in the liquid phase under operating conditions.

Corrosion rate for CO_2 corrosion may be calculated using De Waard – Milliams equation, formulated in the '70s:

$$\log\left(v_{CO_2,dWLM}\right) = 5.8 - \frac{1.710}{T+273} + 0.67 \times \log\left(p_{CO_2}\right)$$

where $v_{CO_2,dWLM}$ is the corrosion rate in mm/year and p_{CO_2} the partial pressure of CO_2 in the gas phase. Starting from this basic equation, other factors are corrections determined empirically, taking into account fugacity for pressures above 100 bar, formation of deposits and pH.

But how CO_2 changes pH in the moisture and how much does it changes?

pH variations are difficult to measure directly in pipelines, so some empirical formulas have been developed to estimate pH from moisture composition.

Two cases may be: the first one, characterized by presence of bicarbonates, and the second one, characterized by absence of bicarbonates.

- In the presence of bicarbonates:

$$pH = 4.4 - 0.475 \cdot \ln\left(p_{CO_2} + p_{H_2S}\right) + 0.5 \cdot \ln\left(HCO_3^-\right) + 0.00375 \cdot T$$

- In the absence of bicarbonates:

$$pH = 3.8 - 0.195 \cdot \ln\left(p_{CO_2} + p_{H_2S}\right) + 0.00375 \cdot T$$

where p_{CO_2} and p_{H_2S} are partial pressures of CO_2 and H_2S, T is the temperature and (HCO_3^-) the concentration of bicarbonates in solution [meq/L].

Although, concentration of bicarbonates may be unknown or difficult to measure, so we may estimate it: it is assumed as zero in case of condensates alone and equal to 10 meq/L in presence of formation water.

Other models has been proposed in order to calculate pH, taking into account more factors, for example CO_2 diffusion.

Which are the reactions that, taking place, modify pH conditions?

When CO_2 is dissolved in water reacts with this, as follows:

$$CO_2 + H_2O \leftrightarrow H_2CO_3$$

Carbonic acid is diprotic and dissociates:

$$H_2CO_3 \leftrightarrow H^+ + HCO_3^-$$
$$HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$$

originating CO_3^{2-}, that tends to form carbonates, but also ionic hydrogen, leading to various forms of hydrogen corrosion.

When the steel corrodes:

$$Fe + 2H_2CO_3 \rightarrow Fe^{2+} + 2HCO_3^- + H_2$$

Because pH in the solution increases, concentrations of Fe^{2+} and CO_3^{2-} increase above the solubility limit, leading to precipitation of iron carbonate:

$$Fe^{2+} + CO_3^{2-} \rightarrow FeCO_3(s)$$

Solid iron carbonate is formed at the same velocity as steel corrodes, so pH remains constant in the whole system.

As already said, solubility of this carbonate is strongly dependent on p_{CO_2} and pH, making difference between protective or non-protective scale.

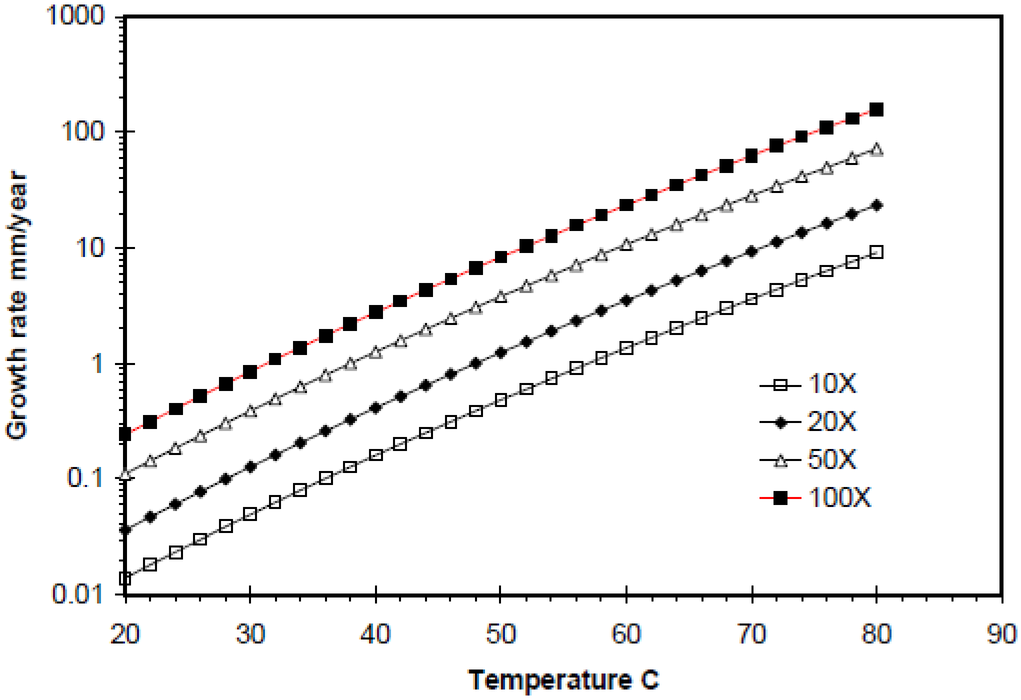


Figure 9: calculated growth rate of iron carbonate as a function of temperature and different supersaturation (NaCl = 1 wt%).

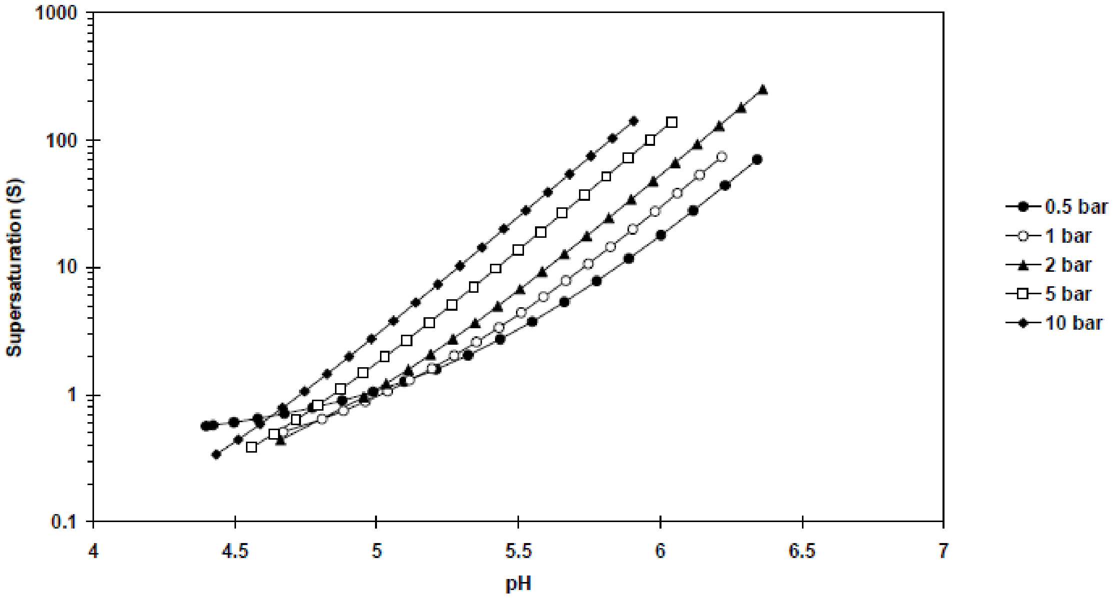


Figure 10: supersaturation obtained in the brine when it is assumed that the corrosion process releases 30 ppm dissolved Fe2+ in the water. The pH is the one in the brine before corrosion starts (NaCl = 1 wt%).

Coming back to empirical model of corrosion, the glycol factor, FGLY, takes into account glycol effects on CO_2 corrosion rate and is added to De Waard – Milliams model.

Condensation factor applies to gas systems when cooling is expected. Condensation Factor applies to gas systems when cooling is expected. Water condensing under a high partial pressure of CO2 is acid and quite corrosive, but iron bicarbonate FeCO3 produced as corrosion product is highly soluble in the thin water film and behaves as an excellent pH controller. Corrosion rate of steel exposed to water phase condensing from wet gas, quickly decreases with time in slowly cooling systems.

For the calculation of the condensation factor, two different cases may be expected: slow cooling systems and rapid cooling systems as heat exchangers or coolers. In the latter case, condensation factor is equal to 1.

To provide a rough calculation of the corrosiveness of hydrocarbons containing CO2, the American Petroleum Institute proposed an empirical rule in the ‘50s based on the partial pressure of the CO2:

- P_{CO2} < 7 psi (0,5 bar): CO_2 corrosion is almost negligible;
- P_{CO2} > 14 psi: CO_2 corrosion becomes significant.

However, this is an insufficient and too rough method to evaluate CO_2 corrosion.

So, an empirical model was developed in the '80s, providing a classification of CO_2 corrosion as high, medium or low, based on:

- p_{CO2};
- pH;
- acetic acid content;
- Ca^{2+}/HCO_3^- ratio.

In Oil&Gas applications, acetic acid content may be neglected; Ca^{2+}/HCO_3^- ratio takes into account a reaction parallel to formation of iron carbonate that is in conflict with it but that also form a carbonate that may be protective. Anyway , for condensed water, corrosiveness is low if p_{CO_2} <0.05 bar or if p_{CO_2} <0.2 bar and acetic acid<0.1 meq/L; medium if 0.2< p_{CO_2} <5 bar and acetic acid<0.1 meq/L; in other cases, corrosiveness is high. For formation water, corrosiveness is low if p_{CO_2} < 0.05 bar or pH>5.6 or 0.05< p_{CO_2} <10 bar and Ca^{2+}/HCO_3^- <0.5 meq/meq; medium if acetic acid<0.1 meq/L or Ca^{2+}/HCO_3^- <1000 meq/meq; in other cases, corrosiveness is high.

