CATHODIC PROTECTION WITH SACRIFICIAL ANODES.

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ABSTRACT

On the basis of the theory of bimetallic and multimetallic corrosion, the fundamentals of cathodic protection with sacrificial anodes were discussed. The exact reaction kinetic treatment of the process of this kind of cathodic protection is described. The -0.85 V and the 100 mV polarization criteria are analysed on the basis of the reaction kinetic theory described in this paper. The basic concept of sizing sacrificial anodes, including an experimental method is described. Concepts of the choice of anode materials and the role of anode beds are outlined. The chemical and physical effects (effects of oxidizing agents, organic materials, complex forming agents, catalysts, dry backfill, hydrogen embrittlement, alternating and stray current) disturbing the operation of a cathodic protection system are analysed.

The most important technological applications are also reviewed. The application of galvanic anode cathodic protection for protection of pipelines and tanks is briefly summarized. Because of the great attention devoted recently to the corrosion of reinforced concrete structures, a more detailed summary is given. Owing to its importance, a separate summary of the protection of reinforced concrete bridges has been made. Finally, a brief description of microbiologically induced corrosion in cathodic protection is given.

Keywords: galvanic anode cathodic protection, fundamentals, practical aspects

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1. INTRODUCTION

Cathodic protection with sacrificial anodes is perhaps one of the oldest methods used in the cathodic protection industry /1, 2/. In spite of the long history of the method, its current application is far below its potentials and desirable degree of utilization. As it requires no outside source of electrical energy (consequently, converters, rectifiers and complicated wiring), it can be applied under conditions where building and operating impressed current cathodic protection would be difficult or impossible. Because of the complicated theoretical background of its operation, the peculiarities of sizing and operating sacrificial anodes, which depends mainly on local conditions, there is still some aversion to the application of the method.

Cathodic protection with sacrificial anodes is built of two electrically connected redox systems with different redox potentials. As a result of electrical (first order or electron conducting) connection, the redox system with more negative redox potential cathodically polarizes the redox system (the protected structure) with more positive redox potential, resulting in decreasing its electrode potential, and consequently, in reducing corrosion.

One of the most important conditions for proper operation of a cathodic protection system with sacrificial anodes is the regulation of corrosion with adequate corrosion rate of the anodes. If there is any discrepancy in this process, the efficiency of cathodic protection decreases or ceases, therefore, in addition to corrosion protection of the protected structure, the operator has to deal with the corrosion of sacrificial anodes as well. Since the corrosion of sacrificial anodes depends also on local conditions, the construction and operation of this kind of cathodic protection systems requires greater care than the construction and operation of impressed current cathodic protection. Solution of these technical problems requires a deeper understanding of redox and corrosion processes than required for impressed current cathodic protection. In continuation of our earlier paper /3/, our current efforts aimed at helping companies with the work of planning, construction and operation by offering an easily understandable description of cathodic protection with sacrificial anodes and, thus, stimulating practical application of the method in a wider field.

2. ON CATHODIC PROTECTION WITH SACRIFICIAL ANODES IN GENERAL

It follows from the above that, as a result of electric connection (connection with first order (electron) conductor), between any redox system with different redox potentials is a cathodic protection of the redox system with more positive electrode potential by the redox system with more negative electrode potential. The general description of the basic concept of this method can be applied to similar systems in the field of scientific and technological practice, in addition to corrosion and corrosion protection. Naturally, in these cases the same laws of metal corrosion apply as in the field of corrosion protection. A very important example is the Raney-Ni catalyst. In this catalyst the Al remnant in the system will act like a sacrificial anode, cathodically protecting the Ni from corrosion, preventing it, in this way, from losing its catalytic activity.

Of course, in the field of corrosion protection not any redox system can be applied as the sacrificial anode. In practice mostly zinc, aluminium, magnesium and their alloys are used /2 - 6/.

2.1. Theoretical basis of cathodic protection with sacrificial anodes

The theoretical basis of cathodic protection with sacrificial anodes can be understood most easily by the help of the analysis of a cathodic protection used in practice or by the use of some model system. A practical example can be cathodic protection of iron with zinc sacrificial anodes and the model system may be a dry battery working with a zinc cathode /5/. In the dry battery the carbon rod may be replaced, in thought, by the protected structure which is connected electrically with the zinc. When the protected structure is connected to the sacrificial anode with a metallic (first order (electron) conductor) wire then a bi-metallic corroding system is created, consequently, the theoretical basis of cathodic protection with sacrificial anodes can be found in the field of the theory of bimetallic or multimetallic corrosion. The protected structure is protected from corrosion by the electrical work created by the corrosion of sacrificial anodes. (The situation is similar in the case of a dry battery, but the electric work which is generated by the oxidation of zinc is used here for corrosion protection and not for lighting, etc.)

In the field of corrosion protection the protected structure is almost

always iron, therefore, the operation of a cathodic protection system with sacrificial anodes can be easily understood by studying cathodic protection built of iron and zinc. The iron-zinc metallic couple is a good choice, because the zinc on the surface of electroplated or hot deep galvanized steel, similarly to cathodic protection with zinc sacrificial anodes, cathodically protects the iron covered.

2.1.1. The processes of a working cathodic protection system with sacrificial anode

In order to understand the operation of a cathodic protection system with sacrificial anodes, we must study the charge transfer processes taking place in the course of the working of the sacrificial anodes and on the surface of the protected structure. The transport processes, inevitable during the operation of a cathodic protection system, have to be taken into consideration only if their role is rate determining in the operation.

As is well known, a piece of zinc and iron dissolves, corrodes in acidic solution, while hydrogen evolution can be observed /4, 6/. The corrosion of the two metals does not effect each other, even if corrosion takes place in the same electrolyte (beaker, flask, soil, etc) . The two corrosion processes are independent of each other, at most, an adsorbed zinc layer may form on the iron surface /7, 8/, somewhat decreasing thereby the rate of iron corrosion.

Under the above discussed circumstances the following charge transfer processes are taking place /3, 9/:

During iron dissolution (corrosion):

$$Fe \leftrightarrow Fe^{2+} + 2e \qquad E^{o}_{Fe} = -0.44\ V \qquad (1)$$

$$2H^{+} + 2e \leftrightarrow H_2 \qquad E^{o}_{H2} = 0.000\ V \qquad (2)$$

During zinc dissolution (corrosion):

$$Zn \leftrightarrow Zn^{2+} + 2e \qquad E^{o}_{Zn} = -0.76\ V \qquad (3)$$

$$2H^{+} + 2e \leftrightarrow H_2 \qquad (2)$$

If the corrosion of these metals takes place under aerated conditions, the reduction of dissolved oxygen must also be taken into consideration. In

practice, however, it must be dealt with only if hydrogen evolution and oxygen reduction take place at a similar rate (at higher p_H values).

Reduction of oxygen in acidic solutions:

$$O_2 + 4H^+ + 4e \leftrightarrow 2H_2O \qquad E^\circ_{O2} = 1.23\ V \qquad (4)$$

Under industrial conditions, in open systems this reaction has always played an important role as the cathodic process of metal corrosion, but in closed systems (in tubes, pipes, tanks, etc) it can play a role only if the quantity of oxygen carried into the system by the flowing media is relatively high. In strongly acidic systems, however, its role even in open systems is of secondary importance.

2.1.2. The electrode potential of the corroding metals

The electrode potential of the corroding metals is a mixed potential determined by the anodic and cathodic processes of corrosion. Since it is a mixed potential, it is the mixture of individual (at least two (a cathodic and an anodic)) electrode potentials of the electrode reactions. The rate (i) of individual electrode reactions can be described with the Erdey-Gruz–Volmer–Butler equation /10-14/ if the charge transfer process is activation controlled /13/, i.e. the rate determining step is the charge transfer itself:

$$i = i^\circ \left(\exp\left(\frac{\alpha z F}{RT} \eta \right) - \exp\left(-\frac{(1-\alpha) z F}{RT} \eta \right) \right) \qquad (5)$$

where i° is the exchange current (the exchange rate of the given charge transfer process), α is the charge transfer coefficient, z is the number of electrons taking part in the charge transfer reaction, η is the overvoltage, the difference between actual (E) and equlibrium(E_e) electrode potential, that is $\eta = E - E_e$, and other symbols have their usual meanings.

If the charge transfer reaction is not a simple charge transfer reaction (like $Fe^{3+} + e \leftrightarrow Fe^{2+}$) but it is also a surface reaction where the surface material and state take part in the charge transfer process (like $2\ H^+ + 2\ e \leftrightarrow H_2$ /15, 16/) then i° is the measure of surface catalytic activity /15, 16/, because the chemical part of activation energy (U°_a or U°_c) of the charge transfer reaction is in the i° as can be understood from the following equation /3, 9-13/:

$$i^{o} = k_1 AzFc_R \exp\left(-\frac{U_a^{o} - \alpha zFE_e}{RT}\right) = k_2 AzFc_O \exp\left(-\frac{U_c^{o} + (1-\alpha)zFE_e}{RT}\right) \quad (6)$$

where k_1 and k_2 are the reaction rate constants, A is the surface area on which the charge transfer reactions take place, c_R is the concentration or activity of the reduced and c_O is the oxidized form of a redox system and U^{o}_a is the chemical part of the activation energy of the anodic and U^{o}_c is the cathodic process of the same redox system. In the field of metal corrosion, the quantity of U^{o}_a and U^{o}_c, however, depends on the catalytic activity of the corroding surface, on which the charge transfer surface reactions take place, therefore, U^{o}_a and U^{o}_c are constant only if the surface catalytic activity is constant/3, 15, 16/. Under the conditions of metal corrosion, U^{o}_a and U^{o}_c may change stochastically and considerably.

It follows from the above, that the electrode potential of corroding metals (the corrosion potential) cannot be an equilibrium potential even if it is constant for a long time /10 - 14/ and because of the changing activation energies at the same corrosion potential there can be different corrosion rates.

