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# APPLICATION OF PERCOLATION THEORY FOR DESCRIPTION OF ELECTRICAL PROPERTIES OF CONDUCTING COATINGS

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**Summary**: In this paper electrical and electrochemical measurements of the organic coatings conducting electric current and able to work as anodes in cathodic protection of reinforced concrete have been presented. Evaluation of coating resistance as a function of graphite content was performed with the use of impedance measurements. On this basis a threshold of percolation of epoxide coating modified with electrographite was assessed. A current loading of conductive coatings was evaluated by potentiodynamic measurements. Basing on the performed measurements it has been stated that the minimum graphite content in the coating cannot be lower than 35%.

***Key words*** *Percolation theory, conductive coating, impedance, cathodic protection, reinforced concrete.*

## INTRODUCTION

Cathodic protection of reinforced concrete based constructions is realized in various ways. Its quite popular form is protector protection. In this case an anode is a thin layer of metal (most often zinc) applied on concrete surface by metal spraying [1]. The other method is application of the cathodic protection with an external source of current. In this case the anode must be a hardly soluble material and has to be connected to the external source of current [2]. Many construction solutions of anodic systems are known. The most widespread form is application of the anodes on concrete surface, inside thin surface layer of concrete jacket [3]. In this type of solution the anodes are made of titanium or titanium covered with active oxides and platinum. Due to very good electrochemical properties of the applied material imposed polarization current densities can be very high even up to 1000 $A/m^2$ [4]. The cost of installation of such solution is relatively high. Another form of reinforced concrete protection is application of conducting coatings. In this case protection against corrosion is realized in two ways. On one hand coating layer constitutes a barrier protecting concrete surface from surrounding electrolytic environment. The second form of anticorrosion protection is cathodic protection, in which an anode is electricity conducting, organic coating. Electrical conductivity of the organic coating is provided by the active pigments, which conduct electric current. Physical properties of this type of coatings must differ from classical protective coatings because of severe exploitation conditions connected with the influence of variable pH of the environment, concrete structure and external atmosphere. Also electrochemical processes occurring as a result of the cathodic protection impose a significant impact on chemical conditions. In such situation epoxide, polyurethane or siloxirane binders can be applied as they exhibit high resistance to aggressive chemical environment [5].

In order to provide effective cathodic protection a coating must be characterized by high electrical conductivity, which depends on electrical properties and the content of conducting pigments in the coating structure. The phenomena of electric current conductivity by composite materials, just as organic coatings, are described by so-called percolation theory [6]. This theory describes the phenomenon of current conduction in composite materials. It allows evaluating the magnitude of conductivity in relation to the content of conductive component, related to the mass of the entire composite. The factors influencing conductivity are size of conducting and non-conducting molecules in the composite, their conductivity and spatial organisation of the material [7]. The structure of electric current conducting composite can be compared to a certain spatial grid, inside which conducting and non-conducting points can be found. Fig.1 presents an example of spatial grid of the composite.

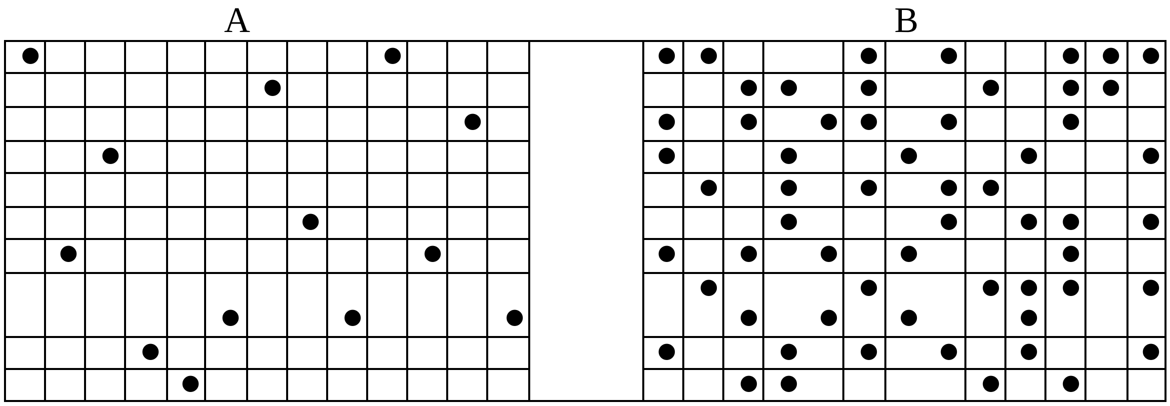


**Fig.1.** Spatial grid of the composite containing electric current conducting component [ ● ].
A - for low contents of conducting component
B - for contents of conducting component exceeding the threshold of percolation

In case when the content of conducting component inside the composite is relatively low the conducting points in grid structure (fig. 1a) are not connected with each other and due to that conductivity of such material is very low. The filling of the grid with molecules of conducting component increases, as its content in the composite increases. For higher contents conducting molecules join into groups till for a certain critical value (so-called threshold of percolation) the conducting grid combines into one big, irregular unity (fig. 1b) [7]. In such conditions conductivity of composite material rapidly rises. Further increase in the content of conducting component results only in thickening of the cluster, without significant improvement in conductivity of composite. In case of conducting coatings it is important to maintain the content of conducting component above the threshold of percolation. Assessment of this value is possible basing on a series of electrical measurements for different compositions of composite material [7].