Let's briefly talk about electrodes reactions that take place in *CO_2* corrosion.

At the cathode, supposing absence of acetic acid, we have carbonic acid and hydrogen reduction, with the development of molecular hydrogen and carbonate ions:

$$H^+ + e^- \rightarrow {}^1\!/_2 H_2$$
$$H_2CO_3 + e^- \rightarrow {}^1\!/_2 H_2 + HCO_3^-$$

Relative contribution of both reactions depends on concentrations, temperature, pH and other factors.

The presence of CO_2 affects the mechanism modifying H^+ concentration and/or amount of undissociated H_2CO_3.

In formation water, typical pH values are around 5: at this value, hydrogen is not fully dissociated; the rate of hydrogen evolution develops according to the first of the two previous reactions and cannot exceed the rate at which H^+ ions are transported to the surface from the bulk solution. So, in this situation, the second reaction, involving H_2CO_3, serves as an additional source of H^+ ions, enabling hydrogen evolution reaction to proceed at higher rate than in a solution of a strong acid at the same pH.

Some experimental results indicate that also reduction of bicarbonate ions and water can become important at low p_{CO2} partial pressure and high pH:

$$2HCO_3^- + 2e^- \rightarrow H_2 + 2CO_3^{2-}$$
$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

Concentration of HCO_3^- increases with pH but, although it can be very high, “the low dissociation constant makes bicarbonate and water poor proton donor and it is believed that the contribution from these reactions will be negligible under normal sweet conditions.” (Fundamentals aspects of CO_2 metal loss…..)

High HCO_3^- concentration may origin H_2CO_3 regeneration, affecting corrosion rate.

At the anode, instead, we have iron oxidation:

$$Fe \rightarrow Fe^{2+} + 2e^-$$

Suggested mechanism for oxidation is the following:

$$Fe + H_2O \leftrightarrow FeOH + H^+ + e^-$$
$$FeOH \rightarrow FeOH^+ + e^-$$
$$FeOH^+ + H^+ \rightarrow Fe^{2+} + H_2O$$

For strong acidic environments.

pH dependence decreases rapidly increasing pH and the same for OH^- concentration; presence of CO_2, instead, is relevant.

An experimental equation to evaluate iron dissolution has been proposed by Nesic:

$$i_a = k\left[OH^-\right]^{a1} \cdot \left(p_{CO_2}\right)^{a2} \cdot 10^{\frac{E}{b_a}}$$

where:

- pH < 4 → $a_1 = 2$, $b_a = 0{,}03$V per decade;
- 4 < pH < 5 → $a_1 = 2 - 0$, $b_a = 0{,}03$V – 0,12V per decade;
- pH > 5 → $a_1 = 0$, $b_a = 0{,}12$V per decade.

and

- $p_{CO_2} < 10^{-2}$ bar → $a_2 = 0$;
- 10^{-2} bar < $p_{CO_2} < 1$ bar → $a_2 = 1$;
- $p_{CO_2} > 1$ bar → $a_2 = 0$.

It was also proposed an alternative mechanism for iron dissolution, valid for pH > 5:

$$\begin{aligned}
&Fe + CO_2 \leftrightarrow Fe_L \\
&Fe_L + H_2O \leftrightarrow Fe_L OH_{ad} + H^+ + e^- \\
&Fe_L OH_{ad} \rightarrow Fe_L OH_{ad}{}^+ + e^- \\
&Fe_L OH_{ad}{}^+ + H_2O \rightarrow Fe_L(OH)_{2ad} + H^+ \\
&Fe_L(OH)_{2ad} \leftrightarrow Fe_L(OH)_{2sol} \\
&Fe_L(OH)_{2sol} + 2H^+ \leftrightarrow Fe^{2+} + CO_2 + 2H_2O
\end{aligned}$$

Where Fe_L stays for $Fe – CO_2$ complex.

We already talk about pH dependence of protective film formation and precipitation reactions: as known, precipitation depends on supersaturation of $FeCO_3$ and is generally a slow process, requiring high degree of supersaturation.

Precipitation process divides in two steps: nucleation and growth.

$$\begin{aligned}
&S = \frac{\left(C_{Fe^+} \cdot C_{CO_3^{2-}}\right)}{K_{sp}} \\
&RS = \frac{\left(Q - Q_{eq}\right)}{Q_{eq}} = (S - 1)
\end{aligned}$$

where S is saturation, RS is relative saturation, Q is solute concentration, Q_{eq} is equilibrium solubility, K_{sp} the solubility product for $FeCO_3$.

The nucleation rate increases exponentially with *RS*, instead growth rate shows linear dependence on it. So, growth step dominate at low *RS*, while at high relative supersaturation nucleation occurs at high velocity, forming a colloidal solution close to the steel surface or inside the film. Then, coagulation becomes important in this situation to form a protective film; it is accelerated by heating.

At high T (T > 60 °C), precipitation rate is fast and supersaturation is low: dense crystalline film is often granting good protection. Lowering temperature, precipitation rate decreases, supersaturation is high and crystallinity of carbonate layer is low. The formed film is porous, low adherent and not protective.

From experiments, it is assumed that growth rate of iron carbonate has to be equal or higher than corrosion rate to form an iron carbonate film close to the metal surface. To have a growth rate able to match a corrosion rate of 1mm/year at 40 °C, about 50 times supersaturation is necessary: this value is supposed to be established at the metal surface when dissolved iron content is high and a surface layer restrict the transport of reactants and corrosion products. "The maximum supersaturation will then be a balance between the corrosion rate, nucleation rate and the rate of transport." (Fundamental aspects of CO_2 metal loss…)[28] [29]

2.2.2 Corrosion by H_2S

As for CO_2, presence of H_2S leads to various forms of corrosion: generalized corrosion (carbon steel), formation of blisters (HIC, Hydrogen Induced Cracking), SSCC (Sulphide Stress Corrosion Cracking), SOHIC (Stress Oriented Hydrogen Induced Cracking, a combination of HIC and SSCC).

Let's start talking about **generalized corrosion by H_2S**. H_2S is not a strong acid, but can cause severe corrosion attacks forming iron sulphide FeS, with a very low solubility product: this leads to a decrease in anodic potential of iron and the consequent availability of a driving force even in neutral solutions.

Sulphide is not always compact and protective, leading sometimes to localized corrosion by galvanic mechanism: in fact, sulphide is more noble than iron.

Corrosion rate is strictly dependent on temperature and H_2S concentration. At T < 60 °C corrosion rate is negligible, at least until H_2S concentration is below 40 ppm: if not, corrosion rate may be significant (0,5 mm/year); at T > 60 °C, corrosion rate is about 1 mm/year (again for H_2S concentration higher than 40 ppm).

The most dangerous mechanisms in sour environment are ones that involve hydrogen.

The first one is **hydrogen induced cracking (HIC)**; it is caused by the entry of atomic hydrogen into the metal, causing blistering. Blisters and cracks are caused by recombination of ionic hydrogen into molecular form after entry in the metal, where ions are trapped in form of inclusions or microvacuums. So, after recombination, H_2 becomes too large and accumulates high internal stresses and pressures, causing local plastic deformations.

The mechanism has already been explained in the chapter 2.4.7, when we talked about hydrogen embrittlement. The characterizing aspect in this situation is the origin of ionic hydrogen. Hydrogen ions come from reaction between metal and H_2S, with the formation of metal sulphide and hydrogen released as a byproduct. The acidic environment cause hydrogen dissociation and lead to migration of ions into the metal. Obviously, this phenomenon is linked to the quantity of hydrogen that penetrate into the metal and for how much of time penetration takes place. If the partial pressure of H_2S is above 0,1 bar, it comes to the surface in a very long time (15-20 years).

When the concentration arises and partial pressure $p_{H2S} > 0{,}3$ bar, two ways are possible to reduce HIC: use of corrosion inhibitors or use of less vulnerable materials.

Sulphide stress corrosion cracking (SSCC) is again a form of hydrogen embrittlement, particularly a cathodic cracking mechanism.

It is easy to confuse SSCC with SCC, stress corrosion cracking, but the second one is completely different.

Again, vulnerable metals react with hydrogen sulphide, producing metal sulphides and atomic hydrogen as byproducts; atomic hydrogen recombines at the surface or penetrates into metal. Although, recombination is hindered by presence of sulphur, so these is an increasing in the amount of hydrogen that can diffuse into the metal. This is the reason for that H_2S environment is so dangerous in this case. This phenomenon depends on numerous factors: steel’s composition, heat treatments, microstructure, mechanical resistance, pH, partial pressure of H_2S, applied load, temperature and time.

SSCC development is evaluated on H_2S partial pressure.

As for CO_2 and relative corrosion, it is often difficult to calculate H_2S partial pressure directly, so sometimes it is estimated starting from mass balance of H_2S according to procedures described in specialist manuals.