Because of the uncertainity of the surface area, in the field of metal corrosion, instead of current density, electric current is used in kinetic equations, therefore, in each equation the different "**i**" and "**i°**" values mean electric currents and not current densities /13/.

2.1.2.1. The electrode (corrosion) potential of corroding iron

The corrosion potential of iron is determined by reactions (1) and (2). If the actual electrode potential of these processes is far enough from their equilibrium potential then the cathodic branch of the rate equation for reaction (1) and the anodic branch of the rate equation for reaction (2) can be ignored /10-14/.

2.1.2.1.1. On the basis of reaction (1) the dissolution (corrosion) rate (i^{Fe}_{corr}) (the anodic process of corrosion) of iron is:

$$i^{Fe}_{corr} = i^{o}_{Fe} \exp\left(\frac{\alpha 2F}{RT}\eta_{Fe}\right) \quad (7)$$

where i^{o}_{Fe} is the exchange current of corroding iron, η_{Fe} is the overvoltage of iron corrosion(reaction (1)):

$$\eta_{Fe} = E_{Fe} - E_{el\text{-}e} \tag{8}$$

where E_{Fe} is the actual electrode potential $E_{el\text{-}e}$ is the equilibrium electrode potential of reaction (1) under given conditions.

2.1.2.1.2. The rate of hydrogen deposition (the Volmer reaction (reaction (2))) $(i_{H_{2Fe}})$ (the cathodic process of corrosion) on iron is:

$$i_{H_{2Fe}} = -i^{o}_{H_{2Fe}} \exp\left(-\frac{(1-\alpha)F}{RT}\eta_{H_{2Fe}}\right) \tag{9}$$

where $i^{o}_{H_{2Fe}}$ is hydrogen exchange current on the corroding iron surface and $\eta_{H_{2Fe}}$ is the hydrogen overvoltage on iron:

$$\eta_{H_{2Fe}} = E_{Fe} - E_{e_{H_2}} \tag{10}$$

where $E_{e_{H_2}}$ is the equilibrium potential of hydrogen (reaction (2)) in the given system.

2.1.2.1.3. The rate of oxygen reduction on iron surface

If the electrolyte is not acidic enough and corrosion takes place under aerated conditions then oxygen reduction (reaction (4)), as the cathodic process, cannot be ignored anymore. Since the corrosion of metals usually takes place very far from the oxygen equilibrium potential, the anodic branch of the kinetic equation can be ignored. The complicated mechanism of oxygen reduction is also ignored here and the oxygen reduction is regarded as a simple four electron charge transfer process /10, 12/. To understand the basic processes of cathodic protection with sacrificial anodes, this ignoration does not affect the understanding of cathodic protection with sacrificial anodes.

The rate of oxygen reduction $(i_{O_{2Fe}})$ (another cathodic process (process (4))) under aerated circumstances) on iron surface is:

$$i_{O_2Fe} = -i^{o}_{O_2Fe} \exp\left(-\frac{(1-\alpha)4F}{RT}\eta_{O_2Fe}\right) \tag{11}$$

where $i^{o}_{O_2Fe}$ is the oxygen exchange current on the corroding iron surface and η_{O_2Fe} is oxygen overvoltage on iron, which is :

$$\eta_{O_2Fe} = E_{Fe} - E_{eO_2} \tag{12}$$

where E_{eO_2} is the equilibrium electrode potential of oxygen (reaction (4)) in the given system.

2.1.2.1.4. The potential of corroding iron

In the course of metal corrosion the sum of anodic and cathodic processes of the corrosion are equal to each other (with opposite sign) /13/. It follows from this statement that the relationship can be written for corrosion current (i_{corr}) /13/:

$$i_{corr} = \sum i_a = -\sum i_c \tag{13}$$

From eqn. (13) it follows that the corrosion current of the corroding iron is:

$$i^{Fe}_{corr} = -i_{H_2Fe} - i_{O_2Fe} \tag{14}$$

On the basis of eqn. (14) the rate equation of iron corrosion can be written:

$$i^{Fe}_{corr} = i^{o}_{Fe} \exp\left(\frac{\alpha 2F}{RT}\eta_{Fe}\right) = i^{o}_{H_2Fe} \exp\left(-\frac{(1-\alpha)F}{RT}\eta_{H_2Fe}\right) + i^{o}_{O_2Fe} \exp\left(-\frac{(1-\alpha)4F}{RT}\eta_{O_2Fe}\right) \tag{15}$$

The electrode potential of a piece of corroding iron (E_{Fe}) is determined by three redox procesess (1), (2) and (4) and described by eqns. (13) and (15).

Of course, in practice, only E_{Fe} (eqns. (8), (10) and (12)) can be measured.

2.1.2.2. The electrode (corrosion) potential of corroding zinc

In the same electrolyte where iron corrosion takes place, zinc corrosion must be studied also because in the case of a running cathodic protection system the protected structure and the sacrificial anode are either in the same electrolyte or connected to each other with an ionic conductor.

The zinc corrosion potential (E_{Zn}) can be calculated in the same way as the corrosion potential of iron had been done. The very first step of determination of the zinc corrosion potential is also determination of the rate equation of zinc dissolution (corrosion) (i_{corr}^{Zn}). It can be made on the basis of redox equation (3), supposing that the rate of the reverse reaction can be ignored, therefore, it is /10- 13/:

$$i_{corr}^{Zn} = i_{Zn}^{0} \exp\left(\frac{\alpha 2F}{RT}\eta_{Zn}\right) \tag{16}$$

where i_{Zn}^{0} is the exchange current of reaction (3) (zinc corrosion) and η_{Zn} is the overvoltage of zinc corrosion, which is:

$$\eta = E_{Zn} - E_{eZn} \tag{17}$$

where E_{Zn} is the actual and E_{eZn} is the zinc equilibrium potential under given conditions.

As can be seen from the redox equations (2) and (4), the cathodic processes of zinc corrosion are the same as those of iron corrosion. Since these processes are catalytic surface reactions (see eqn (6)), their rate depends on the material and state of the surface /15, 16/. It follows from this statement that rate equations of cathodic processes (i_{H_2Zn} and i_{O_2Zn}) of zinc corrosion are formally the same as those of iron, but the values of constants and overvoltages are different. On the basis of this concept and equation (15), zinc corrosion rate equation can be written as follows:

$$i_{corr}^{Zn} = i_{Zn}^{o} \exp\left(\frac{\alpha 2F}{RT}\eta_{Zn}\right) = i_{H_2Zn}^{o} \exp\left(-\frac{(1-\alpha)F}{RT}\eta_{H_2Zn}\right) + i_{O_2Zn}^{o} \exp\left(-\frac{(1-\alpha)4F}{RT}\eta_{O_2Zn}\right) \quad (18)$$

where $i_{H_2Zn}^{o}$ and $i_{O_2Zn}^{o}$ are the exchange currents of hydrogen deposition (reaction (2)) and oxygen reduction (reaction (4)) on the corroding zinc surface, η_{H_2Zn} is hydrogen overvoltage ($\eta_{H_2Zn} = E_{Zn} - E_{e_{H_2}}$) and η_{O_2Zn} is oxygen overvoltage ($\eta_{O_2Zn} = E_{Zn} - E_{e_{O_2}}$) also on the corroding zinc surface.

On the basis of the above, it can be stated that zinc corrosion potential in an aerated electrolyte is determined by (2), (3) and (4) redox equilibriums and described by eqns. (13) and (18). Also in this case, the potential of metal, E_{Zn} can be measured, only.

2.1.3. The driving force of cathodic protection with sacrificial anodes

With the help of eqns. (15) and (18), the corrosion potential of iron (E_{Fe}) and zinc (E_{Zn}) can be described mathematically. Because of the unknown exchange current densities and equilibrium potentials, numerical calculation is impossible. In spite of this, the study of the exact kinetical description of the corrosion processes has several advantages as can be seen below.

Until the sacrificial anode (Zn) is not connected electrically to the protected structure (Fe), the following inequality exists:

$$E_{Zn} < E_{Fe} \quad (19)$$

The nature of cathodic protection with sacrificial anodes can be characterized with inequality (19). The numerical value of this kind of inequalities is the lowest for the iron-zinc couple and the highest for iron-magnesium.

According to the data in scientific literature, the electrode potential of zinc dissoluting in acidic electrolyte $E_{Zn} \approx$ -0.75 V /17/, and the electrode potential of iron under similar conditions $E_{Fe} \approx$ -0.25 V /18/ (with respect to the standard hydrogen electrode). It can be seen from these data that the electrode potential difference between zinc and iron corroding in the same electrolyte is about ~0.5 V. This is the open circuit potential difference (the

corrosion potential difference) of iron and zinc in the same electrolyte. It is the driving force of a cathodic protection system built of zinc anodes for protection of steel structures. If the sacrificial anode is aluminium or magnesium then the driving force, naturally, is considerably higher.

2.1.4. The united potential - p_H (Pourbaix) diagram of iron, zinc, aluminium and magnesium

Based on the original potential - p_H (Pourbaix) diagrams of iron, zinc, aluminium and magnesium /19/, a combination of the diagrams of these metals is derived resulting in their united potential - p_H (Pourbaix) diagram (Fig. 1). From the Pourbaix diagram of zinc, aluminium and magnesium those parts were placed in the iron Pourbaix diagram, which are important for consideration of the thermodynamic character of different sacrificial anodes. With the help of this diagram (Fig. 1) one can easily evaluate the driving force of an operating cathodic protection system (the electrode potential difference between iron and the sacrificial anodes used). These data can be applied succesfully in planning and operating cathodic protection systems.

