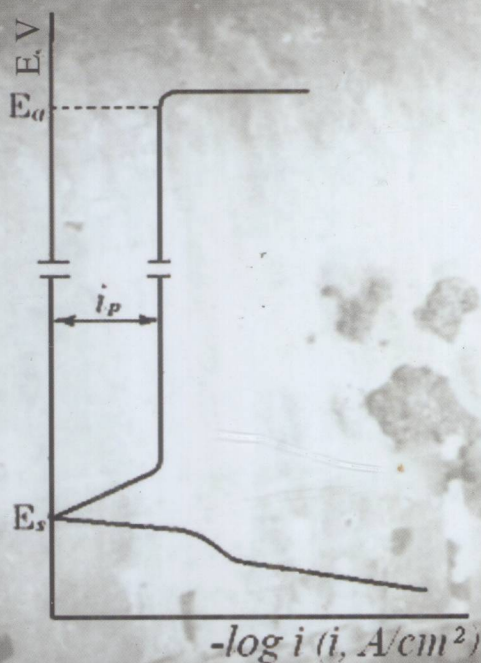


Joseph Riskin

Electrocorrosion and Protection of Metals

General Approach with Particular Consideration to
Electrochemical Plants



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ELECTROCORROSION AND PROTECTION OF METALS

GENERAL APPROACH WITH PARTICULAR CONSIDERATION
TO ELECTROCHEMICAL PLANTS

JOSEPH RISKIN



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ELECTROCORROSION AND PROTECTION OF METALS

*In memory of my father
Martin Fruman, who perished
in a Soviet concentration camp*

PREFACE

The present book may be considered as a first attempt to regard as a whole the problems of corrosion and protection of metals under the attack of external currents in water-containing environments. Corrosion processes in melted environments are not included in this book, since they are characterized by quite other mechanisms and laws.

Corrosion of metals under the attack of external currents is usually defined by the term "electrocorrosion." This general term of generalizing character is given in the title of the book. However, in the text it is not used too often, as specific questions connected with corrosion under the attack of stray currents or of leakage currents are considered. Besides, in the text it was necessary to specify additional current characteristics (anodic, cathodic, variable, etc).

Based on the general approach to the problems of electrocorrosion and protection of metals, the main focus attention was concentrated on the results of the researches of metal electrocorrosion in aggressive media of electrochemical plants, where these problems were most acute and least studied. These results formed the basis for developing methods and means of protection of metallic equipment and pipelines from corrosive attack by external currents in these plants. The well-known problems of corrosion and protection of metals in the field of stray currents are given in the form of a review.

Alongside the available literary data are given the results of long-term work carried out by a specialized division on the protection of metals against electrocorrosion, headed by the author, in the Moscow R&D Corrosion Institute. These results provide the main content, since available data on the electrocorrosion of metals in aggressive environments are rather limited. It must be noted that all the activities of research and development activities were carried out in constant close contact and cooperation with different operating electrochemical plants of chemical and non-ferrous metallurgical industries.

The successful solution to many problems connected with the design and calculation of models of metallic structures operating in the field of external currents and with researches of corrosion and hydrogenation of metals at cathodic polarization in many respects, is credited to the fruitful cooperation of Dr. J. B. Skuratnik, a brilliant scientist of the Moscow Scientific-Research Institute of physico-chemical researches in the name of Karpov.

The author thanks all colleagues with whom he has had the fortune to collaborate and without whose teamwork this book could not have been born.

The author has pleasure in expressing his special gratitude to the director of the Moscow R&D Corrosion Institute, Professor V. A. Timonin, who, for many years, encouraged this work. His benevolent attitude to the work, professional recommendations and advice given at discussions on the results of the studies promoted a successful solution to many problems.

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INTRODUCTION

CORROSION AND ELECTRIC CURRENT – 200 YEARS TOGETHER

The first electric current source was invented 200 years ago, at the boundary of the eighteenth and nineteenth centuries. In 1800, Volta built the famous “column” pile, the first electric battery: a series of alternating copper and zinc disks, separated by cardboard disks soaked with acid or salt solution. Between the copper–zinc pairs, an electric current was generated as a result of zinc dissolution or, in other words, as a result of zinc corrosion. Since then the two phenomena, corrosion and electric current, are closely allied and achievements in the studies of one of them promoted successes in the development of the other.

