Pro-Ecological Aspects of Application of Cathodic Protection

K. Darowicki, W. Bohdanowicz, J. Walaszkowski

Department of Anticorrosion Protection
Chemical Faculty of the Technical University of Gdansk,
ul. G. Narutowicza 11/12, 80-952 Gdańsk, Poland

Abstract

This paper presents the most significant information on the corrosion of steel structures, which can be a source of environmental pollution. It has been recognised that early detection of the hazard and application of appropriate protection are the basic conditions of elimination of pollution as a result of corrosion processes.

Basic information has been given on principles of cathodic protection, scope of application of the technique and its practical aspects. It has been stated that this highly effective anticorrosion technology can guarantee trouble-free operation of objects such as underground and underwater tanks, steel pipeline storage, or transporting oil products and aggressive chemical media.

Keywords: steel pipelines and underground tanks, ecological hazard, anticorrosion protection, cathodic protection

Introduction

The development of civilization is unavoidably connected with pollution and degradation of the natural environment. Hazards to the environment can be of natural character (eruptions of volcanoes, earthquakes, hurricanes, fires, draughts, floods), but most frequently are the result of the "rational" activities of man. Damage caused by natural factors are difficult (or impossible) to avoid, but nature is able to cope with them; results of incorrectly analysed human activities are much more difficult to eliminate. Some sad examples of environmental pollution are large areas of Siberia affected by breakdowns of oil pipelines or fuel leaks from corroded tanks on former Soviet army bases in Poland, threatening the potable water sources of some towns.

As a result of the burning of natural fuels (mainly coal and oil) huge quantities of carbon, sulphur and nitrogen oxides, as well as dust, enter the atmosphere, causing its pollution. In 1990 in Poland over 6.5 mln tons of hazardous gases and dust were emitted to the atmosphere by heat generating plants and electric power stations, factories, municipal buildings and vehicles [1].

The intensity and form of corrosion attacking ferrous alloys, a typical construction material, depends on many factors. A significant role is played by the corrosion aggressiveness of the atmosphere, waters, soil and other media. Production activities of factories, formation of highly saline waste storage areas, emission of hazardous components to the atmosphere, contamination of waters and soils with sewage of different origin, increase the corrosion hazard degree to many technical objects, including tanks storing fuels, oil pipelines, brine and other chemical media. Corrosion of these objects can in turn be the cause of dangerous contamination of the environment. A leak of 1 dm^3 of oil products to underground waters can contaminate 1 mln dm^3 of potable water [2].

Due to the above, protection from corrosion is essen-
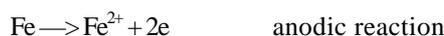
Correspondence to: Prof. K. Darowicki

tial of the huge national property in the form of buried and underwater installations and metal structures. Today's knowledge of science and technology allows early detection of the corrosion hazard and application of modern anticorrosion techniques.

The American Environment Protection Agency (EPA) has since 1989 required that users of underground steel tanks and pipelines with fuels and aggressive chemicals apply effective anticorrosion protection in the form of double walls, cathodic protection or polyester linings reinforced with fibreglass. New structures, if they do not meet the above conditions, are not permitted to be used. For used structures, including private house tanks for fuel oil, a ten-year period was anticipated for preparation of the above anticorrosion protection [2].
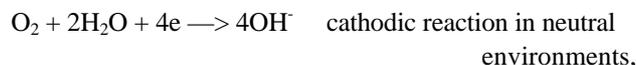
Corrosion of Structures - The Source of Pollution

Corrosion of metals in electrolytic environments is an electrochemical process, with which respective oxidation and reduction reactions are linked.
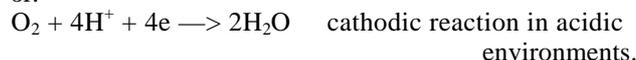
In the case of corrosion of carbon steel in a moist atmosphere, in natural waters and soil, oxidation of iron (dissolution) occurs:
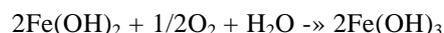
$$Fe \longrightarrow Fe^{2+} + 2e \qquad \text{anodic reaction}$$

and reduction of oxygen (depolariser):

$$O_2 + 2H_2O + 4e \longrightarrow 4OH^- \qquad \text{cathodic reaction in neutral environments,}$$

or:

$$O_2 + 4H^+ + 4e \longrightarrow 2H_2O \qquad \text{cathodic reaction in acidic environments.}$$

In the environment near the steel surface secondary reactions occur, e.g.:

$$Fe^{2+} + 2OH \longrightarrow Fe(OH)_2$$

$$2Fe(OH)_2 + 1/2O_2 + H_2O \longrightarrow 2Fe(OH)_3$$

leading to the formation of corrosion products (rust).