2.2. Building a cathodic protection system of known redox systems

Of the redox systems, discussed above (of iron (reaction (1)) and zinc (reaction (3))) a working cathodic protection system can be made if the two redox systems are electrically connected, i.e., iron and zinc are connected to each other with a first order (electron) conductor (with a metallic wire). In this way, an electric circuit is created with about 0.5 V voltage as the driving force. After the electric connection between zinc and iron, zinc sacrifices itself while it cathodically polarizes, and in this way protects the iron. An ammeter, connected into the electric circuit (into the wire which connects zinc and iron) facilitates the measurement of the protecting current enforced by the sacrificial anode upon the protected structure.

2.2.1. Thermodynamic and kinetic conditions after connecting the anodes and protected structure

After connection of the sacrificial anodes to the protected structures, the electrode potential difference disappears between the protected structure and the sacrificial anode. In our model system, the electrode potential of iron and zinc will be the same value:

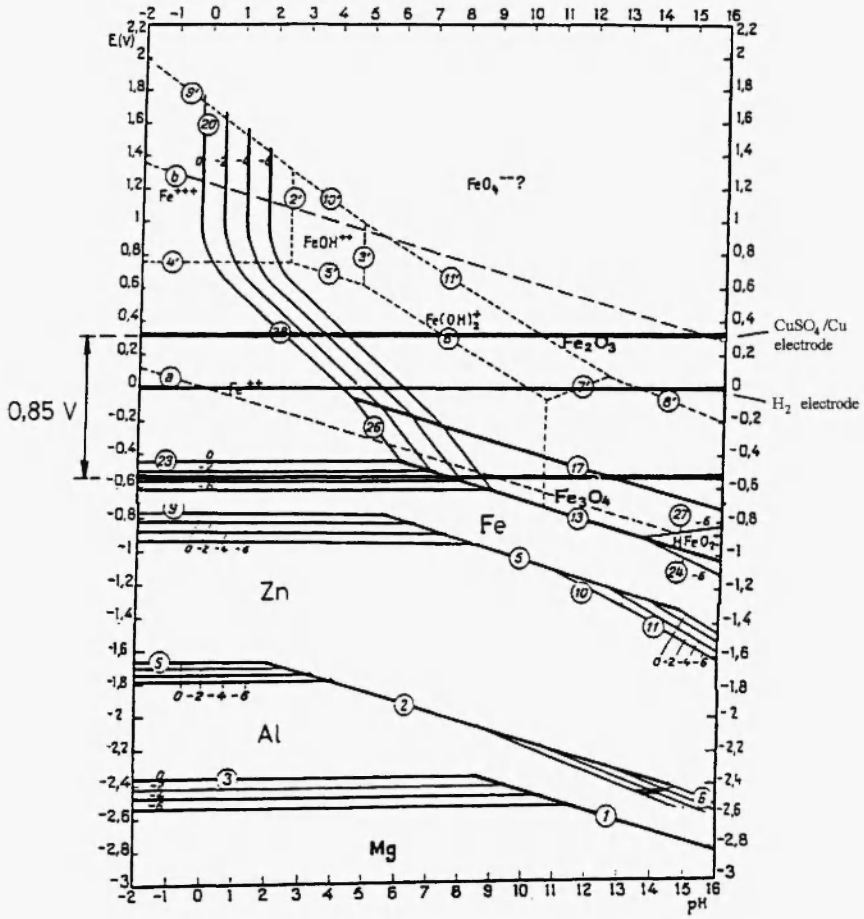

Fig. 1: The united potential-p_H (Pourbaix) diagram of iron (Fe), zinc (Zn), aluminium (Al) and magnesium (Mg).

$$E_{Fe} = E_{Zn} = E \tag{20}$$

where **E** is the common electrode potential, which comes into being after electrical connection (with electron (metallic) conductor) of iron with zinc.The value of **E** will be more negative than $E_{I\,e}$, and more positive than E_{Zn}. **E** is the mixed potential brought about by all the redox systems taking part in the processes of cathodic protection with sacrificial anodes. These

redox processes are the corrosion of iron and zinc as anodic processes, the hydrogen deposition and oxygen reduction as cathodic processes. On the basis of eqn. (13) the following relationship can be written /13/:

$$i_{corr}^{cath} - i_{corr_{Fe}}^{cath} + i_{corr_{Zn}}^{cath} = -i_{H_2}^{cath} - i_{O_2}^{cath} \qquad (21)$$

where i_{corr}^{cath} is the rate of corrosion of iron and zinc put together, in the course of operation of cathodic protection, $i_{corr_{Fe}}^{cath}$ and $i_{corr_{Zn}}^{cath}$ are corrosion currents of iron and zinc in a running cathodic protection system, $i_{H_2}^{cath} = i_{H_{2Fe}}^{cath} + i_{H_{2Zn}}^{cath}$, that is, the rate of hydrogen deposition taking place both on iron and zinc surface, $i_{O_2}^{cath} = i_{O_{2Fe}}^{cath} + i_{O_{2Zn}}^{cath}$, that is, the rate of oxygen reduction taking place both on iron and zinc surface under the conditions of a working cathodic protection system.

On the basis of eqn. (21) the complete corrosion rate equation for a running cathodic protection system where the protected structure is iron and the sacrificial anode is zinc:

$$\begin{aligned} i_{corr}^{cath} &= i_{Fe}^{o} \exp\left(\frac{\alpha 2F}{RT}\eta_{Fe}^{cath}\right) + i_{Zn}^{o} \exp\left(\frac{\alpha 2F}{RT}\eta_{Zn}^{cath}\right) = \\ &= i_{H_2}^{o_{cath}} \exp\left(-\frac{(1-\alpha)F}{RT}\eta_{H_2}^{cath}\right) + i_{O_2}^{c_{cath}} \exp\left(-\frac{(1-\alpha)4F}{RT}\eta_{O_2}^{cath}\right) \end{aligned} \qquad (22)$$

where the overvoltages (η^{cath}-s) are: $\eta_{Fe}^{cath} = E - E_{e_{Fe}}$; $\eta_{Zn}^{cath} = E - E_{e_{Zn}}$; $\eta_{H_2}^{cath} = E - E_{e_{H_2}}$ and finally $\eta_{O_2}^{cath} = E - E_{eO_2}$. These overvoltages come into being spontaneously, when the cathodic protection system works. $\eta_{H_2}^{cath}$ and $\eta_{O_2}^{cath}$ denote hydrogen and oxygen overvoltage under the conditions of an operating cathodic protection system. After connecting the zinc sacrificial anodes with the steel protected structure, these overvoltages form spontaneously from $\eta_{H_{2Fe}}$ and $\eta_{H_{2Zn}}$ for hydrogen deposition, and from $\eta_{O_{2Fe}}$ and $\eta_{O_{2Zn}}$ for oxygen reduction.

When iron and zinc are connected, in this case, both hydrogen deposition and oxygen reduction take place both on the surface of zinc and iron, therefore $i_{H_2}^{o_{cath}}$ and $i_{O_2}^{c_{cath}}$ are the united exchange currents which can be

measured after electric connection of zinc with iron. These exchange currents are the measure of exchange rate of reactions (2) and (4) on both metals put together, and they are the sum of the individul exchange currents , i.e., $i^{0cath}_{H_2} = i^{0}_{H_2Fe} + i^{0}_{H_2Zn}$ and $i^{0cath}_{O_2} = i^{0}_{O_2Fe} + i^{0}_{O_2Zn}$. Since iron is a better catalyst of hydrogen deposition (the equilibrium of (reaction (2))) than zinc /15, 16/, therefore, $i^{0}_{H_2Fe} >> i^{0}_{H_2Zn}$, which means that in acidic solution a more vigorous hydrogen deposition can be expected on iron than on zinc, if their electrode potential is the same **E** (and this is the case, because they (the iron and the zinc) are electrically connected to each other), as confirmed also by experimental observation /4/.

In eqn. (22) overvoltages may be replaced by corrosion potential (**E**) but in this case, exchange currents must be replaced by reaction rate constants and concentrations /10-12/. The advantage of using corrosion potential is that eqn.(22) demonstrates that the same corrosion potential (**E**) can be measured everywhere in the operating cathodic protection system. On the other hand, only **E** can be measured.

2.2.1.1. The role of oxygen diffusion

As in the case of impressed current cathodic protection /3/, also here oxygen diffusion can be the rate determining step, but under somewhat more complicated conditions. If diffusion is the rate determining step of oxygen reduction, then in the place of the last term of eqn. (22) describing the rate of oxygen reduction, the rate equation of the oxygen diffusion current must be written /10-12/:

$$i_{d_{O_2}} = 4FD\frac{c_{bulk} - c_{surf}}{l} \qquad (23)$$

where $i_{d_{O_2}}$ is the diffusion current of oxygen, F is the Faraday number, D is the diffusion constant, c_{bulk} is the oxygen concentration (activity) in the soil, atmosphere, water, etc, and c_{surf} is at the surface of sacrificial anodes and the protected structure. l is the thickness of the diffusion layer.(Number 4 comes from oxygen redox reaction for 4 electrons are exchanged in reaction (4).)

Since oxygen reduction takes place both on sacrificial anodes and the protected structure, the value of c_{surf} can change considerably from anodes to protected structure in a working cathodic protection system. The difference in

oxygen activity may result in an additional corrosion current between the surface areas with different c_{surf} (differential ventillation cell) which renders conditions even more complicated.

In the case of impressed current cathodic protection /3/, the possibility of the formation of the differential ventillation cell on a protected structure, caused by different oxygen activity on the surface of the cathode was ignored because this process may result only in some overprotection where lower oxygen activity can be found on the surface of a protected structure. Atmospheric oxygen does not play any role in the work of anodes of impressed current cathodic protection.