Nevertheless, only in the third decade of the twentieth century, after publications by Evans and Hoar, did the idea of the electrochemical nature of the corrosion processes of metals in contact with electrolytes finally become established [1].

The development of direct current sources made it possible to use an electric current as a means of influencing the metal–electrolyte system in further investigations. The laws of electrolysis that were discovered by Faraday as a result of these investigations promoted intensive development of theoretical and applied electrochemistry.

The fact that corrosion processes of metals have an electrochemical nature turned corrosion science into a branch of electrochemistry. Methods that are used for studies of corrosion processes are, to a large extent, similar to the electrochemical methods of investigation. Most of these methods (different kinds of polarization measurements, potentiometry, coulometry, impedance, etc.) are based on the influence of external currents on metals. The results of investigations of metal dissolution or deposition kinetics, adsorption and desorption processes, etc., obtained by electrochemists, are of interest to corrosion specialists and vice versa.

Processes based on electrochemical reactions in which electric current plays a part found widespread application in applied electrochemistry (electrolysis processes). The first electrolysis process was used in electrodepositing, the process that is the opposite of the corrosion process. Further investigations led to the development of electrolysis processes without metal deposition in aqueous electrolytes. Among them are water electrolysis for producing hydrogen and oxygen and electrolysis of sodium salts and other chloride solutions for producing chlorine, alkali and oxygen–chlorine compounds. Not only chlorine and oxygen–chlorine compounds, but many other oxidizers: hydrogen peroxide, manganese compounds, persulfates and other peroxides are also produced by electrolysis.

Processes of electrolytic refining and extraction of copper, nickel, cobalt, zinc, chromium, metals of the platinum group and of many other metals were developed.

Some of the metals (aluminum, magnesium, alkali and alkaline-earth metals) are produced by the electrolysis of melted salts.

Electrolysis processes are also applied for organic and inorganic electrosyntheses.

For a number of reasons, including the relative ease of execution and monitoring of electrochemical processes, electrochemical plants are now amongst the leading enterprises in the chemical industry [2].

It was possible to create large-scale and energy-consuming enterprises owing to the appearance of high-power sources of electric current. At some of such plants, current magnitudes attain hundreds of kiloamperes.

The use of electric current in electrochemical plants gave rise to problems connected with corrosion effects of leakage currents penetrating to metallic piping and equipment from electrolytic cells. This became a major problem for many plants, since it hindered the further development of the electrochemical plants. It was very difficult to find corrosion-resistant structural metallic materials for such plants, since these materials were attacked not only by media of high aggressiveness, but also by external currents.

Thus, corrosion phenomena promoted the development of different branches of science and technology connected with the processes stimulated by electric currents. In turn, extensive development of these processes engendered serious problems connected with the corrosion of metals under attack by leakage currents appearing in these processes.

So, we have a two-century long history of studies of the relationship between corrosion and electric current, and there are a huge number of investigations connected with the influence of an electric current on metal–electrolyte systems. It is amazing, but, in spite of these facts, the number of researches devoted to studying the direct corrosion attack of metals by external currents in aggressive environments is rather limited. Even fewer are the number of works devoted to methods and means of metal protection against corrosion by external currents in the aggressive media of electrochemical plants where the action of external currents on the metal structures is unavoidable.

Considered the corrosion problems connected with the attack by stray currents on underground and underwater piping and other structures can be considered an exception. Extensive investigations have been carried out in this field. Methods of control and protection of metals used in the said structures against corrosion attack by stray currents were developed. There is a rich library of books containing chapters on the corrosion of underground structures by stray currents. Therefore, only a limited review on this subject is given in Chapter 2 of this book. Such a review was necessary not only to enlarge the scope of the problems connected with the electrocorrosion of metals, but also to analyze the extent to which the experience that was accumulated in the field of corrosion and protection of metals against the attack by stray currents may be appropriated for solving the problems of electrocorrosion in the aggressive media of electrochemical plants.

The relatively low aggressiveness levels of soil, fresh water and seawater enables the application of carbon steel as a major structural material in these media. Extensive and comprehensive investigations of carbon steels that usually have rather similar corrosion and electrochemical characteristics in these media made it possible

to unify most methods and means of protection of underground piping and other structures against corrosion by stray currents. For engineers who are designing and carrying out corrosion protection of these objects today and are using existing standards for these purposes, knowledge in the field of electrical engineering is often more important than knowledge in the field of corrosion and protection of metals.

