CHAPTER 2

Environmental deterioration of metals

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1 Introduction

To make metals usable for people, energy must be supplied for their production. This gives rise to an energetically rich product that is not environmentally stable and deteriorates spontaneously, i.e. corrodes. The energy supplied for its production is thus released into the environment. During its corrosion, a metal merges into a more stable state with a low energy content and a less coordinated structure, into corrosion products which in appearance and content resemble their parent raw material – the ore. Therefore, corrosion is sometimes called reverse metallurgy. People’s experiences with metals are supported by findings that most of them (except gold and platinum) with their exposure to the environment spontaneously turn into corrosion products. The best-known corrosion product is that of the most common metal, iron – rust. The deterioration of metal objects by turning into rust is mentioned even in the Bible, ‘Do not store up for yourselves treasures on earth, where moth and rust destroy, and where thieves break in and steal’ (Matthew 6:19).

Since ancient times, corrosion of metals has been understood as an undesirable process, as illustrated in its definition. ‘Corrosion is physicochemical interaction between a metal and its environment which results in changes in the properties of the metal, and which may lead to significant impairment of the function of the metal, the environment, or the technical system, of which these form a part’ (*Standard ISO 8044 – Corrosion of metals and alloys – Basic terms and definitions*).

No metallic material (with the exception of metallic coatings) is used merely because it is corrosion-proof. The use of a metal depends, in particular, on its primary utility properties, such as mechanical properties (strength, elasticity), excellent electric or heat conductivity, surface look or other properties. To be able to meet its function, a metal should to have sufficient corrosion resistance, which will ensure that the primary utility property shall be usable in a given environment without any
serious constraint in the course of the whole service life of a metal product. The period of the required service life may vary to a great extent, from minutes (e.g. rocket nozzles) to centuries (e.g. objects of great historical and artistic value).

Corrosion reduces the primary utility properties; it may even cause a complete loss of function of certain parts (corrosion perforation of a tank wall, cracks in piping, outward deterioration, etc.). Additionally, in most cases corrosion may significantly participate in an unacceptable contamination of the environment. Of course, corrosion is not the only degradation process inherent in the metallic material. Purely physical deterioration, e.g. wear, deformation, formation of cracks and fractures, embrittlement, also takes place. However, given the presence of a corrosive environment physical deterioration co-acts with a chemical deterioration – corrosion. Even if the physical and chemical deterioration processes are insignificant for a given system, the two being complementary together cause the failure of the metal function.

Corrosive environment contains substances that, when in contact with a given metal, cause corrosion. Besides the chemical composition of the environment, temperature and flow rate significantly influence corrosion. The chemical composition is characterized both by the presence of certain components (or their combination) and by the concentration of single components. Corrosion resistance is most significantly affected by the environment pH and by the presence of substances having an oxidation effect.

Since in most cases corrosion is impossible to be suppressed, the term corrosion intensity allowance was introduced to indicate a technically acceptable corrosion rate, according to which it is possible for a metallic part to be exposed in a corrosive environment over a long term without unacceptable changes of its utility properties or worsening of other observed parameters (appearance, worsening of heat transfer or electrical conductivity, etc.). A corrosion rate exceeding 1 mm per year is technically acceptable exceptionally, or in cases where the required service life of the part is very short. For corrosion engineering, the values exceeding 1 mm per year are practically uninteresting, as any construction material exposed over a long term should not reach such a state. It can happen only under exceptional conditions, i.e. conditions difficult to anticipate, or because of stray currents or poor choice of material for a given environment. Limits for acceptable corrosion rate depend on the required service life of a part during which it should safely meet its function or on the extent of tolerable contamination of the environment by corrosion products. In the corrosion data surveys, an upper limit of entire resistance is set out to 0.1 mm per year which is valid only for a uniform corrosion and utilization of metals in industrial facilities having their service life between 10 and 20 years, and not for, to give an example, conditions of a long-term atmospheric exposure of metals, for concrete reinforcement, or for metallic materials in a human body (a hip bone substitute, a denture, tooth filling, etc.). Generally, the uniform corrosion rate limit ranges in the interval of approximately five orders, and practically in the interval of three orders (0.1 up to 0.0001 mm per year).

Corrosion deterioration represents a large group of failures caused by the environment affecting particularly the surface of a metal. For the scope of the deterioration
we identify the so-called general corrosion, which progresses over the whole surface exposed to the corrosive environment in a more or less uniform manner, and the localized corrosion, which progresses more intensively only in some areas of the exposed surface of metal.

In case acceptable corrosion is accompanied by any form of localized corrosion, then the technical acceptability is constrained either by the absolute elimination of localized corrosion or, more often, by the low (acceptable) probability of its formation.

A still more important viewpoint for the limitation of maximum acceptable corrosion rate is the requirement for the least possible contamination of the environment by the corrosion products, e.g. in case of human body substitutes, despite preserving of the functional properties of the metal implants, the release of soluble corrosion products (metal cations) may lead to unpleasant health complications. In copper coverings without practical reduction of their service life, the atmospherically exposed metal is released in unacceptable amounts into natural waters and soil. Some of the effective methods of corrosion protection used are restrained by ecological viewpoints. This is the case with, for instance, chromating, coatings with lead pigments, and certain types of inhibitors. The coating compositions with organic solvents are continuously replaced with water-solvent coatings. This is the main reason why at least equal substitutes are intensively searched for.

The task of corrosion protection is to reduce corrosion losses, to reach technically acceptable corrosion rate and to exclude the origination of localized forms of corrosion that could endanger a function of the construction material. The selection of construction material and coating constitutes the basic procedures and the modification of the environment and of electrochemical protection the specialized procedures. The efficiency of anti-corrosion measures is in a significant manner influenced by the construction of a metallic product.

In most of the corrosion cases of metals in electrolytes – that is, the environments where the components are dissociated into ions – the main degradation mechanism is the electrochemical one, i.e. anodic dissolution. But ‘non-electrochemical corrosion’ of metals, such as corrosion in gases at higher temperatures, and hydrogen damage also inhere chemical reactions in their mechanisms.

2 Electrochemical corrosion of metals

2.1 Basic electrochemical terms

The rate of an electrochemical reaction, which proceeds at the electrodes and during the course of which the oxidation state of the reaction components changes, may be expressed in terms of the electric current. A reaction during which electrons are released (e.g. when a metal forms its ions) is called oxidation (anodic process). Each anodic process is followed by a cathodic process (reduction), during which the released electrons are consumed. Regardless of whether the process taking place within the electrochemical cell is spontaneous or forced, oxidation prevails
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at the anode while reduction prevails at the cathode. The polarity of the electrodes depends on whether the process is spontaneous or forced.

If the passage of current is forced, the anode is positive (the electrons are consumed), and the cathode is negative (for corrosion, it applies to the electrochemical protection methods and the corrosion resulting from stray currents). If the passage of current is spontaneous, the anode is to the contrary negative (the electrons are released), and the cathode is positive (with respect to the corrosion engineering, it applies to the acceleration of corrosion resulting from galvanic or concentration cells actions).

Compared with a reference electrode, an electrode potential is a measurable value. Standard equilibrium potentials of the electrochemical reactions are upon agreement tabulated against the so-called hydrogen electrode for which the value of its equilibrium potential was stipulated as zero at all temperatures (Table 1). From a macroscopic point of view, no process advances at the equilibrium potential ($E_r$) that is caused by the equality of the oxidation rate at such potential and the reduction rate (following the same reaction scheme). Thus it deals with dynamic equilibrium (Fig. 1). Oxidation and reduction may theoretically appear in the same area of the electrode surface.

So, as the current passes through the electrode ($j$), it is necessary for it to surpass the overpotential that is caused by slow transfer of charge from the electrolyte to the electrode (or vice versa), as expressed by $j = j_a + j_c$. Four types of overpotential

<p>| Table 1: Standard equilibrium potentials in volts (the electrochemical series at 25°C). |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|</p>
<table>
<thead>
<tr>
<th>Mg</th>
<th>Al</th>
<th>Ti</th>
<th>Cr</th>
<th>Zn</th>
<th>Fe</th>
<th>Ni</th>
<th>Pb</th>
<th>H</th>
<th>Cu</th>
<th>Ag</th>
<th>Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>−2.36</td>
<td>−1.66</td>
<td>−1.63</td>
<td>−0.91</td>
<td>−0.76</td>
<td>−0.44</td>
<td>−0.25</td>
<td>−0.13</td>
<td>0.00</td>
<td>+0.34</td>
<td>+0.80</td>
<td>+1.45</td>
</tr>
</tbody>
</table>

Figure 1: Equilibrium electrode potential.
are distinguished: activation, concentration, reaction and crystallization. Activation 
(charge transfer) overpotential is caused by a slow process of the charge transfer 
via the electrode–electrolyte interface. This is applicable throughout the process 
of electrochemical corrosion but does not necessarily have to be decisive. Concent-
tration overpotential is entailed by a slow transport of electroactive component 
from the volume phase to the interface and vice versa. As to corrosion, normally 
the oxygen reduction in the neutral or alkaline environment is concerned. Reaction 
overpotential is caused by a slow chemical reaction (upon the electrode surface, or 
in the electrolyte bulk) prior to or after the electrode reaction itself. At corrosion it 
may deal with weak acids dissociating for formation of reducible $\text{H}^+$, or with the 
rate of hydrogen atoms re-combination. Crystallization overpotential is significant 
for electrochemical deposition of metals and is practically not related to corrosion.

2.2 Thermodynamic assumptions of metallic corrosion

The thermodynamic stability of a metal is indicated by the so-called nobility that 
is represented by the standard equilibrium potential (Table 1). The more positive 
the metal potential is, the nobler the metal is. With respect to the standard potential 
value, it is possible to line the metals into the so-called galvanic series. The metals 
that are considered noble are those whose standard potential is more positive than 
the stipulated zero potential of the hydrogen electrode. The galvanic series stems 
from the condition of equilibrium with ions of the relevant metal in solution, but 
the corrosive environment usually contains very few of these ions and therefore the 
equilibrium is reached very rarely. The series set up in accordance with the nobility 
of metals does not take into account the formation of solid corrosion products 
and is also valid only for aqueous environments without other complex-forming 
substances.

The formation of insoluble products is reflected in potential–pH diagrams. To 
begin with, we may consider the potential to be an extent of the oxidation abilities 
of the environment expressed with the so-called redox potential, which is a mea-
surable value for at-inert (corrosion-proof) electrode. E–pH diagrams define the 
areas of oxidation abilities and pH, in which either metal (immunity) or its soluble 
products – cations, alternatively oxoanions (activity-corrosion), or insoluble oxides 
or hydroxides (passivity) are thermodynamically stable. Borders of these areas are 
usually determined for very low concentrations of metal ions in a solution and 
for constant temperature. Lines limiting the stability area of water are set down in 
the diagrams. Theoretically, water decomposes above this area at the evolution of 
oxygen, and below this area at the evolution of hydrogen (Fig. 2a).

Areas of conditions corresponding with several types of environment may be 
marked also for orientation in the potential–pH diagrams (Fig. 2b). The value of 
potential that is held by a metal constitutes a compromise between the oxidation 
abilities of the environment and the oxidability of a given metal. Within the area 
for a given environment, more negative potentials are held by less noble metals in 
their active state.
The diagrams originated speculatively with regard to the tabulated thermodynamic data, i.e. on the condition of chemical equilibrium between all of the possible species in the metal–water system. Potential–pH diagrams may be exploited for some estimation of metal stability with relation to the oxidation ability and acidity, or alkalinity of the environment; however, it is essential to take into consideration the fact that the diagrams do not convey anything about the reaction rate which is a decisive criterion for the utilization of metals in the corrosion perspective.