Then, according to NACE indications, environment is described as "sour" when H_2S partial pressure and H_2S concentration exceed given thresholds. Following, a graph showing parameters for gas wells:

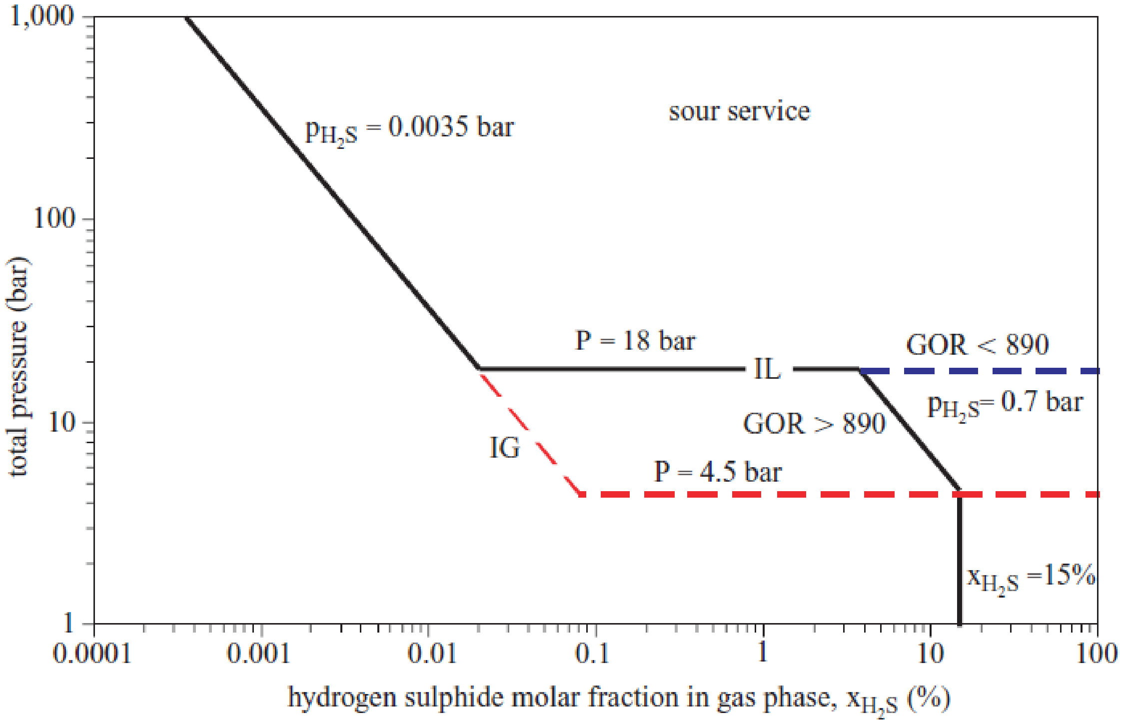


Figure 11: identification of conditions for the onset of SSCC (according to NACE, 2003).

In presence of a multiphase system (liquid-gas), the conditions of non-onset are:

- Gas Oil Ratio (GOR) < 890 Nm^3/m^3;
- Mole fraction of H_2S in gas < 15%;
- $p_{H_2S} < 0,7$ bar;
- working pressure P < 18 bar.

Only in the presence of a high water content should the definition of sour environment be reconsidered, with the possible onset of SSCC in the system.

On the other hand, if the considered system does not fall in above considerations, we may have sour corrosion if:

- P > 18 bar and $p_{H_2S} > 0,0035$ bar;
- P ≤ 18 bar and $p_{H_2S} > 0,0035$ bar and GOR > 890 Nm^3/m^3;
- 4,5 < P < 18 bar and $p_{H_2S} > 0,7$ bar and GOR > 890 Nm^3/m^3;

- P < 4,5 bar and C_{H_2S} > 15% and GOR > 890 Nm^3/m^3.

This is NACE standard to define sour environments. Also another criterion exists, according to ISO-EFC, that integrates the previous one; it is based on three parameters: p_{H_2S}, pH of aqueous phase (pH_{act}) and temperature.

So:

- Very severe sour conditions:
  - $pH_{act} \leq 3,5$;
  - 0,01 bar < p_{H_2S} < 1 bar and $pH_{act} \leq 5,5 + \log(p_{H2S})$;
  - p_{H_2S} > 1 bar and $pH_{act} \leq 5,5$.

- Severe sour conditions:
  - 0,001 bar < p_{H_2S} < 0,01 bar and $3,5 < pH_{act} \leq 6,5 + \log(p_{H_2S})$;
  - 0,01 bar < p_{H_2S} < 1 bar and $5,5 + \log(p_{H_2S}) < pH_{act} \leq 6,5 + \log(p_{H_2S})$;
  - p_{H_2S} > 1 bar and $5,5 < pH_{act} \leq 6,5$.

- Moderate sour conditions:
  - 0,001 bar < p_{H_2S} < 1 bar and $pH_{act} \leq 6,5 + \log(p_{H_2S})$;
  - p_{H_2S} > 1 bar and $pH_{act} > 6,5$.

- Non-sour (sweet) conditions:
  - p_{H_2S} < 0,001 bar and $pH_{act} < 3,5$.

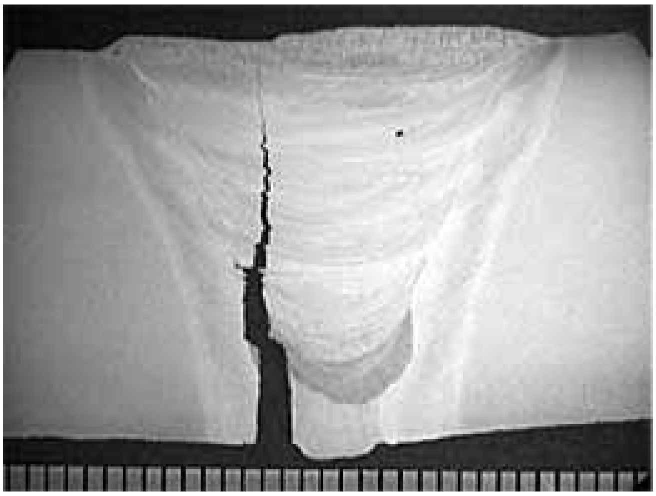


Figure 12: sulphide stress corrosion cracking case, with an intergranular/transgranular branched appearance (www.twi-global.com)

Last but not least, **corrosion by sulphur**. Sulphur may be present in petroleum reservoirs in association with H_2S. his melting point is at 113 °C and boiling point at 445 °C.
Formation of sulphur may occur in reservoirs starting from sulphates ions and methane:

$$SO_4^{-} + CH_4 \text{ ® } S + 2H_2O + CO_2$$

Other mechanisms consist in catalytic composition of hydrogen sulphide or oxidation of hydrogen sulphide by oxygen. Sulphur reacts with hydrogen sulphide to form polysulphides which in turn release sulphur to form deposits and slugs.
So, according to this mechanisms, presence of sulphur implies presence of CO_2 and/or presence of slugs at the bottom of the pipe: so we may have a lot of different corrosion mechanisms because of sulphur formation or presence. Although, these are secondary effects. Directly , “sulphur is an effective cathodic reagent, acting as an electron acceptor through the catalytic action of the sulphide films which have electron conductivity, and gives rise to high corrosion rates when it comes into direct contact with steels; if it is present in an hydrocarbon solution, the corrosion rate is controlled by diffusion processes. At high temperatures, above 120 °C, sulphur reacts becoming H_2S and sulphuric acid, breaking passivation films and leading to localized corrosion (crevice corrosion and SSCC)”. [30]
Corrosion rate, then, strictly depends on temperature. If T < 120 °C, corrosion rate increases because sulphuric acid is formed; above 150 °C, corrosion products become

protective and corrosion rate tends to decrease; at 180 °C, or above, corrosion rate becomes so high to require different materials to be employed (~10 mm/year).

2.2.3 Other corrosion mechanisms in Oil&Gas

2.2.3.1 Erosion-corrosion

Fluids from reservoirs are usually characterized by presence of slugs and suspended solids: this situation, associated to an high fluid velocity, may lead to erosion-corrosion. This synergy between corrosion (chemical) and mechanical action of the fluid may affect practically all metallic materials if given conditions of critical erosion corrosion rate are exceeded.

Erosion-corrosion, then, takes place when assisted by high turbulence, causing impingement.

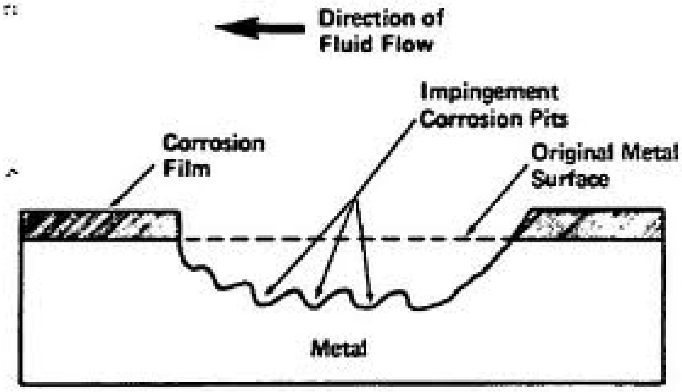


Figure 13: impingement mechanism.

