

# Corrosion resistance of common metals and stainless steels in water

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## 1. Introduction

Because of their extremely commonplace nature, waters intended for human consumption might at first thought be considered as "simple" fluids with regard to corrosion. In fact, this is by no means the case, since aqueous electrolytes possess specific features, which must be clearly understood in order to avoid corrosion problems.

An ordinary water generally has a low mineral content. The quantity of dissolved salts is often less than 1g/l, and more rarely between 1 and 2 g/l. This means that the intrinsic corrosiveness is fairly low. However, all waters contain dissolved oxygen, which is the principal corrosive species. Furthermore, if the mineral concentration of a water is relatively low, the corrosion reactions readily induce large variations in composition in regions where the fluid is little renewed. Thus, water which penetrates into a crevice will be converted more or less rapidly to hydrochloric acid, due to corrosion, and its corrosiveness becomes markedly enhanced. The rate and extent of this process will naturally depend on the initial medium, as well as on the nature of the metal and the operating conditions within the system. It is for this reason that the corrosiveness of a water is meaningful only with respect to a particular metal, and is never the only cause of the various types of corrosion encountered. Moreover, each circuit represents a specific problem, which must be examined in the light of all the factors mentioned above. Consequently, there is no typical case, which can be used as a simple reference. In the present paper, the corrosiveness of water will be considered only with respect to bare and galvanised carbon steels and stainless steels, after first discussing the problems associated with the water composition.

## 2. The importance of water composition

Most practitioners wrongly consider that a complete water analysis is a luxury that can be avoided by performing a few summary measurements. While it is true that this approach can prove sufficient in 80% of cases, the problems that arise in the remaining 20% are generally serious, and may even be catastrophic.

### 2.1. The analysis report

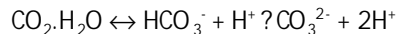
The first step to be taken by the user is therefore to ensure the availability of a satisfactory water analysis. Water analysis is a complex task and should be left to specialists, who should be requested to make a complete type C3 chemical analysis (according to the European directive EC 98/83). The analysis report is an important document. Most laboratories are used to supplying water analyses intended to determine drinkability, and it should be clearly specified that the aim here is quite different and that the analysis must include certain measurements and details that are often omitted, being considered of little interest (cf. analysis model in additive 4 of the 1970 DTU, given in Appendix 1).

It will be seen that the temperature of the water *under analysis* must be indicated and that the pH and resistivity must also be measured at the temperature of the water *under analysis*. In the case of necessity, calculations can then be made which would be impossible without this information. It is also essential to determine the dissolved oxygen and free CO<sub>2</sub> contents and to *indicate separately* the concentrations of calcium and magnesium ions and not simply their total level (TH). It may also be useful to make several analyses, at different times, when the water varies in the course of the year. The analysis obviously requires the presence *in the field* of a skilled person.

Once the analysis report has been established, it is necessary to understand the chief indications and their consequences with respect to corrosion. It must also be checked that the results obtained are self-consistent, particularly as regards the ion balance and the correlation between pH and free CO<sub>2</sub>.

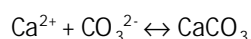
## 2.2. The aggressiveness of water

All waters, without exception, contain inorganic carbon, in the form of dissolved carbon dioxide, that is, CO<sub>2</sub> that has reacted with the water to form carbonic acid, H<sub>2</sub>CO<sub>3</sub> or CO<sub>2</sub>.H<sub>2</sub>O, bicarbonate ions, HCO<sub>3</sub><sup>-</sup>, or carbonate ions, CO<sub>3</sub><sup>2-</sup>. Furthermore, all waters contain calcium, even those considered to be lime-free. This important feature has significant practical consequences. From a chemical standpoint, the HCO<sub>3</sub><sup>-</sup> ion is an *ampholyte*, permanently combining both acidic and basic characteristics, and is therefore always associated with the base CO<sub>3</sub><sup>2-</sup> and carbonic acid H<sub>2</sub>CO<sub>3</sub>. The overall carbonic system is then fully determined by the following equilibria :



Moreover, the concentrations of dissolved CO<sub>2</sub> and of the base CO<sub>3</sub><sup>2-</sup> are limited respectively by exchanges with the atmosphere and by the precipitation of CaCO<sub>3</sub>. These equilibria, which involve H<sup>+</sup> ions, also control the pH of the solution.