In the corrosion process a strict relation exists between occurring reactions. Any limitation in the course of one reaction (e.g., reduction) leads to a decrease of the rate of the second one, and the reverse. This interrelation is used in practice, amongst others, for decreasing the corrosion aggressiveness of water used in the power industry by chemical or thermal removal of oxygen. On the other hand, the necessity of continuous feeding of oxygen to sewage in the biological technology for their purification increases the corrosion hazard to steel chambers and the aerating fittings.

In general, the corrosion of steel structures in natural environments is limited by the rate of the cathodic reaction. If it is reduction of oxygen, then access of oxygen to the environment and the rate of its inflow to the surface of the metal will decide on the intensity of the corrosion attack [3-6].
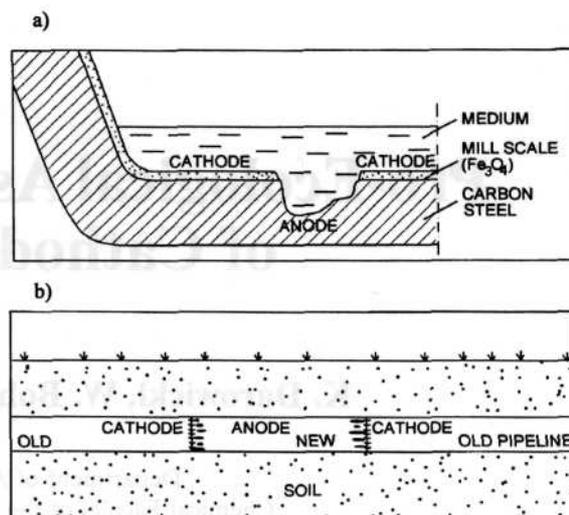

Fig. 1. Examples of occurrence of galvanic corrosion cells.

Steel structures are usually prone to interaction of additional corrosion factors connected with exploitation of different materials in non-uniform environmental conditions. Corrosive macrocells such as galvanic and concentration cells are formed.

Galvanic cells are formed as a result of electric contact (short-circuit) between two or several different metals in the same electrolytic medium. Under these conditions the metal characterised by the most negative potential is the anode in relation to the second material and undergoes accelerated corrosion. A classic example of such a cell is galvanic corrosion of bottom sieves of heat exchangers. Bottom sieves are usually made of carbon steel, while tubes placed in their openings are brass. In the presence of water the steel bottom exhibits a more negative potential and undergoes corrosion [3-6].

A non-metallic conducting component, e.g. magnetite, can become an electrode in a galvanic cell. As a result of the operation of a carbon steel-scale cell (Fig. la) perforation occurred of the wall of an underground tank for storing mazout.

During exploitation of the tank, in its lower part aggressive reflux was gathered, causing accelerated corrosion of steel in places in which scale was partially removed. Corrosion cells on repaired or developed structures can be troublesome for users. For example, during repair of a buried steel oil pipeline a new section of the same grade of steel was welded in (Fig. lb). However, the old pipeline, partially corroded, exhibits a more positive potential in relation to the new pipe section. This leads to accelerated corrosion of the welded-in section. Similarly, placement of a new transfer pipeline next to one operated for a long time, or realisation of new pipe branches, becomes a serious hazard of occurrence in a short time of corrosion centres on the new object.

Corrosion concentration cells are very widespread. They are formed as a result of contact of a metal or alloy with an environment with different concentrations in various places of substances taking part in electrode reactions, e.g. oxygen. A part of a metallic element contacting the environment with a smaller concentration of reagent
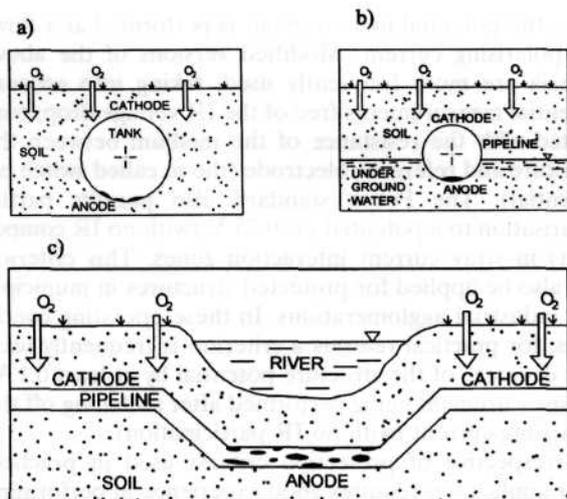
Fig. 2. Examples of occurrence of corrosion concentration cells.