In Oil&Gas industry, critical erosion-corrosion rate is calculated with an empirical formula:

$$v_e = C \Big/ \sqrt{r_m}$$

where v_e is the critical erosion-corrosion rate (m/s), C is a constant depending on the metal and ρ_m is the density of the fluid under operating conditions (Mg/m^3). "Constant C takes on different values depending on the type of material, the type of service (continuous or intermittent) and the presence of a corrosion inhibitor. The values of constant *C* in the absence of inhibitors are 40 for copper, 60 for copper-nickel 70/30, 120 for carbon steels and 500 for stainless steels. Whenever aggressive conditions are particularly severe, it becomes necessary to use hard and corrosion resistant coatings such as stellites and ceramic coatings.” [31]

2.2.3.2 Microbiologically Induced Corrosion (MIC)

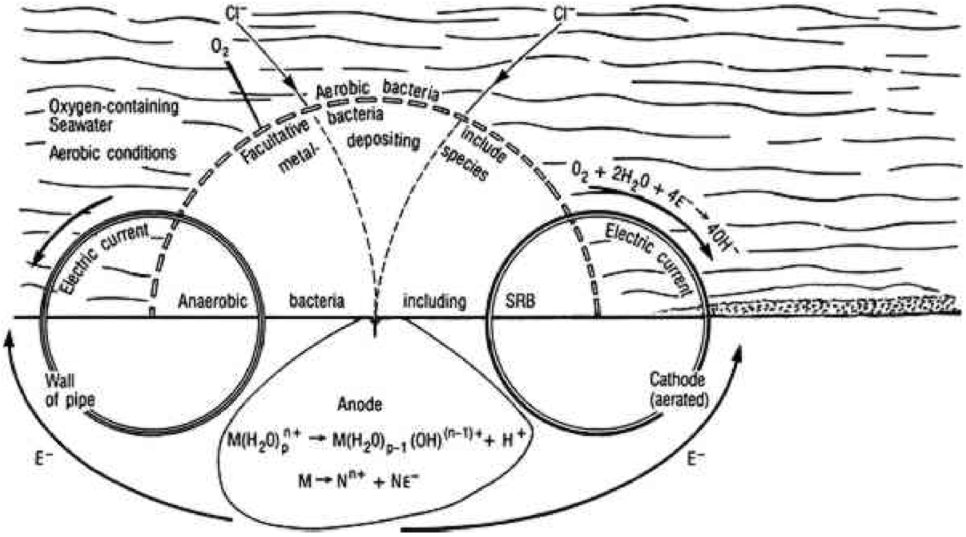


Figure 14: MIC mechanism.

MIC is a mechanism that may be present both in soil or in water; it is due to the presence and action of bacteria, aerobic or anaerobic. In Oil&Gas application, most frequent situation is the anaerobic one, where live anaerobic bacteria, growing in absence of oxygen. A perfect environment for these bacteria, usually SRB (Sulphate Reducing Bacteria), consists in slugs and mud at the bottom of pipelines: there, SRB may live and grow in a lot of temperature and pressure conditions, causing damages on pipes.

Absence of oxygen is an ideal condition to avoid every corrosion process, but, at the same time, it is the ideal condition of life for SRB: corrosion rates above 1mm/year have been reported.

“Anaerobic bacteria are extremely adaptable and able to resist temperatures of up to 80°C and pressures of 400 bar. In aerobic environments they are inactive, but can survive, ready to grow if anaerobic microenvironments are created (for example, beneath deposits).” [32]

2.2.3.3 Stress Corrosion Cracking

As already explained, the term stress corrosion cracking (SCC) is used to describe phenomena involving the formation and propagation of cracks in a metal subject to the combined action of tensile (but not compressive) mechanical stresses and a corrosive environment.

In Oil&Gas application, we already talk about SCC describing SSCC and relative hydrogen embrittlement mechanism. Also chloride induced corrosion by anodic dissolution may be present in this environment, but it is less relevant than others.

We may also have Stress Corrosion Cracking by Chloride: it requires a temperature above 60 °C (but initiation temperature depends on chloride concentration), chloride concentration above 10 ppm (but depending on composition of the steel, so may be higher), an applied (or residual) tensile stress higher than about 30% of the braking load. [33]

2.2.3.4 Naphthenic acids corrosion

When organic acids are present in crude oil, especially those with a naphthenic structure, carbon and low alloy steels are subject to corrosion at temperatures between 200 and 400 °C with a peak at 275 °C (Corrosion in the oil refining industry conference, 1998). The corrosion attack is often associated with erosion-corrosion phenomena due to high turbulence. The corrosion mechanism entails the formation of iron complexes with the organic acids. [34]

Usually, in a pipeline, different mechanism are presents and interact each other: this leads to more dangerous situation and higher corrosion rates than ones specific for every mechanism, often also higher than the sum of them.

An example of dangerous “collaboration” is that between erosion-corrosion and sweet corrosion (CO_2): because of mechanical action of sands and slugs transported by flowing moisture, protective carbonate layer is destroyed or cannot form, neither in presence of favourable conditions of temperature and concentration. This obviously depends on flow conditions, like velocity and dimensions of aggregates. Experimental analysis on this phenomenon has been conducted by O.Klein, H.Hoffmeister, M.Soppa, R.Klatt and M.Jung. Results are reported as follows:

“Experiments presented in this paper were performed at room temperature (RT) and at 80°C +/-2°C as noted, as well as at atmospheric pressure. The quartz sand used had diameters between 0.7 and 1.2 mm; the grains were sharp edged. The distribution of the erosion particles was dictated by the rotational speed of the rotor as it would be dictated by the rotational speed of the screw in a multiphase pump. CO_2 was continuously introduced into the system throughout the length of the experiments in order to insure Carbon Dioxide saturation including a pH of around 4.2. The oxygen content was not measured.

The following test series were carried out:

1. Investigation of the effect of various rotational speeds (rpm) at constant sand loads and temperatures.
2. Investigation of the effect of different sand loads at constant rotational speeds at room temperature
3. Investigation of the effect of elevated temperature (80°C) with different sand loads and constant speed

In addition to the total wear by weight the electrochemical wear as part of the total wear was determined from the measured corrosion current densities.

[…]

The experimental results are summarized as follows:

1. With a constant sand load fraction of 10 wt.%, the highest wear is recorded at speeds below 550 rpm and above 1700 rpm due to gravity forces prohibiting an even distribution of the erosion particles at low speeds and the kinetic energy of the erosion particles combined with a reduction of the boundary diffusion layer at high speeds.
2. At room temperature, the mean corrosion current densities rise with the velocity due to a reduction of the boundary diffusion layer.
3. With identical sand loads at room temperature, the radial extension of the area of wear remains constant above the critical low speed.
4. At experiments run at a constant speed of 1180 rpm, sand rates from 0.1-3 wt.% delivered almost the same result. A further increase in sand load raises the wear exponentially.
5. At 1770 rpm and a sand load of 10%, the wear rate rises by more then 50 % when the temperature is elevated from room temperature to 80°C.

For the operation of multiphase pumps and the choice of materials the following conclusions are drawn:

1. A reduction of speed when operating with high sand loads is a feasible measure to reduce wear on the screws.
2. There is, however, a critical speed, below which the wear will increase due to an uneven distribution of the erosion particles. This critical speed will depend on the type and size of pump used.
3. The data further indicates, that when operating at sand loads below 3 wt.%, little erosive wear can be expected and the material should be optimized regarding corrosive attack.
4. With increasing temperatures, the corrosion part of the total wear rate will increase which means that higher corrosion resistances should be considered for the materials." [35]

Increasing wear by particles collision on the pipe walls, we increase the amount of surface available for sweet corrosion, destroying continuously protective carbonate film (just in case of favourable conditions for formation).

The same thing may happen in presence of sour environment or chlorides, creating more aggressive environments.

About this problem, there is also an article, by A. Akbar, X. Hu, A. Neville and C. Wang, investigating about real influence of flow rate on use of inhibitors and protective layer. Briefly:

"[…]The influence of sand on total degradation of as-received X-65 carbon steel can be recognized by comparing the thickness losses between erosion-corrosion tests carried out with and without sand. It is clearly shown that the thickness loss with sand (3.24 mm/year) is higher compared with thickness loss without the presence of sand (2.4 mm/year) […]

According to this results and as we said previously, combinations of different corrosion mechanisms are much more dangerous than simple sum of singular effects.

Another possible interaction is that between corrosion by sulphur and MIC. Corrosion by sulphur has got the effect of producing slugs at the bottom of the pipe, as a consequence of the reaction of sulphur reduction: this slugs, accumulating also for several millimetres, form an anaerobic environment perfect for SRB life and growth, leading to two different corrosion mechanisms, MIC at the bottom and by sulphur (or generally sour) at the top of the pipe.

Other studies has been conducted about, for example, interaction between H_2S, CO_2 and acetic acid, not strictly related to Oil&Gas industry but useful to understand mechanisms that have not yet been fully understood" [36].

Last but not least, it's important to mention possible interaction between flow corrosion and use of protective coatings. The effect of erosion-corrosion is analogous to that on protective carbonate film in the first analyzed situation, but here protective layer cannot regenerate reducing flow velocity or generally the effect of flow corrosion.

In the next chapter we will talk about possible solution and criteria to make a choice about materials to use in these corrosion situations.

2.3 Solution and materials for corrosion problems in Oil&Gas

As described in previous chapters, a lot of different corrosion combination are possible in a Oil&Gas pipeline, so it is difficult to establish which material is the best for every situation, particularly if we need to use also inhibitors or coatings in association with it.

"The materials selection process should reflect the overall philosophy regarding design life, cost profile, inspection and maintenance philosophy, safety and environmental profile, failure risk evaluations and other specific project requirements. Materials selection should be optimized and provide acceptable safety and reliability. At a minimum, the following should be considered:

- Corrosivity, taking into account specified operating conditions including start up and shut-down conditions;
- Design life and system availability requirements;
- Failure probabilities, failure modes and failure consequences for human health, environment, safety and material assets;
- Resistance to brittle fracture;
- Inspection and corrosion monitoring; and
- Access for maintenance and repair." [37]

Last but not least, we have to consider costs and material accessibility in design phase.

Then, let’s start analyzing ideal materials for every kind of corrosion mechanism and relative countermeasures, trying, at the end, to make some general considerations.