Investigation of elastic composit e anodes based on EPDM or polyethylene binder revealed that during their operation in cathodic protection system electrical properties of anodic material considerably deteriorate. Due to electrochemical reactions taking place during long lasting polarization a process of consumption of conductive component occurs [8]. It was found that the resistance of anode surface layer significantly increases; in order to fight it an application of significantly higher than the threshold of percolation content of conductive components to the structure of the composite is indispensable [8]. In such cases the time of non-damage anode operation can be considerably elongated. Conductive coatings due to their structure resemble elastic composite materials. That is why when planning the content of conducting component earlier experiences should be taken into account [9].

## EXPERIMENTAL

Samples of the coating subjected to the examination were manufactured on the basis of epoxide resin of middle molecular mass and with addition of graphite from 25% to 50% by weight. The coating was applied with the use of brush in form of four layers of total thickness equal to 300 μm. The ST3 steel substrate was prepared by sandblasting. Application of the coating, the intervals between deposition of succeeding layers were carried out according to the accepted schedule. Measurements were conducted for five samples, for each content of graphite.

The measurements of coatings resistance were carried out using impedance measurement method in two-electrode system employing mercury electrode. The measurement set-up consisted of a frequency response analyzer SCHLUMBERGER SI 1255 with high impedance countershaft ATLAS 9181. Evaluation of electrochemical properties was performed by potentiodynamic measurements with the use of Gamry Instruments CMS105 set-up in three-electrode system. Silver/ silver chloride electrode was used as a reference electrode, an auxiliary electrode was platinum mesh and investigated conducting coating served as a working electrode. The measurements were conducted in 1% NaCl electrolytic environment.

## RESULTS

Impedance measurements in two-electrode system were conducted in order to observe the influence of graphite content on coating resistance. Application of mercury electrode facilitates direct contact between the electrode and coating surface. Impedance measurement allows registration of coating resistance deposited on the metal surface. Fig. 2 presents an exemplary impedance spectrum of the conducting coating containing 45% of graphite determined in two-electrode system.