(e.g. less oxygenated) becomes an anode and undergoes accelerated corrosion. The following are the result of action of concentration cells: corrosion of the water line of a structure partially immersed in water, corrosion of steel elements partially covered with deposits, corrosion in crevices, and also corrosion of buried metal structures of large dimensions [3-6]. In Fig. 2 examples have been presented of an occurrence of concentration cells on buried steel structures.

Practically, each large-dimensional buried steel structure (amongst others, brine pipelines, oil and gas pipelines, fuel tanks) is endangered by the action of concentration cells of differentiated oxygenation. Soils of different structure and moisture content occur along the pipeline route. Inflow of oxygen to the buried structure in sandy soils is much easier than in clayey soils. Thus, on the route of the pipeline macrocells can be formed resulting from changes in soil character. Oxygen content in soil also decreases with the depth of buried structures (Fig. 2a) or as a result of the presence of water (Fig. 2b). Hindered access of oxygen to the structure also occurs in places of intersection with terrain obstacles, e.g. roads or water-courses (Fig. 2c).

In each presented situation in places of hindered inflow of oxygen an anodic zone is formed and an increased corrosion hazard appears. Therefore, corrosion defects and leaks connected with them occur most frequently in lower parts of structures.

Hence, corrosion of steel structures can be a source of pollution. In many cases damage to structures occur due to corrosion cells formed as a result of incorrect design, careless execution, application of insufficient anticorrosion protection, improper operating conditions, increase of aggressiveness of the corrosion factor or other causes. Early detection of hazards and application of appropriate protection is the basic condition of elimination of pollution resulting from corrosion.

Cathodic Protection

Cathodic protection is a modern anticorrosion technology for structures in electrolytic corrosion environ-

ments. The scope of application is wide. The following can be protected by this technology: vessels, docks, berths, piers, gas pipelines, water pipelines, hot water pipelines, deep wells, metal tanks, elements of sewage treatment plants, heat exchangers and chemical apparatus. In recent years cathodic protection has been implemented for protection of steel in concrete, e.g. in underground and ground reinforced concrete structures, roadways and bridge supports [7].

Cathodic protection can guarantee failure-free operation of such objects as underground and underwater tanks and steel pipelines storing or transporting oil products and aggressive chemical media. This is significant due to the danger of pollution of the natural environment by such objects. In the USA and almost all European countries (including Poland) arterial oil and gas pipelines (even with very good insulation) have to be protected from corrosion by cathodic protection. Among others cathodic protection has been applied for protection of the transit Yamal-Europe gas pipeline together with the infrastructure of all compressors on the territory of Poland.

Principles of Cathodic Protection

Electrochemical cathodic protection is based on changing the structural potential in the direction of more electronegative values (cathodic polarisation) [8-11].
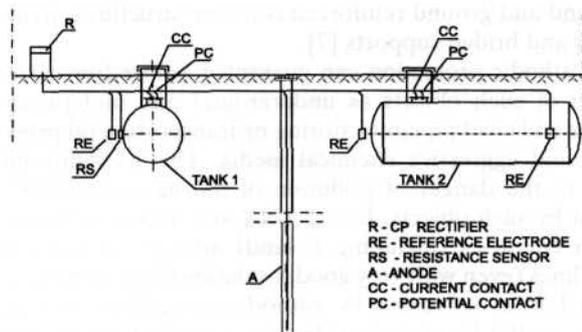
A change of potential of a buried metal structure can be obtained by a purposeful formation of a galvanic cell, i.e. linking to a so called galvanic anode made of a metal of a more electronegative potential than the potential of the protected structure (the so called sacrificial protection) or by applying an external DC power source and an auxiliary anode (impressed current protection). In both cases the anodic reaction is shifted from the protected metal structure to the sacrificial or auxiliary anode.

