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INTRODUCTION IN CORROSION OF METALS AND CORROSION CONTROL

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INTRODUCTION IN CORROSION OF METALS AND CORROSION CONTROL

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The book presents basic knowledge on thermodynamics and kinetics of corrosion of metals. Development of corrosion in different environment compartments (atmosphere, soil, water) and concrete, as well as bio-corrosion are revealed - with respect of mechanism, controlling factors, and peculiarities. Most important forms of corrosion are described. Essential knowledge on corrosion control by metallic and non-metallic inorganic coatings, organic coatings, including principles of surface preparation and coating technology, are presented. Knowledge on cathodic protection and use of inhibitors is given. A basic knowledge and understanding of the main methods for corrosion detection, assessment and monitoring are introduced.

The book aimes at ensuring broader background for students and engineers working in the non-energy (metallic and non-metallic) and energy raw materials supply chain - from prospecting through mining to beneficiation and processing. It may be useful reading also for construction engineers.

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1. PREAMBLE

1.1. Definition of corrosion and its economic consequences

Corrosion is a material destruction due to its reaction with its environment.

In simple terms, corrosion processes may be considered as reactions of metals with species in the environment to form chemical compounds.

The international standard definition of corrosion is as follows: "Physicochemical interaction between a metal and its environment which results in changes in the properties of the metal and which may often lead to impairment of the function of the metal, the environment, or the technical system of which these form a part". (ISO 8044:2020 - Corrosion of metals and alloys - Vocabulary). The term "corrosion" *applies to the process, not to the result*, which is "corrosion damage", deterioration or effect. Implicit in the concept of corrosion as a process is the rate of corrosion reaction; implicit in the damage caused is the extent and nature of the damage in relation to the function of the systems concerned.

A broader, but widely accepted alternative definition, from the International Union of Pure and Applied Chemistry (IUPAC) encompasses the degradation of non-metals as well as metallic materials, as follows: "Corrosion is an irreversible interfacial reaction of a material (metal, ceramic, polymer) with its environment which results in consumption of the material or in dissolution into the material of a component of the environment. Often, but not necessarily, corrosion results in effects detrimental to the usage of the material considered. Exclusively physical or mechanical processes such as melting or evaporation, abrasion or mechanical fracture *are not* included in the term corrosion."

Various estimates have been made of the annual economic loss resulting from corrosion. There is no general agreement as to just what should be included in calculating this loss, for example, should we include the coating on tin cans which would not be needed if the contents were not corrosive to steel. It is, therefore, fruitless to argue about the figure that should be used. However, there is evidence that annual losses attributable to corrosion in North America amount to several billions of dollars and, depending on what is included in the estimate, could well surpass the $10 billion.

1.2. Corrosion indicators

The values by which the degree of corrosion destruction is judged are called corrosion indicators. They are divided into qualitative (observation of the appearance of the metal, of the corrosion environment, use of color indicators to detect corrosion products) and quantitative. Quantitative indicators are:

1) The change Δm of the weight of the sample per unit of time τ, referred to a unit of surface S, i.e.

$v_{cor} = \Delta\ m / (S\ .\ \tau)$, g/(m^{2}h) (1);

2) The depth of penetration of corrosion damage in the metal, taken per unit of time (year). It is called the corrosion permeability P and for uniform corrosion

$P = 8.76.\ 103\ v_{cor} / \rho$, mm/y (2),

where ρ is the specific density of the metal, kg/m^3. Corrosion permeability can be used to evaluate the corrosion resistance of metals according to a corresponding scale given in standardized tables. Indicators 1) and 2) are called corrosion rate.

3) The current density corresponding to the electrochemical corrosion i_{cor}, A/cm^2. The following relationship exists between v_{cor} [g/(m^{2}h)] and i_{cor} [A/cm^2]:

$v_{cor} = A\ .\ i_{cor}\ 0.373 / n$ (3),

where A - the atomic mass of the metal, n - its valence. Current, mass and depth indicators are used to characterize general and relatively uniform corrosion.

4) The volume of absorbed or released gas, per unit of metal surface and unit of time, cm^3/(cm^2.h);

5) Time for appearance of first corrosion damage, min.

6) Number of corrosion spots that occupied by corrosion damage, %

8) Indirect indicators:

a) change in mechanical properties;

b) change of electrical properties;
c) change in the reflectivity of the metal surface.

In uniform corrosion, the choice of indicator is practically irrelevant, but in local corrosion, it is extremely important to select an appropriate indicator for research.

The transition from one to another way of expressing the corrosion rate can be done using the Table. 1.

Table 1. Metal or steel corrosion rate conversion factors

	mA/cm^2	**mm / y**	**mpy**	**g / (m^2 day)**
mA / cm^2	1	3.28 M/nd	129 M/nd	8.95 M/n
mm / y	0.306 nd/M	1	39.4	2.74 d
mpy	0.00777 nd/M	0.0254	1	0.0694 d
g / (m^2 day)	0.112 n/M	0.365 /d	14.4 /d	1

where: mpy = milli-inch per year; n = number of electrons (e^-) involved in the corrosion reaction; M = atomic mass of the metal; d = density of the metal.

The table is read from left to right, i.e.

$$1\ mA/cm^2 = (3.28\ M/nd)\ mm/y = (129\ M/nd)\ mpy = (8.95\ M/n)\ g / (m^2\ day)$$

1.3. Classification of corrosion processes

According to the possibility of identifying the destruction, corrosion can be divided into three groups:

Group 1 – corrosion that is easily identified visually: general corrosion; pitting corrosion; crevice corrosion (classical, filiform, compacted rust); galvanic corrosion; lamellar corrosion.

Group 2 – corrosion that requires identification aids: erosion corrosion; cavitation; fretting corrosion; intergranular corrosion, exfoliation; selective (de-alloying) corrosion.

Group 3 – corrosion identified by microscopic examination: environmental cracking (corrosion cracking, corrosion fatigue, hydrogen embrittlement).

The classification of corrosion processes (of metals and alloys) can be carried out according to three main characteristics: a) according to the mechanism of occurrence - chemical and electrochemical; b) according to the nature of destruction - general and different forms of local corrosion; c) according to the medium in which they occur.

The operating conditions and the type of facility determine which of the types of corrosion is most dangerous for it. For example, for electrical contacts, general corrosion is the most dangerous, for load-bearing elements of structures - corrosion cracking, etc. In principle, local forms of corrosion are more dangerous for equipment and structures compared to general corrosion, regardless that the mass of corroded metal is less.

Depending on the environment in which it occurs, the following types of corrosion are distinguished: a) gaseous - corrosion in gas environments in the complete absence of moisture on the surface of the metal; b) in non-electrolytes - corrosion in liquid non-conducting organic media; c) atmospheric - corrosion in the atmosphere, d) soil - corrosion in the soil, e) in electrolytes - corrosion in liquid conductive media, f) electro-corrosion (including stray current corrosion) - corrosion in electrolytic media under the influence of an externally applied current, g) contact - corrosion caused by the contact of dissimilar metals, h) under tension - corrosion under the simultaneous influence of a corrosive environment and mechanical stresses, i) in crevices - corrosion as a result of the action of an electrolyte trapped in narrow crevices, j) corrosion erosion - corrosion destruction due to simultaneous frictional impact of the corrosion medium itself or other solid bodies, k) corrosion cavitation - corrosion with simultaneous shock impact of the corrosion medium, l) biocorrosion - corrosion with the participation of products released by microorganisms or by using part of the corrosion products in the living cycle of microorganisms. Except for the first two (which occur by a chemical mechanism), all other types of corrosion occur by an electrochemical mechanism.

2. CHEMICAL AND ELECTROCHEMICAL CORROSION MECHANISM

2.1. Corrosion proceeding by a chemical mechanism

2.1.1. General features

In chemical corrosion, destruction is the result of a heterogeneous chemical reaction taking place on the surface of the metal in contact with a liquid or gas medium. Its characteristic features are: a) The oxidation of the metal and the reduction of the oxidizing component are carried out in one act; b) The further development of the corrosion process is determined by the structure, chemical and mechanical properties of the resulting coating, due to the fact that the corrosion products, in general, remain on the surface of the metal.

Corrosion attack can be caused by both oxidizing and reducing conditions. Environments that can cause corrosion at high temperature are corrosive gas environments, ashes, molten salts and metals. Corrosive gas environments are: a) air, oxygen - however, in most industrial environments, corrosion is not due to oxidation only by the oxygen of the air, but also to the action of gases - pollutants; b) water vapor – oxidizes Fe and affects the content of C in the steel; c) CO_2, CO, CH_4 - affect the content of C in the steel and from there - its mechanical properties; d) S-containing gases; e) H_2 – upon contact with steel causes its decarburization by the reaction $C(Fe) + 2H_2 = CH_4$; f) N_2 – only the active N_2 obtained by the decomposition of NH_3 at a temperature below 540 ^oC has a corrosive effect; g) waste gases from the combustion of organic fuels - contain CO_2, CO, water vapor and N_2, and in case of incomplete combustion - CO, O_2 and hydrocarbons. Most fuels contain S, so combustion releases highly corrosive SO_2 and even H_2S; h) Cl_2 and HCl – dry gases do not cause corrosion, but the situation changes dramatically in the presence of moisture and rapid local corrosion is developed.

The most common chemical corrosion process is the oxidation of the metal by O_2 from the air. The ongoing process can be presented in the following manner:

$$mMe(solid) + (mn/4)O_2(gas) = Me_mO_{mn/2}(solid) \qquad (4).$$

There are several methods for measuring the degree of high-temperature corrosion - optical, electronographic, X-ray structural, etc. The most popular is the determination of the change in mass of the specimen per unit time per unit area, but this is not directly related to the thickness of the corroded metal (i.e. the depth of corrosion penetration), which must be known in assessing the strength of the components of a given facility. It is best to work with the thickness of the layer obtained as a result of corrosion destruction, which is determined metallographically.

2.1.2. Thermodynamics of corrosion proceeding by a chemical mechanism

Chemical corrosion of metals is due to their thermodynamic instability under the given environmental conditions. If the equation of the reaction isotherm for reaction (4) is written, it can be found that the process is arbitrary (the change in the Gibbs free energy[1] $\Delta G < 0$) when the partial pressure of O_2 in the gas medium

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[1] Gibbs free energy is a measure of a system's ability to do work. It is defined by the expression:
$G=H–T.S$, where G is the energy received or released during a reversible process at constant pressure and constant temperature T (expressed in degrees Kelvin), H is the enthalpy, and S is the entropy of the system. The change in G (i.e. ΔG) is an indication of the conditions under which a given chemical reaction will occur. At $\Delta G > 0$, a reaction will only occur if energy is introduced into the system to move the system from the equilibrium state (where $\Delta G = 0$). At $\Delta G < 0$, the reaction proceeds spontaneously until equilibrium is reached. Enthalpy (H) is a thermodynamic function describing the system and is defined by the expression: $H=U+p.V$, where U is the internal energy of the system, p is the pressure, and V is its volume. When the reaction takes place in atmospheric conditions, the pressure remains practically constant and the enthalpy of reaction is equal to $\Delta H=\Delta U+p.\ \Delta V$. In exothermic reactions $\Delta H < 0$. Entropy (S) can be considered as a measure of the lack of energy in a system to do work. In closed systems (systems that do not exchange matter with their surroundings), an increase in S is accompanied by a decrease in the available energy in the system. When the system undergoes a reversible change, S changes by the amount of energy (q) transferred to the system by heat divided by the thermodynamic temperature T, i.e. $\Delta S = \Delta q/T$. All naturally occurring processes are irreversible, and in an adiabatically isolated system (a system that does not exchange energy with its surroundings), irreversible processes are always accompanied by an increase in S. The internal energy (U) of the system roughly could be considered as the sum of the kinetic energies of its constituents particles and the potential energies associated with the interaction between these particles. It does not include the kinetic and potential energy of the system as a whole, nor the nuclear energy of its constituent particles. It is impossible

$P_{(O2)}$ is greater than the dissociation pressure of the metal oxide $(P_{O2})_p$ (this is the equilibrium pressure of O_2 in the Me-MeO system) under the relevant conditions, i.e. $P_{(O2)} > (P_{O2})_p$.

Usually, the stability of materials at high temperature is evaluated using Ellingham diagrams, which represent the dependence of the standard free energy of the metal oxide formation reaction (ΔG^o) as a function of temperature. The lower a given line is on the diagram, the more stable the given oxide is at the corresponding temperature. At temperatures for which $\Delta G^o > 0$, spontaneous decomposition of the metal oxide to metal and oxygen takes place.

2.1.3. Kinetics of corrosion proceeding by a chemical mechanism

2.1.3.1. Mechanism of oxide coating growth

At first, with pure metal surface, a chemical reaction takes place between the metal and oxygen - a certain oxide coating is formed.

The oxygen adsorbed on the coating takes electrons from the metal and turns into O^{2-} ions that diffuse through the oxide coating to the metal surface against metal ions that diffuse from the metal surface to the "metal oxide/gas phase" phase boundary. The ratio of the velocities at which the two types of ions diffuse determines the area in which the metal coating grows. Generally, at high temperatures, metal ions are more mobile. As a result, the growth of the oxide coating is mainly observed in its outer part - near the "oxide/gas phase" boundary. The oxide cover formed on the metal surface can make the further corrosion process more difficult.

In order for an oxide coating to have protective properties, it is necessary:

1) To be continuous and dense i.e., to cover the entire surface of the metal, which is fulfilled when the specific volume of the formed oxide V_{ox} is greater than the specific volume of the metal V_{Me}, i.e., $V_{ox}/V_{Me} > 1$ (Pilling-Bedworth ratio). The dependence is preserved up to $V_{ox}/V_{Me} \cong 2$ (except for Ag, Cd, Ti). It is believed that at $V_{ox}/V_{Me} > 2$, significant stresses appear in the oxides, which lead to their cracking. This ratio can also be used for alloys.

2) To have good adhesion to the metal and to have sufficiently good mechanical properties (strength, elasticity);

3) To be physically and chemically resistant under the relevant conditions of the corrosive environment;

4) To have a low ionic conductivity, i.e., to make it difficult for the reactants (Me^{n+} and oxidizer) to access each other.

2.1.3.2. Growth laws of the oxide coating

The rate of high-temperature corrosion (i.e., the rate of growth of the oxide coating) depends on the protective properties of the resulting oxide coating.

When a porous, poorly adhered or cracked oxide coating is formed (usually at $V_ox/V_{Me} < 1$), the oxidizing agent penetrates unhindered to the metal phase and reacts with it. In this case, the rate of corrosion depends on the rate of the chemical reaction and does not depend on the thickness of the oxide layer.

$Y = k_C.C_o.\tau$ (5),

where Y - thickness of the oxide coating, k_C - rate constant of the chemical reaction - depends on the temperature, C_o - the concentration of oxygen on the outside of the oxide coating, τ - time. Oxide coatings on alkali and alkaline earth metals grow linearly. Some of the metals, whose oxidation kinetics obey a linear law, at a certain temperature show a tendency to the so-called "catastrophic oxidation" - very rapid oxidation. The phenomenon is associated with the formation of low-melting oxidation products that sublimate. Metals that are prone to this type of oxidation are Mo, W, Os, Re, V and Mg (where even self-ignition is reached).

At $V_{ox}/V_{Me} > 1$ (i.e., with non-porous and continuous oxide coatings on the metal surface, which have protective properties), the access of the oxidizer to the metal surface becomes difficult and corrosion is slowed down. Access of the oxidizer to the metal surface is achieved by diffusion through the oxide coating, which

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to measure the absolute value of U, its change is measured, i.e. ΔU. For a closed system, ΔU is equal to the heat introduced (from its surroundings) into the system, minus the work done by the system W, i.e. $\Delta U = q - W$. The Van't Hoffs reaction isotherm presents the relation between the Gibbs free energy and equilibrium constant, see also eq. (32).

obeys Fick's first law. If the diffusion is slower than the actual chemical reaction taking place on the metal surface, it can be shown that the oxide coating grows according to a parabolic law:

$Y^2 = D_o.C_o.\ \tau$ (6),

where Y– thickness of the oxide coating, D_o – diffusion coefficient of oxygen in the oxide layer – depends on temperature, C_o – oxygen concentration on the outside of the oxide coating, τ – time. According to this law, oxide coatings on iron, carbon steels (over 700 ^oC), copper, nickel (over 500 ^oC) grow.
When the rates of diffusion of the oxidant through the oxide layer to the metal surface and of the chemical reaction are commensurate, the oxide coating increases as follows:

$K_1Y^2 + K_2Y = K_1K_2\tau$, (7),

where $K_1 = k_C.C_o$, $K_2 = D_o.C_o$, τ - the time. According to this law, oxide coatings on iron and steels grow during oxidation at high temperatures and environments containing water vapor and carbon dioxide.
It is possible that the corrosion rate decreases with increasing thickness of the coating on the metal surface more strongly, compared to the case described by the parabolic law. Then the oxidation is described by the dependence:

$Y = \ln(K_3.\ \tau + b)$ (8),

where K_3 and b – empirical constants, τ - time. According to this law, oxide coatings on copper, aluminum, zinc grow at not very high temperatures (100-250 ^oC).
Laws (5-8) are based on relatively simple models of oxidation. The partial destruction of the oxide coatings, due to the internal stresses that have arisen in them or as a result of external mechanical effects, leads to changes in the laws of their growth. Changes in the laws of oxidation are also observed in alloys that are oxidized by a more complex mechanism. Small changes in their composition can lead to significant changes in corrosion rates. Therefore, for practical purposes it is better to have in mind the accumulated empirical data on the corrosion of the material in question under similar conditions than to rely only on calculations obtained using models of the type described above.

2.1.4. Influencing factors

The factors that influence the rate of chemical corrosion are:
a) The type of metal - especially the qualities of the coating formed on its surface (V_{ox}/V_{Me}, porosity, adhesion to the metal surface);
b) The surface of the metals – the larger the surface, the better the metal-gas contact and the easier the corrosion;
c) The purity of metals - usually the presence of various impurities in technical metals accelerates their corrosion;
d) Temperature - the relationship between corrosion rate and temperature is approximately the same as that derived by Arrhenius for the rate of chemical reactions:

$v = \text{const.} \exp[-E_a / (R.T)]$, (9),

where v – corrosion rate, const - value that includes the pre-exponential factor (parameter characterizing the probability of the reaction) and the speciffic reaction conditions, E_a – activation energy, R – the universal gas constant, T – the temperature in K. The dependence is not followed in the oxidation of Zn and in the interaction of Cu and Ag with the halogen elements.
e) The pressure (concentration) of oxidizing gas in the oxidizing gas phase: for example, at a constant temperature, the rate of oxidation increases with an increase in the concentration of oxygen in the gas phase, until reaching a partial pressure of O_2 corresponding to the maximum saturation of the oxide coating with O_2, after whereby the rate of oxidation becomes almost independent of the pressure (concentration) of oxygen in the oxidizing gas phase.

2.2. Corrosion proceeding by an electrochemical mechanism

2.2.1. Fundamentals of electrochemistry related to corrosion

2.2.1.1. Electrolyte solutions

Substances whose solutions and melts conduct electricity are called *electrolytes*, their solutions are called solutions of electrolytes or (for short) just electrolytes. Their representatives are acids, bases, salts, their solutions in water (or in other solvents) and their melts. Current carriers (positive and negative ions) move under the action of the external electric field. Their temperature coefficient of conductivity is positive.
The breakdown of electrolytes into ions is called *electrolytic dissociation*. Electrolyte molecules dissociate into ions spontaneously when the electrolyte is dissolved in a suitable solvent. A quantitative estimate of the tendency of an electrolyte to dissociate is the degree of electrolyte dissociation α, which is represented by the relation:

α = number of dissociated molecules / total number of molecules = C_{diss}/C_{total} (10),

where: C_{diss}, C_{total} - the concentration of the dissociated molecules and total (initial) concentration of the electrolyte. α is a dimensionless quantity varying within the limits $0 < \alpha < 1$. Depending on the size of α, electrolytes are divided into strong (for them $\alpha \approx 1$) and weak (for them $\alpha << 1$). Examples of strong electrolytes are: HCl, H_2SO_4, HNO_3, NaOH, NaCl, KCl, KOH, and for weak ones - CH_3COOH, NH_4OH. Experience has shown that the degree of electrolyte dissociation is not a constant value, but depends on the concentration of the solution. As the concentration decreases, α grows and at infinite dilution (for strong electrolytes) it reaches 1.
Electrolyte dissociation is a reversible process, i.e. an equilibrium can be established between dissociated and undissociated molecules. For a binary electrolyte CA (C- cathion, A - anion) the equilibrium can be written:

$CA = C^+ + A^-$ (11).

The equilibrium constant characterizing the dissociation is called the dissociation constant K_D and is represented by the expression:

$K_D = [C^+]. [A^-] / C_{CA}$ (12),

where $[C^+]$, $[A^-]$ and [CA] are respectively the concentrations of the obtained cations, anions and undissociated molecules. At constant temperature, K_D depends on the nature of the electrolyte and the solvent and does not depend on its concentration. Since dissociation is always an endothermic process, an increase in temperature leads to an increase in the value of the dissociation constant. Stronger electrolytes have a higher K_D value.
According to the classic theory of Arrhenius, acids are substances that dissociate in aqueous solutions giving only one type of cations - hydrogen ions, and bases - substances that dissociate giving only one type of anions - hydroxyl ions. This simple and clear definition is sufficient only when considering dissociation in aqueous solutions. It does not consider the role of the solvent. Taking into account the interactions in the solutions, acids can be defined as substances that, upon interaction with water, give only one type of cations – H_3O^+. Even in its expanded form, Arrhenius' definition of acids and bases can only be used for aqueous solutions.
Water is a weak electrolyte and dissociates to a small extent according to the equation:

$2H_2O = H_3O^+ + OH^-$ (13).

The dissociation constant characterizing the dissociation of water has the form:

$K_D = [H_3O^+] . [OH^-] / [H_2O]^2$ (14).

Considering that the dissociation is very weak, one can assume $[H_2O] = [H_2O]^2 \cong 1$ = const. Then

$K_D = [H_3O^+] . [OH^-] = K_W$ (15).

is called the ion product of water. For pure water under standard conditions (25 °C, 101.3 kPa) $Kw = 1.10^{-14}$ was found. Therefore, for a neutral aqueous solution[2] $[H_3O^+] = [H^+] = [OH^-] = 10^{-7}$, mol/dm^3 .

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[2] Often, for greater convenience, we work with $[H^+]$ instead of with $[H_3O^+]$

If H^+ predominates (i.e. $[H^+] > 10^{-7}$) the water medium is acidic. If there are more OH^- (i.e. $[OH^-] > 10^{-7}$, respectively $[H^+] < 10^{-7}$) the medium is alkaline. To eliminate the inconvenience of working with so small numerical values, Sørensen introduces the parameter pH:

$pH = - lg [H^+]$ (16).

Analogous to pH for hydroxyl ions, the value pOH is introduced:

$pOH = - lg [OH^-]$ (17).

For aqueous solutions, pH is represented as a numerical sequence from 0 to 14, and at pH = 7 the aqueous solution (medium) is neutral, at pH < 7 - acidic, at pH > 7 - alkaline.

The pH and pOH definitions given in terms of concentrations can only be used for dilute solutions. In more concentrated solutions, the interaction between their ions must be taken into account. Therefore, more generally, pH is defined as the negative decimal logarithm of hydroxonium ion activity[3]:

$pH = -lg\ a_{H3O+}$ (18).

respectively

$pOH = - lg\ a_{OH-}$ (19)

and $pH + pOH = 14$ (20).

The Arrhenius theory explains hydrolysis as the interaction of salt ions (electrolyte) and water ions, resulting in an acid and a base:

$CA + H_2O = C^+ + A^- + H^+ + OH^- = HA + COH$ (21).

In a system in which there is a deviation from equilibrium, non-equilibrium phenomena are observed, leading to the establishment of a new equilibrium state. Such are diffusion, convection and migration.

Diffusion in electrolyte solutions is a non-equilibrium phenomenon in which a substance is transferred from a place of higher to a place of lower concentration. In general, the rate of diffusion increases with increasing temperature.

Convection in electrolyte solutions is a non-equilibrium phenomenon in which there is a directed movement of liquid from the warmer to the colder part of the solution. It is due to differences in solution density as a result of unequal temperatures. It continues until the temperatures at all points of the solution are equal.

When in all points of the solution the electric potential has a different value (i.e. there is a potential gradient) migration is observed - a process of transporting ions under the action of the electric field in the solution. In doing so, the solution conducts an electric current. A quantitative characteristic of electrical conductivity is given by Ohm's first law:

$I = U / R = (1 / R) . U = G . U$ (22),

where I – the current, A; U – the voltage, V at the ends of the wire (in the case of an electrolyte - the potential difference between the two electrodes immersed in the electrolyte). The quantity G=1/R is called conductivity, it is measured in Siemens (S) $\equiv \Omega^{-1}$. G characterizes the ability of a wire (electrolyte medium) to conduct an electric current and is numerically equal to the current flowing through it when the voltage applied to its ends is 1 V. Since conductivity is proportional to the number of ions (current carriers) and their speed, it is a more appropriate quantity for use with electrolytes.

The specific electrical conductivity (χ) is defined using Ohm's second law:

$R = \rho . L / S = (1 / \chi) . L I / S$ (23),

where L - wire length, m; S - its cross section – m^2; ρ - specific resistance, Ω.m. The quantity $\chi = 1/\rho$ is called specific electrical conductivity and is measured in S/m.

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[3] Activity is a quantity that is used instead of concentration in relationships derived for ideal solutions in order to use them to correctly describe real solutions. Most often, the relationship between activity (a) and concentration (C) is represented by the expression a = f . C, where f - activity coefficient - takes into account the interactions between particles in real solutions. For dilute solutions ($C \rightarrow 0$), ($f \rightarrow 1$) and instead of a, we can work with C, or expressed also as [].

$\chi = (1 / R) . (L/S)$ (24).

This is the electrical conductivity of a cube of the solution with an edge of 1 m when a voltage of 1V is applied between its two sides. χ depends on the nature of the electrolyte and the solvent, on the concentration and on the temperature. Fig. 1 shows the generalized dependence of χ on the concentration.

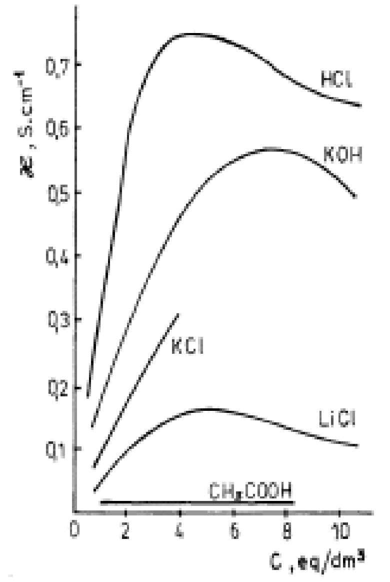


Fig.1. Dependence of the specific electrical conductivity of various electrolytes on the concentration of the solution

2.2.1.2. Electrochemical systems, electrode reactions, electrode potential

Processes that occur with the transition of electrons (e^-) are called oxidation-reduction. The substance that donates electrons is called a reducing agent (reductant). The substance that accepts electrons is called an oxidizing agent (oxidizer). The process of donating electrons is called oxidation. In doing so, the reductant is oxidized and its degree of oxidation increases. The process of accepting electrons is called reduction. During the process, the oxidizer is reduced and its oxidation state decreases. A substance can be said to be involved in an oxidation-reduction process if its oxidation state changes during the process. An electron-accepting process can only exist if there is an electron-donating process and vice versa, i.e., the oxidation-reduction reaction is a sum of two inextricably linked half-reactions. Therefore, the redox process is actually a single process. The number of electrons gained in the reduction reaction is equal to the number of electrons lost in the oxidation reaction. Each oxidation-reduction reaction can proceed by two different mechanisms - chemical and electrochemical. When the oxidation-reduction reaction takes place according to a chemical mechanism, the exchange of e^- occurs when the reacting particles are in direct contact, it is carried out chaotically in both directions, and as a result, the change in the energy of the system is manifested in the form of heat. According to an electrochemical mechanism, oxidation-reduction processes take place in the so-called electrochemical systems. Simultaneously occurring oxidation and reduction are spatially separated, and the sections on which they occur (generally called electrodes) are connected with an external metal conductor, ensuring the transition of electrons between them. In this case, the movement of e^- is directed (current flows), i.e. the change in energy of the system is in the form of electrical energy. The appearance of an electric current can only be explained by the performance of a partial electrode reaction (half-reaction) at each of the electrodes. This reaction is characterized by exchange of e^- between the metal and the solution. The overall redox reaction is the sum of the two partial reactions (oxidation and reduction).

A system made up of conductors of the first (e^- are the charge carriers) and second kind (ions are the charge carriers), placed in electrochemical contact with each other, is called an electrochemical system. An electrochemical system consisting of a single metallic conductor in serial contact with one or more non-metallic conductive phases, the last of which is a conductor of the second kind is called an electrode or half-cell. In it, reactions with charge transfer, i.e., electrochemical reactions, take place at the phase boundary between conductors of the first and second kind. Two or more electrodes (half-cells) placed in contact with each other by means of a conductive medium, called an electrolyte, form a galvanic (electrochemical) circuit. A galvanic circuit in which chemical reactions take place at the expense of electrical energy from an external source at the "electrode/electrolyte" interphase boundaries is called a galvanic bath (electrolysis cell, electrolyzer). A galvanic circuit that produces electrical energy at the expense of chemical reactions taking place in it (at the "electrode/electrolyte" interphase boundaries) is called a chemical source of power (CSP). Depending on the nature of the current-giving reactions, CSPs are divided into: galvanic cells - GC (primary sources of electrical energy), accumulators - AC (secondary sources of electrical energy) and fuel cells. *The electrode on which oxidation (donation of electrons) takes place is called the anode, the ongoing electrode reaction – an anodic reaction (anodic process). The electrode on which reduction takes place (acceptance of electrons) is called the* *cathode, the ongoing electrode reaction - cathodic reaction (cathodic process).* An electrochemical reaction is realized as a result of the simultaneous occurrence of spatially separated anodic and cathodic processes. The potential difference occurring between the two electrodes is the main characteristic of GC. In this case, only the potential difference arising at the ends of a reversible GC (GC in equilibrium, i.e. when no current flows through it) is subject to a theoretical description. This potential difference is called electromotive force - EMF. Experience has shown that the EMF of a GC depends on the nature of the occurring chemical reactions (the electrical work that is obtained is exactly equal to the heat capacity of the reaction), the concentration of the substances involved in the reaction, the temperature and the pressure (for electrochemical systems, involving gaseous substances).

The potential difference that occurs at the metal/electrolyte boundary is called the *electrode potential* (potential of the metal) - E. It corresponds to the part of the EMF of a circuit, which is due to the progress of one half-reaction of the oxidation-reduction process. The electrode potential determined when no current flows through the electrode is called the *equilibrium electrode potential*.

The concept of equilibrium potential is most easily demonstrated for the case of the simplest electrode – a metal immersed in a solution of its own ions. When a metal and a solution containing the ions of the metal are placed in a contact, it is possible that metal ions (Me^{n+}) pass from the metal to the solution or vice versa. An idea about the direction of Me^{n+} movement can be obtained by comparing the hydration energy of the ion E_H and its work function E_M (energy needed to separate a metal ion from the solid metal and remove it into the solution to a such distance that it can not be returned into the solid metal). At $E_M < E_H$, the metal ions pass from the metal lattice into the solution, and the electrons remaining in the metal lattice led to charging the metal surface with a negative charge; for $E_M > E_H$ the reverse process is valid and the metal surface is positively charged. The charged metal surface attracts and holds (through electrostatic forces) ions of opposite charge from the solution. As a result, the so-called double electric layer (d.e.l.) is formed. It is a set of opposite charges located at a certain (very small) distance between them. In general, d.e.l. is electroneutral. According to Stern's theory, the counterions in the d.e.l. are located in one ordered and one diffuse part (in which the charge density decreases exponentially from the surface of the metal to the volume of the electrolyte).

The process of Me^{n+} leaving the metal lattice in the solution and their attraction from the volume of the solution to the phase boundary takes place until equilibrium is reached, when the rates of the two reactions are equalized and virtually no charge transfer is observed. The potential difference occurring at the metal/electrolyte interface under these conditions is called the *equilibrium electrode potential*.

Only potential differences can be measured experimentally, but not the values of electric potentials at a given point. Therefore, E remains an undefined quantity. But the concept of EMF makes it possible to solve the problem of the value of the electrode potential. The value of the potential of an arbitrarily chosen electrode, with a reproducible potential under given conditions (called a standard electrode), is assumed to be 0 (at any temperature) and relative to it the the potential of all other electrodes is determined. For such an electrode, the standard hydrogen electrode (standard hydrogen electrode - SHE) *is adopted*. It is realized by immersing a platinized (to obtain a highly developed surface) platinum wire in a solution with $a_{H^+} = 1$, through which gaseous H_2 with a pressure of =101.3 kPa (=1 atm) is blown. The potential of each electrode determined with respect to this notional zero (i.e., with respect to 0.000 V) has the character of a relative quantity. With the use of SHE, the EMF of a given GC can be expressed as: $EMF = E_x - E_{SHE} = E_x - 0$, therefore $E_x = EMF$. In this case E_x is relative electrode potential. Based on the above considerations, in modern electrochemistry, electrode potential is understood as the EMF of GC, made up of SHE (working as an anode) and the electrode (working as a cathode), the potential of which is measured. The use of relative electrode potentials instead of their absolute values does not affect the final result for the EMF because the electrode potentials are measured relative to the same zero and the EMF is independent of the choice of zero. The equilibrium potential of a given electrode, at which the concentrations (more correctly, the activities) of the oxidized and reduced form are equal to unity (1 mol/liter), measured at 25 °C relative to SHE, is called the *standard (normal) electrode potential.*

Standard conditions include pure substances or elements and for gases - a pressure of 100 kPa. The arrangement of the electrodes in ascending order of the value of their standard electrode potentials gives the so-called *table of standard electrode potentials*, Table 2.

Table 2. Standard electrode potentials E° of some electrodes at 25 °C

Electrode	Electrode reaction	E°,V
$Li^{+}\|Li$	$Li^{+} + e^{-} <=> Li$	-3,045
$K^{+}\|K$	$K^{+} + e^{-} <=> K$	-2,925
$Ba^{2+}\|Ba$	$Ba^{2+} + 2e^{-} <=> Ba$	-2,900
$Ca^{2+}\|Ca$	$Ca^{2+} + 2e^{-} <=> Ca$	-2,870
$Na^{+}\|Na$	$Na^{+} + e^{-} <=> Na$	-2,714
$Mg^{2+}\|Mg$	$Mg^{2+} + 2e^{-} <=> Mg$	-2,360
$Be^{2+}\|Be$	$Be^{2+} + 2e^{-} <=> Be$	-1,850
$Al^{3+}\|Al$	$Al^{3+} + 3e^{-} <=> Al$	-1,660
$ZnO_2^{2-}\|Zn$	$ZnO_2^{2-} + 2H_2O + 2e^{-} <=> Zn + 4OH^{-}$	-1,220
$Mn^{2+}\|Mn$	$Mn^{2+} + 2e^{-} <=> Mn$	-1,050
$CNO^{-}\|CN^{-}$	$CNO^{-} + H_2O + 2e^{-} <=> CN^{-} + 2OH^{-}$	-0,970
$HSnO_2^{-}\|Sn$	$HSnO_2^{-} + H_2O + 2e^{-} <=> Sn + 3OH^{-}$	-0,910
$Zn^{2+}\|Zn$	$Zn^{2+} + 2e^{-} <=> Zn$	-0,763
$Cr^{3+}\|Cr$	$Cr^{3+} + 3e^{-} <=> Cr$	-0,740
$S\|S^{2-}$	$S + 2e^{-} <=> S^{2-}$	-0,510
$Fe^{2+}\|Fe$	$Fe^{2+} + 2e^{-} <=> Fe$	-0,440
$[Cu(CN)_2]\ \|Cu$	$[Cu(CN)_2]^{-} + e^{-} <=> Cu + 2CN^{-}$	-0,429
$Cd^{2+}\|Cd$	$Cd^{2+} + 2e^{-} <=> Cd$	-0,400
$T1^{+}\|T1$	$Tl^{+} + e^{-} <=> Tl$	-0,336
$Co^{2+}\|Co$	$Co^{2+} + 2e^{-} <=> Co$	-0,280
$Ni^{2+}\|Ni$	$Ni^{2+} + 2e^{-} <=> Ni$	-0,250
$Cu(OH)_2\|Cu$	$Cu(OH)_2 + 2e^{-} <=> Cu + 2OH^{-}$	-0,224
$Mo^{3+}\|Mo$	$Mo^{3+} + 3e^{-} <=> Mo$	0,200
$Sn^{2+}\|Sn$	$Sn^{2+} + 2e^{-} <=> Sn$	-0,136
$Pb^{2+}\|Pb$	$Pb^{2+} + 2e^{-} <=> Pb$	-0,126
$W^{3+}\|W$	$W^{3+} + 3e^{-} <=> W$	-0,050
$[Cu(NH_3)_4]^{2+}\|Cu$	$[Cu(NH_3)_4]^{2+} + 2e^{-} <=> Cu + 4NH_{3(aq)}$	-0,050

Electrode	Electrode reaction	E°,V
$Fe^{3+}\vert Fe$	Fe^{3+} + 3e$^-$ <=> Fe	-0,040
$2H^+\vert H_2$	$2H^+$ + e$^-$ <=> H	0,000
$Sn^{4+}\vert Sn^{2+}$	Sn^{4+} + 2e$^-$ <=> Sn^{2+}	0,150
$SO_4^{2-}\vert SO_3^{2-}$	SO_4^{2-} + $4H^+$ + 2e$^-$ <=> H_2SO_3 + H_2O	0,200
$Bi^{3+}\vert Bi$	Bi^{3+} + 3e$^-$ <=> Bi	0,220
$Cu^{2+}\vert Cu$	Cu^{2+} + 2e$^-$ <=> Cu	0,340
$[Fe(CN)_6]^{3-}$ I $Fe(CN)_6]^{4-}$	$[Fe(CN)_6]^{3-}$ + e$^-$ <=> $[Fe(CN)_6\vert^{4-}$	0,360
$O_2\vert OH^-$	O_2 + $2H_2O$ + 4e$^-$ <=> $4OH^-$	0,401*
$Cu^+\vert Cu$	Cu^+ + e$^-$ <=> Cu	0,520
$I_2\vert 2I^-$	I_2 + 2E$^-$<=> $2I^-$	0,530
$Fe^{3+}\vert Fe^{2+}$	Fe^{3+} + e$^-$ <=> Fe^{2+}	0,770
$Ag^+\vert Ag$	Ag^+ +e$^-$ <=> Ag	0,800
$Pd^{2+}\vert Pd$	Pd^{2+} + 2e$^-$ <=> Pd	0,830
$Hg^{2+}\vert Hg$	Hg^{2+} + 2e$^-$ <=> Hg	0,850
$NO_3^-\vert NO_2$	NO_3^- + $2H^+$ + 2e$^-$ <=> NO_2 + H_2O	0,940
$Br_2\vert 2Br^-$	Br_2 + 2e$^-$ <=> $2Br^-$	1,065
$Pt^{2+}\vert Pt$	Pt^{2+} + 2e$^-$ <=> Pt	1,190
$O_2\vert 2O^{2-}$	O_2 + $4H^+$ + 4e$^-$ <=> $2H_2O$	1,230**
$Cl_2\vert 2Cl^-$	Cl_2 + 2e$^-$ <=> $2Cl^-$	1,360
$Cr_2O_7^{2-}\vert 2Cr^{3+}$	$Cr_2O_7^{2-}$ + $14H^+$ + 6e$^-$ <=> $2Cr^{3+}$ + $7H_2O$	1,360
$Au^{3+}\vert Au$	Au^{3+} + 3e$^-$ <=> Au	1,500
$MnO_4^-\vert Mn^{2+}$	MnO_4^- + $8H^+$ + 5e$^-$ <=> Mn^{2+} + $4H_2O$	1,520
$MnO_4^-\vert Mn^{4+}$	MnO_4^- + $4H^+$ + 3e$^-$ <=> MnO_2 + $2H_2O$	1,670
$Pb^{4+}\vert Pb$	Pb^{4+} + 2e$^-$ <=> Pb^{2+}	1,69
$Au^+\vert Au$	Au^+ + e$^-$ <=>Au	1,69

*1,230 - at pH<7; **0,820 - at pH=7; 0,410 - at pH=14

In Table 2 all reactions are presented as reduction. When at connecting the corresponding electrode to the SHE, oxidation actually takes place on the studied electrode and e$^-$ pass from it to the SHE, this is marked with a "-" sign in front of the number indicating the standard potential of this electrode. The "+" sign indicates that the arbitrary process when connecting SHE and the studied electrode is oxidation of SHE and transition of e$^-$

from it to the studied electrode occurs. At the beginning of the table there are the electrodes that easily give and difficult receive e^-, and at the end (bottom) - the electrodes that easily receive and difficult release their e^-.
When two electrodes are combined, GC is obtained, in which the upper (more negative) electrode from the Table 2 works as an anode (i.e., oxidizes), and the lower electrode (more positive) - as a cathode (i.e., it is reduced). As a consequence, if there are two oxidation-reduction pairs in GC: $ox_1 + red_2 \leftrightarrow red_1 + ox_2$, the reaction will proceed spontaneously to the right if: $E^o_{ox_1/red_1} > E^o_{ox_2/red_2}$. Therefore, any metal with a more negative potential can reduce (separate / precipitate) a metal with a more positive potential from a solution containing the ions of the more positive metal. Metals with a negative potential can release hydrogen from solutions containing hydrogen ions. Metals with the most negative potentials displace hydrogen ions from water, releasing active hydrogen.
Based on the knowledge of the electrode potentials and the oxidation-reduction properties of the substances related to these potentials, the following conclusions can be drawn: a) During the electrolysis of aqueous solutions containing several dissolved salts (with comparable concentrations), reduction at the cathode takes place first of the ions with the most positive electrode potential (in particular, the cations of the metal with the most positive potential are deposited first). At the anode, ions with the lowest potential are most easily oxidized; b) In galvanic cells and in galvanic corrosion, the role of the anode is played by the metal with the most negative potential.
Each electrode can accept or give e^-. When combining two reversible electrodes, it cannot be said in advance in the specific case which electrode will give e^- and be the anode and which will accept e^- and be the cathode, i.e., uncertainty arises. It was removed by a special convention of the International Union of Chemistry (IUPAC, Stockholm, 1953), according to which the following basic rules must be observed when recording galvanic circuits:
1) At first, the material of one electrode is recorded - a conductor of the first kind, then the solution that is in contact with this electrode, then the solution in which the second electrode is immersed (if this solution is different from the first) and finally the second electrode - conductor of the first kind.
2) The boundary between two different phases is indicated by a vertical line; between two liquid phases - with a broken vertical line; between two liquid phases when the diffusion potential is removed - with two broken vertical lines; if the electrode or solution consists of several different substances or has different concentrations, they are listed by separating them from each other with a comma.
3) The circuit starts (on the left) with the electrode on which oxidation takes place, i.e. the anode. On the right (at the end of the chain) is written the electrode on which reduction takes place, i.e. the cathode.
4) EMF of the galvanic circuit is defined as the difference between the potentials of the right and left electrodes:

$EMF = E_C - E_A$ (25).

If following these rules for the calculated value of EMF of a given GC, EMF > 0 is obtained, it means that the reaction in the GC takes place spontaneously to the right. If EMF < 0 is obtained, the reaction in the GC does not take place arbitrarily in the right direction; in fact, it proceeds arbitrarily in the opposite direction.

An expression for calculating the EMF of GC can be reached by using the relationship known from chemical thermodynamics between the change in Gibbs energy during the course of a given electrochemical reaction and the maximum work done by the system ($\Delta G = - W_{max}$). When a charge Q is moved through an electric field of potential E = EMF, the electrical work done, at constant temperature and pressure, is

$W_{el} = Q \cdot E$ (26).

If we assume that the current carriers are electrons, since

Q = number of moles e^- x (charge/ mole) (27),

or for n moles

$Q = n. F$ (28),

where F - Faraday's constant (Faraday) = 96484 C/mol(e^-), it follows

$\Delta G = -n.F.E$ (29)

or for standard conditions

$\Delta G^o = -n.F.E^o$ (30).

Since, according to chemical thermodynamics, processes proceed spontaneously at $\Delta G < 0$, it follows that the electrochemical reaction will proceed spontaneously at $E = ЕДН = E_C - E_A > 0$.
Let us consider a reaction occurring in GC and written in the most general form:

$aA + bB = cC + dD$ (31),

where a, b - are the stoichiometric coefficients of the starting substances A and B, c and d - the stoichiometric coefficients of the reaction products C and D. According to chemical thermodynamics, the change in the Gibbs energy of the system during the course of the reaction can be represented by the equation of the reaction isotherm:

$\Delta G = - R . T . \ln K_T + R . T . \ln [(a_C^c a_D^d) / (a_A^a . a_B^b)]$ (32).

where R - universal gas constant, J/(mol.K); T - the absolute temperature, K; a_A, a_B, a_C and a_D – non-equilibrium activities of the substances involved in the reaction, K_T – the equilibrium constant of the reaction and

$K_T = (a^*{}_C^c a^*{}_D^d) / (a^*{}_A^a . a^*{}_B^b)$ (33),

where $a^*{}_A$, $a^*{}_B$, $a^*{}_C$ and $a^*{}_D$ – activities of the substances involved in the reaction at equilibrium.
At equilibrium $\Delta G = 0$ and

$\Delta G^o = - R . T . \ln K_T$ (34).