In electrochemical plants, the situation is quite different since aggressive media and applied structural materials are characterized by their great variety. This variety must be taken into account when the corrosion of metals by external currents and methods of protection against their attack are considered.

This approach to the problem means that a profound analysis of the metal state (passive, active, etc.) in the given aggressive environment of corrosion and electrochemical characteristics (corrosion and activation potentials of the metal, oxidation or reduction potentials of medium components on the metal surface, ratio of external current density to the current density of metal in the passive state, polarization characteristics, etc.) has to be carried out. Under such an approach, the external current is considered to be not just one of the factors of environmental aggressiveness, but the most aggressive one.

A very important point in this approach involves the fact that in the majority of cases, the metals that are used in aggressive media are initially in a passive state. Concentrating on this fact enabled the elaboration of fundamentally new very effective methods and means of protection of metals from electrocorrosion in aggressive media. The major concept of these methods consists of retaining by all means the potential of the protected metal within the limits of its passive field.

Further, it will be shown that such an approach turned out to be the most fruitful, particularly for the development of effective methods of metal protection against electrocorrosion in electrochemical plants.

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DEPENDENCE OF THE CORROSION BEHAVIOR OF METALS ATTACKED BY AN EXTERNAL CURRENT ON THEIR INITIAL STATE

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1.1. STATE OF METALS IN AGGRESSIVE MEDIA IN THE ABSENCE OF ATTACK BY EXTERNAL CURRENTS

When a pure metal comes into contact with an aqueous solution of its salt, an equilibrium electrode potential, E_{eq} , is established on the metal. This potential corresponds to the equality of speeds of metal atom ionization and of metal ion discharge on its surface. The value of the equilibrium potential of a metal in a 1 N solution of its salt at a temperature of 25°C is identified as the standard electrode potential, which is considered an important metal characteristic. To compare the thermodynamic stabilities of various metals, a so-called electrochemical series was established in which the metals are located in ascending order of their stability. In general, the more positive the standard potential of a metal, the higher is its thermodynamic stability. Values of standard electrode potentials are specified with respect to the standard potential of a hydrogen electrode, which is conventionally accepted as equal to zero.

During electrochemical corrosion, the process of metal dissolution in the electrolytes, which proceeds in accordance with the electrochemical mechanism, two conjugated reactions take place: anodic reaction of metal ionization



and cathodic reaction of reduction of any solution component on the metal surface

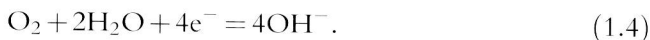


The spontaneous course of a corrosion process according to reaction (1.1) is possible only if the electrode potential of the metal is more negative than the potential of the cathodic reaction (1.2). Such a relationship between the potentials is a thermodynamic condition for the occurrence of the corrosion process. During the course of an irreversible corrosion process, a compromise potential, E_s , is established on the metal. It is called the stationary or corrosion potential.

The hydrogen ion is the component that is most often reduced on the cathode in acid media. The summarizing reaction of cathodic depolarization of a hydrogen ion is characterized by the equation



In many media, particularly in water, dissolved oxygen is reduced on the cathode. The summarizing reaction of this reduction is as follows:



The reversible potential of this reaction in a neutral solution in an atmosphere of air (i.e., at a partial oxygen pressure of 0.21 atm) is equal to 0.805 V.

The agent (oxidizer) that is reduced on the cathode is defined in the existing corrosion terminology as the depolarizer of the cathodic process. Accordingly, a corrosion process at which a cathodic reaction (1.4) takes place is termed as corrosion with oxygen depolarization.

Dissolved chlorine, ions of metals of the highest valence, for example, Fe^{3+} and Cu^{2+} and so forth can act as oxidizers in corrosion processes.

The condition of the metal, which can be characterized as stable or unstable in a given aggressive medium, depends on the nature of the metal and on the properties of the aggressive medium. Metals of the first group – lithium, potassium and sodium – are the most unstable, being at the left end of the electrochemical series of metals. The electrode potentials values of these metals (–3.045, –2.925 and –2.714 V, respectively) belong to the most negative. On contact with water, their dissolution is accompanied by strong evolution of hydrogen.

Iron is positioned in the middle of the electrochemical series. The standard potential of the reaction $\text{Fe} = \text{Fe}^{2+} + 2\text{e}^-$ is equal to –0.44 V. The standard potential of the reduction of hydrogen ions in water at pH 7 is equal to –0.414 V,