Application of galvanic anodes is the oldest and at the same time the simplest method of electrochemical protection. A sacrificial protection system is made up of the metal structure, a sacrificial anode placed in the same environment and electric cables linking the structure with the sacrificial anode. The current flowing through the environment from the sacrificial anode to the structure causes cathodic polarisation of the structure and its protection from corrosion. However, this process is accompanied by anodic dissolution of the sacrificial anode material and its irreversible loss. Sacrificial anodes are applied mainly in cases when only small currents are needed for ensuring protection (e.g. underwater and underground metal structures with a good insulation coating). Also, they are used for local protection of especially endangered structural fragments (amongst others in cases presented in Figs, lb and 2c) or supplementing cathodic protection with impressed current in zones of insufficient protection. Due to a low EMF and a small current efficiency of the cell made up of the given structure and the galvanic anode, the range of sacrificial protection is limited. This depends on the presence and state of insulation on the structure, the resistivity of the environment and the type of applied sacrificial material.

Cathodic protection with the use of an external power

source and auxiliary anodes is realised when a higher demand for polarisation currents is required. In Fig. 3 a schematic diagram is presented of a cathodic protection installation of buried petrol station fuel tanks [12].

Fig. 3. Schematic diagram of an impressed current cathodic pro-

tection installation.

A cathodic protection installation is made up of two electric circuits:
- a polarising (current) circuit, the main elements of which are: protected tanks, DC power source (cathodic protection station) and an auxiliary anode,
- a potential (control) circuit, containing a potential ter minal, a reference electrode and a potential meter (DC voltmeter) placed in the cathodic protection sta tion.

The protected tanks are connected to the negative end of the power source and the anodic system to the positive end in the polarising circuit. The control circuit is used to apply a potential to protected tanks vs. the reference electrode, controlling in this way the degree of polarisation of tanks and the effectiveness of protection.

A cathodic protection installation should ensure a possibly uniform distribution of the polarising current on protected surfaces. The realisation of this aim in practice is very difficult. The current and potential distribution on the structure surface depends on such factors as: polarisation ability of the structure, resistance of the corrosive environment, the presence of insulation and its resistance, dimensions, shape and location of the structure, its metallic connections to other objects, distance and placement of anodes, etc. The largest potential changes occur on structure surfaces nearest the anode [8-10].

Cathodic Protection Criteria

Potential protection criteria are most frequently used [13]. In the case of steel structures with good insulation, operated in natural corrosive environments, cathodic polarisation to a potential of -0.85 V (measured versus the $Cu/CuSO_4$ reference electrode placed in the direct neighbourhood of the protected structure) should ensure retardation of corrosion processes. For a structure with poor insulation or with no insulation a decrease of the structure potential by 0.3 V is recommended. In both

cases the potential measurement is performed at a flowing polarising current. Modified versions of the above criteria are more frequently used, taking into account potential measurements free of the IR voltage drop, connected with the resistance of the medium between the structure and reference electrode (the so called switch off potential). The Polish standard also permits partial polarisation to a potential of -0.75 V (with no IR component) in stray current interaction zones. This criterion can also be applied for protected structures in municipal and industrial agglomerations. In these operating conditions, for practical reasons a criterion is frequently used of a decrease of the structure potential by at least 0.1 V, the measurement being performed after switching off the polarising current (with no IR participation).

Irrespective of protection criteria used in practice, their application requires good experience in performing measurements and their interpretation.

Protection Effectiveness

The degree of retardation of corrosion processes on a steel structure depends on the magnitude of its cathodic polarisation. Any potential shift in the negative direction reduces the steel corrosion rate. In most cases full inhibition of corrosion, so-called full cathodic protection, is obtained for a potential change to -0.85 V. The potential of the protected structure in natural media should not be more negative than -1.1V. This will ensure a possibly uniform distribution of the polarising current and maintaining the desired potential. Buried pipelines are typical structures with a non-uniform distribution of polarising current. In Fig. 4a a schematic diagram is presented of a cathodic protection installation which started in 1990 for water and sewage collectors, made up of four steel pipelines, 1020 mm in diameter and 7400 m in length [11].

Bituminous insulation is the passive protection of the pipelines. A bad state of the insulation on a large area of the pipelines forced the application of a greater number of cathodic protection stations and higher current densities. Fig. 4b presents results of potential measurements of collectors before installing protection and after several years of operation. The switch off potential of protected collectors is in the -0.85 to -1.1 V range, pointing out correct operation of the installation and meeting of the potential protection criterion.