For calcium, the equilibrium to be considered is :



This is the "calcium-carbonate" equilibrium. When the product [Ca<sup>2+</sup>] [CO<sub>3</sub><sup>2-</sup>] is equal to the solubility product K'<sub>s</sub>, the water is said to be in equilibrium with respect to calcium carbonate. If the product is less than K'<sub>s</sub>, the water is considered to be "aggressive". This means that, thermodynamically, it is liable to dissolve calcium carbonate. In contrast, if the product is greater than K'<sub>s</sub>, the water is said to be "calcifying", indicating that, thermodynamically, it is capable of precipitating calcium carbonate.

This concept of *aggressiveness* (with respect to calcium carbonate) is not directly related to the notion of *corrosiveness* of the water (with respect to a particular metal). An aggressive water may be non corrosive towards a stainless steel, for example. Nevertheless, the situation of the water with respect to the calcium-carbonate equilibrium can have an indirect influence on the corrosion of a metal. Some types of corrosion in cold water are practically never observed unless the water is aggressive (e.g. type I pitting in copper, corrosion of galvanised steel). Moreover, metals, which owe their corrosion resistance to the presence of a layer of corrosion products at the surface can show highly variable behaviour depending on whether the conditions are on one side or the other of the calcium-carbonate equilibrium.

When one of the water parameters varies ( $\text{CO}_2$  level, local excess concentrations, treatments, etc.), the equilibria are displaced and the other parameters are also affected. Several precise calculation techniques have been proposed to determine their individual changes [1] [2].

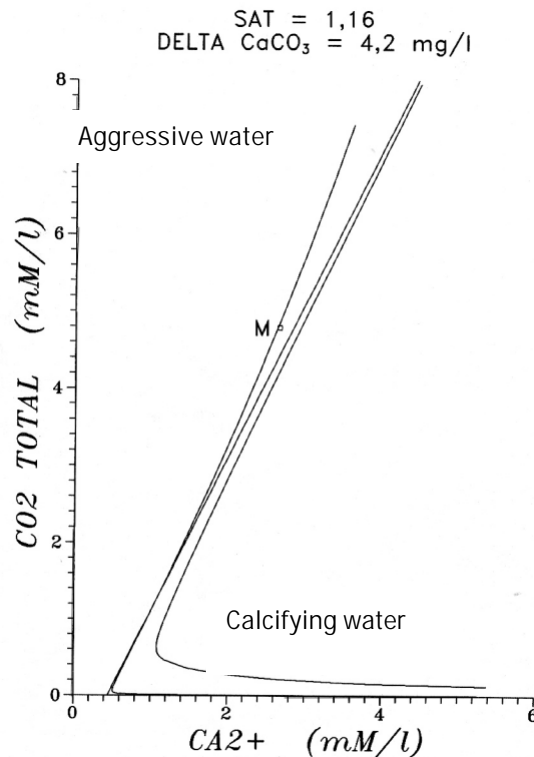


Figure 1 : Calcium-carbonate equilibrium curves for a water as a function of temperature (scales in m.moles/l).

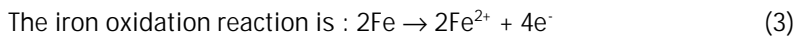
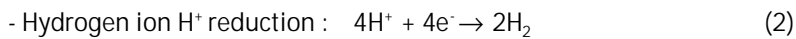
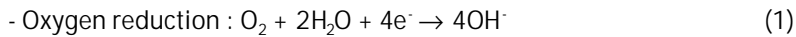
However, it is also possible to use graphical methods enabling the different parameters to be displayed. That due to Legrand and Poirier [1], developed in France 30 years ago, is the only one, which combines both simplicity and rigour. It takes into account the effect on the equilibrium constants of all the analytical parameters, together with the ionic force and the temperature. Furthermore, it can be applied to all industrial and natural waters, provided that their mineral concentration is not excessive. The use of linear coordinates for the Total  $\text{CO}_2$  /  $\text{Ca}^{2+}$  diagram allows immediate determination of the quantities of matter involved. The method has been fully computerized and is extremely easy to use. Equilibrium curves can be obtained in a few minutes. Each water, which represents a particular case, can therefore be situated with respect to the calcium-carbonate equilibrium (Figure 1).