2.3.1 Sour corrosion

In sour environments, two main problems must be solved: generalized corrosion by sulphur and hydrogen adsorption. So, we have to exclude carbon steel and duplex stainless steel, because they undergo generalized corrosion by sulphur also at room temperature. The same happens for austenitic stainless steels but only above 120 °C, so they give acceptable performances for our temperature range.
Passing to martensitic steels, the problem becomes mechanical resistance, often very low compared with austenitic ones; it may be increased adding chromium, molybdenum, nickel, but it also rises costs of the resulting alloy.
About hydrogen embrittlement, we have to avoid as much as possible migration of hydrogen ions into the metal and consequently recombination inside it. So, we must avoid trap formation inside steel, choosing correct elements to add and correct quantities of everyone. [38]

“The inclusions with the greatest impact on this phenomenon are those of manganese sulphide (MnS_2 type II), which during the hot lamination of the carbon steels used for pipelines and the sheets for pressurized containers are squeezed and arranged parallel to the direction of lamination, thus forming an easy trap for the hydrogen atoms. The phenomenon is linked to the quantity of hydrogen penetrating into the metal and time; if the partial pressure of H_2S is above 0.1 bar (concentration in the aqueous phase of about 400 ppm), it emerges on vulnerable steels in a time comparable to the mean project life of oil facilities (15-20 years); at partial pressures below 0.1 bar, the phenomenon is nonetheless present on vulnerable steels and emerges over a longer time. When the concentration of H_2S is significant, for example $p_{H_2S} > 0.03$ bar, two different strategies can be adopted (or both) to limit HIC: the use of corrosion inhibitors, which reduces the quantity of hydrogen produced, and the use of steels which are not vulnerable to this phenomenon. The latter may be of two types: steels treated with rare earths, in which the sulphur contained in the steel is combined with elements whose affinity is higher than manganese, such as calcium and caesium which form hard sulphides that are not squeezed during hot lamination; steels with a low sulphur content (20-50 ppm) so that the quantity of Mn sulphide able to form is insufficient for the phenomenon to set in.” [39]

The second option, use of steels containing rare earth, is better than use of inhibitors cause does not ask continuous intervention and avoid difficulties about injection of inhibitors and homogeneously distribution in the flow. On the other hand, rare earth may be more and more expensive than inhibitors on thousands of kilometres of pipelines. So every case must be valued carefully also on the economic side.

2.3.2 Sweet corrosion

Presence of CO_2 is very dangerous for carbon steel, comparable to the presence of a strong acid, instead of a weak acid like carbonic one. So, it is necessary to add other elements to steel to improve resistance to sweet corrosion; in this case, chromium is the right choice. In fact, chromium improve formation a more stable protective carbonate film on the steel surface, also at very low concentration: a typical concentration is 0,5%, so this is an effective and quite cheap solution to avoid sweet corrosion.
If this countermeasure is not sufficient, we may employ CRA (Corrosion Resistant Alloy), but this is usually an expensive choice to do, so the first one is preferable if possible.
In every case, corrosion inhibitors are useful and can be employed, so they must be taken into account.

“In summary, when CO_2 corrosion takes place, the procedure is: Base corrosion rate, $v_{dWM,B}$ according to dWM; correction by introducing correction factors; calculation of the expected corrosion rate on the basis of Water wetting factor, FWW; and finally calculation of corrosion rate in the presence of a corrosion inhibitor. When inhibitors are used, a corrosion allowance has to be taken into account.” [40]

Referring to the last sentence, let’s a cite experimental results by L. D. Paolinelli, T. Pérez, S. N. Simison, titled “The Influence Of Cr Content On The Efficiency Of Inhibitor Of C-Mn Steel CO_2 Corrosion”. The aim of that work was to analyze dependence on Cr content and other factor (i.e. steel microstructure) of efficiency of a commercial imidazoline-based product to control CO_2 corrosion. Here the results:

“• Cr addition has a remarkable detrimental effect on the efficiency of the studied inhibitor.
• Microstructure influence was also observed (the tempered martensite structure presented a better performance compared to ferrite-perlite one), but the effect is secondary to that of Cr. In addition, pre-corrosion decreases efficiency and its impact is also microstructure dependent.
• More work has to be done in order to provide additional evidence on the effect of microstructure and corrosion products films characteristics on inhibitors efficiency. Particularly, in order to clarify the influence of chromium enrichment it will be very useful to monitor the system for different periods of pre-corrosion and longer inhibitor film formation time.
• The effect of steel composition and microstructure on inhibitor efficiency should be taken into account for inhibitor selection.” [41]

So, every couple material – inhibitor must be carefully valued before applying it, because it may have exactly the effect opposite to that expected.

2.3.3 SCC by chlorides

Stress corrosion cracking by chlorides mainly affects stainless steels (i.e. AISI 304 and 316) and austenitic-ferritic stainless steels. Lowering Ni content below 4% in ferritic stainless steels we obtain practical immunity. Austenitic stainless steels with high nickel content (above 15%) and nickel alloys offer increasing resistance to stress corrosion cracking as the content of alloying elements rises.
High alloy austenitic stainless steels, characterised by a nickel content above 15%, show a higher resistance to SCC; martensitic stainless steels (with both ferritic and martensitic microstructure) are less susceptible to stress corrosion because of low nickel content (often below 1%). On the other hand, nickel alloys with nickel content above 45% are practically immune to chloride stress corrosion cracking. [42]

2.3.4 Other forms of corrosion

In the erosion-corrosion we need materials that show correct mechanical behaviour, leading to a low value of C constant in empirical formula of corrosion rate:

$$v_e = C / \sqrt{r_m}$$

in order to minimize v_e, according also to combined effects of inhibitors.
C values, reported by literature (in absence of inhibitors) are 40 for copper, 60 for copper/nickel 70/30, 120 for carbon steels and 500 for stainless steels. [43]
In addition to inhibitors, there is another possible countermeasure: use of coatings.
Coatings, applied on the internal surface of the pipe, increase toughness of the material, reducing considerably erosion-corrosion rate. This coatings may be stellites and ceramic coatings.
About coatings and their development, here is a paper by Dr. J. K. Pratt & M. Mallozzi and Dr. A. D'Souza:

"Fusion bonded epoxy (FBE) coatings have been used on pipelines as protection against corrosion for 50 years. They have been used as a stand-alone product in single layer systems and as a primer in dual layer FBE and three layer polyolefin systems. Pipeline coating systems require physical properties that minimize damage during transit, installation and operation. Damage to the coating leads to higher potential corrosion sites on the metallic surface and could ultimately lead to a decrease in service life.
There are several ways that have been used conventionally to attempt to make a FBE coating more resistant to mechanical damage. In one conventional approach, the thickness of the overall coating is increased to provide added absorption of impact and abrasion. However, as the thickness of the coating increases, the coating has a increased tendency to crack. Another conventional approach to enhance damage resistance is to add an abrasion resistant overcoat that has a high filler loading to increase abrasion resistance and decrease impact damage. However, higher filler loadings can dramatically decrease the flexibility of the FBE coating. Yet another conventional approach to enhance damage resistance is to use a three layer polyolefin coating system. Unfortunately, when damage does occur in these systems, cathodic shielding may allow corrosion to develop unchecked. This paper will present a novel coating system that incorporates both damage resistance and flexibility in a system that is not subject to cathodic shielding.

[…]

A number of different pipe coatings products with different coating thicknesses prepared and evaluated. The dual layer coatings utilized a standard single layer FBE coating from 3M as the base coat. The top coats evaluated were a standard ARO coating and a new experimental ARO that has been designed to have improved flexibility.

[…]

As can be seen in the data, there is a significant improvement in the flexibility of the flexible ARO samples at all thicknesses both at -30°C and at -50 °C. At -30°C, the flexible ARO coatings passed 4%PD bend versus 2 to 2.5%PD for the standard ARO coated samples. The data also suggests that there is minimal decrease in flexibility with increasing coating thickness for the flexible ARO formulation. […]At room temperature, the impact energy for both the standard ARO coating and the flexible ARO coatings increased from 15 J for a 30 mil thickness to 19 J for a 70 mil thickness coating. At -30°C there is a much larger effect of coating thickness. For a 30 mil thickness coating the impact energy is only 8 J but at 70 mil thickness the impact energy increased to about 15 J. […]The data show that the gouge depth ranged from 20 mil gouge thickness for a 100 kg normal load to a maximum of 60 mils gouge depth at 130 kg of normal load for both the standard ARO coating and the flexible ARO coatings. In contrast, it is well know that 3 layer polyolefin systems have significantly worse gouge resistance with gouge depths in the 1mm to 3mm range under similar testing conditions." [44]

Also in MIC conditions coatings may be effective, but the most common way to reduce corrosion by SRB is the use of inhibitors. These inhibitors, that are biocides, are added to the moisture at the origin of the pipe or along the whole length at regular intervals. There are no steels completely immune to MIC without use of biocides.

2.3.5 General view

Generally speaking, there isn't an unique and final solution for corrosion problems in Oil&Gas industry, or a specific steel or alloy to use in every case, ensuring good performances in every environment. Every case must be analyzed as unique and the right material, or coating, or inhibitor must be chosen from time to time.

Nevertheless, some general guidelines can be provided, to make this choice easier.

First, how to put corrosion under control?

Corrosion process is prevented if the available driving force is zero or negative. This happens choosing a material whose nobility is higher than one of the cathodic process.

In non-oxygenated acidic environment, cathodic process consists in hydrogen ion reduction and its potential is given by $E_c\left(H^+/H_2\right)$ = -0.059 pH. If metals potential is higher than cathodic one, corrosion does not occur. From this consideration, common metals not subjected to corrosion in acidic environments are Cu, Ag, Hg, Pt, Au. On the other hand they may be corroded by formation of complexes, lowering their potential: this happens for copper alloy, forming copper-ammonia complexes in ammoniac environments (what a misfortune, copper was the cheaper of the metals cited above!).