In the case of noble metals, immunity overlaps the area of water stability (metals are thermodynamically stable in pure water). The existence of passivity area of a relevant metal (particularly in the area of water stability) enables practical utilization in aqueous solutions. Overlapping of areas of metal stability (immunity + passivity) and areas of water stability is caused by the requirement that water should not spontaneously decompose when the metallic construction material is in contact with the aqueous environment. If we consider the sizes of the immunity area and the passivity area together as the extent of thermodynamic corrosion resistance, then we get to a sequence of metals which corresponds with a general framing experience (the experience that assesses the corrosion resistance in a general way, i.e. regardless of the environment) better than the resistance implied by the electrochemical series. Especially titanium, aluminum and chromium are shifted among the 'noble' metals.

The whole area of water stability is overlapped only by the immunity of gold (Fig. 3a). Should any complex-forming reagent be added to the environment, e.g. cyanides, the border of the immunity area would be shifted to significantly lower potentials, and also gold would, in the presence of the oxidizing agent, actively dissolve (this is used in hydrometallurgical processing). Platinum acquires a large immunity area; nevertheless, in strongly oxidizing environment it is protected by a passive layer.
Figure 3: Potential–pH diagrams for different metals at 25°C. Dark area – activity, grey – passivity, white – immunity.
The copper immunity area interferes with the area of water stability only in part; corrosion resistance is normally based on copper oxides stability. Increase of oxidizing ability in the acidic environment is very undesirable for copper; copper does not resist namely in oxidizing acids (Fig. 3b). Silver acts in a similar way as copper, only the immunity area is a little bit larger.

Theoretically, it is possible to use iron, thanks to its passivity in the area of water stability, but it is not possible to use iron in the acidic environment. Both the change of pH and the change of the oxidizing ability of the environment, or potential, lead to passivity (Fig. 3c). Chromium is a non-noble metal with an immunity area lying deep in the region of negative potential values. Similar to iron, the stability of its oxides and hydroxides and the possibility of passivation are exploitable. Zinc and aluminum are amphoteric metals and thus soluble in acidic as well as alkaline environments. Passivity may be reached only by the change of pH, not by the change of oxidizing ability (potential) (Fig. 3d). Titanium and tantalum are very non-noble metals, but thanks to their very stable oxides they are passive almost within entire area of water stability (Fig. 3e and f).

The E–pH diagrams clearly demonstrate that the stability of the two metals most resistant against corrosion, gold and tantalum, is based on totally diverse causes. In case of gold, the entire area of water stability is overlapped by immunity, whereas in case of tantalum by passivity.

A solid corrosion product with a low solubility may not necessarily mean formation of a well-protecting passive layer. In addition, to reach a pH value beyond the neutral area the presence of other ions is essential, and thus the condition for the validity of the diagrams, considering pure aqueous environment, is not fulfilled. In the case of acidic solutions, another anion, which is not considered in the diagrams, is always present; conversely, in alkaline solutions there is a cation. Other ions are also present in neutral solutions. These may significantly influence the areas of metal stability by formation of insoluble products or by formation of soluble complexes, which fundamentally shift the equilibrium conditions. Should another cation or anion change only the oxidizing ability of the environment, then its influence is already present in the potential value at a given pH.

### 2.3 Corrosion reaction kinetics

In the usual corrosion system not only the species acting on the metal ions equilibrium are electroactive in electrolyte, but several totally diverse oxidation and reduction reactions may also simultaneously proceed at the electrode surface. The total rate of all oxidations has to be equal to the total rate of all reductions, i.e. the sum of all anodic currents has to be equal to the sum of all cathodic currents. The potential spontaneously established by the achieving of the final zero current in a given system is a combination of equilibrium potentials for individually proceeding reactions. Therefore it is referred to as mixed potential. It is not an equilibrium potential, as the equilibrium is impossible to be achieved – a stationary state, at the most. The so-called free corrosion potential is the most frequent case of
mixed potential, which is established while metal anodic oxidation and environment cathodic reduction proceed at the same time (Fig. 4).

The ability of an electrode to be polarized (i.e. to change its potential by current passage) is characterized by polarizability that is closely connected with a value of exchange current density \( (j_0) \), which, in case of free corrosion potential, is a value corresponding with corrosion current density \( (j_{corr}) \). Out of this value and Faraday laws it is possible to determine the corrosion rate.

### 2.3.1 Anodic dissolution of metals

At anodic dissolution, metal usually passes into aqueous electrolyte in the form of a hydrated cation. The formation of cation proceeds in several steps. Upon the metal surface, initially the ad-atom generates, which is bound to a water molecule in the other step. The reaction is often facilitated by anions (e.g. \( \text{OH}^- \) or \( \text{Cl}^- \)) while an unstable intermediate product is formed. In an aqueous environment, the hydroxide mechanism is always, or at least partly, applied, which may lead to formation of passive layer. With regard to frequent presence of chlorides in the corrosive environment, the so-called chloride mechanism of anodic dissolution of metals is possible and is, for intermediate products, less energy-demanding.

In a number of practical corrosion systems, the chloride and hydroxyl anions mutually compete, as the hydroxide mechanism for, e.g. iron and its alloys, enables to form an oxide-type passivity, whereas the chloride mechanism does not. In these cases we may distinguish between the conditions for passivation and activation of a given metal merely upon the knowledge of the ratio of chloride and hydroxyl ions concentrations in the environment, and of the boundary condition specific for the given metal material. The chloride mechanism is an example of catalytic anions effect. It resembles the sulfate mechanism, which applies to iron under atmospheric conditions.

![Free corrosion potential for active metal in acidic electrolyte.](image)
2.3.2 Cathodic reactions

The process of anodic oxidation of metal is conditioned by the consumption of electrons released during its ionization by cathodic reactions. These are the electrode reactions in the course of which a species of the environment is reduced. Such cathodic reactions have to proceed at the same potential as the anodic reaction of the metal dissolution. In aqueous electrolytes, cathodic reductions of oxygen or hydrogen ions and/or water (evolution of hydrogen) are the most usual one.

Hydrogen evolution may be described with the following two equations:

\[ 2\text{H}^+ + 2e^- \rightarrow \text{H}_2 \] (in acidic electrolyte)
\[ 2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^- \] (in neutral or alkaline electrolyte).

The first one is applied mainly in the acidic environment with sufficient amount of hydrogen ions; the second one is applied mainly in neutral and alkaline environment (especially at cathodic polarization). Both of these reactions may be followed by corrosion of non-noble metals. The rate of hydrogen evolution depends on the potential. The rate of the reaction may be decisive for the metal corrosion rate. Potential dependence of the cathodic reaction rate and the value of its exchange current density are essential in this case (Table 2).

The most usual cathodic reaction in electrolytes which are in a contact with the air atmosphere is oxygen reduction which proceeds in accordance with the following equations:

\[ \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2e^- \rightarrow 2\text{OH}^- \] (in neutral or alkaline electrolyte)

With respect to low oxygen solubility in the aqueous environment, the corrosion rate at corrosion in active state may be limited by slow oxygen transport. Oxygen reduction may proceed even in the area of water stability and thus may follow the corrosion of noble metals (gold only in presence of complexing substances). Regarding the fact that the most common corrosion system consists of a combination of iron and neutral aqueous solution, oxygen reduction supports the transformation of the greatest volume of metallic material into corrosion products.

2.3.3 Heterogeneity in corrosion systems

Anodic and even cathodic reaction may theoretically proceed in the same area of metal surface, and as to the course of corrosion process, geometrically separated

<table>
<thead>
<tr>
<th>Metal</th>
<th>Pt</th>
<th>Fe</th>
<th>Ni</th>
<th>Cu</th>
<th>Sn</th>
<th>Al</th>
<th>Zn</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>( j_0 ) (A/m²)</td>
<td>( 10^1 )</td>
<td>( 10^{-2} )</td>
<td>( 10^{-2} )</td>
<td>( 10^{-3} )</td>
<td>( 10^{-4} )</td>
<td>( 10^{-6} )</td>
<td>( 10^{-6} )</td>
<td>( 10^{-9} )</td>
</tr>
</tbody>
</table>
anodic and cathodic areas are not necessary. However, there are heterogeneities in real corrosion systems that facilitate the process of anodic or cathodic reaction. Therefore, the reduction proceeds in a simpler manner in areas with lower overpotential and anodic reactions where metal is more easily ionizable.

Heterogeneities are inherent in the structure of most metal materials. These differences lead to activities of the so-called microcells which are given by structural arrangement inhomogeneity (crystal planes, lattice defects), or chemical inhomogeneity (gradient of chemical composition of a phase, various phases, precipitates, inclusions – electron-conductive or chemically unstable in environment) or inhomogeneity of the internal mechanical stress.

In addition to microcells activities, cells with anodic and cathodic areas at a distance of more than mere tens of µm frequently form within the corrosion system. Such cells are designated as macrocells and the distance to which the metal potential is influenced by their activities may reach even hundreds of meters (e.g. in case of lined buried facilities – piping and cables).

Connections of two differently noble metals having dissimilar anodic behavior may serve as a classical example. The metal with more negative free corrosion potential turns into anode, and the metal with more positive potential becomes cathode. Activities of such galvanic cells lead to the acceleration of the anodic metal corrosion, and frequently, as a result of geometrical arrangement, to localized attack.

The heterogeneity of the environment that is in contact with the metal surface often leads to the formation of cells that are called concentration cells. The most common example of such cells is the one with differential aeration, when the cell is activated by different accessibility of a certain part of the surface in neutral aqueous environment for atmospheric oxygen. The prevailing anodic reaction upon the surface in lesser contact with oxygen leads to the acidification of the adjacent electrolyte as a result of metal ions hydrolysis. Electrolyte aggressiveness at the anode increases (also as a result of migration of frequently present chlorides), and electrolyte aggressiveness at the cathode decreases. The final consequence is the passivation of the surface with better access to oxygen and increase of corrosion of the surface where access to oxygen is limited. The original heterogeneity in access to oxygen has therefore turned into heterogeneity of composition (pH, Cl−) initiated by the corrosion cell activity. At construction crevices, in cracks, semi-closed pits, at level meniscus, under sealings, coatings, deposits and corrosion products, the same mechanism leads to the formation of what are known as occluded solutions. Likewise, the microbial activity upon the metal surface leads to formation of occluded solutions and concentration cells. Formation of occluded solutions follows the localized forms of attack, such as pitting and crevice corrosion, stress corrosion cracking, corrosion fatigue, etc.

Heterogeneity in the composition of the environment does not have to be related to access to oxygen but may have connection with concentration differences of other species of the environment that affect the corrosion process. Likewise, heterogeneity in physical parameters at the metal surface (temperature, heat flow, flow rate) leads to formation of cells.
2.3.4 Passivity of metals

Should the suppression of corrosion reaction on a metal be caused by a protective layer generated spontaneously upon the surface (referred to as passive layer), we call it a passive metal. Various barrier effects of non-oxide corrosion products are involved in constituting passivity. The oxidation type of passivity is caused by a very thin, non-porous layer of oxides-hydroxides on the phase interface metal–electrolyte. Salt passivity occurs almost in every metal under conditions where the solubility product of forming salts is exceeded upon their surface.

Most frequently, upon the passive metal surface, there is a very thin layer of hydrated oxides which is of amorphous, almost microcrystalline character, usually electron-conductive (very little conductive at aluminum, titanium, and tantalum), and whose composition is given by the basis metal (alloy). The passive layer becomes continuously enriched with some elements, such as chromium and silicon in stainless steels. It is anticipated that the protective effect is given by the function of the layer as bipolar membrane, which prevents penetration of anions from the electrolyte (outer part) and penetration of metal cations into the electrolyte (inner part). The penetration of OH\(^{-}\) ions is essential for the formation of the layer from the metal–layer interface ensured by the splitting of molecules of water by electric field within the layer.