Combining (29), (32) and (34) and transforming, not forgetting that E = EMF, we arrive at the expression

$EMF = EMF^o + [(R . T) / (n . F)] . \ln [(a_A^a . a_B^b) / (a_C^c a_D^d)]$ (35),

known as the (generalized) Nernst equation, where

$EMF^o = [(R .T) / (n . F)] . \ln K_T$ (36)

is the standard electromotive voltage ($E^o{}_C - E^o{}_A$), n-number of exchanged e^- (i.e. e^- passing through the circuit during a single reaction); R - the universal gas constant, J/(mol.K); T - the absolute temperature, K; F - Faraday's constant;
Let's consider a GC made up of an electrode whose potential is being measured and SHE. Let the electrochemical reaction occurring on the studied electrode be

$Ox + ne^- = Red$ (37),

where Ox – the oxidized form of a given chemical species – is taken as the starting substance; Red – the reduced form of the same chemical species – is assumed to be the product of the reaction; n – number of e^- participatings in the reaction. When applying the concept of measuring the electrode potential with respect to the SHE, the rules of the IUPAC convention, taking into account (35) it is obtained:

$EMF = E_C - E_A = E_{Ox/Red} - E_{2H+/H2} = E_{Ox/Red} - 0 = EMF^o{}_{Ox/Red} + [(R . T) / (n . F)] . \ln (a_{Ox} / a_{Red})$ (38),

where $EMF^o{}_{Ox/Red}$ - characteristic of the studied electrode, a_{Ox} – activity of the oxidized form, a_{Red} – activity of the reduced form.
In compliance with the requirements for recording the reaction as a reduction and assuming that the starting substance is the oxidized form, $E_{Ox/Red} > 0$ means that when combining the studied electrode with SHE, the electrode reaction (37) will proceed spontaneously in the right direction, i.e., the investigated electrode will be a cathode (its potential is positive compared to the potential of the hydrogen electrode ($E_{2H+/H2}$). At $E_{Ox/Red} < 0$, the electrode, in combination with SHE, will play the role of an anode (its potential is negative compared to $E_{2H+/H2}$. It *should not* be forgotten that the Nernst equation is valid only when a single oxidation-reduction reaction takes place at the electrode. It follows from the Nernst equation that under standard conditions (including activities of the substances involved in the electrode reaction $a_{Ox} = a_{Red} = 1$) $E_{Ox/Red} \equiv EMF^o{}_{Ox/Red.}$ The

$EMF^{o}_{Ox/Red}$ (written as $E^{o}_{Ox/Red}$) is called the *standard electrode potential*. It is equal to the EMF of the galvanic circuit composed of the investigated electrode and SHE, determined under standard conditions.

$E_{Ox/Red} = E^{o}_{Ox/Red} + [(R . T) / (n . F)] . \ln (a_{Ox} / a_{Red})$ (39).

This equation is also known as the Nernst equation.

If the electrode reaction in question (37) is the reduction of a metal ion, i.e.

$Me^{n+} + ne^{-} \leftrightarrow Me^{o}$ (40),

then $a_{Red} = 1$ (solid phase activity) and the Nernst equation transforms into:

$E_{(Me^{n+}/Me)} = E^{0}_{(Me^{n+}/Me)} + (RT / nF).\ln a_{Me^{n+}}$ (41).

This dependence is the most commonly used form (when calculating electrode potentials) of the Nernst equation. When replacing R and F with their values, T = 25 °C, and when switching to a decimal logarithm (41) transforms into:

$E_{(Me^{n+}/Me)} = E^{0}_{(Me^{n+}/Me)} + (0{,}059 / n).\lg a_{Me^{n+}}$, V (42).

Taking into account the dependences (25) and (39) for the EMF of a GC made up of two different electrodes (none of which is a SHE), it can be written:

$EMF = E_C - E_A = \{E^{o}_{C} + [(R . T)/(n . F)] . \ln (a_{Ox(C)})/(a_{Red(C)})\} - \{E^{o}_{A} + [(R . T)/(n . F)] . \ln (a_{Ox(A)})/(a_{Red(A)})\}$ (43).

Considering the definition of a galvanic bath (electrolyzer), *electrolysis* can be defined as a process of simultaneous oxidation-reduction reactions on the electrodes at the expense of electrical energy from an external source. In the electrolysis cell, the negative electrode is called the cathode - C, and the positive - the anode - A, as (as in GC) oxidation takes place at the anode and reduction at the cathode.

Let us place a solution of HCl in an electrolyser and dip two platinum wires into it. The acid dissociates into H^+ and Cl^-. When a direct current is passed through the system, the H^+ will move to the cathode where they are reduced. Cl^- are directed to the anode and are oxidized there. The reactions taking place can be written as follows:

On C (-):$2H^+ + 2e^- \rightarrow H_2$;
On A(+):$2Cl^- \rightarrow Cl_2 + 2e^-$ ..
Total: $2HCl \rightarrow H_2 + Cl_2$ (44).

If one plots the dependence of the current, I flowing in the electrolysis cell as a function of the applied potential ΔU, it will be seen that there is a value U_T of the potential at which the current increases sharply. This value is the minimum potential difference needed to start the process. When current is passed through the electrolysis cell, a voltage drop ($I.R_I$) is observed due to the internal electrical resistance of the cell. During electrolysis processes, the electrodes are polarized and the overvoltage of the electrodes must also be overcome by the applied external voltage in order for the process to proceed. Therefore, the actual voltage (ΔU_{el}) that must be applied to the electrolysis cell in order for the electrolysis to proceed is represented by the expression:

$\Delta U_{el} = U_T + I . R_I + \eta_a + \eta_k$ (45),

where η_a and η_k are the anode and cathode overvoltages, respectively (for polarization and overvoltage see below).

When electrolysis of a solution containing different ions is carried out, the ions are reduced on the cathode in the order of electrode potential decreasing of the corresponding oxidation-reduction pair, until reaching the hydrogen evolution potential $E_{ev.H2}$:

$E_{ev.H2} = - 0{,}059 . pH + \eta_{H2(C)}$ (46).

Metals whose potentials are more negative than the potential of the standard hydrogen electrode can be deposited on the cathode in acidic solutions only if they have a large H_2 evolution overvoltage ($\eta_{H2(C)}$). This allows the deposition of such metals as Pb, Zn, Ni, Co, Cd, Cr, Sn and Mn (the latter from neutral solutions).

Faraday's laws apply to electrolysis.
First law: "The mass (Δm) of the substance reacted as a result of an anodic or cathodic reaction is proportional to the amount of electricity ΔQ that passed through the system":

$\Delta m = k_e . \Delta Q = k_e . I . \tau$ (47),

where I - the current, A; τ - electrolysis time, h; The proportionality factor k_e=E/F is called the electrochemical equivalent, g/(A.h); k is a quantity characteristic of the reacting substance and is equal to the reacted mass of the electrode when one coulomb of electricity flows through the system.
Second law: "When the same amount of electricity flows through solutions of different substances, the reacted quantities Δm_1, Δm_2,... relate to each other as the chemical equivalents E_{x_1}, E_{x_2} ... of these substances":

$\Delta m_1 : \Delta m_2 : ... = E_{x_1} : E_{x_2}$ or $\Delta m_1/E_{x_1} = \Delta m_2/E_{x_2} = ... = const . (\Delta Q)$ (48).

It is clear that the number of reacted equivalents does not depend on the nature of the substance, but only on the amount of electricity passed. Combining the first and second laws yields:

$(k_{e_1} . \Delta Q) : (k_{e_2} . \Delta Q) : ... = E_{x_1} : E_{x_2} : ....$ (49).

Therefore, the equivalent of a substance is proportional to its electrochemical equivalent, i.e.

$E_x = F . k_e$ (50),

where the proportionality factor F is called Faraday's constant (number) and represents the amount of electricity required to convert one equivalent substance of the electrode.

2.2.1.3. Kinetics of electrode processes, electrode polarization

Electrode reactions are heterogeneous processes because they occur at the solid phase (first-order conductor) / liquid phase (second-order conductor) interface. They are multi-step reactions, proceeding mainly as a sequence. Therefore, the slowest stage is rate-determining (limiting). The main stages of electrochemical reactions are, for example if a cation is discharged (or molecule ionized) at the solid surface: a) transfer of particles from the depth of the solution to the diffuse part of the e.d.l.; b) transfer of particles through the diffuse part of the e.d.l. to its dense part in close proximity to the metal electrode; c) an actual electrochemical reaction with electron transfer (it mainly covers the process of particle discharge / ionization); d) formation of the final product of the reaction - consisting of several sub-stages, mainly related to the construction or degradation of a new phase; e) moving the reaction products away from the electrode surface. When one of the diffusion stages a), b) or e) is limitingwe, we speak of diffusion control of entire the process. When the reaction stages are limiting, we speak of electrochemical kinetics control of the total process.
The rate of electrode reactions can be expressed by the current density i flowing through the electrode:
It is known from chemical kinetics that the rate of a heterogeneous reaction v is

$v = \Delta m / (S . \Delta\tau)$ (51),

where Δm - the amount of reacting substance for time $\Delta\tau$, S - the surface of the interphase boundary.
If the current flow is the result of only the electrode process, the relationship between the reaction rate and the current can be established by considering Faraday's first law (proportionality between Δm and the amount of electricity passed ΔQ). For current carriers of charge n, the quantity of electricity Q can be represented by

$Q = \Delta m . n. F$ (52),

where Δm – the amount of substance, expressed as moles, that underwent an electrochemical change; n – number of e^- exchanged by each mole; F - Faraday's constant.
According to the definition of quantity of electricity

$Q = i . S . \Delta\tau$ (53),

where i - the current density, S - the surface of the interphase boundary, τ - the time.
From (52) and (53) one can write

$i = \Delta m \, . \, n \, . \, F / (S \, . \, \Delta\tau)$ (54),

and from (54) and (51) it follows

$i = n \, . \, F. \, v$ (55),

i.e., about the rate of the electrochemical reaction it can be judged by the density of the current flowing in the circuit.

The rate of the electrode process depends on the concentration of the reacting particles. E.g., for reaction (37) the rate of the forward reaction is

$v^{\rightarrow} = k^{\rightarrow} .C_{ox} \, . \, C_{e^-}{}^{n}$ (56)

the rate of the reverse reaction (oxidation) is

$v^{\leftarrow} = k^{\leftarrow} .C_{Red}$ (57),

and the total rate

$v = k^{\rightarrow} .C_{ox} \, . \, C_{e^-}{}^{n} - k^{\leftarrow} .C_{Red}$ (58),

where: $k^{\rightarrow}$ and $k^{\leftarrow}$ - rate constants of the forward and reverse reaction; C_{ox}, C_{Red} and C_{e^-} - concentration of the oxidized, reduced form and of the exchanged electrons respectively, n – number of exchanged e^-.

A peculiarity of electrochemical reactions is that the reaction rate depends (most often) exponentially on the potential of the electrode through which current i flows. The graphically expressed dependence between the current (or current density) and the potential (or the polarization) of the electrode is called a *polarization curve*. The general polarization curve of an electrode is a sum of two partial polarization curves describing the oxidation and reduction occurring simultaneously on the electrode.

The electrode potential changes its value when current flows through the electrode. The *phenomenon* of displacement of the electrode potential from the equilibrium electrode potential is called *electrode polarization*. A *quantitative measure* of the polarization is the difference $\eta = E_i - E_r$, called the *overvoltage* (η). In this case, E_r and E_i - potentials of the electrode in equilibrium (when no current flows through it) and when current flows through it, respectively. It follows from the definition that in the case of cathodic polarization (i.e., when the electrode potential deviates in a more negative direction from the equilibrium potential) $\eta_c < 0$, and in the case of anodic polarization (i.e., when the electrode potential deviates in a positive direction from the equilibrium potential) - respectively $\eta_a > 0$. The overvoltage gives an idea of the additional energy that is needed (the loss of energy in the form of heat) to ensure that the electrode reaction proceeds at the desired rate (or at its equivalent current density).

The polarization existence is an indicator of difficulty in one of the stages of the electrode process. When this is due to some of the stages associated with diffusion, leading to a change in the concentration of the electrochemically active particles, we speak of *concentration polarization*. When the difficulties are in stages related to the true electrochemical reaction, we speak of *activation polarization*. Even in the simplest case, the overvoltage is the combined result of concentration and activation polarization. The dependence between the overvoltage) and the current density i at activation polarization is given by the *Tafel equation*:

$\eta = E_i - E_r = a + b \, . \, \log i$ (59),

where a and b are empirical coefficients depending on the specific conditions of the electrochemical process. Tafel's equation is obeyed quite precisely only for the hydrogen overvoltage. The values of **a** and **b** for the H_2 overvoltage, depending on the nature of the electrode and the current density, as well as for other oxidation-reduction pairs, can be found in electrochemical tables. The overvoltage also depends on the nature of the ongoing electrode reaction, i.e., on the magnitude of the exchange current I_o, as with a faster reaction (larger I_o) the overvoltage is greater. The exchange current characterizes the rate of the opposite reactions occurring on the electrode when it is in dynamic equilibrium, i.e., when the rate of the two opposite reactions (oxidation and reduction) is equal and the total rate of the reaction, respectively, the total current is 0. In this case, there is no loss or increase in the mass of the electrode material. The exchange current is determined experimentally (usually, for the purpose of normalization, its density $i_o = I_o / S$, S – the area of the electrode is determined) and depends on the nature of the metal (composition of the alloy), the roughness of the electrode surface (greater at - rough surface), the impurities present on the surface and the concentration of reactants and products of the reaction taking place on the electrode.

The polarization curve at activation polarization of an electrode on which an oxidation-reduction reaction takes place is represented by the Butler-Volmer equation:

$i = i_o . \{ \exp [- (\beta . n . F . \eta_{act}) / (R . T)] – \exp [(1 - \beta) . n . F . \eta_{act} / (R . T)] \}$ (60),

where: i – anodic or cathodic current density; i_o – exchange current density; β and $(1-\beta)$ - transition coefficient[4] for the cathodic or anodic reaction – its typical value is around 0.5; η_{act} - the overvoltage ($\eta_c < 0$; $\eta_a > 0$); n- number of exchanged e^-; R - the universal gas constant; T - the absolute temperature; F - Faraday's constant;

At anodic polarization ($\eta_a > 0$) the first term of dependence (60) becomes negligibly small and the current density i_a is represented by the expression:

$i_a = - i_o . \exp [(1- \beta) . n . F . \eta_a / (R . T)]$ (62)

or in logarithmic form:

$\eta_a = b_a . \lg (i_a / i_o)$ (63),

where b_a is the Tafel coefficient (slope). It can be determined from the slope of the line

$\eta_a = f (\log i)$, i.e. (64)

$b_a = 2,303 . R . T / [(1- \beta) . n . F]$ (65).

Similarly, with cathodic polarization ($\eta_c < 0$) the second term of dependence (60) becomes negligibly small and the current density i_c is represented by the expression:

$i_c = i_o . \exp [(- \beta) . n . F . \eta_c / (R . T)]$ (66)

or in logarithmic form:

$\eta_c = b_c . \lg (i_c / i_o)$ (67),

where b_c is the Tafel coefficient (slope). It can also be determined from the slope of the line $\eta_C = f (\log i)$, i.e

$b_c = 2,303 . R . T / (\beta . n . F)$ (68),

where the cut gives the value of i_o.

An expression for the polarization curve for concentration polarization can be derived using the example of the cathodic reaction of oxygen reduction. The rate of electrode reaction is proportional to the concentration of O_2 at the electrode surface. When the actual electrochemical reaction proceeds rapidly, the concentration of O_2 at the electrode surface rapidly decreases to 0, and the rate of the overall cathodic reaction will be determined by the rate of O_2 transfer. When the transfer of O_2 takes place by diffusion, the process rate, at an electrode surface area S=1 cm^2, is described by Fick's first law:

$v = \Delta m / (\Delta\tau) = D . (\Delta C / (\Delta x)$ (69)

From (69) and (55) it follows

$i = n . F. D . (\Delta C / (\Delta x)$ (70),

---

[4] The transition coefficient characterizes the degree of influence of the electric field of the electrode on the activation energy of the corresponding partial electrode reaction and determines the symmetry of the energy diagram of the reaction. The activation energy of the electrode reaction can be considered as the sum of the energy of the redox reaction in the absence of an electric field and the additional energy associated with the contribution of the field. The activation energy E_a is defined as the difference in the energy of the active particles (the particles of the starting substances that are capable of reacting) and the average energy of all the particles of the starting substances in the system. The larger E_a, the more difficult a given reaction proceeds. The relationship between the rate constant of a given reaction (k), i.e. the reaction rate at reactants concentrations = 1, and E_a is represented by the Arrhenius dependence:

$k = A . \exp (- E_a/(R.T)]$ (61)

where R - the universal gas constant; T - the absolute temperature; A – factor taking into account the influence of the solvent, steric factors, etc.

When the solution with which the electrode is in contact is stirred, a stationary layer is formed near the electrode surface, the so-called Nernst diffusion layer with a thickness δ in which layer the concentration of the reactant decreases from the concentration in the volume C_o to 0 - Fig. 2. In this layer, the concentration of the reactant c is controlled only by diffusion. Due to the stirring, the concentration in the volume remains constant, C_o and does not depend on diffusion.
The concentration gradient within the Nernst diffusion layer is

$\Delta C / \Delta x = (C_o - C_x) / \delta$ (71),

Taking into account that on the electrode surface the concentration C_x is =0, it follows

$\Delta C / \Delta x = C_o / \delta$ (72),

Under these conditions, the electrode reaction rate reaches its maximum value i_{max}, known as the "limiting current" i_L.

$i_{max} = i_L = n . F . D . C_o / \delta$ (73)

When oxygen at the electrode surface is not completely depleted, (71) applies to the concentration gradient. For this case, it can be proved that the relationship between the concentration polarization η_{conc}, the current density i and the limiting current density i_L is represented by:

$\eta_{conc} = [2,303 . R . T / (n . F)] . \lg (1 - i / i_L)$ (74),

where n-number exchanged e^- (in this case =4); R - the universal gas constant; T - temperature, K; F - Faraday constant and $2.303 \cdot R \cdot T/F = 0.059$ V at T = 298.16 K.

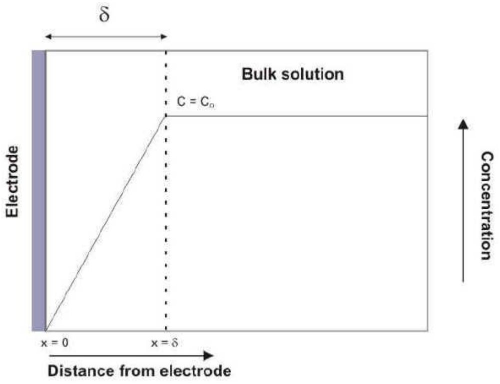


Fig. 2 Formation of a diffusion layer at the metal-solution interface

When determining the EMF of GC, the three types of polarization that occur must be taken into account:

$EMF_i - EMF_r = \eta_{total} = \eta_{act} + \eta_{conc} + iR$ (75),

where η_{act} – activation overvoltage – prevails at small values of the polarizing current and the voltage; η_{conc} – concentration overvoltage - prevails at high values of the polarizing current and the voltage; η_{act} and η_{conc} are recorded on both electrodes forming GC; iR - ohmic voltage drop - describes the polarization that occurs when an electric current flows through a phase.

2.2.2. General characteristics of electrochemical corrosion

2.2.2.1. Essence

Electrochemical corrosion is the spontaneous destruction of metals (and alloys) due to an electrochemical reaction proceeding during their interaction with an electrolyte medium. In it, the oxidation (ionization) of metals and the reduction of the oxidizing component of the corrosion medium do not occur in one act, and the rates of both processes (oxidation and reduction) depend on the potential of the metal. This type of corrosion is most common in practice.
The characteristic features of electrochemical corrosion are:
1) The general corrosion process is divided into two independent but simultaneously occurring and mutually conditioning electrode processes: anodic (oxidation) - passage of metal ions into the solution, leaving an equivalent number of e^- on the metal:

$Me \rightarrow Me^{n+}.mH_2O + ne^-$ (76)

and cathodic (reduction) - assimilation of the remaining excess e^- on the metal by an ion (or molecule) located in the corrosion environment and called a depolarizer:

$D + ne- \rightarrow Dne^-$ (77).

The unimpeded course of the cathodic depolarizing reaction accounts for the impossibility a reaction equilibrium to be reached. In this case, the equilibrium potential of the corroding metal described by equation (41) cannot be reached, and usually its potential is more positive than its equilibrium potential.

In the process of exchange between the metal and the solution, not only the ions of the metal, but also the ions (molecules) of the depolarizer are involved. Therefore, the potential developed on the metal *is non-equilibrium* - Fig. 3.

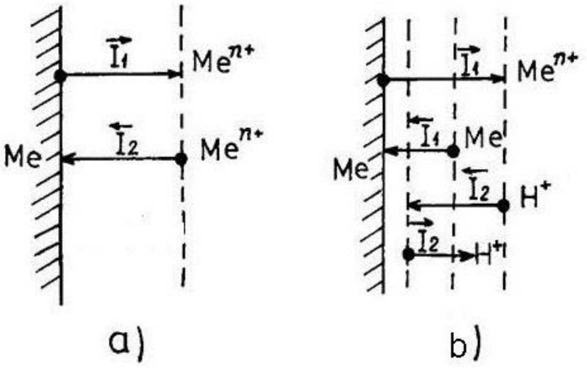


Fig. 3. Scheme of establishment of equilibrium (a) and nonequilibrium (b) potential

The non-equilibrium potential of a given electrode is established when at least two oxidation-reduction pairs are involved in the electrode process taking place on a given surface, where the anodic process is mainly carried out by one pair, and the cathodic process by the other. (For example, in Fig. 3, the anodic process is mainly carried out by the ions of the metal $I_1^{\rightarrow} \gg I_1^{\leftarrow}$), and the cathodic process – by H^+ ions. When equalizing the sums of the rates of the anodic and cathodic processes (i.e. $I_1^{\rightarrow} + I_2^{\rightarrow} = I_1^{\leftarrow} + I_2^{\leftarrow}$) a *stationary (mixed)* potential of the metal is established, in which there is a balance of charges, but not a balance of the substance in relation to the mass of the metal. In this case, the mass of the metal continuously decreases as $I_1^{\rightarrow} \gg I_1^{\leftarrow}$. Non-equilibrium potentials cannot be calculated using the Nernst equation, but are only determined experimentally. The value of the mixed potential lies between the values of the equilibrium potentials of the two redox reactions taking place. In corrosion, the steady-state non-equilibrium potential established is called the *corrosion potential*.

2) Dependence of the rates of the cathodic and anodic process, and therefore of the rate of corrosion, on the potential of the metal that corrodes. This makes it possible to control the corrosion process by affecting the potential of the metal (for example, in the electrochemical protection);

3) In most cases, the cathodic and anodic processes are localized on different sections of the metal surface (cathodic and anodic sections). The material effect of corrosion (destruction) occurs mainly on the anodic sections. Due to the presence of anodic and cathodic sections, electrochemical corrosion is reminiscent of the Galvanic cell (GC) operation, where the anode and cathode are short-circuited Fig. 4.

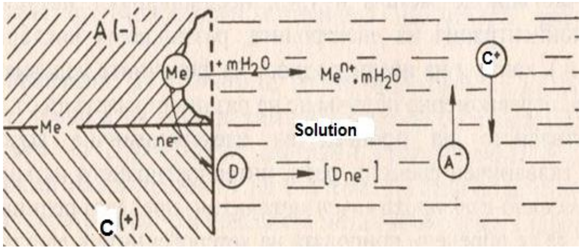


Fig.4. Scheme of the action of a corrosion galvanic cell

In this corrosion GC, e^- move inside the metal from the anodic to the cathodic region, and the ions (of the metal and the depolarizer) move in the electrolyte. The current flowing between the anode and cathode sections is called the *corrosion current*. It is a *measure of the rate of corrosion*. The electromotive force (EMF) of the corrosion GC is given by the expression:

$EMF_{cor.\ GC} = E_{r(c)} - E_{r(a)}$ (78),

where $E_{r(c)}$ - the equilibrium oxidation-reduction potential of the cathodic reaction; $E_{r(a)} \equiv E_{r(Me)}$ - the equilibrium oxidation-reduction potential of the anodic reaction, i.e. the equilibrium potential of the metal.

For $EMF_{corGC} > 0$, i.e. for the corrosion process to be arbitrary, $E_{r(c)} > E_{r(a)} = E_{r(Me)}$. Therefore, for the spontaneous progress of electrochemical corrosion, it is necessary to have a depolarizer in the solution, whose oxidation-reduction potential is more positive than the equilibrium potential of the metal, under the given conditions.

In natural conditions, electrochemical corrosion occurs mainly with two types of depolarization: hydrogen and oxygen.

In corrosion with hydrogen depolarization, the depolarizer is the H^+ ion adsorbed on the surface of the metal. The generalized cathodic reaction is:

$H^+ + e^- \rightarrow \frac{1}{2} H_2$ (79).

The equilibrium potential of this reaction is represented by the expression:

$E_{r,H+/H2} = E^o_{H+/H2} + [(R\ .\ T) / F]\ .\ \ln (a_{H^+} / p_{H2}^{1/2})$ (80),

where $E^o_{H+/H2}$ is the standard potential, p_{H2} is the partial pressure of hydrogen gas, R, T and F have their usual meaning, i.e., the universal gas constant, temperature in K, and Faradey's constant.

The potential at which this reaction occurs in a corrosion process, i.e., with current flowing, at 25 °C and partial pressure of H_2 0.101 MPa is:

$E_{2H^+/H2} = – 0,059\ .\ pH + \eta_{H_2}$ (81),

where η_{H_2} is the hydrogen overvoltage on the cathode of the corrosion GC.

Hydrogen depolarization corrosion is possible when $E_{r(Me)} < E_{2H+/H2}$ and usually occurs in acidic environments (i.e. pH < 3.5 - 4.0). Apart from environments with high activity of H^+, this type of depolarization takes place in corrosion environments with low activity of metal ions (e.g., corrosion of some metals - Fe, Pb - in a highly alkaline environment) and for metals with highly negative potentials (alkaline and alkaline earth metals in water and in neutral aqueous solutions).

In corrosion with oxygen depolarization, the depolarizer is O_2 dissolved in the electrolyte. The generalized cathodic reaction in this case can be represented by the expression:

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ (82).

The equilibrium potential of this reaction is represented by the expression:

$E_{r,O2/OH^-} = E_{O2/OH^-} + [(R\ .\ T) / (4\ .\ F)]\ .\ \ln (p_{O2} / a_{OH^-}{}^4)$ (83),

where E_{O2/OH^-} is the standard potential, p_{O2} is the partial pressure of hydrogen gas, a_{OH^-} is the hydroxyl ion activity, R, T and F have their usual meaning.

The potential at which this reaction occurs in a corrosion process at 25 °C and a partial pressure of O_2 of 0.101 MPa is (η_{O_2} is the oxygen overvoltage on the cathode of the corrosion GC):

$E_{O2/OH^-} = 1,229 – 0,059\ .\ pH + \eta_{O_2}$ (84).

Corrosion with oxygen depolarization is possible if $E_{p(Me)} < E_{O2/OH^-}$. Corrosion occurs with O_2 depolarization usually in environments with pH ≥ 4.5 - 5.0. At pH = 4.0 - 4.5, both types of depolarization occur. With O_2 depolarization, the corrosion of metals occurs in: the atmosphere, fresh and salt water, soil, neutral aqueous solutions of salts.

Apart from H^+ ions and O_2, cathodic depolarization can also be performed by other depolarizers:

- ions, e.g., NO_3^-; $Cr_2O_7^{2-}$; Fe^{3+}:

$NO_3^- + 3H^+ + 2e^- \rightarrow HNO_2 + H_2O$ (85)

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$ (86)

$Fe^{3+}.mH_2O + e^- \rightarrow Fe^{2+}.\ mH_2O$ (87)

- neutral molecules H_2O_2, Cl_2

$H_2O_2 + 2e^- \rightarrow 2OH^-$ (88)

$Cl_2 + 2e^- \rightarrow 2Cl^-$; (89)

- oxide or hydroxide layers on the metal

$Fe_3O_4 + 2e^- + H_2O \rightarrow 3FeO + 2OH^-$ (90)

$Fe(OH)_3 + e^- \rightarrow Fe(OH)_2 + OH^-$ (91);

- organic compounds

$R + 2H^+ + 2e^- \rightarrow RH_2$ (92)

$RO + 4H^+ + 4e^- \rightarrow RH_2 + H_2O$ (93)

where R is an organic radical or compound.
Reactions (76) and (77) are primary processes of electrochemical corrosion. The resulting primary products can react with each other, with the electrolyte or with the gases dissolved in it - that is, secondary reactions can occur. For example, as a result of reactions (79) and (82), the pH of the environment around the cathode increases. It is possible to reach a pH at which low soluble hydroxides of the corroding metal are formed:

$Me^{n+}.mH_2O + nOH^- \rightarrow Me(OH)_n\downarrow + mH_2O$ (94).

Rust on Fe and steels is precisely a layer of secondary corrosion products. Its composition and physical properties depend on the conditions of obtaining the corrosion products (access to O_2, presence of Cl^-). Corrosion of Fe at pH >5.5 results in a slightly soluble product - the so-called "green rust":

$Fe^{2+}.mH_2O + 2OH^- \rightarrow Fe(OH)_2\downarrow + mH_2O$ (95).

Green rust oxidizes with free access of O_2

$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4\,Fe(OH)_3\downarrow$ (96).

The resulting porous $Fe(OH)_3$ layer with poor adhesion to the metal surface is not stable and decomposes, producing hydrated oxides of Fe^{3+}, i.e. $Fe_2O_3.H_2O$ with red-brown color.
At a lack of O_2, magnetite is obtained from the complete oxidation of $Fe(OH)_2$:

$6Fe(OH)_2 + O_2 \rightarrow 2Fe_3O_4 + 6H_2O$ (97).

The layers of secondary corrosion products formed on the metal surface can have protective properties and change the corrosion resistance of the respective metal - e.g., the formation of insoluble sulfates explains the increased resistance of Pb in H_2SO_4, of Fe in concentrated H_2SO_4.

In order for corrosion GCs to form and function, it is necessary that the metal surface can function as an anode, a cathode and a metal conductor between them, i.e., it is necessary to create conditions for distinguishing anodic and cathodic sections of the metal surface - sections with different potential (electrochemically heterogeneous sections). The reasons for the creation of such sections are non-uniformity of the metal phase; non-uniformity of the electrolyte contacting the metal and non-uniformity of the physical conditions acting on the metal.

- Inhomogeneity of the metal phase

- Structural heterogeneity of the metal:
a) Contact of different metals - the metal with a more negative potential is anode of the corrosion GC;
b) Presence of inclusions (metallic and conductive non-metallic) in the base metal - inclusions with a more positive potential are cathode sections;
c) Difference in the concentration of solid solutions in different sections of a metal alloy - sections of the alloy richer in the component with a lower potential are anodic sections;
d) Presence of defects on the metal surface - the places with defects are anodic sections;
e) Anisotropy of the metal crystals – the planes with lower density are anodic areas;
f) Presence of boundaries between the metal grains - usually the boundaries are anodic areas.

- Microscopic heterogeneity:
a) Presence of heterogeneous atoms in a given solid solution in the alloy - the atoms of the nobler metal form a microcathode section;
b) Existence of fluctuations in the energy of the atoms from the metal surface - the energetically richer ones form a microanode section.

- Non-uniformity of natural and artificial protective coatings on the metal surface:

a) Presence of defects in protective coatings (conversion, varnish-paint, polymer, etc.) - the metal in the pores is usually an anodic section;
b) Presence of defects in naturally formed oxide coatings - the metal in the pores is an anodic section;
c) Uneven distribution of secondary corrosion products on a metal surface - usually the metal areas located under a thicker layer of corrosion products are anodic.
- Non-uniformity of internal stresses and deformations
a) Irregularity of applied mechanical load on the metal - sections with higher resultant stress are anodic;
b) Uneven deformation – more deformed areas are anodic
c) Non-uniformity of the defects and internal stresses as a result of different processing of the alloys - the sections subjected to cold processing are anodic.
• Non-uniformity of the electrolyte contacting the metal
- Difference in the concentrations of the ions of the corroding metal in the electrolyte - the sections of the metal surface that are in contact with the electrolyte (water, solution, soil) with a lower concentration of these ions are anodic.
- Difference in concentrations of salts dissolved in the electrolyte
a) Areas of the metal that come into contact with a more concentrated solution of activating ions (e.g. Cl^-) are anodic;
b) The parts of the metal that come into contact with a more concentrated solution of passivating ions (e.g. $Cr_2O_7^{2-}$) are cathodic;
- Difference in the acidity of the electrolyte contacting the metal – e.g., in corrosion of unalloyed steel, the areas in contact with a more acidic electrolyte are anodic.
- Difference in the concentrations of O_2 in the electrolyte – the sections that are in contact with an environment richer in O_2 are cathodes.
• Non-uniformity of the physical conditions acting on the metal
- Difference in metal temperatures – usually the hotter sections are anodic;
- Uneven distribution of radiant energy – more intensively irradiated areas are anodic;
- Uneven imposed external electric field - anode are the areas where positive charges leave the metal to the electrolyte.

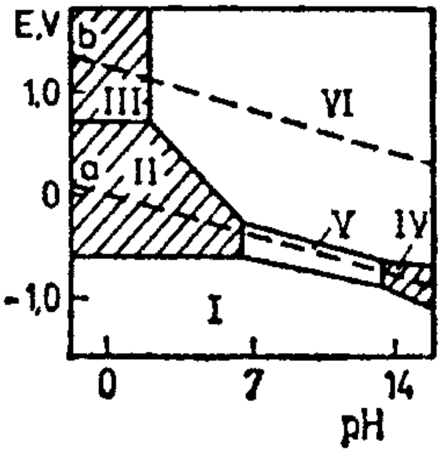
The nature of the electrochemical inhomogeneity and the size of the formed cathodic and anodic areas lead to the formation of corrosion GCs of different sizes:
- Corrosion macro-GC - are formed as a result of contact of two different metals or in case of non-uniformity of the external conditions. Their operation depends on the kinetics of the ongoing anodic and cathodic processes and on the resistance of the corrosive environment. They are characterized by a stable distribution of the cathodic and anodic sections over time, which leads to highly pronounced local corrosion.
- Corrosion micro-GC – formed as a result of electrochemical micro-heterogeneity (e.g., boundaries between metal grains, non-uniform metal structure). Their operation depends on the efficiency of the ongoing anodic and cathodic processes and almost does not depend on the resistance of the corrosive environment. Their work leads to pronounced local corrosion, but on a micro scale, e.g., intergranular corrosion, corrosion cracking. A change in the location of the cathode and anode sections is possible, e.g., stopping the action of the micro anode due to its dissolution.
- Corrosion submicroscopic GC - are formed as a result of inhomogeneity of the metal surface at the atomic level and are characterized by an unstable distribution over time of the cathodic and anodic sections.

2.2.2.2. Thermodynamics of corrosion proceeding by an electrochemical mechanism

The thermodynamic possibility of an electrochemical corrosion proceeding and the thermodynamic stability of metals in relation to corrosion with hydrogen and oxygen depolarization can be estimated by using the Pourbaix diagrams. These diagrams are isothermal phase diagrams of the metal-water-air system in equilibrium potential vs. pH coordinates and reflect the metal-oxide (hydroxide) equilibrium.
The diagrams are composed of graphical dependences of equilibrium potentials on solution pH for three types of equilibria: potential-dependent (with e^- exchange); dependent only on pH (no e^- exchange, but involving H^+ or OH^- ions) and equilibria dependent on both potential and pH (i.e., involving e^-, H^+ and OH^-). Some equilibria

in the metal - water system depend not only on the activity of the hydrogen ions, but also on the activity of the other ions involved in the equilibrium. Then, in full Pourbaix diagrams, instead of a single line corresponding to a given equilibrium, a family of lines is drawn, each of which corresponds to a certain activity of the given ion. Fig. 5 shows a simplified Pourbaix diagram for iron at 25 °C.

Lines **a** and **b** correspond to the equilibrium of the hydrogen and oxygen depolarization reactions.



$2\,H_2O + 2\,e^- = H_2 + 2\,OH^-$ (a)

and the relationship between pH and potential at 25 ^oC and H_2 pressure 101.3 kPa is described by:

$E_{H^+/H2} = E^o_{H^+/H2} - 0.059\ pH$ (98)

$2\,H_2O = O_2 + 4\,H^+ + 4\,e^-$ (b)

and the relationship between pH and potential at 25 ^oC and an O_2 pressure of 101.3 kPa is described by:

$E_{O2/H2O} = E^o_{O2/H2O} - 0.059\ pH$ (99).

Fig. 5. Simplified Pourbaix diagram for iron

Water is thermodynamically stable in the region between lines **a** and **b**. At potentials above line **b**, it oxidizes (decomposes with the release of O_2), and below the line **a** it is reduced (decomposes with the release of H_2). All metals whose potentials lie below line **a** can corrode with hydrogen nd oxygen depolarization, metals with potentials between lines **a** and **b** - only with oxygen depolarization, while metals (Au, Pt, Ag) whose potentials are above line **b** do not corrode neither with oxygen nor with hydrogen depolarization. They can corrode only if they are in contact with another depolarizer whose oxidation-reduction potential is more positive than the potential of these metals. At the bottom of the diagram is the region I of thermodynamic stability (immunity) of iron. Regions II and III are the zones of stability of Fe^{2+} and Fe^{3+} respectively, i.e. in these regions iron is thermodynamically unstable and can corrode with formation of Fe^{2+} and Fe^{3+}, i.e. these are corrosion regions. In areas V and VI, respectively, $Fe(OH)_2$ and $Fe(OH)_3$ are stable. These are areas of passivity. In them, iron is thermodynamically unstable, but its corrosion rate is low due to the presence of protective layers of the corresponding hydroxides. Region IV (at very high pH) is also a corrosion region corresponding to the thermodynamic stability of $HFeO_2^-$.

Purbe diagrams exist for all technically important elements. With the help of Pourbaix diagrams for the various metals, the thermodynamic potential for corrosion, the possible cathodic reaction, the expected corrosion products and the rational directions for corrosion control can be determined - changing the potential of the metal (electrochemical protection), changing the pH of the medium or addition of oxidizers.

Pourbaix diagrams represent the theoretical possibility / probability of corrosion of a given metal or alloy in a given corrosion situation if the chemical composition of the corresponding corrosion environment is known. From a practical point of view, it is important to understand that the corrosion environment is not constant and can change over time and with changing conditions. It is also important to consider that there are differences between the parameters of the corrosion medium inside its volume and the parameters of this medium near the corroding surface - the latter are the ones that actually act most strongly on the corroding metal.

It should be emphasized, however, that the determination of the corrosion region by the Pourbaix diagram for a given metal is only an indication that that metal is thermodynamically unstable under the relevant conditions and may corrode. But only the area of immunity can be determined with some certainty. In the areas of corrosion and passivity, kinetic factors control the rate of formation and dissolution of films on the surface of the corroding metal and are a more important factor in the progress of the corrosion process than the thermodynamic stability of the formed metal oxides and hydroxides.

The diagram *does not give information about the actual corrosion rate.* The rate of corrosion is determined by electrochemical kinetics.

2.2.2.3. Kinetics of corrosion proceeding by an electrochemical mechanism

2.2.2.3.1 Corrosion polarization diagrams

Corrosion reactions include the transition of e^- and ions between the metal and the solution, and the speed of this transition is equivalent to the generated electric current. The rate of these reactions depends on the potential difference between the metal and the solution, i.e., from the electrode potential of the metal. As described above, the corrosion destruction is due to the operation of the spontaneous corrosion GCs. The current generated as a result of the operation of a given corrosive GC is called the *corrosion current* - I_{cor} and it is a measure of the rate of the ongoing corrosion.

Diagrams built in potential / current coordinates and graphically expressing the dependence of the potential of the anode and cathode on the magnitude of the current in the corrosion cell are called *corrosion polarization diagrams = diagrams of Evans* - diagrams with a mixed potential (Fig. 6). According to the mixed potential theory, any electrochemical reaction can be divided into separate oxidation and reduction reactions, which occur without a general accumulation of electric charge. In the absence of an externally applied potential, the oxidation of the metal and the reduction of the oxidizing component present in the solution occur simultaneously at the metal / electrolyte interface, the total measured current being zero and the corroding metal being electroneutral. Therefore, in this case, the flowing anodic (characterizing the dissolution of the metal) and cathodic (characterizing the corresponding reduction reaction current) are equal, but their densities may be different for different areas of the anode and cathode. In most studies, the data concerning the corrosion current is presented as the corrosion current density i_{cor}, but in the Evans diagrams one works with the absolute values of the current, since then the electric charges can be balanced. The coordinates of the intersection of the anodic curve (A) and the cathodic polarization curve (C) correspond to the stationary corrosion potential of the metal (the potential due to the corrosion of the metal) - E_{cor} and the maximum corrosion current I_{cor}. In corrosion with H_2 depolarization, with negligible resistance of the corrosion GC, the corrosion current coincides with the maximum possible current $I_{cor}=I_{max}$ - Fig. 6a, and with significant resistance it is determined by the resistance, as $I_{cor} < I_{max}$ - Fig. 6b.

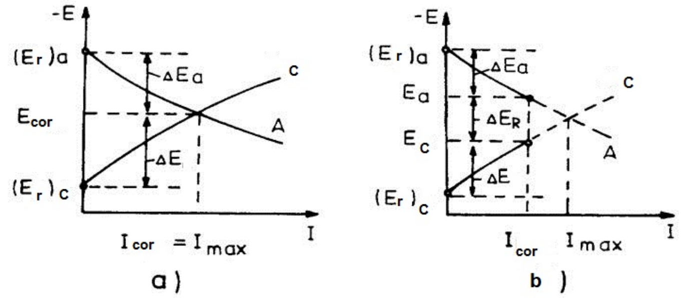


Fig. 6. Corrosion polarization diagrams for: a) ongoing corrosion, with hydrogen depolarization at negligible resistance of the corrosion GC (R=0); b) ongoing corrosion, with hydrogen depolarization at significant resistance of the corrosion GC (R≠0).

In O_2 depolarization corrosion, the maximum corrosion current, and therefore the corrosion rate, is determined by the cathodic reaction and more precisely by the rate of diffusion of O_2 to the corroding surface.

Evans diagrams are used to explain and qualitatively predict the influence of various factors changing the course of polarization curves on E_{cor} and I_{cor}. Corrosion polarization diagrams are constructed from experimental data collected using a potentiostatic setup. Graphical determination of E_{cor} and i_{cor} ($i_{cor} = I_{cor} / S$, S - electrode surface) using experimental data is shown schematically in Fig.7.

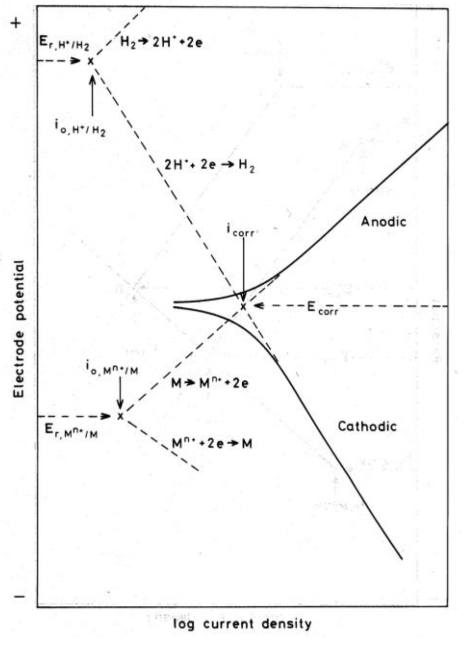


Fig. 7. Graphical determination of corrosion potential and current

The obtained data for the anodic (metal dissolution) and cathodic (H^+ reduction) polarization curves are plotted on a common diagram. The case of a metal corroding in an acidic environment is presented in Fig 7 - the solid curves. The current and the corrosion potential are determined by the coordinates of the intersection of the continuations of the rectilinear Tafel sections of the curve E = f (log i). The determination of the equilibrium potentials and exchange currents of the reaction of hydrogen depolarization and dissolution of the metal is represented by dotted lines.

When polarizing the corroding metal (shifting its potential from E_{cor} using a potentiostat), its potential is a linear function of the current density when the shift is small (in the order of 10 mV). The slope of the linear part of the polarization curve dE/di is called the polarization resistance R_p.

The measurement of R_p is used to determine the instantaneous rate of corrosion. It is inversely proportional to the corrosion rate, expressed as corrosion current density:

$i_{cor} = B / R_p$ (100),

where the constant B is determined electrochemically or by the weight method.

Further polarization of the corroding metal (more than 10 mV) leads to deviations from the linear dependence between the potential and the current density and reaches the logarithmic dependence described by the Tafel equation - dependence (59), as for the case of corrosion instead of with E_r, we work with E_{cor} and the constant a = i_o, determined at E_{cor}. If the experimental curve is described by the the Tafel dependence this is an indicator that only one corrosion reaction (anodic or cathodic, depending on the direction of polarization) actually takes place on the electrode, and the rate of the other reaction is negligibly small.

Fig. 8 shows a corrosion polarization diagram of a metal corroding with oxygen depolarization. The maximum corrosion current is determined by the limiting diffusion current.

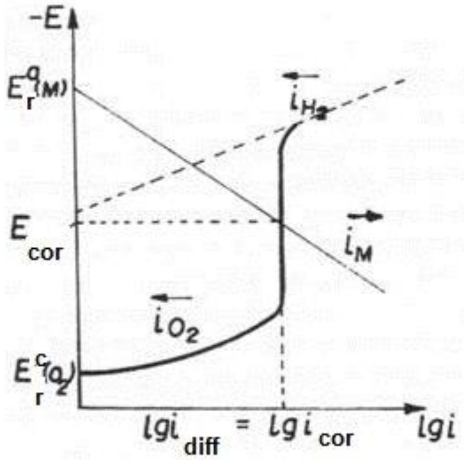


Fig. 8. Corrosion polarization diagram for determination of limiting diffusion current

Figures 7 and 8 illustrate case where a pure metal corrodes and there is only one depolarizer in the medium. In technical metals and alloys, oxidation of two (or more) metals is possible, or in the medium, more than one cathodic depolarizing process is possible. Then the anodic curves (for the oxidation of the individual metals) and the cathodic curves (for the individual processes) are summed and the corrosion current and potential are determined by the coordinates of the intersection of the summed anodic and cathodic curves.