In oxygenated solutions, cathodic process is oxygen reduction, with a potential equal to $E_c\left(O_2/OH^-\right)$= 1.23 – 0.059 pH. In this case only Pt and Au are practically always immune; Ag and Hg only in pH close to neutrality.

Practically, in industry, these metals are useless, due to very high costs. So, it is necessary to find alternatives among less noble materials and alloys that can become more noble after a passivation process.

Then, stainless steels, nickel and titanium alloys can operate in aerated solutions, if there is no factors able to destroy passivity film; these factors may be chlorides, erosion-corrosion, etc..

In case of destroying of passivity film, localized corrosion may occur.

If change material is impossible (because of cost, materials accessibility, …), another possibility is to change the environment, reducing aggressiveness.

Most common procedure in this way is use of oxygen scavengers in alkaline environments or increase of pH where oxygen is already absent; for acidic environments, corrosion inhibitors are used.

In addition, use of coatings of various nature is everyday more diffuse, especially with development of new kind of materials and deposition techniques.

Finally, cathodic protection is widely used, since processes are of electrochemical nature, to keep metal in immunity conditions.

How does cathodic protection work?

Cathodic protection is an electrochemical method of corrosion prevention which can be applied to metals exposed to conductive environments. It controls corrosion of a metal surface by making it the cathode of an electrochemical cell. [45]
Some historical notes by Wikipedia:

“Cathodic protection was first described by Sir Humpry Davy in a series of papers presented to the Royal Society in London in 1824. The first application was to the HMS Samarang in 1824. Sacrificial anodes made from iron attached to the copper sheath of the hull below the waterline dramatically reduced the corrosion rate of the copper. However, a side effect of the cathodic protection was to increase marine growth. Copper, when corroding, releases copper ions which have an anti-fouling effect. Since excess marine growth affected the performance of the ship, the Royal Navy decided that it was better to allow the copper to corrode and have the benefit of reduced marine growth, so cathodic protection was not used further.

Davy was assisted in his experiments by his pupil Michael Faraday, who continued his research after Davy's death. In 1834, Faraday discovered the quantitative connection between corrosion weight loss and electric current and thus laid the foundation for the future application of cathodic protection.

Thomas Edison experimented with impressed current cathodic protection on ships in 1890, but was unsuccessful due to the lack of a suitable current source and anode materials. It would be 100 years after Davy's experiment before cathodic protection was used widely on oil pipelines in the United States — cathodic protection was applied to steel gas pipelines beginning in 1928 and more widely in the 1930s.” [46]

The simplest method of cathodic protection is the use of a sacrificial anode that corrodes instead of metal surface. It is made from a metal alloy with a more "active" voltage (more negative electrochemical potential) than the metal of the structure. The difference in potential between the two metals means that the galvanic anode corrodes, so that the anode material is consumed in preference to the structure.
The other CP method is the one by impressed current. In ICCP (Impressed Current Cathodic Protection) systems, current is provided by a DC feeder through an anode which is able to supply current to the environment. The impressed current anode supplies current

by means of an anodic reaction, which depends on the anodic material and the environment.

In sea water and inside equipment, anodes with different shapes are directly exposed to the environment. In soil applications, a backfill, typically calcinated carbon coke debris, is used to obtain low anode resistance , even in relation to a maximum feeding voltage of 50V. When high current output is required, a group of multiple anodes called a *groundbed* (GB) is used. There are three main types: horizontal, shallow vertical and deep vertical.

A CP system, as for any other industrial plant, may be subject to a failure probability assessment or reliability analysis. For example, an ICCP system may be split into components such as the feeding system, the cable, the cable-anode connection, the anode and the anode-environment interface, which are all linked in series and therefore the system's reliability is inherently conditioned by the weakest component. In soil applications the weakest component is the anode, which can easily loose contact with soil because of its consumption. In this case, a thicker cable is unnecessary, while it is important to use a backfill.

Common applications of cathodic protection are: steel pipelines, storage tanks (such as heaters), steel piers piles, ships and boats, offshore oil platform, offshore oil well casing. In some cases, cathodic protection may also prevent SSC. [47]

We already saw which kind of materials should be avoided for every corrosion mechanism; but what about ideal materials for various pH conditions (roughly corresponding to principal different corrosion mechanisms in Oil&Gas)?

Let's suppose to be in an alkaline environment, approximately corresponding to sweet environment with low CO_2 content, absence of H_2S and relevant presence of salts in the moisture.

Alkaline environments are slightly aggressive due to the formation of hydroxides and low soluble salts that are partially protective.

Selection of materials depends on presence or absence of oxygen. Since pH is much above neutrality, hydrogen evolution as cathodic reaction can take place for active metals more negative than iron, only; therefore, carbon steel and more noble materials resist corrosion in oxygen-free alkaline solutions. If oxygen is present, corrosion will take place on metallic materials not passivating, because of high nobility of oxygen reduction as cathodic reaction. If a protective passivity film is formed, they will not undergo corrosion.

So, in oxygen-free solutions, carbon steel and low alloy steels are available materials until high temperatures, as in a boiler; also in high alkali content solutions they are corrosion resistant, because of formation of a passivity film, regardless the presence of oxygen. Although, at higher temperatures, carbon steel and low alloy steels begin to corrode, then stainless steels or nickel alloy must be used; alternatively, we can increase amount of chromium and nickel in low alloy steels.

Carbon steel can suffer SCC in the presence of mechanical stresses induced by cold plastic deformation and welding if the temperature is higher than 50-80°C depending on the alkaline concentration. It is possible to extend the range of operating temperature performing a thermal treatment at 600°. Austenitic stainless steel present similar problem : in this case thermal treatments required higher temperature and are not advisable, both for the costs and for avoiding the carbide precipitation. Nickel and nickel alloys do not suffer SCC in alkaline environment at high temperature.

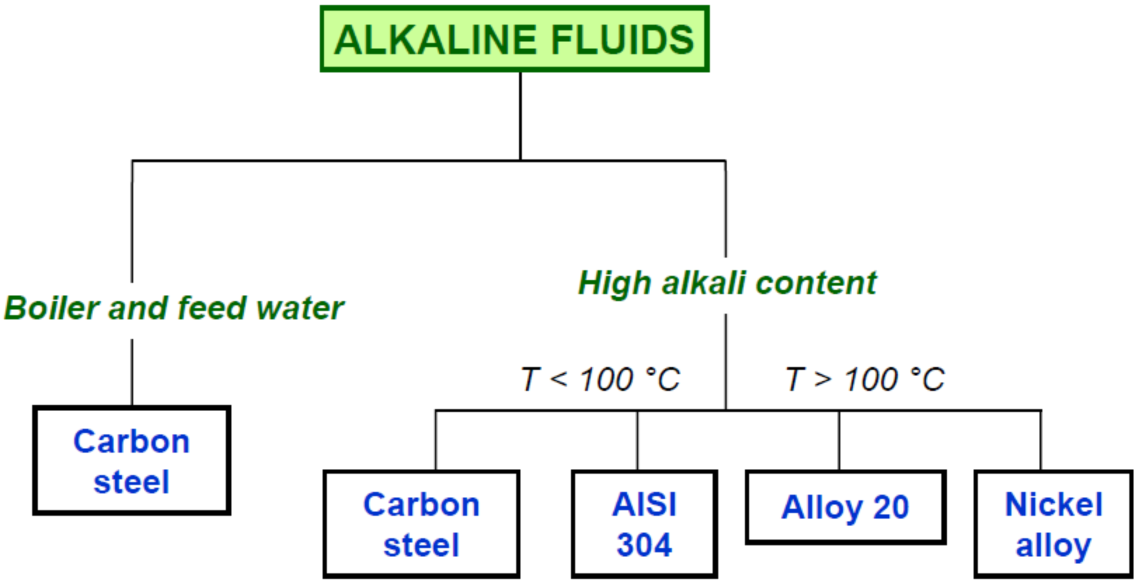


Figure 15: material selection for alkaline environments.

Then, pass to analyze acid solutions, initially without presence of chlorides.

Thermodynamically, favoured reaction at the cathode is hydrogen reduction: so we have to select materials more noble than hydrogen. According to this reason, at room temperature, copper-based alloy can be used. Monel can resist also at high acid concentration and high temperatures.

If chlorides are not present, also passive materials can be used, such as stainless steels, provided that passive film resists at low pH, because film will not be destroyed by chlorides. AISI 316 does not resist in nitric acid, all other Mo containing steels resist because of strong passivation effect. At high concentrations and high temperatures, materials have to be selected on the basis of the presence of oxidants, which helps formation of strong passive film. When useful oxidants are not present, monel and hastelloy grades must be employed, because they don’t require film formation to resist to corrosion.

If pH < 5, carbon steel must be necessary avoided and substituted by stainless steel.

Fundamental criterion to decide about employ of austenitic instead of austeno-ferritic stainless steel is the presence of nitric acids. Nitric acid require use o stainless steel without molybdenum, like AISI 304, 347, duplex 2304 and, for higher temperatures, AISI 310 with low or very low carbon content.

In the case of other acids molybdenum plays an important role, since in the presence of oxidising agents corrosion resistance increases increasing chromium and molybdenum content and decreasing the iron content (alloys 20 and nickel alloys); in the absence of oxidising agents even if alloys 20 and nickel alloys can be used, the better performances are achievable using alloy 400 and alloy B. These two alloys are very vulnerable in the presence of oxidising agents; for this reason is mandatory to guarantee their absence during the operating conditions.