In a number of electrolytes, passivable metals exhibit dependence of corrosion rate on environment oxidation ability corresponding with the curve from Fig. 5. There are four areas with different corrosion resistance. In the area of immunity, metals are thermodynamically stable. In the area of activity, the metal oxidation rate, expressed by corrosion current, is exponentially dependent on the oxidation ability of the environment expressed by a potential. Increase of oxidation ability of the environment leads to increase of corrosion rate. In active passivable metals, after oxidation under given conditions has reached a certain level there is a sudden drop in the corrosion rate, which in a relatively broad interval of conditions sustains low value – the metal is passive.

Figure 5: Dependence of passivable metal corrosion rate on oxidation ability of environment.
Figure 6: Dependence of current on the potential for passivable metal.

Any further increase in the oxidation ability of the environment results in the failure of the protective function of the passive layer, and the corrosion rate significantly increases. Where the environment does not contain ions locally damaging the passive layer, we talk about transpassivity in which metal corrodes practically uniformly all over the surface. If there are any aggressive ions in the environment (e.g. chlorides for steels or aluminum), it causes local breakdown of passive layer and localized attack of metal.

Qualitative dependence, expressed in Fig. 5 in general coordinates corrosion rate–oxidation ability, may be expressed in coordinates current–potential (Fig. 6) where current is an expression of the electrochemical reactions rate upon the metal surface, and potential is a formulation of oxidation conditions upon its surface. This experimentally observable dependence is a sum of partial currents of all electrochemical reactions proceeding upon the surface. In the whole potential range, the polarizing curve does not express merely the corrosion rate of metal; it corresponds with the observed current at potentials at which neither reduction nor oxidation of the solution species occur. The basic characteristic current values in dependences are passivation current density (\(j_{\text{crit}}\)) – current necessary for passivation of metal surface unit (\(10^{-10^{4}}\, \text{A/m}^2\)) and passive current density \(j_p\) which usually corresponds with the corrosion rate of passive metal. Passive current largely depends on time and partially on potential and reaches values of \(10^{-4}–10^{-1}\, \text{A/m}^2\).

Passivation potential \(E_p\) is the potential the exceeding of which results in passivation. Potential, at which metal may be considered as persistently passive, is often somewhat more positive, and thus the passivation potential cannot be considered as an unambiguous border of usable passivity on the negative side. Transpassive potential \(E_t\) limits the passivity on the positive potentials side from transpassivity. In case a solution contains aggressive ions causing local breakdown of passive layer, the stable passivity is limited by breakdown potential \(E_b\) on the side of...
positive values. The range between passivation and transpassive or breakdown potential is a passive area in which corrosion protection is applied by passivation. This area is broad, of the order of hundreds of millivolts; for titanium, tantalum and aluminum, it is of the order of tens of millivolts.

2.3.4.1 Factors affecting passivability and corrosion resistance in passive state

Passivability is considered to be a range of adversity for a metal’s transfer in a given environment from active to passive state. It is identified by values of passivation potential and passivation current density. Corrosion resistance in passivity and the stability of passive state are characterized by a value of passive current density and width of the passive range, i.e. potential difference between passivation potential and transpassive or breakdown potential.

Technically significant passivable metals are iron, nickel, chromium, aluminum, copper, titanium, tantalum and their alloys, such as stainless steels and nickel alloys. The composition of a metal is the most distinctive factor affecting its passivability, even the corrosion rate in the potential area of passivity.

Passivability of metal is simplified by alloying elements that decrease the passivation current density and shift the passivation potential to negative direction. Stability of passive state is supported by metals that decrease passive current and broaden the passive range.

Passivability of iron alloys is most significantly influenced by chromium which, added in amount exceeding 12 wt.%, considerably simplifies passivation. The mechanism of chromium effect may be explained with a shift of passivation potential to negative direction that enables easy, spontaneous passivation. Neither decrease of the rate of a partial anodic reaction should be omitted. Iron alloys containing more than 12 wt.% of chromium (stainless steels) have corrosion resistance just from easy passivability and resistance in passive state. Nickel in iron alloys decreases passivation current and the corrosion rate in active state.

In addition to composition, another important factor is the metal structure, which may be affected by the composition as well as heat or mechanical treatment of the material. Formation of structural non-homogeneity of metal constricts the passive area and increases characteristic currents. This usually results in occurrence of localized forms of attack, such as intergranular and pitting corrosion.

The environment affects passivability of a metal and its resistance in passive area mainly by composition and temperature, and alternatively by motion. Metals passivate not only in aqueous solutions but also in environments with distinctively low water content, such as certain organic solutions or in waterless solutions as a melt with ionic conductivity.

The influence of chemical composition is given by the content of species with activating or passivating effects. Unambiguous distinction of solution species regardless of the protected metal is impossible, as the components with activating effect on one metal may have passivating effect on another.

Substances with oxidation effects normally come under the category of passivators. Chloride, fluoride and sulfide anions usually have activating effects.
Several different states may be a result of the oxidation effect of the environment on a metal which is passivable under given conditions. Where the oxidation ability is low for passivation as well as for the sustaining of the metal in the area of passivity, the metal corrodes in activity. Should the oxidation ability of the environment be sufficient to sustain the metal in the area of passivity but insufficient to passivate the active metal, then the passive state is unstable and any local failure of the passive layer leads to overall spontaneous activation. Should the oxidation ability of the environment be sufficient for spontaneous passivation and the passive state is stable, then the passivity is a basis for the corrosion resistance of the metal. In case the oxidation ability of the environment is too high, corrosion proceeds in the area of transpassivity, or the pitting corrosion occurs above breakdown potential, then the passivable metal does not resist any longer.

2.3.5 Biologically influenced corrosion
In some cases, the corrosion attack of construction materials is impossible to be explained merely on the basis of abiotic corrosion mechanisms. In most cases microorganisms participate in the stimulation of the corrosion process. Various types of organisms are present in all natural environments. In aqueous environments, the microorganisms incline to attach to the surface of solid substances and grow thereupon. It results in formation of more or less uniform layer of biofilm. The activity of microorganisms in the biofilm upon the surface of metals causes a change of chemical composition of the environment and physical conditions on the interface metal–environment.

In the first case, the microorganisms stimulate the corrosion process by using the environment components or corrosion products during their metabolism. The ability of sulfates reducing bacteria to exploit hydrogen and the ability of iron bacteria to oxidize Fe\(^{2+}\) to Fe\(^{3+}\), and thus permanently support the corrosion process, may serve as examples. Microorganisms may also evolve aggressive substances for metals (evolution of hydrogen sulfide by sulfates reducing bacteria, production of sulfuric acid by sulfates oxidizing bacteria, etc.). Only the formation of biofilm enabling the formation of concentration corrosion cells shall be considered as a physical change on the interface metal–environment. These two changes that mainly influence the corrosion process simultaneously do not lead to the origination of a new type of corrosion attack but affect the initiation or the rate of already known corrosion processes.

The origination of heterogeneities of a physical and chemical nature on the metal–environment interface following the formation of biofilm is characterized by changes of the environment (pH, oxidation ability, temperature, rate and character of flow, concentration of certain components of the environment, etc.). In this respect, the value of a certain parameter on the surface of the metal under the biofilm may totally differ from the value outside the biofilm, and conditions appropriate for a function of concentration cells may arise. It may result in change of corrosion attack arrangement (e.g. from uniform to localized), or in the initiation of the corrosion attack in conditions under which the attack would not occur if that biofilm did not exist (under abiotic conditions).
3 Types of corrosion

3.1 Uniform corrosion

Uniform corrosion is a general corrosion that proceeds at an almost identical rate upon the whole surface. It occurs in case when the complete surface is either in active or passive state. In uniform corrosion in active state, those microcells significantly apply that are mainly uniformly distributed within the surface. As a result of metal corrosion, the localization of anodic and cathodic areas continuously changes. This localized attack on a microscopic scale leads more or less to uniform loss of the metal upon the surface.

3.2 Galvanic and concentration cells (macrocells)

The action of macrocells (see Section 3.3) intensifies corrosion upon the surface of the metal which is anodic under given conditions (it has more negative corrosion potential) (Fig. 7) and conversely, corrosion of the material which is cathodic is reduced by connection. The action of the cell is always developed by heterogeneity of composition or other conditions which acts even during the acceleration of uniform corrosion (microcells) and is related to a range of other types of localized corrosion.

The acceleration of the corrosion rate upon the metal surface caused by the cells activity depends on many factors. In addition to the difference of free corrosion potentials in a given environment and the polarizability of connected metal surfaces, electrolyte conductivity, geometrical arrangement and the ratio of surface areas also factors in this process.

For the cell activity, electric connection of at least two materials is essential, while the cathodic material does not have to be metallic. As the conductivity of
electron-conductive materials, metals in particular, is high, the resistance of electrodes and their connection should not be constraining for the function of the cell. The most important is the electrolyte resistance, which is remarkably higher due to low conductivity of the corrosion environment as well as frequently due to geometrical arrangement. For instance, cells in atmospheric conditions may act in a very thin layer only, and therefore their reach is small and the effect is localized. Vice versa, in the volume of conductive electrolyte, corrosion of anodic metal is intensively influenced by the effect of the cell, but the effect is not so localized in the area adjacent to the connection (though the total effect is the greatest in this place).

In conductive environments, the extent to which cells are affected by corrosion also depends to a large extent on the ratio of the areas of anodic to cathodic materials. When a small anode is connected to a large cathode, the intensification of corrosion reaches its maximum. Conversely, when the anodic surface (compared with the cathodic surface) is large, the extent of corrosion exhibited is small. Due to the high resistance of a thin layer of electrolyte, the ratio of the areas of connected surfaces is not considered to be a distinctive factor under atmospheric conditions.

Protection against the effects of macrocells consists namely in the selection of an appropriate combination of materials. It is possible to connect materials with considerably close, free corrosion potentials, or materials the connection of which does not change the corrosion potential outside of the passive area. Corrosion impacts of the macrocells may be limited by decrease in corrosion aggressiveness of the environment. In some cases it is possible to eliminate the cells activities by electrical insulation (e.g. insulating flange), cathodic protection or extension of the closest distance of the surfaces in electrical contact.

### 3.3 Crevice corrosion

Crevice corrosion is a localized form of attack which is related to narrow crevices or slots between metal surface and other surface (metallic or non-metallic). One of the dimensions at the slot orifice is usually smaller than 10 μm. Though it enables the electrolyte inside the crevice to ionically communicate with the electrolyte volume outside, the dimensions impede convection and limit diffusion. Such situation occurs in case of construction crevices, thread connections, pores of welds, locations where a weld is not continuous, at the edge or riveted joint, under sealings (Fig. 8), under deposits, under corrosion products or under disbonded coatings. The crevice effect follows a range of other forms of corrosion, such as stress corrosion cracking, corrosion fatigue, intergranular and pitting corrosion. In the first phase of crevice corrosion, oxygen is relatively quickly consumed from a very small inner electrolyte volume. In the second phase, a slow corrosion of the inner passive surface continues with the cathodic reaction outside the crevice, and the excess of positive charge in the inner electrolyte is compensated by migration of anions (usually chlorides) from the outside electrolyte to the inside of the crevice. In the third phase, the increase of chloride concentration, followed by hydrolysis, continues.
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Inside the crevice it leads to a formation of an occluded solution which leads to activation of the originally passive surface.

An example of this is the formation of crevice corrosion of stainless steel in aerated water with a content of chlorides that still enables a long-term stability of the passive state. Crevice corrosion of stainless steel in water may be anticipated on the basis of various models which use mathematical description of migration, diffusion, chemical equilibrium and even empirically assessed conditions for activation of various types of stainless steels.