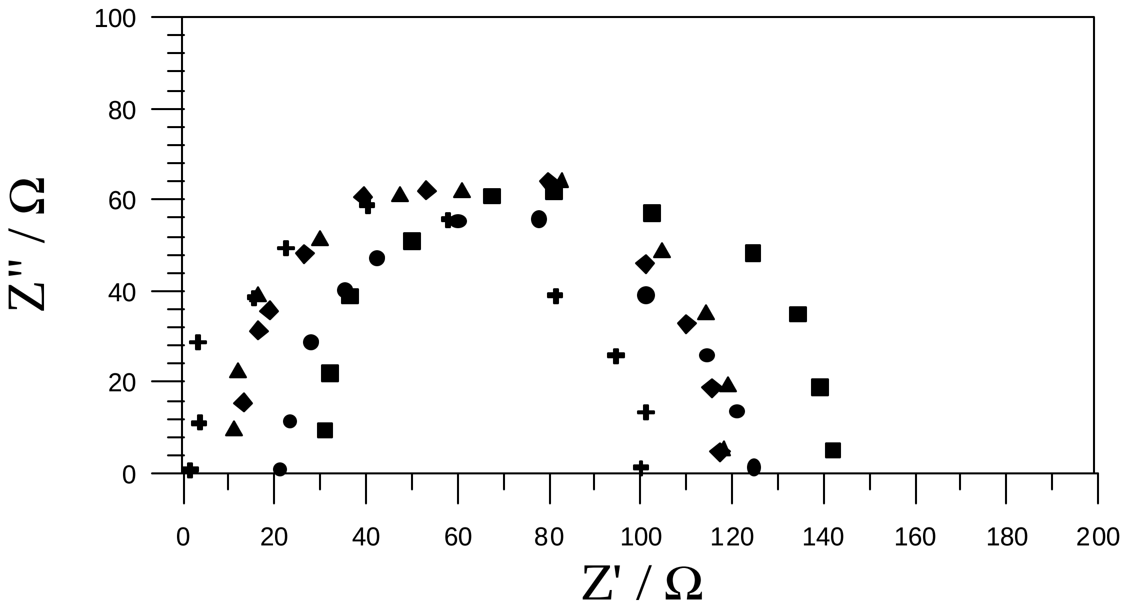


**Fig. 2.** Impedance spectrum of the conducting coating containing 45% of graphite determined in two-electrode system.

Obtained impedance spectra exhibit dispersion of the results. Averaged results were subjected to further analysis. Determined impedance spectra are characterized by existence of one time constant. The magnitude of the chord of the semicircle on real part axis corresponds to coating resistance. The values of resistance obtained in such way are lower by several orders of magnitude than the resistance of the coating without conducting components. Obtained spectra were analyzed employing Boukamp software [10]. In order to evaluate the threshold of percolation, that is to assess the content of conducting component in the coating, above which a significant increase in conductivity appears, a relation between coating resistance and graphite content was determined. The relation is presented on fig. 3.

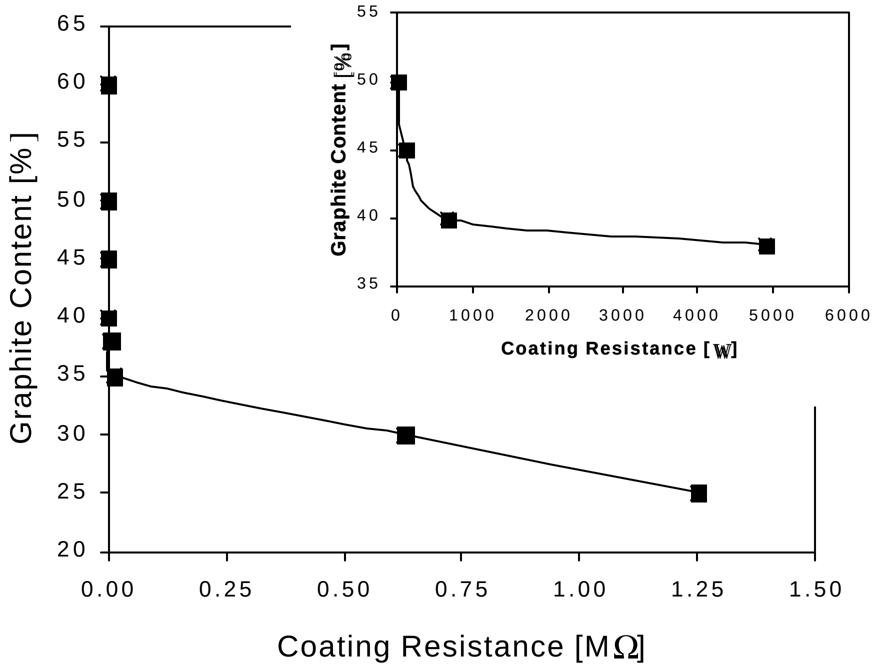


**Fig.3.** Coating resistance as a function of graphite content in the coating

Data presented on fig.3 show that the threshold of percolation for conducting epoxide coating modified with graphite equals to about 35%.

Presented graph of coating resistance is in accordance with the percolation theory given by Navarro-Laboulais and others [6]. According to the percolation theory creation of the conducting paths resulting from direct contact between graphite molecules in a non-conductive binder leads to a significant drop of composite resistance. This phenomenon is evident when graphite content exceeds 35%. In turn at higher graphite content (over 45%) additional content of conductive component does not significantly influence on a drop of composite resistance [6]. Basing on performed measurements it can be stated that satisfactory resistance values are characteristic for the coatings containing over 38% of graphite. For resistance higher than $10^4$ Ω a decrease in protective current of cathodic protection would be too significant [9]. In this case one should remember about the economic factor connected with higher power consumption of cathodic protection station and with faster wearing of coating anodic material. The measurements on conducting composites based on ethylene-propylene terpolymer indicated that the samples characterized by higher resistance exhibited low durability as anodes in cathodic protection [8].

The other parameter characterizing electrochemical properties of an anode is its current loading. Evaluation of the current loading can be done on the basis of potentiodynamic measurements. On fig. 4 there are presented characteristics of current in function of polarization potential for the coatings with different graphite content.