### 2.3. The driving forces for corrosion

In waters, the essential "driving force" for corrosion is generally dissolved oxygen. However, this role can be taken over by acidity. In order to understand the effects of these parameters, it must be remembered that the reactions that lead to corrosion are electrochemical in nature and that a corrosive medium is an electrolyte in

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which certain ions can capture electrons from the metal, becoming "reduced". Conversely, the metal, which loses the electrons is said to be "oxidised". Any corrosion phenomenon can thus be described by "oxidation-reduction" or "redox" reactions. For example, in the majority of waters, the reduction reactions for iron are :



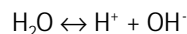
It should be noted that the electrons (e) captured by the oxygen or H<sup>+</sup> ions are those released by the iron.

The reduction reactions (1) or (2) therefore occur at the same rate as the oxidation reaction (3). This point is of capital importance, since it is generally the reduction reactions that impose their rate on the system as a whole.

Consequently, the concentration of dissolved oxygen in the water is a fundamental factor. It depends both on the origin of the water and the type of circuit in which it is employed. A water is said to be *aerated* when the oxygen content is greater than 4 mg/l. This value can rise to about 10 mg/l before reaching saturation. However, even higher oxygen contents can be encountered in distributed waters disinfected with ozone.

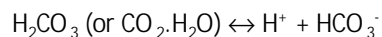
When oxygen is absent, or present in only very small amounts, the most readily reduced species is the hydrogen ion H<sup>+</sup>. The concentration of H<sup>+</sup> ions is expressed by the pH value, and is lower the higher the pH (pH = -log[H<sup>+</sup>]). To a first approximation, it can be considered that it is the dissolved CO<sub>2</sub> concentration, which determines the pH of a water. This can be illustrated by the following example :

- A perfectly demineralised water out of contact with the air will be partially decomposed according to the reaction :



The dissociation constant is  $K_0 = 10^{-14}$ , leading to concentrations of OH<sup>-</sup> and H<sup>+</sup> each equal to  $10^{-7}$  (whence pH= 7).

If this water is placed in contact with the atmosphere, part of the CO<sub>2</sub> in the air dissolves and an equilibrium is gradually established between the CO<sub>2</sub> dissolved in the water and the CO<sub>2</sub> in the atmosphere (Henry's law). The dissolved CO<sub>2</sub> partially reacts with the water and the carbonic acid formed subsequently decomposes to hydrogen and bicarbonate ions :



The equilibrium constant  $K_1$  is of the order of  $10^{-11}$ , leading to HCO<sub>3</sub><sup>-</sup> and H<sup>+</sup> concentrations of around  $10^{-5.5}$  (pH = 5.5). In this case, it is clearly the CO<sub>2</sub> level that determines the pH, since the quantity of ions generated by this decomposition is considerably higher than that produced by the *self-dissociation* of water.

For a non demineralised water, the same situation will hold, but the effect of the dissolved CO<sub>2</sub> on the acidification will be attenuated by the buffering effect of the bicarbonate ions. This can be illustrated by a theoretical calculation for two waters whose initial pH is identical (8.05), to which are added half a millimole (22 mg) per litre of CO<sub>2</sub>. The two waters contain the same quantity of dissolved salts. The only differences are their concentrations of bicarbonate and calcium ions.

The results are as follows :

First water, TAC = 10°F

initial pH = 8.05 → final pH = 6.86

Second water, TAC = 25°F

initial pH = 8.05 → final pH = 7.23

It can be seen that the addition of CO<sub>2</sub> has less effect on the second water, which is more highly buffered than the first, because it is richer in bicarbonate. A similar situation would arise, in the opposite direction, in the event of a loss of CO<sub>2</sub> due to outgassing.