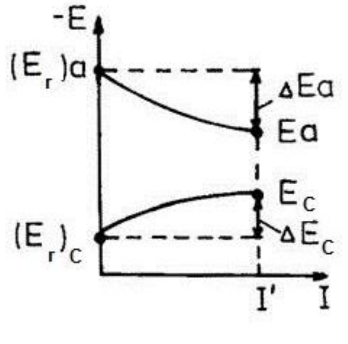
2.2.2.3.2 *Polarization of a corrosion galvanic cell*

The rate of corrosion depends on the performance of corrosion GCs. Theoretically, the current (I) generated by GC can be calculated by Ohm's first law

$I = (E_{r(c)} - E_{r(a)}) / R$ (101),

where $E_{r(c)}$ and $E_{r(a)}$ are the equilibrium potentials of the anode and cathode, R – the resistance of the GC.

The operation of any GC, including the corrosion GC, is hampered by the polarization of its electrodes, which leads to a decrease in the corrosion current, i.e., of corrosion destruction. The polarization of the anode (ΔE_a) and cathode (ΔE_c) is represented by the expressions:



$\Delta E_c = E_{r(c)} - E_{(c)}$, $\Delta E_a = E_{(a)} - E_{r(a)}$,

where $E_{(a)}$ and $E_{(c)}$ are the anode and cathode potentials when a corrosion current I' flows through the corrosion GC, the so-called effective potentials (Fig. 9) and:

$I' = (E_{(c)} - E_{(a)}) / R < I$ (102).

Fig. 9. Polarization of the electrodes of a corrosion galvanic cell

The change in the initial difference between the potentials of the electrodes of the corrosion GC, leading to a decrease in the flowing corrosion current, is called the *polarization of the corrosion GC*. Polarization is due to difficulties in one of the stages of the ongoing anodic and cathodic reactions. The reason for the cathodic polarization can be delayed consumption of electrons by the depolarizer (compared to their release from the corroding metal) - *activation polarization* or delayed diffusion of the depolarizer from the volume of the solution to the surface of the corroding metal - *concentration polarization*. The reasons for the anodic polarization can be: (a) slowing down of the ionization reaction of the corroding metal - *activation polarization*; (b) slowing of the diffusion of metal ions from the surface of the corroding metal to the volume of the corrosion medium – *concentration polarization* and (c) emergence of anodic passivity – *passivation polarization*. Anodic polarization causes the measured corrosion potential to be more positive than the corresponding standard equilibrium potential of the same metal. The total cathodic and total anodic polarizations are the sum of the respective polarizations. The activation polarization is described by the Tafel equation applied to the anodic or cathodic reaction respectively:

$\Delta E_{a, act} = a_a + b_a . \lg i_a$ (103)

$\Delta E_{c, act} = a_c + b_c . \lg i_c$ (104).

The concentration polarization is described for the anodic and cathodic reactions respectively with dependences (105) and (106):

$\Delta E_{a, conc} = [(R . T) / (n . F)] . \lg (a'_{Me^{n+}} / a_{Me^{n+}})$ (105)

$\Delta E_{c, conc} = [(R . T) / (n . F)] . \lg (a_D / a'_D)$ (106),

where $a'_{Me^{n+}}$ and $a_{Me^{n+}}$ - the activities of the metal ions of the corroding metal at its surface and in the volume of the electrolyte, respectively; a_D and a'_D – the activities of the depolarizer in the volume of the electrolyte and on the surface of the corroding metal, respectively; R, T, n and F have the usual meanings.

The anode (ΔE_a) and cathode (ΔE_c) polarizations are determined graphically using the corrosion polarization diagrams as shown in Fig. 9. Using the diagrams, the ohmic voltage drop ΔR can also be determined when R is significant ($R \neq 0$).

The general corrosion process consists of inextricably linked anodic, cathodic and current flow processes (which depend on the resistance of the medium). Generally, the most effective corrosion protection is achieved by further hindering the limiting=controlling stage of the general corrosion process. It is therefore essential to know which is the controlling stage.

The degree of control (C_a, C_c or C_R) of the general corrosion process of a given stage is determined by the dependencies:

$C_a = \Delta E_a/(E_{r(c)} - E_{r(a)})$ (107);

$C_c = \Delta E_c/(E_{r(c)} - E_{r(a)})$ (108);

$C_R = \Delta E_R/(E_{r(c)} - E_{r(a)})$ (109).

The stage with the greatest degree of control determines the rate of the entire corrosion process. Knowledge of the controlling stage is necessary to properly influence (slow down) the corrosion process. As a rule, in most cases the controlling stage is influenced in such a way as to be hindered.

There is a direct relationship between the corrosion effect (loss of metal per unit corroding surface) and the action of corrosion microgalvanic cells. If we denote by **d** the corrosion effect caused by the action of one cell, by I_{cor} - the corrosion current of the same element, by τ - the time of the cell's action, the relationship between the current and the corrosion effect is represented by the expression:

$d = k_e . I_{cor} . \tau$ (110),

where k_e is the electrochemical equivalent of the metal. If we denote by N the number of active corrosion cells on a unit of metal surface and take into account the polarization of the electrodes leading to a decrease in the maximum corrosion current for each of the corrosion GCs, for the total corrosion effect D per unit surface we get:

$D = N \,.\, d = N \,.\, k_e .\, \tau \,.\, (E_{r(c)} - E_{r(a)}) / (\Delta E_c + \Delta E_a + \Delta E_R)$ (111).

Corrosion processes of technical metals, alloys and structures made of different (not isolated from each other metals) comprise the operation of multi-electrode galvanic elements. The component with the most negative potential is the (main) anode and the component with the most positive potential is the (main) cathode. The behavior (anode or cathode) of the remaining components depends on a number of factors (the composition and resistance of the corrosion medium, the ratio of the areas of the various components, the polarization characteristics of each of the components, the internal resistance of the structure, etc.). Patterns in a multi-electrode corrosion system are determined by constructing a corrosion diagram on which the polarization curves of each component are plotted and summed. The current and corrosion potential of the system are determined by the coordinates of the cross point of the averaged anodic and averaged cathodic polarization curves. All electrodes whose initial electrode potentials are more negative than the thus determined corrosion potential are (intermediate) anodes, and all electrodes whose initial electrode potentials are more positive than the corrosion potential are (intermediate) cathodes. All factors contributing to an increase in the potential of the main cathode (stirring, addition of an oxidizer) reduce relatively the potential of the intermediate cathodes and can turn them into anodes. Increasing the area of the main cathode relative to the main anode can turn intermediate cathodes into anodes and vice versa - intermediate anodes can become cathodes when the area of the main anode is increased relative to that of the main cathode. The greater the electrical resistance of the system (high internal resistance, contact with a weakly conductive aggressive medium, the presence of weakly conductive layers between the contacting metals of the structure), the smaller the influence of the polarization of the individual electrodes and the greater the influence of the initial difference between the electrode potentials of the base electrodes and of the electrical resistance. The greater the electrical resistance of a given electrode, the less the influence of this electrode on the work of the other electrodes of the system, and the weaker their influence on it. The smaller the area of a given electrode, other conditions being equal, the weaker the influence it can have on the performance of the other electrodes. The stronger the polarizability of a given electrode, the weaker its influence on the other electrodes of the multi-electrode system. At low external resistance or with close external resistances of all electrodes, the intermediate electrodes located closer to the main cathode have a greater chance to become anodes, and those located closer to the main anode - to become cathodes. Factors reducing cathodic polarization (increasing the oxidizing power of the medium, lowering the pH, increasing the total electrical resistance, increasing the area of the cathodes) enhance the work of the main cathode (cathodes) and thus promote the conversion of weak cathodes into anodes, i.e. lead to an increase in the number of anodes in the system. The inclusion of a new, stronger cathode leads to the same result. Conversely, an increase in cathodic polarization leads to a weakening of the performance of the cathodes and the conversion of weak anodes into cathodes. The disconnection of a strong cathode from the system also leads to such a result. Raising the potential of the anodes at the expense of anodic polarization or excluding the strongest anode from the system or reducing the area of the anodes leads to the conversion of weak cathodes into anodes. Incorporating a new strong anode into the system or reducing the anodic polarization leads to the conversion of weak anodes into cathodes.

2.2.2.3.3. Passivity

Under certain conditions, metals can pass into a passive state. *Passivity* is a state of increased corrosion resistance of the metal (in conditions where, from a thermodynamic point of view, it is fully reactive), caused by slowing down of the anodic process. A diagram of a metal prone to anodic passivity is presented in Fig. 10.

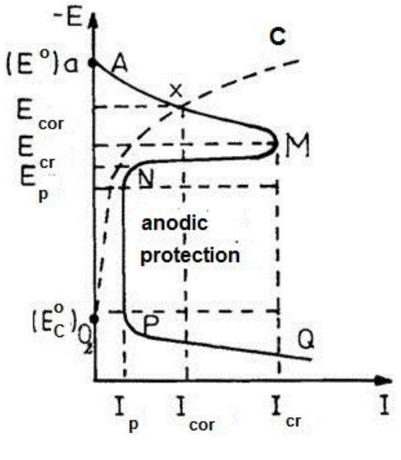


Fig. 10. Corrosion diagram of a metal prone to anodic passivity

The passivity is not due to a high thermodynamic resistance of the metal and is not caused by a hindrance of the cathodic process as a result of polarization. It most often occurs when the metal comes into contact with strong oxidizing agents.

The passive state has the following characteristic features: a) the rate of corrosion of the metal sharply decreases, but the corrosion process continues; b) the potential of the metal shifts significantly in the positive direction; c) the passive state is most often associated with the action of oxidizers (oxygen, chromates, dichromates) or external anodic current; d) the presence of halides, the impact of an external cathodic current, mechanical stresses can disrupt the passive state, i.e. cause depassivation; e) the increase in the temperature of the corrosion environment makes passivation difficult; f) some metals are self-passivated (Al, Cr, Ti) under the influence of air or solutions containing dissolved oxygen, others are passivated under certain conditions (Mo, Ni, Fe). The passive state caused by the action of oxidizers-passivators is called *chemical passivity*. Passivity induced by the action of an external anodic current is called *anodic passivity*.

Point X in Fig. 10 corresponds to the spontaneous corrosion of the metal. Its coordinates give the corrosion current and the corrosion potential. At point M, the metal begins to passivate (its coordinates give the critical values of the current I_{cr} and the potential E_{cr}). The value of the critical passivation potential (the primary passivation potential) depends on the acidity of the corrosion medium, and when the pH of the electrolyte increases by one unit, it is usually shifted by 60 mV in the negative direction. E_{cr} also depends weakly on the composition of the corrosion medium, especially on the content of Cl^- ions, which induce localized destruction of the passivating oxide film. At a concentration of aggressive ions significantly exceeding the concentration of ions that stabilize the passive state, i.e. oxidizers, active development of pitting corrosion is possible. The corrosion current increases rapidly even before the transpassive region is reached. The region NP starting from the potential of complete passivation E_p (often called Flade potential) is a region of passive state, and the corrosion current corresponding to this state I_p is much smaller than I_{cor}. The $E^o{}_{(a)}$M region is called the active dissolution region. The curve PQ (transpassive region) corresponds to a new anodic process (evolution of O_2 by the reaction $4OH^- \rightarrow 2H_2O + O_2 + 4e^-$), and not to dissolution of the metal. If a peak in the corrosion current is observed in this region of the experimental curve of a given metal (or alloy, e.g. Cr-alloyed steel), it is related to the oxidation of the metal or the alloying component.

The passivity is explained by the occurrence on the metal surface of an adsorption or phase protective oxide layer, which hinders the transition of metal ions in the solution, but does not prevent the movement of e^- through it. Alloying the metal with a more easily passivable metal facilitates the passivation of the former, e.g. the alloying of Fe with Cr. The tendency to form such a film depends on the standard electrode potential of the corresponding metal oxide. Usually, these potentials for the different metals change parallel to the standard potentials of the metals, but there are also exceptions related to the solubility of the corresponding oxide and to the presence and action of corrosive-aggressive ions.

2.2.2.3.4. Peculiarities of corrosion processes occurring with hydrogen depolarization

In most cases, soluble corrosion products are produced and the metal surface is in an active state, so the corrosion rate and associated losses are significant. Cathodic polarization is mainly due to difficulties in the H^+ reduction reaction, and in this case the measure of the displacement of the potential of the corroding electrode from its stationary potential is called the *hydrogen overvoltage* η_{H_2}. The value of η_{H_2} significantly affects the rate of the corrosion process. The characteristics of corrosion (of metals) occurring with hydrogen depolarization are:

1) The rate of corrosion is weakly dependent on the agitation of the corrosion medium, especially in acidic media;

2) The corrosion rate is highly dependent on the pH of the medium (since $E_{2H^+/H2}$ and η_{H_2} are highly pH dependent), generally increasing as the pH decreases.

3) The rate of corrosion strongly depends on the nature of the corroding metal and mainly - on the cathodic impurities in it (the lower η_{H_2} on them, the corrosion proceeds at a greater rate);

4) The rate of corrosion increases with time, due to the exhibition of additional cathodic areas on the surface of the metal, as a result of its dissolution;

5) There is a possibility of hydrogen embrittlement.

2.2.2.3.5. Peculiarities of corrosion processes occurring with oxygen depolarization

In O_2 depolarization corrosion, cathodic polarization can be attributed to two factors:

1) Difficulties in the O_2 ionization reaction. In this case, the measure of polarization is called the *oxygen ionization overvoltage*; The overvoltage depends on the material of the electrode and the condition of its surface, the temperature and the density of the flowing current, and the last dependence is described by equation (104).

2) Difficulties in supplying O_2 to the cathodic sections of the corroding metal. In this case, we speak of concentration polarization due to delayed diffusion of O_2 to the metal surface. The polarization is described by dependence (106), where n=4. At the maximum possible (for the given conditions) rate of diffusion, the maximum possible corrosion current, called limiting current, is reached. It corresponds to the maximum possible corrosion rate under the given conditions. In this case, the boundary diffusion current is described by equation (73), and the relationship between it and the polarization – by dependence (74), and in both cases the number of exchanged e^- is 4.

The main features of corrosion occurring with O_2 depolarization are:

1) The rate of corrosion strongly depends on the agitation and movement of the electrolyte;

2) The nature of the cathodic and anodic sections and the ohmic resistance of the electrolyte have little effect on the rate of corrosion;

3) The rate of corrosion depends on the dimensions of the cathodic areas - when using macrocathodes, the rate of corrosion is proportional to their area, and when using microcathodes - to their linear dimensions;

4) There is a possibility of the occurrence of corrosion GC due to uneven aeration (the cathodic process takes place on the more strongly aerated sections of the metal surface, and the anodic process on the less aerated).

2.2.2.3.6. Internal factors effecting electrochemical corrosion

Internal factors include:

1) The nature of the metal - especially its equilibrium electrode potential - metals with a more negative potential corrode more easily; the cathodic reaction is the same for different metals in a given corrosion environment, the standard potential of the metal determines the course of the anodic reaction (provided that no corrosion-resistant oxide coating is formed on the metal surface, e.g. in solutions containing Cl^-) and from here the total corrosion rate – Fig. 11.

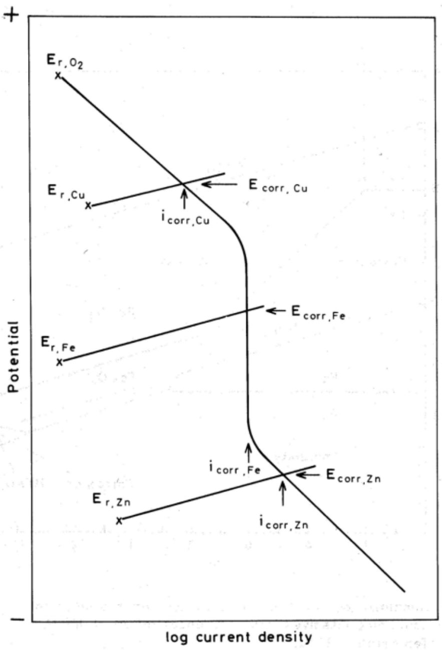


Fig. 11. Schematic polarization diagram illustrating the influence of the reversible electrode potential of Cu, Fe and Zn on their corrosion rate in an aerated solution containing Cl^-

Figure 11 shows that the corrosion potential becomes more negative and the corrosion rate increases in the order Cu < Fe < Zn, corresponding to the more negative values of the standard equilibrium potentials of these metals.

2) The state of the surface of the metal - the fine treatment of the surface increases the corrosion resistance of the metal, because it reduces its actual contact surface with the corrosive environment and facilitates the formation of uniform protective films on the metal surface. This factor manifests itself mainly in the initial stages of the corrosion process.

3) The composition and structure of the alloys - the anodic structural impurities (with a potential more negative than the potential of the base metal) do not significantly change the corrosion resistance of the alloy if they are in insignificant amounts and uniformly distributed or lead to local corrosion if they are located in separate sections of the metal. Cathodic structural impurities, in general, lower the corrosion resistance of the alloy if corrosion is controlled by the cathodic reaction.

4) The mechanical factor (microstructure, composition along the boundaries of the metal grains, residual stresses in the metal - from bending, during welding, during mechanical processing of the metal, including grinding) - in general, mechanical stresses reduce the corrosion resistance of the metal.

3. TYPES OF CORROSION DAMAGE

Depending on the type of corrosion damage, the following types of corrosion can be distinguished: a) general; b) local – point-like (pitting), localized biocorrosion, galvanic corrosion, etc; c) influenced by metallurgical factors - intergranular, selective; d) corrosion aided by the action of mechanical factors - erosion corrosion, fretting corrosion, corrosion cavitation; e) environmental cracking – stress corrosion cracking, hydrogen embrittlement, corrosion fatigue.

3.1. General corrosion

In general corrosion, the corrosion damage covers almost the entire metal surface in contact with the corrosion medium. It is observed when the naturally formed or artificial films on the metal surface dissolve in the corresponding corrosion medium or do not have good adhesion with the metal. General corrosion is uniform - corrosion proceeds at the same rate on the entire metal surface and uneven - corrosion proceeds at different rates on different sections of the metal surface - Fig. 12. This type of corrosion is responsible for destroying the largest amount of metal. It is relatively easy to measure (weight method can be used), predict and control (using suitable materials including coatings; inhibitors; cathodic protection; reduction of conductivity of the corrosion medium).

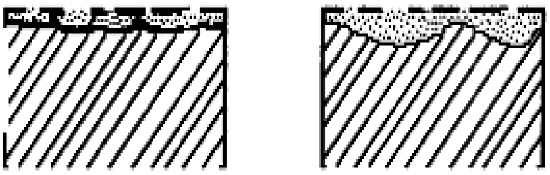


Fig. 12. Schematic of uniform (left) and non-uniform (right) corrosion

3.2. Local corrosion

Local corrosion covers only some areas of the metal surface - Fig. 13. It occurs at local destruction of resistant natural or artificial films existing on the metal surface. Local corrosion accounts for about 70% of corrosion damage, because the damage occurs without prior signs and in a relatively short time after the equipment is exposed. In spot corrosion, the destruction spreads over relatively large but comparatively shallow areas; in the case of pitting - the corrosion is in the form of individual small in area, but deep destructions.

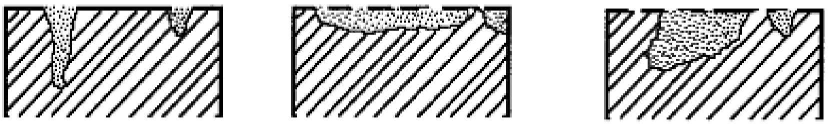


Fig. 13. Local corrosion - scheme: pitting - left, spot - middle and right

3.2.1. Pitting corrosion

In this type of corrosion, the corrosion destruction is in the form of separate points with a diameter of 0.1-2 mm and considerable depth (the diameter of the pitting is less than or equal to the depth) - Fig. 14. Pitting corrosion is one of the most destructive types of corrosion. Structures fail due to perforation, with relatively low overall metal loss. Pitting corrosion is relatively difficult to detect, due to the small diameter of the pitting or because they are covered with corrosion products. It is difficult to be predicted, measured and quantified due to variations in the number of pittings per unit area and their depth. Pitting can also be a cause of stress corrosion. Pitting corrosion is initiated by: local chemical or mechanical disruption of a protective oxide film; local change in the composition of the corrosion environment – low concentration of O_2, increased acidity, increased concentration of Cl^-; local destruction or poor-quality protective layer; local changes in the composition of the material – e.g. non-metallic inclusions in a metallic structure or inclusions of a more easily corroding metal in the parent.

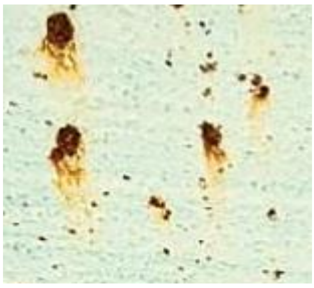


Fig. 14. Pitting corrosion

The depth of pitting is determined with a special micrometer or with a specially calibrated microscope. Qualitative determinations can be made by radiographic method. The weight method is not useful, and the results of applied stress tests can be misleading. The control over this type of corrosion is carried out by choosing a suitable material, ensuring a sufficiently high speed of movement of the fluids contacting the material or its frequent washing; control of the composition of the fluids contacting the metal and the use of corrosion inhibitors.

3.2.2. Crevice corrosion

Local corrosion is usually due to the presence of stagnant electrolyte near the metal (in cracks; under coatings; under deposits; in places where there are connections, clips, clamps) - Fig. 15. It is initiated by local changes in the composition of the electrolyte in the crack: decomposition of the inhibitor, reduction of the amount of O_2, acidification, accumulation of corrosive-aggressive ions, for example Cl^-.

The insufficient amount of O_2 in the crack cannot support the cathodic reaction and an anodic region forms in the crack. As a result of the anodic reaction, the environment in the crack becomes acidified and enriched with corrosive-aggressive ions. The rest of the metal acts as a cathode. Detection and monitoring of crevice corrosion is a difficult task. Special sensors are used. This type of corrosion is avoided by proper construction (without sharp edges, use of sealants, use of welds instead of bolts), selection of appropriate material.

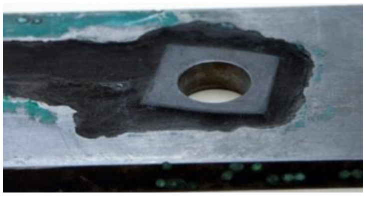


Fig. 15. Crevice corrosion of a facility in seawater (https://corrosion-doctors.org/Forms-crevice/Crevice.htm)

A special type of crevice corrosion is filiform corrosion, in which an aggressive corrosion environment is formed under the protective coating - Fig. 16. It occurs under paint coatings through which moisture has penetrated. Fast-drying paints are the most susceptible. Their use should be avoided unless their effectiveness has been proven through field trials. It starts with small, sometimes microscopic defects in the coating.

Fig. 16. Filiform corrosion
https://www.rustbullet.com.au/technical/how-it-works/introduction-to-corrosion-and-process/attachment/filiform-corrosion/

Compacted rust (Fig. 17) is a localized form of corrosion typical of components where crevice corrosion develops in atmospheric conditions – e.g., the rust between the steel sheets of bridges.

Fig. 17. Compacted rust

3.2.3. Galvanic corrosion

Rapid corrosion destruction, which is due to the operation of a corrosion galvanic element, that occurrs when two different metals (alloys) came into contact - Fig. 18. The two metals, before coming into contact, may corrode. When the contact is made, the corrosion of the more electronegative metal is enhanced, and the corrosion of the more electropositive metal is reduced or stopped. Destruction is especially dangerous when the ratio of the anode area to the cathode area is small. In order for galvanic corrosion to occur, the following conditions must be met:

Fig. 18. Galvanic corrosion

a) To have an electrolyte connecting the two metals which is not necessarily aggressive to the metals individually when not connected. The electrolyte can be a solution, a film of condensate, soil, a layer of corrosion products or sediments; b) there must be an electrical connection between the metals - direct electrical contact, through an insulated wire, through grounding, etc. It is not necessary for the metal connection to be immersed in the electrolyte; (c) Sufficient difference in the electrode potentials of the two contacting metals so as to produce a significant galvanic current.

The factors that effect galvanic corrosion can be grouped into several main categories:

- Properties of the material – composition, electrode potential, production conditions, surface condition, including the presence of protective natural and artificial films;
- Properties of the environment – composition (pH, electrical conductivity, biological components, presence of corrosive-aggressive ions, presence of pollutants), temperature, volume, speed of movement, duration of impact on the pair of metals, height of the electrolyte layer above the pair of metals, conditions for diffusion, migration and convection in the electrolyte;
- Geometric factors – ratio of the areas of the connected metals, distance between the metals, shape, type of connection (welds, clamps, separate metals but connected by an external connection).

The value of the electrode potential for each metal (alloy) is influenced by a number of factors (temperature, speed of movement of the electrolyte contacting the metal, presence of biocides, presence of complexing ions, pH, intensity of aeration, etc.). In the case of metals with close values of the corrosion potential, the ratio between their areas has a significant influence on it. The value of the difference between the potentials of the two contacting materials is not sufficient to predict the magnitude of the risk of galvanic corrosion. The rate of corrosion also depends on the kinetics of the process, which in turn depends on the flowing corrosion current.

Measures to protect against galvanic corrosion must be taken already at the construction stage. Its prevention is based on: a) selection of materials that are close to each other in the galvanic series; b) breaking the electrical contact between different metals - by using rubber, plastic insulation, wood, etc.; c) preventing the movement of the electrolyte around the contacting metals and the access of O_2 with a suitable coating at the places of the connections or by ensuring a dry environment and the impossibility of collecting electrolyte near the places of contact of the different metals; e) providing a maximum "anode area / cathode area" ratio; f) use of appropriate corrosion inhibitors; g) cathodic protection with sacrificial anodes; h) cleaning of the connected metal surfaces after welding, since residual fluxes can cause corrosion in the otherwise non-aggressive environment for the connected metals.

3.2.4. Corrosion due to the formation of concentration galvanic cells

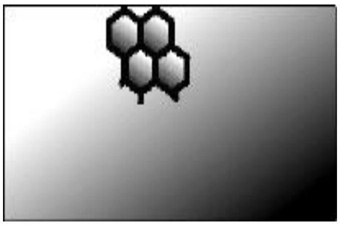
Concentration galvanic cells can occur in the presence of different concentrations of the corroding metal ions in the corrosion medium that contacts different parts of the metal surface. The part of the metal in contact with a solution with a lower metal ion content is the anode, and that part in contact with a solution with a higher metal ion content is the cathode. Concentration galvanic cells can also occur in the presence of different concentrations of dissolved O_2 in the corrosion medium. This type of corrosion occurs when two metal surfaces are in contact (e.g., under rivets, under bolts), in cracks, under layers of a different nature on the metal surface (bacterial slime, sediment of solids), in metal piles driven into the soil. The part of the metal in contact with more O_2 is the cathode and the part in contact with less O_2 is the anode. This type of corrosion is avoided by proper construction (use of sealants, use of welds instead of bolts), selection of appropriate material.

3.2.5. *Corrosion influenced by metallurgical factors*

3.2.5.1. Intergranular corrosion

Corrosion damage is concentrated at the boundaries between the crystal grains (while their interior remains unattacked) and leads to the separation of the metal grains from each other and to the loss of strength of the alloy - Fig. 19. It is caused by the segregation of impurities in the base metal, accumulated at the boundaries of the metal grains; from enrichment or depletion at the boundaries of one of the alloying elements - an example of the latter cause is the corrosion of Cr-alloyed steels due to the depletion of Cr in the boundary regions.

This type of corrosion can be prevented by selecting stable materials and controlling the heat treatment of the alloys.



A specific type of intergranular corrosion, the so-called "knife corrosion", that is observed in the welding of alloy steels, due to the interaction of Cr in the heat-affected areas with C from the steel. The problem is remedied by reheating the area heated during welding.

Fig. 19. Intergranular corrosion - scheme

A variety of intergranular corrosion is layer corrosion, which develops horizontally, parallel to the surface, mainly along the boundaries of metal grains, and the formation of corrosion products and destruction of the metal has a layered character - Fig 20. This type of corrosion affects mainly aluminum alloys.

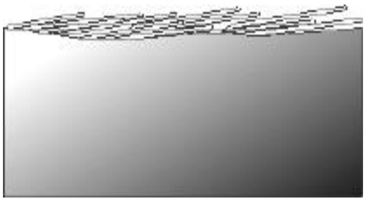


Fig. 20. Scheme of layered corrosion

3.2.5.2. Selective corrosion

There are two types: structural-selective, in which a given phase in a heterogeneous alloy is primarily destroyed (e.g. preferential dissolution of ferrite during corrosion of cast iron in acid) and component-selective, in which one of the components of the alloy is primarily attacked. The most common example is dezincification of brass. This type of corrosion is prevented by choosing a material suitable for the given conditions, reducing the aggressiveness of the corrosion environment, using coatings, applying cathodic protection.

3.2.6. Corrosion aided by the action of mechanical factors

3.2.6.1. Erosion corrosion

This type of corrosion represents an acceleration destruction of the metal, due to the movement of the corrosive fluid relative to the corroding surface - Fig. 21. Usually, this movement is quite rapid and leads to the inclusion of mechanical wear or abrasion. Natural or artificially created films on the metal surface are quickly destroyed.

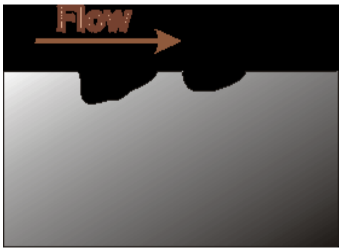


Fig. 21. Scheme of occurrence and development of erosion corrosion (https://corrosion-doctors.org/Forms-Erosion/erosion.htm)

The metal is separated from the surface in the form of ions or solid corrosion products, which are exfoliated mechanically. Erosion corrosion is characterized by the appearance of channels, waves, rounded holes, which are usually directed in a certain direction. Often this type of corrosion appears soon and unexpectedly (because the corrosion tests were done in static conditions and the erosive effect was not taken into account). Increasing electrolyte turbulence accelerates erosion corrosion. The high hardness of a given metal (alloy) does not necessarily mean high resistance against erosion corrosion. The development of this type of corrosion is prevented (reduced) by reducing the speed of movement of the corrosive fluid; removal of abrasive particles from fluids contacting the metal; reducing the roughness of the metal surface, smoothing the welds, appropriate construction (ensuring laminar flow; absence of sharp changes in the direction of fluid movement; inlet pipes for vessels should not be directed to the walls, but to the center; increase the thickness of the susceptible of this type of corrosion areas and ensuring their easy replacement); fluid deaeration; use of corrosion inhibitors; use of protective coatings and cathodic protection.

3.2.6.2. Fretting corrosion

This is corrosion destruction of the irregularities of contacting surfaces, caused by simultaneously applied load and small repetitive surface movement (e.g., caused by vibration). Pitting, channels, and oxide debris characterize this type of corrosion, typical of bolted machinery and equipment. This type of corrosion is also observed on contacting surfaces subjected to vibration - Fig. 22.

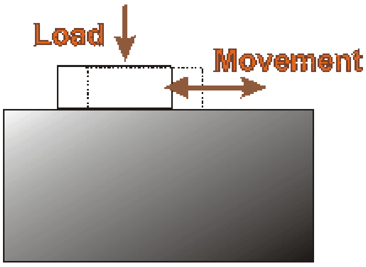
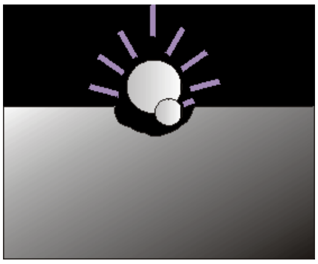


Fig. 22. Scheme of occurrence of fretting corrosion

Friction can destroy protective coatings and cause fretting corrosion. This type of corrosion is avoided by avoiding vibration, lubricating the metals in the rubbing section, increasing the load between the surfaces in order to stop the movement, surface treatment of the metals, which leads to an increase in the coefficient of friction.



3.2.6.3. Corrosion cavitation

Cavitation is observed when the working pressure of the fluid falls below its vapor pressure, which leads to the formation of gas bubbles and their bursting - Fig. 23.

Fig. 23. Corrosion cavitation - scheme of genesis

This type of corrosion is found in pumps, valves, pressure regulators, pipelines (especially elbows and extensions), near ship propellers. The fight against this type of corrosion is carried out by selecting a suitable material in terms of composition and structure; design leading to reduction of hydrodynamic pressure gradients and avoidance of sharp reduction in fluid working pressure; use of resistant coatings and cathodic protection.

3.2.7. Environmental corrosion cracking

Generally, environmental corrosion cracking is called a failure due to a combination of conditions that can lead to one of the following types of corrosion - corrosion cracking, corrosion fatigue, hydrogen embrittlement. Cracks appear and propagate at nearly right angles to the direction of the applied stress and at a stress much lower than that required to achieve the same failure without contact with a corrosive medium. The load-bearing section of the structure is reduced to the state of failure of the structure due to overload. It occurs in metals where, if they were not exposed to the action of a corrosive environment, destruction would not be observed or it would be very little. The stresses that cause corrosion cracking caused by environmental action can be residual (from the production of the metal, from its cold or hot processing, from welding, grinding, hardening); generated by reaction products or externally applied during operation of the facility (thermal cycling, thermal expansion, vibration, rotation, bolting, application of pressure) and must be tensile stresses to be effective.

3.2.7.1 Stress corrosion cracking

This is corrosion destruction, in which cracks (intergranular and trans-granular) appear in the metal as a result of the simultaneous impact of a specific (for the given material) corrosion environment and static mechanical tensile stresses - Fig. 24.

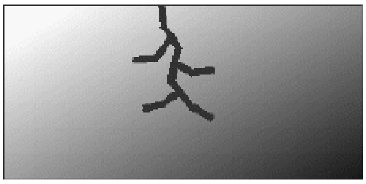


Fig. 24. Schematic of the occurrence of stress corrosion cracking (SCC)

This type of corrosion usually occurs under a specific combination of "given type of alloy - environment - stress".

Stress corrosion cracking is not inevitable. The most effective means of protection against SCC are: 1) Appropriate construction (avoiding stress concentrators, thermal and residual stresses), using suitable and properly processed materials in their manufacture (e.g. low alloyed mild steels are more slightly susceptible to SCC, compared to high-alloy steels, except for water containing Cl^-; 2) Reduction of the stresses acting on the metals by appropriate heat treatment or machining of the entire article or of critical areas (e.g. around welds); 3) Removal of critical from the point of view of the development of SCC environmental components (chlorides, hydroxides, dissolved O_2); 4) Avoiding stagnant areas and crevices where chlorides and hydroxides can concentrate. In addition, protective measures may include the use of appropriate protective coatings; application of cathodic protection; reduction of the temperature of the environment in contact with the product.

3.2.7.2 Hydrogen embrittlement

This type of corrosion represents a destruction of the metal as a result of the development of cracks caused by the existence of the combination "hydrogen inclusions in the metal in a critical concentration, applied tensile stresses, microstructure of metal that is susceptible to this type of corrosion" - Fig. 25.

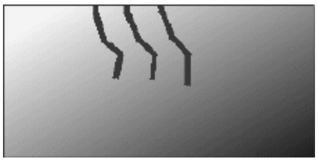


Fig. 25. Scheme of occurrence of hydrogen embrittlement

Examples of hydrogen embrittlement are the cracking of welds or high-strength steels when exposed to an environment where H_2 is generated or injected. Susceptible to hydrogen embrittlement are also titanium and aluminum alloys.

Sources of hydrogen leading to the appearance of hydrogen embrittlement are the cathodic reaction of hydrogen depolarization in corrosion processes, application of metal coatings, welding, phosphating, pickling, poorly controlled cathodic corrosion protection. This type of corrosion is also observed with a significant displacement of the potential of high-strength steels in a positive direction compared to the natural corrosion potential. Hydrogen diffuses easily into the metal crystal lattice due to its small size. It is attracted to those lattice sites that are under tensile stress. There, it promotes the destruction of the metal, possibly through the development of local deformation. This leads to an increase in the brittleness of the metal, the load resistance decreases. Usually, corrosion cracking due to hydrogen embrittlement develops very quickly, in the most extreme cases the speed is up to 1 mm/s. Only high-strength steels are susceptible to hydrogen embrittlement under static loading.

Measures to prevent this type of corrosion include using materials resistant to this type of corrosion; avoiding sources of H_2 (cathodic protection, pickling, some types of welding); heating the metal at 200°C for several hours to remove H_2; development of processes for the application of galvanic coatings in which no H_2 is released or the amount released is small.

3.2.7.3 Corrosion fatigue

Corrosion destruction (appearing as deep localized cracking) that is a result of the combined action of alternating cyclic stress and a corrosive environment - Fig. 26.

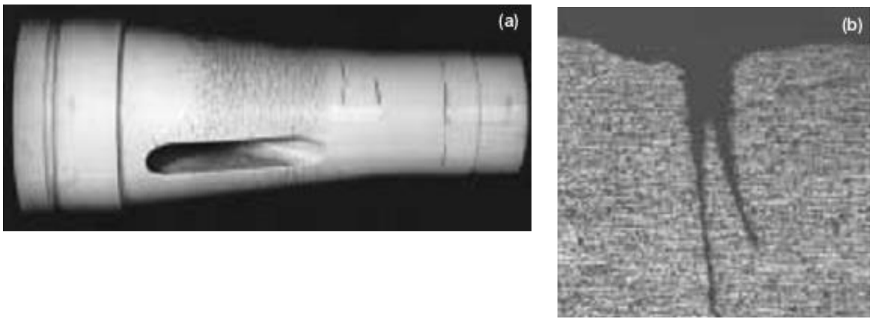


Fig. 26. Corrosion fatigue of a pump: left - general view; right - microsection (x 70)

It can be described as a reduction in the fatigue resistance of the material caused by the action of the corrosive environment. In a corrosive environment, the stress level at which a material can be considered to have an infinite life decreases significantly or disappears. In contrast to pure mechanical fatigue of a material, corrosion fatigue has no fatigue limit. Much lower stresses and much shorter failure times are observed in the presence of a corrosive medium than when alternating stresses are applied to the same material not in contact with a corrosive medium. Destruction can be reached even at low loads and after their short action.

4. CORROSION IN VARIOUS ENVIRONMENTS

The environment with which a metal or alloy contacts is a major factor that determines the type and intensity of corrosion. Minicomponents of the environment can be critical in terms of the development or termination of corrosion attack. The geographical location and climatic conditions during the construction or repair of the facilities are also of great importance.

4.1. Atmospheric corrosion

All corrosion processes taking place in a moist gas environment are called atmospheric corrosion. Generally, the average atmospheric corrosion rate of unalloyed steel ranges from about 0.048 mm/year in rural unpolluted areas, through 0.079 mm/year in marine unpolluted atmospheres to 0.170 mm/y in some industrial polluted atmospheres. In very dry areas it can be of the order of 0.003 mm/y. In principle, in all but the most aggressive atmospheres, the average corrosion rates of technical metals in atmospheric conditions are generally lower than the corrosion rates in water and soils. Often, constructions and machines that are only partially wetted or are periodically wetted and dried corrode faster than articles of the same metal that are continuously flooded with water or are under a thick layer of moisture. The explanation lies in the catalytic properties of the initially formed rust.

The corrosion products of iron and steel are called rust. In contact with an uncontrolled corrosive atmosphere, other metals also corrode. A green film of corrosion products containing hydrated sulfates, carbonates or chlorides of copper forms on the copper. The rate of corrosion is much lower than that of steels, but the dependence on the relative humidity of the atmosphere is similar. Aluminum shows very low atmospheric corrosion rates in most cases, but in the presence of alkaline copper salts or wood preservatives, it corrodes very rapidly in atmospheric conditions. The corrosion rate of zinc products that are fully exposed to atmospheric conditions is relatively low due to the formation of basic zinc carbonates or sulfates with protective properties. However, with increased concentrations of SO_2 in the atmosphere or in the presence of conditions leading to increased condensation, the rate of corrosion increases significantly. Stainless steels (containing at least 12% Cr) have increased resistance to atmospheric corrosion, austenitic alloys (containing 8% Ni and 18% Cr) are even more resistant, and alloys containing an additional 2-3% Mo practically do not destroy in industrial atmospheres. Low alloy steels containing 0.2-0.3% Cu and other additives in small amounts corrode about 4 times slower than unalloyed steels and can be used unprotected in dry climates but not in wet climates / rainy conditions.

As a result of precipitation and condensation of water vapor from the air, as well as due to temperature differences on the metal surface, a layer of moisture is formed. The time of existence of this layer on the metal surface (Time of Wetness - TOW) is a very important parameter effecting the rate of atmospheric corrosion.

The layer of moisture facilitates corrosion processes. Atmospheric corrosion proceeds according to an electrochemical mechanism - the anodic reaction of metal destruction and the cathodic reaction, which is most often oxygen depolarization, are balanced. Oxygen from the atmosphere easily reaches the metal surface through the thin layer of electrolyte. The intensity of corrosion destruction and the rate of corrosion depend on the properties of the electrolyte formed on the metal surface, which in turn depend on the humidity and pollution of the atmosphere. Depending on the thickness of the layer of moisture on the metal surface, dry, moist and wet corrosion are distinguished. We speak of dry corrosion when the thickness of the moisture layer is below 10 nm. This type of corrosion takes place by a chemical mechanism, the corrosion damage is very small, practically it does not occur. Moist atmospheric corrosion is observed at a relative humidity of the atmosphere below 100% and a thickness of the moisture layer on the metal surface of 10 to 100 nm. The moisture layer is formed as a result of capillary, adsorption or chemical condensation. This mechanism is also observed in corrosion in a wet layer of corrosion products. It proceeds trough an electrochemical mechanism. The change in the mechanism of corrosion from chemical to electrochemical leads to a sharp acceleration of corrosion processes. Wet atmospheric corrosion occurs when the relative humidity of the atmosphere approaches 100% or when water directly falls the metal surface. A layer of moisture with a thickness of 1 μm to 1 mm is formed. This subtype proceeds by an electrochemical mechanism. The increase in the thickness of the electrolyte layer leads to an increased cathodic polarization, due to difficulties in the transport of O_2 to the metal surface, i.e. to a decrease in the corrosion rate.

The rate of corrosion depends on the magnitude of the local current in the corrosion micro galvanic cells and on the number of these cells. The magnitude of the local current depends on the efficiency of the cathodic process, the efficiency of the anodic process and the magnitude of the ohmic resistance. The efficiency of the cathodic process is in most cases determined by the rate at which oxygen depolarization occurs, which in practice is determined by the rate of O_2 diffusion to the metal surface. The small thickness of the moisture layer on the metal surface facilitates diffusion and increases the efficiency of the cathodic reaction, and therefore of the overall corrosion process. With very thin layers of moisture (e.g. with adsorption layers of moisture) on the metal surface, the reduction of oxygen (O_2+$2H_2O$ + $4e^-$ = $4OH^-$) becomes difficult, due to a lack of water. It should be considered that SO_2, Fe^{3+} can also act as cathodic depolarizers. The efficiency of the anodic process decreases with a decrease in the thickness of the layer of moisture on the metal surface, due to: a) the appearance and subsequent increase of concentration polarization, since the thin layer of moisture contains an insufficient amount of anodic depolarizers; b) anodic passivation as a result of practically unhindered (in the beginning) reaching of O_2 to the metal surface; c) lack of moisture to maintain a normal anodic process. As the thickness of the moisture layer decreases, the ohmic resistance increases. This leads to a reduction in the radius of action of the microcathodes and microanodes and to a relatively uniform nature of corrosion damage. In summary, in general - in wet atmospheric corrosion (corrosion under a visible layer of moisture) the cathodic reaction with the rate-determining step the diffusion of oxygen to the metal surface is controlling. In moist atmospheric corrosion, the anodic reaction is controlling. The ohmic factor has a significant influence only in relatively dry conditions and is of greater importance only in smaller sizes of micro galvanic sections.

The thickness of the electrolyte layer formed on the metal surface and its electrical conductivity depend on the relative humidity of the atmosphere, the presence of pollutants, the hygroscopicity of corrosion products.

The factors that affect the rate of atmospheric corrosion are:

a) The relative humidity of the atmosphere - in most cases, the increase of the relative humidity above some critical value leads to a sharp increase in the rate of corrosion. This critical humidity is not a constant value and depends on the pollution of the air, being lower at more polluted air. It usually fluctuates between 60-75%. The critical humidity value also depends on the type of corroding material, the hydroscopic properties of the corrosion products, and the substances naturally deposited on the corroding metal surface.

b) The temperature and its variation - the increase in temperature accelerates atmospheric corrosion, *if* drying of the metal surface does not occur. The influence of temperature on atmospheric corrosion is not unambiguous. An increase in temperature leads to an increase in the rate of corrosion, due to the acceleration of electrochemical reactions and diffusion processes. At constant relative humidity, an increase in temperature will accelerate corrosion. On the other hand, an increase in temperature generally leads to a decrease in the relative humidity of the atmosphere and a faster evaporation of the electrolyte layer formed on the metal surface. The time during which a layer of moisture exists on the metal surface with the necessary thickness, facilitating the corrosion processes, is reduced - and from there, the rate of the entire corrosion process decreases. It has been shown that in confined spaces an increase in relative humidity due to a decrease in temperature has a predominant effect on the rate of corrosion. This means that cooling the air through air conditioning, without taking additional measures to reduce the humidity of the atmosphere, leads to the acceleration of atmospheric corrosion.

c) Presence of various air pollutants – solid particles, salty fog and gases. Solid particles (dust, sand, soot, welding residues) accelerate corrosion, especially in the initial stage, through their role as centers of condensation of atmospheric moisture and as sources of corrosion-acting anions. In addition, C-containing solid particles can act as additional microcathodes. Polluting gases (SO_2, H_2S, NO_x, CO_2, NH_3, HCl, Cl_2) play the role of depolarizers or create an acidic electrolyte environment with moisture from the air. Hydrogen sulfide is extremely aggressive towards most metals/alloys; HCl and Cl_2 in the presence of moisture lead to acidification of the environment and to more intense corrosion, compared to the case of the presence of chlorides in the atmosphere. Various salts (of natural origin - in the marine atmosphere or of anthropogenic origin), most metal oxides, plant fibers, many polymers have hygroscopic properties and their presence on the metal surface leads to acceleration of corrosion in a humid atmosphere.

d) The atmospheric conditions under which the product is initially exposed to the action of the corrosive atmosphere (winter-summer, rainy-dry period).

e) The protective properties of the obtained corrosion products (depend on the nature of the metal, on the alloying additives) - e.g., in the case of iron (steel), at first the rate of atmospheric corrosion is small, then it increases sharply and decreases again with a significant thickness of the layer of corrosion products (with known protective properties, weaker in the presence of corrosive salts, e.g. chlorides) on the metal surface. For Cu, Sn, Pb, the "corrosion effect-time" curve has a parabolic character, which means that with an increase in the thickness of the layer of corrosion products, their protective effect does not increase.

f) The frequency of alternating between wet and dry conditions - more frequent alternation leads to acceleration of corrosion.