2.2.1.2. The polarity reversal

Under certain conditions in aerated electrolytes the zinc, instead of being galvanically corroded, is actually cathodically protected by Fe /17/. This phenomenon is called polarity reversal /17/. In this case the zinc passivates $\left(i^{o}_{Zn} \approx 0\right)$. On the passivated zinc and corroded iron surface the rate of H_2 deposition is also near to 0 $\left(i^{o_{cath}}_{H_2} \approx 0\right)$ but rate of O_2 reduction $\left(i^{o_{cath}}_{O_2}\right)$ can even increase by catalytic effect of the materials causing zinc passivation; therefore, in case of polarity reversal, anodic process is only Fe corrosion, cathodic process is only O_2 reduction, consequently, the second (Zn corrosion) and third (H_2 deposition) terms of eqn. (22) will be zero.

On the other hand, the condition of polarity reversal is $i^{o}_{Fe} \ll i^{o_{cath}}_{O_2}$. In this case O_2 overvoltage $\left(\eta^{cath}_{O_2}\right)$ is small, but Fe overvoltage $\left(\eta^{cath}_{Fe}\right)$ is high $\left(\eta^{cath}_{O_2} \ll \eta^{cath}_{Fe}\right)$, which results in a shift of corrosion potential (E) towards positive direction (this potential ennoblement is the indication of polarity reversal if Fe and Zn are electrically connected.

For catalytic reasons, the value of $i^{o_{cath}}_{O_2}$ depends on the quality and size of the zinc surface; therefore, a relatively small Fe/Zn surface ratio is another condition of polarity reversal. Of course, at a high Fe/Zn ratio the polarity reversal cannot come into existence because $i^{o_{cath}}_{O_2} = i^{o}_{O_{2Fe}} + i^{o}_{O_{2Zn}}$ and when the Zn surface is small, $i^{o}_{O_{2Zn}}$ is also small, i^{o}_{Fe} is increased, and the $i^{o}_{Fe} \ll i^{o_{cath}}_{O_2}$ condition can no longer be fulfilled. The influence of decreasing

Zn surface on Fe corrosion gradually disappears and the reaction of O_2 and Fe takes place according to eqn. (15).

Finally, it must be remarked that polarity reversal can be observed (measured) only if Fe and Zn are corroding in the same aerated electrolyte and they are not connected electrically /17/. The condition of polarity reversal in this case is also a small, practically zero i^{0}_{Zn} and a high $i^{0}_{O_2Zn}$ (eqn. 18)) which result in $E_{Fe} < E_{Zn}$. E_{Fe} and E_{An} (corrosion potential of Zn and Fe) are determined by eqns. (15) and (18). In this case Fe/Zn surface ratio does not play any role in polarity reversal.

2.2.2. Conditions of sufficient protection

According to internationally accepted practice, conditions required for sufficient protection of steel are that the corrosion potential of iron must be at least -0.85 V with respect to a saturated $CuSO_4/Cu$ reference electrode /3, 4, 13, 14, 20, 21/. It follows from this condition that the value of **E** (corrosion or operating potential) cannot be more positive than -0.85 V, therefore, the condition of sufficient protection is:

$$E < -0.85V \tag{24}$$

NACE RPO 169-96 describes three potential criteria for cathodic protection, one of which is a negative potential of at least -0.85 V vs $Cu/CuSO_4$ reference electrode /21/.

It follows from the -0.85 V criterion that the value of **E** in eqns. (20) and (22) cannot be higher (more positive) than -0.85 V, if there are no disturbing chemical and electrical processes in the system /3/. On the basis of this condition it can be stated that the electrode potential of the electrically connected zinc sacrificial anode and the steel protected structure must be -0.85 V or lower.

According to our calculations in our earlier paper /3/ -0.85 V is the equilibrium potential ($E_{e_{Fe}}$) of an iron electrode in 10^{-3} M Fe^{2+} ion electrolyte, therefore, at -0.85 V the corrosion potential can be regarded as an equilibrium potential:

$$E = E_{e_{Fe}} \tag{25}$$

Since on the basis of eqn. (22):

$$\eta_{Fe}^{cath} = E - E_{e_{Fe}} \tag{26}$$

therefore, at -0.85 V operating potential, the value of η_{Fe}^{cath} will be zero (or near to zero if Fe^{2+} ion activity is lower than 10^{-3} M). In this case, in eqns. (21) and (22) the terms describing iron corrosion will also be zero (near to equilibrium the cathodic branch of the kinetic equation of iron corrosion in eqn. (22) cannot be ignored, anodic and cathodic exponential terms will be 1, (and the sum of anodic 1 and cathodic -1 results in 0), consequently, the term describing iron corrosion will be 0). On the other hand, in eqn. (21) the value of $i_{corr_{Fe}}^{cath}$ will also be zero.

On the basis of corrosion rate equations (eqns. (21) and (22)) of a cathodic protection system with sacrificial anodes, therefore, it can be stated that at -0.85 V operating potential there is no iron corrosion, i.e., the burden of corrosion is taken over by the zinc sacrificial anode alone. In other words, this means that hydrogen deposition proceeds on both iron and Zn surface and oxygen reduction on both iron and and zinc surface only at the expense of the Zn anode. Iron does not take part in the processes because it is in equilibrium state (or near to equilibrium if Fe^{2+} ion activity around the protected steel structure is not exactly 10^{-3} M).

2.2.2.1. On the 100 mV cathodic polarization criterion

This method is applied to old and ineffectively coated structures. On bare structures it can be very difficult to achieve a polarized off potential of -0.85 V vs $Cu/CuSO_4$ electrode. Successful application of the 100 mV (or more precisely -100 mV) polarization criterion may achieve the desired protection level at reduced current requirement /22/. In this case, the value of operation potential (E) is not equal to $E_{e_{Fe}}$ but somewhat more positive, therefore, η_{Fe}^{cath}, consequently, $i_{corr_{Fe}}^{cath}$ will not be zero /23/. According to industrial experience a rather good cathodic protection can be achieved by the 100 mV polarization criterion, although the corrosion of steel is not zero under this condition, moreover the corrosion rate is unknown, as it is highly dependent on local conditions /22-25/. The protection is independent of the polarization method (performed either by impressed current or sacrificial anodes).

2.3. The sacrificial anodes

Planning, building and operating sacrificial anode systems is much more complicated than the operation of anodes in the case of impressed current cathodic protection, because – as demonstrated earlier – anodes and protected structure make up a bimetallic corroding system. The corrosion protection ability of cathodic protection with sacrificial anodes is determined by the thermodynamic and kinetic character of this bimetallic corroding system. The conditions affecting the operation of sacrificial anodes will determine the working and protecting efficiency of cathodic protection with sacrificial anodes.

2.3.1. The basic concepts of sizing sacrificial anodes

The question is now, how the **E** value (in eqns (20) and (22)) can be changed without any outer electric polarization. It can be achieved only by the regulation of i^{o}_{Zn} (exchange current of the zinc sacrificial anode) for the higher the value of i^{o}_{Zn}, the more negative is the value of **E** (the protective potential). The exchange current /10-12/, the anodic branch of rate equation (6) where c_R is the concentration or activity of the reduced form of the redox system taking part in the redox reaction (here it is unit because c_R solid metal (Zn, Al, Mg (in the case of alloys, however, the activity of sacrificial metal must be taken into consideration)), depends only on constant quantities except for A, the anode surface area.

On the basis of eqn. (6) it can be stated that the value of i^{o} (the exchange current) can be changed by increasing or decreasing only A (the anode surface area). In other words, this means that the anode surface area must be large enough to force upon the protected structure the required protective electrode potential (**E**). After selection of the metal used as the sacrificial anode, sizing the surface area of anodes is the most important question in this technology.

Determination of the anode surface area (A) required is one of the most crucial questions in the field of planning, building and running cathodic protection with sacrificial anodes, because the potential of operation (**E**) of a working system depends on the surface area of A. There is enormous difference in sizing anodes for pipelines, water boilers or, for instance, for offshore structures, etc. Determination of the mass of anode to be built into a cathodic protection system is somewhat simpler. Mass of the anode depends on the protective current and the time interval of anode exchange, and can

easily be calculated on the basis of Faraday's law and anode effeciency.

Good working conditions of a cathodic protection system with sacrificial anodes are: proper surface area, largest possible reaction rate constant (k) and lowest activation energy (U°_{a}) for the anodes, i.e., a good anodic backfill and appropriate size anode surface area.

2.3.2. The backfill

In order to provide adequate ionic contact between the sacrificial anode and the protected structure and the highest possible exchange rate for equilibrium (3), a special structure is built for this purpose, which is termed the anode bed. Since this kind of cathodic protection works with very low voltage, the anode bed must be near to the protected object. The anode bed is filled with the backfill. The role of backfill /4, 6, 20/ is:

- to maintain sufficient moisture around the sacrificial anode,
- to ensure good ionic contact between the anode and the protected structure,
- to ensure the slightest possible ohmic resistance between the anode and
- protected structure,
- to prevent passivation of the sacrificial anode,
- to ensure the uniform corrosion of the anode.

A very common backfill for zinc sacrificial anode is: 5% Na_2SO_4 + 20% bentonite + 75 % gypsum /4, 6, 20/.

Occasionally, there is no need for the anode bed and backfill, for instance in water heaters /4/.

2.3.3. Determination of the sacrificial anode surface area

The surface area of the anode can be determined on the basis of the magnitude of protective current and by the current intensity the anode can be loaded. The electric current by which the anode can be loaded, depends on the anode surface area and the state of the anode bed. In a good backfill k and U°_{a} (eqn. 6) are of optimal value. For instance, the value of rate constant k can be very low and U°_{a} relatively high (eqn. 6) in a dried backfill.