When a public or private water distribution circuit is interrupted, the configuration becomes that of a *closed* circuit. In this case, corrosion rapidly consumes both the oxygen and acidity, but can continue nevertheless, since other species can still be reduced. These include nitrates NO<sub>3</sub><sup>-</sup> which can be reduced to nitrites NO<sub>2</sub><sup>-</sup>, then to ammonium ions NH<sub>4</sub><sup>+</sup>, and sulphates SO<sub>4</sub><sup>2-</sup> which can be reduced to sulphites SO<sub>3</sub><sup>2-</sup>, then to hydrogen sulphide ions HS<sup>-</sup>. Eventually, corrosion stops. It should be noted that these reduction mechanisms can also occur in open circuits that include *dead legs* or *confined zones*.

Nevertheless, as a rule, in a correctly designed and operated distribution circuit, the reducible species that comes into action first is almost always dissolved oxygen.

#### 2.4. Interface compositions

Because corrosion phenomena are electrochemical in nature, the reactions occur at the liquid/metal interface. In flowing water, the composition at the interface changes and depends on the flowrate. Figure 2 shows the form of the velocity-concentration curves for a medium flowrate (e.g. 1 to 2 m/s). The degree of enrichment of redox reaction products in the boundary layer is difficult to evaluate accurately. However, the variation of the pH level in the boundary layer can be estimated by simulation techniques. Thus, in the case of a bare carbon steel pipeline carrying water from the Seine, it has been calculated that in certain circumstances the pH could increase by one unit in the vicinity of the interface. For metals such as copper and zinc which do not corrode due to a protective layer of corrosion product, the existence of the boundary layer is essential for an equilibrium to be established between the metal, the metal ions and the protective oxide. If this is not the case, the solubility product of the protective compound cannot be attained in the interface zone and an erosion-corrosion phenomenon sets in.

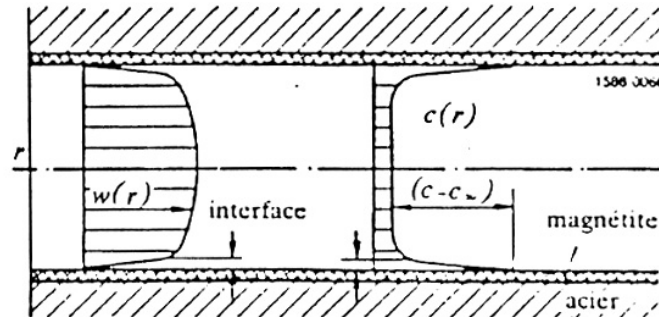


Figure 2 : Velocity profile  $w(r)$  and concentration profile  $c(r)$  inside a steel tube, according to [3].

For pseudo-laminar flow, the larger the Reynolds number, the thinner the boundary layer, and consequently, the greater its chemical enrichment. However, beyond a critical velocity, for which flow becomes turbulent, the boundary layer is destroyed and protective layers are difficult to maintain, as indicated above. This leads to the erosion-corrosion phenomenon, which should not be confused with cavitation, whose origin is purely mechanical.

### 3. The corrosiveness of water towards metals

#### 3.1. Bare carbon steels

Plain carbon steel normally corrodes in water in a predictable uniform manner that is not dangerous. This is no longer true for relatively low pH levels (less than 5 or 6). However, in practice, the presence of dissolved oxygen and the existence of fluid flow are such that the local pH is always higher. The metal then tends to passivate in a more or less uniform manner. In zones that are poorly passivated, there is a risk of initiating local corrosion. In aqueous media, the corrosion products commonly formed on iron are amorphous or poorly crystallised hydroxides ( $\text{FeOOH}$ ), which are strongly hydrated. Their adherence is only moderate and they are little protective. Indeed, on the contrary, they promote the formation of confined zones. This can be illustrated with the aid of potential-time curves plotted for the same steel in two otherwise identical waters differing only by their pH (Figure 3). The curve for  $\text{pH} = 5.2$  corresponds to uniform corrosion, whereas that for a water at its natural pH (equilibrium with the atmosphere,  $\text{pH} = 8.3$ ) reflects the tendency for pitting. The corrosiveness of water with respect to bare carbon steel is therefore highly dependent on the flow conditions and on the free  $\text{CO}_2$  and  $\text{HCO}_3^-$  concentrations liable to limit the increase in pH at the interface. In practice, uncoated carbon steel can nevertheless be used in public water networks transporting slightly calcifying waters. Indeed, slight corrosion of iron promotes the precipitation of calcium carbonate, since the  $\text{Fe}^{2+}$  ions enable the nucleation of  $\text{CaCO}_3$  at low supersaturations [4]. The mixed  $\text{CaCO}_3$  and  $\text{FeOOH}$  deposit is generally protective and its growth is self-limiting in waters close to the calcium-carbonate equilibrium, provided that the surface coverage is complete.