Corrosion in atmospheric conditions can be significantly influenced by local conditions - wind direction and speed, humidity, presence of dust, fibers, electrolytes. These local conditions can change significantly within just a few meters depending on the air turbulence grid (e.g., in winter around roads where anti-icing liquor is used).

The assessment of the corrosion aggressiveness of a given atmosphere is mainly carried out by two methods:

1. The first method (direct assessment of the corrosion aggressiveness of the environment) consists in exposing standard samples (a copper or steel bolt around which an aluminum wire is wrapped) in the corrosion environment and classifying the environment based on the established resulting corrosion destruction - so called CLIMAT samples and tests. Special attention is paid to the selection of the test site, the method of mounting (including the angle of exposure) and the collection of the specimens.
2. The second method involves measuring several parameters of the atmosphere and classifying the atmosphere by corrosive action based on the determined values using ISO 9223. The standard classifies atmospheres by corrosive action based on the time during which there is a layer of moisture on the metal surface (TOW) and based on the established concentrations of precisely defined air pollutants (SO_2, Cl^-). The standard is not used for extremely corrosive environments, e.g., the atmosphere in chemical or metallurgical plants. It applies to the natural environment. Although widely accepted and applicable, the standard also has shortcomings - it underestimates some and overestimates other factors affecting atmospheric corrosion.

The time during which there is a layer of moisture (TOW) on the metal surface is a key parameter that directly determines the duration of electrochemical corrosion. This is a complex parameter, since all the ways of formation and evaporation of the moisture layer on the metal surface must be taken into account. For the purpose of standardization, it is defined that there is a layer of moisture on the metal surface at a relative humidity above 80% and a temperature above 0 ^oC. The measurement unit for TOW is hours/year during which the relative humidity (RH) > 80% and the temperature is > 0 ^oC – resulting in a categorization where the most aggressive environments are of the highest category. The 0 ^oC limit is artificial and does not take into account the corrosion that occurs in cold climates when using anti-icing salts. It should be noted that TOW depends not only on the relative humidity of the atmosphere and temperature, but also on the hygroscopicity of the corrosion products.

Chloride ions falling on the metal surface can directly accelerate the corrosion process, more important from a practical point of view is the initiation and development of pitting corrosion and crevice corrosion, compared to general corrosion. The average annual rate of chloride deposition on the metal surface, mg/(m^2day) is the parameter by which, according to ISO 9223, atmospheres are classified according to corrosion aggressiveness table.

Sulfur dioxide (SO_2) is important as a corrosive agent in rural and industrial atmospheres. It is adsorbed on the metal surface and due to its high solubility in water, in the presence of moisture, forms H_2SO_4 (acid rain). According to ISO 9223, the categorization of the atmosphere by corrosive action is based on the deposition rate of SO_4^{2-}, mg/(m^2day).

Depending on the corrosion rate (CR) of steel for one year, g/(m^2year) or for 20 years, μm/year, the atmosphere is classified into 5 categories.

According to ISO 9223, by combining the categories reflecting the corrosiveness of the atmosphere, estimated by TOW, the concentration of chlorides and the concentration of SO_2, it is possible to estimate the corrosive action of this atmosphere and convert it into a short-term corrosion rate, g/(m^2year).

Measures to protect against atmospheric corrosion include:

- Surface cleaning and protection from dust and dirt;
- Use of protective coatings (metal, enamel, conversion, paints, polymer). Coatings may contain additives that slow down the anodic or cathodic reaction;
- Use of alloys;
- Alloying;
- Appropriate construction;
- Reduction of the relative humidity of the atmosphere below 60% - by heating, by using chemical dryers and moisture sorbents;

- Maintaining an appropriate temperature and avoiding exposing the metal products to sudden temperature changes;
- Purification of the atmosphere from gaseous and solid pollutants;
- Use of volatile corrosion inhibitors.

4.2. Corrosion in soil

Corrosion in soil refers to all corrosion processes occurring in moist or wet soil. In general, the soil can be considered as an electrolyte, corrosion proceeds by an electrochemical mechanism, but with some peculiarities. The corrosion process is due to the operation of the following types of corrosion cells:

- Long-length macro-GCs caused by the different O_2 permeability of the different soil sections contacting the facility. In sandy soils, the access of O_2 is facilitated, as a result, oxide films with some protective properties are formed on the surface of the metal, and the part of the facility located in or in contact with this soil plays the role of a cathode - it does not corrode. The part of the structure located in clay soil plays the role of an anode - it corrodes.
- Macro-GCs due to local heterogeneity of the soil: Occurs in soils composed of inclusions of different size and composition. Anodic areas (i.e., corrosion damage) on the metal facility form below the inclusions with the lowest O_2 permeability. Corrosion in small anodic areas and large cathodic areas is especially dangerous, since then the anodic current density is very high (i.e., the destruction is deep).
- Macro-GCs due to differences in the depth at which the various elements of the structure are located. Such corrosive GCs can appear even in uniform soils, as a result of unequal aeration, and not only in vertically located structures, but also in horizontally located ones, as a result of differences in the topography of the area. It is more dangerous than corrosion due to the action of corrosive micro-GCs, which, as a rule, is more uniform. The anodic sections in these macro-corrosion cells, i.e., corroding parts of a lengthy structure, appear where less air permeability is observed.
- Macro-GC, due to the so-called "end effect" - to the ends of iron (steel) electrodes located in soil or in a liquid electrolyte, the access of O_2 is easier. This leads to some passivation of the metal surface and the formation of a cathodic region. In the middle of the structure, where the access of O_2 is less, an anodic section is formed, with significant corrosion damage.
- Micro-GCs due to microstructural heterogeneity of the soil.
- Micro-GCs due to structural microheterogeneity of the metal itself.
- Macro- and micro-GCs due to poor adhesion of corrosion products to the metal surface.

Usually, when the corrosion is due to the action of micro-GCs, the corrosion damages have a more uniform character, and when the cause is the operation of the macro-GCs, the corrosion damages have a local character. For small details, the effect of corrosion micro-GCs is of the greatest importance. In medium-sized equipment, corrosion is due to the operation of macro- and micro-corrosion couples. In very large and long underground facilities (e.g., pipelines), the action and importance of corrosion macro-couples prevails.

For most soils (except very light dry or very loose soils, or very thin soil layers on the surface of the corroding metal) cathodic control predominates, the main cathodic depolarizing process being oxygen depolarization, with the slowest step being diffusion of oxygen to the metal surface. In very loose and relatively dry soils, as the oxygen permeability of the soil increases, a gradual transition from predominantly cathodic to predominantly anodic control takes place. Ohmic or cathodic-ohmic control is only observed in corrosion in very dry soils.

Soil corrosion is a complex phenomenon, not fully understood, with many variables. The relative importance of these variables changes and differs from material to material.

The factors that influence soil corrosion are:

a) Soil porosity - in general, with greater porosity, corrosion is greater, due to better aeration (the amount of O_2 decreases with depth). For neutral and alkaline soils, O_2 concentration is an important factor because corrosion proceeds with O_2 depolarization. Excavation of soils can increase the corrosion rate by supplying more O_2 to the metal surface. A measure of the degree of soil aeration is the redox potential. Its high value is an indicator of high O_2 content. Its low value is a likely indicator of the existence of corrosion conditions under the action of anaerobic microorganisms. The measurement of the redox potential should be carried out with as little disturbance as possible to the natural integrity of the soil.

b) Electrical conductivity of the soil - in most cases, corrosion is higher with greater electrical conductivity of the soil. Soil resistivity generally decreases with increasing soil moisture and the concentration of various ions. The soil resistivity is widely used as an indicator of the corrosion aggressiveness of the soil – Table 3. It can be taken as a dominant parameter in the absence of action of microorganisms.

Table 3. Classification of soils according to corrosion aggressiveness depending on their resistance

Soils resisivity (Ohm-cm)	Corrosive action
>20,000	not corrosive
10,000 ÷ 20,000	very weak corrosive effect
2,000 ÷ 10,000	weak corrosion effect
1,000 ÷ 2,000	corrosive
500 ÷ 1,000	highly corrosive
<500	extremely corrosive

According to this classification, sandy soils have the lowest corrosion aggressiveness, and clay soils, especially those that are saline, have the highest. Soil resistivity *cannot* be considered as the only parameter influencing corrosion in soils. The high resistance of soils *does not* guarantee the absence of conditions for serious corrosion. The data in the table is only an indication that intense corrosion is not normally observed at high resistances. Soil resistivity is determined in different ways, the most commonly used being the 4-point method of Wenner (ASTM G-57 - 20). In order to predict the corrosion action of the soil, not only the value of its resistivity is essential, but also whether it changes along the given route. Corrosion of pipelines is significantly affected by changes in soil resistivity along the route, as opportunities are created for the development of corrosion macro-GCs. Parts of the facility that are in soil with lower resistance act as anodes and corrode. More quantitative information on existing infrastructure could be gathered through physical inspection, non-destructive testing and statistical analysis. For this purpose, in a predetermined number of places (depending on the length of the facility and the corrosive action of the soil), the soil above the facility along its extension is excavated. In the statistical processing of the data, pittings with the greatest depth are taken into account. This method is applied alongside the study of resistivity, soil moisture and other factors that affect soil corrosion in order to predict the intensity of expected corrosion problems.

c) Salts dissolved in the soil: salts containing depolarizing ions (e.g. Cl^-) accelerate corrosion because they directly participate in the depolarization of the anode and reduce the soil resistance. Concentrations above 50 ppm should be considered quite corrosive. The concentration of Cl^- in the soil electrolyte varies when the conditions in the soil change from wet to dry, and the influence of Cl^- on corrosion also changes accordingly. The presence of S^{2-} in the soil is an indicator of the existence of sulfate-reducing bacteria. The presence of SO_4^{2-} has a negative effect on metal structures, if there is a possibility that sulfates can turn into highly corrosive sulfides. The presence of SO_4^{2-} is particularly dangerous for concrete structures. Salts containing passivating ions (e.g. NO_2^-) slow down corrosion.

d) Soil moisture - moisture of the order of 16% and more is necessary to maintain the corrosion processes. Corrosion is facilitated with increasing soil moisture until the so-called critical moisture is reached. Corrosion then becomes more difficult due to the impeding of O_2 access to the metal surface. Critical moisture is different for different soil types and depends on the size and distribution of soil pores, soil structure and texture, and soil organic matter content; It is also different for different metals in contact with the same soil.

e) The acidity of the soil - usually the pH of the soil is in the interval 5-8. In this range, pH is generally not a dominant soil corrosion factor. A serious corrosion risk for common steels, cast iron and zinc-coated products are acidic soils, and as soil acidity increases, so does corrosion. In the case of soils with a relatively high total acidity (acidic humus, clay), it is assumed that this acidity can serve as a criterion for the corrosion aggressiveness of the soils. In soils with a pH of the water extract between 6 and 7.5 (as it is in most cases), the total acidity of the soil, including the content of organic acids, is a better indicator of the corrosion aggressiveness of the soil. The acidity of soils can also affect the solubility of corrosion products and the nature of microbiological corrosion. Alkaline soils contain high concentrations of Na^+, K^+, Mg^{2+} and Ca^{2+} and have a tendency to form carbonate deposits (with certain protective properties) on structures in the soil.

f) Temperature - in general, as the temperature increases, the rate of corrosion increases, until a condition is reached where the amount of soil moisture decreases to such an extent that this begins to impede the corrosion process. The rate of corrosion greatly increases when the aggregate state of soil moisture changes from solid to liquid (i.e., when the soil thaws).

g) The depth at which a facility is located - in general, the rate of corrosion increases with depth, but this increase is uneven and different for different types of soils and metals.

h) Presence of microorganisms - sulfate-reducing and iron-bacteria are particularly dangerous. As a result of the action of sulfate-reducing bacteria, the rate of soil corrosion can be much higher under anaerobic conditions than corrosion under aerobic conditions.

The difficulty in finding accurate relationships that describe the influence of different factors on soil corrosion is explained by the different way in which these factors affect macro- and micro-GCs elements. Table 4 summarizes the influence of various factors on the performance of corrosion micro-GCs. In general, soil with high humidity, high electrical conductivity, high acidity, high concentration of dissolved salts is the most corrosive-aggressive. Areas of lower aeration allow corrosion to develop under the action of sulfate-reducing anaerobic bacteria.

The American Water Association (AWWA) has developed a numerical scale for evaluating the corrosion aggressiveness of soils, and this scale is applicable to cast iron and steel (AWWA C-105 Standard). Depending on the values of the various parameters affecting corrosion, different points are awarded and when the sum of all points is > 10, it is necessary to take protective measures. The parameters included are soil resistivity, pH, redox potential, sulphide concentration and moisture.

The assessment of the corrosion aggressiveness of the soil can also be made based on the ratio $\Delta I / (\Delta L \,.\, \rho)$, where ΔI is the change in current when using a constant source for polarization of the structure with a potential of 1.1 V, ΔL – the distance along the length of the route, ρ - the average specific resistance of the soil in the given section.

It should be noted:

- Corrosion tests carried out on individual samples in different sections (different soils) do not give a correct assessment of the intensity of corrosion of long equipment passing through the same sections of soils in which the small samples are located.
- The characterization of the corrosion aggressiveness of soils compiled from the experience of operating old pipelines does not give a correct assessment of the corrosion aggressiveness of similar soils along other routes, where the soils may be located in a different sequence.
- In the case of small objects, the determination of the corrosion aggressiveness of soils can be made based on finding the anodic and cathodic polarization characteristics under the given conditions. At large sites, the determination of the corrosion activity of the soil can be based on the assessment of the change in O_2 permeability (or its proportional value, cathodic polarizability) along the length of the track and on the average ohmic resistance of the section.
- The ordering of metals by their equilibrium electrode potential can be used to judge which metal will corrode. However, *it should not be forgotten* that the so-called "galvanic series" refer only to a precisely defined corrosion environment. Therefore, in order to properly combine construction materials in soils, it is necessary to take into account the arrangement of metals and alloys according to the value of their equilibrium electrode potential in soil.

Measures to protect against soil corrosion include the use of various means: Appropriate construction; Use of alloys; Alloying; Application of electrochemical protection; Use of protective coatings (metal, paint, polymer, insulation, cement). Coatings may contain additives that slow down the anodic or cathodic reaction. The insulation coating of the pipelines must be especially good on the anode sections, otherwise the corrosion process will concentrate on the sections with poor quality coating and the corrosion damage in this case can be greater, compared to the case of no coating.

Other anicorrosion measures include:

Table 4. The influence of various factors on the operation of corrosion micro-GCs.

Nature of change in soil corrosion conditions	Anodic process	Cathodic process	Ohmic resistance	Total corrosion rate under the action of micro-GCs
Increase in soil moisture	Facilitates	Hinders	Decreases	Passes through a maximum
Increased aration (loose soil)	Hinders	Facilitates	Increases	Passes through a maximum
Increase in soil salinity (Na_2SO_4, NaCl)	Facilitates	Slightly hinders	Decreases	Usually increases
Increase in total acidity and decrease in pH	Facilitates	Facilitates	Increases	Increases
Increase in H_2S content	Facilitates	Facilitates	Increases	Increases
Activity of sulfate-reducing bacteria	Facilitates	Facilitates	Increases	Increases
Increase in soil resistivity	Does not change immediately	Does not change immediately	Increases	Almost does not change

- Modification of the soil that is in contact with the threatened facility - the goal is to make the soil uniform and with greater O_2 permeability;
- Reduction of soil acidity around the facility – e.g. by applying slaked lime or limestone to the soil;
- Isolation of the individual sections of a long structure at the transition from one section of the soil to another with highly differing values of O_2 permeability, which will reduce the probability of formation of corrosive macro-GCs caused by unequal aeration and therefore reduce the intensity of the corrosion. This measure is poorly effective if stray current flows through the threatened structure with a voltage sufficient to overcome the electrode potential jump of the isolated parts of the facility.
- Turning the pipes at 180 ° (if possible), in case of pitting corrosion - when the lower part of the facility is more corroded.

The above measures are most often used in combination. Which combination will be chosen depends on the type of material used, the electrical continuity of the facility and the soil around it, the location of the facility in relation to neighboring structures and environments. Protection by coatings, electrochemical protection must be combined with increasing the uniformity of the soil immediately adjacent to the metal surface. The presence of pieces of clay in sandy soil is especially dangerous and has to be avoided.

4.3. Stray current corrosion

Stray current is the leakage of direct (less often alternating) current from sources or users of such current in contact with the soil. An electrical installation can be a source of stray current if some of the conductors included in the circuit or some other part of the installation are grounded at more than one point. Sources of stray current are railway lines and tram lines where the rails are used to conduct current; transport signaling systems; networks in electricity supply; electrical substations; high-voltage direct current transmission lines; industrial equipment operating on direct current; the cathodic protection stations. As an example, we will consider rail transport - Fig. 27. The poor insulation of the rails, the high resistance at the points of connection of the rails and the increased electrical conductivity of the adjacent soil become the reason for the diversion (leakage) of a part of the electric current to the soil. If metal underground facilities (various installations, water pipes, etc.) are located near the rails, stray currents pass through them and when they encounter areas of high resistance (near the rail) they are diverted back through the soil to the rails. The places where stray currents pass from the ground to the metal structure become cathodic sections, and the places where the current passes from the metal structure into the soil are anode sections.

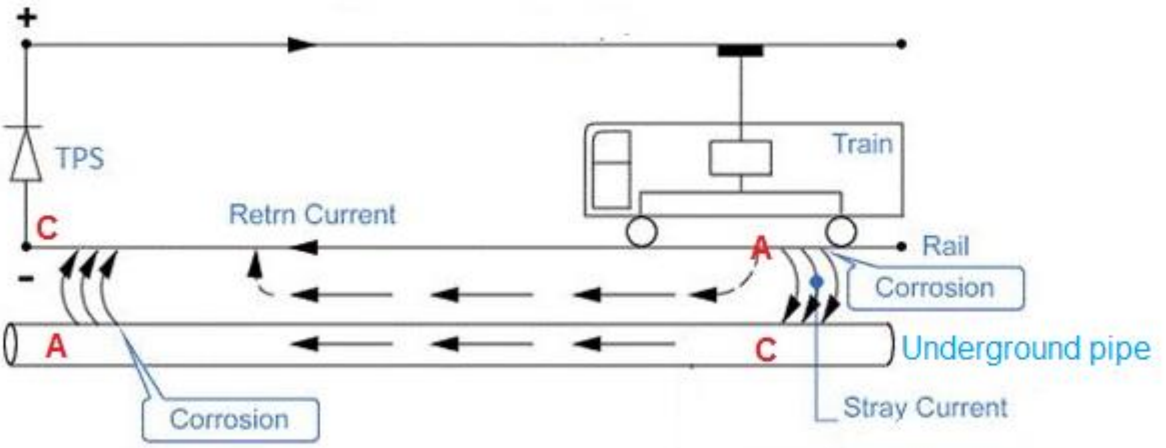


Fig. 27. Stray current corrosion in rail electric transport, TPS - traction power substation
(https://railsystem.net/stray-dc-current/)

The figure presents a "snapshot" of the change in potential of the threatened unprotected structure. In reality, the potential of the structure is constantly changing over time.

Anodic sections are subject to corrosion (only if the metal structure is made of amphoteric metals – Pb, Al, destruction is also possible in the cathode area). Sometimes the cathodic sections can be subjected to the negative effects of "overprotection". Corrosion losses are significant (usually much greater than corrosion of the same facility in the same soil, in the absence of stray current effects), since they are proportional to the current flow, and the currents that flow are large. This particular case of electrochemical corrosion is also called electrical corrosion, because the destruction of the metal is due to the action of an electric current obtained from an external source. Corrosion proceeds by an electrochemical mechanism, similar to corrosion due to the operation of corrosive GCs, but the destruction is more significant due to the large flowing currents. The protection measures are also different. Corrosion under the action of stray currents operates over significantly longer distances than corrosion due to the operation of galvanic corrosion cells, occurring near some heterogeneity of the material or medium, since the anodic and cathodic sections are usually at a considerable distance one from another. Seeking the path of least resistance, the stray current from the external installation can travel a considerable distance along the length of the pipeline, causing significant corrosion destruction at the point where it exits. In such a case, cathodic protection of the pipeline with the sacrificial anodes is not efficient. Therefore, it is essential to know if there are stray currents. Stray current can be expected to cause the corrosion of a facility if the corrosion process is rapid and there is a large direct current installation nearby.

Stray current is dynamic in nature, its amplitude varies depending on the use of the transit system (source of stray current), the relative location of the electric vehicles to the corroding facility and their acceleration. Identification of the presence of stray currents is the fluctuations in time of the potential of the pipeline with respect to the ground in a given section of the affected structure. Stray currents are detected by: a) measuring the potential difference between two perfectly identical standard electrodes attached to the threatened facility at a certain distance between them. The absence of a potential difference is an indication that the facility is not at risk of corrosion under the action of stray currents. If there is a potential difference, its sign determines whether the section is cathodic or anodic. b) Measurement of the potential of the threatened facility against a reference electrode. The sign of the measured potential determines whether the section is cathodic or anodic.

The parameters of the soils and waters in contact with a facility subjected to stray current corrosion affect the corrosion rate similarly to the case of corrosion due to the operation of corroding galvanic cells in soil and water.

Factors influencing the intensity of stray currents are: soil resistance, amplitude of stray current, distance between substations, method of substation grounding, resistance of running rails, use and location of cross-ties and isolated joints, resistance of rails to ground, tension of the mechanical traction system.

Solidly grounded systems are a sure source of stray current. Older transit systems operating on direct current are the sources of the most dangerous corrosion problems associated with the action of stray current for the following reasons: a) relatively high electrical resistance of the running rails (smaller cross-sections, bolted connections, breaking of connections with time, etc.); b) poor insulation of the running rails from the ground (deliberate grounding of the negative rails, absorption of moisture by the wooden traverses, etc.); c) large distances between substations leading to a greater voltage drop in the rails. The stray current corrosion problem has been reduced in modern transit systems by two fundamental sets of measures: a) reducing the electrical resistance of the electrical circuit that returns the current and b) increasing the electrical resistance between the rails and ground. The first group makes it unlikely that the current will return through the ground – the group of methods includes using heavier rails, continuously welding the rails, improving the connections between the rails, reducing the distance between substations. It is desirable to combine the electrical substations with the passenger stations. This provides a very short return path for the maximum currents arising as a result of the trains accelerating. The resistance between the rails and the soil can be increased by placing insulation between the rails and the wooden or concrete traverses and by using insulated fasteners. The danger of stray current corrosion is particularly significant where old and new transit systems are in contact. The higher current required in new high-speed trains increases the risk of stray current corrosion in older systems. Theoretically, ungrounded systems are not sources of stray current. In practice, due to the presence of multiple parallel clamps, grounding exists and stray current is observed. Diode grounded systems represent a compromise between solidly grounded and ungrounded systems. They are used to eliminate the problems that occur with solidly grounded systems and to keep the electrical potential within safe limits. Corrosion under the action of stray current can still be observed with them, the destruction on the rails and their supporting brackets is particularly significant.

Measures to protect against corrosion under the action of stray current include:

- Isolation of the facility from the stray current source;
- Grounding of the stray current source and/or the protected structure;
- Application of drainage protection;
- Application of cathodic protection with an external voltage source - cathodic protection with sacrificial anodes is usually not efficient.

4.4. Corrosion in natural waters

Natural waters are a typical electrolyte with a complex composition - they contain dissolved salts (exactly which ones - it depends on the rocks and soils with which they come in contact), gases, and often - microorganisms.

Corrosion in natural waters proceeds by an electrochemical mechanism with the following features:

a) For most metals (and especially for steels) corrosion proceeds with cathodic control. Since most natural waters are approximately neutral, corrosion proceeds with oxygen depolarization, with the most common (in calm water or at moderate motion) rate-determining step being oxygen diffusion to the metal surface. This determines the relatively weak influence of alloying additives and the composition of low-alloy steels on the corrosion rate of equipment fully immersed in water. In most cases, the anodic reaction proceeds with little difficulty. Due to the sufficiently high electrical conductivity of natural waters, corrosion occurs with little ohmic resistance. This leads to a strong influence on the corrosion process not only of micro-, but also of corrosive macro-GCs.

b) Due to the difficulty of reaching a passive state of iron and steel in natural waters, the corrosion macro-GCs caused by different aeration are not essential.

c) In addition to the primary anodic and cathodic processes, secondary processes can also occur. Around the cathode section of the corroding metal facility, the concentration of OH^- increases as a result of the reactions:

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^{-}$ (112)

or $2H^+ + 2e^- \rightarrow H_2$ (113),

leading to a decrease in the acidity of the medium.

It is possible soluble hydroxides of the corroding metal to be formed, e.g. for iron (steels):

$Fe^{2+} + mH_2O + 2OH^- \rightarrow Fe(OH)_2 + mH_2O$ (114)

With free access of O_2 to the water, the resulting $Fe(OH)_2$ is oxidized:

$4\ Fe(OH)_2 + O_2 + H_2O \rightarrow 4\ Fe(OH)_3$ (115).

The resulting $Fe(OH)_3$ is unstable and decomposes to give hydrated reddish oxides ($Fe_2O_3.H_2O$). If the amount of O_2 is insufficient for the complete oxidation of $Fe(OH)_2$, magnetite is obtained:

$6\ Fe(OH)_2 + O_2 \rightarrow 2\ Fe_3O_4 + 6\ H_2O$ (116).

The formed layer of hydrated iron oxides on the surface of iron and steel is called rust. In most cases, rust consists of several layers. The innermost is of green-black magnetite (Fe_3O_4), followed by hydrated magnetite ($Fe_3O_4.H_2O$), and the outermost consists of $Fe_2O_3.H_2O$ (red-brown). The layered construction of the cover from corrosion products explains the difficult access of O_2 to the inner layers.
d) For partially submerged equipment, maximum corrosion occurs around the waterline.

4.4.1. Factors affecting corrosion in natural waters

1) The acidity of water - directly effects the rate of corrosion by effecting the cathodic process of H^+ or O_2 depolarization and indirectly - by changing the possibility of formation and solubility of corrosion products. The potential of the hydrogen and oxygen depolarization reaction changes by 0.059 V for a unit change in pH. As the pH decreases, the cathode potential becomes more positive, which facilitates the cathodic process (of hydrogen or oxygen depolarization) and the corrosion rate increases, which is felt more strongly in corrosion with hydrogen depolarization. When increasing the acidity of the environment during corrosion with H^+ depolarization, the cathodic curve shifts parallel to itself (from AB to CD), which leads to an increase in the corrosion current density from i_{corr} to i'_{corr} - Fig. 28.

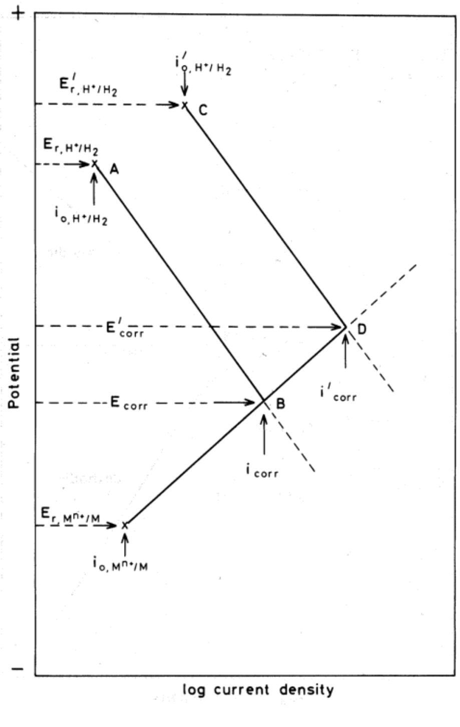


Fig. 28. Schematic illustration of the effect of pH on the corrosion rate of a metal in an acidic environment

Depending on the influence of the acidity of the corrosion environment on the corrosion process, metals are divided into five groups:
- Metals stable in acidic, neutral and alkaline environments, i.e. in the interval pH = 0 - 14 – e.g. Au, Pt, Ag;
- Metals unstable in acidic, insufficiently stable in neutral and stable in alkaline (pH < 14) environments – e.g. Fe, Mg, Mn;
- Metals unstable in acidic but stable in neutral and alkaline (pH < 14) environments – e.g. Ni, Co, Cd;
- Metals stable in acidic and neutral, but unstable in alkaline environments - e.g. Mo, W;
- Metals unstable in acidic and alkaline environments, but stable in neutral environments - e.g. Al, Zn, Sn, Pb.

The formation of corrosion products on the metal surface and their solubility in environments with different acidity complicates the influence of pH on the corrosion of metals.

The influence of pH on the corrosion resistance of iron (non-alloyed and low-alloyed steels) can be generally described as follows: strong corrosion is observed in an acidic environment; corrosion is weaker in neutral and alkaline environments; in a highly alkaline environment, especially at elevated temperature, corrosion is observed due to the formation of soluble compounds of iron - ferrates and ferrites. In this highly alkaline region, corrosion proceeds by hydrogen depolarization, with H^+ ions produced by water decomposition.
2) Gases dissolved in water - mainly O_2 and CO_2. Dissolved O_2 mainly effects corrosion proceeding with O_2 depolarization. As the oxygen concentration increases, corrosion is initially accelerated due to the facilitation of the cathodic reaction of oxygen depolarization and hence of the entire corrosion process. A further increase in

the amount of dissolved oxygen (by an anthropogenic activity - usually to above 15 mg/dm^3) leads to a certain reduction in corrosion due to the formation of oxide films with some protective properties.

In hard waters (waters with a high content of di- and polyvalent metal ions, mainly Ca^{2+} and Mg^{2+}), protective covers, consisting mainly of $CaCO_3$, are usually precipitated on the metal surface. In the presence of CO_2, these covers dissolve and lose their protective properties:

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca(HCO_3)_2 \qquad (117)$$

In water saturated with CO_2, the corrosion products formed on the surface of the metals are easily exfoliated and have no protective effect. Therefore, the rate of corrosion does not decrease over time (as is the case in the absence of CO_2), but remains constant.

It should be borne in mind that the solubility of gases in water decreases with increasing temperature and the amount of dissolved salts.

3) Salts dissolved in water – the main ions found in natural waters are Ca^{2+}, Mg^{2+}, HCO_3^-, SO_4^{2-}, Cl^- and NO_3^-. The presence in small amounts of Fe_{tot}, Mn^{2+}, Na^+, K^+ is possible. The presence of small amounts of acid anions - NO_2^- and PO_4^{3-} is not essential from a corrosion point of view. There are several main cases of effects of salts dissolved in water:

a) In solutions of hydrolyzable salts, the influence of the salt is determined by the change in pH of the medium after hydrolysis.

b) Presence of ions determining water hardness - layers of slightly soluble metal corrosion products (e.g. $CaCO_3$ and $MgCO_3$) are formed on its surface, which reduces corrosion. These layers make it difficult for O_2 to reach the metal surface and from there – the entire corrosion process.

c) In solutions of salts forming sparingly soluble metal corrosion products, corrosion decreases with increasing salt concentration due to the formation of protective layers on the metal surface (e.g. Fe in phosphate solutions);

d) The presence of salts with oxidizing properties ($NaNO_2$, K_2CrO_4, $KMnO_4$,) in sufficiently high concentrations, can lead to a decrease in the corrosion rate, due to the passivation of the metal, in the absence of active ions (such as Cl^- I^-) in the water. At insufficiently high concentrations, these ions act as cathodic depolarizers and accelerate the corrosion process.

e) Salts acting as cathodic depolarizers ($FeCl_3$, $HgCl_2$, $CuCl_2$) accelerate the cathodic process and from there - the entire corrosion reaction. Their action is primarily due to the presence of metal ions of variable valence, which are very good cathodic depolarizers (e.g. Fe^{3+}/Fe^{2+}). At the cathode, the ion of increased valence acts as a depolarizer. In solution, the ion reduced at the cathode is oxidized by O_2 to its higher valence. The solubility of such a depolarizer may be much greater than that of O_2. The oxidation of the ions of lower valence takes place in the volume of the solution at a sufficiently high speed, which also determines their significant corrosion stimulating effect.

f) The presence of salts forming complexes with the metal ions accelerates corrosion (within certain limits), with an increase in salt concentration, due to the facilitation of the anodic process.

g) Anodic corrosion stimulator ions (sulfate, halide) destroy the protective cover of the anodic sections of the metal surface, remove the ions of the corroding metal from the reaction zone, thus preventing the reaching of equilibrium. The most dangerous anodic stimulator of corrosion are Cl^- ions, since after they have taken the corroding metal ions from the metal surface to the volume of the solution, they are autocatalytically restored:

$$Me^{n+} + 2\,Cl^- \rightarrow Me(OH)_2 + 2H^+ + 2Cl^- \qquad (118).$$

Chlorides can reduce the effectiveness of the natural protective films on the metal surface. The action of nitrates is similar to that of chlorides, but in practice it is not significant due to the low concentrations of NO_3^- in natural waters. Water with high concentrations of SO_4^{2-} has increased corrosion aggressiveness towards concrete and has a negative effect on corrosion inhibitors.

h) Generally, the dependence of the corrosion rate of Fe and carbon steels on the concentration of neutral salts is a curve with a maximum. As the concentration of the salt increases, the conductivity of the solution and its corrosive effect increase, but the solubility and diffusion rate of O_2 decrease, which makes the cathodic process more difficult and, from there, corrosion.

4) The rate of movement of the corrosion medium has little effect on the corrosion rate in corrosion with hydrogen depolarization. At cathodic control, corrosion with O_2 depolarization and rate-determining reaction O_2

diffusion to the metal surface, the corrosion rate first increases (due to facilitation of the cathodic reaction due to greater O_2 influx) - Fig. 29, then decreases (due to the formation of oxide films with certain protective properties on the metal surface, related to the abundant flow of O_2, which is possible if the water does not contain corrosion-aggressive ions in high concentrations). At very high flow velocities (turbulence), corrosion again increases as a result of corrosion erosion. In the areas of a sharp change in the gradient of the speed of movement of the corrosion medium, conditions for the development of corrosion cavitation can be created. The rate of corrosion increases when in contact with two- and multiphase fluids, as well as with liquids carrying bubbles, particles and droplets of water-immiscible liquid.

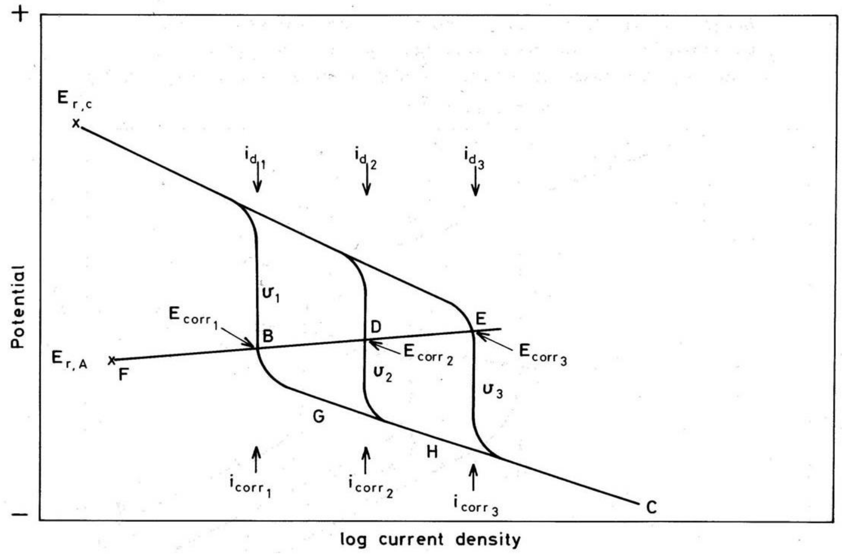


Fig. 29. Schematic illustration of the effect of increased velocity of the corrosion medium ($v_1 < v_2 < v_3$) on the cathodic polarization curve and corrosion current in diffusion-controlled corrosion of the cathodic depolarizer

5) The temperature of the corrosion medium - the corrosion rate increases almost exponentially with temperature in corrosion with H^+ depolarization. In corrosion with O_2 depolarization in an open system, the corrosion rate initially increases (due to an increase in the diffusion rate of O_2 and decrease in η_{O_2}), and at temperatures above 70 - 80 °C - decreases (due to a decrease in the solubility of O_2 in the corrosion medium). If the electrode reaction where electron transition or diffusion (mostly of O_2 to the metal surface) are rate-determining factors, the Arrhenius equation (equation (61), where E_a is the effective activation energy of the process) is observed with sufficient accuracy.

6) The presence of inhibitors in the corrosion environment.

7) Microorganisms growing in water – the most important are anaerobic sulfate-reducing bacteria (which reduce SO_4^{2-} to S^{2-} and cause sulfide corrosion of steel) and aerobic bacteria of the type *Acidithiobacillus thiooxidans*, formerly known as *Thiobacillus Thiooxidans*, which generally oxidize S to H_2SO_4 by the scheme: $S \rightarrow SO_2 \rightarrow SO_3$ (these reactions are catalyzed by bacteria); $SO_3 \rightarrow H_2SO_4$ (the reaction is not catalyzed by bacteria). The final product H_2SO_4 greatly increases the corrosive aggressiveness of the medium. The most suitable environment for the development of *Acidithiobacillus thiooxidans*, is slightly acidic water located near oil and S deposits, wastewater from oil refining and other industrial wastewater containing organic compounds. Another type of bacteria that accelerates the corrosion of iron and steel is iron bacteria. They obtain the energy needed for their development by oxidizing Fe^{2+} to Fe^{3+}. The resulting Fe^{3+} are strong cathodic depolarizers and their presence significantly accelerates corrosion. In addition, a fibrous precipitate of $Fe(OH)_3$ is obtained (according to the reaction $Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H_2$), which favors the development of other corrosive microorganisms, the emergence and operation of corrosion GCs due to different aeration and reduces the efficiency of the useful cross-section of the equipment.

8) Contact of materials with different standard potential - it has been proven that the overall corrosion effect of uncovered and partially covered with some kind of protective coating (metallic, non-metallic) facilities is the same, due to the acceleration of corrosion on the uncovered part of the partially covered facility.

4.4.2. Indices of water saturation with respect to calcium carbonate - as an indicator of the corrosive aggressiveness of water

The property of water to precipitate saponified fatty acids is called "water hardness". It is determined by the concentration of all divalent and polyvalent cations present in the water. In practice, for freshwater it is determined by the total content of Ca^{2+} and Mg^{2+} ions. With a content of Ca^{2+} and Mg^{2+} above 1.4 mmol/l, the water is hard, with a content below 1.4 mmol/l, the water is soft. Soft waters are more corrosive to iron and steel than hard waters. In hard water, a film of $CaCO_3$ naturally forms on the metal surface, which makes it difficult for the O_2 to reach the cathode areas by diffusion - and from there the general corrosion process. A protective film of $CaCO_3$ does not form in soft waters. The precipitation of $CaCO_3$ depends not only on the hardness of the water, but also on its pH and dissolved solids. The water is in equilibrium with $CaCO_3$ when it neither dissolves nor precipitates $CaCO_3$.

The saturation coefficient (equilibrium coefficient) of water relative to $CaCO_3$ (K_s) is defined by:

$K_s = (a_{Ca}{}^{2+} \, . \, a_{CO3}{}^{2-}) / SP_{CaCO3}$ (119),

where $a_{Ca}{}^{2+}$ and $a_{CO3}{}^{2-}$ the activity (concentration) of Ca^{2+} and $CO_3{}^{2-}$, SP_{CaCO3} – the solubility product of $CaCO_3$. The equilibrium condition ($K_s = 1$) is based on the assumption that the water is calm and at a constant temperature and that this state remains undisturbed for an infinitely long time. Water that is unsaturated with respect $CaCO_3$ ($K_s < 1$) dissolves it. Water supersaturated with respect to $CaCO_3$ ($K_s > 1$) precipitates it.

Saturation indices characterizing the saturation of water relative to $CaCO_3$ have found wide distribution.

4.4.2.1. Langelier Saturation index - LSI

Langelier Saturation index - LSI – can be interpreted as the necessary change in pH of water in order to bring it to equilibrium with $CaCO_3$:

$LSI = I_s = \lg (a_{Ca}{}^{2+} \, . \, a_{CO3}{}^{2-}) / SP_{CaCO3}$ (120),

where $a_{Ca}{}^{2+}$ and $a_{CO3}{}^{2-}$ the activity (concentration) of Ca^{2+} and $CO_3{}^{2-}$, SP_{CaCO3} – the solubility product of $CaCO_3$. Special nomograms for determining I_s can be found in the literature (when the composition and temperature of the water are known). I_s can also be determined experimentally:

$I_s \equiv \Delta pH = pH_{experimental} – pH_s$ (121),

where $pH_{experimental}$ – the pH value of the water, pH_s – the pH value of the same water, measured in a water sample, after adding marble powder (1-2 g per 100 cm^3 of water) and waiting for equilibrium to be reached, i.e. a constant value of pH. It is possible to calculate pH_s according to the dependence:

$pH_s = (9.3 + A + B) - (C + D)$ (122),

where:

$A = (Log_{10} [TDS] - 1) / 10$ (123)

$B = -13.12 \times Log_{10} (^oC + 273) + 34.55$ (124)

$C = Log_{10} [Ca^{2+} \text{ as } CaCO_3] - 0.4$ (125)

$D = Log_{10} [\text{alkalinity as } CaCO_3]$ (126).

LSI evaluates the possibility of corrosion. At $I_s \equiv pH < -0.05$ water is aggressive towards $CaCO_3$, i.e. if a $CaCO_3$ coating is pre-formed on the metal surface, it will dissolve, no new one will form. Therefore, water is corrosive and aggressive to iron and steel. At $I_s \equiv \Delta pH > +0.05$, water is oversaturated with respect to $CaCO_3$, it is possible to deposit a coating of $CaCO_3$ on the metal surface, water is less corrosive to iron and steel. Such water is more prone to scaling. At $-0.05 < \Delta pH < +0.05$, the water is in a state of calcium-carbonate equilibrium and its corrosion aggressiveness is determined by other factors.

The saturation index introduced by Langelier is the most widely used indicator for evaluating the ability of water to form scale. The index characterizes the thermodynamic possibility for the formation and growth of the $CaCO_3$ layer, but does not provide information on the amount of $CaCO_3$ that will precipitate to reach equilibrium.

The corrosiveness of soft water can be reduced by treating the water with $Ca(OH)_2$ - lime or with Na_2CO_3 - soda or both at the same time.

When using I_s data as an indicator of the corrosiveness of water, the following *limitations* must be taken into account:

1. In natural waters containing colloidal particles, quartz or organic matter, precipitation of $CaCO_3$ is possible on them, and not on the metal surface. In this case, the corrosion aggressiveness of water remains high, regardless of the positive ΔpH value.
2. In the presence of dissolved salts of halides in the water (e.g. NaCl), corrosion can proceed, regardless of the positive value of ΔpH. Corrosion has a pitting character and is due to the loss of the protective properties of the $CaCO_3$ cover in some areas under the action of halide ions.
3. If complexing ions (e.g. polyphosphates) are added to the water during any chemical treatment, the formation of $CaCO_3$ is hindered/slowed down and I_s can no longer serve as an indicator of the corrosive aggressiveness of the water.
4. When $\Delta pH < -0.05$ as a result of water deionization and deaeration, the Langelier index cannot serve as an indicator of corrosion aggressiveness - this water is not corrosion aggressive.

If one of the above cases is not reached, I_s is a useful indicator indicating the relative corrosion aggressiveness of fresh water in contact with a metal whose corrosion rate depends on the diffusion of O_2 to the metal surface (as is the case with the corrosion of iron, steel, copper, brass, zinc, lead in natural waters). Is *is not* applied to assess the corrosion aggressiveness of waters in contact with passive metals (i.e. they corrode less the higher the concentration of O_2 on their surface, e.g. alloy steel). LSI does not give actual information about the corrosion aggressiveness of water without taking into account the other factors - concentration of Cl^-, SO_4^{2-}, dissolved O_2, speed of water movement, buffer capacity, presence of suspended particles. LSI does not provide information on the tendency to form other sedimentary layers – from $CaSO_4$, $Mg(OH)_2$, $Ca_3(PO_4)_2$.

4.4.2.2. Ryznar index - RSI

Ryznar index - RSI - connects empirical data on the thickness of the $CaCO_3$ layer formed in freshwater with the chemical composition of the water. Like LSI, RSI is based on the concept of equilibrium between water and $CaCO_3$ and is defined by the expression:

$RSI = 2(pH_s) – pH_{experimental}$ (127),

where: $pH_{experimental}$ and pHs are respectively the pH of the water and the pH value of the same water measured in a water sample after adding marble dust and waiting for equilibrium to be reached.
Empirically established values are:
- If $RSI < 6$ - the probability of precipitation of $CaCO_3$ increases when the value of the index decreases;
- If $RSI > 7$ - probably the formed film of $CaCO_3$ will not hinder the progress of corrosion;
- If $RSI > 8$ - corrosion of unalloyed steel is a significant problem.

