Impedance Measurements Of Coating Properties On Bridge Structures

Jacek Bordziłowski, Kazimierz Darowicki, Stefan Krakowiak, Agnieszka Królikowska*)
Department of Anticorrosion Technology
Technical University of Gdansk
*)Road and Bridges Research Institute
Warsaw

Key words: electrochemical impedance spectroscopy, organic coatings, steel bridges.

Abstract.
Impedance measurements allow early evaluation of the protective properties of paint coatings and linings. They are applied for comparison of coatings, monitoring of their properties and determination of the protection mechanism. This methodology is being used more and more frequently in laboratory investigations. On site studies are more difficult due to the need of using complex computer controlled apparatus and its susceptibility to atmospheric conditions, electric fields and mechanical damage. In this lecture a proposal has been made of application of the impedance methodology of paint coating evaluation in „in situ" conditions on bridges. Good correlation has been stated with results obtained in the laboratory, allowing application of this methodology for non-destructive evaluation of the properties of thick coatings and organic linings on industrial structures.

1. Introduction

The impedance technique is becoming more and more important in the evaluation of properties of metals and coatings on a metal base [1-25]. In the initial period of application of the impedance method it found application in investigations of the corrosion rate of different metals and thin porous coatings and was used mainly in basic research [1-8]. In 1989, basing on these investigations, the ASTM G 106-89 standard was issued in USA[9], which determined the methodology of impedance measurements in laboratory conditions. This standard determined the procedure for investigation of metals in 0,005 M sulphuric acid and 0,495 M aqueous sodium sulphate solution to verify the apparatus and algorithm of impedance measurements. Investigations were performed in a 3 electrode system at the stationary potential or one provided by a potentiostat.

In later years the impedance methodology began to find wider application in investigations of organic coatings and in this way in 1984 a conference "Application of Electrochemical Techniques to Organic Coatings" was organised in Genua by Prof. P.L. Bonora, attended by such known scientists as: Funke, Deloui, Scantlebury and Drazic. Initially, thin coatings were investigated, and next, with improvement of measurement apparatus and computer techniques, investigations were initiated of coatings up to 1 mm in thickness, and lately of linings up to 10 mm [10-25].

The first results of „in situ" measurements performed in a scrubber of a flue gas desulphurisation plant (IOS) were presented at a conference in Poraj in November 2000 [26,27]. The aim of this presentation is the summary of results obtained on bridge structures.

2. Research methods

Impedance on site investigations of coating systems require specially prepared apparatus. The main assumptions of the apparatus system are:

- High internal impedance of the measurement system
- Measurements in a two electrode system
- Measurement frequency range: at least 10^{5}-10^{-1}Hz
- Adjusted amplitude of the measurement signal in the range to min. 500 mV
- Own power supply
- Measurement in lock-out conditions of electrode polarisation
- Appropriate measurement cells
- Appropriate system of measurement cell mounting to the surface.

As the result of performed trials measurement apparatus was set up made up of:

- A Sycopel spectrostat modified by cutting off the potentiostat and attaching a high-impedance interface enabling investigations of thick coatings in the 10^{4}-10^{-0}Hz range
- A portable PC notebook computer
- Screened cables with capacitor lock-out of electrodes
- Measurement cells of area 78.5 cm^2
- A battery power supply with converter, ensuring an independent source of AC current.

Laboratory tests were performed with modernised Polish **ATLAS** apparatus**,** made up of a 9121 Analyser and a 9181 Impedance Interface and a PC computer. Software was delivered by Soft - Kar from Elbląg, Poland.

Measurements were performed in a two electrode system in which a platinised titanium mesh was the auxiliary electrode and the investigated sample the working electrode. Measurement was performed one hour after immersion in a 3% NaCl aqueous solution. Measurements were performed by perturbation of the system with a sinusoid signal in the 100 kHz - 0.01 Hz frequency range at an amplitude of 100 mV.

Numerous trials allowed determination of optimum measurement amplitudes in the 100 - 400 mV limits, depending on the type and thickness of investigated linings. Three measurement cells were investigated at each location.

Measurement results were obtained on the basis of analysis of impedance spectra by the Boukamp programme.

3. Scope and results of investigations

The scope of performed investigations was as follows:

- Investigations on bridge structures
- Control measurements in the laboratory

In this presentation results have been presented of coatings on two bridges over the Vistula river (bridge in Fordon and bridge in Swiecie) in comparison with results obtained in laboratory conditions for an analogous coating system. Results of investigations have been presented in Figs. 1-3 and Table 1.

4. Experimental

4.1. Materials and conditions

The investigated coating system was consisted of:

- 2 coats of epoxy primer
- 1 coat of polyurethane finish

On bridges the measurements were performed on reference painting areas, where supervision of coating application was best. Depending on the structure of the bridge measurement cells were placed on the following elements of bridge structures:

- Vertical surfaces of bridge girders (Fordon and Swiecie)
- Horizontal surfaces of bridge girders (Fordon)

The total thickness of the system was:

Fordon Bridge (2 years after renovation):

- Vertical surface: 255-352 μm (average 286 μm)
- Horizontal surface: 259-450 μm (average 309 μm)

Swiecie Bridge (3 years after renovation):

- Vertical surface: 286-334 μm (average 312 μm)

There were carried out three measurements in each position.