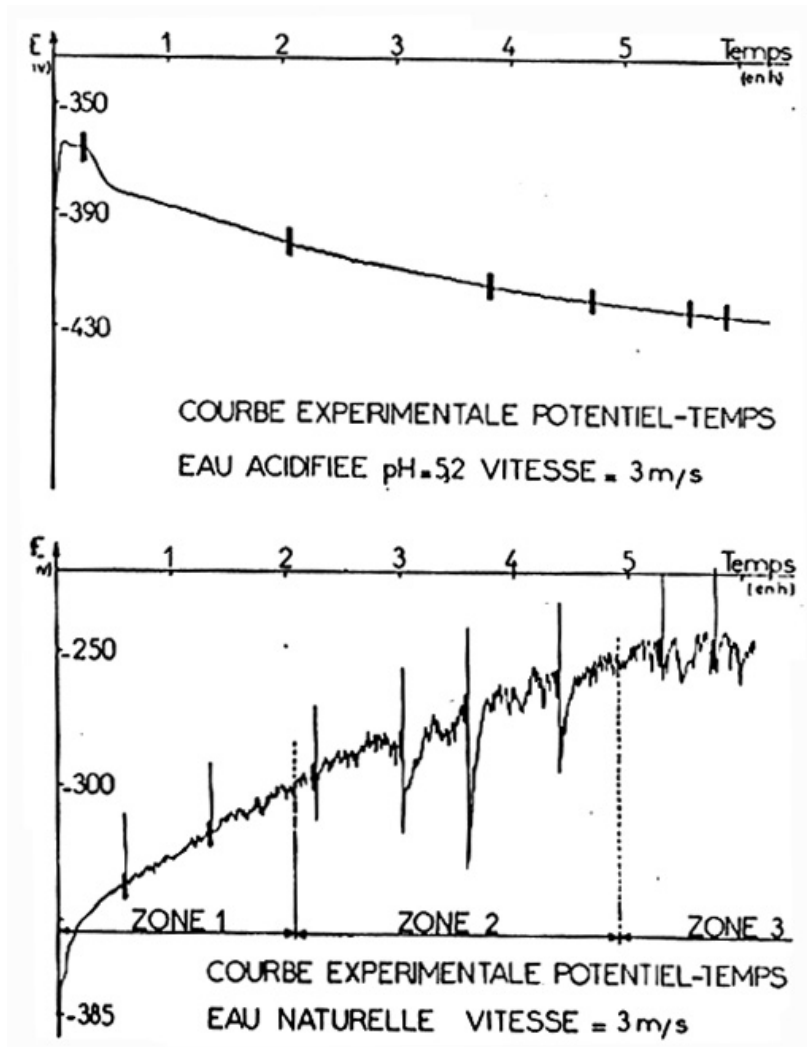


Figure 3: Top : pH = 5.2 (uniform corrosion)  
 Bottom : pH = 8.3  
 Zone 1 reflects almost uniform corrosion.  
 Zone 2 reflects incipient pitting.  
 Zone 3 reflects generalised pitting.