4.4.2.3. Puckorius Scaling Index -PSI

Puckorius Scaling Index (PSI) - gives a quantitative relationship between the equilibrium state of water saturation and the precipitation of $CaCO_3$, and the index includes an estimate of the buffering capacity of water. It is defined by the expression:

$PSI = 2 (pH_s) - pH_{eq}$ (128),

where: pH_s - pH of water measured in a water sample after adding marble powder and waiting for equilibrium to be reached;

$pH_{eq} = 1.465. lg [Alkalinity] + 4.54$ (129);

$[Alkalinity] = [HCO_3^-] + 2 [CO_3^{2-}] + [OH^-]$ (130).

4.4.2.4. Larson-Skold Index - LI

Larson-Skold Index - LI - describes the corrosion aggressiveness of water against unalloyed steel. It is defined by the expression:

$LI = (epm\ Cl^- + epm\ SO_4^{2-})/(epm\ HCO_3^- + epm\ CO_3^{2-})$ (131),

where epm (ion) – concentration of the corresponding ion in equivalent parts per million. The introduction of the index is based on correlation with experimentally observed corrosion rates of mild steel in Great Lakes waters. Extrapolation of index value to other water types, e.g. to waters with low alkalinity or waters with extremely high alkalinity is not correct. The index is interpreted as follows:
- If LI is < 0.2, the water is not corrosive;
- If LI < 0.8 it is likely that chlorides and sulfates in the water do not interfere with the formation on the metal surface of a natural film with certain protective properties;
- If $0.8 <$ LI < 1.2 it is likely that chlorides and sulfates in the water interfere with the formation on the metal surface of a natural film with certain protective properties; higher than permissible corrosion rates are expected;
- If LI > 1.2 a tendency to increase the rate of local corrosion is expected, which will increase with increasing index value.

4.4.2.5. Stiff-Davis index (SDI) and Oddo-Thomson index - OTI

Stiff-Davis index (SDI) is based on the concept of equilibrium between water and calcite, but overcomes the disadvantages of LSI in terms of high concentrations of dissolved salts. It is defined by the same expression as the LSI, but the SP_{CaCO3} used to calculate the equilibrium pH is modified based on empirical data. It is interpreted in terms of the corrosion aggressiveness of water, similarly to LSI. The SDI calculation will predict a given water to have less scale forming capacity than the LSI calculation. The difference between the results obtained with the two indices increases as the ionic strength of the water increases.
Oddo-Thomson index (OTI) - takes into account the influence of pressure and partial pressure of CO_2 on the pH of water and the solubility of $CaCO_3$. This empirical approach also includes corrections for the presence of three phases (water, gas and oil). It is interpreted in the same way as LSI and SDI.

It should not be forgotten that the specified indices give information about the possibility of forming low soluble compounds on the metal surface. In principle, these compounds can protect the metal from corrosion, but this possibility depends on how well they adhere to the metal surface and how free they are of cracks and defective structure. The influence of substances suspended in the water is not included in the calculation of the indices, and these substances can adsorb reagents that control the formation of $CaCO_3$. Full knowledge of the corrosion aggressiveness of a given water is obtained through the collection of experimental data, but still the saturation indices provide (at least qualitative) information on the tendencies for the formation of sediment layers on the metal surface and from there - on the corrosion aggressiveness of the water.
Measures to protect against corrosion in natural waters include: Use of alloys; Alloying; Appropriate construction; Use of protective coatings (metal, paint, polymer, insulation). Coatings may contain additives that slow down the anodic or cathodic reaction. The application must be tailored to the properties of the coating - e.g. the phosphate coating is only suitable for protection in a neutral environment; Application of electrochemical protection.
In closed systems containing corrosive-aggressive waters, in addition to the above measures, the following can be applied: Introduction of inhibitors into the corrosion environment - according to the specifics of the water and the metal; Deaeration of water; Decreasing the concentration of other than O_2 possible cathodic depolarizers (e.g. Fe^{3+}); Reduction of the concentration of corrosive-aggressive ions in water (as a special case – neutralization of water to pH= 6-8).

4.4.3. Peculiarities of corrosion in seawater

It should be borne in mind that the arrangement of metals and alloys by their potential in seawater is most often different from their arrangement by their standard potentials, which is related to the peculiarities of seawater: constant ratios between the concentrations of macrocomponents of water in world Ocean; high concentration of salts - mainly NaCl; high electrical conductivity; relatively high and constant pH value; buffering capacity; great influence of the solubility of gases (the most important of which are O_2 and CO_2) on the corrosion effect; presence of many organic substances in the water; presence of micro-fouling (bacteria, films of microorganisms) and macro-fouling (mussels, snails, small animals, fish) organisms on equipment

immersed in seawater; significant possibility of the occurrence of "hydrogen embrittlement" in equipment completely immersed in water and protected by cathodic protection.
When cathodic protection is applied, the pH around the facility increases as a result of oxygen or hydrogen depolarization reactions taking place:

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ (132)

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ (133).

In principle, the pH of seawater is controlled by CO_2 equilibria described by the following interrelated reactions:

$CO_2 + H_2O \leftrightarrow H_2CO_3$ (134)

$H_2CO_3 \leftrightarrow H^+ + HCO_3^-$ (135)

$HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$ (136).

The increase in the pH of the water near the metal surface, as a result of the cathodic reaction, favors the precipitation of carbonate layers on the metal surface according to the reactions:

$CO_2 + OH^- \leftrightarrow HCO_3^-$ (137)

$OH^- + HCO_3\text{-} \leftrightarrow H_2O + CO_3^{2-}$ (138)

$CO_3^{2-} + Ca^{2+} \leftrightarrow CaCO_{3(s)}$ (139).

The equilibria represented by equations (137) to (139) indicate the participation of OH^- formed according to (132) and (133). Equilibria (135) and (136) are drawn to the right, i.e. to increasing H^+ concentration. This counteracts the increase in pH and accounts for the buffering capacity of water. However, equations (134) to (139) show that the buffering action is accompanied by the formation of a sedimentary layer of carbonates on the cathodic surfaces of the equipment in contact with seawater. The formation of magnesium compounds, especially $Mg(OH)_2$, can also contribute to the protective nature of the films formed on the metal surface. But seawater is not supersaturated with respect to $Mg(OH)_2$ and it forms only at water pH around and above 9.5.
Fig. 30 shows the corrosion profile of a steel column immersed in seawater. The development of oil and gas deposits located underwater places more serious requirements (compared to the case of land-based facilities) to the selection of corrosion-resistant materials and structures. It is necessary to take into account the following factors: composition of the produced fluids; operating temperature and pressure; presence of galvanic effects due to contact of dissimilar materials; resistance of the materials used for the manufacture of parts to close the equipment to corrosion in crevices; resistance of materials used to make moving parts to corrosion fatigue; temperature and chemical resistance of non-metallic materials; compatibility of materials in terms of their weldability; compatibility of materials with injected fluids; efficiency of cathodic protection; effectiveness of protective coatings; availability and cost of materials.

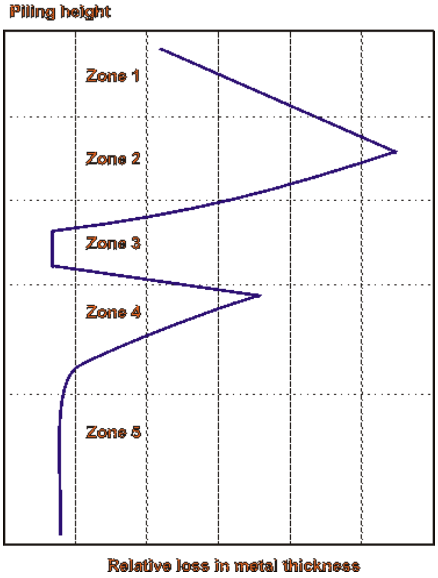


Fig. 30. Corrosion profile of a steel column immersed in seawater:
Zone 1: Atmospheric corrosion in a sea mist-rich atmosphere; Zone 2: Corrosion in the splash zone above high tide - there are "wet" and "dry" cycles; Zone 3: Corrosion in the tidal zone; Zone 4: Corrosion under fully immersion in water; Zone 5: Corrosion in contact with the bottom soil conducive to crevice corrosion
https://corrosion-doctors.org/Seawater/piling.htm

4.5. Corrosion by microorganisms (biocorrosion)

This type of corrosion is influenced by the presence or activity of microorganisms (bacteria, fungi or other microorganisms) and/or their metabolites. Most of the metals and their alloys can be affected by biocorrosion.

Strictly speaking, biocorrosion is not a separate form of corrosion, but is the destruction of metals / alloys by conventional corrosion processes that are stimulated or modified as a result of the activity of organisms. Biological activity can affect corrosion in a variety of environments – fresh and salt water, soil, natural petroleum products, oil emulsions and even air. This type of corrosion can cause extremely rapid destruction of metals and alloys in soils and waters. Microorganisms can negatively affect the corrosion resistance of materials in different ways: a) by creating slimy layers and sediments that serve as a basis for the development of crevice corrosion; b) by forming biofilms that reduce the amount of O_2 dissolved in the water; c) the products of their metabolism increase the intensity of the corrosive action of the environment around the facilities and structures; d) by breaking down the corrosion inhibitors; e) direct effect on corrosion rate.

Mechanisms potentially involved in biocorrosion are:

- Cathodic depolarization, in which the rate-determining step is accelerated by microbiological action;
- Formation of corrosion GC, due to occlusion, as a result of the formation of colonies of microorganisms on the metal surface.
- Supporting the anodic reaction and formation of pitting, under the action of microorganisms;
- Attack under the surface of protective coatings under the action of acidic end products of the metabolism of microorganisms.

Some microorganisms live in anaerobic, others in aerobic conditions. The presence of nutrients in the environment, the pH and the temperature of the environment significantly influence the development of microorganisms and the corrosion caused by their activity. Some species can, in the form of spores, survive extremely unfavorable conditions for a long time and reproduce very quickly under favorable conditions. The main microorganisms associated with corrosion damage are classified into bacteria (aerobic and anaerobic), fungi and algae. Anaerobic bacteria produce highly corrosive substances as a result of their metabolism. Aerobic bacteria produce corrosive mineral acids. Fungi produce corrosive byproducts of their metabolism, e.g. organic acids. Both classes of microorganisms can form slime layers and sediments that serve as a basis for the development of corrosion.

Biocorrosion is most often associated with the action of the following types of microorganisms:

- Fungi that produce organic acids that cause the corrosion of steel and aluminum. In addition, fungi can create anaerobic conditions in which sulfate-reducing bacteria (SRB) can grow and can produce metabolic products that are beneficial for the growth of corrosion-acting bacteria.
- Anaerobic bacteria that produce films of extracellular polymers, commonly called "slime". These films make it difficult for O_2 to reach the metal surface and create ideal conditions for SRB development. Some of the enzymes released by the anaerobic bacteria can transform the biocides added to the water into substances that are nutritious for the bacteria.
- Iron bacteria that obtain the energy needed for their development by oxidizing Fe^{2+} to Fe^{3+} (see also factors affecting corrosion in natural waters). This type of bacteria (and *Gallionella* bacteria in particular) is responsible for numerous cases of alloy steel corrosion. The biofilms formed by them accumulate Mn, which is noted as the main cause of some cases of corrosion of stainless steels in aqueous systems in the presence of Cl^- and Br^- -containing compounds.
- Microorganisms producing methane (methanogens). They consume H_2 and therefore can act as cathodic depolarizers. They usually exist in symbiosis with SRB in natural habitats.
- Bacteria that produce organic acids – e.g. *Clostridium*. They are a major problem in confined water environments where anaerobic conditions have been created and in gas pipelines.
- Sulfate-reducing bacteria, which function most effectively as corrosion-acting factors in an anaerobic strongly reducing environment, but survive in aerobic conditions, including in the presence of chlorine and other disinfecting oxidants. SRBs reduce SO_4^{2-} to S^{2-} (in the form of H_2S or FeS). Some subspecies consume H_2 and thus facilitate cathodic depolarization. Most subspecies develop best at a temperature of 25-35 °C, but there are some subspecies that develop effectively at temperatures above 60 °C.

SRBs can adversely affect the corrosion resistance of cast iron, unalloyed steel, ferritic stainless steel, high-alloy steels, copper-nickel alloys and nickel-molybdenum alloys - in soils and waters. A major sign of the involvement of SRB in the corrosion process of Fe alloys is the presence of local fractures filled with black corrosion products containing sulfides.

- Bacteria that oxidize S and S^{2-} - this type of bacteria obtain energy for their activity from the oxidation of S to SO_4^{2-}. Some *Thiobacillus* species can oxidize S to H_2SO_4 and acidify the medium to pH=1. This type of bacteria is one of the main causes of acid mine drainage. They can also cause corrosion of concrete and reinforced concrete structures. Usually, when *Thiobacillus* are the main cause of corrosion damage, they are found together with SRB. The simultaneous presence of two absolutely different types of microorganisms (under optimal living conditions) is proof of the formation of the micro-corrosion environment in contact with the metal surface and its great importance in corrosion processes.

Measures to combat biocorrosion include:

- Use of corrosion-resistant materials;
- Frequent cleaning of facilities;
- Controlling the chemical composition of the environment that comes into contact with the materials and alloys and removing substances that are nutritious for microorganisms;
- Use of biocides;
- Application of cathodic protection.

4.6. Corrosion of reinforcement in reinforced concrete

Reinforced concrete is a complex composite material whose structure and properties change over time. It does not "behave" as a simple corrosive medium. The need for repair of reinforced concrete structures is usually due to corrosion of rebar. The two most important causes of reinforcement corrosion are: a) local disturbance of the passive state of the steel by chloride ions that have penetrated to it through the concrete and b) general disturbance of the passivity by neutralizing the alkaline conditions of the concrete, mainly due to the reaction with the atmospheric CO_2. Clean concrete is an ideal anti-corrosion medium for steel rebar, which is usually made of carbon or low-alloy steel. The presence of large amounts of $Ca(OH)_2$ and relatively small amounts of Na^+ and K^+ leads to a high alkalinity of the concrete (pH = 12-13). At the beginning of the operation of the reinforced concrete structure, this high alkalinity is the reason for the formation on the steel surface of the reinforcement of a film with very good adhesion, consisting of 2 layers - internal - dense with a spinel structure and external - of $Fe(OH)_3$. This film passivates and protects the steel from corrosion until it is disturbed. Corrosion damage usually occurs when the facility is exposed to the environment for many years. The volume of corrosion products formed can be 10 times greater than the volume of steel from which the rebar is made. This leads to the occurrence of stresses and subsequent cracking and delamination of the concrete coating.

As a result of Cl^- contamination, for example - due to the use of anti-icing mixtures, chloride ions penetrate through the concrete and accumulate on the surface of the steel reinforcement. When a certain critical concentration is passed, the protective film is broken, and if moisture and oxygen are present at the "steel/concrete" boundary, corrosion of the steel begins. This critical value was found to be around 0.033 weight % (based on the weight of the concrete) of total chloride. The critical value was found to vary depending on the type of cement and concrete used, which is mainly due to changes in the content of tricalcium aluminate (C3A) and hydroxyl ions in the concrete. Therefore, as a more appropriate index, it has been proposed to use the ratio $[Cl^-] / [OH^-]$, with the limit value being within 2.5 to 6.0 range. Once initiated, corrosion proceeds by an electrochemical mechanism, with anodic and cathodic sites localized on the steel. Corrosion induced by chlorides manifests itself mainly as a local form of corrosion and, in addition the increasing stresses (as a result of the formation of corrosion products) significantly reduce the load-bearing section of the reinforced concrete structure. Due to inhomogeneities in the structure and composition of the steel reinforcement, under the action of an electrolyte, numerous microgalvanic cells appear on its surface. Concentration galvanic cells also appear on the surface of the reinforcement, due to the different aeration of the reinforced concrete or the different composition of the electrolyte in contact with the reinforcement.

Corrosion of the reinforcement can also start in the absence of Cl^-. This happens when the concrete comes into contact with carbonic acid, which is formed from CO_2 and air moisture. $Ca(OH)_2$ from the cement paste is transformed to $CaCO_3$ and this leads to a decrease in the alkalinity of the medium to pH 8.5, which allows corrosion of the rebar. The speed of carbonation depends directly on the "water/cement - w/c" ratio, with a higher ratio, carbonation penetrates deeper into the cement. The rate of carbonation is generally very low in good quality, good density and crack free cement. For example, at a w/c ratio of 0.45, it will take more than

100 years for the carbonation front to reach the steel reinforcement in the concrete of structures built using classical technologies. It is essential to establish the critical value of pH below which the steel is not passivated, i.e. the corrosion process of the reinforced concrete reinforcement proceeds at a measurable rate. It has been experimentally proven that this value is pH = 12.0 with free oxygen access and pH = 11.5 with limited oxygen access. Therefore, during the operation of reinforced concrete, it is necessary to create conditions for the long-term maintenance of the steel in a passive state, i.e., the concrete coating retains its high alkalinity and low permeability to chlorides.

The initial stages of corrosion of steel reinforcement in reinforced concrete are imperceptible. Usually, in practice, that moment is established when the corrosion products of the reinforcement significantly increase in volume and destroy the surface layer of concrete - characteristic longitudinal cracks are observed. Later, the protective layer of concrete in individual sections crumbled and heavily corroded reinforcement was discovered. When the cross-section of the supporting reinforcement is significantly reduced, parts of the structure may collapse, and in some cases, the entire structure may collapse.

Considering the significant economic losses caused by the corrosion of reinforced concrete structures, it is extremely important to take all possible measures to control corrosion, both in new construction and in existing ones. If corrosion is detected in its early stages, it is possible to take measures to regenerate the passivation layer on the surface of the steel reinforcement or to isolate the surface of the concrete in order to prevent the penetration of Cl^- ions. If corrosion has progressed to a stage where structural failure has occurred, repair is much more expensive because it requires replacing the damaged concrete.

Good design, adequate concrete cover thickness, use of corrosion-inhibiting admixtures, reduced water/cement ratio of concrete, and compacted concrete do not solve the problem, as concrete has a tendency to crack unevenly and leave the steel uncovered. Therefore, it is necessary to cover the reinforcing steel with an epoxy or other organic coating and even with a metal coating. In addition, various coatings can be applied to the concrete that isolate it from the surrounding environment or it can be covered with semi-permeable membranes. Until now, no organic coating has been found for steel reinforcement that can withstand the extreme combination of constant salt water wetting, high temperature, high relative humidity of the atmosphere to which reinforcing steel is subjected in marine conditions. Numerous studies have shown that if epoxy-coated steel rebar is not in contact with permanently wet concrete, the coating can provide significant protection to the rebar and delay the onset of the corrosion process in non-marine environment.

For existing chloride-contaminated concrete deck bridges, cathodic protection using Ti anodes is a reliable method of arresting rebar corrosion if the relevant cathodic stations and electrical connections are properly maintained. Electrochemical chloride extraction is a good method to rehabilitate and stop corrosion of chloride-contaminated reinforced concrete, although with less consistent success. This alternative has the advantage of moving the rectifier and wires after the treatment is stopped. Although reducing the chloride concentration in the concrete and stopping the dissolution of the steel is achieved, the steel cannot usually be re-passivated.

In new reinforced concrete structures, it is necessary to use a combination of different anti-corrosion measures: the adequate thickness of the concrete cover, the quality of the concrete, the use of corrosion-inhibiting mixtures, corrosion-resistant reinforcement and alternative reinforcement.

Various rehabilitation methods can be used for existing reinforced concrete structures. Each of the methods, used after all the damaged concrete has been removed and the necessary concrete backfill has been made, operates on one of the following principles:

- A barrier layer is created on the surface of the concrete to prevent chlorides from entering; conventional methods of rehabilitation fall into this category.
- Modification of the concrete in order to reduce its corrosion effect - this is how the electrochemical extraction of chlorides works;
- Control of the flow of electrons in the reinforcement - this is how the cathodic protection works.

The application of cathodic protection places certain requirements on the anodes: to withstand the load and the impact of the environment; have a longer lifespan than the protected surface; have sufficient surface area to prevent premature failure of the concrete; their use is economically beneficial.

The main reason for the corrosion of conventional concrete bridges is the violation of the passive state of the steel by the chloride ions that have penetrated to it through the concrete, originating from the used anti-icing mixtures. The following corrosion prevention measures for this type of bridges can be mentioned: a) preventing the penetration of Cl^- ions to the steel surface (through the creation of physical barriers on the surface of the concrete, the use of appropriate coatings on the surface of the steel, the use of concrete with low permeability to Cl^-); b) use of additives to concrete that make it less corrosive at a given concentration of Cl^- in it; c) increasing the corrosion resistance of the reinforcement itself by using corrosion-resistant or clad steels or composite materials.

The prevention of corrosion of prestressed bridges is realized mainly through the use of high-quality concretes and the addition of corrosion-inhibiting ingredients in them. It is possible to apply cathodic protection, but strict measures must be taken not to reach excessively negative potentials, which would lead to the occurrence of hydrogen embrittlement of the high-strength steels used in the reinforcement. Electrochemical extraction of chlorides cannot be used, because this method releases significant amounts of H_2, which can cause hydrogen embrittlement.

5. CORROSION CONTROL BASICS

5.1. Introduction to protection methods against electrochemical corrosion

Corrosion is an electrochemical reaction that proceeds by a mechanism that responds to the specific combination of material(s), environment and geometry of the products. It can be controlled by hindering the electrochemical processes taking place or changing the structure, provided the processes taking place are properly understood. Therefore, the first step in corrosion protection measures is to identify the general mechanism of the corrosion process taking place.

There are various anti-corrosion measures, the aim of which is to reduce the risk of corrosion to an acceptably low level. At the same time, when selecting protection measures, the entire life cycle of the construction (product) must be taken into account, since corrosion damage can occur at any stage of the cycle.

The methods of protecting metals from corrosion can be systematized into five main groups:

1) Rational design and material selection;
2) Impact on corroding metal;
3) Impact on the corrosion environment;
4) Protection through coatings;
5) Electrochemical protection.

5.2. Impact on corroding metal

The methods of increasing corrosion resistance by influence on the corroding metal include alloying, the selection of an appropriate mode of heat treatment of metals and alloys, and the appropriate treatment and cleaning of their surface. Alloying is the mixing of the base metal with another metal(s) or non-metal(s) in order to produce an alloy with increased corrosion resistance (compared to the base metal) or to remove (decrease) the possibility of developing dangerous forms of local corrosion. Corrosion-resistant alloying is carried out in the following main directions: a) introduction of components supporting the formation of a protective layer of corrosion products on the surface of the metal, for example, alloying steel with small amounts of copper increases its corrosion resistance in atmospheric conditions; b) introduction of components reducing the anodic activity of the metal, i.e. introduction of easily passivable components (e.g. Cr in steels) or of components facilitating the passivation of the base metal (e.g. alloying of chromium or chromium-nickel steels with copper - to facilitate their passivation in H_2SO_4); c) introduction of components reducing the cathodic activity of the metal (usually introduction of elements with high η_{H_2}); d) introduction of specific alloying components - e.g. Ti or Nb, which form carbides more easily than Cr due to their greater affinity for C and thus reduce the likelihood of corrosion of the alloy steel in the areas subjected to heating during welding.

Corrosion resistance is increased by avoiding defects on the surface of the products (e.g. scratches from processing); of traces of oils, lubricants, dust and of internal defects and stresses caused by inappropriate heat treatment or non-compliance with technological requirements during casting.

The corrosion resistance of alloy steels is increased by their passivation - facilitating the formation of a passive film on their surface and removing contaminants from their surface (cast iron, unalloyed steel - carbon or low carbon), the presence of which leads to the occurrence of pitting corrosion. Passivation usually involves treatment with solutions or pastes based on HNO_3, and it should be ensured that only the contaminants from the surface are dissolved, but not the alloy steel itself. The quality of the passivation carried out is checked by ensuring a 6-minute contact of the passivated surface with a $CuSO_4$ solution. The appearance of red color on the surface of the steel where the solution is dropped (i.e. copper reduction deposition) is evidence of poor passivation.

5.3. Impact on the corrosion environment

The method aims to reduce the aggressiveness of the corrosive environment. It is most often applied in cases where the medium is liquid and of limited volume. The impact on the corrosion environment is carried out mainly by:
1) Reducing the content of the depolarizer;
2) Introduction of corrosion inhibitors;
3) Other effects - lowering the temperature, the speed of movement of the medium and the concentration of the ions in the medium (or of the most corrosive-acting ions in it).

In case of corrosion in an aqueous environment, proceeding with O_2 depolarization, the reduction of the depolarizer content is achieved by:

a) thermal de-aeration (heating of water, during which gases dissolved in it are released, including O_2); b) desorption de-oxygenation (purging the water with an inert gas); c) chemical de-oxygenation (reductants, binding O_2, are introduced into the water).

In corrosion proceeding with H^+ depolarization, the corrosion medium is neutralized (by addition of $CaCO_3$, CaO, NaOH) to reach at least pH $\gtrapprox$ 5.

In case of atmospheric corrosion, the following measured can be applied: a) dehydration using substances that adsorb or absorb moisture from the air; b) cooling the air below the dew point temperature - in this case the moisture from the air condenses and is separated in advance. The treatment prevents the formation of a film of moisture on the metal surface, which is a necessary condition for the corrosion processes to occur.

5.4. Material selection and rational construction

The rational choice of construction material *requires*: a) establishing the causes of corrosion of metals under the operating conditions of the facility - nature of the corrosion environment, type of depolarization, controlling factor; b) knowledge of the operating conditions of the facility - presence of vibrations, mechanical loads; c) evaluation, albeit only qualitatively, of the influence of the main internal and external factors of corrosion; d) knowledge of the properties (including corrosion resistance) of construction materials; e) selection of suitable material and welding conditions and treatment of the areas around the welds; f) selection of suitable binders and sealing materials; g) knowledge and application of the permissible norms of corrosion under the specific conditions; h) consideration of economic factors; i) during repair - use of materials that are compatible with the material of the structure.

The choice of material is usually the result of a compromise involving evaluation of the mechanical properties of the material (strength, weldability), corrosion resistance and cost. The choice of material also depends on whether a new facility will be built or an old one will be modified or repaired.

From an economic point of view, it is not the initial cost of the material that is important, but the cost of its use throughout the life of the facility. It is more economically efficient to use a material with a higher initial cost, especially in parts of the facility where subsequent repairs will be difficult. The cheaper, but also less corrosion-resistant materials (carbon steel, cast iron) are a reasonable choice in the case when such material is easily available, the labor to replace the corroded parts of the facility is paid cheaply, and the demand for reliable and trouble-free operation of the facility are not particularly high. Where corrosion conditions are such that carbon steel cannot be used or coating protection is not sufficient, alloy steel is used.

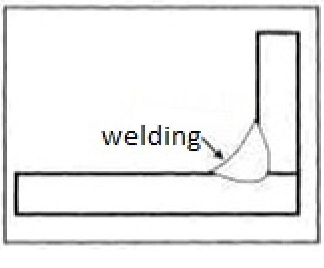
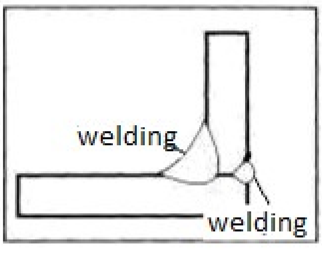
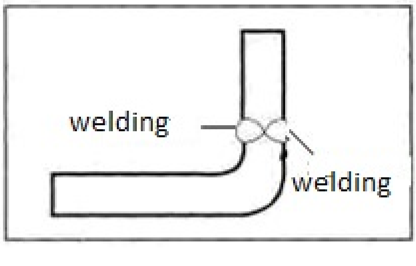
When selecting suitable materials, the possibility of welding and compatibility of the different materials must be taken into account, which is often very important.

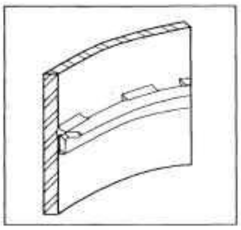
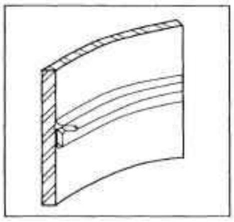
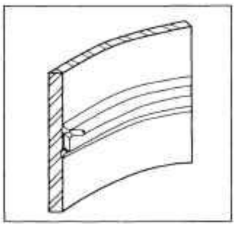
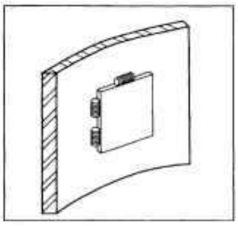
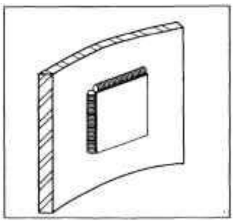
Binders are used to protect joints by preventing the accumulation of moisture and dirt. They also serve as a reservoir of inhibitors. Sealing materials are used to prevent the leakage of various fluids, but they also prevent the accumulation of moisture. The binding substances must be elastic and allow easy disassembly of the individual parts of the facility. Different rubbers are used for this purpose. They have to harden enough to be painted, but to remain flexible enough in order not to crack. Most often, polysulfide sealing materials are used that contain inhibitors. They are particularly effective when used to protect connections in equipment operating in wet conditions and to isolate dissimilar metals from each other.

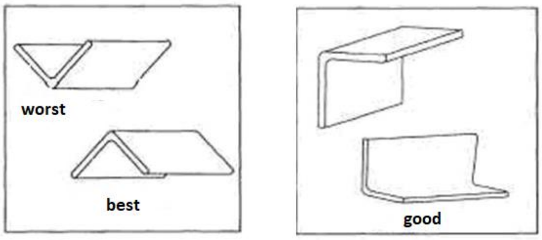
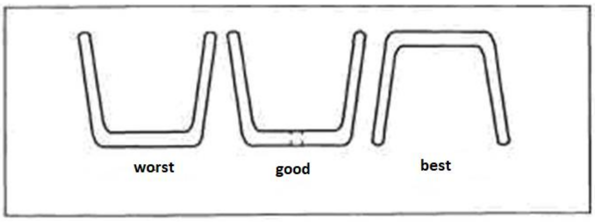
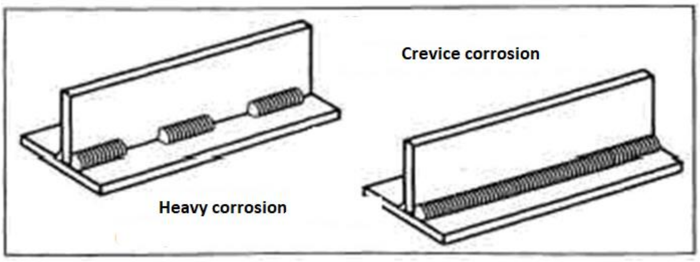
Rational design requires compliance with some basic requirements: a) avoiding contacts between dissimilar metals or between metals and conductive non-metals (e.g. magnetite – Fe_3O_4, FeS), and if such contacts are unavoidable - to isolate them (e.g. with a coating that plays the role on a protector or with a coating that has a high electrical resistance); b) avoiding contact with non-metals that can absorb moisture; c) avoiding stagnant areas for liquids and dust; d) avoiding and filling with inert material the cracks and narrow openings; e) avoiding mechanical stresses, stresses caused by heat treatment and stress concentrators; f) preferring welded joints to screw and riveted joints, and the welds must be made with the same or a more noble metal and the mechanical stresses arising during welding have to be removed (through heat treatment); g) avoiding the creation of conditions causing inhomogeneity of the corrosion environment; i) ensuring the possibility of laminar movement of the corrosion medium contacting the equipment and reducing the speed of movement of the corrosion medium; j) when applying the permissible corrosion norms, the thickness of pure metal (alloy) should be taken into account, and not the scale obtained during the metallurgical preparation of the material; k) ensuring the greatest possible "anode/cathode area" ratio of the facility; l) use for the preparation of joints (braces, bolts) of material that is from the material of the structure or more noble; m) ensuring the possibility of easy inspection of facilities and constructions; n) ensuring the possibility of easy replacement of the corroded parts of the structure; o) planning of maintenance anti-corrosion measures in the long term, taking into account the fact that the natural course of corrosion processes, repairs and local changes may require some change in anti-corrosion measures.

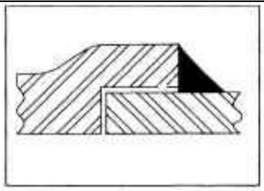
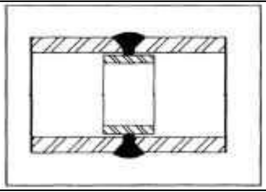
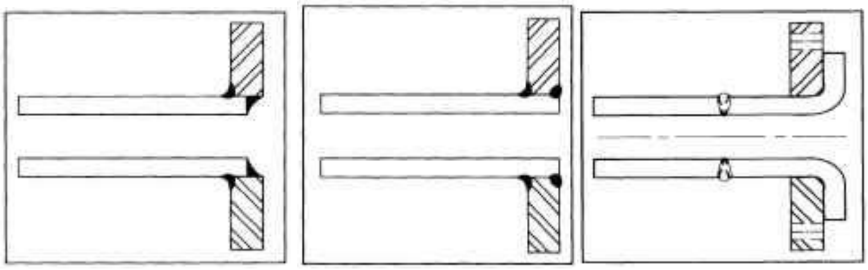
The facility design stage is perhaps the most important phase in corrosion control. In general, good practice requires: providing adequate ventilation and drainage to minimize the accumulation of condensate; avoiding concave and flat areas with inadequate drainage; avoiding contact of asbestos, felt, cloths with the metal surfaces; adequate preparation of metal surfaces before applying protective coatings; using "wet installation" to create an effective sealing barrier; providing access for corrosion inspections and maintenance activities; making it possible to use corrosion inhibitors. Fig. 31 presents various options for bottom corner welding, which are common in practice. Fig. 32 presents possibilities for designing structural elements with strengthening devices. Various design solutions, from the point of view of increasing the corrosion resistance of the equipment, are presented in Fig. 33. Fig.34 shows different welding options for pipelines.

Stagnant fresh or salt water at the bottom of alloy steel vessels causes their destruction.

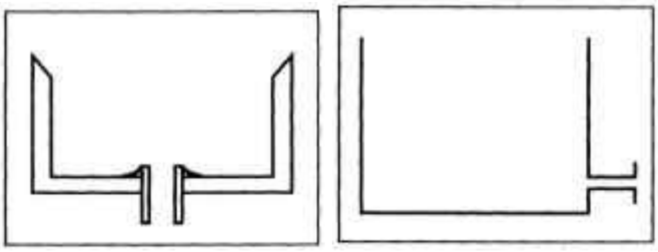
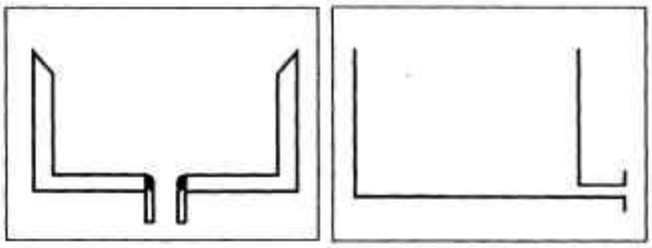
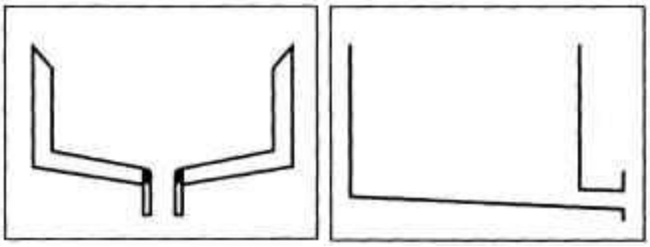
		
(a) **Bad design inside, worst design outside** - when the sidewalls are at right angles to the bottom, the fillet weld is rarely as smooth as shown in the figure. It is often rough, its thickness varies, and this compensates for the insufficiently good fit of the walls and bottom. The location makes it very difficult to apply the weld material smoothly on adjacent sides. Dendrites are formed, which are difficult to detach and allow crevice corrosion to develop.	(b) **Bad design inside, good design outside** – welding outside prevents the development of crevice corrosion. Fig. 31. Different ways to weld bottom corners	(c) **Best design inside, good design on the outside** - fatigue resistant - rounding the corner and offsetting the sidewall weld avoids the disadvantages described in (a) and (b). The construction has much higher corrosion and fatigue resistance.

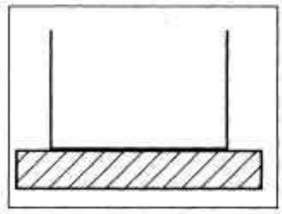
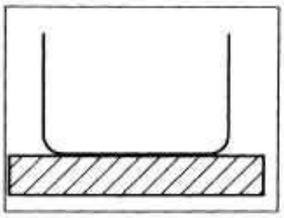
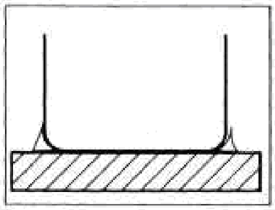
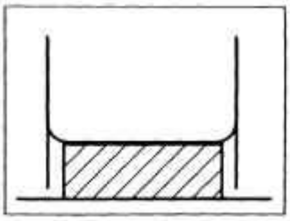
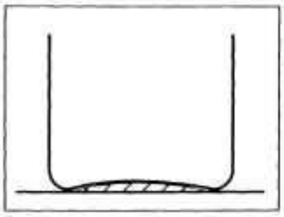
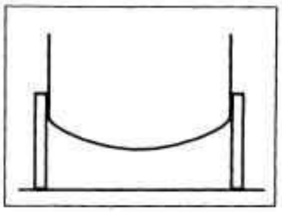
				
(a) All additional attached parts create potential opportunities for development of crevice corrosion. The structure reinforcing angle is attached with interrupted welds. There are large gaps between the structure and the angle, which will be filled with debris and cause early failure of the structure due to crevice corrosion - **adequate reinforcement, high risk of corrosion.**	(b) The construction of (a), but the reinforcing angle is welded with a continuous top weld, which prevents waste material from getting into the gaps between the reinforcing angle and the structure and greatly reduces the risk of corrosion in cracks (it still exists, however less dangerous, as there is a loose fault below which allows vapor condensation and the possibility of corrosion to develop) – **good resistance to crevice corrosion.**	(c) The gap between the structure and the reinforcing angle is filled from both the top and the bottom - **best resistance to crevice corrosion.**	(d) Reinforcement support, to which other fixtures are often attached by interrupted welds, which create the possibility of severe crevice corrosion - **adequate strength, but poor corrosion resistance.**	(e) Continuous welding -**increased resistance to crevice corrosion** Fig. 32. Different possibilities for designing structural elements with strengthening devices

	Fig. 33. Design of structural elements (a) The positioning of structural corners - it is necessary to ensure their drainage
	(b) Where channels are used, drainage holes must be drilled every 300 mm on center unless it is possible to position them as shown on the right
	(c) The continuous weld (right) of the stiffeners prevents the possibility of significant crevice corrosion occurring as is the case with the discontinuous weld (left)

	(a) For small diameter alloy steel pipes, side socket welding is usually used instead of butt welding. For large diameter pipes, an annular pad is often used. The two designs can only give satisfactory results in cases where the alloy steel is sufficiently resistant to crevice corrosion
	(b) Due to the clearances created, these designs can lead to crevice corrosion and are not recommended. In addition, the annular pad enters the flow, leading to unwanted turbulence and sediment build-up of the carried fluid. Best from a corrosion point of view are full penetration butt welds
(c) The figures show 3 good welds of pipes and flanges of the same material. The first 2 are not suitable when carbon steel flanges are welded to alloy steel pipes. In this case, a shortened end is used	 Fig. 34. Possibilities for welding in pipelines

Various design options for vessel outlets are presented in Fig. 35. In Fig. 36, six vessel bottom designs are presented, with relevant comments regarding rational design from a corrosion point of view. Figure 37 shows the tendency for a water film to remain in horizontal pipelines and how it drains in inclined pipelines.

	(a) The side drain and bottom hole shown here allow convenient construction, but cause relatively rapid corrosion damage to the bottom of the vessel. Not only does a layer of stagnant water remain, but sediments cannot be easily washed off the bottom - **poor design.**
	(b) The flush mounted side drain and recessed bottom hole allow the bottom to drain completely and wash away all sediment and debris, keeping the bottom clean and dry - **good design**.
	(c) Slanted solutions allow easier drainage and washing - **best design** Fig. 35. Design of outlet openings of vessels

		
(a) **Worst case -** square corner and flat bottom lead to rapid corrosion problems inside the corner where weld material collects to initiate crevice corrosion. Moisture penetrating the flat bottom through the gasket causes rapid corrosion in crevices on the outside	**(b) Good angles, bad design outside** - a rounded bottom is much more resistant to corrosion inside; the design is actually worse than (a) from the outside because the condensate enters directly into the gap between the bottom and the seal.	**(c) Very poor design both inside and outside** - the molding used here to deflect condensation helps at first but soon bends and itself requires repair
		
(d) Good design both inside and outside - the cylindrical drains shown are a good solution for flat bottom vessels	**(e) Good design both inside and outside, fatigue resistant** – bent vessel bottom and hemispherical bottom support body excel not only in corrosion resistance but also in fatigue resistance designs compared to (a) - (d) cases. Fatigue due to vessel filling and emptying is rarely reported in flat-bottomed vessels, but can be significant and lead to destruction. In this case, much greater load resistance is provided.	**(f) Best design both outside and inside** -- hemispherical bottom Fig. 36. Designing a vessel bottom

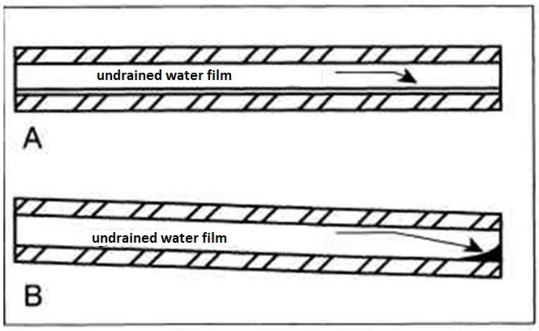


Fig. 37. Tendency to retain water film in horizontal pipelines (A) standard design – poor; (C) inclined design – good

5.5. Use of inhibitors

Inhibitors are chemical compounds that, introduced in small but sufficient quantities into the corrosion environment, slow down the rate of corrosion. They adsorb onto the metal surface or react with it or with the corrosive medium in contact with the metal, resulting in some corrosion resistance to the surface. Inhibitors slow down the corrosion process by increasing the anodic or cathodic polarization of the corroding metal, by hindering the movement of corrosive ions to the metal surface, or by increasing the electrical resistance of the metal surface. They are usually introduced into the corrosion environment in the form of solutions or in dispersed form, and less often they are included in the composition of protective coatings.

A quantitative assessment of the effect of inhibitors is given by the degree of protection Z (%) = efficiency of the inhibitory action and the coefficient of protective action γ, as:

$$Z = (v_o - v) \, . \, 100 / v_o , \quad \% \qquad (140)$$

and $\gamma = v_o / v$ (141),

where v_o - corrosion rate in the given medium without inhibitor, v - corrosion rate in the same medium, with added inhibitor.

In general, the effectiveness of the inhibitor increases as its concentration in the corrosion medium increases. Typical good inhibitors show 95% efficacy at 0.008% concentrations and 90% inhibition at 0.004% concentrations.

The change in corrosion potential upon addition of inhibitor can be used as a useful indication of the degree of corrosion inhibition. A significant shift of E_{cor} in the positive direction usually indicates a hindrance of the anodic reaction, while a shift of the E_{cor} in a negative direction - a hindrance of the cathodic reaction. A slight change in the E_{cor} value suggests difficulty in proceeding both the cathodic and anodic reactions.

The following *should be considered* when using inhibitors:

1) In principle, there are no universal inhibitors - i.e., different inhibitors, in different concentrations, are suitable for different metals and different corrosive environments;

2) The introduction of inhibitors into the corrosion environment should not adversely affect technological processes, the environment and human health;

3) The use of inhibitors is economically most expedient in systems with a constant or slightly renewed volume of the corrosion medium.

According to their chemical nature, inhibitors are divided into organic and inorganic, and according to the mechanism of electrochemical action - into cathodic, anodic and mixed (Fig. 38).

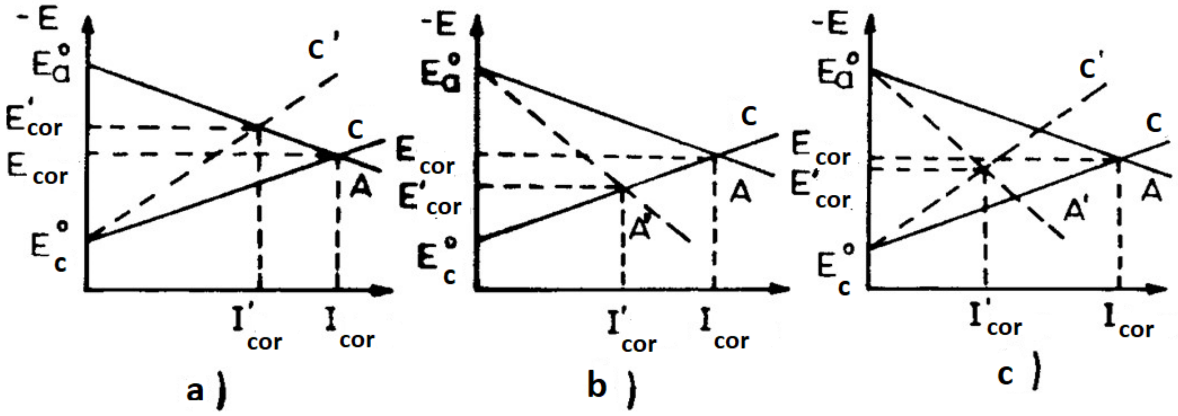


Fig. 38. Schematic representation of corrosion polarization diagrams in the presence of (a) cathodic; (b) anodic and (c) mixed inhibitors

Cathodic inhibitors hinder the cathodic reaction. They are divided into:

a) Reducers (e.g. Na_2SO_3, $N_2H_4.H_2O$), binding O_2 from the corrosion environment and thus hindering the cathodic reaction and therefore - the entire corrosion process. The efficiency of their action is increased by reducing the foam and dissolved gases in the corrosion environment by mechanical methods;

b) Shielding cathodic inhibitors (e.g. $ZnSO_4$, $ZnCl_2$, $Ca(HCO_3)_2$) - by forming on the cathodic areas of low soluble compounds, isolating the metal surface from the corrosion environment, they hinder the cathodic reaction of O_2 depolarization;

c) Increasing the overvoltage of H_2 release (eg S, CN^-, salts of As, Sb, Bi, Se, Te) - by hindering the recombination of hydrogen atoms. This type of inhibitors can increase the metal's susceptibility to corrosion cracking as a result of facilitating the penetration of hydrogen atoms into the metal crystal lattice ("hydrogen embrittlement").