Protection against crevice corrosion consists of construction modifications which impede the formation of construction crevices, discontinuous weld seams, preventing construction connections from forming crevices and restricting the formation of deposits. It may also be restrained by the elimination of porous sealing materials and materials releasing aggressive components. The problem of crevice corrosion may obviously be solved by selection of appropriate material with greater corrosion resistance (which resists even to occluded solutions), or by modification of the environment.

3.4 Pitting corrosion

Pitting corrosion is localized corrosion process in which deep pits are generated upon the metallic surface and the surrounding surface remains without observable attack. This form of attack is generated on a number of passivable metals; however, it is typical for stainless steels (Fig. 9) and aluminum. In the incubation phase, pitting corrosion of stainless steels is normally generated on the basis of competition between hydroxide and chloride ions at the surface. The chloride ions attack the
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Figure 9: Pitting corrosion of stainless steel sheet.

passive layer, the hydroxide ions form it. The initiation mechanism consists in attacking the metal in areas with lower protective properties of the passive layer (inclusions, grain boundaries) in the presence of various aggressive ions in solution. In the area of passive layer failure, a pit is generated, inside which the concentration of aggressive ions increases by migration, and the value of pH decreases by the hydrolysis of corrosion products. Localization of the attack is caused by actively corroding inside of the pit, which serves as a sacrificial anode for the remaining passive surface.

The generation and propagation of pitting corrosion are enhanced by increased concentration of an aggressive ion (usually chlorides), by presence of oxidizing substances, increased temperature and low pH value.

Protection against pitting corrosion is based on selection of resistant metallic material. Improved resistance of stainless steels may be achieved, e.g. by alloying with molybdenum. The decrease in the probability of pitting corrosion development is supported by the decrease in the environment oxidation ability, the presence of certain ions with an inhibitive ability (e.g. \( \text{NO}_3^- \), \( \text{SO}_4^{2-} \)) and the increase of pH value. Pitting corrosion is supported also by roughly machined surface, occurrence of scales and inclusions (sulfides) in the metal structure. Motion and reduced temperature of the environment help to eliminate the pitting corrosion. It is possible to exploit the electrochemical protection, mainly cathodic, which decreases oxidation conditions upon the surface by polarization. Aluminum and its alloys suffer from pitting corrosion; beside chlorides, aluminum is also attacked by very low concentrations of noble metal ions (Cu, Hg). Pitting corrosion occurs even in copper in certain types of water.

3.5 Intergranular corrosion

Intergranular corrosion is a form of localized corrosion attack which is manifested in stainless steels after heat treatment, during which, on the grain boundaries, it leads to
Environmental Deterioration of Materials

Figure 10: Intergranular corrosion of stainless steel (specimen after bending).

generation of areas depleted of chromium as a result of formation of carbides rich in chromium, or of other phases with different electrochemical properties. The metallic material corroding intergranularly loses its mechanical strength without any visible surface change. It is because under certain conditions, it preferentially corrodes in a narrow band at the grain boundaries, which lose then their mutual cohesion (Fig. 10). The area at the grain boundary becomes inclined to be attacked by corrosion in an aggressive environment, mostly as a result of decrease of chromium under the limit of 12%, which enables easy passivability of alloy. The decrease of the chromium content at the grain boundary is caused by precipitation of carbides with high content of chromium (Cr$_2$C$_6$, M$_6$C) at heat treatment in a critical temperature area. The inhomogeneity generated by heat treatment is reversible – it is possible to remove this sensitization by annealing at the temperature of approximately 1050°C, followed by immediate cooling.

The critical area of heat treatment (sensitization) is allocated by the time and temperature of isothermal annealing. Mainly the content of carbon affects the sensitization of austenitic stainless steels – the less carbon is contained in steel, the less sensitive the material is. Intergranular corrosion is fastest under conditions when the depleted part of metal corrodes in active state while the remaining surface is passive.

Intergranular corrosion of ‘active boundary–passive grain’ type may be prevented by heat treatment beyond the area of critical temperatures, or where applicable, may be protected by the so-called stabilization by adding titanium or niobium which has greater affinity to carbon than chromium is. The presence of carbon in austenitic stainless steels is not essential for absolute majority of their applications due to their mechanical properties; therefore utilization of low carbon steels (<0.03 wt.%) constitutes the best solution for elimination of the danger of austenitic stainless steels intergranular corrosion after welding.

Intergranular corrosion attack is not solely related to austenitic steels but also concerns all other stainless steels and nickel alloys – in addition also alloys of aluminum, copper, zinc, silicon and lead. The so-called exfoliation may serve as an example of intergranular corrosion of aluminum alloys (Fig. 11).
3.6 Selective corrosion

In selective corrosion, corrosion processes cause removal of one component of alloy. A typical example of this form of corrosion is dezincification of brass, when part of the original material, alloy of zinc and copper, turns to spongy copper. It happens either in the whole layer at the surface (Fig. 12), or locally. The spongy copper has no strength, and it continuously causes wall perforation. Dezincification plays its role in the formation of corrosion cracking of brass. All brasses having a Zn content higher than 15 wt.% incline to dezincification. The mechanism of dezincification lies in dissolution of Cu and Zn, and Cu subsequently re-deposits. The dezincification often happens in waters containing chlorides and is a frequent cause of failing of the brass fittings in water circuits. Dezincification is significant in waters with high content of oxygen and carbon dioxide, at low or no flow.
Acidic waters with low salinity usually lead to uniform dezincification at normal temperature; neutral waters with high salinity lead to local dezincification especially at elevated temperatures.

Where a problem with dezincification may occur, it is recommended to use red brass (\(<15\% \text{ Zn}\)) (mostly they are inappropriate due to their bad mechanical and processing properties) to limit the oxidation ability of environment by decreasing the oxygen content to increase flow, apply cathodic protection, alloy brasses (\(\alpha\)) with arsenic, tin, and phosphorus – the so-called admiral brass.

Other cases of selective corrosion may be observed in aluminum bronzes (dealuminification), silicon bronzes (desiliconification), tin bronzes (detinification), gold alloys (decopperification) and dental amalgams (selective removal of tin).

Graphitic corrosion of gray cast iron with continuous graphite network is another example of selective corrosion. The graphitic corrosion appears in water and in soil. Graphite is continuous in the gray cast iron structure and forms a distinctly noble phase compared with iron. That leads to galvanic cell and selective corrosion of metal matrix. The original gray cast iron turns to non-metallic material in which the iron is completely transformed into corrosion products and has practically no strength.

3.7 Environmentally induced cracking

Straining metal below the yield strength or fatigue strength may, even in environment with low corrosion aggressiveness, result in cracking. The tensile component of stress is always remarkable; the compressive component does not cause the attack. From a technical point of view, this is a very important degradation mechanism as it causes sudden failure of metallic materials, often with high strength and corrosion resistance. Cracks develop, while any other more significant damage of the material surface does not occur.

Various forms of cracking induced by the environment have the same result for users, while the causes and conditions of its development are different. Individual forms have several features in common; there is no exact border between them. In aqueous solutions, cracking developed by the environment may be divided into three types: stress corrosion cracking, corrosion fatigue and hydrogen-induced or -assisted cracking.

3.7.1 Stress corrosion cracking

Corrosion cracking occurs when static tensile stress affects metallic material exposed in specific environment (at certain temperatures and concentrations). In corrosion cracking, cracks propagate in the metal structure, either at grain boundaries – intergranularly (Fig. 13) or via grains – transgranularly (Fig. 14). The mechanism of stress corrosion cracking of a number of technically important materials is explained by active dissolution in the crack front which simultaneously acts as a stress concentrator. The outer mechanical stress is not always necessary for the development of corrosion cracking, but the residual stresses are sufficient, e.g. after
Each irregularity of the surface may cause a localization of stress – tensile stress is greater in this area. Therefore, the formation of a crack is frequently related to the area of crevice or pitting corrosion – the crack may propagate more easily out of a pit or from a crevice; a specific, more aggressive environment develops therein – occluded solution. A typical example of corrosion cracking is the so-called caustic embrittlement. It would occur in boilers made from carbon steel for which water is cold working or at weld seams. The more homogenous the material is, the less susceptible it is (pure metals are the most resistant).

Figure 13: Intergranular stress corrosion cracking.

Figure 14: Transgranular stress corrosion cracking.
was alkalized to eliminate uniform corrosion (pH above 9). In areas of riveted joints, hydroxide got concentrated by overheating, and the tensile-stressed rivets cracked.

Another example is the so-called season cracking of brass. Brass cartridges with great inner stress (in the area of a pressed-in projectile) in humid atmosphere, in the presence of ammonia vapors (decomposition of organic waste), crack, and thus the ammunition is depreciated. Up to now, this form of failure of brass may be observable, and the main cause is the inner stress originated in cold working. The corrosion cracking of carbon steel in soil environment (in the presence of \( \text{CO}_2 \text{(aq.)/HCO}_3^- \) or \( \text{HCO}_3^-/\text{CO}_3^{2-} \)) which relates to gas pipelines behind the compression stations, where temperature is elevated, is also significant. Another considerable problem is also corrosion cracking of stainless steels which crack in chloride environment. The structure of austenitic chromium-nickel stainless steels is susceptible; therefore, it is more appropriate to use duplex steels (growing of the crack is stopped in ferritic grains) or ferritic steels.

Protection against corrosion cracking is based on the decrease of tensile stress in material and even in construction, on elimination of specific components from the environment, or on transformation of metallic material which under given conditions does not suffer from corrosion cracking. Electrochemical protection and addition of inhibitor may be effective as well.

### 3.7.2 Corrosion fatigue

Corrosion fatigue is a form of attack which requires co-operation of a corrosive environment and cyclic mechanical stress with a tensile factor. While in cyclic stress, the metal integrity is violated by development of cracks, even if stressed below the yield strength and even without any corrosive environment. In corrosion fatigue, the crack is transcrystalline and is propagated discontinuously that results in development of striations. Frequency of stress greatly influences the attack: the lower it is, the greater the change of the crack length per cycle is. The frequency of \( 10^{-6} \) Hz (approx. once a week) is sufficient for the process of corrosion fatigue. In fast opening and closing cracks (at high frequencies), the corrosion attack is not enough to apply, and the mechanical effect prevails. In some cases, the corrosion fatigue is confused with heat fatigue damage.

Protection against corrosion fatigue is based on the elimination of the cyclic tensile factor, decreasing of fatigue amplitude, choice of more resistant material, decreasing of the environment aggressiveness (inhibitors) and on utilization of inorganic (metallic) coatings.

### 3.8 Erosion corrosion

Among the various forms of purely mechanical damage (abrasive, adhesive and erosive) in corrosive environment erosion corrosion has the greatest significance. When in contact with a flowing liquid or gas, it may lead to purely mechanical failure of metallic material and the damage grows if the flowing medium contains some species (solid or liquid particles in gas, gas bubbles or solid particles in liquid) – even under conditions when the material’s mechanical failure is very small. This is
because most of technical metals derive its corrosion resistance from passivity, i.e. the existence of a surface layer of corrosion products which restrains the anodic dissolution. In case of salt passive layers, the effect of the flowing medium may be based solely on intensive removal of the liquid layer close to the surface saturated with dissolved components of salt passive layer.

Much greater effects may be observable for turbulent flow (Fig. 15) than for laminar flow. Turbulence in a liquid may lead to mechanical failure, particularly at thicker layers, and to a substantive increase of the corrosion rate. Beyond a certain rate of flow, the corrosion rate begins to increase as well.

If the electrolyte contains particles, the attack increases even at low flow rates. Particles with sizes of the order of tens of micrometers to tens of millimeters are thicker than the passive layer, and in the area of impact they deteriorate the passive layer completely and even damage the metal below the passive layer; this gives rise to an area for new passivation of the surface. The tendency of a metal to undergo corrosion damage depends on many factors that are determined by the properties of the metal, the electrolyte, the suspension and the suspended particles as well as the geometric arrangement.

