Controlling Factors in the Protection of Metals from Corrosion

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Great interest is attached to the development of existing methods for the prevention of corrosion of metals, starting from the inhibition of the basic step of electrochemical corrosion. Apart from providing the most rational scientific classification of the possible methods of anti-corrosive protection, such an approach might indicate the best conditions for using each method and their most effective combinations.

There exist a very large number of different methods for preventing corrosion. These methods are so various in character that it appears impossible to see in them any general factor, such as is necessary for a rational classification based on a single scientific system. Let us recall the basic methods which are widely used to protect metallic structures from corrosion, and arrange them firstly, as is generally done, according to the different ways in which they are carried out: 1. Protective coatings. Organic coatings (paints, high-polymers, greases). Inorganic coatings (oxides, phosphates, chromates, etc.). Metallic coatings of various types (metallization, sublimes, diffusion, plated). The protective coatings can differ very much in their thicknesses, starting from very thin protective layers like the adsorbed passive films (tens of angstroms), up to thick linings (refractories) constructed from protective materials, the layers of which are some 2-3 cm thick. 2. Treatment of the corroding medium to reduce its corrosive activity. As examples one can cite neutralization and deoxygenation of liquid media, the use of different types of inhibitor, especially volatile ones, which have been widely used to protect metallic parts in atmospheric conditions, and some others. 3. Electrochemical protection based on the methods: a) cathodic protection and the use of protectors; b) anodic electrochemical protection; c) protection from stray currents by use of electrodrainage. 4) Development and use of new metallic constructional materials with increased corrosion stability. 5. Rational construction and exploitation of metallic installations and parts.

From the scientific point of view it is more interesting to analyze and classify the various methods enumerated not on the basis of their conditions of use or the technology of their application, but by the application of the electrochemical theory of corrosion and discussion of the mechanism of the protective effect of each method. It is possible to carry out such a classification, but it is essential to establish correctly for each protective method the stage of the corrosion process which is retarded by the given protection method i.e., to establish the basic controlling factors of the particular protective method.

It appeared that one could choose with sufficient certainty for each method of corrosion protection the step of the corrosion process whose deceleration determines the general reduction in rate of the corrosion process. It is known \[7,9\] that the dependence of the corrosion current (which characterizes the rate of corrosion) on the basic factors of electrochemical corrosion is defined by the equation:

\[
I = \frac{V^0_k - V^0_a}{P_k - P_a + R}
\]

where \(V^0_k - V^0_a\) is the difference between the initial equilibrium potentials of the cathodic depolarization process \(V^0_k\) and the anodic reaction of the dissolved metal \(V^0_a\). These values, which are equal to the EMF of the corrosion element, will be proportional to the decrease in free energy of the system when the corrosion process occurs. The value \(V^0_k - V^0_a\) can be regarded as the degree of thermodynamic instability of the system. The denominator of the expression given will represent the more general inhibition of the system; in the formula it is expressed by three
terms with ohmic dimensions; the mean cathodic and anodic polarizabilities (P_k and P_a) and the general ohmic resistance of the system (R).

Consequently the strength of the corrosion current (I) will, in the general case, depend on at least four factors: 1) the degree of thermodynamic instability of the system (V^t - V^2); 2) the mean cathodic polarizability (P_k); 3) the mean anodic polarizability (P_a); 4) ohmic resistance of the corrosive elements. These four factors rationally form the basis for a scientific classification of the different means for decreasing the rate of corrosion.*

For metals, decrease in corrosion is connected with inhibition of the cathodic process. Hence, for example, the use of cathodic inhibitors which increase the over-potential of the cathodic depolarization reaction, the decrease in the concentration of cathodic depolarizers in solution, e.g., hydrogen ions or dissolved oxygen, the decrease in active cathodic inclusions in the alloy, and some other things. To cathodic inhibition also belong the widely used methods of cathodic electrochemical protection, especially the use of protectors. The fact that cathodic electrochemical protection belongs to the methods which inhibit the cathodic process follows directly from the simple definition of the type of control.

As has been described previously [7-9] quantitative determination of the control can be carried out starting from the known value of the corrosion potentials (V_x) and the initial potentials of the cathodic (V^c_k) and anodic (V^c_a) processes. In particular the extent of cathodic control (C_k) will be determined by an expression:

\[ C_k = \frac{V^c_k - V_x}{V^c_k - V^c_a} \times 100 \]

It is obvious that with constant values for V^c_k and V^c_a any decrease in the value of V_x, i.e., a shift of the corrosion potential (V_x) in the negative direction, will correspond to an increased degree of cathodic control. Thus, cathodic protection, which is connected with a shift of the potential of the corroding surface (V_x) in the negative direction, can be interpreted as a decrease in corrosion due to an increased degree of cathodic control of the corrosion system. The mechanism of the principal inhibition of cathodic processes using cathodic electrochemical protection or the use of protectors can be understood thus: When the corroding surface is polarized cathodically with a surface current the microcathodes are so energetically overloaded from the surface circuit with its more energetic anode that they cease to work in the internal circuit because the corroding surface is a less active anode than the applied protector, for example.

Many methods of protection are based on inhibition of the anode process, for example: introduction of anodic inhibitors or general "passivating" reagents into the solution; increasing the ability of metal to be rendered passive by alloying it, and also special additions of noble metal ions to the solution, or introduction of noble metals into the metal structure. To anodic inhibition also belongs the recently discovered form of corrosion prevention with anodic electrochemical protection which may be carried out when the metal easily undergoes anodic passivation in the given conditions [10-14].

The possibilities of methods of protection against electrochemical protection based on increased ohmic inhibition are more limited. This is connected with the decreased role of ohmic control on electrochemical corrosion processes, especially in those cases in which the corrosion process is determined by the work of a micro- or submicro-cell [14]. However, for example, the method of protection against subterranean corrosion (which arises as a result of the effects of macroscopic cells) by drainage of the soil around the subterranean structure should certainly be placed in this category.

Many methods of protection against corrosion should be connected with lowering the degree of thermodynamic instability of the given corrosion system. The degree of thermodynamic instability of the system is determined not only by the character of the metal itself but also by the surrounding corrosion medium and the general physical properties of the system under discussion. Covering a thermodynamically active metal with a compact layer of a thermodynamically more stable metal (e.g., covering copper or copper-steel with gold, or steel with nickel) and also alloying the metal with a sufficiently large quantity of a more stable component (e.g., nickel with copper, or chrome steel with nickel) are examples of combating corrosion by lowering the degree of thermodynamic stability of the system.

* Analogous ideas are used not only to analyze the inhibition of electrochemical corrosion of metals but also to analyze the more general case of the course of electrochemical heterogeneous reactions.