Inhibitors from subgroup a) and b) are suitable for protection against corrosion occurring with O_2 depolarization, while those from c) - for corrosion with H^+ depolarization.

Cathodic inhibitors are less effective than anodic inhibitors, but they are safer (with respect to corrosion facilitation) than them.

Anodic inhibitors hinder the anodic reaction. They are:

a) Screening anodic inhibitors called film formers (e.g., NaOH, Na_2CO_3, phosphates, benzoates, borates). They form on the metal surface phase or adsorption films of low soluble compounds, as a result of the interaction of the protected metal with the inhibitor, with the participation of O_2 from the corrosion environment or from the atmosphere. As a result, the effective surface of the anode decreases, the anodic reaction becomes more difficult and, as a consequence, the entire corrosion process. The effectiveness of their protective action depends strongly on the pH and the saturation index of the water with respect to $CaCO_3$, which in turn depends on the temperature and composition of the water.

b) Passivators - they are oxidizers (chromates, dichromates, nitrates, nitrites) that can passivate the metal surface in the absence of O_2 and molybdates, phosphates, vanadates, which require the presence of O_2 in the corrosion environment for their passivating effect to appear. Passivators have *a dual nature* - as depolarizers they accelerate the cathodic reaction. Their total impact depends on the corrosion conditions and on their concentration. At insufficient concentration, they accelerate the cathodic reaction and from there - the entire corrosion process. In the presence of active ions (Cl^-) they change the nature of corrosion (usually cause pitting corrosion). That is why they are called dangerous inhibitors. Anodic inhibitors are mainly applied for protection in water and in neutral aqueous solutions and, in sufficient quantities, are much more effective than cathodic ones (they can lead to an almost complete cessation of the corrosion process). Inhibitors based on chromates and dichromates are the cheapest and are used in recirculation cooling systems of internal combustion engines, cooling towers, refrigeration plants. They are usually used in a concentration of 0.04-0.1% at a water pH of 7.5-9.5 and room temperature. Increasing the temperature or freshwater Cl^- concentration to 10 mg/L requires increasing the amount of inhibitor added to maintain its effectiveness.

Mixed inhibitors hinder both the anodic and cathodic reactions. These include silicates - $xSiO_2.Me_2O$, polyphosphates $(MePO_3)_n$ and a number of organic inhibitors (containing amino $-NH_2$, carboxyl -COOH or phosphonate $-PO_3H_2$ groups). The action of silicates is expressed in the neutralization of CO_2 dissolved in water and the formation of a protective film on the surface of the metal, composed mainly of amorphous SiO_2. Organic inhibitors usually form films on the metal surface that hinder the access of corrosion-acting agents. Mixed inhibitors are not as effective as nitrites and chromates, but are not toxic. Silicates are commonly used to prevent corrosion of steel plumbing systems. They also protect relatively well some non-ferrous metals - lead, tin, aluminum and their alloys. The effectiveness of the mixed inorganic inhibitors depends on the pH of the corrosive water and the temperature, and of the organic ones, in addition, it depends on their chemical composition and molecular structure and the pressure in the system. For each organic inhibitor there is an optimum concentration for the given corrosion medium and corroding metal, e.g., for the protection of unalloyed steel in water with pH=7.5 and containing 17 mg/l NaCl, the required concentration of sodium benzoate is 0.05%, and sodium cinnamate - 0.2%. Organic inhibitors are applied in the protection of water-cooling systems, steam circuits, etc. The advantage of these inhibitors over inorganic ones is that at low concentrations in the solution, they do not cause an increase in the corrosion rate of steel. Phosphonates can be used at elevated temperatures and are environmentally friendly.

In addition to mixed inhibitors, mixtures of cathodic and anodic inhibitors are also used in practice, and in their composition the synergistic action of Zn^{2+} and CrO_4^{2-} is used, and as the effectiveness of the action of the anodic inhibitors is preserved, the risk of pitting corrosion is reduced. To protect water cooling systems, complex additives are applied, including inhibitors, anti-scale agents, biocides (reagents limiting the development of biological formations), pH stabilizers, etc.

Contact and "volatile" inhibitors are used to protect against atmospheric corrosion in closed spaces. They can be substances that neutralize the action of acidic CO_2 (morpholine, hydrazine) or substances that release protective ions during their hydrolysis (dicyclohexylamine, cyclohexylamine, hexamethyleneamine).

Contact inhibitors are applied directly to the surface of the metal or in packaging materials (paper). Their action is limited in the place of their contact with the metal surface. The most used inhibitor of this type is $NaNO_3$, which adsorbs well on the steel surface and forms a passive film with high protective properties. Its application is carried out by immersing the steel products and details in aqueous solutions of $NaNO_3$.

Volatile inhibitors (vapor phase inhibitors) are substances that evaporate easily, quickly fill the air atmosphere around the metal and, being adsorbed on its surface, provide protection against atmospheric corrosion. The use of volatile inhibitors requires good cleaning of the metal surface and hermetic packaging that limits the volume of atmosphere surrounding the product. Protection can be ensured by wrapping the articles with inhibitor-impregnated paper or impermeable polymer film, using containers containing the inhibitor. Various organic compounds are used as volatile inhibitors - nitrites, carbonates and chromates of secondary amines, esters and salts of carboxylic acids. A disadvantage of volatile inhibitors is that the duration of their protective action depends strongly on the hermeticity of the packaging of the products.

The selection of an inhibitor begins with the selection of its required physical properties (solid or liquid; its melting and freezing points are important; is its degradation over time critical; it must be compatible with other additives in the system in which it will be used; any specific dissolution characteristics). The rules, dependencies, or theories for selecting an appropriate inhibitor are very strict. Synergism is often observed between different inhibitors and the controlled environment; usually mixtures of different substances are the choice of commercial inhibiting compositions.

The challenge in evaluating inhibitor performance is designing experiments that simulate properly the conditions of a natural corrosion system. The variables to be considered are temperature, pressure, medium velocity, metal properties, chemical composition of the corrosion medium. Adequate testing should include the most severe conditions that would be observed in the system and should not be limited to macro- and averaged conditions, but should also consider the influence of micro-conditions. The tested samples must be of the same metal that will be protected with the corresponding inhibitor; even very small changes in metal composition can lead to significant changes in inhibitor behavior. The effect of inhibitors can vary greatly for different metals and therefore the ordering of inhibitors in terms of their effectiveness determined against a given metal is not universal. The preparation of the metal surface in the study of inhibitors should be as close as possible to that of the real system being modeled. (A suitable methodology for preparing the metal surface is described in ASTM G 1).

The transportability of the inhibitor from the corrosion medium depends on its solubility in it. In general, inhibitors are divided into oil-soluble, water-soluble, oil-soluble-water-dispersible, etc. The solubility of inhibitor compositions cannot be estimated from the tabulated distribution coefficients of one of the compounds or of all the compounds involved in the composition - these coefficients must be measured for the particular inhibitor composition. The effectiveness of inhibitors against a given metal and a given corrosion medium is most often determined by the weight method - by immersing metal samples for a certain time in a corrosion medium with the corresponding concentration of the inhibitor. The specimens are then removed, washed, dried, observed - visually and using a magnifying glass to determine the areas of localized corrosion (ASTM G 46) or the corrosion products are removed to determine the corrosion rate. The effect of volatile inhibitors is studied by hanging the samples in special chambers in the corrosive atmosphere to which the inhibitor has been added. The appearance of the samples is monitored (ASTM B-117). Reporting the protective action of the inhibitor in %, which is commonly used, does not give information about the actual corrosion rate. It can be used to compare the effect of the action of different inhibitors.

The study of the action of film-forming inhibitors is more complicated. The test metal is immersed for a certain time in a solution containing an inhibitor (i.e., a film-forming solution) at a certain concentration, then washed and immersed in a corrosive solution for a certain time, after which the rate of corrosion is determined by the weight method. The composition of the film-forming, washing and corrosion-active solution is the same, the difference being that an inhibitor has been added to the film-forming solution in an amount aimed at reaching a corresponding concentration.

Electrochemical methods for investigating the effectiveness of inhibitors have 2 main advantages: a) They are fast – corrosion rates can be determined in minutes, while the gravimetric method requires days; b) Changes in inhibitor behavior are easily determined; thus, the incubation time of the respective inhibitor can also be easily found. The main limitation of electrochemical methods is the need for a corrosion medium that conducts electricity well. Another difficulty is the need to have a model for the action of the inhibitor. The electrochemical methods most commonly used to study inhibitory action are potentiodynamic polarization methods, linear polarization resistance, electrochemical impedance spectroscopy, and electrochemical noise.

5.6. Preparation of the surface before applying a protective coating

Protection of the metal surface from corrosion by modifying it (the use of coatings or the creation of protective layers) includes three main stages - preparing the surface; coating or surface modification; washing the treated surface.

To obtain a protective coating of good quality and good adhesion to the metal surface, it is necessary to prepare the metal surface in advance by cleaning and leveling its microrelief. For the different operating conditions of the facility and the different coatings that will be applied, different preparation is required. Correct surface preparation is the most important factor that determines the protective properties of the coating. About 80 to 90% of premature failures of coatings are due to improper preparation of the metal surface. Insufficient preparation leads to: deterioration of the adhesion of the coating and the base metal; reducing the cleanliness of the surface of the coating; development of corrosion processes under the coating; blistering of the coating; cracking and flaking.

The soluble salts - chemical pollutants invisible to the naked eye (salts containing Cl^-, SO_4^{2-}), attract moisture through the covering systems and lead to their premature destruction. Their more dangerous effect is that these salts, in combination with moisture, also cause corrosion directly on the substrate under the coating. These salts are often chemically bonded to the metal surface and do not wash away easily with water.

An important condition that *must always* be observed is that the cleaned surface should not remain unprotected for more than 6 hours - it begins to corrode quickly. After fire cleaning, the coating must be applied immediately - on a still warm (≈ 40 °C) surface.

Preparation of the metal surface includes the following types of metal surface treatment: mechanical cleaning, degreasing, pickling, polishing.

The mechanical preparation of the metal surface includes the following operations: processing with metal brushes, sandblasting, grinding, polishing and fire treatment, small details are cleaned by placing together with abrasive material in rotating or vibrating drums. The scale formed during the production of metals, as well as oxides, hydroxides, carbonates, etc., are removed from the metal surface by mechanical processing. Removal of compounds formed during storage of metal goods and a certain leveling of the relief is achieved.

Metal brushing is a quick method of preparing a metal surface that has had primer or paint on it and has almost no visible contamination (except for oil and rust contamination). It is applicable for a) light processing to obtain the necessary roughness – the abrasion is small (0.2 - 0.5 mm); b) intensive processing to eliminate coating residues in areas where they are not in good condition and c) abrasion (0.2 - 0.5 / 0.2 - 1.5 mm). The main disadvantage of cleaning with metal brushes is that the corrosion products cannot be completely removed from the cleaned surfaces and that often the surfaces are unnecessarily polished and contaminated with oils. This deteriorates the adhesion of the primer. Mechanical removal of solid deposits from the metal surface with brushes is convenient for small repairs to the coating, but is not suitable for general surface preparation of the entire structure to be painted. It can be used to remove thick layers of rust in order to reduce the cost of subsequent sandblasting.

Hammering is used to remove rust, paint, etc. from corners.

Fire treatment removes all organic and inorganic contaminants deposited on the metal surface, but causes some oxidation. It is not suitable for modern varnish and paint systems.

Sandblasting or centrifugal sandblasting are the best methods for mechanically removing oxides from the metal surface. The size of the abrasive particles is an important factor that determines the cleaning efficiency and the roughness of the cleaned surface. An abrasive with smaller particle sizes is used for the removal of thin lacquer-paint protective films or for the removal of rust from the metal surface, which is the result of pitting corrosion. Thermal spray metal coatings and thicker paint coatings require a rougher metal surface and therefore surface preparation is performed with larger particle abrasives. Wet abrasion using a water jet with very high pressure (> 2000 bar) and a speed of 10 - 12 m/h leads to complete removal of old coatings and rust. The result is comparable to that of dry abrasion, but premature oxidation of the surface of the structure is reached after drying. Wet abrasion using a water jet with high pressure (up to 1300 bar) and a speed of 5 m/h leads to the removal of old coatings, salts and rust. It is used to remove remnants of lower layers of former coating. Wet processing with an abrasive at low pressure (6-8 bar), cleaning speed maximum 10-16 m/h leads to a reduction of abrasion, removes accumulated dust and salts from the metal surface, eliminates the risk of spark formation. The result is comparable to that of dry abrasive treatment, but is accompanied by premature oxidation of the surface of the structure after drying. Steam cleaning with a pressure of 100-120 bar eliminates water-soluble or water-emulsifiable contaminants.

Through degreasing, metal products are cleaned of various fats, oils and polishing pastes left over from preliminary processing. Preliminary (rough) degreasing is achieved with various organic solvents (gasoline, benzene, petroleum, di-, tri-, tetrachloroethane, etc.). It is desirable to avoid chlorine-containing organic solvents, as they decompose and release corrosive ions. After that, chemical or electrochemical degreasing is applied. Chemical degreasing is used for parts with a complex profile and (for ferrous metals and most non-ferrous metals) is achieved by immersing them in hot alkaline solutions. Bases and other alkaline reagents from these solutions saponify vegetable and animal fats, forming soaps readily soluble in water. The mineral oils are separated by adding surfactants called emulsifiers to the solution. Electrochemical degreasing achieves the best cleaning in a very short time. Electrolysis is carried out in an alkaline solution, and the part to be degreased can be a cathode or an anode. If it is a cathode, gaseous H_2 is released on it, which mechanically breaks the oil layers on the metal surface and separates them on the surface of the solution in the form of small droplets. As a result of the release of H_2, the space around the cathode is enriched with OH^-, which leads to the saponification of fats. If the part to be degreased is an anode, O_2 is released on it, which acts analogously to H_2 in cathodic degreasing. For degreasing of thin-walled products, springs, hardened parts, only anodic degreasing is recommended, because the H_2 separated during cathodic degreasing can occlude in the metal lattice of the degreased part and make it brittle.

Pickling is a process of cleaning the metal surface from oxides (and other corrosion products remaining after the previous two treatments) by chemical or electrochemical treatment in solutions of acids (or bases for Al and its alloys). In chemical pickling, the part to be cleaned is immersed in diluted acids (or bases), which interact with the metal oxide on the surface of the part. As a result, easily soluble compounds are obtained. Pickling of ferrous metals is carried out in aqueous solutions of HCl and H_2SO_4 (10 - 15% HCl - at room temperature or 5 - 10% H_2SO_4 - when heated to 50-60 ^{o}C). In the pickling process, the acid often interacts not only with the oxide but also with the base metal. This releases H_2, which can occlude in the metal lattice. To avoid these undesirable reactions, corrosion inhibitors are added to the acid. In electrochemical pickling, electrolysis takes place in acid solutions, and the part to be cleaned can be a cathode or an anode. When the workpiece to be pickled is a cathode, the released H_2 breaks off the oxides from the metal surface and reduces the metal ions. When the workpiece to be pickled is an anode, the oxides are stripped from the metal surface by the released O_2. In addition, a small amount of the base metal beneath the oxide dissolves, this loosens the metal-metal oxide bond and the oxide is mechanically removed.

Additional pickling is a final process of preparing the metal surface, which is mainly applied just before the application of galvanic coatings. It is carried out by short-term processing in dilute acid solutions in order to remove the air-formed (during intermediate operations) oxide films.

Chemical and electrochemical polishing is a treatment (of the metal surface) aimed mainly at leveling the microrelief. Chemical polishing is applied to parts with a complex profile and is achieved by immersing the parts in specially prepared compositions (different for different metals) and under suitable conditions. Solutions for polishing steels are prepared mainly on the basis of H_3PO_4, H_2SO_4, HCl, CH_3COOH. Electrochemical polishing is achieved by electrolysis in suitable electrolytes and under suitable conditions, with the workpiece to be polished always being the *anode.* Anodic dissolution of the peaks of the roughness is carried out, which achieves a fine smoothing of the metal surface.

After each of the stages – degreasing, pickling and polishing, the processed parts are washed abundantly with water.

When selecting reagents for chemical degreasing, pickling or polishing, consideration should be given to whether the steel is hot or cold rolled. Cold-rolled steel has finer metal grains, its surface is smoother and less porous. Therefore, a smaller surface is exposed to the action of the reagents.

Treatment with rust converters also enters the preparation of the metal surface before the application of protective coatings. Rust converters are solutions or primers that are applied directly to a rust-covered surface in order to convert the corrosion products into insoluble products that are harmless to the metal facility, have good adhesion to it and protect it. There are 2 main groups a) compositions based on H_3PO_4, which forms layers of iron phosphates with good adhesion and b) compositions based on tannins.

The first, in addition to H_3PO_4, also contain wetting reagents that reduce surface tension and allow better penetration of the acid into the rust; solvents that remove greasy dirt and other components, varying by manufacturer.

Tannins (natural water- and alcohol-soluble products) react with iron oxides to produce a stable corrosion-resistant product with good adhesion to metal.

Although rust converters are very useful in theory, their application in practice is not easy because they must be applied depending on the thickness of the rust layer. If used in excess, H_3PO_4-based converters leave an acid on the metal surface that causes corrosion. If the same converters are used in insufficient quantities, not all the rust is converted and the remaining rust accelerates corrosion. The use of rust converters is not allowed in many cases.

After applying them, the surface must be washed before applying the coating. To ensure the necessary effectiveness of the application of rust converters, it is necessary to comply with the following requirements: removing dust from the metal surface with a soft metal brush; cleaning the surface with a vacuum cleaner; washing the water-soluble salts from the surface of the metal before applying the converter; degreasing with mineral spirits; applying the converter with a brush or gun; work at a temperature between 10 and 30 ^oC; converters must be with pH 2 - 2.5, homogeneous; the treated surfaces should not get wet for 24 hours (the time required to reach the full effect of the converter) after applying the converter (this period is longer at relative air humidity above 75% - 80 %); before applying the converter, sandblasting of the surface is not allowed; the application of the rust converter must always be followed by covering with a compatible coating; if possible, more expensive converters have to be used, which are better because they are based on tannins.

5.7. Non-metallic inorganic coatings

Inorganic coatings are metallic and non-metallic. Non-metallic inorganic coatings are divided into conversion, enamel, ceramic, silicate, insulating. Inorganic non-metallic protective coatings have good physico-mechanical properties and chemical resistance. The main disadvantages are related to their insufficient adhesion to the protected metal or to the large differences in the temperature coefficients of expansion of the coating and the metal.

5.7.1. Conversion coatings

Conversion coatings are protective layers of chemical compounds of the metal (oxides, phosphates, chromates), which are obtained on its surface under the influence of chemical reagents or electric current. Their main purpose is to protect ferrous and non-ferrous metals from atmospheric corrosion - alone or as a base under a paint coating.

Oxidation is a process of obtaining oxide coatings (with good adhesion) on metal products. Oxidation of steels is carried out by chemical, electrochemical and thermal methods, in which an oxide coating consisting mainly of Fe_3O_4 is obtained. In chemical oxidation, the products are processed in hot alkaline solutions (130-170 ^oC) containing oxidants ($NaOH + NaNO_3$ or $NaNO_2$) or in acidic solutions containing H_3PO_4, $Ca(NO_3)_2$ or $Ba(NO_3)_2$, MnO_2 and additives (different phosphates). Oxide coatings are a good base for applying film-forming substances. The protective properties of the oxide film are increased by impregnating it with oil, grease, varnish, etc. Electrochemical oxidation of steel is carried out by electrolysis in an alkaline (NaOH-based) or acidic electrolyte at elevated temperature (120 °C), with the processed part serving as an anode. Electrochemical oxidation is carried out at a lower temperature, in more dilute solutions (less consumption of reagents) in a shorter time, compared to chemical oxidation. It requires a direct current source, more expensive equipment, it is more difficult to control. Thermal oxidation is carried out by treatment with superheated steam (800 °C).

Oxidation of Al is carried out electrochemically - the so-called anodization, and the resulting coating is composed mainly of $A_{l2}O_3$. Anodic oxide coatings are obtained by processing in solutions based on sulfuric, chromic, phosphoric, oxalic acid. The coating consists of a thin non-porous barrier layer on the metal surface and a thicker, porous outer layer. Pores are closed by hydrothermal treatment in steam or hot water for several minutes. The oxide film (typically 2 μm to 25 μm thick) has good protective properties in atmospheric conditions, in water and some mineral acids, but is unstable in alkaline environments (pH > 8.5) and in highly acidic (pH < 4.0) environments. The coating is relatively fragile, it cracks under stress and therefore its additional protection is necessary, e.g., by painting. Its corrosion resistance is improved by dipping in hot solutions of chromates and dichromates, during which the pores of the outer oxide layer are blocked. The oxide film is a suitable base for further corrosion protection by painting or bonding protective coatings. In addition to increased corrosion resistance, anodizing ensures cleaner surface of the products, increases their resistance to abrasion and wear. Anodizing is also applied to improve the corrosion resistance of Mg and Ti alloys.

Phosphating is a chemical process of forming a water-insoluble film of H_3PO_4 compounds on the surface of ferrous and (less often) non-ferrous metals. The phosphate film has a very good adhesion to the metal surface, high corrosion resistance in atmospheric conditions, in a gas environment (except for H_2S), in liquid fuels, in lubricants, in neutral aqueous solutions. It does not get wet from molten metals, retains the magnetic permeability of the base metal, is heat resistant and has electrical insulating properties. The corrosion resistance of phosphate films is increased by treatment with oils, lubricants, varnishes, during which the pores of the coating are filled.

Phosphating of steel can be slow and accelerated. Conventional slow phosphating is carried out at room temperature, at lower concentrations of reagents in the phosphate bath and for a longer time (usually 30 - 90 min). Thick coatings (10 - 20 μm) are obtained, which are used mainly for corrosion protection, and also to facilitate the cold plastic processing of steel, to increase the wear resistance of products and for insulation (after filling the pores with varnish or grease). Accelerated phosphating takes place at high temperatures (75 - 95 ^{o}C), at higher concentrations of phosphating agents (as accelerators - chlorates, nitrates are added to the phosphating bath) and for a shorter time - up to 10 - 15 min. Thinner coatings (below 10 μm) are obtained, with very high elasticity, which are mainly used as a primer under varnish and paint coatings. In order to ensure maximum anti-corrosion protection, it is necessary to apply the varnish and paint coating immediately after the phosphate coating has dried.

Phosphating should not be applied to nitriding, heat-treated and high-strength steels, as well as to steels containing Al, Mg and Zn.

Chromate coatings are mainly used to protect non-ferrous metals. The coatings are usually obtained by electrolysis in acidic electrolytes containing $Na_2Cr_2O_7$, Cr_2O_3 and additives or immersion in acidic chromate solutions. The protective properties of chromate coatings are related mainly with the availability of Cr^{3+} ions and their action as corrosion inhibitors. The coatings are used as a base for paint or sealing coatings or on their own.

Steels containing nitride-forming elements (Cr, Mo, Al, V) are treated with NH_3, not containing water vapor, at elevated temperatures and **nitride layers** with increased resistance to fatigue, wear and corrosion fatigue are formed on their surface.

Austenitic and hard stainless steels are generally not protected by coatings applied to their surface. Their durability is due to the formed natural oxide films with protective properties. Typically, the formation of these films is assisted by immersing the articles in HNO_3 and dichromate solutions.

During the examination of the conversion coatings, their thickness (by weight or microscopic method), porosity (by contact of the coated article with a suitable solution or paste) and corrosion resistance (by electrochemical and electrical methods, by drop method, visually - after standing for a separate time in the corresponding corrosion environment) are studied.

5.7.2. Enamels

Enamels are inorganic coatings that are mainly used to protect steel and cast-iron products. Enamels practically isolate metals from their surroundings, not allowing H_2O and O_2 to pass through for a very long time. They are resistant to the action of all organic and inorganic acids, except HF and hot H_3PO_3, on salt solutions. They withstand very high temperatures (600 ^{o}C – ordinary enamels and 1000 ^{o}C – special). Enamels are vitreous masses that are obtained by fusing glass-forming materials with melting substances and additives. Glass-forming materials are quartz, quartz sand, feldspar, various clays. Na_2CO_3, K_2CO_3, $CaCO_3$, $Na_2B_2O_7$ are used as melting substances. Additives are colorants (MnO_2, Fe_2O_3, Cr_2O_3), matting compounds (SnO_2, NaF, TiO_2), and substances that increase the adhesion of enamel to the metal ($NiCO_3$, Co_2O_3). The components are taken in the appropriate ratio and after fine grinding and homogenization, they are sintered at 1200-1300 ^{o}C. The resulting material is cooled in water, dried, ground to a fine powder. This powder is used to prepare the enamel. First, primer enamel is applied - by spraying or pouring the product. The goal is to create good adhesion between the coating and the base and to create suitable conditions for applying the enamel. This is followed by drying the primer enamel at 60-80 °C and heating it at temperatures of 850-900 °C until a smooth, shiny surface is obtained. The next stage is the application of a covering layer of enamel with anti-corrosion properties, which is done in 2 ways: a) Dry method – the hot part taken out of the furnace, after of the primer enamel heating, is immediately covered with powder of the covering enamel. The powder is compacted on contact with the hot surface and sticks to it. This is followed by a new heating for sintering the covering enamel. Usually, this operation is repeated several times. b) Wet method – after heating the ground enamel, the object is cooled. A water suspension of the covering enamel is applied to the cooled surface by spraying, dipping or pouring. After drying, the object is placed back into a kiln to heat the enamel. This is followed by a re-application of a suspension of the covering enamel and again drying and heating. The operation is repeated several times.

5.7.3. Coatings from refractory materials

Redractory materials are high-temperature (over 1000 °C) melting oxides, carbides and nitrides of some metals. They are obtained by plasma atomization. They have a high resistance to abrasion and the impact of aggressive gases at high temperatures. Correctly selected, they significantly increase the life of the details and lead to savings on expensive and special steels and alloys. Al_2O_3, ZrO_2, WC_3 coatings are most often used. They are applied with special plasma guns. Main disadvantages of this type of coating are: change of the internal structure of the material under the coating when the temperature changes, poor adhesion with the base metal or alloy, porosity, large difference in the coefficient of thermal expansion of the coated metal and the coating. The addition of stabilizers (e.g., CaO and ZnO_2) and the application of interlayers of various metals are used to combat these disadvantages.

5.7.4. Silicate coatings

Coatings of silicate cladding materials are multi-layer systems in which the layer of binder, applied directly to the previously prepared metal surface, fills the joints between the cladding tiles or bricks that constitute the cladding layer. Materials can be applied in more than one layer. This type of coating is used to protect large metal structures. They have high corrosion resistance in highly aggressive environments at elevated temperature and low thermal conductivity, they are resistant to mechanical loads and abrasive wear. Acid-resistant ceramic tiles and bricks, porcelain, sital, and cast stone tiles are used for cladding. Combined linings are also used, consisting of a chemically resistant impervious underlayer (rubber compound, sheet polymer material, etc.) and a protective layer of silicate lining materials. Chemically resistant silicate screeds, acid-resistant cement and screeds based on synthetic resins (phenol-formaldehyde, epoxy, polyester) are used as binders.

Cement and concrete coatings are used to protect large metal facilities and structures from atmospheric and soil corrosion. Acid-resistant cement screeds are particularly effective, and are used both as a binding material in silicate linings and as a stand-alone coating.

Large metal facilities are effectively protected from atmospheric corrosion by shotcrete. Shotcrete is a suspension of sand, water and cement that is applied to the metal surface at high velocity. After the mixture has hardened, a dense, well-adhering to the metal surface coating is obtained, which is resistant to flue gases, but lets water through. Due to the alkaline reaction of this coating, it slows down the corrosion of the metals underneath. It is used to protect large metal equipment.

5.8. Metal coatings

Metal coatings are divided into cathodic and anodic. Cathodic coatings are made of a metal whose potential is more positive than the potential of the metal to be protected in the given corrosion environment. They protect the metal mechanically by isolating it from the environment. Therefore, the main requirements for these coatings are that they are dense, without pores and cracks and with good adhesion to the metal surface. If it is possible for the corrosion medium to come into contact with the protected metal, it is destroyed (it plays the role of an anode, and the coating plays the role of a cathode in the resulting corrosion GC). Anodic coatings are made of a metal whose potential is more negative than the potential of the metal to be protected in the corresponding corrosion environment. They protect mainly electrochemically. If there is a possibility of contact between the corrosion medium and the base metal (mostly through the pores of the coating), the coating is destroyed, i.e. it is an anode, and the base metal is a cathode. In this case, an important requirement for the coating is to have sufficient mass (thickness). The most widely used anodic coatings are made of zinc, which is due to their relatively easy application on steels, their ability to form dense corrosion products with good adhesion and protective properties, and the significantly lower rate of corrosion in atmospheric conditions, compared to unalloyed steel. In general, the corrosion protection provided by a metal coating depends on the nature of the coating metal and the thickness of the coating, with little effect of the method by which the coating is obtained. Metal coatings are obtained by the following methods: immersion in molten metal, metallization by sputtering, plasma deposition, thermal diffusion, mechanochemical, brazing or welding, vapor condensation, galvanic, chemical deposition. The most widespread are immersion in molten metal, metallization by sputtering, galvanic and chemical deposition.

5.8.1. Galvanic coatings

Hot-dip galvanization (immersion in molten metal) and metallization by sputtering are the methods most commonly used in practice to obtain non-galvanic anti-corrosion coatings on structural steel.

The application of a metal coating by hot-dip galvanization goes through the following stages: surface preparation; immersion in fluxes that ensure good contact between the base and the covering metal; immersion in molten cladding metal, during which the two metals react and an alloy of the two metals is formed on the surface of the protected metal; drying, during which a layer of the protective metal is formed on the surface. The method is most widely applied to obtain Zn coatings on structural steel. The thickness of the obtained coating depends on the preparation of the surface, the dimensions of the coated part, the composition of the steel (Si and P content). With a thickness of the coated steel not less than 6 mm, the thickness of the coating must be at least 85 µm (ISO 1461, ISO 14713). Coatings obtained by hot-dip galvanization are in many cases used alone as anti-corrosion protection, but in order to improve anti-corrosion resistance, painting coatings are often applied to them, after appropriate preparation, aimed at ensuring good adhesion between the two types of coating. A limitation of the method is the requirement that the metal used for coating have to possess a relatively low melting point. With some coatings (e.g., aluminum, tin), an intermediate layer of intermetallic compounds of iron is obtained, which is brittle and makes further mechanical or plastic processing of the products difficult. Disadvantages of the method are the relatively large consumption of non-ferrous metals, the difficult adjustment of the coating thickness, etc.

In metallization by thermal sputtering, molten metal is applied to an article whose surface is heated, while its volume is relatively cold and unchanged. This allows modification of the surface properties, without significant changes in the structure and properties of the underlying material. The molten metal is applied to the protected surface with a special spray gun, in which the covering material is melted. The material is fed into the gun as wire or powder. With the help of compressed air or inert gas, the molten material is fed at high speed onto the protected surface to which it adheres. Melting is done with flame burners, electric or plasma arc. No alloy is formed on the surface of the protected metal, the coating is only from the protecting metal. Disadvantages of the method are the significant porosity of the obtained coatings and their insufficiently strong adhesion to the base metal, as well as the significant losses of metal during the application of the coatings. The resulting pores in the coating are filled by applying an organic coating to the metal one. The preparation of the protected surface must necessarily include uniform roughening in order to achieve good adhesion of the coating. The method is used in practice mainly for the application of Al and Zn coatings on structural steel. These coatings are used to protect steel structures and equipment in atmospheric environment and from the action of ordinary and sea water. Aluminum coatings have increased corrosion resistance compared to zinc coatings in industrial atmospheres containing sulfur oxides and in gaseous environments at high temperatures. Typical coating thickness is 150-200 μm for Al and 100-150 μm for Zn coatings. Metallization can also be applied to obtain coatings of Pb, Sn, Ni, brass, chrome-nickel steels. The method is suitable for applying coatings on large structures and for carrying out repair operations. In general, the method is more expensive compared to obtaining a coating by immersion in molten metal. Plasma metallization makes it possible to apply coatings of hard-to-melt metals or their compounds.

Laminating is a process of metallurgical bonding (covering) of the metal to be protected and metal with increased corrosion resistance, the protecting metal being anodic to the protected. Thus, if the coating breaks down, the coating metal will provide cathodic protection to the coated metal. The process is mainly carried out by sheet or tube manufacturers using pressing, extrusion or rolling. A non-porous coating with controlled thickness and very good adhesion to the protected surface is obtained. A disadvantage of the process is that it is applicable only to products with a simple shape, which will not be subjected to large mechanical deformations afterwards. Covering carbon and low carbon structural steel with other corrosion resistant steel can also be done by welding, mechanothermal joining. Almost all corrosion-resistant steels and nickel can be bonded to unalloyed steel. Laminating saves up to 80% of the funds that would be spent if a completely corrosion-resistant steel was used instead of a coating.

According to the thermo-diffusion method, the coating is obtained as a result of diffusion of the atoms of the covering metal in the covered at high temperature. Typically, solid state reaction takes place, where the article to be coated and the coating metal (in powder form) are placed in closed heat-resistant reactors and heated at strictly controlled temperatures for specific time intervals. This is how aluminum, zinc, chrome, silicon coatings are obtained on steels.

The (electro)chemical deposition of the metal is carried out by reduction (without the influence of an external current) through solutions, the composition of which includes the ions of the deposited metal and a reducing agent. Under certain conditions, the reduction of the ions of the deposited metal occurs spontaneously, the reduced metal being deposited on the previously prepared metal surface. Technologies have been developed for the deposition of a number of metals - Ni, Co, Sn, Cu. The main disadvantages of the method are the requirement for very good preparation of the surface of the metal to be coated, the requirement for good electrical conductivity and purity of the electrolyte, the need to maintain a certain pH value of the electrolyte and a certain concentration of its constituent components. The advantage of the method is the possibility to obtain metal coatings on insulators and to deposit coatings of uniform thickness on products with a complex profile, with holes and internal surfaces. Most often in practice, the method is applied to obtain Ni coatings.

Thus deposited Ni coating is actually a composite and usually contains phosphorus and boron. When the process of chemical deposition of Ni coating is strictly controlled and the metal surface is well prepared, a coating with good adhesion, very good corrosion resistance and high hardness is obtained - therefore it is applied to products and structures operating under harsh conditions (oil production, marine industry). With good mixing of the nickel-plating electrolyte, a coating of very uniform thickness is obtained, even on products with a complex profile. Other advantages of chemical nickel plating are: The resulting coatings are less porous and harder compared to coatings obtained by the galvanic method; Hydrogenation of steel as a result of the process is generally 5 times less compared to galvanic nickel plating and 10 times less compared to chrome plating; The coatings have no residual stresses, they are self-lubricating and do not wear easily – unlike galvanic nickel coatings; They are well wetted by oils; Coatings containing small amounts of P, especially B-containing coatings, are easily welded; No dendrites are formed on the corners and edges of the coated products; The low P coatings are very hard and with exceptional uniformity of application even on complex profiles. Parts with medium P coatings are comparable to parts made from alloy steel. They are corrosion resistant in alkaline environments. Coatings with a high P content have the highest corrosion resistance, including in acidic environments, coal mines, oil extraction facilities, but they require additional adjustment of process parameters when obtaining them to avoid the occurrence of internal stresses in the coverage. Nickel coating containing up to 20% Teflon particles is a solution to problems related to friction, wear, slowing down the movement of moving parts or heated surfaces. Testing of nickel coatings on steels includes determination of hardness, thickness, adhesion, and corrosion resistance - 5% neutral spray (ASTM B-117).

5.8.2. Coatings obtained by electroplating

The electroplating (electrochemical deposition) of a coating is carried by reduction of cations of the coating metal by electrolysis of solutions containing the ions of this metal. The protected article plays the role of a cathode, and the anode is most often made of the protecting metal. The electrolyte also contains components that increase its electrical conductivity, adjust the pH and dissolution of the anodes, brighteners, levelers and other additives. For the purpose of anti-corrosion protection, coatings of Zn, Ni, Cu, Cr, Cd, brass, bronze are most often applied.

The advantages of the electropating method for applying metal coatings are: easy management of the process (regulating the thickness and properties of the coating by changing the composition and concentration of the electrolyte and the electrolysis mode - current, voltage, temperature); high purity and uniformity of the coating; good adhesion to the base metal; possibility of obtaining alloys with diverse composition and properties. The main disadvantages of the method are the relatively low productivity, difficulties in obtaining a uniform coating on parts with a complex profile, the requirement for very good preparation of the surface of the metal to be coated, the requirement for the purity of the electrolyte.

When a current flows through the electrolyte at the cathode (part being coated), the metal ions are reduced and the crystal lattice of the coating is formed.

$Me^{n+}.mH_2O + ne^- \rightarrow Me + mH_2O.$ (142)

Electrochemical dissolution of the metal is carried out at the anode (for soluble anodes).

$Me – ne^- + mH_2O \rightarrow Me^{n+}.mH_2O$ (143)

At the same time, hydrogen can be released at the cathode ($2H^+ + 2e^- \rightarrow H_2$), and oxygen at the anode ($4OH^- - 4e^- \rightarrow O_2 + 2H_2O$).

The yield of the deposited metal is usually lower than that corresponding to the amount of electricity passed through the electrolyte, due to the side reactions taking place simultaneously with the main processes of metal deposition and dissolution. For such cases, the concept of "current yield" is introduced - this is the ratio of the amount of substance $m_{experimental}$ actually reacted by a given electrode reaction to the theoretical amount of $m_{theoretical}$, calculated on the basis of Faraday's first law (equation 47) and assuming that only the reaction studied is proceeding:

$\text{yield } \% = m_{experimental} .100/ m_{theoretical}$ (144)

The nature of the deposited metal, the composition of the solution and the mode of electrolysis determine the structure of the galvanic coatings and their physico-mechanical and protective properties. The rate of metal deposition can be most easily controlled by current density, but also by electrolyte composition, temperature, special additives, etc.

Electroplating is usually carried out at a temperature of up to 90 ^oC, which leads to a reduction in equipment requirements and, accordingly, to a lower price.

Conducting the process at near room temperature reduces the problems associated with the different coefficients of thermal expansion of the base metal and the coating that are seen in other metal coating methods. A significant part of the elements can be deposited electrolytically from aqueous solutions of their salts - such are Zn, Ni, Cu, Cr, Cd, Mn, Fe, Co, Ni, As, Se, Y, Tc, Ru, Rh, Pd, Ag, In, Sn, Sb, Te, Re, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi. Some metals (Ti, Al) cannot be deposited electrolytically from aqueous solutions of their salts - for them, electrolysis is carried out only from solutions based on organic solvents. Elements such as Mg, Nb, Ta, and W can only be deposited by electrolysis of molten electrolytes (> 700°C). The elements B, P, V, Nb, Mo, Ga, Ge, and W can only be deposited in combination with each other or with another element in aqueous solution. The elements Co, Ni, Cu, Ru, Rh, Pd, Ag, Sn, Au and Pb can be deposited by both electrolysis and chemical methods.

Nickel plating gives a good appearance to the products by covering the irregularities of the base metal. It increases the hardness of products made of softer metals (Zn, Cu). When it is double-layered, it provides very good anti-corrosion protection. Nickel coatings have a very high resistance in atmospheric conditions, in water, base solutions and organic media as well as magnetic properties. They can be produced with minimal or no internal stresses.

Zinc coatings are applied to protect steel products from atmospheric corrosion, but are not reliable in highly polluted industrial atmospheres.

Chromium coatings have very good corrosion resistance in water, salt solutions, atmosphere and in oxidizing acids, combined with wear resistance. Because they are cathodic to steel and have significant porosity, chromium coatings are used as the outermost layer in multilayer systems (e.g. copper - nickel - chromium).

Tin coatings are used to protect steel mainly in neutral aqueous solutions and nutrient media, in atmospheric conditions.

Copper coatings are applied as functional coatings in electronics and in the composition of multi-layer coatings to protect steel products from atmospheric corrosion.

Chemical metal deposition (which is actually an electrochemical process) and electroplating of metal coatings are often referred to collectively as electrochemical deposition.

Composite metal coatings that combine the properties of metals and non-metals can be also obtained electrochemically.

Metal coatings are tested according to the following parameters: a) thickness - determined metallographically or by weight method; b) porosity - determined by changing the color of solutions or pastes with a suitable composition applied to the surface of the metal coating; c) adhesion to the metal surface - by bending suitably prepared samples, with an applied coating, around metal cylinders of different sizes and taking into account the diameter of the cylinder at which microcracks appear in the coating; d) wear resistance - by taking into account the conditions under which the coating is damaged by falling sand or rubbing with sandpaper; e) impact resistance - by taking into account the height from which, when a standard body is dropped, damage to the coating is achieved; f) hardness - through a special apparatus for determining microhardness and a microscope.

5.9. Organic coatings

Organic protective coatings include paint coatings, rubber coatings, coatings of polymeric materials and anti-corrosion lubricants. The use of organic coatings is based on the presence of one of the following sets of properties:

a) Ability to isolate the metal product from its surroundings, good adhesion to the protected surface and high electrical insulation properties. The ideal impervious coating should be completely unaffected by the relevant corrosive environment for which it is intended, atmospheric humidity, water and corrosive reagents. It must have a high dielectric constant and very good adhesion to the adjacent surface.

b) Good adhesion to the protected surface and the ability to help formation of a film that inhibits the metal surface. These coatings function by reacting with the corresponding corrosive environment to form a protective film or barrier on the metal surface.

c) Good adhesion to the protected surface and the ability to help shifting the potential of the protected metal in the cathodic direction until reaching a potential where the corrosion process is difficult, which is achieved by introducing cathodic protection pigments.

5.9.1. Paint coatings

Paint coatings are the most common, due to their relatively good anti-corrosion resistance, at a relatively low price. Their composition includes a film-forming substance (binder), solvent, filler and additives: pigment(s), plasticizer, hardener, etc.

Film-forming substances (binders) turn the coating after its application into a membrane that is dense, hard, uniform and with good adhesion to the covered structure. Not all film-forming substances have anti-corrosion properties, so a limited number of them are used in anti-corrosion coatings. According to the essential chemical reactions in which they participate, film-forming substances are divided into: a) reacting with O_2 - alkyd resins, epoxy esters, urethane alkyds, silicon alkyds; b) varnishes - polyvinyl chloride polymers, chlorine-containing rubbers, acrylic compounds, bituminous materials; c) substances that convert under the action of heat - hot melts, organizols and plastisols, powdery materials; d) co-polymers - epoxy polyurethanes; e) condensation binders; f) coalescent binders; g) self-hardening silicates soluble in organic solvents.

Pigments are powdery substances that are insoluble in paint and are mixed with it by good dispersing techniques. By origin they are natural and synthetic substances, by chemical nature - organic and inorganic. In one coating, several pigments can be used, which contribute to the improvement of various properties of the coating: color, protection of the binder, increased corrosion resistance, inhibition of corrosion processes, mechanical strengthening of the film, increased covering ability, improved adhesion, avoidance of coating sagging, defect reduction, gloss control. Currently, zinc phosphate is the most widely used anti-corrosion pigment.

It should be noted that for good protection, the compatibility of the pigments, the binder and the metal to be protected is very important - e.g. minium has good corrosion protection properties for ferrous metals, but accelerates the corrosion of non-ferrous metals.

Most coatings are obtained from a material in which more than one solvent is involved. The type of solvent affects viscosity, flow ability, drying speed, sprayability or brushability, gloss. One of the most serious problems (especially with adhesion and curing) that can occur with organic coatings is related to poor solvent selection. There is no universal solvent that can be used for all types of coatings. The best solvent for one type of coating can often be impractical for another.

Fillers are introduced into paint materials to reduce their price and to improve their mechanical properties. Natural inorganic materials (clay powder, andesite, kaolin, barite, mica, talc) and organic materials (graphite, wood, fibers) are used.

Plasticizers give elasticity to the coating and slow down its aging. Liquid rubbers, dibutyl phthalate, dioctyl phthalate, etc. are used.

Hardeners accelerate the hardening of synthetic resins contained in some coatings (epoxy, phenol-formaldehyde).

Multi-layer protective coatings are usually used - Fig. 39, the main requirement being the compatibility of the materials (i. e. belonging to the same generic type) used in all layers.

