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TECHNICAL NOTES FRL-TN-123

THE USE OF RADIOACTIVE INDICATORS
IN STUDYING THE INHIBITION OF
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SUPERIMPOSED FROM THE OUTSIDE

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Nauchnye Doklady Vyshey Shkoly, Khimiya i Khimicheskaya
Tekhnologiya, No. 1, 1958, pp. 32-35

Available literature data are insufficient for understanding the particularities and the mechanism of inhibition of corrosion caused by a current superimposed from the outside [1], and it is difficult to agree with some of the conclusions that have been reached. For example, Salin [2] affirms that the amount of hydrogen, which is formed when zinc is immersed into its acid sulfate solution, is independent of the application of outside current. A further deduction is made that the entire amount of hydrogen separated, as well as of zinc, is the result of a return solution of the metal already settled on the cathode. At the same time, the fact of an electrochemical protection of metals by a superimposed current was established long ago [3]. Later, a supposition was formulated [4] to the effect that the mechanism of the protective action of cathodic polarization lies in the rebuilding of the double electric layer [5] on the boundary between the metal-solution phases.

An attempt at returning to the study of this problem, which is very important to both theory and technology, is reported in this paper. The method of radioactive indicators was used for the carrying out of the experimental part of the study [6]. We had in mind that if the superimposition of an outside current actually

stops any process, the summary result of which is the corrosion of the metal, the presence and the change in contents of the corrosion products can be detected with the aid of marked atoms. This investigation can be done by determining the radioactivity of the medium (solution) in which the ionization of the metal takes place. Zn^{65} with a half-life equal to 250 days was used as a radioactive isotope. Radioactive zinc dissolved in 0.5 n sulfuric acid had at the beginning of the study a specific activity equal to 6.5 mc/ml.

The experiments were carried out in a glass cell with a 150 ml capacity. The cathodic and the anodic spaces were divided by a glass filter, in order to avoid the possibility of contaminating the products of electrode reactions. The observations were carried out in a thermostat at $30^{\circ}C$ ($\pm 0.1^{\circ}C$). Smooth platinum was used for anodes. A platinum tablet (1 cm² of surface) galvanized preliminarily in electrolyte cyanide at $i_k = 2$ a/dm² was used as the cathode. The tested electrode was covered with a firm coat of zinc from the electrolyte sulfate which contained 60 g/l of zinc and 100 g/l of H₂SO₄ with $i_k = 4.2$ a/dm². An indicator solution of radioactive zinc sulfate was also introduced into the same glass cell. This preparation of samples contributed to the production of a particularly dense, smooth, fine crystalline zinc precipitate with an activity of not less than 73,880 imp/min/cm². The cathodes were freshly prepared for each experiment. Their weight before and after the experiment were noted. The radioactivities of the zinc precipitate and of the sulfuric acid solution were determined after the tests with the aid of the surface computer in the type B installation [7].

The study of the speed of zinc corrosion in the absence of polarization and at the given density of the current was carried out in a 2 n sulfuric acid solution. The plotting of $i - \varphi$ curves was carried out with the aid of a cathode voltmeter "LLPU-1" constructed by UNIKh IM [8]. The measurements of the potential and the speed of zinc corrosion in the absence of the current were taken on the same installation.

The tested electrode was kept in 2 n H₂SO₄ for one hour, while the potential was established in time. After that, it was removed from the solution and weighed. The force of the current of cathodic polarization (i_k) was fixed throughout the experiment for each given value of the potential, since this force varied very strongly for

some φ_k .

The variations in the progress of zinc corrosion in an acid solution when cathodic polarization is influenced by an electric current are given in Table 1. The rate of corrosion in this case was characterized by the amount of marked zinc passed into the solution, i.e., by the radioactivity of the sample of the solution under examination.

Table 1 shows us that corrosion of the electrolytic zinc was greatest in the absence of an electric current. It then markedly diminished with the growth in cathodic polarization and, when the protective potential reached a determined value, corrosion stopped completely. For instance, in the case of a prolonged polarization of zinc with potentials $\varphi_k \geq -0.852$ v the radioactivity of the acid solution reached the minimum value; at the same time, the corrosive effect ceased. The fact that after obtaining the protective potential the polarizing current (i_k) remained constant for 1 hour (test 4, Table 1), or even slightly diminished at the end of the exposition (tests 5 and 6), attests to the inhibition of the corrosion process for the cathodic deposit. In this case, the zinc surface remained completely smooth, light, without any traces of corrosion. The weight of the cathode did not change.