In laboratory the measurements were performed on sandblasted steel plates covered with the coating system in laboratory conditions by airless spray. The total thickness of the system was 226- 264 μm (average 248 μm).

The temperature conditions during measurements were as follows:

- Fordon Bridge: 18-20 ^{o}C
- Swiecie Bridge: 16-17 ^{o}C
- Laboratory: 21 ^{o}C.

4.2 Results

Fordon Bridge

Measurements were performed in the region of the reference area . Results have been presented in Fig. 1 and Fig. 2.

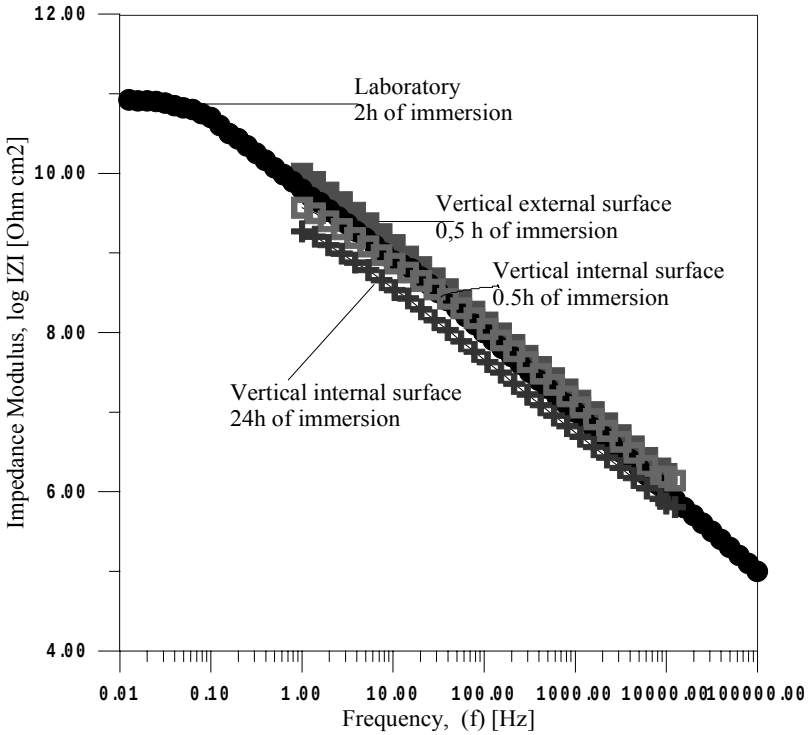

Fig. 1. Impedance spectra of coatings investigated on vertical surfaces of the bridge in Fordon 0,5 h after immersing the cell and 24 h after immersing the cell, in comparison with the spectrum obtained during laboratory investigations 2 h after immersing the cell.

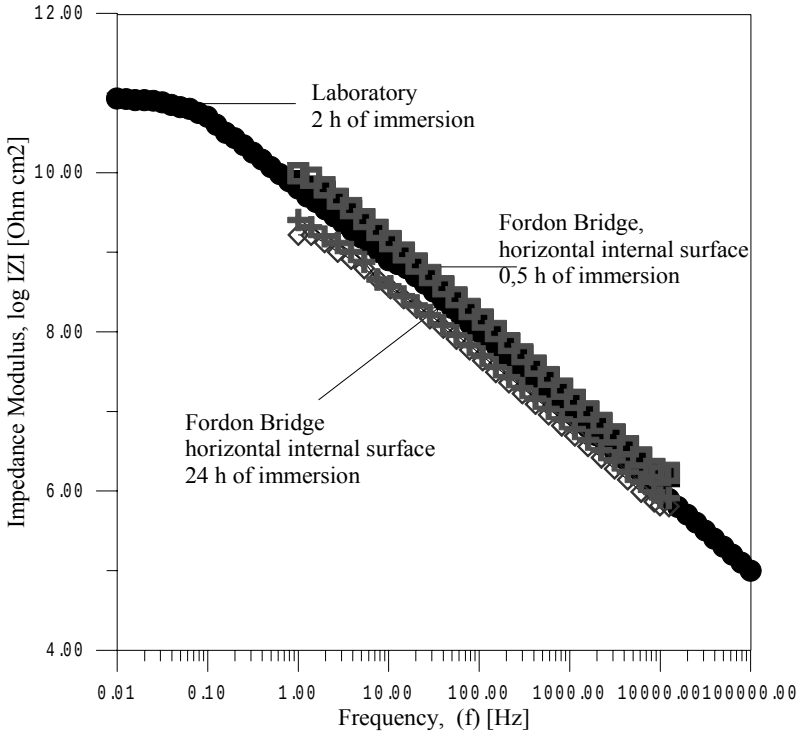

Fig. 2. Impedance spectra of coatings investigated on horizontal surface of the bridge in Fordon 0,5 h after immersing the cell and 24 h after immersing the cell, in comparison with the spectrum obtained during laboratory investigations 2 h after immersing the cell.