### 3.2. Galvanised steel

Galvanised steel is used to avoid the risks of corrosion encountered with uncoated carbon steel when protection by a mixed calcium carbonate-iron hydroxide deposit is not possible. The corrosion resistance of galvanised steel is due to two successive phenomena:

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a) During an initial transient stage, which can sometimes be very long (2 years), the layer of zinc and iron-zinc alloys becomes coated with a protective corrosion product, corresponding in the majority of cases to pentazinc hexahydroxycarbonate (PZHC for short), whose formula is close to  $Zn_5(CO_3)_2(OH)_6$ . The formula indicates that, for the product to form and be maintained, the  $OH^-$ ,  $CO_3^{2-}$ , and  $Zn^{2+}$  concentrations must be sufficiently high in the vicinity of the interfaces. Furthermore, the water must not contain ions or impurities that prevent satisfactory crystallisation. For these conditions to be fulfilled, it is imperative that the water should contain a minimum amount of dissolved oxygen (at least 4 mg/l) to enable the reduction reactions to produce a sufficient quantity of  $OH^-$  ions. It is for this reason that it is absolutely essential to *avoid periods of stagnation* during start-up of the installations. The alkalisation must also be sufficient to locally produce carbonate ions from the bicarbonate ions. The latter must therefore also be present in sufficient quantity. As regards the analysis, this requirement corresponds to a minimum TAC value of 1.6 **mmole** (8°f in French degrees). Moreover, the free  $CO_2$  content must be limited to ensure that the initial pH is not too low. A pH of 6.5 appears to be the minimum. For the practitioner, the limiting values of the different parameters related to the water can be usefully taken from Additive 4 of the DTU number 60.1 (February 1977). Beyond these limits, the use of galvanised steel remains possible, but it is then appropriate to consult a specialist to be on the safe side.

b) In a subsequent stage, when the zinc and its alloys have been consumed by the corrosion, the underlying iron will corrode. However, the corrosion of iron begins beneath a protective deposit, which, if it is correct, limits hydration of the corrosion products. The iron corrosion products then formed are different from those usually obtained in water, and can continue to protect the metal when all the zinc has disappeared [5]. Consequently, galvanised steel can reasonably be used only in flowing waters with fairly high mineral contents, that are aerated and tend to be calcifying, and have a pH greater than 6.5, together with a minimum concentration of bicarbonate ions. These conclusions have been confirmed by numerous experimental studies performed in Germany over a period of several years, leading to the definition of empirical corrosion rate formulae allowing for :

- 1- the nature of the water
- 2- the quality of the installation

The term "quality of the installation" includes the regularity of the flow conditions (in the hydraulic sense) and the regularity of the galvanised layer on tubing and fittings (a clearly defined constant thickness, conformity with the NF A35503 standard). To illustrate the effect of a parameter such as the pH, Figure 4 shows the variation of the polarisation resistance (which, to a first approximation, is proportional to the corrosion resistance) as a function of pH, for a same water in which only the free  $CO_2$  concentration is changed.



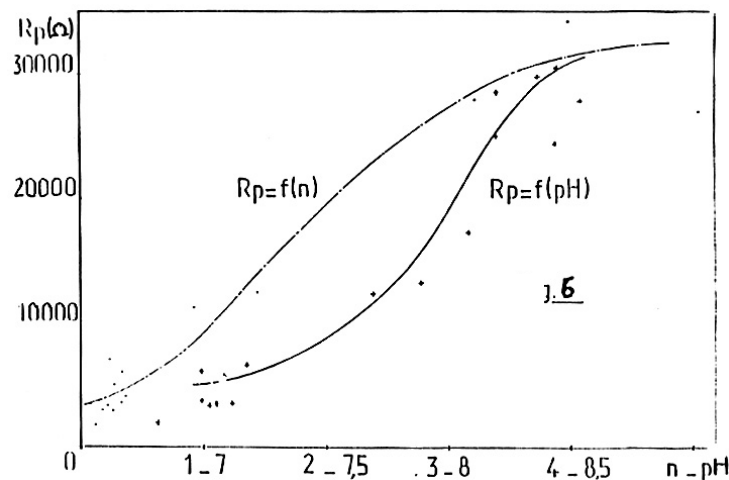


Figure 4 : Variation of the polarisation resistance of zinc as a function of pH ( $7 < \text{pH} < 8.5$ ) and the degree of supersaturation ( $0 < n < 4$ ).