The potential measurement of the polarised structure is not the only technique which allows evaluation of the protection effectiveness. The resistive corrosimetry technique is used, amongst others, for the quantitative monitoring of protection effectiveness [14, 15]. In the installation presented in Fig. 3 tanks exhibit a switch off potential value in the -0.86 ÷ -0.95 V range, showing that the potential protection criteria are met. A resistance sensor mounted on one tank allows continuous monitoring of the tank corrosion rate and the quantitative evaluation of the protection effectiveness. In Fig. 5 results are presented of long-term resistance measurements of a protected tank. The dependence is given for comparison of corrosion losses of a steel pipeline buried in the same area out of reach of cathodic protection of the
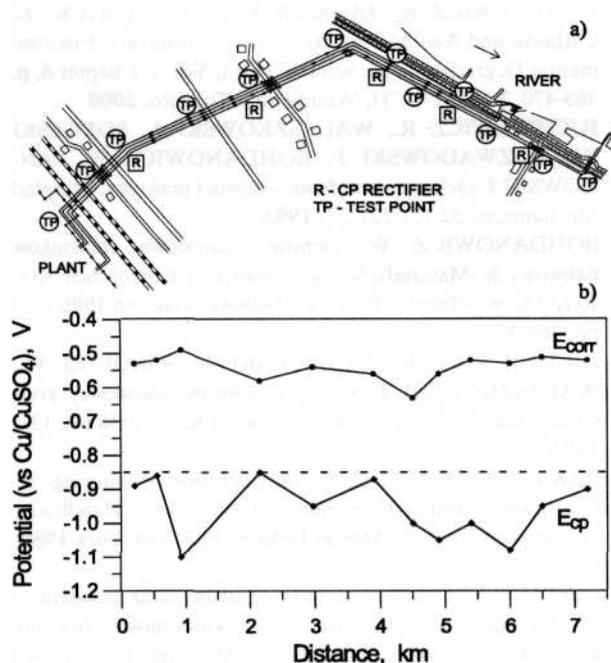
Fig. 4. Schematic diagram of a cathodic protection installation of water and sewage collectors: a - location of installation elements, b - potential distribution along the route of protected collectors.

tanks. The mean corrosion rate of the non-protected pipeline was approx. 55 µm/year, while that of cathodically protected tanks approx. 4 µm/year. The second value would have been even smaller, if there had not been an interruption in the power supply of the protection installation (repair of the electric substation). In comparison with the classic potential measurements the resistance corrosimetry technique allows to obtain significantly more accurate information on the anticorrosion protection degree of tanks.

In general, the effectiveness of cathodic protection depends on many factors, primarily on the choice of protection criteria, correct design, application of reliable elements, scrupulous execution of the whole installation and systematic supervision during operation.

An effective and economic anticorrosion protection of main objects, e.g. arterial pipelines, is obtained by simultaneous application of appropriately chosen insulation coatings and cathodic protection. Both types of protection supplement each other; the better the quality of insulation, the smaller essential outlays for operation of cathodic protection.

Introduction of a new generation of insulation coatings creates new conditions of application of cathodic protection. The role of cathodic protection is limited primarily to protection of the metal surface in places of damage of the insulating coating. Additionally, cathodic protection enables control of the process of aging of the insulation, as well as detection of each accidental or purposeful damage. At the same time, when a cathodic protection installation is correctly realised and monitored, the risk of occurrence of corrosion failures is significantly decreased.

Summary

Accelerated corrosion resulting from an increased aggressiveness of the environment is the cause of breakdown of many industrial objects (pipelines, tanks). Leaks of harmful media can be the cause of dangerous pollution of the environment.

Knowledge of corrosion processes, possibilities of formation of corrosion cells and activities preventing corrosion can facilitate observation of corrosion hazards to structures and connected negative effects for the environment. It can also help in the execution from users of ecologically dangerous objects of the realisation of modern, verified anticorrosion means.

An effective and economic anticorrosion protection of structures in soils and natural waters is ensured by cathodic protection. The effectiveness of this technology depends on: choice of criteria, its proper application, correct choice of elements, accurate execution, systematic supervision and professional maintenance. Correctly applied cathodic protection guarantees almost 100% hindering of corrosion processes, and what is equally important - it can be applied on existing, used installations and structures without any interruptions in operation and without full uncovering and cleaning of the surface.