In practice, the surface area of anodes is calculated on the basis of protective current intensity required, but the protective current is calculated by the help of Ohm's low /20/. For an iron zinc (where $(E_{Fe} - E_{Zn}) \sim 0.5V$ (see section 2.1.3.)) system this is:

$$i^{cath}_{corr} = \frac{E_{Fe} - E_{Zn}}{\Sigma R} = \frac{\sim 0.5}{\Sigma R} \qquad (27)$$

where ΣR is the sum of ohmic resistance in the protective electric circuit /20/. The value of ΣR contains also the resistance of sacrificial anodes, which can be calculated with suitable formulas, /4, 20, 26/. Since the different ohmic resistances (soil resistance, resistance of connecting wires, etc) in the circuit are constant, decrease in ΣR can be achieved only by the increase of the anode surface area. The higher the anode surface area (and the better the anode bed and backfill), the smaller the resistance of anodes, and the larger the anode surface with respect to the protected surface, the nearer the operating potential (**E**) to zinc potential (E_{Zn}).

2.3.4. Determination of sacrificial anode surface area by an experimental method

The formulas published in the literature cannot be applied under all conditions for calculation of the sacrificial anode surface area. For this reason, newer and newer methods are published /26, 27/. In spite of the above, the anode surface area must be determined occasionally by experimental method. The theoretical basis of experimental method can be described with eqns. (22) - (24) .

Under similar conditions as in the planned cathodic protection system, an experimental system must be built. For example, an experimental system may be assembled to size anodes for cathodic protection in soil (Fig. 2). The size of sacrificial anodes must be increased until the system meets the requirements determined by eqn. (24) (in the case of water heaters, for

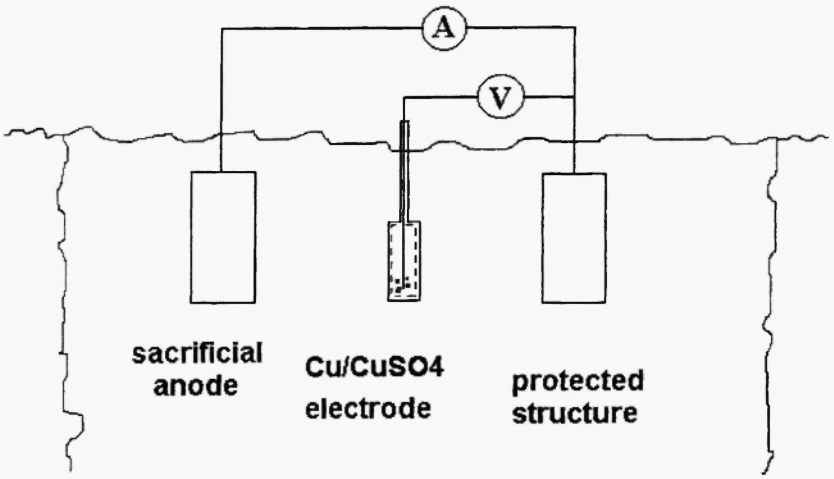

Fig. 2: Determination of the surface of sacrificial anodes with experimental method.

instance, this experiment must be carried out in tapwater). Technically this means that the surface or number of sacrificial anodes must be increased until the V voltmeter (in Fig. 2) displays at least -0.85 V (with respect to saturated $CuSO_4/Cu$ electrode) if the protected structure is made of steel. By this method the size of the anode surface area required for the protection of 1 m^2 surface can be measured under given conditions without tedious and unreliable calculations. (In Fig. 2 the ammeter (A) reads the current generated by sacrificial anodes.)

2.3.5. Choice of a sacrificial anode material

Since there is only 0.5 V electrode potential difference between iron and zinc, and the standard potential of zinc is -0.76 V, zinc can be used as a sacrificial anode only in the presence of air and water. If the protective potential must be more negative than -0.85 V then, depending on the required protective potential, either aluminium or magnesium or their alloys can be used as sacrificial anodes.

There are rather different anodes for the cathodic protection of steel. There are, for instance, Zn-Ni alloy /28/, aluminium alloys /29, 30/. A critical review of aluminum anode activation was also published /31/. A high-driving potential and high-efficiency Mg anode: a Mg-Ca alloy /32/ has been developed. An excellent anode material is an Al-Zn alloy activated with RuO_2 /33/. Sometimes three component (Al-Zn-Mg) alloys are used for cathodic protection application /34/.

2.3.5.l. Zinc-rich coatings

Another possible choice for sacrificial anodes are zinc-rich coatings. This technology combines the advantages of electroplated and hot dip galvanized systems with application methods of paint systems. Zinc-rich coatings are available with organic and inorganic binders /35/. The binder in the paint cannot prevent metallic contact between zinc particles and the surface to be protected. The size and distribution of Zn particles play an important role in the cathodic protection /36/. The deterioration of cathodic protection of zinc-rich coating in atmosphere is discussed in /37/. The development of zinc-rich paint for automotive application has also been attempted /38/.

2.3.6. Anode quality

On the basis of industrial experiences the quality of anode to be used can

be determined. A very important question is the alloying material. When a zinc anode is used, a very important requirement is the appropriate iron content of zinc, which cannot exceed 0.15 %, for at higher concentration passivation may take place. According to other authors, iron content must be less than 0.003 % /20/. In practice mostly the zinc anode, American Standard No. ASTM B418-88, is used /20/. An elevated content of iron, however, improves the electrochemical properties of zinc /39/

The anodes made of aluminium are generally apt to passivate. For this reason a suitable alloy must be used. Very often, the alloying metals are indium, zinc, tin, mercury /4, 30, 40, 41/. A study of the role of modifying elements in the behaviour of an indium activated aluminium-zinc anode has been made /42/. Development and testing of In and Hg free aluminium anodes was also carried out /43/. Current capacity of Al-Zn-In anode could be achieved by improved casting parameters and Mg addition /44/. The influence of Ti and Sr alloying elements on properties of Al sacrificial anodes has also been studied /44/. Of the ternary alloy systems the Al-Zn-Mg ternary system is the most efficient /45/. Activation of an Al-Zn-Mg-Li alloy by the presence of precipitates to be used as a sacrificial anode is described /46/. Electrochemical characteristics of Al-Zn-Mg alloys as sacrificial anodes in sea water is also a very important question. It is shown that by increasing Mg content an improvement in properties could be observed /47/.

In the case of magnesium, the self dissolution is considerable, therefore, the alloying material must decrease this character of Mg. This problem is discussed from the aspect of high potential Mg anodes for cathodically protecting iron water mains /48/. The performance of high potential Mg anodes and the factors effecting their efficiency was published recently /49/. A review of Al sacrificial anodes used for protection against corrosion of structures submerged in marine environment and the characteristics and superiority of Al alloys over other sacrificial anodes is also published /29/. Aluminium alloys (In/Hg free) suitable as sacrificial anodes for cathodic protection, have been developed and tested /50/.

The results of tests conducted for evaluating initial electrochemical characteristics of In activated Al alloy sacrificial anodes were reviewed /51/.

A new Al and Mg bimetallic sacrificial anode for cathodic protection of offshore structures was developed and tested in the last decade /52/. The addition of Ca to Mg anodes resulted in higher driving potential and efficiency. Mg-Mn-Ca anodes had the highest efficiency and driving

potential /53/.

2.3.7. Calculation of the quantity of sacrificial anodes

As mentioned above, the quantity of electric charge liberated by way of corrosion of 1 kg sacrificial anode can be calculated with the help of Faraday's law. Taking into consideration the magnitude of the required protecting current and the efficiency of the anode, the quantity of anode material consumed in one year can easily be calculated /4, 6, 20/.

Energy characteristics of a few well known and widely used sacrificial anodes have been calculated as follows /4, 6, 20/. Parameters of zinc: its energy capability ~ 810 A.h/kg , consumption rate 10.5-11.5 kg/A.yr. The same data for aluminium are: energy capability ~2500 A.h/kg, consumption rate 3-5 kg/A.yr and finally data for magnesium: energy capability: ~1100 A.h/kg, consumption rate: 7-8 kg/A.yr.

2.3.8. Wiring

Where it is important, a first order (electron) conductor (a metallic wire) must be used to connect the sacrificial anode electrically to the protected object. Very often it is insulated, but insulation is not of vital importance /4, 6, 20/. A more important question is the material of the wire. It cannot be a less noble metal than the material of the sacrificial anode. For instance, a zinc sacrificial anode cannot be connected to a protected structure with aluminium wire because aluminium, as the less noble metal in the system, will dissolve first. Copper cannot be a good choice either, for the copper pollutes its environment with copper ions and thus may catalytically accelerate reaction (2).

In the case of a zinc anode and steel protected structure, zinc plated (hot dip galvanized) iron wire is the best choice. When aluminium and magnesium anodes are used, this is also a good choice.

There are circumstances where cathodic protection with sacrificial anodes can be operated without an anode bed, backfill and wiring, e.g. in water boilers. Sacrificial anodes can be riveted, sputtered, plated, etc. onto the protected object without the use of anode beds.

2.3.9. Current efficiency of sacrificial anodes

Since anode metals are less noble metals than hydrogen (their electrode potential is much more negative than hydrogen potential under the

circumstances of operation of a cathodic protection system) and must not have passivated surface, therefore, to a certain extent they react with water, and naturally, with the oxygen of the air. These side reactions decrease the current efficiency of the sacrificial anodes. Of the sacrificial anodes zinc has the highest efficiency. Only about 5 % loss can be experienced. The current efficiency of aluminium sacrificial anodes is about 50-90 %, depending on the alloying metals and the possible impurities/20/. The less efficient anode is the magnesium anode, because it is the less noble metal and its current efficiency can be as low as 25 % /20/. The current efficiency can be increased by the use of appropriate inhibitor, which decreases the exchange current of reactions (2) and (4) but does not influence the ionization (the exchange current) of anode material (in the case of a zinc, anode reaction (3)).

2.3.10. The design of sacrificial anodes

In anode beds, anodes may be sheets or rods /4, 6, 20/. These are the most common forms but in practice there are various other designs. Very often the sacrificial anode is electrodeposited onto the protected structure /28, 30/. Flame spraying, hot dipping is also very often used to deposit a sacrificial anode layer on the protected structure /54/. It is proposed to design sacrificial anode cathodic protection systems for marine steel structures based on the slope associated with the linear relationship between potential and current density that arises as each of these parameters decays with time /55/.