Protection against the effects of erosion corrosion is based on selection of material, on elimination of areas with unacceptable flow rates by appropriate construction solution and on removal of solid particles and gas bubbles.

With relation to erosion corrosion, the so-called fretting corrosion is indicated. It occurs under atmospheric conditions upon the surface in areas of connection of metal parts that mutually move on one another with very low amplitude. This form of corrosion occurs even under conditions of low relative humidity of the atmosphere when the corrosion effect of the atmosphere is irrelevant. Periodical removal of a thin oxide layer leads to periodical reaction of the pure surface with oxygen and following loss of material, which is transformed into corrosion products. It is usually related to textile or printing machines, bearings and other machine parts subject to vibrations. Protection is based on improving of the parts lubrication, change of material and elimination of vibrations or increasing of their amplitude.
3.9 Hydrogen damage

An important damaging process in chemical and petrochemical plants is interaction of metallic construction material with hydrogen. At temperatures below 190°C hydrogen is developed upon the surface mainly due to corrosion attended by H^+ reduction, and enters into steel in the atomic form. The hydrogen atom is notably small which enables simple diffusion into the metal structure. Generation of atomic hydrogen upon the surface of metal is also possible in water electrolytes in cathodic polarization upon the metal surface in electrochemical technologies in cathodic protection at stray current’s entry.

In metals, atomic hydrogen gets caught in places identified as ‘hydrogen traps’, e.g. dislocations, lattice defects, grain boundaries, inclusions, blisters, cracks. Recombination of hydrogen atoms to H_2 molecule in appropriate areas of the structure results in development of cavities and cracks. The re-combination in the areas of steel structure defects causes the development of great inner compressions (tens to hundreds of MPa), which without the presence of another stress field lead to mechanical failure (the so-called hydrogen blistering) (Fig. 16). The so-called hydrogen-induced cracking is construed as a form of blistering, when as a result of formed inner hydrogen cracks, at tensile stress of a metal part, it leads to a fracture. Loss of ductility and toughness of metallic materials is demonstrated by hydrogen embrittlement. If the embrittled material is tensile stressed, then cracks occur (hydrogen-assisted cracking). The development of hydrides in the structure of metals such as titanium, tantalum, niobium and zirconium greatly affects degradation of mechanical properties (hydride cracking).

Having entered the structure, hydrogen which had no opportunity for re-combination, may be removed by heating up to temperatures of 100°C–150°C. To prevent hydrogen embrittlement, it is also essential to avoid welding of moist surfaces which leads to thermal decomposition of water and entering of hydrogen into the structure.

Figure 16: Hydrogen blistering of carbon steel.
The entering of hydrogen into the structure may also be possible at elevated temperatures when any aqueous environment is not present. At temperatures of 200°C–480°C molecular hydrogen undergoes thermal dissociation into atomic hydrogen on the steel surface. The atomic hydrogen diffuses into the steel, combines with carbon, and produces high-pressure methane which causes damage to the steel; this process is the so-called hydrogen corrosion (attack) which is represented by the formation of blisters.

In a proper sense, the negative effects of hydrogen on metals do not belong to corrosion processes, as an electrochemical or a chemical reaction often does not directly participate in the deterioration mechanism. The deterioration itself is of a purely mechanical type, though the causes are of a chemical nature.

4 Corrosion environments

4.1 Atmosphere

Atmospheric corrosion causes a great part of losses resulting from corrosion. The reason is that the largest surface of the construction material, mostly of carbon steel, is exposed to the effects of the atmosphere. Many metallic objects, such as building constructions, vehicles, etc are exposed to the corrosion effect of the outdoor atmosphere. Similar to the corrosion of metals in electrolytes, atmospheric corrosion is an electrochemical mechanism at normal temperatures. As the interaction of dry air with construction metals at normal temperatures is negligible, atmospheric corrosion occurs only due to atmospheric humidity. Conditions of what is known as ‘critical humidity’ lead to the formation of a sufficiently thick electrolyte film essential for the process of corrosion reactions. Such conditions are met where the relative humidity of the atmosphere exceeds a critical value of 60–80% (corresponds with 10–14 g H$_2$O/m$^3$ of air at 20°C). Under subcritical humidity, the corrosion rate is not zero, but for the majority of technical applications of metals it is insignificant. The corrosion effect of the atmosphere in a territorial locality is given by time for which the relative humidity of the atmosphere is above critical at temperatures of the surface electrolyte liquidity (time of wetness). Atmosphere aggressiveness is influenced by the presence of a range of substances, the most significant corrosion stimulator of which is sulfur dioxide and chlorides.

Rust, the porous precipitate of hydrated iron oxides with no especially notable protection effect, mostly visually devaluating, develops upon the surface of steel or cast iron. The protective and decorative effects of rust is exploited only in case of what are known as weathering steels, i.e. low alloyed carbon steels used in the atmosphere usually without any surface finishing, the corrosion rate of which is only a quarter to a half compared with the corrosion rate of carbon steels, and the rust layer is cohesive and uniformly colored.

The main polluting component of the atmosphere in local conditions – sulfur dioxide is oxidized by other components of the atmosphere (by atomic oxygen, NO$_x$) and it leads to formation of sulfate ions stimulating active dissolution of iron. Sulfates act here as a catalyst of anodic oxidation.
In case of copper and zinc, sulfates or chlorides from the atmosphere transform into solid corrosion products (basic sulfates or chlorides), which cannot repeatedly enter into the mechanism of their active dissolution as it is in the case of iron.

Atmospheric corrosion of metals is also influenced by contents of other substances: solid substances (dust) enhance condensation (saline particles may be hygroscopic), have erosive effects; and conductive particles may work as an electrode (iron oxides, carbon) and accelerate corrosion with the effect of galvanic cells. Ammonium causes corrosion cracking of brass. Corrosion under atmospheric conditions may even be accelerated by microorganisms and accumulation of aggressive components of the atmosphere in permanently moist crevices.

Carbon steel is necessary to be protected by organic coatings or galvanizing. Modification of construction may constrain retention of moisture (orientation of profiles, elimination of heat bridges, crevices). Corrosion losses caused by atmospheric corrosion are mainly related to coating systems, their application and the necessity of their regular restoration on steel structures and objects. A frequent cause of failing of corrosion protection is application of the coating on an inappropriately prepared surface.

Protective layers formed upon copper are based on basic sulfates and chlorides (patinas). The maximum corrosion rate is approximately 1 µm per year. Wider utilization of copper in atmospheric conditions should be prevented for ecological reasons (transmission of Cu²⁺ in the living environment – the so-called run-off has been assessed to be 5 g Cu²⁺/m² per year in local conditions). Copper is transmitted into the environment in concentrations of the order of ppm due to corrosion of copper roofing by draining rainwater.

Protective layers formed upon aluminum are based on modifications of Al₂O₃, or even Al(OH)₃. Aluminum is sensitive to pitting corrosion in the presence of chlorides. The corrosion rate is approximately 0.1–1 µm per year, and aluminum, under conditions of normal atmosphere without chlorides, is absolutely resistant. Stainless steels – if they are not exposed to chlorides – are absolutely resistant.

Exposure tests for atmospheric corrosion of construction materials are conducted at many stations in the world, and their results, together with the atmospheric pollution and meteorological data, form the basis for empirical calculation relations and for computer processing of the corrosion aggressiveness maps for given territories.

The connection of different metals leads to the formation of galvanic cells, and therefore it is necessary to avoid certain combinations, e.g. copper and iron. The washout of noble metal ions from corrosion products (e.g. Cu²⁺) onto ions of less noble metals (e.g. Zn, Al, Fe), even if they are not electrically connected, leads to acceleration of corrosion.

4.1.1 Atmospheric corrosion of historical objects

The outer atmosphere also affects metallic monuments. Their degradation due to corrosion leads to their continuous depreciation, which requires costly restoration. The emergency conditions of copper and bronze statues are caused mainly by the
corrosion of their iron framework that results in mechanical damage of a copper or a bronze shell. Construction defects of statues allow easy leakage of rainwater to the inside, and conversely, create conditions for internal retention of water. Good electrical and electrolytic contact of the framework and the copper shell aids the corrosion damage of the iron parts as well.

With regard to corrosion resistance of iron, ill-informed literature and media often cite the example of the so-called ‘non-corrodible’ Iron Pillar in Delhi, though iron corrosion products apparently cover its surface. This column, made of malleable iron (length 7.2 m, weight approx. 6 tons), is an evidence of the admirably high technical skills of the inhabitants of India 1600 years ago. In its aboveground part, the column corrodes very slowly, mainly owing to the clean atmospheric conditions that existed in Delhi in the past and which are still unfavorable for the long-term condensation of aerial humidity. The great heat capacity of the column, given by its weight, ensures that corrosion occurs very seldom, even in times when the relative humidity of the atmosphere exceeds the critical value. On average, the percentage of rainy days in a year is only approximately 10%. The thin layer of corrosion products formed during the periods when the atmospheric aggressiveness was lower compared to the rainy days has protected the column till date. The underground part of the column has obviously undergone corrosion. The composition of the column is well known, and considerable variation has been observed based on the area of the sampled specimen owing to the production technology (malleable iron) used. To a certain extent, the composition contributes to the atmospheric resistance of the column as well (low content of sulfur, higher content of phosphor). The rust structure partly resembles the rust developed on weathering steel. According to some sources, the higher content of phosphor (tenths of wt.%) was achieved on purpose, as during production a certain wood with higher content of phosphor was used. Specimens of the metal sampled from the column did not exhibit any significantly better corrosion protection in comparison with other carbon steels. With respect to the current scientific knowledge, neither corrosion nor technological mystery is related to the column in Delhi.

4.2 Aqueous solutions

4.2.1 Water

The term, water, for our purpose includes not only chemically pure water, but also various weak-concentration aqueous solutions with a content of substances that get into water during its natural and industrial hydrological circle. Not only do natural waters aggressively affect water constructions and ships; their aggressiveness passes into the industrial waters obtained from them and also into drinking water.

The aggressiveness of industrial waters is influenced either by intentional modifications or by the substances that get into the water during its use or that concentrate during its circulation. Although there are several requirements imposed on various kinds of water, there is a range of common factors influencing the aggressiveness of the water.
The metal surface exposed to absolutely pure water corrodes only irrelevantly. Mainly additional agents, a certain amount of which are always present in both natural and industrial waters, are responsible for the process of corrosion reactions in the water.

Water aggressiveness is affected by the content of oxygen and other aggressive gases, by the amount and type of dissolved salts, by the presence of organic substances and microorganisms, by pH, temperature and flow rate, and by the content of solid particles.

Oxygen is the most influential of gases dissolved in water as corrosion in water is mostly controlled by the rate of oxygen reduction. The uniformity of the oxygen access to the surface is also very important – if the access is not uniform it leads to the formation of cells with differential aeration that results in local attack.

Oxygen is not only a stimulator of corrosion, but also supports formation of protective layers and if its content in water is sufficient, it may limit the corrosion. However, the content of oxygen dissolved in pure water that is in contact with a free atmosphere at room temperature (up to 10 mg O₂/l) is not sufficient for passivation of carbon steel.

Carbon dioxide is another important component influencing aggressiveness of water. Thus, in acidic waters, cathodic reactions of types other than oxygen reduction may apply. The presence of CO₂ also negatively influences the inhibitive effect of Ca²⁺ and HCO₃⁻ ions. Similar effect is also caused by sulfur dioxide dissolved in water from the polluted atmosphere. Hydrogen sulfate and ammonium may cause corrosion cracking.

Salts dissolved in water change the pH of the solution by hydrolysis, increase conductivity, influence formation of layers upon the metal surface and may be a cause of localized corrosion.