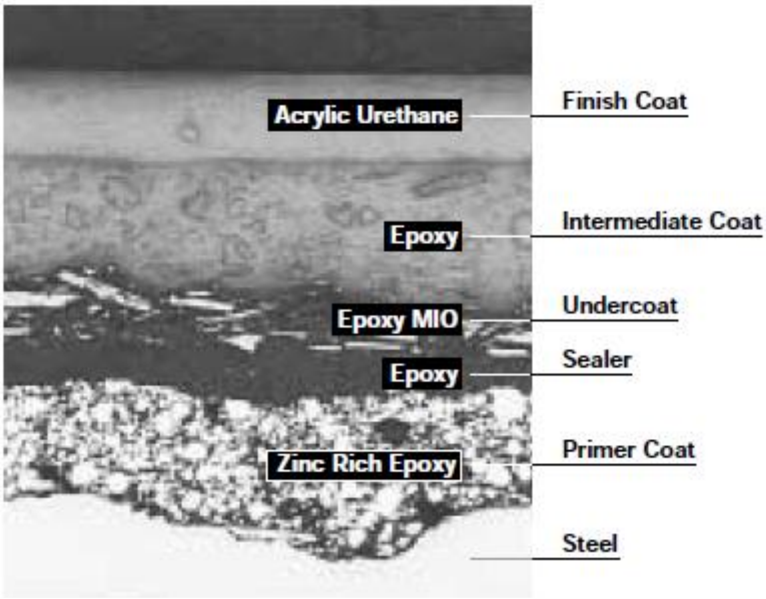


Fig.39. Protective paint system

The primer coat is the main and most important component of all anti-corrosion coatings. It is applied directly to the cleaned metal surface. A good primer slows down the development of non-uniformities in the coating (point defects, defect areas, cracks) that facilitate corrosion. In order to protect well, the primer must have good adhesion to the metal surface or the possible conversion coating on it. The primer may contain a leaching inhibitor in the appropriate concentration (e.g., chromate pigment). The main functions of the primer are: to ensure good adhesion or a strong bond with the substrate; to improve the internal strength and provide adequate flexibility of the coating; to ensure inertness to the environment; to ensure a good bond with the intermediate layer of the coating. There are two main types of primers: a) primers pigmented with metals (e.g., Zn) which are anodic to the metal of the structure being protected – when the protective coating is broken, the metal from the pigment in the primer acts as an anode and protects the relevant construction; b) primers pigmented with inhibiting substances (e.g. $Zn_3(PO_4)_2$), which have a protective effect after breaking the upper layers of the coating. The most widely used are primers rich in zinc or zinc silicates. The sealing layer is made of film-forming substances. The undercoat and intermediate layers are used to reduce water and oxygen permeability, improve resistance to tensile stresses and (when containing inhibiting pigments) to increase the overall protective properties of the coating. The covering layer provides the desired appearance and resistance of the product's surface to the surrounding environment. Depending on the conditions of use, this coating must be resistant to moisture, solar radiation, various atmospheric polluting gases, bacteria and fungi, solid particles.

Paint materials are classified in different ways, but most often by the type of pigments or their film-forming substances. The primers for steel are classified mainly according to the inhibiting pigments used in their composition. Materials for under-coat, intermediate and covering layers are usually classified according to the binding substances included in their composition (epoxy, vinyl, urethane).

The main generic types of paints are the following:

- Air-drying (alkyd) paints – these materials, when drying, form a film through oxidation processes involving the participation of O_2 from the atmosphere. This necessitates limiting their thickness to about 40 μm. Already formed films have limited solvent resistance and (usually) low chemical resistance.
- One-component (acrylic, vinyl, bituminous) - these materials form a film on the surface of the protected product by evaporation of the solvent (without the inclusion of an oxidation process). They can be applied in

the form of a film with a thickness in the order of 50-75 μm, bearing in mind that the evaporation of the solvent is somewhat difficult for films with a thickness close to the upper limit. The formed film remains relatively soft, with poor resistance to organic solvents, but good resistance to other chemicals.

- Two-component chemically resistant materials (epoxy, urethane) - they consist of two components (base and hardener), which are mixed directly before use. The formation of the protective film is based on the polymerization processes that continue even after the coating has been applied to the article. After evaporation of the solvent, films are obtained that are dense and rigid, with good resistance to organic solvents and inorganic chemicals. This type of coating is called "solvent-free coating" and can be used in the form of quite thick films (around and above 1000 μm.)

The method of application and the conditions under which the paint coating is applied play an essential role in its protective properties and durability. The main technological operations in the application of coatings are surface preparation, application of primer, application of the upper layers of the coating and drying.

The standard methods used to apply paint coatings to steel structures are brush application, air (pneumatic spraying) and airless (mechanical, electrostatic) spraying. For small details, the dipping method (in molten paint) and electrophoresis can also be used. Application with a roller should be avoided due to the impossibility of uniformly covering hard-to-reach areas. Brush application is the simplest, but at the same time the slowest and the most expensive method (with high labor cost). Its advantages are ensuring better wetting of the metal surface with the paint, which after hardening provides better adhesion of the coating, the possibility of application in hard-to-reach and small areas, less sensitivity to the quality of the preliminary preparation of the metal surface, less environmental pollution. Disadvantages include harsh working conditions, uneven coverage, difficulties in using quick-drying materials. Painting by dipping is mainly used for coating serial parts and small-sized products. The painted objects are hung on special devices and dipped (manually or by mechanized means) into the bath with the paint. The thickness of the resulting coating is difficult to adjust. During spraying, the paint is supplied in the form of fine droplets to the metal surface. In pneumatic spraying, the droplets are formed by mixing the paint with compressed air in conventional air guns. The disadvantage of the method is the significant loss of the applied material and the poor working conditions. In mechanical airless automated spraying, droplets are formed by hydraulic compression and delivered by airless guns. The loss of paint is less, the method makes it possible to use materials with greater viscosity and to reduce the consumption of solvents. In electrostatic airless spraying, the paint droplets are charged using an external voltage source, and the protected surface is oppositely charged. The applied high voltage (100 - 150 kV) between the covered part and the charging device creates an electrostatic field that directs the dispersed and identically charged paint particles to the surface of the part to be covered. A high degree of utilization of the paint material is ensured. Airless spraying equipment is more expensive, highly skilled labor is used, and the method is applied for so-called "solvent-free coatings" when long-term protection of important structures is needed. In electrophoretic application, the paint is deposited on the protected metal surface by electrophoresis. The method is highly productive, with possibilities for full automation, easy adjustment of coating thickness and exclusion of expensive organic solvents from the technological process. The resulting coatings are uniform (even on parts with a complex shape) and of high quality. Disadvantages of the method are the need for special paints, expensive equipment and its inapplicability for painting non-conductive materials.

Temperature and humidity are the most important painting process conditions, which effect the coating quality. The temperature of the air and of the surface to be protected effect the evaporation of the solvent, the viscosity of the paint, the drying and curing process. Where heating is required, it should always be indirect. A coating should not be applied when the relative humidity of the atmosphere is high, making it possible to create a condensation layer of moisture on the surface. Normal practice is to measure the temperature of the surface to be protected with a contact thermometer and maintain its temperature at least 3 ^{o}C above the dew point.

The final operation in the application of a paint coating is drying, which, depending on the type of film-forming substance, is carried out at room or elevated temperature. Drying at elevated temperature in special dryers (radial or convective) is applied in cases where the coating is obtained as a result of polycondensation processes.

The advantages of paint coatings are: low price, possibility of application on constructions with a complex profile and for combination with other means of protection, easy repair. Their disadvantages are: relatively low heat resistance, mechanical strength and hardness, tendency to aging, insufficient resistance in water corrosive environments. These coatings provide sufficiently reliable protection against atmospheric corrosion, with proper selection and application technology (including preparation of the metal surface).

Painting materials based on vegetable oils are suitable for painting external surfaces of metal structures and equipment located outdoors or indoors, but in the absence of aggressive gases. Nitro-cellulose and alkyd paint materials are suitable for protection against atmospheric corrosion. Perchlorvinyl materials are used for protection in an atmosphere contaminated with vapors of mineral acids, Cl_2 and other aggressive gases, they are resistant to the effects of water and mineral oils. To improve their elasticity and adhesion to the base, alkyd or other resins are added. Bituminous and chlorinated rubber painting materials protect well in diluted and moderately concentrated aqueous solutions of salts, acids and bases and in an atmosphere of aggressive gases. In practice, they are used in paint materials based on compositions of bituminous materials and synthetic resins (mainly epoxy), which have very good anti-corrosion properties. Materials based on phenol-formaldehyde resins are resistant to most aggressive environments (mineral acids, salt solutions and a number of organic solvents) with the exception of strong oxidizers and bases. A disadvantage of these materials is the need for heat treatment to harden the coatings, which makes it difficult to apply them on large-sized equipment. Materials based on urea-formaldehyde and melamine-formaldehyde resins are used to obtain waterproof and weatherproof coatings with good hardness and wear resistance, the elasticity and adhesion of which are improved by the addition of alkyd resins. Materials based on epoxy resins are resistant to acid solutions, bases, the most commonly used organic solvents (gasoline, acetone, oils) and atmospheric conditions. They are characterized by high hardness, wear resistance and chemical resistance. Epoxy-phenol-formaldehyde materials have particularly high protective properties. Their main disadvantage is insufficient resistance to the action of ultraviolet rays. Furyl paint materials have good heat resistance (up to 150°C) and are resistant to mineral and organic acids, alkaline solutions and organic solvents (kerosene, gasoline), but are not resistant to HNO_3 and hot alkaline solutions. Polyurethane materials combine resistance to: aqueous solutions of acids and bases, etc. aqueous aggressive media, of organic solvents with hardness and increased resistance to abrasive wear. The same qualities, supplemented with significant heat resistance, are also possessed by the paint materials based on organosilicon polymers.

There is no simple rule for selecting the most suitable coating anti-corrosion system. In addition to the needed duration of use of the protected product, other factors that influence the choice are the price and prestige of the protected structure, the type of protected material, the cost of possible repairs, the cost of the coating. Increasing requirements for safe and healthy living conditions lead to the cessation of the use of organic coatings that contain toxic or flammable substances. In addition, legislation and increased public awareness of environmental protection requires the use of environmentally safe organic coatings - this means coatings that are water-based or with a reduced content of organic toxic solvents and an increased content of solid components.

The factors that effect the quality of the paint coating are the following:

1. The method and quality of the preparation of the metal surface; The durability of the coating is increased several times when using abrasive jet cleaning - compared to manual preparation of the surface to be protected. In most cases, shot blasting with round particles of the abrasive material is used, but for coatings and primers that are applied by thermal injection molding, processing with hard, sharp-angled particles is more suitable.
2. The compatibility of the type of protective coating with the conditions under which the painted article will be operated - e.g. for sea water and marine atmosphere (cathodic control, oxygen depolarization) it is suitable to use in the coating Zn and Al pigments which have a protective role. For oxidizing environments, under anodic control, it is appropriate to use paints with passivating pigments, e.g. chromates.
3. The type of primer and its compatibility with the method of preparing the surface and with the paint; Many of the modern primers that are based on synthetic resins are not compatible with manual preparation. In general, oil and alkyd primers should not be covered with layers of materials that contain strong solvents, i.e. they should not be used with epoxy paints, bituminous coatings, etc.
4. Compliance of the conditions of application of the coating with the method of its application: e.g. paint coatings should not be applied at relative humidity >80%; coatings should not be applied with a brush at a temperature < 5 °C and by mechanical spraying at a temperature < 15 °C;

5. The conditions of application and drying of the coating - viscosity of the paint, the change of which must be taken into account with the temperature and humidity of the atmosphere; the temperature and duration (at least about 72 h are necessary) of drying the paint. The best quality coatings are obtained when painting is carried out in closed and heated rooms - elements of bridge and building structures can be painted in this way and then connected. Coatings obtained by thermal injection molding are porous and require treatment with a low viscosity pore sealing agent, preferably followed by a further application of a top coat. Special attention should be paid to the treatment of weld areas (removing residual fluxes and electrode material) and tapered parts to ensure the same quality of preparation as the rest of the surface of the structure. Connections made with raw bolts are usually protected with primer only. For connections that must withstand significant friction and stress, the contacting surfaces must be thoroughly cleaned of any dirt or coating that would reduce sliding between the parts. Only certain zinc-silicate primers or thermally applied metallic coatings (serving as a primer) may be used, but organic coatings should not be used. Bolts and brackets used in the structure must be provided with the same degree of coating protection as the main steel.

6. The thickness of the coating - in general, the thicker the coating, the better its protective properties (except for excessively thick coatings, in which stresses and other defects occur); e.g., for mine conditions, the coating thickness should not be less than 200-250 μm; to take into account possible mechanical effects after painting.

The importance of the various factors that influence the quality of the varnish and paint coatings can be assessed according to a point system.

In order to avoid the preparation of low-quality coatings, it is necessary: a) To take into account at the design stage that this protection measure will be applied - e.g. inaccessible places, cracks, places that can retain moisture should be avoided; b) The coating must be planned considering the "worst case" scenario, (type, method of surface preparation, number of coating layers and their thickness, method of application); c) The application of the coating must strictly follow the prescribed methods and conditions; d) The covering material must comply with fire prevention measures.

The following factors determine the choice of anti-corrosion specification: the expected "life" of the structure and the possibilities for maintenance repair; the environment in which the structure will be used; the size and shape of structural elements; the possibilities that exist in the workshops for applying the coating; the possibilities of applying the coating on site, after assembling the structure; the price.

The following defects and damages are observed in the paint coatings:

a) Loss of color (darkening) – due to applying too thick layer of paint, and painting at too high relative humidity and too low a temperature;

b) Loss of gloss – it is due either to the use of material unsuitable for the relevant conditions or to non-compliance with the technological conditions when applying the coating (too high relative humidity and/or too low temperature);

c) Appearance of dust on the surface of the painted article as a result of the decomposition of the film-forming substance under the action of atmospheric factors and UV radiation - due to the use of material unsuitable for the relevant conditions;

d) Wrinkling of the coating during its drying - due to the application of a very thick layer of paint;

e) Paint drip - due to painting an inclined surface with insufficiently thin paint;

f) Granular coating - due to the presence of dust or grease on the article to be coated, paint contamination;

g) Loss of elasticity and plasticity of the paint and cracking of the paint layer (formation of the so-called "crocodile skin") - due to drying of the paint at too high a temperature, insufficient drying of the primer and intermediate layers before applying the covering layer or the natural aging of the paint during operation;

h) Peeling and flaking of the paint - due to poor preparation of the covered metal surface;

i) Blistering in the coating - due to painting on an oily surface, presence of moisture in the paint, application of too thick layers of paint, excessive agitation of the paint during dip application. The nature of blistering depends on many factors related to the specific combination of primer, paint, surface preparation of the metal to be protected, metal coating and environmental conditions.

The most common forms of the loss of adhesion of the paint and the substrate are:

a) Transverse development of corrosion from a crack in the coating or from the ends of the product, where the base metal, intermediate coating, primer and paint are simultaneously exposed to a corrosive environment. The end result is the loss of adhesion.

Corrosion can be due to a chemical reaction at the "finishing coat / intermediate coating" interface, which causes the destruction of the adhesion bond, or to a reaction in the volume of the intermediate coating located between the protected metal and the coating layer - in this case, the "paint/metal" bond is completely destroyed".

b) Blistering under the paint - caused by corrosion reactions occurring under the paint. This defect is due to the fact that the paint finish is not impervious to water reaching the metal surface when the painted surface is wet. If the initial strength of the bond is not good, if atmospheric pollutants are particularly hazardous to this type of paint, etc., blisters may develop under the paint even if there are no inhomogeneities in the coating. As the blisters develop, they begin to coalesce, and the overall effect is that the paint cracks and peels over large areas of the surface.

The transverse development of corrosion and the formation of bubbles under the paint is particularly dangerous, as it combines all elements of corrosion in cracks - a small local anode and a large cathode (outer surface), formation of an acidic environment, formation of gaseous H_2. In order to minimize the loss of paint adhesion, all the requirements prescribed by the paint manufacturer for the preparation of the metal surface, the thickness of the primer layer and the coating layer, the type of paint used in the top layer must be observed. The manufacturer's recommendations take into account: the type and concentration of the corrosion-acting environment (acid rain, sea salts, polluting fluids from various industries, the humidity of the environment), the amount of ultraviolet light to which the coating is exposed, the appearance expectations.

Usually, the durability of paint coating products is less than the planned service life of the protected structure (product). This necessitates renewal and repair of existing coatings. First, it is necessary to establish whether the coverage will be renewed in full or in part. The coating is washed to remove any possible contaminants. Where the damaged coating has good adhesion to the metal being protected, it can be used as a base for the repair coating. This is the case when no rust is observed on the coating, but only a loss of color and shine. Hard coatings (e.g. epoxy) are lightly scraped to ensure good adhesion of the newly applied coating. When the coating is destroyed only in individual areas (bubbles, flakes, paint cracks, light rust), and the majority of the protected structure has preserved its integrity, only these areas are prepared for the application of the new coating. The coating on these areas is repaired by applying the preparation methodology, materials and technology of applying the protective layers, which were used in the previous coating procedure. Then the whole structure is painted. When rust is observed on the coating in the form of numerous spots covering almost the entire surface, then the coating is completely removed, the metal surface is cleaned according to the appropriate technology and a new coating is applied.

In all cases of application of paint coatings on the metal surface, a "wet film" is formed at first, which later dries. The thickness of the "wet film" can be measured by using a thread gauge. The thickness of the resulting "dry film" can be determined with a sensor operating on the basis of magnetic induction. The relationship that exists between the "wet film thickness - WFT" and the "dry film" (final) film thickness - DFT is determined by the percentage composition of solid particles in the paint (% VS) and is represented by the expression:

$$DFT = WFT \times \%\ VS \qquad (145).$$

To characterize the protective properties of the coatings, the following parameters are determined: porosity, adhesion, exfoliation, hardness, elasticity, mechanical strength, moisture permeability, water absorption, presence of bubbles, corrosion of the metal under the coating, wear resistance, dielectric properties, change of gloss and color, pollution containment and paint dust formation. Appropriate standardized methods are used.

The following methods are used when testing the corrosion resistance of paint coatings:

1. Testing in a humid atmosphere - in special chambers
2. Test with periodic spraying with salt solution in special chambers
3. Test by immersion in a corrosive environment
4. Accelerated electrochemical studies
5. Field trials

Testing in a humid atmosphere is one of the most realistic methods for determining the corrosion resistance of paint coatings, due to the good correlation of the results with the real behavior of the coatings. It should not be forgotten, however, that the obtained value for the corrosion rate is a relative value and is determined by many parameters that must be controlled. The test is carried out in pressurized chambers in which a constant relative humidity is ensured. The samples, with paint coatings on their surface, are hung at an angle of 15 or

30^{o} from the vertical and after staying in the chamber are inspected (up to 5 min after removal from the chamber!) from the upper side for irregularities in the coating. The appearance of bubbles in the coating is evidence of the beginning of the process of destruction of the coating.

The intermittent salt spray coating test involves more variable parameters than the wet atmosphere test and the results are generally less representative. It is carried out in chambers in which a salt fog is created by mixing a 5% NaCl solution and air saturated with water vapor. The salt used must not contain iodide. The saline solution is changed every 48 h, it is operated at a temperature of 35 ^{o}C. On the samples, with the paint applied to them, with the help of a special device or a sharp knife, cuts in the form of "X" are made at an angle specified by the standards. After the samples have been in the chamber, they are inspected for blisters greater than 3 mm in diameter or rusted areas greater than 3 mm in size around the cuts. The rusting of the samples on the edges is normal, since there the paint coating is thinner and this destruction is not taken into account. Specimens must be examined within 5 min of removal from the chamber. The results may be affected by the washing and drying conditions of the samples removed from the chamber and therefore all these operations should strictly follow the descriptions of the standards or be the same for different samples.

In the test by immersion in a corrosive environment, the metal samples, with a paint coating applied to them, are immersed in distilled (deionized) water for a certain time at a temperature of 35 ^{o}C. As variations of this standard, half-immersion of the specimens and observation of the development of corrosion processes around the water-line are used; replacing distilled water with potable water; temperature variation from 25 to 100 ^{o}C; immersion in aqueous solutions or in organic solvents instead of d.H_2O.

Accelerated electrochemical studies are used to quickly compare the performance of different coatings in a given corrosion environment or the resistance of a given coating to different environments.

Accelerated comparative semi-quantitative testing of different coatings in terms of their corrosion resistance can be done by using the current generated in a corrosion GC constructed of a steel specimen on which the test material is coated and a Zn plate. The electrolyte is 3% p-p of NaCl, the distance between the electrodes is 3 cm. To better model the natural operating conditions of the coating, instead of Zn, a steel plate (which is the substrate of the investigated coating) can be used. It works with the so-called "zero resistance" circuit, in which the voltage drop in the investigated galvanic pair and the additional resistance (from the wires) is compensated by applying an equal magnitude and opposite sign voltage from an external source. (The control of the regulation of the scheme is carried out with a galvanometer.) At a higher measured current, the coating has weaker corrosion-protective properties.

For quantitative studies, the impedance methods (which are often the only suitable methods for examining the coating at the beginning of its contact with the corrosive environment), recording and analyzing the electrical noises (current and potential) and the method of measuring the linear polarization resistance are applied.

Field tests give the most reliable results on the behavior of the coating, the rate of corrosion and the course of the process of coating breakdown and corrosion development, but require at least a period of about 2 years. The samples are placed in the corresponding corrosion environment (while complying with the requirements for their location; volume of the corrosion environment corresponding to a unit area of the sample, etc.) and are removed and analyzed at certain time intervals, according to a previously developed program.

The methods described in this section for testing organic coatings are also used for testing rubber and polymer protective coatings.

5.9.2. Coatings of layers of polymeric materials

Coatings made of polymeric materials are usually applied to protect pipelines.

Thermoplastic and thermoreactive polymers are used: fluorolon - 4, PVC, polyethylene, polyamide, polymethyl methacrylate, polystyrene, epoxy resins, etc. The choice of polymer coating material is determined by the operating conditions, the dimensions and construction of the protected facility and the protective properties of the polymer.

In practice, four types of coatings from polymeric materials are used: a) thin layers obtained from powdery materials (applied by gas-plasma and electrostatic spraying, in a pseudo-fluidized bed); b) sheet polymer coatings; c) coatings of liquid and pasty polymeric materials; d) coatings obtained from suspensions of polymeric materials.

Powder polymer coatings (polyethylene, polymethyl methacrylate, polystyrene, polyvinyl chloride, fluorine-containing polymers) are used to protect small-sized products. Special stabilizers are added to the polymer powders to reduce thermal destruction during coating application, and fillers are added to improve the adhesion of the coating to the metal.

Gas-flame spraying is carried out using special guns, which, with the help of compressed air, direct the particles of the thermoplastic polymer to the surface to be protected. At the exit from the gun, the particles are heated and softened by an air-acetylene flame, and falling on the preheated metal surface, they melt completely and form a uniform coating.

In flameless sputtering, the powdered polymer material is applied directly to the preheated work piece (the surface of which has been cleaned and roughened) without the use of a flame. In electrostatic sputtering, the polymer particles are charged and moved in the electrostatic field created between the sputtering device and the coated part. After creating the powder layer on the parts, they are subjected to heat treatment to seal the coating. Advantages of the method are the better use of the polymer material, the uniformity of the coatings and the elimination of the need to pre-heat the parts.

The formation of coatings in a fluidized bed of thermoplastic polymer powders is the most productive of the considered methods and is suitable for applying coatings to small-sized parts with a simple shape. The preheated work piece is immersed in a special vessel and the polymer particles, hitting the heated metal surface, soften and fuse into a uniform, continuous coating.

Coatings made of sheet polymer materials (polyvinyl chloride, polyethylene, polypropylene, isobutylene) are used to protect large-sized equipment. Various thermosetting adhesives are used to attach the sheet materials to the protected (pre-scratched to improve adhesion) surface. In practice, two-layer sheets of different polymer materials are also used, e.g. polyethylene / polyisobutylene, polypropylene / rubber, polyethylene or polypropylene / cotton fabric, which combine the properties of both materials. Sheet materials are also used as an impermeable underlay in combined silicate linings.

Coatings made of liquid and pasty polymer materials are used to protect metal and concrete structures of various shapes and sizes. The most widely used are liquid polymer compositions based on thermoreactive resins - epoxy, phenol-formaldehyde, polyester, furan and various combinations between them. In addition to resin, these materials contain hardeners, plasticizers, fillers, solvents and other additives. The type and amount of resin and filler determine the viscosity and properties of the various resulting compositions. Coatings made of liquid polymer materials can be applied by all the methods used in the paint coatings technique. Coatings of pasty polymeric materials (usually polyvinyl chloride based) are applied by spraying or dipping with subsequent heat treatment. Coatings obtained by using suspensions of polymeric materials can be obtained from all thermoplastic polymers. They are applied by dipping, spraying or manually with a brush. The fluorine-containing polymers are widely used, as they combine high chemical resistance with wear resistance, a low coefficient of friction and excellent electrical insulation properties.

The advantages of coatings made of polymer materials are: high water, atmospheric and chemical resistance, good thermal and electrical insulation properties, relatively low price. Their disadvantages are insufficient heat resistance and tendency to aging.

The application of polymer protective coatings on pipelines and other structures depends on the corrosion environment.

5.9.3. Rubber coatings

Different rubber materials are used: polysulfide (thiocol), chloroprene (nairite), organic silicon, isoprene, rubber materials based on butyl rubber, such as fluoro-rubber, butadiene nitrile and silicone rubber, which have increased chemical and heat resistance (e.g., silicone).

The application of the rubber coatings is done by: lining the protected surface with an unvulcanized rubber mixture with subsequent vulcanization, gluing pre-vulcanized lining materials, applying rubber solutions and pastes with subsequent vulcanization. The first method has found the widest application. The technology for coating metal surfaces with sheet rubber materials includes the following operations: preparation of the protected surface and the sheet material, application of glue, tight fastening (gluing) of the coating, heat treatment (vulcanization at temperatures of 120 - 160 °C in autoclaves - for small-sized products or directly in the protected product itself by heating with steam or warm air - for large-sized equipment) of the coating.

When lining structures with pre-vulcanized rubber sheets, the quality of the coating is highly dependent on the adhesion of the sheets to the substrate and to each other. The adhesives used for gluing are based on rubber derivatives, synthetic resins and other high molecular compounds. Rubber gluing should not be carried out at a temperature of the air, the lining material and the protected structure lower than 10 ^{o}C. The covering of metal surfaces by applying rubber solutions and pastes is a suitable method for objects with a complex profile and to obtain seamless and more uniform coatings in terms of physico-mechanical properties and chemical resistance. Chloroprene, silicone and polyurethane rubbers, as well as some thiocols are suitable for this application technology. The advantages of rubber coatings are: good chemical resistance to inorganic compounds (with the exception of strong oxidizers), wear impact and deformation resistance, high adhesion with the covered metal surface. Their disadvantages are: relatively low heat resistance (120-130 °C, and for natural rubber-based coatings up to 70 °C) and relatively low resistance to organic solvents and petroleum products, tendency to aging.

5.9.4. Anti-corrosion lubricants and sealing systems

Anti-corrosion lubricants are used for temporary protection against corrosion. They are cheaper than the coatings described above, do not require such careful preparation of the metal surface, allow the introduction of inhibitors, are easily removed. They protect relatively well from atmospheric corrosion (including in aggressive gas environments), have relatively good water resistance. Their main disadvantage is the difficulty in applying them.

Bonding compositions are used to protect bonds by preventing the ingress of moisture and contaminants and serving as a reservoir of passivating inhibitors. These compositions must remain flexible throughout the operation of the facility and allow for easy disassembly.

Sealing compositions are used to prevent the leakage of fluids from the connection points, the ingress of moisture into the facility through the connections, and the isolation of various metals in the area of their connection.

Various synthetic rubbers are used as binding and sealing compounds. These compositions harden enough to be paintable, but remain flexible enough not to crack when bent. The most used sealants are those based on polysulphides. They also contain corrosion inhibitors.

Hydrophobizing compounds provide additional protection in the event of damage of paint coatings. They displace water from surfaces and cracks. They are applied by dipping the products in them, using a brush or spraying. They are usually prepared on the basis of lanolin, contain various solvents and inhibitors. Evaporation of the solvent may leave thin soft films, semi-hard films or hard films on the protected metal surface, providing varying degrees and durations of protection.

5.10. Electrochemical protection

During corrosion, the anodic current (characterizing the dissolution of the metal) and the cathodic current (characterizing the corresponding reduction reaction) are equal. The rate of the anodic and cathodic reactions can be altered by additional supply or withdrawal of electrons (e^-) from the corroding metal surface, thereby changing the potential of the corroding metal. For example, according to the well-established principle of mobile equilibrium, the supply of e^- from an external energy source to the corroding metal will accelerate the cathodic and hinder the anodic reaction. Electrochemical protection is based on the possibility of changing (reducing) the rate of corrosion by changing the potential of the corroding metal - Fig.40. Its application is only possible for corrosion in a relatively *well-conducting medium*, i.e., it is not suitable for protection against atmospheric corrosion. This type of protection is most effective for large-sized products in a high-volume corrosive environment. The advantages of electrochemical protection are: easy to implement; reliable; applicable to powerful installations; with great economic effect.

Electrochemical protection is carried out by:

a) Shifting the potential of the metal of the facility to be protected in the negative direction (cathodic polarization) to a value at which the speed of the anodic reaction decreases strongly or its course is energetically disadvantageous - the so-called cathodic protection.

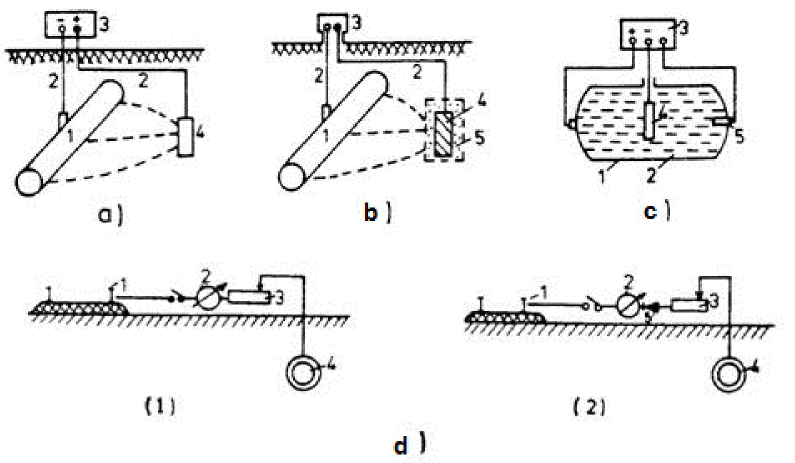


Fig. 40. Basic schemes of electrochemical protection: a) cathodic protection with an external energy source (impressed current cathodic protection): 1) protected object; 2) wires; 3) direct current source; 4) anode; b) cathodic protection with sacrificial anodes: 1) protected object; 2) wires; 3) measuring device; 4) sacrificial anodes; 5) groundbed; c) anodic protection: 1) protected object; 2) electrolyte; 3) potentiostat; 4) cathode; 5) reference electrode; d) protection against stray current by electrical drainage: (1) direct drainage; (2) polarized drainage: 1) stray curren source; 2) ammeter; 3) variable resistance; 4) protected object; 5) valve

b) Shifting the potential of the metal to be protected in the positive direction (anode polarization) to values where the metal is passivated - the so-called anodic protection.

c) Returning stray currents to their original source by means of a metal joint (called a drain) connecting the endangered structure and the source of stray current.

5.10.1. Cathodic protection

In cathodic polarization, the metal to be protected, receives electrons, becomes a cathode and therefore does not corrode. The principle of this action is shown in Fig. 41. In the conditions of spontaneous corrosion, the corrosion current and the corrosion potential are I_{cor} and E_{cor}, respectively. If cathodic polarization is carried out with an external (for the corrosion GC) current I_1, the potential of the metal shifts to E_1 and the corrosion current decreases - I'_{cor}. Under these conditions, the metal is partially protected. If the externally applied current is increased to I_2, E_2 becomes equal to the equilibrium potential of the anode and only a cathodic process will occur on the metal surface.

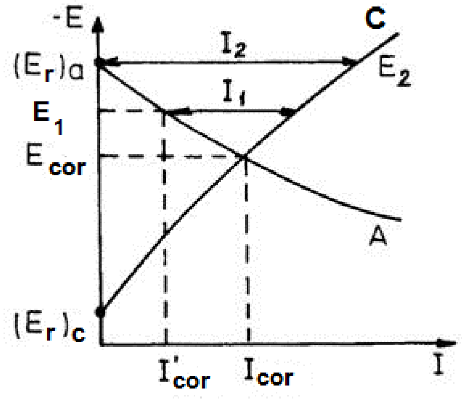


Fig. 41. Corrosion diagram illustrating the principle of action of cathodic protection (at E_1 - partial, at E_2 - full protection)

In this case, the metal is completely protected. Therefore, complete protection is certainly achieved when the corrosion potential is shifted to values more negative than the equilibrium (under the given conditions) potential of the metal to be protected. The minimum potential at which full protection is implemented is called the protective potential, and the density of the corresponding external (polarizing) current - the protective current density i_{prot}. In all cases $i_{prot} > i_{cor}$.

Further cathodic polarization to potentials more negative than E_2 leads only to energy loss. Better protection is not achieved, on the contrary, negative phenomena from the corrosion point of view may occur (it is said that the metal is "over-protected"). Protection by cathodic polarization is effective and economically most advantageous in corrosion conditions with O_2 depolarization, under diffusion control of the process. Therefore, it is suitable for the protection of underground metal facilities and facilities in contact with fresh, sea water and neutral process solutions. In this case, the rate of corrosion is determined by the rate at which O_2 reaches the metal surface. Increasing the water velocity or turbulence will increase the amount of O_2, increase the corrosion rate and therefore increase the current required for cathodic protection. The required protective current density in sea and river water varies significantly. The presence of fouling and calcareous deposits, the change in pH of the water significantly affects the value of the protective current density. Therefore, the current density required to maintain effective protection depends on the operating conditions of the facility. Consequently, a better parameter to judge the efficiency of cathodic protection is the potential. For example, the most commonly used criterion for the protection of steel equipment in an aerobic neutral environment is that the potential of the protected equipment is -850 mV against a $Cu/CuSO_4$ electrode or -800 mV against an Ag,AgCl/KCl electrode. In the presence of sulfate-reducing bacteria in the medium, the potential must be more negative (-950 mV against Ag,AgCl/KCl). In practice, the potential of the facility with respect to the corrosive medium is measured using reference electrodes that are placed very close to the facility in order to minimize errors. The values of the potential will depend on the cathodic and anodic reactions taking place, on the geometry of the facility, its internal electrical resistance and above all - on the presence, properties and condition of the protective coating. In general, the potential of the protected facility is lowest near the anodes and rises to the natural corrosion potential away from the anodes. For example, in cathodic protection using an external power source, a single cathodic station can provide protection of a very well-coated pipeline for 150 km, while in the absence of coating, the same station provides protection for 2 km.

At over-protection, the potential falls into the range of potentials at which the reduction of water takes place ($2H_2O + 2e^- \rightarrow H_2 + 2OH^-$), energy is wasted, and the evolved hydrogen can cause hydrogen embrittlement of steels (the problem is especially significant for high-strength structural steels). Excessively negative potentials accelerate the corrosion of lead and aluminum because they lead to alkalization of the environment. This alkalization can also be the reason for the deterioration of the quality and destruction of some paint coatings. It is possible to break the adhesion of the coating to the metal surface - in this case, corrosion develops under the coating, while at the same time the coating isolates the metal from the action of the protective cathodic current.

The application of cathodic protection is economically most advantageous when applied to protect equipment that is covered with paint coatings. The coating significantly reduces the required polarizing current. Ideal for joint application with cathodic protection are coatings with high electrical resistance and good adhesion to the metal surface, which are resistant to the corrosive action of the environment (including highly alkaline environment), as well as abrasion. In this case, the main protective function is performed by the coating, and the effect of the cathodic protection is reduced to the protection of the areas under the defective / destroyed coating. As the quality of the coating deteriorates over time, the role of cathodic protection increases. This type of protection applies when even the smallest leaks from the facility negatively affect people and the environment. It is mainly used to protect steel products, but it can also be applied to protect copper alloys and, in exceptional cases and with very carefully controlled cathodic potential, aluminum alloys and lead-coated cables. Its action is also effective for protecting reinforcement in reinforced concrete from corrosion in water, soil and wet atmosphe conditions - ports, bridges, buildings. The latter is possible because the concrete itself contains enough moisture to act as an electrolyte.

Cathodic polarization can be accomplished in two ways:

1) With the help of direct current from an external source (Fig. 41a) - the so-called impressed current cathodic protection (or only cathodic protection).

2) With the help of a polarizing current obtained from the work of GC, built from the metal to be protected and a metal with a more negative (in the given corrosion environment) potential, called a protector (Fig. 41b) the so-called cathodic protection with sacrificial anodes.

In general, cathodic protection with sacrificial anodes is used for small equipment, with a good paint coating, where a small polarizing current is required, or for local corrosion protection. Impressed current cathodic protection is used for large, complex equipment that is not coated or has a poor paint coating.

5.10.1.1. Cathodic protection with an external power source (impressed current cathodic protection)

The protected metal is connected to the negative pole of an external direct current source. The anode is made from a material soluble in these conditions (cast iron, steel), semi-soluble (graphite, high-silicon cast iron, lead alloys) or - from insoluble (platinized Ti, Ta, Nb, metal oxides, magnetite). The anodes are electrically connected to the protected structure by welding or brazing. For anodes connected by bolts or clamps, the electrical resistance must be below 0.10 Ω.

The supply voltage is selected to provide the required protective current density. The highest current density on the protected facility is in the section closest to the anode. In order to provide protection at the ends of the facility (e.g., pipeline) some overprotection must be assumed in the areas closest to the anodes. This effect is minimized by using more than 1 anode, which in turn is associated with an increase in installation costs.

5.10.1.1 1. Anodes for impressed current cathodic protection

Insoluble anodes

The material for insoluble anodes must meet the following conditions: low corrosion rate, good electrical conductivity, good mechanical properties, easy processing, low cost, not to form barrier oxide films when high current flows, withstand high voltage (up to 100 V).
The anodic reaction that occurs at insoluble anodes is:

$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ (146).

In saline corrosion media, chlorine can form on the anode and this can be a significant problem in confined spaces.
Platinized substrates - Platinum is an ideal material for making insoluble anodes because it is resistant to corrosion in virtually all corrosive environments and has a high exchange current for most anodic reactions. Due to its high price, it is used in the form of thin coatings (1-5 μm) on Ti, Ta, Nb. Platinized Ti is most often used in seawater. In order to avoid dissolution of Ti in the places where it is not covered with Pt, the anodes should be used at a maximum voltage of up to 8 V, which corresponds to an output current density of 1 kA/m^2. Where a higher voltage is required, anodes based on Ta and Nb are used. Their consumption is 8 mg/(A.y). Pt consumption increases in the presence of alternating current, especially at frequencies below 50 Hz. To avoid this phenomenon, it is recommended to use single-phase or three-phase two-half-cycle rectifiers.
Magnetite is a cheap natural material. Because of its fragility, it is cast in the form of a cylinder that is closed on one side. The inside of the cylinder is coated with Cu and the cylinder is filled with polystyrene. The remaining spaces are filled with epoxy resin. The conductive cable is welded to the copper. This anode is suitable for use in soil and sea water. The maximum current density at which it works is 0.115 kA/m^2 at an electrode consumption of 1 to 4 g/(A.y).
Lida electrodes have been developed in recent years. They are made of an inert metal oxide (ruthenium oxide) coated with titanium. They are considered to have better mechanical and electrochemical properties and operate at less dissolution than conventional electrodes. The current density at which they work is 0.8 kA/m^2 at a consumption of 0.8 mg/(A.y).

Semi-soluble anodes

Graphite electrodes – graphite electrodes with good electrical conductivity are used, often impregnated with resins to reduce penetration of corrosive solution and increase mechanical strength. This type of electrodes is stable in an environment containing an increased concentration of chlorides, but if the main anodic reaction is the release of O_2, the graphite is oxidized to CO_2. Graphite is also destroyed when the pH decreases and the concentration of SO_4^{2-} increases. Graphite electrodes are not suitable for closed systems due to the possibility of galvanic corrosion occurring when broken pieces come into contact. At a temperature above 50 ^oC, the consumption of graphite electrodes in an aqueous environment increases sharply. The consumption depends strongly on the corrosion environment and is from 0.045 in seawater to 0.45 kg/(A.y) in fresh water, correspondingly the operating current density is from 2.5 to 10 A/m^2. The maximum voltage at which these electrodes can operate is determined by the brittleness of the material and the increased self-dissolution. The main disadvantage of graphite electrodes, compared to other pressed electrodes, is the low operating current density and relatively low mechanical strength. They are generally used in combination with carbonaceous back-fills to form anode system.
High silicon iron alloys are widely used anodes. They contain 14.5% Si, some also contained 4.5% Cr, which has been replaced by Mo. A protective film of SiO_2 is formed on the surface of this type of electrodes. A necessary condition for the formation of this film is the anode to corrode afresh for several hours. This type of electrodes is very hard, difficult to process, and are therefore produced by casting. Although brittle, they are more resistant to abrasion and erosion than graphite. They are used usually in conjunction with carbonaceous

backfills to form the anode systems applied in soils. The maximum operating current density is determined by the type of alloy used and the corrosion environment. For example, in soils the current density is 10-20 A/m^2, due to gassing problems, while in seawater high iron chromium anodes can operate at a current density of 50 A/m^2. The consumption of this type of electrodes depends on the nature of the corrosion medium and is of the order of 0.10 - 0.50 kg/(A.y), decreasing with decreasing polarizing current density and increasing in the presence of SO_4^{2-}.
Lead alloys - their operation is based on the formation of a protective and electrically conductive film of PbO_2, which is stable in the presence of chlorides, due to the formation of insoluble $PbCl_2$. This determines the behavior of the Pb/PbO_2 electrode as inert and allows the evolution of Cl_2 and O_2 at high polarization. In order to form a stable and well-adhered PbO_2 film, usually Pb is alloyed with Sb and Ag. Due to the low Cl_2 evolution overvoltage, this type of electrodes is used in seawater, but are not suitable for operation at depths greater than 30 m. The maximum operating voltage and current density are 24 V and 1 kA/m^2, respectively, the electrode consumption is 1-10 g/(A.y). The introduction of a Pt pins into the Pb electrodes facilitates the formation of PbO_2.

Soluble anodes

Scrap, steel or cast iron are usually used. They can be used in soils and waters. The anodic reaction taking place is:

$Fe \rightarrow Fe^{2+} + 2e^-$ (147).

Their consumption is 9 kg/(A.y), and the maximum current density at which they can be used is 5 A/m^2. This type of anodes is rarely used, mainly because of their high consumption.

5.10.1.1. 2 Cathodic protection in reinforced concrete structures

External current protection is applied to protect the steel reinforcement. Typically, a total cathodic current of the order of 5 mA/m^2 is sufficient for protection in most corrosive environments. The potential difference that is reached in the volume of concrete is a function of the applied current density, the presence and type of coating, the distance between the metal ribs, the resistance of the concrete. A potential difference $\geq$ 45 mV is usually sufficient to significantly reduce the content of corrosion-aggressive Cl^- in the concrete, even if the structure is immersed in seawater, and to raise the pH value of the corrosion environment near the steel surface, thus hindering the development of corrosion.
The advantages of cathodic protection are: high efficiency; using a relatively small number of anodes, the possibility for: protection of large metal surfaces having damaged insulation (or without it) in environments with different specific resistance, regulation of the polarizing current, automation, constant monitoring of the effectiveness of protection. Applying cathodic protection right from the start of facility operation ensures a possibility to make relatively thin products without the need to provide a certain thickness to offset thinning due to corrosion destruction. The main disadvantages of cathodic protection are: high initial cost of the facility; need for systematic control and preventive maintenance; the possibility of harmful effects on adjacent unprotected equipment (the cathodic protection station can be a source of stray current), the possibility of sparking when supplying current to structures located in explosive areas, the impossibility of avoiding significant potential variations along the length of large structures. Adverse effects on adjacent structures can be reduced by carefully designing the system so that it protects successfully at the lowest possible current density and the greatest possible distance between the threatened structure and the protected structure, and between the threatened structure construction and anodes' groundbeds of the cathodic protection system.

5.10.1.2. Cathodic protection with sacrificial anodes

The main requirements for the sacrificial anodes are to be from active, non-passivable metals with a low cost. Mg, Al, Zn alloys are used, which are more electronegative than iron and its alloys. The sacrificial metal dissolves (metal ions pass into the corrosion medium), the separated e^- pass to the metal to be protected (more electropositive metal) and polarize it cathodically. The sacrificial metal is cast around a steel core that helps to fix the anode and maintains electrical continuity and mechanical strength at the end of the anode's life. The core may be directly welded or bolted to the structure to be protected, or the anodes may be connected to the structure by insulated wires (most commonly copper).

The sacrificial anode is placed in a groundbed whose main tasks are:

- Maintaining the necessary humidity and electrical conductivity of the environment around the sacrificial anode and reducing the resistance to current leakage from the sacrificial anode;
- Preventing the passivation of the sacrificial anode through preventing the formation of resistant corrosion products on its surface;
- Ensuring the uniform dissolution of the sacrificial anode and stabilization of the flowing current over time;
- Increasing the electrical efficiency of the sacrificial anode.

Sacrificial anodes are produced in different shapes (blocks, rods, wires). They are mounted individually or in groups. They are located as close as possible to the structure to be protected in order to reduce the resistance of the electrical circuit. The action of the sacrificial anode is limited to a certain distance, depending on its potential and the conductivity of the medium.

The criteria determining the practical applicability of metals and alloys for sacrificial anodes are: a) sufficiently high negative steady-state potential of the sacrificial anode in the given corrosion-acting (electrolytic) environment; b) uniformity of the anodic dissolution of the sacrificial anode; c) absence of anodic polarization of the sacrificial anode; d) negligible self-dissolution; f) high practical current output.

5.10.1.2. 1. Sacrificial anode performance

A good sacrificial anode should have a high number of e^- per unit mass and should efficiently transfer charge. The electrical performance of the anode is represented by the capacity of the delivered current, which is expressed in Ah/kg or kg/(A.y). The output current capacity is determined by the electrochemical equivalent, density and efficiency of the anode material. Efficiency is determined by many factors, including the nature of the corrosion environment, the operating current density, the metallurgical microstructure of the anode. A weak cathodic reaction on the sacrificial anode determines its minimal self-dissolution and, accordingly, high efficiency. The type of corrosion to which the anode is subjected also significantly affects the anode's efficiency. For example, significant pitting and trans-granular corrosion of the sacrificial anodes can cause partial electrical disconnection and the inability to use all of the electrical charge released by it.