2.4. Chemical and physical effects disturbing the operation of cathodic protection

Chemical and physical effects influencing the cathodic protection of the structure to be protected were discussed in our earlier paper /3/. In this paper the effects will be discussed mostly that can disturb the expected operation of cathodic protection system with sacrificial anodes.

As mentioned previously, reliable operation of galvanic anode cathodic protection system is based on the good performance of sacrificial anodes. Chemical and physical processes that can disturb the working of anodes will disturb the operation of the whole system. Sacrificial anodes can contact substances which may react with anode material, decreasing in this way the current efficiency of anodes and disturbing the operation of cathodic protection system.

2.4.1. The effect of oxidizing agents

Omnipresent oxygen or other oxidizing agents can react directly with the anodes decreasing their current efficiency. In planning the anode bed, we must take into consideration that except for air, other oxidizing agents must not get into the anode bed and backfill because these materials simply oxidize anode material, thus disturbing the operation of the whole system. Oxidizing agents in the backfill result in increased anode consumption because the current of reduction of oxidizing agents is added to the cathodic processes (reactions (2) and (4)) in the form of an unknown cathodic process ($i_{un.ox}^{cath}$) therefore, eqn. (21) must be modified as follows:

$$i_{corr}^{cath} = i_{corr_{Fe}}^{cath} + i_{corr_{Zn}}^{cath} - i_{H_2}^{cath} - i_{O_2}^{cath} - i_{un\ ox}^{cath} \qquad (27)$$

and, of course, this unknown process proceeds at the expense of anode material. In other words, in the presence of an unknown oxidizing agent, higher protective current is needed to force upon the system the -0.85 V protective potential, otherwise the potential of operation (**E**) is increased, consequently, η_{Fe}^{cath} will not be zero. This means that the system has moved out of the domain of thermodynamic immunity. The answer to the problem is: larger anode surface area.

2.4.2 Effects of organic materials

Different organic substances, sewage water, etc, may disturb the operation of cathodic protection for either the protected structure or the anodes can react directly with organic materials. If the presence of organics is inevitable, their presence must be taken into consideration in planning, sizing and operating anodes. Sometimes the parameters of operation have to be determined by experimental methods (see section 2.2.3.3. and Fig. 2).

In planning, construction and running a cathodic protection system it must be taken into consideration that iron has numerous organic reactions /9/, and in an environment contaminated with organics, working of cathodic protection may be disturbed /3/. The situation is very similar to the effects of complex forming agents /56/.

2.4.3. The effect of complex forming agents

In the presence of complex forming agents, the thermodynamic character

of the sacrificial anodes changes. Their influence is more favourable than not, because in the presence of complex forming agents the potential of ionization of the sacrificial anodes will be more negative, but a faster consumption of anodes may be expected.

Complex forming agents or those of ions, which are bonded to the protected structure (in the case of iron, for instance: CN^-, S^{2-}, NH_3, CO_2, etc) more strongly than the simple ionic bond, change the thermodynamic character of the protected structure as well /56/. Under these conditions iron must be polarized to a more negative electrode potential than -0.85 V. Of course, under these conditions zinc anodes cannot be used.

The effect of complex forming agents has to be taken into consideration very carefully in the course of planning and operating a cathodic protection system.

2.4.4. The effects of materials with catalytic action

When planning and operating a cathodic protection system with sacrificial anodes we must take into consideration that hydrogen deposition (reaction (2)) and oxygen reduction (reaction (4)) are catalytic processes, therefore, their reaction rate depends on the corroding material and the state of its surface /15, 18, 57/. Exchange current and consequently the reaction rate of processes (2) and (4) changes considerably if some material with catalytic character appears either on the surface of the sacrificial anode or on the protected structure. In this case the current efficiency of the anode decreases while the operation potential, the potential of the protected structure, increases. In this case a higher protective current is needed to force upon the system the protective potential (-0.85 V vs $Cu/CuSO_4$ electrode).

In reaction rate equation (22) values of exchange currents of hydrogen and oxygen ($i_{H_2}^{0cath}$ and $i_{O_2}^{0cath}$) will be increased in the presence of suitable catalysts on the surface. In order to keep the protective potential below -0.85 V (to fulfill the condition described by eqn. (24)), the value of i_{Zn}^{0} must also be increased. This can be realized only by increasing the anode surface. If the anode surface area cannot be increased then η_{Fe}^{cath} will not be zero because **E**, the potential of operation, will be more positive than -0.85 V; therefore, corrosion of the protected steel structure can be expected. In other words, catalytic effect decreases the reliability of the cathodic protection because the system may easily move out of the domain of the thermodynamic immunity

(the protective potential will be over -0.85 V). (Even in high quality theoretical papers it is not stated definitely that oxygen reduction and hydrogen deposition are catalytic processes.)

A rarely studied field of metal corrosion is adsorbate catalysed anodic dissolution and oxidation at corroding surfaces. Adsorbed materials can enhance metal corrosion, therefore, can influence the working of a cathodic protection system/7, 56 - 59/.

2.4.5. The effect of dried backfill and the environment

Drying has two effects. At first, the ohmic resistance is increased in the protective electric circuit. The value of ΣR in eqn. (27) is increased, therefore, only an increased anode surface area is capable of generating the suitable protective current; therefore, to assure the protective potential a larger anode surface area is needed.

On the other hand, the exchange current of the anode, in the case of zinc anode i^{0}_{Zn} in rate eqn. (22) is decreased in a dry backfill which results in a decreased corrosion current of the anode (eqns. (16), (18), (22)). The low corrosion current of the sacrificial anode is not enough to keep the protective potential in the domain of thermodynamic immunity, i.e., below -0.85 V if steel is protected (see eqn. (24)). In other words, the value of η^{cath}_{Fe} will not be zero (see eqns. (24) and (26)); therefore, corrosion of the protected steel structure can be expected.

The drying can be dangerous. When the anode bed is dried out but the protected object is not in dry environment, in this case there is no cathodic protection and the corrosion of the protected structure occurs. If the anode bed, the backfill becomes moisturized again, protective current regenerates and normal operation of the system is re-established.

2.4.6. Hydrogen embrittlement

In an earlier paper a detailed theoretical analysis of the conditions of hydrogen embrittlement was given /3/. Naturally, this harmful phenomenon can cause difficulties even in the operation of cathodic protection with sacrificial anodes if hydrogen activity on the surface of the protected structure is high enough. But how can it be too high? In the case of a bad choice and sizing of sacrificial anodes, overprotection may take place which may result in hydrogen embrittlement.

The condition of overprotection, and consequently hydrogen

embrittlement, is :

$$E << -0.85V \tag{28}$$

i.e., the potential of operation (E in eqns. (20), (22) (if not Zn is the anode)) must be much more negative than -0.85 V and somewhat acidic p_H /3/. In addition to the surface hydrogen activity, reaction kinetic effects of hydrogen deposition and ionization can also play an important role in the appearance of hydrogen embrittlement /15/.

A newly patented Al, 0.1 % Ga alloy has a working potential of -0.80 to -0.83 V vs Ag/AgCl (-0.89 V to -0.92 V vs $Cu/CuSO_4$ electrode) in sea water and its use has been described. This anode is used instead of Zn or Al-Zn-In anodes which potential is 1.0 V and 1.1 V vs Ag/AgCl /60/. In the case of high strength 13 % Cr stainless steel value of E, the protective potential cannot be more negative than -0.80 V (vs. Ag/AgCl) (which is -0.89 V vs. $Cu/CuSO_4$ electrode) /61/. The optimum protective potential region for cathodic protection of welded high strength steel without hydrogen embrittlement is between -0.77 V and -0.875 V (vs. SCE) (which is -0.845 V and -0.95 V vs $Cu/CuSO_4$ electrode) /62, 63/.

This paper deals with the influence of cathodic protection conditions on hydrogen absorption with underground steel pipes for natural gas transport media containing thiosulfate /64/.

If a zinc sacrificial anode is used then, theoretically, the value of E cannot be more neagtive than: -0.75 - 0.316 ≈ -1.066 V /17, 60/, where -0.75 V is the corrosion potential of zinc in acidic electrolyte and -0.316 V is the potential of the $Cu/CuSO_4$ reference electrode, both measured against a standard hydrogen electrode /3, 4, 12, 20/. At -1.066 V and the usual p_H values, generally, there is no serious risk of hydrogen embrittlement; therefore, when zinc sacrificial anodes are used, there is no danger of hydrogen embrittlement (but there are exceptions /60/). (Exact calculations are given in our earlier paper /3/.)

In the case of Al or Mg anodes, however, thermodynamic conditions are greatly different, and hydrogen embrittlement can be counted on as demonstrated by corrosion of Cd and Al based sacrificial coatings /65/. On the basis of united Pourbaix diagram of Fe, Zn, Al and Mg (Fig. 1) it can be calculated that with the use of an Al anode, maximum polarization potential cannot be more negative than: -1.720 - 0.316 ≈ - 2,04 V and in the case of

Mg anode, it cannot be more negative than : -2.448 - 0.316 ≈ -2,76 V , with the assumption that Al and Mg anodes dissolve at -1.72 V and -2.45 V, respectively. From these data it can be seen that application of Al and Mg sacrificial anodes may result in hydrogen embrittlement. Because of the multi-step reaction mechanism of hydrogen deposition and ionization, catalytic effects may also play a role in hydrogen embrittlement /15, 16, 55, 59, 63/. Based on the measure of back pressure P_{H2}, construction of a universal scale of severity for hydrogen cracking in differential media was studied /66/.

Hydrogen absorption studies confirmed that the absorption by steel in wet non-acidic NH_4HS and other H_2S environments is accelerated even in CN^- free conditions /66, 67/.