Practical application of cathodic protection is, however, significantly more complex than would result from the principles of the presented technology. A non-uniform configuration of the protected surface (e.g. of metal underground installations in municipal areas), stray currents, untypical corrosion media and construction materials require a an individual design of a cathodic protection installation. Increasing requirements for protection of the natural environment demand a much wider application of cathodic protection, especially of underground and underwater pipelines, tanks and other metal structures for storage and transport of oil products and chemicals.
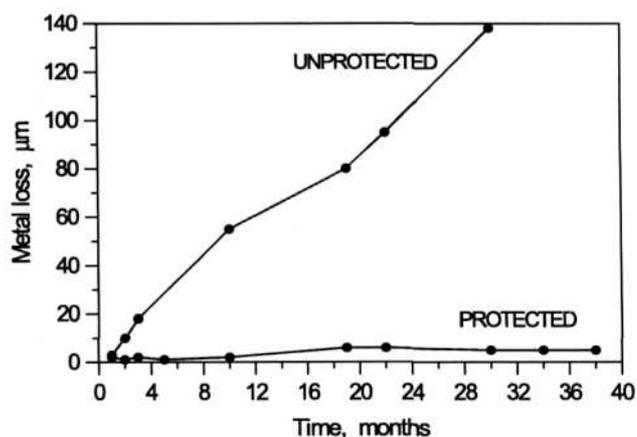

Fig. 5. Effect of cathodic protection on the corrosion of buried fuel tanks (Fig. 3).

Acknowledgement

References

1. JUCHNIEWICZ R. Gospodarcze i ekologiczne skutki korozji. Analiza przyczyn oraz zapobieganie, Przeglad Mechaniczny, 52 (21-22), 5, **1993.**

2. Federal Register, Vol. 53, No. 185. Underground Storage Tanks, EPA, Washington, **1988.**

3. MATTSON E. Basic Corrosion Technology for Scientists and Engineers, Ellis Horwood Ltd., John Wiley & Sons, New York - Toronto, **1989.**

4. FONTANA M.G. Corrosion Engineering, McGraw-Hill Book Company, New York, **1986.**

5. BRASUNAS A.deS. (Ed.): Corrosion Basics, NACE, Houston, **1984.**

6. SHREIR L.L., JARMAN R.A, BURSTEIN G.T. (Eds.). Corrosion, Vol. 1 Metal - Environment Reactions, Butterworth - Heinemann Ltd., Oxford - London, **1994.**

7. SHREIR L.L., JARMAN R.A., BURSTEIN G.T. (Eds.). Corrosion, Vol. 2 - Corrosion Control, Butterworth - Heinemann Ltd., Oxford - London, **1994.**

8. BAECKMANN W.von, SCHWENK W, PRINZ W. (Eds.). Handbook of Cathodic Corrosion Protection. Theory and Practice of Electrochemical Protection Processes, Third Edition, Gulf Publishing Company, Houston, **1997.**

9. MORGAN J. Cathodic Protection, Second Edition, NACE, Houston, 1987.

10. JUCHNIEWICZ R., JANKOWSKI J., DAROWICKI K. Cathodic and Anodic Protection, in: Corrosion and Environmental Degradation, M. Schiitze (Ed.), Vol. 1, Chapter 8, p. 383-470, WILEY-VCH, Weinheim - Toronto, **2000.**

11. JUCHNIEWICZ R., WALASZKOWSKI J, SOK6LSKI W., ROZWADOWSKI J., BOHDANOWICZ W., JANKOWSKI J. Ochrona katodowa - teoria i praktyka, Przeglad Mechaniczny 52 (21-22), 21, **1993.**

12. BOHDANOWICZ W. Ochrona katodowa zbiornikow paliwowych, Materialy V Ogolnopolskiej Konferencji KOROZJA '96 -Teoria i Praktyka, Gdansk, wrzesien **1996,** t. 2, pp. 369-372.

13. JUCHNIEWICZ R., JANKOWSKI J., SOKOLSKI W., WALASZKOWSKI J. Kryteria ochrony katodowej konstrukcji stalowych, Cz. 1, Ochrona przed Korozja **36** (6), 121, **1993.**

14. RAK G.F., SCHWEITZER P.A. Corrosion Monitoring, in: Corrosion and Corrosion Protection Handbook, P.A.Schweitzer (Ed.), Marcel Dekker, Inc., New York **1989,** p. 547-553.

15. JANKOWSKI J., SZUKALSKI J. Zastosowanie korozymetrii rezystancyjnej do pomiarow skutecznosci ochrony katodowej konstrukcji podziemnych, Materialy IV Krajowej Konferencji "Pomiary korozyjne w ochronie elektrochemicznej", Jurata, **1996,** pp. 51-58.