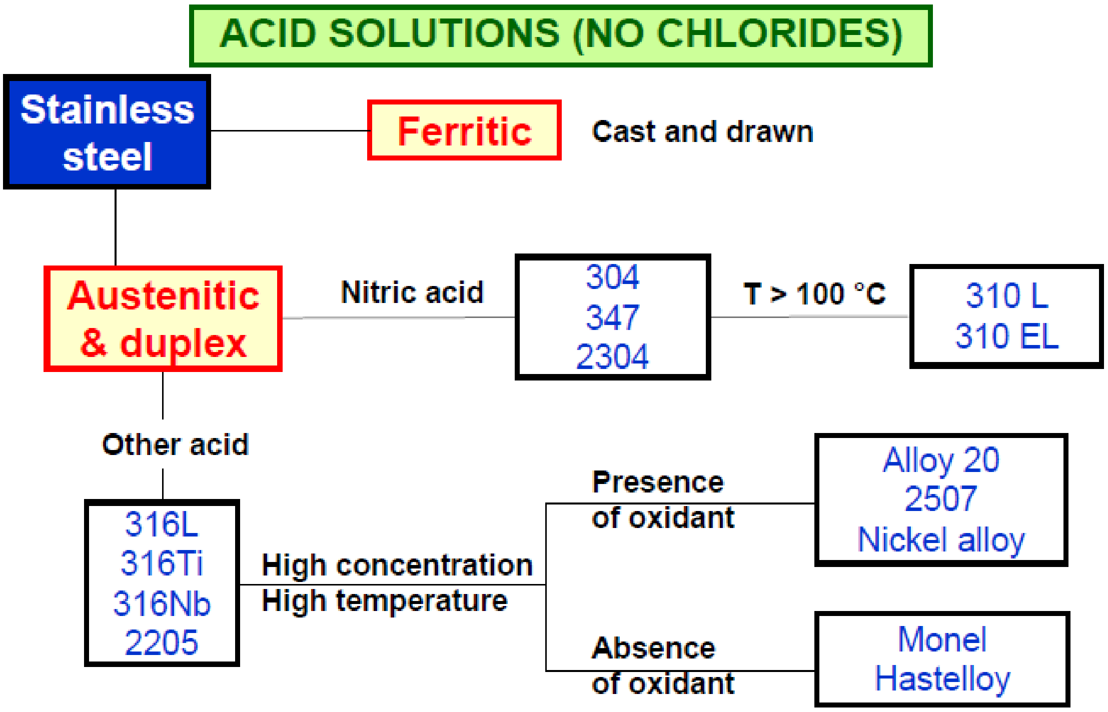


Figure 16: material selection for acid environment without chlorides.

In case of environments containing chlorides, material selections is based principally on pH.

In neutral or alkaline solutions, copper alloy can passivate and so they are suitable, but only in the case that chlorides content is not too high.

In neutral or alkaline environments, if chlorides concentration is above 100 ppm and oxidizing species are presents, stainless steels such as 316L will suffer localized corrosion, particularly pitting if temperature is below 60 °C, crack if it is above 60 °C (and in presence of mechanical tensile stresses). To avoid holes formation, nickel alloys must be considered, instead of stainless steels like AISI 316L.

If holes formation is not so considerable and tensile stresses not so high to cause SCC, there is another solution: austenitic stainless steels like 2205 and 2507, avoiding SCC because of biphasic structure.

Copper alloys and titanium are immune from the attack even in the presence of high concentration of chlorides.

In the presence of oxidising agents if the chloride contents is lower than 100 ppm, stainless steel AISI 316 can be used; this material is the temperature is higher than 60°C, can suffer SCC. In the presence of neutral-alkaline fluids containing high chlorides content but without oxidising agents, it is possible to use stainless steels that belong to the AISI 316 family, copper alloys and even carbon steel.

In acid solutions, stainless steels can resist localized corrosion even if chloride are present, provided the presence of oxidants which enhance passivation. Very resisting alloys must be used in the absence of oxidants. When using stainless steels, attention must be paid on risk of pitting, crevice and chloride-induced stress corrosion cracking.

In chloride content higher than 100 ppm, materials selection must consider only complex materials, like alloy B, C, titanium alloys, all of them resisting in an acid environment.

In other chlorides concentrations, selection criteria are the same of that for simply acidic environment. [48]

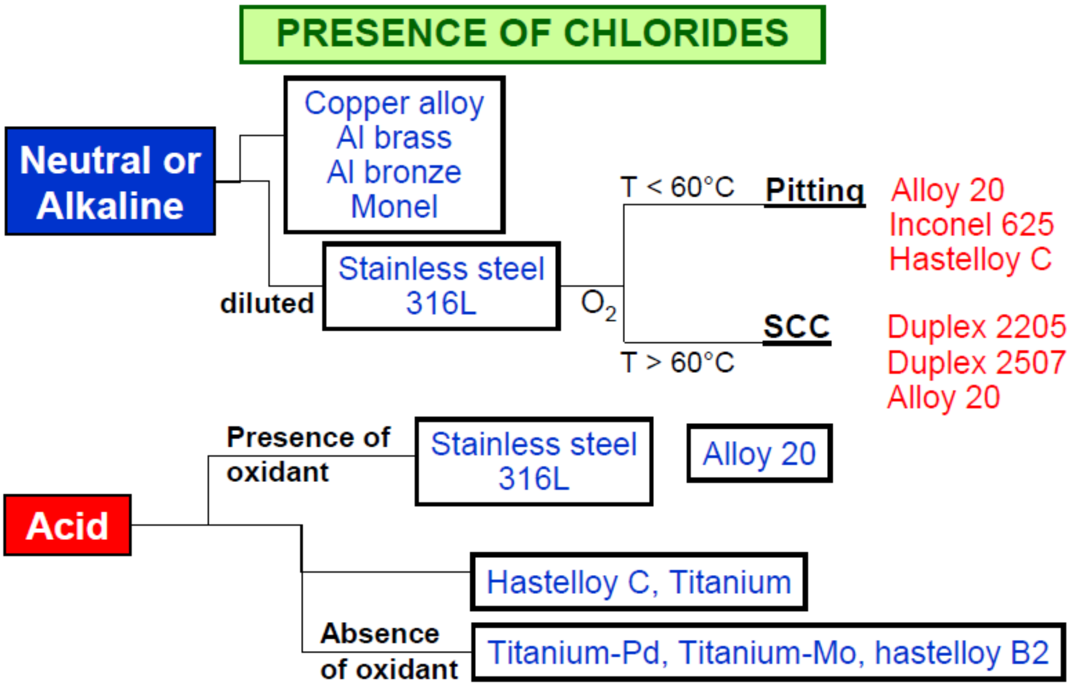


Figure 17: material selection in acidic environments in presence of chlorides.

2.4 Possible future developments and conclusions

As already said, it is fundamental to research continuously about new technology to reduce corrosion and save as much money as possible. Today’s research are about almost all possible way to reduce corrosion of metals: new alloys, new coatings, new inhibitors, new deposition technologies.

New alloy compositions are expressed every day and tested on the field or in laboratory; they concerns both different concentration of “classical” materials, like chromium, molybdenum, vanadium, nickel, and use of new materials, never considered before, like some rare earths.

A possible direction of research may be explore possibilities and combinations of materials to reduce use of nickel, whose cost is sometimes high and always very instable; it may be interesting to investigate about the possibility to increase chromium content, substituting nickel and reducing costs of alloy.

Moreover, a lot of research are about new inhibitors, especially against MIC, and new kind of coatings; widely diffusion of nanostructured materials, development of organic materials and recent improvements in deposition techniques give great boost to research of new coatings.

A challenge in this way may be the development of coating increasingly more resistant to erosion-corrosion and impingement, but, at the same time, able to reduce chemical corrosion of metal, for example by passivation. Another target may be the creation of a combination of coating and inhibitor, able to avoid or at least decelerate practically all corrosion process.

Some examples of new researches (and relatively new developments) are treated in the following papers; the first one is about a new alloy formulated to resist both in reducing and oxidizing environments:

“As is to be expected, nickel-chromium-molybdenum alloys combine the good resistance to corrosion of nickel-molybdenum alloys under reducing conditions with the good resistance to corrosion exhibited by nickel-chromium alloys under oxidizing conditions.

The most important for engineering purposes are the so-called C-type alloys, the first of which was introduced as long ago as the 1930s. This was a nickel alloy with typically (figures in mass-%) 16 % chromium and 16 % molybdenum which also contained 4 % tungsten and 6 % iron together with 0.7 % silicon and 0.05% carbon; this alloy is no longer in common use. With the discovery that to reduce precipitation readiness it is important to reduce both the carbon and the silicon content of such materials to very low levels, it was developed into the alloy UNS N10276 which is in use today, as shown in Table 1.

Low silicon contents of typically 0.04 mass-% and very low carbon contents of typically 0.005 mass-% are nowadays characteristic of all the commonly used C-type nickel-chromium-molybdenum alloys, which also include the alloys UNS N06455, UNS N06022 and UNS N06059 in Table 1.

Whereas according to Table 1 the chromium contents of nickel-chromium-molybdenum alloys are in a range between 16 and 23 %, the molybdenum contents are in most cases at about or near to 16%, with exception of alloy UNS N06625 which contains only 9 % molybdenum. There is no alloy in common use where the molybdenum content is essentially above 16 % which would allow handling more corrosive reducing acids.