Several failures of cathodically protected duplex stainless steel made it quite clear that the risk of hydrogen embrittlement under cathodic protection must be carefully assessed when using these materials /68, 69/. Hydrogen embrittlement from cathodic protection on supermartensitic stainless steel was discussed on the basis of case history and recommendations are made for new qualification methods /70, 71/.

Hydrogen embrittlement of corrosion resistant alloys used in the oil and gas industry was discussed, and finally, a flow plan was put forward indicating the procedures that can be followed /72/. Effect of cathodic potential and strain rate on hydrogen embrittlement of alloyed steel was studied between -2.0 V and -0.8 V vs SCE (-2.075 V and -0.875 V vs $Cu/CuSO_4$) /73/.

2.4.7. The influence of alternating and stray current

Owing to electric network and electric traction and other industrial equipments in towns and big cities, the effect of alternating and stray current on cathodic protection must be taken into account /20, 74-77/. It has been observed that potential distribution on a pipeline can change upon the effect of stray current interactions. These currents can greatly affect the effectiveness of cathodic protection /78/. On the basis of the measurement of IR drop-free potential, the alternating current corrosion of buried steel under cathodic protection could be estimated /79/. A method for elimination of the IR ohmic drop component from the structure potential in regions of interaction of a dynamic stray current with carbon steel gas pipelines is developed /80/. Characteristic parameters have been observed for 24 hrs and

presented on the interaction of steel pipelines with randomly changing stray current leaking out of tram tractions /81/.

Fluctuating AC was observed on a pipeline where the pipeline was parallel to an AC powered rail transit system. AC was decreased by connecting the pipe to a bare steel casing pipe through a solid state DC decoupling device /82/.

Another interesting and hardly known phenomenon is the effect of telluric current on cathodic protection. Practical telluric current compensation was developed to improve the accuracy of cathodic protection close interval survey measurements /83/. Pipe to soil potential variations created by telluric currents were described, based on the results of recent studies involving extensive observations and modelling of telluric current /84/.

In the course of planning and operating of galvanic anode cathodic protection, the above discussed possibilities must be taken into consideration and the surface area, material and setting of sacrificial anodes must be planned accordingly.

3. TECHNOLOGICAL APPLICATIONS

After theoretical consideration of cathodic protection with galvanic anodes, the most important technological application of the method must be summarized. Recently, a great many scientific papers and lectures have been devoted to the questions of technological application of the latest results of development of cathodic protection. The protection of pipelines, tanks, and reinforced concrete structures is perhaps the most important problem of corrosion protection, the solution of which requires tremendous efforts all over the world today. Theoretical development has greatly contributed to a better understanding of corrosion problems and led to the elaboration of simpler and cheaper methods for solution of the technical problems involved.

In this section the most important papers and monographs published recently are cited and briefly summarized. The technological information given by summary of the latest results offers a closer insight into the corrosion problems and makes it possible for the readers to deepen their knowledge by getting acquainted with the original publications cited.

3.1. Protection of pipelines

In the case of pipelines impressed current cathodic protection is usually applied. There are, however, a few pipelines which are protected against corrosion with sacrificial anodes /60, 85, 86/. They are mainly in sea water where building the electric network is rather complicated. Other structures built offshore are often protected with sacrificial anodes /4, 6, 47, 52, 55/.

3.2. Protection of tanks

A well known corrosion protection question is the internal protection of hot water tanks of water heaters. This is solved by environmentally and biologically indifferent sacrificial anodes /4, 6/.

Above-ground storage tanks, mainly their bottoms, create a unique corrosion protection challenge for even small leaks may cause great cleanup expenses /87, 88/. Both sacrificial anode and impressed current techniques are applied to above-ground tank bottoms /89/. Improved cathodic protection testing techniques for above-ground storage tank bottoms have made the technology even more reliable /90/. Usual cathodic protection problems with underground storage tanks are described in /91/.

3.3. Protection of reinforced concrete

The corrosion of steel in global reinforced concrete infrastructures is a worldwide problem today /92 - 94/. After the catastrophic collapse of some reinforced concrete buildings and bridges, a great number of scientific research papers are devoted to the study and solution of corrosion problems of reinforced concrete. An overview of concrete corrosion and control practices was published in /95/. A modelling of the effect of corrosion on the lifetime of reinforced concrete structures is shown in /96/. Rapid development in the field can be observed, but there are still a great many scientific and technological questions to be solved. New concepts have been developed for cathodic protection and cathodic prevention in the maintenance of reinforced concrete buildings /97/.

A very important question is the application of steel reinforced concrete in chloride environment, that is, the protection of offshore structures and the structures where salt is used for de-icing.

Reinforced concrete structures are very often far from electric energy

supply systems. On the other hand sometimes the form of these structures makes the building of impressed current cathodic protection rather difficult. For this reason, in recent years increasing attention has been focused on galvanic anode cathode protection for the corrosion control of steel in reinforced concrete. This technology has two fields: Protection of rebars and protection of the reinforced concrete structures. The selection of guidelines for using cathodic protection systems on reinforced and prestressed concrete structures has been discussed in a recent publication /98/.

Innovative corrosion mitigation solutions for existing concrete structures have been developed and applied /99/. New development and use of galvanic corrosion protection systems has increased significantly in the protection of reinforced concrete structures /100/.

3.3.1. The protection of rebars

It seems obvious that prevention of the deterioration of reinforced concrete structures can be achieved by application of corrosion resistant steel (rebars). The only question is how corrosion resistant steel can be manufactured for reinforced concrete industry. The first attempt was application of hot dip galvanized (zinc coated) rebars /101-104/. The drawback of zinc coating is its sensitivity to the p_H of concrete. Even hydrogen evolution has been observed in the course of corrosion of zinc on rebars /105/.

Inorganic treatment and corrosion inhibitors can also be used for the corrosion prevention of rebars /106 - 111/. Zinc compounds as corrosion inhibitors act via adsorption (underpotential deposition) on steel /7, 107, 109/. On the other hand, in application of zinc coated rebars the advantage is that the corrosion products of zinc are corrosion inhibitors /107, 109/.

Instead of protection, sometimes high chromium steel or stainless steel rebars are used to ensure the long lasting usage of reinforced structures /112-114 /. Because of the high costs involved in the application of stainless steel, different reinforcement materials are being developed and tested /115/.

3.3.2. The protection of reinforced concrete structures

A more frequent solution for the protection of reinforced concrete structure is cathodic protection of the structure itself. In the protection of a completed concrete structure the problem is the electric contact between the rebars and anodes, for electric conductivity is not very reliable between the

corroded steel bars /116/. An analytical evaluation of galvanic anode cathodic protection systems for steel in concrete was carried out /117/. The evaluation of a new sacrificial anode cathodic protection systems for highway bridge decks is described in papers /118, 119/. The galvanic cathodic protection of reinforced concrete structures in marine environment is even more important /120/.

Different sacrificial anodes are used for cathodic protection of steel in reinforced concrete. The most frequent anode is the zinc or alloy zinc /118, 119, 120 - 124, 127, 128/. Aluminum and its alloys are also widely used /119, 120, 124 - 126, 129/, as well as magnesium and its alloys /130, 131/. An Indian (CECRI know-how) Mg alloy anode is described /132/. The application of titanium is also more and more popular /133 - 136/. Titan is used as the sacrificial anode, but also as a corrosion resistant anode for impressed current cathodic protection.

There are alternate anode materials for cathodic protection of steel reinforced concrete. These anodes are different alloys of Zn, Al, In, Ti and Co (Co is used to activate Ti anode) /137, 138/.

When titan is used as an anode for impressed current cathodic protection then its surface is covered with mixed metal oxide coating /4, 6, 139 - 141/. For characterization of the IrO_2 - RuO_2 film on Ti surface the Taguchy Method is used /142/.

The geometry of sacrificial anodes is rather different and depends on the geometry of reinforced concrete to be protected. The use of an anode metal sheet is simplest , but there are also mesh /121, 122, 128/, sputtered, arc or thermally sprayed metal anodes/123, 124, 127, 133 - 137/. Arc spraying is a tool for the durable corrosion protection of reinforced concrete /143, 144/.

Sacrificial anodes have been very often activated or modified. Aluminium anodes were activated with In, Sn, Hg, Ti /126, 129/. Activating elements were found to overcome the passivating influence of the insulating oxide layer which forms spontaneously on aluminium /129/. Zinc was activated with $LiNO_3$, LiBr /145, 146/. Titanium anodes were activated with cobalt nitrate and subjected to accelerated electrochemical aging to test their durability /147/.

Sometimes the anode was a conducting paint coating applied to the concrete surface /148, 149/. Conductive fibre in cementitious mortar was also used as anode for cathodic protection of steel in concrete. The conductive material was nickel-coated carbon fibres. Anodic current densities were in the

range of 10-100 mA/m^2 /150/. The carbon fibre mesh was embedded in a special mortar layer and then used as the anode of an impressed current cathodic protection system /151/. Conductive carbon fibres were found to cause galvanic corrosion /152/.

According to other authors, very often there are conducting organics, e.g., hydrogel and humectant between the anode metal and the concrete surface /120, 123, 137, 153 - 157/ .

Occasionally, cathodic protection of reinforced concrete could be afforded by an intermittent current. In most cases pulsed current resulted in significant reduction in the Cl^-/OH^- ratio of pore solution in the vicinity of the cathode /158/. It was observed that an integrated protection current of just 6 mA/m^2 induced the passivation of steel exhibiting an initial corrosion rate of 60 mA/m^2 /159/. Investigating the application of intermittent cathodic protection corrosion as a means for advancing corrosion control of reinforced concrete structures while extending the service life of thermal sprayed zinc anodes was carried out /160/. Pulsed current cathodic protection was used for the protection of oil well casing systems /161/. Similar protective effect could be experienced at the electrochemical treatment of reinforced concrete. It could be shown that the protective effect of a negative shift enforced on the rebars with cathodic polarization might be negligible compared to the protective effect caused by the improvement of the environment around the steel cathode in atmospherically exposed concrete where oxygen access is not restricted /162/. It means that sometimes the passivation and the favourable chemical environment around the rebars are more important than to keep the -0.85 V protective potential.