Chlorides are present in almost all types of water and cause problems mainly when stainless steels are used, such as pitting and crevice corrosion, and also corrosion cracking at higher temperatures. Aluminum is also easily attacked by pitting corrosion due to the effect of chlorides in water. With the exception of seawater and brackish water, the usual concentration of chlorides in water lies within the range 10–200 mg Cl⁻/l. Compared with chlorides, the corrosion effect of sulfates and nitrates on steels in normal concentration is low.

Natural and industrial waters have pH usually ranging from 3 to 9, and therefore on a majority of metals, a layer of insoluble corrosion products is formed. The quality of this layer often determines corrosion resistance.

In the formation of a protective layer, the hydrogencarbonate, calcium (II) and magnesium (II), ions, with their inhibitive effect for steel given by the ability of aerated water to form protective layers consisting of iron oxides and calcium carbonate, constitute a significant component of water.

In power plants, water is used for cooling and heat transmission in armatures of district and central heating, as hot water in open circuits and is supplied to boilers. Water for the production of steam, upon which special requirements are imposed, is treated to the lowest salinity by demineralization, depleted of oxygen (thermically, by hydrazine) and alkalized with sodium phosphate. With water supply depleted...
of oxygen, corrosion of a boiler steel surface depends at higher temperatures on the formation of well-protecting layers of oxides (Fe₃O₄). The protective layer of magnetite is damaged by higher pH and oscillation of temperature.

Power plant cycles coming into contact with supplied water are most frequently made of carbon steel, brass and stainless steel. Brass, with a higher content of Zn, is affected by dezincification. At elevated temperatures, in the presence of chlorides, stainless steels are affected by corrosion cracking.

It is necessary to soften and deaerate water for heat transmission in closed circuits. Water for armatures of central heating is modified by addition of inhibitors. For the water in closed power plant cycles, it is important, much as in the case of water supply, not to let the water get into contact with the atmosphere, not to change the water and not to replenish it, as corrosion depends mainly on the amount of oxygen entering the loop. In this case, oxygen is depleted by addition of sulfite. For the distribution of utilized warm service water, drinking water is sometimes modified by adding silicates or phosphates. If the water is sufficiently conductive, it is possible to cathodically protect certain steel parts of the system (boilers, tube sheets).

Cooling water used in the circuit systems of industrial plants (e.g. chemical) and in power plant cycles are almost always aerated, as it is in contact with the atmosphere in the cooling towers. Therefore, corrosion may not be limited by the decrease of the content of oxygen. Where necessary, the inhibitors (phosphates) and other substances, which constrain the activity of microorganisms (biocides), keep the insoluble substances floating and limit deposition of calcium carbonate even if the solubility product is exceeded, are charged.

Cooling water for flow through systems is cleansed of dirt and is not treated any further. To constrain formation of deposits, the appropriate flow rate for water distribution systems is from 1.5 to 3 m/s. For erosion corrosion, the appropriate maximum flow rate is 1.5 m/s.

The equipment coming into contact with cooling water is made of carbon steel, stainless steels or brass. Carbon steel may be protected by coatings. Brass may suffer from dezincification and, in the presence of ammonia, also from corrosion cracking. In the presence of greater amount of chlorides in water (>100 mg Cl⁻/l), stainless steels may crack and is affected by crevice and pitting corrosion.

In the mine water environment, increased aggressiveness is caused not only by the presence of anions (chlorides, sulfates, carbonates), but also by cations which may, for instance, participate in cathodic reaction (copper deposition).

The aggressiveness of drinking water depends on the composition of natural water out of which it is modified. Drinking water should have an equilibrium composition and normally have a content of salts 300 ± 200 mg/l and chlorides 10 to 100 mg/l. Equipment made of carbon steel, galvanized carbon steel, brass and copper are used for drinking water. Carbon steel is often protected by organic coatings (paints). In the drinking water-distributing armatures, extensive iron corrosion products frequently occur under which it leads to localized corrosion.

It is essential to note that in warm waters (service, cooling), the zinc coating protects carbon steel only up to 50°C; in warmer waters carbon steel becomes...
nobler than steel and results in the formation of macrocells of the small anode (steel in the area of the coating defect) and the large cathode (zinc coating).

The combination of copper and galvanized steel or aluminum in the same circuit is also inappropriate. When copper, which is transferred in very small amounts to the solution due to corrosion, comes into contact with a galvanized steel or aluminum surface, it deposits resulting in the formation of local cathodes which cause local attack.

The aggressiveness of natural waters is very variable and depends not only on contents of substances naturally present in water, but also on the grade of pollution caused by the humans. The corrosion resistance of the same material therefore differs in different localities, and the aggressiveness of water is determined by chemical analysis.

Seawater contains on average 35 g/l of dissolved salts (mainly chlorides) and is alkaline (pH 8) and well conductive. In the coastal areas, seawater is used for industrial cooling, but the main corrosion problems occur in ships and water constructions. In seawater, carbon steel, which is protected by coatings or cathodic protection, is used again as the main construction material. As to metallic materials, titanium, nickel and its alloys exhibit a very good resistance. Stainless steels suffer from pitting and crevice corrosion and stress corrosion cracking. Corrosion problems in brackish waters (fresh water polluted with seawater) are similar to that observed in seawater.

4.2.2 Industrial electrolytes

The aggressiveness of industrial electrolytes depends on the kind of anions and cations present in the solution, and it is impossible to completely identify it by rules generally valid for different chemical substances.

Acids are characterized by a low value of pH, and therefore, evolution of hydrogen is the main cathodic reaction in the corrosion of most of technically utilized metals. If oxygen is present, its reduction also plays a role. The aggressiveness of acids largely depends on the type of anions and the presence of substances which may have oxidation effects or may attack the passive layers (Cl\(^-\) in stainless steels, F\(^-\) in titanium).

The presence of oxidizing agents is harmful for non-passivable metals under given conditions. For passivable metals, such as stainless steels, the presence of oxidizing agents is favorable, but only when their concentration is adequate. Positive influence is also reported for anions that show no oxidative effect. Their positive influence is thus based on formation of protective insoluble products.

After the dissociation of salts in solution, both cations and anions may participate in the electrochemical processes related to corrosion of metal. In case hydrolysis of salt occurs, the pH of the solution is also influenced. If the dissolution of salt results in acidic solution, its aggressiveness corresponds to the solution of acid with the relevant anion of the same pH. The case is similar with alkaline solutions, the aggressiveness of which corresponds to solutions of relevant hydroxides. The effect of individual ions may be inhibitive, stimulating or indistinctive. Both ions (cation and anion) may act negatively as well as positively, or against one another. Similar to
other environments, the basic as well as accompanying solution components with oxidation effect are of great importance.

Concentration of salt solutions has an obvious effect on their aggressiveness. Along with increase of concentration (up to a certain limit), corrosion aggressivity also increases. Sometimes it is related to increase of solution conductivity and intensification of the cells function. The corrosion rate in neutral salt solutions is mostly controlled by the rate of oxygen reduction. Corrosion of non-noble metals proceeds in alkaline environment with hydrogen evolution. For noble metals, oxygen reduction is decisive.

Occurrence of certain forms of localized corrosion (pitting, corrosion cracking) is related to the presence of certain ions. Of all anions, chlorides cause probably the most harmful corrosion problems as they accelerate the uniform corrosion and also cause development of crevice and pitting corrosion and corrosion cracking.

4.3 Soil

Most of the metallic structures (tanks, pipelines) buried in the soil are made of steel. Against the effects of soil electrolytes it is protected mainly by coatings based on tar and bitumen, or more perfectly by polymeric coatings (polyethylene, polypropylene, etc.). This protection is usually completed by cathodic polarization. The selection of optimal protection depends on the significance of the equipment, aggressiveness of soil and the type of protected metal. The type and cohesion of the soil, the homogeneity, humidity, chemical composition of soil electrolyte (including gases), pH and redox potential, buffer capacity and oscillation of ground water level are significant for aggressiveness of the soil. Corrosion attack of metallic materials in a soil would be absolutely indistinctive without the presence of humidity.

In addition to the depolarizing effect (cathodic reduction), oxygen supports decomposition of organic substances, oxidation of sulfides up to sulfuric acid. Carbon dioxide negatively affects spontaneously generated protection layers (so-called calcareous rust consisting of hydrated iron oxides and calcium carbonate). Aqueous solutions of carbon dioxide are claimed to attack ferritic–pearlitic steels along the boundaries of the grains. Metal corrosion induced by aqueous solution of carbon dioxide at pH 4.5–5 is greater than the corrosion induced by aqueous solution of HCl at equal pH. Aqueous solutions of CO2 also stimulate selective corrosion of gray cast iron – graphitic corrosion. In the deeper layers of the soil, the concentration of CO2 is considerably higher than it would obtain in the composition of air.

In most of the soils, pH ranges from 5 to 9. The dividing value is 6.5, below which aggressiveness is high; above 8.5, the soils are deemed as unaggressive. However, under mechanical stress, increased alkalinity at higher temperatures (exceeding 50°C) may commence attack along the grain boundaries. Besides, increased alkalinity may result in serious defects of amphoteric metals (aluminum, lead).

From the corrosion perspective, the presence of soluble salts is always unfavorable as they increase conductivity and thus enable function of macrocells, retain humidity and have activating effects. Cl\(^{-}\) (road salting in winter, soil in coastal
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territories), Na\(^+\), Ca\(^{2+}\) and Mg\(^{2+}\) occur in soils. Ions of Cl\(^-\) in the presence of Mg\(^{2+}\) shift pH to lower values (hydrolysis). A similar but less significant effect is also exhibited by SO\(_4\)^{2-}. The presence of S\(^2-\), HS\(^-\) is unfavorable at any time, as it considerably stimulates the corrosion effects.

To assess the aggressiveness of soil, the value of apparent resistivity is used: this is sometimes the basic criterion of aggressiveness. Resistivity is determined in corrosion analysis in natural conditions and constitutes a basis for application of cathodic protection (cathodic protection is necessary at values below 10 \(\Omega\)m). The soils are considered as unaggressive at resistivity exceeding 100 \(\Omega\)m.

Corrosion defects of buried structures occur in areas of damaged insulation, more so with insufficient cathodic protection. Soil aggressiveness is further increased by microbial activity and presence of stray currents, and alternatively by excessive polarization resulting from incorrectly installed cathodic protection and by increased temperature.

Metallic constructions in soil conditions are frequently exposed to stray currents which may lead to their quicker failure if they are not sufficiently insulated, are buried incorrectly in relation to the source of stray currents, and not protected against stray currents by means of electric or electrochemical protection.

Coating is the most widespread means of corrosion protection against soil affecting steel pipelines and other buried structures. The efficiency of this protection is mainly influenced by adhesion to metal, slight decrease of the coating resistivity even after long exposure to soil or water, low coating’s inclination to swelling and ageing, impermeability for water and gases even at higher temperatures, and resistance against mechanical stress. No coating completely meets the abovementioned requirements, but when polymers were introduced in coating techniques as a substitute of traditional bitumen insulations, resistance significantly improved. Cathodic protection which secures protection in areas of damaged insulation serves as a complementary protection.

4.4 Concrete

The required mechanical properties are usually reached with use of reinforcing bars which in most cases are made of carbon steel. Carbon steel is passive in fresh concrete as after the intrusion of water, the reserves of calcium hydroxide produce pore solution with pH of 12.5–13.5 (depending on the contents of alkali metals in cement). Such alkalinity ensures spontaneous passivation of steel and very low corrosion rates. The oxidizing power of the pore solution is given by oxygen accessibility from the atmosphere. The pore solution corrosion aggressiveness depends on the access of the carbon dioxide and chlorides to the reinforcement. When carbon dioxide from the atmosphere intrudes into moist concrete, free calcium hydroxide reacts and turns into calcium carbonate (so-called concrete carbonation), which is accompanied by decreasing pH of the pore solution.