### 3.3. Stainless steels

The stainless steels used in water circuits are generally either austenitic or ferritic grades. In waters intended for human consumption, the stainless steels show perfect corrosion resistance, thanks to their *passive layer*. Their corrosion resistance does not depend on the formation of a protective layer of corrosion products, but on the existence, *over the whole of their surface*, of a suitable passive layer. In all strictness, they should be described as *self-passivating steels*. If the metal surface is clean, the passive layer forms spontaneously in all waters complying with the EC Directive 98/83. However, if the service conditions are not correct, these materials are unable to passivate normally and may then develop two types of localised attack known as "pitting" and "crevice" corrosion.

Whereas uniform corrosion equally affects the whole of the metal surface, "pitting" and "crevice" corrosion are purely localised electrochemical phenomena.

The cause of crevice corrosion is not the material itself, but the change in composition of the medium in confined zones. In such regions, the oxidising medium (the water in the present case) is unable to sustain a suitable protective passive layer. The metal is locally depassivated or poorly passivated and the anodic dissolution reactions become concentrated in this area, while the cathodic reduction reactions occur outside the occluded region. The local dissolution leads to gradual *acidification* of the confined medium. In this region, the stainless steel, which was initially in contact with water, becomes progressively exposed to increasingly concentrated hydrochloric acid. In these conditions, the metal rapidly loses its corrosion resistance.

For each grade of stainless steel there is a critical pH level, called the depassivation pH ( $\text{pH}_d$ ), below which passivity disappears. The value of  $\text{pH}_d$  varies with composition. Additions of molybdenum lower  $\text{pH}_d$  and enhance the resistance to crevice corrosion.

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Thus, since the corrosion resistance of stainless steels is due to a protective passive layer formed in contact with « fresh water » or moisture from the air, it is essential that the surfaces of stainless steel components remain clean throughout their life (absence of contamination, high temperature oxide scale, unwanted deposits, etc.). It is also necessary that any surface cleaning operations include final rinsing with « fresh water », that is, with a low chloride ion content and free from chlorine or hypochlorite (contained in detergents such as Javel water). Wiping is not essential, but represents an additional safeguard if the water used for rinsing is of doubtful quality.

The depassivation phenomena encountered in practice have four principal origins:

- contamination by ferric ions
- the creation of confined media
- corrosion beneath deposits
- the use of prohibited cleaning products

When carbon steels are in contact with stainless steels, the presence of corrosion products from the carbon steels (ferric ion contamination) can promote the occurrence of pitting or crevice corrosion. Stagnant media, due to shut down without draining, the presence of dead legs or anfractuosités, are dangerous since, in the absence of oxygen, they can lead to depassivation and rapid corrosion. Scale and sludge deposits can also promote the same type of phenomena [6] [7] [8].

In summary, stainless steels should be used preferably under steady flow conditions, without prolonged periods of stagnation, and components should be designed with simple geometries. The presence of molybdenum in the steel is necessary to limit the risk of crevice corrosion.

There are four essential rules for the correct use of stainless steels :

- 1) Choice of the most suitable grade.
- 2) Design of equipment to avoid the creation of confined or retention zones [9].
- 3) Construction and implementation according to the rules of the art [10].
- 4) Avoidance of abnormal working conditions [11].

## 4. Conclusions

Natural water is not inherently corrosive towards common metals, provided that corrosion remains uniform and that the normal protective corrosion products are able to form at the water/metal interface. The principal corrosive species is usually dissolved oxygen, but paradoxically, its presence is *necessary* to maintain the protective layers.

In the case of stainless steels, the corrosiveness of waters complying with the European directive EC 98/83 is a secondary factor, since these waters normally ensure the formation of protective passive layers, provided that the metal surface is perfectly clean.

The problems that can be encountered in practice are generally related to the occurrence of *localised corrosion*, which can sometimes lead to complete perforation. It is for this reason that the design, construction, operation and maintenance of stainless steel circuits are much more important than the intrinsic corrosiveness of the

water.

## 5. References

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