3.3.3. Hydrogen embrittlement of rebars

Hydrogen embrittlement of rebars and prestressed wires is a special field of hydrogen embrittlement which was discussed in our earlier paper /3/ and section 2.4.6.. It is a serious technological problem even in the field of cathodic protection of reinforced concrete structures, because the toughness of rebars and wires is changed by hydrogen absorption /163 - 168/. The long term effect of cathodic protection on prestressed concrete structures, the hydrogen embrittlement of prestressed steel was studied /163/. The relationship between steel mobile hydrogen and fracture initiation stress was studied. In the absence of mobile hydrogen, fracture initiation stress was found to be independent of environment and p_H value. The previously

reported fixed cracking threshold of -0.9 V vs SCE (-0.975 V vs. $Cu/CuSO_4$) was also explained /163/.

In the case of the impressed current cathodic protection of steel-reinforced concrete pilings, hydrogen production and uptake occurred at current densities as low as 0.33 $\mu A/cm^2$, critical hydrogen concentration for embrittelement (i.e. $2x10^{-7}$ mol H/cm^3) was not exceeded even at area averaged current densities <1.33 $\mu A/cm^2$. Even at this high current density the -0.78 V (SCE) (-0.855 V vs. $Cu/CuSO_4$) criterion was not met /165/. It has been stated that thermosprayed aluminium cannot be used in prestressed concrete piles for cathodic protection because the very negative potential (<-1.1 V vs. $Cu/CuSO_4$ electrode) Al supplies to the reinforcement can lead to hydrogen embrittlement /166/.

In another study it was stated that the ASTM A648 steel prestressed wire showed high susceptibility to hydrogen embrittlement at cathodic potentials below -1.2 V vs (SCE) (-1.275 vs. $Cu/CuSO_4$), resulting in severe loss of toughness, therefore, catastrophic failure may be expected under sudden action of force /167, 168/.

Based on the conclusions drawn from the above cited papers it may be stated that it is extremely important to avoid the overprotecting of reinforced concrete structures, when using either impressed current or galvanic cathodic protection in order to improve life expectancy.

3.4. Protection of bridges

Because of the salt used for de-icing and in coastal area for the sea water, the cathodic protection of bridges built of reinforced concrete is especially important. In spite of the tremendous corrosion danger, most bridges were built without corrosion protection and cathodic protection was constructed and built later onto the structure. For this reason, cathodic protection is generally not so efficient as it would be if the cathodic protection had been planned and realized simultaneously with the construction of the bridge. Both impressed current cathodic protection /139, 149/, and cathodic protection with sacrificial anodes /118, 119, 124, 132, 134, 137/ were applied for the protection of reinforced concrete bridges.

Another serious technical problem is the corrosion evaluation /169, 170/ and monitoring /171/ of reinforced concrete bridges. Degradation mechanisms of prestressed concrete bridges include: chlorides and corrosion;

concrete carbonation effects; the impact of concrete cracking; electrochemical and pitting corrosion; stress corrosion cracking and steel embrittlement; fretting corrosion; corrosion fatigue can be observed. Current inspection procedures used to assess the condition of bridges involve the use of sounding techniques, half-cell potential test, chloride analysis and cover thickness measurements. Impulse response technique and ground penetrating radar were used in assessing the delamination of concrete at concrete-steel interface. Measurements with radar were also used to determine the depth of cover profile across the bridge member. Corrosion rate measurements using linear polarization technique gave a more realistic result than half-cell potential tests /169, 170/.

Potential mapping is a reliable traditional technique to determine the corrosion state of reinforced concrete structure. Investigations carried out on several bridges and viaducts confirmed that potential mapping made on bituminous pavement can be considered representative of the actual corrosion state of the underlying rebars. In interpretation of the results, however, macrocell formation between upper and lower steel mats must be taken into consideration /172/. Corrosion monitoring based on macrocells indicated that the rebars close to concrete surface acted as anodes, while rebars further acted as cathodes. Ambient temperature strongly affected the galvanic activity. By application of cathodic protection to the structure, galvanic currents in macrocells became more negative. Macrocells appeared to offer a valuable approach to corrosion monitoring and to the monitoring the efficiency of cathodic protection./173/.

Various types of electrochemical corrosion mitigation technology systems including electrochemical treatment, cathodic protection and an overview of corrosion protection attained by electrochemical technologies is presented. The paper gives details on the application of certain specialized technologies including electrochemical treatment (re-alkalization, and chloride extraction), targeted corrosion control with embedded galvanic anodes, and galvanic cathodic protection using embedded strip anodes and humectant activated zinc /99/. Financial aspects of corrosion protection systems for construction and rehabilitation of reinforced concrete bridges are discussed in paper /174/. Assessing the sustainability methods for repairing concrete bridges subjected to reinforcement corrosion a pseudoquantitative method has been developed, which can be used to appraise sustainability. The paper describes the background of the method and discusses its application to three commonly

used bridge maintenance strategies: silane application, concrete repair and cathodic protection /175/. Owing to repair and rehabilitation, reinforced concrete structures must be inspected from time to time. In these inspection reports the initial signs of corrosion such as rust staining, efflorescence, cracking and spalling are well documented /176/.

A new technique called passivity verification technique has been developed for the assessment of cathodic protection of concrete bridges. This method is based on the passivation of rebars rather than on the level of the polarization potential of cathodic protection. Passivity measurements are carried out using electrochemical impedance spectroscopy. The results are not quantitative, but properly define the passivity of the rebar under protection and its resistance to corrosion /177/. This technique is supported by the observation that the principal protective effect of a cathodic current applied to steel in atmospherically exposed concrete improves the environment of steel and this promotes the formation of a stable passive film on the rebars. It can be shown that in this case the protective effect of the negative potential shift may be negligible compared to the protective effect of the passivity layer and the improved environment of steel in concrete /162/. In another case the 100 mV criterion was accepted as an indication of effective cathodic protection system for highway bridge decks /118/.

3.4.1. The anode materials

When impressed current cathodic protection is applied to bridges, then mixed metal oxide titanium anodes, conductive rubber, conductive coatings, conductive polymer and coke asphalt based anodes are mostly used /139, 149, 178, 179/. Maximum current of polarization is less than 10 mA/m^2 of steel surface area. /178/.

Galvanic anodes used for cathodic protection of bridges are made of zinc, aluminium, titanium or magnesium /132, 137, 138/. Naturally, not pure metals are used but their alloys because the pure metals apt to passivation and for this reason activating metal alloyed in the anode is required to eliminate this possibility. These metals sometimes alloyed also with each other /34, 45, 180/. Alloying metals for the activation of galvanic anodes are In, Hg, Co, Li, Sr, Ga /124, 126, 129, 137, 138/. The use of Al-Zn-In alloys /119, 120, 124, 153, 166, 181- 183/ as galvanic anodes is very common. Al-Zn-In alloy used for protection of reinforced concrete structure exposed to brackish water was the best at potentials in the order of -0.9 V vs $Cu/CuSO_4$ /183/. Alternative

consumable anodes (zinc-hydrogel, Ti, Zn, Zn-15Al, Al-12Zn-0.2In) for cathodic protection of reinforced concrete bridges were also published /181, 182/.

Galvanic anodes were applied in mesh form /118, 120 - 122, 128, 179/, in the form of metal sheets activated with hydrogel or humectant /119, 120, 123, 137, 156, 157/, thermally or arc sprayed onto the concrete surface to be protected /119, 120, 123, 124, 127, 133 - 135, 181, 182/.

3.5. Cathodic protection and microbiologically influenced corrosion

In all fields of corrosion and corrosion protection microbially induced corrosion must be taken into account, naturally, also in the field of cathodic protection /184 -186/. When cathodic protection is applied, electrochemical changes on the metallic surface influence the chemistry of water and favour the settlement of fouling organisms /185/.

Cathodic polarization led to the formation of a protective calcareous layer on the surface. Attachment of bacteria to metal surfaces and subsequent biofilm formation changed some physical and chemical parameters at the interface, consequently, influenced also the corrosion. Both low p_H induced by bacterial metabolism and exopolymers affected the deposition process and the stability of the calcareous layer /184/. Pseudomonas and Vibrio were selected to study their effect on current demand at potentials from -0.7 V to -1.2 V vs. SCE (-0.775 V to -1.275 V vs $Cu/CuSO_4$). The amount of current required for maintaining the protective potential was appreciably lower in the presence of these species, but only up to -1.0 V vs SCE /185/. Experiments were carried out with natural strains of Sulphate Reduction Bacteria (SRB) and Thiosulphate Reduction Bacteria (TRB), with monoculture of Desulfovibrio halophilus (SRB specie) and Dethiosu fovibrio peptidovorans (TRB specie), with cathodic protection between -0.9 V and -1.0 V vs SCE (-0.975 V and -1.075 V vs $Cu/CuSO_4$). The results seem to indicate that upon the effect of cathodic polarization, the metabolism of bacteria changes, which leads to the reduction of their corrosive activity /186/.

Not only reinforcement but the concrete itself may be attacked by microorganisms, mostly under conditions favourable for microbiological processes /187/. In the presence of sulphur containing compounds acidophilic (ASOM) and neutrophilic sulphur-oxidizing (NSOM) microrganisms are able

to attach to initially weathered concrete and then even smaller numbers of these, 1 % ASOM and 3 % NSOM , survive to colonize and further reduce the p_H of the concrete /187/. A review of fungal induced corrosion defines microbiologically induced corrosion and it is stated that microorganisms can accelerate the rate of partial reactions in corrosion processes and/or shift the mechanism for corrosion /188/.

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