A fundamental disadvantage of protection with sacrificial anodes is the relatively low polarizing current, and hence the difficulties in using this type of protection in environments with high specific resistance or for basic protection of large metal equipment. The protection with sacrificial anodes is suitable for soils with resistance below 3000 Ωcm. The protection of large metal facilities requires the use of many anodes, which involves the creation of many electrical connections and significant installation work. For example, the application of systems with Zn and Al anodes whose EMF is around 0.5 V is possible only in environments with a resistance below 5 Ohm.m. Usually, protection with sacrificial anodes is used as an additional means (to organic coatings). Another disadvantage of protection with sacrificial anodes is the irreversible loss of anode metal and environmental contamination. Decrease in the protective properties of the coating leads to an increase in the current flowing from the sacrificial anodes and the need of periodical inspection and installation of additional anodes to maintain the protective effect. The advantages of protection with sacrificial anodes are: independence from an external source of current, the possibility of working in an explosive environment, the possibility to ensure local protection, self-regulation of the protective current, easy installation and maintenance, no harmful effect on neighboring unprotected structures, the impossibility of reaching overprotection, uniform distribution of potential throughout the facility.

5.10.1.2. 2. Materials for sacrificial anodes

Magnesium sacrificial anodes – due to its significantly negative potential (-2.61V vs. SHE) Mg associated with Fe alloys provides their protection. The relatively low efficiency of these sacrificial anodes (50-60%) is attributed to the evolution of H_2 at the local cathode areas on the surface of the sacrificial anodes. The theoretical current capacity of Mg anode is about 2200 Ah/kg, while the actual measured values are of the order of 1200 Ah/kg. To reduce the rapid activation of Mg, alloying elements (Al, Zn, Mn) are added to it. Due to their high EMF, magnesium alloys are used in soils, reservoirs and other corrosive environments with high resistance. This type of sacrificial anodes is not recommended for environments with high electrical conductivity (e.g., seawater) due to the risk of causing overprotection and their high consumption.

Zinc sacrificial anodes - due to the significant potential difference with Fe and its alloys (with an equilibrium potential of -440 mV vs. SHE), Zn (with an equilibrium potential of -763 mV vs. SHE) provides good protection for Fe and its alloys at normal temperatures. But at a temperature above 60 ^{o}C in an aerated environment, the polarity of the Fe/Zn pair changes. The chemical composition of Zn anodes has to be monitored very strictly, because dangerous impurities can weaken the protective effect. Fe impurities are the most harmful. If present in concentrations above 0.0014%, Fe precipitates as discrete intermetallic particles, which cause the development of local corrosion GCs on Zn. This reduces the effectiveness of the sacrificial anodes. The corrosion product of this self-dissolution – $Zn(OH)_2$ passivates the Zn sacrificial anodes. The problem is overcome by adding Si or Al, which form harmless intermetalides with the iron. Cd additions facilitate the development of uniform corrosion of the sacrificial anodes and the formation of corrosion products with poor adhesion. As a result, more than 90% anode efficiency is achieved. Zinc anodes are suitable for the protection of pipelines with paint coatings in environments with high electrical conductivity (e.g., seawater) at room temperatures. They are also used in places where spark formation must be avoided.

Aluminum sacrificial anodes – Al (with an equilibrium potential of -1.90 V relative to SHE) is thermodynamically very reactive, but due to its tendency to passivate in most corrosive environments, it is not used in its pure form as aa sacrificial anode; Al alloys are used (successful alloying elements are Hg, In, Sn, Ga, Bi, Zn, Cd, Mg, Ba). Generally, Al sacrificial anodes containing 0.5-4% Zn and 0.01-0.05% In are used. Their current capacity is 2500 A h/kg with an anode efficiency of over 90%.

5.10.1.3. Cathodic protection design

The design of the cathodic protection should be done at the "facility design" stage. Usually for underground structures it is necessary before starting the actual designing to visit the place where the facility / pipeline will be located, to collect data on the resistance of the corrosion environment, on the areas with lower electrical conductivity of the soil, the presence of power plants in the vicinity, the presence of stray currents, other possible factors that would affect cathodic protection. This research is usually combined with an economic justification of the need for corrosion protection and its type.

The design of a cathodic protection system for a new facility includes the calculation of the electrical resistance of the anodes to the corrosion environment, the resistance between the anodes and the protected structure and from there the required polarizing current, the requirements for the polarizing current source, the quantity and location of the anodes (anode systems), testing and monitoring facilities.

If the facility already exists, the facility-to-soil potentials must first be measured to determine the anode and cathode sections. The required protection current and current distribution over the protected system must be determined experimentally (using temporary cathodic polarization from a convenient direct current source and temporary anodes).

When designing cathodic protection on an unpainted surface (e.g., a pipeline) a protective current density in the order of 11-22 mA/m^2 should be envisaged, provided that the equipment will not operate in any extreme conditions. This value is modified according to the specific conditions. For covered equipment, the required current is estimated using data from field tests. Applying a protection current in the order of 11-22 mA/m^2 is usually not economically viable for large facilities, then protection is applied only in the most threatened areas. Uncoated steel tanks are treated similarly to pipelines. Internal surfaces that come into contact with water at zero or low movement speed require a protective current density of 22-65 mA/m^2, depending on the composition of the water (the low value is for scale-forming water). Protection of equipment in contact with moving water requires experimental determination of the required protective current density. Moving water prevents the formation of carbonate protective layers and in this case a higher protective current density is required.

The location of the anodes must be carefully selected depending on the conductivity of the soil, the presence of adjacent metal structures and the presence of a source of polarizing current. Anode groundbeds for externally sourced cathodic protection can be shallow vertical, shallow horizontal, or deep. The anode material is surrounded by a filling of carbonate materials. This reduces soil resistance, extends anode life, and provides a porous structure for gases to escape. With high soil resistance, it is preferable to use a series of vertical anodes installed in deep well groundbeds, the depth of which is determined on the basis of soil resistance measurements. Deep groundbeds have vents to escape the formed gases, thus reducing the resistance of the groundbeds. A steel casing is usually used to prevent the borehole from collapsing. Several anodes are tied together with a rope and placed in the casing. Then it is filled with carbonaceous material. The carbonaceous filler used typically includes natural graphite, calcined petroleum coke, and coke dust. The purpose of using a filler is to reduce the resistance of the groundbed by increasing the effective size of the anode and to provide sufficient surface area for oxidation reactions to occur. To ensure good electrical contact, the filler should be tamped around the anode.

The resistance of the carbonate filling should be of the order of 50 Ω cm. This extends the life of the anode. When the groundbed starts working, the steel cage is first dissolved, which activates the anode and the filling. Deep groundbed provide good distribution of polarizing current, but are more expensive and more difficult to repair.

The anode groundbeds for sacrificial anodes protection are filled with so-called "chemical fillers" (a mixture of clay, gypsum and salts). A typical composition often used is 75% gypsum powder ($CaSO_4$), 20% granular bentonite and 5% Na_2SO_4. The resistivity of this mixture is 50 Ω cm and it is suitable for high resistivity soils. A mixture of 75% bentonite and 25% gypsum (250 Ω cm) is recommended for soils with low moisture. This creates favorable conditions for the dissolution of the anode and reduces the current leakage resistance. In horizontal cells, individual anodes are not used, but usually many anodes arranged in line are used. Soil resistivity is one of the main factors determining the placement of anode groundbeds, the number of anodes required, the length and diameter of the backfill column, the voltage range of the rectifier, and the cost of the protection. In general, when designing deep groundbeds, the lowest and most uniform soil resistivity distribution should be used. Soil resistivity (ohm-cm) is measured using Werner's 4-pin method. In the design of deep anode groundbeds, experience from the operation of other cathodic protection installations in the relevant area should be taken into account.

Particle size and shape are important factors in filler specification. They determine the contact surface between the anode and the earth and effect the porosity of the filling, which determines the possibility of ventilation. A general-purpose coke breeze, with a resistance of 35 Ωcm, is most commonly used for shallow groundbeds. For the deep groundbeds, a special calcined petroleum coke breeze with a resistance of 15 Ωcm is used, which can be supplied by a pump.

The use of cathodic protection requires, still at the design stage, making basic decisions regarding the type of cathodic protection, the type, number and placement of anodes. The main requirements for cathodic protection are:

A) The sacrificial anodes protection system requires sacrificial anodes, direct welding of the anodes or of a wire connected to them to the structure, secure and minimal resistance electrical connections;

B) The system with an external current source requires a current source, corresponding anodes, electrically well-insulated and with good electrical permeability conductors between the anodes and the current source;

C) Electrical continuity of the environment in which the protected facility is located;

D) Application of a protective coating that is consistent with the application of cathodic protection;

E) Possibility of isolating the facility or a part of it, so that it is possible to limit the spread of the cathode current only in the desired areas;

F) Ensuring the possibility of monitoring the operation of the system (placing reference electrodes, ensuring the possibility of permanent collection of data).

The performance of the cathodic protection system is monitored by measuring the potential of the protected facility in the given corrosive environment (using a high input resistance voltmeter) against a standard reference electrode.

5.10.2. Anodic protection

Anodic protection (Fig. 41c) is carried out by passivating the metal surface, in contact with a liquid electrolytic medium, by anodic polarization using an external source of direct current. The potential of the metal to be protected is shifted and maintained in the passive state region (see Fig.10). Anodic protection can be applied to protect carbon alloyed (passivable) steels. In order to successfully use anodic protection, the following conditions must be met:

- The region of the passive state of the metal of the protected structure is not less than 50 mV wide. In the event that several metals are used in the construction, these areas must at least partially overlap.
- Electric current can pass freely through the structure, ensuring the access of polarizing current to all sections of the structure that come into contact with the corrosive environment.
- The corrosive environment must have good electrical conductivity and stability during operation.

Anodic polarization is achieved with the help of a special electronic device (potentiostat) for setting and maintaining a constant potential, with the positive pole of the voltage source being connected to the protected structure, and the negative - to an auxiliary cathode (made of a material inert in the corresponding corrosion environment - high alloy steels or cast iron, platinum, Ni). The potential of the protected structure is continuously monitored using a reference electrode.

The advantages of anodic protection are: efficiency; possibility for: replacement of expensive and scarce structural metals with cheaper and more accessible ones, implementation of protection in highly aggressive environments, protection of mobile equipment and equipment with a complex configuration; negligible operating costs, relatively low protective current. The applied anodic current is usually equal to the corrosion current in the system – this allows the corrosion rate to be directly monitored. The anodic protection disadvantages are: high initial cost of the equipment; limitation only for anodically passivable metal systems, with not very large dimensions, which are in contact with liquid electrolytes; potential danger in highly aggressive environments - in the event of an emergency interruption of the power supply with polarizing current, the potential of the metal can shift to the area of active dissolution and reach a catastrophic destruction of the metal of the structure.

5.10.3. Protection against stray current

Use of electrical drainage is the most effective method of corrosion protection under the action of stray current (Fig. 41d). Stray current is returned to its original source (in the rail section) by means of a metal joint connecting the endangered structure (in its anode area) and the source of stray current. As a result of the use of an electrical drainage, cathodic polarization of the metal of the protected structure is carried out, the anodic zones caused by the stray current are eliminated, while preserving the cathodic areas (at the entrance of the stray current) on the facility. Therefore, electrical drainage "works" only if the potential difference "endangered facility - element of the rail network" is positive or artificially kept positive. For the normal operation of the electrical drainage, it is necessary that the voltage drop in the electrical drainage cable be less than the potential difference "facility-rail". Therefore, the use of electrical drainage protection is justified only when the protected facility and the stray current source are relatively close. At longer distances, electrical drainage protection may be economically inefficient and cathodic protection is then switched to. Direct drainage is the easiest to implement - Fig. 41d (1). It must have a rheostat to regulate the drained current. This type of electrical drainage has bi-directional conduction and is therefore only applicable in cases where the endangered facility potential is always higher than the rail potential in the drainage section (i.e., the possibility of current flowing through the drainage from the rail to the protected facility is excluded). In addition, in order to avoid leakage of stray current into the ground in the drainage section, which would cause subsequent corrosion of the protected facility, it is necessary that the "facility-rail" potential difference is higher than the "facility-ground" potential difference. The polarized drain - Fig. 41d (2) is distinguished from direct by its unidirectional electro conductivity and is applied in cases where the potential of the protected facility is positive compared to the potential of the rail or has a variable sign (i/e. the direction of stray current changes), as at the same time, the "facility-rail" potential difference is higher than the "facility-earth" potential difference. The polarized drainage prevents reverse flow of current from the rail to the protected facility, when the potential of the rail increases relative to the potential of the facility. The unidirectional conduction of the polarized drainage is achieved by using semiconductor diodes. When the potential of the stray current source is not negative enough to ensure that the drainage reaches the required potential of the protected facility, enhanced drainage is applied. Enhanced drainage is a combination of a valve electro drainage system and a cathodic protection station. Most often, automated installations for enhanced drainage are used. It is applied at positive or sign-changing (with respect to ground) potential of the facility to be protected (which is usually the result of the action of more than 1 source of stray current) and when the use of reinforced drainage is more economically advantageous than increasing the cross-section of the drainage cable. In this application, the protected facility is cathodically polarized (until the protective potential is reached) at a time when the section of the rail (in which the current returns) has a more positive potential than the potential of the protected structure. Advantages of reinforced drainage (compared to other types of drainage) are: a greater range for adjusting the protective potential, the possibility of reducing the cross-section of the drainage cables used, a weaker influence on adjacent unprotected structures (compared to the use of cathodic protection). However, enhanced electrical drainage is relatively rarely used, since the inclusion of an additional current source leads to losses of electricity and the use of the rails as an anode grounder increases their wear.

The choice of the type of drainage used and the place for drainage is based on the synchronous measurement of the potential differences "facility-rail" and "facility-ground" during the experimental use of electrical drainage installations.

5.11. Methods of protection against gas corrosion

The following methods are used to protect metals from gas corrosion: a) heat-resistant alloying; b) rational mode of heating the metals; c) use of protective atmospheres; d) use of protective coatings.

The heat resistance of steels is significantly increased by alloying, the main alloying components being Cr (up to 30%), Al (up to 10%) and Si (up to 5%). The mechanical properties of alloys at high temperatures are preserved with the help of additions of Ni (up to 25%), Mo (up to 2%) and W (up to 4%). The higher the Cr content, the higher the heat resistance of chromium steels. It is further increased with additions of Si (up to 4%). Iron alloys alloyed simultaneously with Cr, Si and Al are characterized by even higher heat resistance (900 - 1150°C). Very high heat resistance (up to 1000°C) is possessed by iron-chromium alloys additionally alloyed with Al (up to 7%). The heat resistance of chromium-nickel steels is very good (800 - 1100°C), especially of steels with an increased content of Cr (up to 25%) and Ni (up to 20%).

Chrome-alloyed nickel-based alloys (e.g., Inconel) are characterized by very high heat resistance (1100 – 1200 ^{o}C) and good mechanical properties at high temperatures. Silicon, aluminum and high-chromium cast irons are characterized by good heat resistance.

A significant reduction in losses from gas corrosion can be achieved by finding a rational mode of heating metals during their heat treatment and in various metallurgical operations, namely: a) Combustion of fuel with decreased amount of air, thus the oxidizing ability of the combustion products is decreased, which leads to a reduction of high-temperature oxidation of metals when they are heated in flame furnaces before rolling and forging or during their heat treatment. This regime is applied to the heating of products made of carbon and low-alloy steels; b) Combustion of the fuel with an excess of air, which leads to the formation of oxide coatings with protective properties and a subsequent significant reduction in oxidation.

With the help of artificial gas environments (protective atmospheres), conditions can be created in which the oxidation of the metal is thermodynamically impossible. With the application of such atmospheres, the operations for cleaning the articles from sinter after the processing of the metals by plastic deformation and other metallurgical productions are avoided. The main task is the correct selection of the atmosphere for the specific conditions of heating the metal, which should not oxidize, decarburize or carburize the products. The composition of such an atmosphere is calculated from the equilibrium constant of the corresponding oxidation reaction of the metal. Inert media used when heating steel are argon, nitrogen, hydrogen, carbon monoxide, methane. It should be borne in mind that hydrogen decarburizes, and carbon monoxide and methane carburize the surface of steel products. In practice, gas mixtures with the main component nitrogen and with a greater or lesser content of H_2, CO and CH_4 are usually used. In the heating of non-ferrous metals, protective atmospheres are used, obtained by burning natural gas, purified from sulfur compounds, and in the case of zinc alloys - from carbon dioxide and water vapor. It should be borne in mind that most atmospheres are explosive, flammable or can be poisonous.

The use of coatings allows combining the mechanical properties of the base metal with the heat resistance and other functional properties of the coating (hardness, wear resistance) and with the economy of expensive and scarce heat-resistant alloys. Metallic and non-metallic heat-resistant coatings are used.

Metal heat-resistant coatings are applied using the same methods that are used to apply coatings for protection against electrochemical corrosion. Heat-resistant coatings of Al, Cr and Si on steel and cast iron are produced by thermal diffusion. Spray metallization is used to apply heat-resistant coatings of Al, Ni and some alloys to steel products and entire structures. Aluminum coatings obtained by electric arc metallization are most widely used. Through plasma metallization, alloy coatings with very high heat resistance are obtained and with a wide assortment of applied alloys. The welding of heat-resistant alloys on separate parts of low-alloyed steel parts is also applied. Coatings of heat-resistant alloys and chromium-nickel steels on carbon steels are obtained by hot rolling or pressing (i.e., by thermo-mechanical method). The galvanic method is used to apply heat-resistant coatings of Cr and Ni on steel parts. Thin coatings are obtained for protection against gas corrosion at relatively low temperatures. For the application of aluminum coatings on steel products, immersion in molten metal is used, but the method is not widely used, since brittle intermediate layer is obtained.

Non-metallic coatings for protection against gas corrosion include heat-resistant enamels, coatings of refractory compounds, and metal-ceramic and ceramic coatings. Heat-resistant enamels are obtained by fusing vitreous ceramic materials that contain maximum amounts of refractory oxides (Cr_2O_3, SiO_2, Al_2O_3, TiO_2) and a minimal amount of alkali metal oxides and PbO. The resulting enamels are characterized by heat resistance, excellent adhesion to the metal surface, high hardness and wear resistance. The best heat-resistant enamels withstand up to about 1100 °C, and in some cases - up to 1400 °C. A disadvantage of enamels is that they are not sufficiently resistant to sudden temperature changes.

Coatings of refractory compounds are obtained on the surface of the metal as a result of a chemical reaction in the solid or gas phase at high temperatures. This is how coatings of carbides, silicides, borides and other compounds are obtained, which provide protection against gas corrosion at very high temperatures (e.g., silicides - up to 2000 °C).

Metal-ceramic and ceramic coatings are mainly applied by gas flame sputtering and subsequent heat treatment of the details in an inert atmosphere or vacuum. In this way ceramic and metal-ceramic compositions with different chemistry and properties can be applied to sheet materials, details with a complex profile and other products made of carbon or low-alloy steels. By introducing metal additives into the oxides, the thermal conductivity and plasticity, as well as other mechanical properties of the coatings are changed, and it is possible to achieve coefficients of thermal expansion close to those of the metal base, which significantly improves the resistance of the coatings.

5.12. Corrosion detection, assessment and monitoring

5.12.1. Corrosion detection and monitoring methods

Some of the so-called non-destructive inspection and evaluation methods are used to detect corrosion. Table 5 summarizes the main corrosion detection methods (with their advantages and disadvantages) and the corrosion mechanisms for which they are used.

No single detection method is ideal or suitable for detecting all types of corrosion damage.

Visual inspection is most commonly used as a complementary method to identify where structural failure is expected to begin. The reliability of the method depends on the experience of the inspector. Visual inspection can be carried out directly or remotely using special devices to facilitate access and observation (borescopes, fiberscopes, video cameras).

The penetrating liquid is applied to the examined surface and the places of its penetration show the defects and destroyed areas.

Eddy current testing is an electromagnetic technique that is only applicable to electrically conductive materials. When an electrically charged coil is placed near the surface of a metal component, eddy currents are induced in the latter. They create a magnetic field that is opposite to the original magnetic field. The impedance of the coil, close to the metal sample, is affected by the eddy currents induced in it. When the eddy currents are changed as a result of the existence of various defects in the metal, this changes the impedance of the winding. The change is measured and presented in a way that is indicative of the type of defect. While the classical eddy current technique uses a continuous signal, the "pulsed eddy current" technique uses a pulsating or step-like initial signal, which allows deeper penetration into the investigated substrate and the possibility of obtaining quantitative data on the thickness of investigated metal walls.

Table 5. Summary of non-destructive corrosion detection methods

Method	Advantages	Disadvantages	Corrosion mechanisms for the detection of which it is applied
Visual inspection	Relatively inexpensive, can be used for large surfaces, fast, tools used are easily portable	Very subjective, measurements are not precise, limited to surface inspection only, labor intensive, requires good cleaning and accessibility of the inspected surface	Surface corrosion, exfoliation, pitting and integral annular corrosion
Advanced visual inspection	Can be used for large surfaces, very fast, very sensitive to lap joint corrosion, can be used to investigate multi-layer coatings	Difficult to obtain quantitative results, subjective - requires an experienced expert, requires preparation of the study surface	Same as visual inspection, but enhanced by means of image magnification and ease of access
Inspection using penetrating fluids	Flexible and relatively easy to use, sensitive to small defects and corrosion damage, fast inspection of large surfaces and volumes (including complex geometries), direct visualization on the real surface, relatively inexpensive	Only defects that destroy the surface are detected, applicable only to well-cleaned relatively non-porous and smooth surfaces, need for direct access of the inspector, need to control multiple operations and to clean the facility after the inspection, work with chemicals	Inspection of all materials (metals, glass, ceramics, rubber, plastics)
Eddy currents	Relatively inexpensive, provides good resolution, can be used in the investigation of multilayer coatings, the tools used are easily portable	Low productivity, the possibility of different interpretation of the results, the need for special training of the operator, tedious to apply	Surface and subsurface defects such as cracks, exfoliation corrosion around fasteners and corrosion thinning
Ultrasound	Good resolution, material loss and thickness reduction can be determined	Single-sided, requires contact fluid (couplant), cannot be used for multi-layer evaluation, low throughput, requires cleaned smooth test surface	Mass and thickness loss, delaminations, voids in laminated structures
Radiography	Best resolution (~1%), ability to interpret images	Expensive, need to comply with requirements for safe handling of radioactive materials, bulky equipment	Surface and subsurface defects due to corrosion
Thermography	A large area can be scanned, relatively high performance, a “macro picture” of the structure condition	Complex equipment, layered structures are a problem, insufficient precision of corrosion damage thickness measurement	Surface corrosion
Inspection using magnetic particles	Can be used underwater and in the open sea	Effectiveness decreases rapidly with increasing depth of defect and depends on type of defect, need for careful surface preparation prior to inspection	Mainly for surface defects due to cracking (fracture), but can also locate subsurface defects

Ultrasonic inspection uses sound waves of short length and high frequency. An ultrasonic signal is generated in a piezoelectric crystal, passes through the metal surface and is reflected from the back wall. The thickness of the metal surface is determined by the delay time of the return signal. Defects in the specimen reflect the ultrasound back to the transducer. The size of the defect can be determined and its distance from the surface of the construction. By using a "scanning" ultrasonic device, the inspector can map the corrosion damage. The use of ultrasonic sensors fixed to the structure constitutes "on-line" monitoring.

Ultrasonic guided waves are used to inspect large surfaces. In combination with Locus mapping, they can be used to determine defects and inhomogeneities on surfaces with complex geometry.

In radiography, X-rays are obtained with a special machine, and usually using the isotope Ir-192. The choice of radiation source depends on the thickness of the investigated material. The rays pass through the examined material and are captured on film on the other side. Appropriate precautions are required when working with radiation.

Thermography is a non-contact optical method in which 2-dimensional mapping of the stationary and variable thermal effects is carried out based on the measurement of IR energy emitted by the object under investigation, which is previously heated with the help of short-term energy pulses generated by quartz lamps. The changes in the radiation of the object caused by the corrosion damage are considered. The method can be used to detect defects in coatings and corrosion on the metal surface under the coating.

Inspection using particles with magnetic properties is based on the following concept: When a piece of magnet is broken in half, 2 pieces are obtained with the corresponding magnetic poles on each of them. If the piece of magnet is cracked rather than completely split, magnetic poles still form on each side of the crack. If Fe shavings are sprinkled on the cracked magnet, they are attracted not only to the edges of the magnet but also to the poles around the crack and help to detect it.

Inspection and monitoring are key activities in ensuring system integrity and controlling corrosion. Corrosion monitoring is a series of investigations planned and organized to obtain extensive and reliable information about the condition of the system over time, while inspection is a "snapshot" of the corrosion conditions at a given time. Monitoring can help maintain the integrity and full capacity of the facility by:

a) early provision of information warning of the presence or development of dangerous (from a corrosion point of view) conditions; b) revealing the dependencies between the changes in the environmental parameters and their impact on the corrosion resistance of the facilities; c) diagnosis of the specific corrosion problem - identification of the causes of its occurrence and the parameters controlling the rate of corrosion; d) evaluating the effectiveness of the corrosion control/prevention program; e) providing management with the information necessary to implement the maintenance program in the relevant conditions.

Corrosion monitoring is a complex task, because usually several types of corrosion damage occur at the same time, the rate of corrosion can vary significantly even in close areas. There is no single technique that can detect and measure all different types of corrosion. During the inspection and monitoring, besides the various types of corrosion damage, the parameters of the working environment and the development of biological activity should be followed and evaluated. The selection of the points where the monitoring and inspection will take place is extremely important. The selection should be based on a comprehensive knowledge of the operating conditions, the materials used in the facility, the geometry of the system, the construction factors (such as welds, presence of cracks, turbulence conditions, etc.), galvanic mismatch, external factors (chemical composition of the corrosion medium, speed of its movement - in a fluid medium) and records of the history of the facility and corrosion problems. In order to reduce monitoring costs, the "worst case" is usually observed in the areas where the most severe corrosion is expected. In practice, monitoring and inspection locations are often determined by their accessibility. When it is difficult, even impossible to install the corresponding sensor in a given location, then a bypass is prepared and the sensors are placed in it, under the conditions of the construction.

Each monitoring system consists of equipment for collecting, transmitting, storing, processing and presenting and recording the data. The analysis of corrosion monitoring data includes: the trend in the period of use of the facility, the correlation trends of different monitoring and inspection techniques, the correlation trends with the operating parameters, the prediction of the remaining lifetime of the system, the application of appropriate statistical analysis in order to realize correct extrapolation of the data to the entire structure. Corrosion monitoring system software must combine data from sensors monitoring the corrosion status of the system with data from sensors monitoring environmental and working environment parameters. Ideally, it should be able to automatically send warning messages indicating the type of corrosion that is developing and its causes.

"In-line" monitoring is the installation of samples, biopins, devices and sensors directly in the facility, which are removed for the purpose of corrosion analysis. "On-line" monitoring involves the use of devices that are permanently attached to the equipment or constantly exposed to the action of the corrosive environment, for example, sensors measuring electrical resistance, sensors measuring polarization resistance, fixed ultrasonic sensors, etc. "Off-line” monitoring is mainly realized through the use of the above described non-destructive assessment and inspection methods and laboratory analysis. These techniques are used throughout the "life" of the facility. Corrosion sensors can be intrusive (which are introduced directly into the structure / facility) and non-intrusive. Corrosion monitoring techniques can be classified as direct (where the mass of metal lost or corrosion rate is directly measured) and indirect (which indicate the existence of a corrosion environment and assess its aggressiveness).

The following techniques are used for direct monitoring: measurement of change in the mass of samples of the material under study, measurement of electrical resistance, measurement of inductive resistance, measurement of linear polarization resistance, electrochemical impedance spectroscopy, measurement and analysis of electrochemical noises, measurement of galvanic currents (amperometry at zero resistance), polarization methods, the electric field signature method (FSM), acoustic emission, thin film activation. For indirect monitoring, the following techniques are applied: measurement of the potential of the corroding metal, monitoring of the volume of evolved H_2, chemical analysis.

When measuring the change in mass of samples of the material under investigation, the weighed samples are placed in the corrosion medium, left for a certain time, removed, cleaned and weighed again. The corrosion rate is calculated according to dependencies (1) and (2) and Table 1. The method is suitable for monitoring general corrosion, corrosion at contact of 2 dissimilar metals, corrosion due to differential aeration, corrosion under stress. Local corrosion can also be identified. It is applicable to corrosion in liquid, gas medium and in soils. The accuracy and reproducibility of the results strongly depend on the correct preparation of the samples. Because the method assumes that corrosion develops uniformly, the determined corrosion rate is actually a lower bound on the actual rate. The method is not suitable for real-time corrosion rate determination, it may even fail to register large changes in corrosion rate.

In the electrical resistance measurement technique, the change is determined in resistance of a metal element immersed in a corrosive medium with respect to a protected reference element (sensor) immersed in the same environment. The change in resistance is due to corrosion. Sensors can be permanently attached to the facility and provide information. The method makes it possible to determine the mass loss of the specimen as a result of corrosion at any time and as often as necessary. It is possible to register large changes in the corrosion rate, but the response to the changes is not particularly fast. No distinction can be made between general and local corrosion. Data can be corrupted by the formation of electrically conductive corrosion products and large variations in temperature. Sensors that measure inductive resistance are at least an order of magnitude more sensitive than those that measure electrical resistance. They can also be used in environments with low electrical conductivity.

The linear polarization resistance (LPS) measurement technique is based on electrochemical theory. Polarization resistance R_p is defined as the slope of the “potential/current density” curve at the corrosion potential E_{corr}. In activation response control, it is defined as

$$R_p = B/i_{corr} = (\Delta E)/(\Delta i), \text{ at } (\Delta E) \to 0 \qquad (148),$$

where i_{corr} - corrosion current density, B - a constant characteristic of the studied system - is determined experimentally or calculated using the anodic (b_a) and cathodic (b_c) slopes of the Tafel dependence:

$$B = (b_a \, . \, b_c) / [2.303 \, . \, (b_a + b_c)] \qquad (149),$$

with the slopes determined experimentally from the polarization curves. The technique is used by applying a small polarization (from E_{corr}) to an electrode of the material under study and reading the flowing corrosion current. The determination of the corrosion rate takes place in real time. Although the identification of a temporary stoppage of the corrosion process is possible, the method determines an average overall corrosion rate. It is not possible to measure local corrosion. The method is very sensitive to the cleanliness of the examined surface and to changes in the electrical conductivity of the corrosion medium.

In electrochemical impedance spectroscopy (EIS), a small-amplitude signal is applied to samples of the test material at a series of frequencies. The EIS instrument records the real and imaginary components of the impedance response of the system. The results are interpreted using models of the "specimen / corrosion medium" interface that are fitted to the obtained data. In doing so, parameters are found that correlate with the state of the coating on the metal and with the corrosion of the metal beneath the coating.

The measurement and analysis of electrochemical noises is based on the natural fluctuations of corrosion processes and their electrochemical nature. Fluctuations in current and potential of the corroding system are simultaneously measured and correlated with corrosion damage and corrosion rate by appropriate transformations of the records. With this method, it is possible to differentiate between general and local corrosion. The method is extremely sensitive to changes in the corroding system. Problems with its application arise only in corrosive environments with low electrical conductivity.

In zero-resistance amperometry, two electrodes of dissimilar metals are exposed to the corrosion medium and short-circuited through a zero-resistance ammeter. A natural potential difference occurs between the two metals and as a result a current is generated which is proportional to the corrosion rate of the more active metal. The magnitude of the current is directly proportional to the corrosion aggressiveness of the environment and the thickness of the moisture layer on the metal surface (in case of atmospheric corrosion). The method is suitable for monitoring corrosion in crevices and pitting corrosion, corrosion cracking, corrosion of welds, corrosion resulting from the contact of 2 dissimilar metals.

In polarization methods, the potential of the corroding metal is varied and the resulting change in current is monitored as a function of potential or time. In addition to LPS measurement, several other polarization methods are used: In potentiodynamic polarization, the potential of the electrode is changed at a selected rate by passing a current through an electrolytic corrosion medium. It is used to study uniform corrosion. The problems are related to the effect of the changing corrosion environment and corroding surface during the measurement and to the effect of the speed of the potential scan on the results obtained. The electrochemical potentiodynamic reactivation technique is based on a potentiodynamic change of the potential from a passive state to the reactivation potential and allows determination of the degree of sensitization of steel. Cyclic polarization is used to assess pitting corrosion. The potential is varied in one (or less than 1) cycle and the hysteresis formed is examined, simultaneously with the difference between the values of the initial corrosion potential and the passivation potential. The presence of hysteresis is an indication of pitting or crevice corrosion, and its size is an indicator of the intensity of pitting. Cyclic voltammetry involves changing the potential in a positive direction to a predetermined value, then immediately changing the potential in a negative direction until the initial value is reached. In some cases, the potential scan is repeated multiple times to determine changes in the current/potential curves due to the scan that are indicative of the corrosion mechanism. The potential of the polarizing electrode can also be changed by a series of steps, at each new value of the potential it is held constant for a certain time and the current is allowed to stabilize before the potential is changed by the next step. In this way, information about the mechanism of corrosion is collected.

In the electric field signature method, an induced current is applied to the monitored part of the facility and the resulting voltage distribution is measured to detect corrosion damage. The data are presented as streamlines and equipotential surfaces (depending on the geometry of the structure and the material from which it is made) normal to the streamlines. The first measurement (signature) is unique to the geometry of the studied object. When corrosion damage occurs, the structure of the electric field changes, compared to the "signature". An array of permanently installed pick-up pins is positioned around the outside of a pipe to produce an electric potential map of the structure. The reduction in the wall thickness of the facility can be determined by appropriate interpretation of the observed changes. The method is sensitive and fast, suitable for studying inaccessible areas. It is mainly applied to monitor the corrosion of pipelines.

Corrosion monitoring by the acoustic emission method is based on the capture of the sounds (often imperceptible to the human ear) that are generated during the rapid release of energy accumulated in stressed materials. The technique involves attaching one or more piezoelectric transducers to the structure and analyzing the captured sounds with appropriate instruments. Sounds arise from friction, growth of cracks, material changes due to the development of corrosion. It is possible to detect and localize microscopic changes. The entire construction can be observed from only a few points.

In thin-film activation, a small area of the material is subjected to high-energy irradiation with charged particles, resulting in a radioactive surface layer. It can be formed directly on a working facility. The concentration of radioactive particles is low enough not to change the metallurgical properties of the studied material. The change in the γ-radiation emitted by the investigated surface layer is measured with a suitable detector in order to study the rate of release of the material from the surface. The method is suitable for monitoring the corrosion of internal surfaces, e.g. in case of corrosion of gas pipelines.

In monitoring the potential of a corroding metal, its potential is measured against a reference electrode immersed in the corrosion medium or electrically connected to the metal under study. In the context of

Pourbaix diagrams, the potential value is an indicator of the thermodynamic possibility of corrosion risk. Relatively big changes in the potential are an indicator of the beginning of a corrosion process or a change in its intensity. The technique is widely used to track the corrosion condition of reinforcement in reinforced concrete, of pipelines in soil.

The volume of evolved hydrogen, which is monitored with special sensors, can be used to monitor the corrosion of iron and steel occurring in an acidic (and highly alkaline) environment or in an environment containing hydrocarbons (refineries, petrochemical plants).

The various chemical and physicochemical analyzes (monitoring / measurement of the pH and electrical conductivity of the medium, the concentration of dissolved O_2, the concentration of metal ions - especially the ions of the corroding metal, of other ions - Cl^-, SO_4^{2-}, of organic pollutants, of inhibitors, of suspended substances) can provide valuable information in corrosion monitoring programs. A large part of these measurements can be realized with special sensors attached directly to the operating equipment.

Monitoring of reinforcement corrosion in reinforced concrete ensures long-term and reliable operation of facilities and structures. It provides information on the changes occurring in the structure needed for the timely and cost-effective measures that must be taken to prevent unacceptable damage to the structure and to extend its service life. It is impossible to directly inspect the armature or the formed corrosion products. Existing methods and techniques for corrosion monitoring and assessment include electrochemical techniques (primarily monitoring the potential of the rebar steel against a reference electrode); installation of sensors based on the measurement of the electrical resistance of reinforced concrete or the linear polarization resistance; ultrasonic methods; determination of the concentration profile of chlorides in concrete; determining the penetration of carbonation into concrete; concrete integrity and permeability tests; visual inspection.

In the construction of new structures, sensors for corrosion monitoring can be installed, which work on the basis of linear polarization, and the potential of the "steel/concrete" phase boundary is measured against a suitable reference electrode - Fig.42.

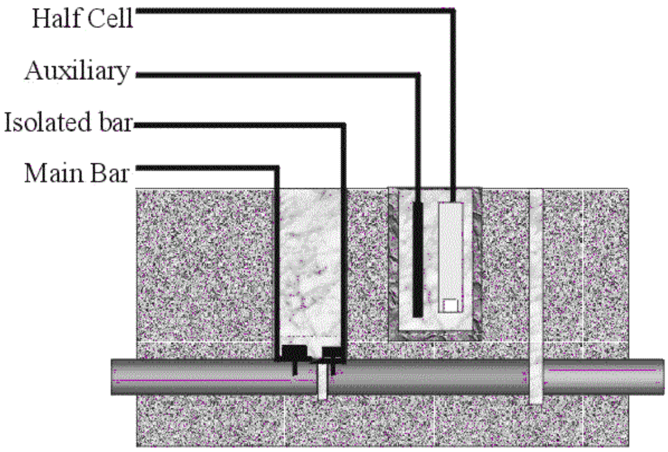


Fig. 42. Sensor scheme for corrosion monitoring of new reinforced concrete structures (Broomfield et al. 2002)

The obtained values are correlated with empirical data on the corrosion of the rebar and further used to predict the probability of corrosion. The low carbon steel of the armature is used as the working electrode, and the auxiliary electrode is alloy steel. The system is placed inside the structure. A suitable terminal is attached to the sensor, which, even after the final construction of the structure, is available for contact with mobile or permanently fixed data collection instruments.

Existing reinforced concrete structures can be fitted with corrosion monitoring sensors to be installed in holes made in the concrete. Isolating a small portion of the reinforcement enables controlled representative measurements of the potential of the steel/concrete interface in an undisturbed reinforced concrete corrosion environment – Fig. 43.

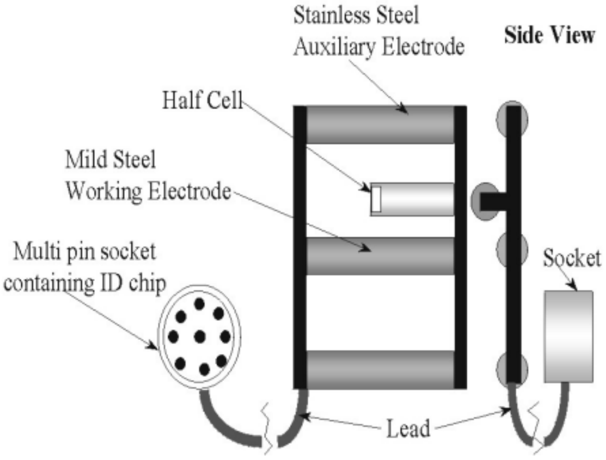


Fig. 43. Schematic of a sensor for monitoring the corrosion of existing reinforced concrete structures, (http://corrosion-doctors.org/Concrete/newstructures.htm)

Corrosion phenomena are complex, influenced by many different factors and cannot be limited to one type of corrosion. Each individual corrosion monitoring technique has certain limitations and therefore it is best to use several techniques simultaneously. The advantages of this approach are: the ability to follow the development of different types of corrosion destruction, greater reliability and accuracy of the collected data, more data and correlations between them, making it possible to create a "complete picture" of the corroding system, early warning of the emerging danger by the most sensitive techniques. It should not be forgotten that together with the monitoring of corrosion damage of structures and facilities, the parameters of the corrosion environment should also be monitored.

In so-called risk-based inspection (RBI), facility inspection programs are developed based on the principles of risk analysis. RBI has been used in the development of cost-effective inspection and maintenance programs for nuclear power plants and petrochemical plants. Usually, the greatest risk to a facility is associated with a small number of its details. Efforts are focused on the most critical details, selecting the most appropriate methods and optimizing the inspection plan. In the development of an RBI plan, it is assumed that the operating conditions of the facility, the parameters of the corrosion environment and the degradation mechanism will not change significantly. If significant changes are present, the result will be a significant change in corrosion rate and/or in the type of corrosion damage and other inspection methods will be required. When there is no historical data on the corrosion behavior of the facility and the parameters of the corrosion environment, a baseline study is conducted to determine the conditions against which the inspection and monitoring are carried out.

5.12.2. Risk related to corrosion

The primary task of a corrosion risk assessment (CRA) is to guide the development of an inspection and monitoring plan aimed at locating and measuring potential corrosion problems and the selection of corrosion management procedures. The corrosion risk is presented as a product of the probability of failure (failure, accident) and the consequences. The probability is estimated based on the corrosion damage expected for a given component and the types of corrosion. Consequences include the impact of corrosion damage, assessed using a matrix including types of failure probability (high, medium, low) and at a minimum the following types of consequences: worker safety (high, medium, low), environmental (high, medium, small), for the production and overall operation of the facility (large, medium, small). The corrosion risk assessment is done on two levels: I - system including a group of components subjected to similar working conditions and II - specific components (more detailed assessment). The CRA identifies the corrosion and degradation hazards of each piece of equipment, estimates its remaining "life time" and feeds this information to the overall risk assessment system of the respective facility/equipment. The risk is assessed for a particular facility/machine, for particular conditions and (most often) for a particular degradation mechanism. The following types of assessments are made:

A) Risk of occurrence of a certain type of corrosion, depending on the available influencing factors - the assessment is made using a matrix of expert opinions, which includes various influencing factors: material (composition, structure, surface condition), working environment (nominal conditions, specific conditions), temperature (variable, constant), design and different possible types of corrosion damage (uniform corrosion, pitting corrosion, corrosion cracking, etc.).

B) Risk of the degree of development of certain types of corrosion under certain conditions (e.g. corrosion of unalloyed steel in soils) – the assessment is made using a matrix with points corresponding to certain values of a given parameter (e.g. specific electrical conductivity, chloride concentration, presence of microorganisms, etc.). The influence of each factor is assigned a certain number of points, and the total number of points corresponds to a certain possibility of corrosion and determines what protective measures should be taken.

C) Corrosion risk due to human errors - the assessment is made using a matrix of expert opinions, which includes different types of errors (operational, structural, manufacturing, installation / construction errors, maintenance errors, underestimation of the problem). Each of the errors is assigned a certain weight (points) related to the failure of the machine / facility, and the assessment is made for a certain type of machine / facility and certain conditions.

REFERENCES AND FURTHER READING

Antropov L., Theoretical electrochemistry, Visshaia shkola, Moscow, 1984 (in Russian).

Baboian R, NACE Corrosion Engineer's Reference Guide, Fourth Edition, NACE Press, Houston, 2016.

Bastidas D. M., Ed., Corrosion and Protection of Metals, MDPI, Basel, 2020.

Brandes E. A, Brook, G. B., Eds., Smithells Metals Reference Book, 7th Edition, Butterworth-Heinemann, Oxford, 1998.

Broomfield J. P., Davies K., Hladky K., The use of permanent corrosion monitoring in new and existing reinforced concrete structures, Cement and Concrete Composites, 24 (1), 27-34, 2002.

Corrosion Handbook (Incorporating Corrosion Prevention Directory), MPI Group, (Inst. of Materials, Inst. of Corrosion), 1999.

Fontana M. G., Greene N. D., Corrosion Engineering, 3rd revised edition McGraw-Hill Book Company, New York, 1985.

Fürbeth W., Ed., Advanced Coatings for Corrosion Protection, MDPI, Basel, 2022.

Gavrilov G., Nikolov Ts., Chemical nickel plating and dispersion coatings, Technika, Sofia, 1985 (in Bulgarian).

Hamann C. H., Hamnett A., Vielstich W., Electrochemistry, 2nd, Completely Revised and Updated Edition, Wiley, Weinheim, 2007.

Hudson R., Coatings for the Protection of Structural Steelwork, The National Physical Laboratory, Teddington, UK, 2000.

Hussain C. M., Verma C., Aslam J., Aslam R., Zehra S., Handbook of Corrosion Engineering, Modern Theory, Fundamentals and Practical Applications, Elsevier, 2023.

Munger C.G., Vincent L. D., Corrosion Prevention by Protective Coatings, Third Edition (e-Book), NACE Press, USA, 2014.

Page C. L., Bamforth P., Figg J. W.; Eds., Corrosion of Reinforcement in Concrete Construction, The Royal Society of Chemistry, Ove Arup and Partners, London, UK, 1996.

Panayotova M., Corrosion and corrosion protection in construction, Publishing house "Saint Ivan Rilski" at University of Mining and Geology, Sofia, 2007 (in Bulgarian).

Pedeferri P., Corrosion Science and Engineering, Springer Nature Switzerland AG, Cham, Switzerland, 2018.

Raichev R., Chemical resistance of materials and corrosion protection, Technika, Sofia, 1990 (in Bulgarian).

Rieger, P., Electrochemistry, Prentice Hall, Inc., Engle wood Cliffa, N. Y., 1986.

SchweitzerP.A. , Corrosion Engineering Handbook, M. Dekker, New York,1996.

Tomashov N. D., Theory of Corrosion and Protection of Metals, The Mac Millan Co, New York, 1996.

Treseder R. S., Baboian R., Munger C. G., Eds., NACE Corrosion Engineer's Reference Book, 2nd edition, NACE Press, Houston,1991

Uhli H., Corrosion and Corrosion Control, An Introduction in Corrosion Science and Engineering, J. Willey & Sons, USA, 1985.

Veleva L., Russel D. K., Atmospheric Corrosion, ASTM Series, 2004, 196-209.

Von Baeckmann W. , Schwenk W., Prinz W., Handbook of Cathodic Corrosion Protection, Elsevier Science, USA, 1997.

Yang L. , Techniques for Corrosion Monitoring, Second Edition, Woodhead Publishing Ltd, Sawston, UK 2020.

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