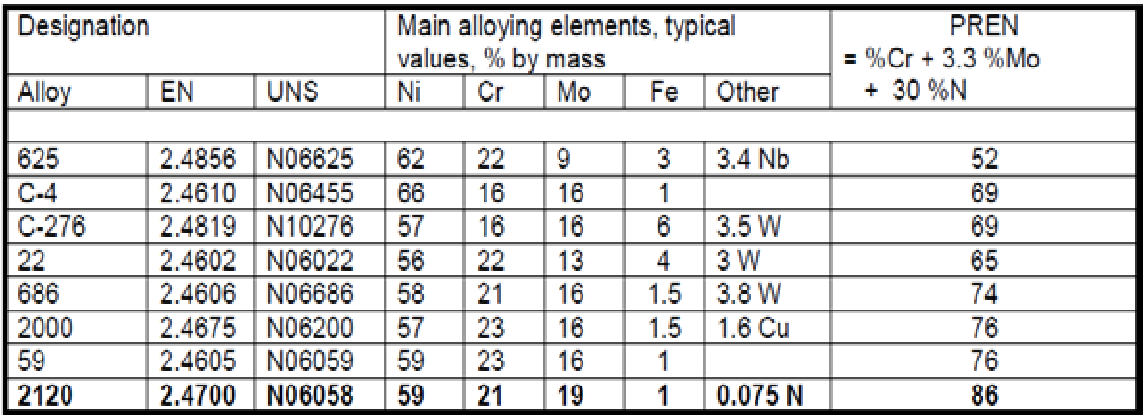
The last column of Table 1 gives the pitting resistance equivalent number (PREN) as calculated from the alloy composition figures in Table 1. Indeed, for resistance to pitting and crevice corrosion, the sum of the chromium content plus approximately 3.3 times the molybdenum content, the so called pitting resistance equivalent number, is the decisive factor. In many cases, 30 times the nitrogen content may also be added to this, as expressed by the following Equation:

PREN pitting and crevice corrosion = %Cr + 3.3 %Mo + 30 %N

Therefore alloys with higher molybdenum contents are used in corrosive environments contaminated with sulphuric acid, halides and especially chlorides, for example in flue gas scrubbers.

As Table 1 shows, the commonly used nickel-chromium-molybdenum alloys from alloy UNS

N06625 up to alloy UNS N06059 are covering a range of PREN-values between about 52 and 76.



Designation			Main alloying elements, typical values, % by mass					PREN = %Cr + 3.3 %Mo + 30 %N
Alloy	EN	UNS	Ni	Cr	Mo	Fe	Other	
625	2.4856	N06625	62	22	9	3	3.4 Nb	52
C-4	2.4610	N06455	66	16	16	1		69
C-276	2.4819	N10276	57	16	16	6	3.5 W	69
22	2.4602	N06022	56	22	13	4	3 W	65
686	2.4606	N06686	58	21	16	1.5	3.8 W	74
2000	2.4675	N06200	57	23	16	1.5	1.6 Cu	76
59	2.4605	N06059	59	23	16	1		76
2120	**2.4700**	**N06058**	**59**	**21**	**19**	**1**	**0.075 N**	**86**

Figure 18: commonly used nickel-chromium-molybdenum alloys in comparison to the new alloy UNS N06058 with (Cr + Mo) in ascending order.

[…]

Typical values of composition of the new developed alloy 2120 – Nicrofer 5821 hMoN(1) – UNS N06058 are indicated in the bottom line of Table 1. When compared to alloy UNS N06059 the chromium content is slightly reduced and the molybdenum content is considerably increased. As comes out from Table 1, alloy UNS N06058 is the first Ni-Cr-Mo-alloy to contain nitrogen as an alloying constituent. Together with the increased molybdenum content this results in a PREN-value of about 86 which is the highest PREN-value of all Ni-Cr-Mo-alloys being commonly in use so far.

[…]

CONCLUSIONS
1) Alloy UNS N06058 is the first nickel-chromium-molybdenum alloy to contain nitrogen as an alloying constituent.
2) The increased molybdenum content of alloy UNS N06058 and alloying with nitrogen results in a PREN value of about 86 which is the highest PREN value of all Ni-Cr-Mo-alloys being commonly in use so far.
3) As a consequence of the high PREN value alloy UNS N06058 is ahead of the other Ni-Cr-Mo alloys with respect to its unique resistance to pitting and crevice corrosion in acidic chloride containing media as they occur e.g. in flue gas desulfurization.
4) Generally the application of alloy UNS N06058 is to be considered where the resistance to pitting and crevice corrosion of other Ni-Cr-Mo alloys is approaching the limits and alternative materials like zirconium or graphite had to be selected in the past.
5) In boiling hydrochloric acid test solutions the corrosion resistance of alloy UNS N06058 proved to be markedly better than with other Ni-Cr-Mo alloys, obviously due to the alloy’s high molybdenum content.” [49]

This above is an example of new alloy with “non-classical” elements inside (nitrogen) and new formulation. The second paper is above coating research:

“As regards FBE (fusion bonded epoxy) coatings, it has already been demonstrated that barrier performance is due to the hydrophobic nature of the coating and consequently its ability to maintain a high glass transition temperature, despite humid and hot surroundings. In order to maintain adhesion under such conditions, good substrate preparation is the key to success.

Common chemical pre-treatments of steel include through the application of chromate or phosphoric acid wash.

A new patented application process for FBEs, used either as monolayer coatings or as primers in multilayer systems, is proposed. This process includes a no-rinse chemical treatment with a solvent free and non toxic product.

This paper demonstrates the improved adhesion performance of FBE coatings immersed in hot water.

[…]

The interest of strengthening the adhesion of FBEs used as single layer coatings or as primers in multi-layer systems is linked to two reasons:

Firstly: the abrupt variations in temperature that occur during the coating application process lead to thermal shocks within each constituent (including the steel). Each layer reacts differently to the thermal shock: the FBE very quickly (in several seconds) goes from a liquid state to a gel state before becoming solid, the adhesive goes from an extruded state to a solid state, and the same is true of the PE or PP based top coat. The dimensional variations of each constituent, due to their change of state, cause mechanical stresses at each interface, which can reduce inter-layer adhesion. Consequently, the adhesion of the coating, and particularly that of the FBE, can already be affected before the pipe is brought into service.

Secondly: in service, the coating is subjected to constraints linked to the temperature of the transported fluid and the corrosive environment in which it is sited. The penetration of species such as water, oxygen and salts into the coating causes a reduction in the affinity between the metal substrate and its protective coating at the interface. 1 This perturbation results in blistering and loss of adhesion, making the coating less integral with the substrate. This process facilitates the influx of corrosive components at the coating – metal interface and therefore increases the risk of corrosion.

In order to strengthen and maintain adhesion despite the abovementioned constraints, it is indispensable to create a strong link between the coating and the substrate. As David Norman has reported, surface preparation is one of the keys to success. The preparation of the substrate to be painted consists in attaining two objectives: to obtain a clean substrate and to modify the surface roughness.

These factors make it possible to improve the wettability of the steel to be protected and the anchoring of the coating to be applied. Nevertheless, this process leads to an affinity between the coating and the substrate to be coated, which is essentially physical and mechanical. It is not likely that covalent bond type chemical bridges are created. Chemical species such as water and salts can, thanks to their small size of around one Angstrom, easily insert themselves between the coating and the substrate and thereby break the electrical type link at the level of the interface .

The force of such linkages is less than that of a covalent chemical bond. Creating such bonds between the coating and the substrate would enable the affinity to be maintained at the level of the interface despite the influx of chemical species. This is why chemical treatments have been used for many years to prepare steel prior to it being coated, including in the field of pipe coatings.

The most widely known method consists in washing the steel with a phosphoric acid solution and rinsing it with demineralized water in order to eliminate any traces of salts. Treatment with a chromate solution without final rinsing has been preferred in some parts of the world, to phosphoric acid, thereby assuring a chemical grafting between the steel and the epoxy. The chromate treatment may be used also after the acid washing stage. This method, also efficient in optimizing the adhesion of the FBE, has disadvantage to use toxic substances, mainly involving the use of hexavalent chromium solution.

This disadvantage is therefore dissuasive and means that this type of chemical treatment will not be widely used in the future due to health, environmental and ecological concerns. It was therefore important to seek to develop an alternative enabling this disadvantage to be overcome, while at the same time meeting the increasingly widespread concerns of pipeline users with regard to numerous cases of losses of adhesion observed with certain external protective coatings of buried or immersed pipelines. The innovative environmentally-friendly® process meets this challenge.

The SILPIPE® process

This patented process is based on a specifically designed Silane Chemical Treatment (SCT) of grit blasted surface that is heated to the proper temperature for epoxy powder coating application. It has therefore been designed to optimize the adhesion of single layer or multi-layer primer FBE powders used as protective coatings of steel pipes and their accessories and to provide a new technology that respects the environment (no volatile organic compounds or toxic waste) and the health of users (no hexavalent chromium).

[…]

The results show significant differences between the chemically treated metal substrates and the non-chemically treated substrates. In fact, the epoxy coating can maintain adhesion when it is immersed in hot water providing the metal substrate is treated by the silane based solution prior to the application of the FBE.

These results demonstrate that, based on a same coating, the difference in performance in terms of adhesion is linked to the creation of chemical bonds at the coating – substrate interface.

[…]

Whatever the concentration and the nature of the chemical treatment solution used, the adhesion of the FBE coatings tested by the pull-off test or the peeling tests was not affected by immersion in tap water at 80°C. These results show that the treatment efficiency of the designed SCT solution used matches the efficiency of the chromate solution.” [50]

It is a good example of how new research are mainly about new deposition and adhesion techniques and fusion between organic and inorganic material.

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