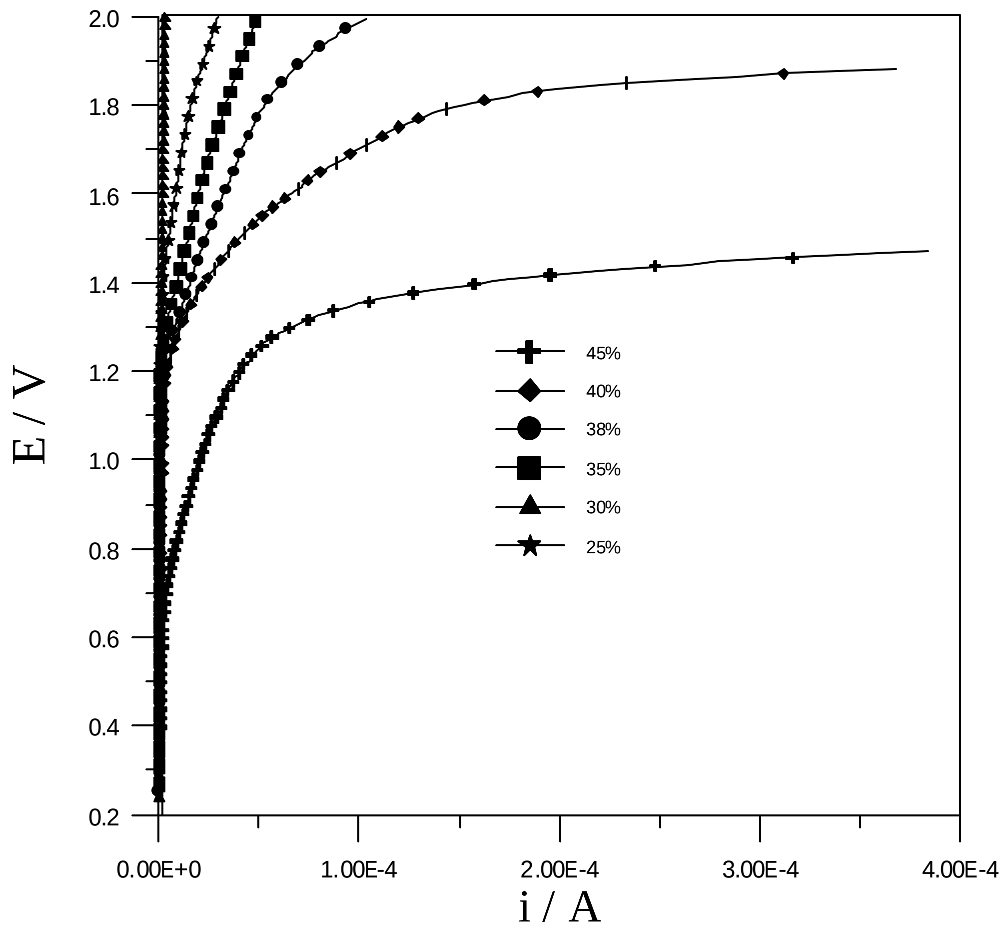


**Fig.4.** Current as a function of polarization potential for the coatings of different graphite content

With rising current loading of anode the effectiveness of cathodic protection increases, this parameter is the main indicator describing electrochemical properties of anodic material. If the current loading of two anodes is analyzed and if for a given current density lower polarization potential of one anode in respect to the second one is observed then the current loading of the first anode is higher [11]. Table 1 presents the values of potentials for a current density of 20 $mA/m^2$.

**Table 1.** Values of potentials of conducting electrodes determined for a current density of 20 $mA/m^2$

| graphite content [%] | potential against Ag/AgCl [V] |
|---|---|
| 25% | > 2 |
| 30% | 1,50 |
| 35% | 1,33 |
| 38% | 1,27 |
| 40% | 1,22 |
| 45% | 0,73 |

Results presented in table 1 point out that the higher graphite content in the coating the higher current loading is.

Electrical and electrochemical measurements show that coating properties improve with an increase in graphite content. Analysing the results obtained on the basis of the measurements one must remember that obtained parameters are characteristic for perfect, intact coatings. During exploitation one may expect deterioration of electrical and electrochemical parameters and this effect should be taken into account while planning coating composition.

## CONCLUSIONS

Results of the investigation of the coating able to work as an anode in cathodic protection of reinforced concrete have been presented. This non-conventional way of protection requires application of electroconducting coatings with special electrical and electrochemical parameters. On the basis of electrical and electrochemical investigations of conductive coatings the following conclusions can be stated:

Electrical and electrochemical properties of conductive coatings depend on graphite content and the type of carbon material. Very high resistances characterize coatings containing less than 35% of graphite due to the fact that the threshold of percolation hasn't been reached. The current loadings of such coatings are not satisfactory. In order to achieve desired current parameters of cathodic protection very high polarization voltage should be applied. Coatings containing higher contents of graphite (over 40%) are characterized by low resistances, high current loadings. However, application of too high graphite content in organic coating may cause negative effects connected with so-called overpigmentation of the coating. Coatings with too high pigment content exhibit poor mechanical properties what reflects in fast loss of barrier properties of the coating.

Obtained results justify the supposition that conducting coatings can act as anodes in cathodic protection of reinforced concrete. Measurements enabling evaluation of mechanical, electrical and electrochemical properties of the coatings are necessary while realization of cathodic protection of steel reinforcement of concrete. These types of measurements allow to assess coating parameters evolution in time and to evaluate cathodic protection effectiveness.

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