In case the carbonation front gets to the reinforcement through the covering layer (20–30 mm), it causes activation of the steel and substantial increase in the corrosion rate. The rate of the carbonation front progress depends on quality of the cement
and concrete. The progress rate (in order of tenths of mm per year) depends not only on the density of concrete and on the presence of cracks, but also on concrete moisture. The pH decrease may be accelerated by the effect of acid rain.

In case the chlorides penetrate into concrete (even if non-carbonated) it also causes activation of the steel without necessarily being related to decrease of the pore solution pH. The critical concentration of Cl$^-\text{ in concrete is approximately 0.2 wt.%/cement.}$ The chloride penetration through concrete is in the order of mm per year.

The steel reinforcement which is exposed to the effects of the outer atmosphere prior to being installed into concrete has a surface covered with rust and its corrosion rate, when it is embedded into the concrete, achieves its bordering limits as concrete alkalinity does not entirely inhibit the rate of active dissolution under the layer of rust. Therefore, it is inappropriate to install pre-rusted reinforcement into concrete; scaling of reinforcement from production has actually no major effect on carbon steel corrosion resistance.

Where steel reinforcement is activated by the effect of carbonation or penetration of chlorides, its corrosion rate is given mainly by transport of oxygen through the concrete covering layer or cracks in the concrete.

Should the concrete be in a passive state, the corrosion rate is lower than 0.1 $\mu m$ per year and the corrosion is uniform. In active state, the corrosion rate exceeds $10 \mu m$ per year – the activation is localized. Corrosion damages are usually non-uniform due to cells with differential aeration.

From the technical point of view, the corrosion rate of 1–2 $\mu m$ per year is acceptable as it corresponds to the 100-year service life of a reinforced concrete structure.

Corrosion damages result in occurrence of voluminous corrosion products (2–3 times greater than the volume of the parent metal), which will cause cracks in concrete and, concurrently, reduction of the reinforcement cross-section (acceptable reduction shall not exceed 10%).

To extend the period before the steel reinforcement activation, it is necessary to utilize the highest-quality concrete (water-to-cement ratio <0.5, sufficient contents of quality cement, chloride-free components for concrete preparation).

The basic methods of concrete reinforcement corrosion protection are:

- Limited intrusion of moisture into the concrete (insulation, concrete surface coating).
- Limited intrusion of corrosion stimulators into the concrete (Cl$^-$, H$^+$, O$_2$).
- Reinforcement coatings (organic, zinc).
- Corrosion inhibitors.
- Alternative materials used for reinforcement (e.g. stainless steels)
- Electrochemical methods (cathodic protection, re-alkalization, chloride extraction)

Powder epoxides are the most reliable and commonly used organic coatings in the world. The price of the reinforcement is about to increase 1.5–2 times. However, organic coatings only extend the service life of a reinforced concrete structure and
do not ensure a long-term service life. Problems are caused by additional bending and connecting of the reinforcement coated with the organic coating. All defects occurring during these operations and other improper treatment must be repaired so that maximum reliability is ensured.

Hot-dip galvanized coatings have thickness of 35–100 µm (proportionally to the thickness, the corrosion resistance increases). The zinc layer eliminates the effects of carbonated concrete; however, the corrosion rate in fresh concrete is still very high. The corrosion reaction is accompanied by development of gaseous hydrogen, which negatively affects the structure, and thereby also the mechanical properties of the concrete interfacing with the reinforcement. Development of hydrogen is not effectively eliminated even by practically utilizable conversion coatings of zinc. Zinc coating doubles the price of reinforcement.

Stainless steels are entirely resistant in carbonated concrete, but concrete carbonation leads to reduction of critical chloride concentration. In the presence of chlorides, there is a danger of pitting or crevice attack. Austenitic chromium-nickel steels (FeCr18Ni10) are suitable in most of the practical cases of chloride contamination. Austenitic chromium-nickel steels containing molybdenum (FeCr17Ni12Mo2) are suitable (including cleaned welding seams) under all conditions. Duplex steels (FeCr23Ni4 and FeCr22Ni5Mo3N) are suitable not only for corrosion resistance, but also when high mechanical strength is required. A decisive factor of corrosion resistance of stainless steels is removing the scales occurring after production or welding of the bars. Chromium stainless steels (FeCr13, FeCr17) are resistant in chloride-free carbonated concrete. However, in concrete contaminated with chlorides, their resistance after removal of scales is higher than in case of scaled chromium-nickel steels. The price of the reinforcement made of stainless steel is about 5–10 times higher compared to carbon steel: the increase in the price of the structure shall not exceed 10%.

Long-term protective effect of corrosion inhibitors is questionable, particularly from the practical point of view.

The corrosion resistance of the steel reinforcement in moist concrete may be significantly affected by direct current passage during which a change of the electrolyte composition takes place that is favorable for spontaneous passivation of steel (increase of OH\(^{-}\) concentration and decrease of Cl\(^{-}\) concentration). The electrochemical methods of concrete reinforcement protection have been used for many years. In particular it concerns the cathodic corrosion protection where the protected reinforcement is permanently connected to the negative pole of a direct current source or to a sacrificial anode. Apart from this method, procedures of non-recurring cathodic polarization are also used, including electrochemical re-alkalization and electrochemical extraction of chlorides.

Cathodic protection in concrete is usually divided into two groups based on whether it is installed preventively or as an additional corrosion precaution after activation of the reinforcement. The preventive cathodic protection in a new unaggressive concrete requires very low protective currents and impedes chloride intrusion (migration acts against Cl\(^{-}\) diffusion) and even carbonation (OH\(^{-}\) occurs due
to oxygen reduction on the reinforcement). Cathodic protection in an aggressive concrete requires increased protective currents and contains both chloride extraction and re-alkalization.

A very important supporting measure against corrosion of steel reinforcement in concrete is corrosion monitoring.

5 Corrosion protection methods

There are four basic groups of corrosion measures which may decrease the corrosion deterioration of metal:

- material selection (metallic, inorganic non-metallic, polymeric),
- coatings and surface treatment,
- modification of corrosive environment (change of physical parameters, destimulation, and inhibition),
- electrochemical protection (cathodic or anodic protection), which is followed by the fifth group of corrosion measure
- corrosion prevention by design.

The selection of the means of protection, or more often of their combination, usually depends on many circumstances. Nevertheless, at any time it is essential to select construction material and design, and often also an appropriate surface treatment. Electrochemical protection and modification of environment belong to complementary or specialized corrosion procedures.

5.1 Material selection

Material selection is a very significant means of corrosion protection, the objective of which usually is to replace carbon steel that in most cases would meet the requirements of primary utilization qualities. The most distinctive material developed for corrosion protection are stainless steels. It is a group of iron-based alloys containing chromium (>12 wt.%) and a range of other elements (Ni, Mo, Ti, Cu, N). From the corrosion perspective, there are three main groups of stainless steels – chromium (martensitic and ferritic), chromium-nickel austenitic and duplex. The stainless steel most exploited (70%) is austenitic steel (FeCr18Ni10). In case stainless steels are high-alloyed (Cr, Mo), they are referred to as superaustenitic, superduplex or superferritic. The nickel alloys with chromium exhibit even higher corrosion resistance. The greatest corrosion resistance in many environments is achieved by the use of titanium and its alloys or tantalum.

The use of copper and its alloys, lead, zinc and aluminum may not be omitted in corrosion protection; however, it is not that universal, as it is related to specific conditions. For substitution of metals, use of polymers, glass and ceramics, or graphite is very significant.
5.2 Coatings

The most widespread procedure of corrosion protection is application of coating onto the basic metallic material which is not sufficiently resistant in a given environment. Carbon steels are the most coated metallic material. Ratios among various surface treatments are the following (according to the area of protected surface): 70% organic coatings, 20% metallic coatings, 10% other types (conversion and cement coatings, enamels).

The basic protection mechanism of coatings is to create a barrier between protected metal and corrosive environment. Depending on the type of coating used, protection side effects may subsequently occur, e.g. galvanic, destimulating and inhibitive.

Among materials of organic types used in corrosion protection are rubber and other polymer coatings, in addition to most frequently used coatings. Materials for production of organic coatings are mixture of polymer substances and special additives (inhibitors, pigments, fillings, etc.). Their protective function is in the nature of a barrier. By selecting appropriate additives it is possible to exploit their inhibitive or destimulating effects (Zn). Organic coatings are used most frequently for corrosion protection of metals. The efficiency of this form of corrosion protection is related not only to the paint quality, but also to the quality of prior surface treatment and the way of its application. Painting systems have a limited service life; therefore, they must be renovated, and they thus constitute the greatest part of total costs incurred by corrosion protection.

The protective effect of metallic coatings depends on the nature of formed composite, that is, on the mutual corrosion resistance of a coating and the basis in a certain corrosive environment. Various protective mechanisms are applied on imperfect coatings. Coatings produced without defects exhibit a basic effect that is in the nature of a barrier. The existence of defects in metallic coatings and the exposure of such area in corrosive environment allows both the materials to perform different electrochemical behavior. If the coated metal is of a more positive free corrosion potential than the coating, it leads to corrosion of the coating and protection of the basic metal (the coating serves as a sacrificial anode). If the corrosion products of the coating metal are insoluble, they continuously fill in the defect of the coating. The presence of pores in this type of coatings is (to a certain extent) not decisive. In case the coated metal is less noble than the coating, its protective function is merely in the nature of a barrier. In case of the failure of coating compactness, cells are formed in which the exposed basic metal forms a small anode (i.e. by corroding area), and the surface of coating metal forms a large cathode. Corrosion of the coating metal often results in undercorrosion of the coating. It is very difficult to achieve zero-defect coatings; therefore, coatings with several layers of coating metals are used.

In a chemical treatment the metal reacts with the treatment agent so that a coating not easily soluble is formed on the metal surface. Examples of chemical conversion treatment are phosphating, chromating and anodizing.
Coatings of a cement nature constitute a specific group of inorganic coatings. They are mostly used for protection of steel surfaces; the most remarkable advantage of their use is the possibility of application directly onto untreated (corroded) surface. The protective effect is in the nature of a barrier as well as destimulating. Enamels belong among significant anticorrosion coatings.

5.3 Modification of corrosive environment

Corrosion processes may be reduced by modification of corrosive environment. The objective of this procedure is to change the concentration of the component causing the attack, or to remove it from the environment—destimulation (removal of oxygen, chloride ions, air humidity, etc.), modification of physical parameters (temperature, flow rate), or inhibition of corrosion reactions (i.e. addition of corrosion inhibitors).

Destimulation is usable in cases when the aggressive component of the environment is not necessary for the production technology, and its elimination does not require excessively high expenses. Destimulation thus is mostly used in cases when the corrosive substance is present in a relatively low amount. The most common case of destimulation is removal of oxygen from an environment in which the corrosion process is regulated by the rate of oxygen reduction. The decrease of oxygen content of water that is used in power plants may be achieved by either physical methods (vacuum, boiling, bubbling with inert gas) or chemical processes (reaction with hydrazine or sulfite). The water treatment is also possible using an ionex or electrochemically. The alkalization of acidic waters or removal of chlorides from water by demineralization on ionex is also considered as destimulation. The chlorides are removed mainly in cases when they might cause pitting and crevice corrosion or corrosion cracking of stainless steels.

The presence of aqueous electrolyte is a basic presumption of a course of the corrosion process; elimination of humidity, e.g. from organic products of solid salts, or from the atmosphere in closed rooms, leads to significant reduction of corrosion. Removal of solid particles from aqueous electrolytes and air constrains attacks related to formation of deposits (crevice corrosion in solutions and the atmosphere) and to erosion-corrosion effects of the environment.