A close examination of the mechanism of corrosive processes shows that they represent a series of successive stages, each of which has an influence on the course of the total process. For instance, when zinc corrodes in an acid in the absence of an outside electric current, the atoms of zinc ionize, liberating electrons (anodic process). Simultaneously, the ions of hydroxonium H_3O^+ attract electrons, forming molecules of hydrogen (cathodic process). Thus, when the sample is immersed in sulfuric acid in the absence of an electric current a certain amount of zinc passes into the solution, as a result of which the metal surface acquires a negative charge at the expense of electrons. In the layer of the solution adjoining the metal will appear, beside the cations Zn^{2+} , a certain excess of positively charged ions of hydrogen. The double electric layer will undergo marked changes and a stationary potential [9] will establish itself on the border of the metal-solution phases. No equilibrium can be established because some atoms of zinc pass into the solution, thus increasing the concentration of zinc cations in the sulfuric acid, and a certain number of ions of hydrogen will be transformed into molecular hydrogen. Therefore, when zinc is immersed

Table 1

The Progress of Zinc Corrosion in 2 n H₂SO₄ in the Absence of an Electric Current and with the Cathodic Polarization by an Outside Current

(Duration of exposure 1 hour, temperature 30° C, sample of the solution under examination 0.5 ml)

No of the experiment	φ k volts	Force of the current ik in ma		Radio-activity imp/min/ml	Quality of the cathodic zinc deposit after testing for corrosion
		Initial	final (after exposure)		
1	-0.743	-	-	1330	Deposit completely dissolved
2	-0.809	4	190.0	207	Corrosion sharply defined
3	-0.852	4	26.0	21	Unclear traces of corrosion. Deposit is good.
4	-0.894	13.5	13.0	0	Smooth, clear, fine-crystalline surface without traces of corrosion
5	-0.937	27.0	21.0	0	The same
6	-0.979	36.0	30.0	0	The same

into sulfuric acid without electric current, only a balance of charges will result; the balance of substance will not be achieved, since different ions participate in the transfer of charges in the direct and reverse direction.

The superimposition of a direct current from outside provokes sharp displacements in the course of electrode reactions. Such displacements manifest themselves in changes both of concentration and of composition of ions in the electrolyte, particularly, near the electrodes (concentrating polarization). In addition to the concentrating polarization, or along with it, a chemical polarization arises when the current passes. This polarization is related to various stages of the process of discharge of hydrogen ions.

The hydrogen-formation reaction can be divided into two stages. During the first one a hydrated ion of hydrogen (H_3O^+) gains an electron. In this case an adsorbed layer of atoms of hydrogen is formed on the surface of the electrode.

During the second stage, the atoms of hydrogen transform themselves into molecules. In order that this process might proceed with a sufficient speed, it is necessary to weaken the bond between the cation of hydrogen H^+ and the molecule of water. The activation energy necessary for this can be obtained partly from the supplementary energy generated when the charges pass through the electric field of the double layer near the surface of separation between the metal-solution phases, owing to which the electrode's potential increases: it becomes more negative. This has a decisive influence on the rate of the process of the discharge of ions [10]. Hence, when the potential changes from its positive value to a more negative one, the amount of charges on the surface of zinc will vary. We can, therefore, assume that the protective action of the outside current is not directly related to the speed of corrosion of the metal to be protected in the given medium.

The mechanism of the protective action of the current has seemingly a purely electrochemical nature and is related primarily to the process of reconstruction of the double electric layer on the metal-solution border. During the cathodic polarization, electrons flow onto the surface of the metal to be protected. When their numbers near the active sectors become sufficient to prevent the passage of zinc cations from the liquid coating of the double layer into the mass of electrolyte, a passivity (non-solubility)

of the metal must take place. In this case, the cathodic potential increases and the polarizing current i_k (experiments 4-6, Table 1) remains practically constant during the entire time of exposure. From which it follows, that the appearance of some surplus of electrons in the metal lining of the double layer is not only a factor limiting corrosion but also a condition that stabilizes the process of discharge of ions.

The surplus of electrons necessary for the given metal and the medium in which the corrosion takes place depends on many circumstances and principally on the amount of overvoltage of hydrogen and on the speed of discharge of ions (cathodic density of the current). In other words, the protective potential set up on the zinc electrode in the sulfuric acid solution is a result of the compensation of the reaction of ionization of the atoms of zinc by the discharge of the ions of hydrogen. This potential will be by its nature very little equilibrated, since it is very sensitive to the change of conditions under which the direct and the reverse processes take place. The speed of the zinc corrosion, in particular, depends very strongly on the microstructure of its surface, the purity and the concentration of the acid solution, as well as on the particulars and the character of processes of adsorption that take place on the surface of the metal. The ionization of zinc is facilitated by the fact that a discharge of the ions of hydrogen takes place simultaneously and in direct contact with the process of the dissolving of the zinc. At the same time, the surplus energy, which exists in the discharged atom of hydrogen, can be used for the diminution of energy necessary to the pulling out of an atom of zinc from the crystal lattice. It is natural to conclude in this case that a lessened density of current on the cathode will be required for the creation of the necessary protective cathodic polarization for metals which have a great overvoltage of hydrogen. That explains the experimental fact (see Table 1) that the density of the electric current superimposed from the outside, in order to create the necessary cathodic polarization required to protect zinc from corrosion, is relatively small. It is, at any rate, considerably smaller than the current, under which a reverse dissolving of zinc takes place.

We must remark, in conclusion, that a sufficiently complete theory of the "protective" potential still does not exist. However, experimental data given above attests that the protective action of the current superimposed

from the outside is undoubtedly related to the creation of a barrier, which retains the ions of zinc in a double electric layer. The process of self-dissolving of the metal damps at the same time. In this case, the precipitation of hydrogen on the zinc cathode, when φ_k attains a determined value, cannot be explained by the corrosion of the metal already settled on the cathode. The generation of gas is the primary electrode reaction, i.e., it depends only on the rate of interaction of the ions of hydrogen with the electrons.

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