In some cases, corrosion may be limited by small changes of concentration of the substance which causes the corrosion attack. It may be influenced also by a change of ratio of concentrations of substances with inhibitive and stimulating effect. This is mostly the case when conditions for spontaneous passivation of metal or stability of a passive layer are secured by this modification.

Particularly, changes of temperature and the environment flow rate belong to the group of physical parameters modification. Lowering of corrosion aggressiveness may be achieved by decrease of temperature. In some cases, corrosion is conversely suppressed by increasing the temperature which, for instance, leads to decrease of oxygen solubility and the steel corrosion rate in water. Increase of temperature may have a positive effect in reducing atmospheric corrosion in closed rooms, as the relative humidity may drop below the critical level.
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Corrosion attack may also be influenced by adding of substances (corrosion inhibitors) into the corrosive environment, which causes its considerable decrease in low concentrations. The effective concentration of these substances usually ranges from 0.1 to 10 g/l. In industrial conditions, the inhibitors are determined mainly for acid pickling of metals (e.g. thiourea, urotropine), recirculating cooling water systems in industrial plants (e.g. polyphosphates, silicates, phosphoric acid) and protection of equipment used for oil production and refining (e.g. imidazole, amines, thioglycolic acids). A range of inhibitors is determined also for protection of machinery products against atmospheric corrosion.

The volatile corrosion inhibitors, i.e. substances with inhibitive effect and high tension of vapors (amines, organic nitrates) by which the air is treated or packing materials are impregnated, also protect against atmospheric corrosion. The inhibitors soluble in lubrication oils (an inhibitor may be contained in oil emulsions for machining) are determined for protection of machinery products as well. Even organic coatings determined for temporary protection frequently contain substances with inhibitive effect.

5.4 Design

The design of an object, which is exposed to a corrosive environment, should take into consideration the requirements of its effective corrosion protection. It is thus often needed to modify its design, i.e. change its dimensions or shape, or use specific production procedures during mechanical operations. Design changes may affect the corrosion resistance of equipment so that they may cause changes in the properties of the material, influence the quality or effect of corrosion protection and have an indirect effect on the aggressiveness of the environment and on time during which the surface is in contact with the electrolyte.

Machinery operations, such as welding, soldering, mechanical working and machining may significantly decrease resistance against corrosion even of the construction material that might in itself be sufficiently corrosion-resistant. When welding, a change in the structure of the basic metal that causes a disposition to the localized corrosion may occur. Corrosion problems ensuing from the quality of weld seams may be resolved by selection of convenient combination of basic and filler alloys, welding technology, and design of the weld seam. Soldering, similar to welding, may cause changes in structure, formation of cells and crevices.

While producing equipment with weld seams, cold working or working on the machined surfaces, internal strains occur which may cause environmentally induced cracking. Machining also affects the roughness of the surface, and since the corrosion resistance of smooth surfaces is mostly higher, it is appropriate to use technologies that produce surfaces of the lowest roughness.

Overall corrosion also depends on the area of the exposed surface; therefore it is necessary to design equipment with the smallest possible area of exposure (one big vessel is better than more small vessels). Increase of a metal material thickness, the so-called corrosion allowances that, under given uniform corrosion and with correct presumption of its rate, ensure a sufficient cross-section of the material during the
estimated service life of an object, may be deemed as a constructional measure as well. The design must also allow to change the parts attacked more quickly by corrosion.

Coatings generally require the protected surface to be as simple as possible and to be of such shape and dimensions as allow application of a uniform layer all over the surface. Seams that are to be coated are preferred to be welded or soldered. It is important that such design is selected so that it does not lead to unnecessary mechanical damages of the coating during the operation. Certain kinds of coatings (e.g., enamels) require a minimum thickness of the basic material. Design must ensure maintenance of those coatings, the service life of which is shorter than the service life of the equipment. Mainly paints are concerned here. The whole exposed surface is to be sufficiently accessible both for preparation and re-application of the coating.

Reduction of the time during which the surface is exposed to corrosive environment is based on use of devices that do not retain the corrosive environment, or enable a complete emptying. In the outdoor atmosphere, it is vital to use simple structures in which the profiles and their connections are so arranged that rainwater is not retained.

Inhomogeneities on the exposed surface may stem from connections of two differently noble metals – for example, during welding and when the basic metals of different compositions are connected, a macrocell occurs. Similarly, inhomogeneities can occur when the galvanized connecting material is combined with the non-galvanized one, or when two adjacent parts of the equipment are of different metals.

Should a coating be used for elimination of a macrocell, it is to be used on the cathodic material, in particular, since the damaged areas act as small anodes with concentrated corrosion attack when the coating is damaged – which unavoidably happens from time to time. From this perspective, it is more appropriate to apply the coating only on more resistant materials.

Another factor affecting corrosion resistance is the flow character; its size and uniformity are often determined by the object design. Problems appear, for instance, in the area of pipe bends. Areas where the flow rate exceeds acceptable limits for a given material, and where sudden changes of flow occur should be avoided.

5.5 Electrochemical protection

Electrochemical corrosion protection is based on the effects of direct current passing through a protected metallic surface which lead to decrease of corrosion rate. Passage of current results in occurrence of a change of metal electrode potential as well as a change of composition of corrosive environment adjacent to the protected surface. If the changes in the environment composition are insignificant, then it is, in case of cathodic protection (the protected object is a cathode), a reduction of anodic dissolution of metal in activity, and in case of anodic protection (the protected object is an anode), a current-induced passivation. In case of cathodic protection it leads, under conditions of limited convection, to alkalization of the
environment at the protected surface and creation of conditions for the stability of passive state (mainly of steel which is the most cathodically protected metal), even under conditions of cathodic polarization. The stability of passive state is also ensured by depletion of chloride ions by migration off the cathodically protected surface. The cathodic protection in the area of stable passivity is also used for elimination of great oxidation ability of the environment which in case of stainless steels leads to pitting corrosion. Cathodic polarization may be used for elimination of aggressiveness of porous materials, such as carbonated or chloride-contaminated concrete (re-alkalization, extraction of chlorides). The effects of direct current on corrosion resistance of metals may also be negative. It may be observed in the case of improperly operated electrochemical protection and in case of the so-called stray currents, which lead to undesirable polarization of the surface that is in contact with the electrolytically conductive environment.

5.5.1 Cathodic protection
Cathodic protection is mostly a complementary means of surface protection of steel covered with coating. Under certain conditions, such as in seawater, cathodic protection may be used also on uncoated metallic surfaces.

Cathodic polarization of protected metallic surface may be generated by two means: connection of the metal (sacrificial anode) with more negative free corrosion potential in a given environment than the required protection potential (in this case the effect of galvanic cell is used) or connection of the protected metal with the negative pole of direct current supply.

Carbon steel is the most frequently cathodically protected metal in aqueous environment (soil electrolyte, industrial and natural waters). Under these conditions, magnesium, zinc and aluminum may be used for protection. The criterion for use is that the free corrosion rate of the anode is lower so that it is not passivated (therefore aluminum is used mainly in seawater). Localized effect and possibility of usage without any electrical sources are advantages of a sacrificial anode. Replacing the sacrificial anode is disadvantageous. Sacrificial anodes are exploited for protection of ship hulls, boilers for water heating, steel structures exposed to seawater and locally, also of buried structures.

Breaking of greater ohmic resistance and protection of large objects with a small amount of anodes are enabled by cathodic protection using an external source of direct current. However, in this case it is necessary that the operation of protection does not lead to degradation of the anode by corrosion. Therefore, usually those materials are exploited that have electron conductivity and are anodic dissolution-resistant – the main anodic reaction is evolution of oxygen or chlorine (in chloride environment). Silicon cast iron, graphite, magnetite, titanium with platinum or iron oxides coating are suitable anode materials.

For cathodic protection by external source of current it is important to control so that polarization of the surface to the area, where hydrogen is liberated by decomposition of water and the environment is intensively alkalinized, does not take place. It may negatively affect further damages of protective coating of the
protected structure (disbonding), as well as steel properties with the entering of atomic hydrogen.

5.5.2 Anodic protection
Anodic protection is based on intentional passivation of metal by current passage or change of a metal potential within the scope of passivity by current passage when a protected object is an anode. Anodic protection constitutes a primary corrosion measure taken in strongly aggressive industrial solutions, e.g. sulfuric acid.

5.5.3 Protection against stray currents
If direct current passes through an electrolytically conductive environment, it results in drop of potential in the metallic structure that is in contact with the environment which affects the corrosion potential. It leads to formation of anodic and cathodic areas. The corrosion rate increases mainly in anodic areas where a wall may be perforated. Stray currents most frequently affect structures placed in soil, water or in industrial electrolytes. Stray currents in soil may be caused by direct current transportation systems (railways, trams, underground), stations of cathodic protection (interference), electrochemical technologies (galvanizing plants, plants producing sodium hydroxide and chlorine), telluric currents (currents in earth crust generated by the effect of induction from magnetic resonance between ionosphere and the earth) and ore body (currents caused by activities of macrocells on ore body).

Stray currents in line-buried structures (pipelines, cables), stray currents may be limited by several means: measures taken against the source of stray currents (decrease of resistance for back current in direct transportation systems), insulating a metal subject from soil and installation of complementary anodes for the systems of cathodic protection. The limitation may also be achieved by suitable selection of the line equipment route, improvement of line equipment insulation, use of insulation flanges and by drainages, electric connection of the stray current source and the threatened structure. Controlled rectifiers for cathodic protection may also be exploited.

5.6 Corrosion testing and monitoring
Although we are coming to know more and more about the patterns regulating the corrosion processes and are able, to a certain extent, to anticipate behavior of materials in the environment, it is still essential to experimentally obtain most of information on corrosion resistance.

The reason is the complexity of the corrosion process and the possibility of this process to be affected by a range of random factors. Under laboratory or operational conditions, experimental works for obtaining information on corrosion may be summarized in terms of corrosion tests. Some kind of a corrosion test is always related to the purposes of its execution, the type of corrosion system (material/product/environment) and the form of corrosion which causes possible or factual deterioration. A range of laboratory and industrial corrosion tests procedures are standardized.
The principles of corrosion tests are based on evaluation of visual, dimensional and mass changes; metallographic evaluation, evaluation of changes in mechanical properties, evaluation of changes in the corrosive environment composition and analysis of corrosion products are exploited. A significant part of it are electrochemical methods that are based mainly on dependence between corrosion potential and the current passing through the metallic surface and their time dependence. In corrosion tests, other physical methods are also exploited, such as resistance, inductive, acoustic, radiation, magnetic, thermographic procedures, etc.

Corrosion monitoring is important to determine operational reliability of equipment. It is based on technologies that help to obtain relatively fast and continuous, if possible, information on corrosion. A brisk response on acceleration of corrosion is needed to be able to intervene immediately. Corrosion monitoring concerns not only industrial equipment but also reinforced concrete structures, and is also used for tracking atmosphere aggressiveness.

6 Economic impacts

In industrial countries, direct corrosion costs reach approximately 3–5% of the gross national product. The latest evaluation of direct corrosion costs in the USA annually makes for US$ 276 billion. This immense loss, which is 50 times higher than direct annual losses caused by fires, is attributed mainly to the fact that corrosion is not completely avoidable, but also to the fact that the existing technical potentialities of corrosion protection are insufficiently exploited. The types of corrosion costs vary from direct losses on material to hardly assessable environmental and emergency impacts.

It is believed that at least one-fourth to one-third (in some fields up to 70%) of losses caused by corrosion may be avoided. Indirect costs due to metallic corrosion may be substantially higher than direct losses and may have considerable health and environmental impacts (e.g. damages of buried equipment, damages in nuclear power stations or chemical plants).

Literature for further reading