Świecie Bridge

Measurements were performed in the region of the reference area between supports. Results have been presented in Fig. 3.

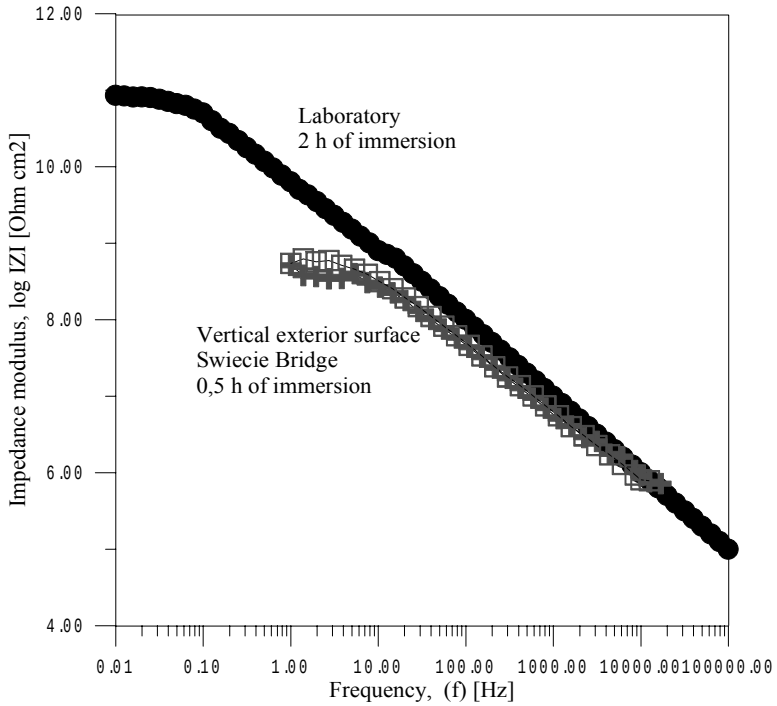

Fig. 3. Impedance spectra of coatings investigated on vertical surface on the bridge in Swiecie on the reference area of the girder 0,5 h after immersion of the cell in comparison with the spectrum obtained in laboratory investigations 2 h after immersion of the cell.

Discussion of results

Results have been presented in Figs. 1-3. The numerical data have been gathered in Table 1.

Table 1. Electric parameters of coatings obtained from impedance measurements for bridges in Fordon and Swiecie.

Measurement position	Impedance modulus Log IZI_{1Hz}, [Ωcm^2]	Coating resistance Rc, [Ωcm^2]	Coating capacitance Cc, [F/cm^2]	Coefficient „n”
Fordon external vertical surface, 0.5 h	9.86 - 9.99	1.32 - 4.26 x 10^{10}	1.62 – 2.18 x 10^{-11}	0.97 - 0.98
Fordon internal vertical surface, 0.5 h	9.32 - 9.56	2,89 - 4.40 x 10^{9}	2.20 – 3.49 x 10^{-11}	0.91 - 0.94
Fordon internal vertical surface, 24 h	8.73 - 9.27	3.11 - 5.42 x 10^{9}	2.95 – 3.23 x 10^{-11}	0.90 - 0.92
Fordon internal horizontal surface, 0.5 h	9.54 – 9.97	1.16 - 14.3 x 10^{9}	1.16 - 1.55 x 10^{-11}	0.97 - 0.98
Fordon internal horizontal surface, 24 h	8.13 – 9.21	1.09 - 4.23 x 10^{9}	4.85 - 6.11 x 10^{-11}	0.90 - 0.92
Swiecie vertical surface, 0.5 h	8.71 - 8.73	3.90 - 6.59 x 10^{8}	4.85 - 5.31 x 10^{-11}	0.92 - 0.93

Analysis of curves presented in Fig. 1 for coatings on vertical surfaces indicates a maintained barrier character of the evaluated coating system on the bridge in Fordon (2 years after renovation) on external surfaces (logarithm of the impedance modulus for 1 Hz approx. 10 Ωcm^2). The coating system is tight, indicated by the capacitive character of graphs inclined at an angle of 45^o in relation to the abscissa axis.

On internal surfaces of the bridge, where more moist conditions are found, a slight bend of the curve was stated already 0.5 h after immersing the cells, at frequencies of approx. 20 Hz, indicating a frequency-resistive character of the dependency, pointing to water reaching the metal base. In this case a decrease has been stated of the logarithm value of the impedance modulus to approx. 9.5 Ωcm^2. In the case of measurements performed 24 h after immersing the coating a distinct decrease of the curves has been stated without change of its shape, pointing to penetration of water into the coating and a change of the associated dielectric constant of the external coating layer. This points to insufficient resistance of the coating to action of water, especially in conditions of continuous presence of moisture.

In the case of the bridge in Swiecie after three years of exploitation (Fig. 3) on vertical, less moist surfaces a capacitive-resistive character of curves was stated already 0,5 h after immersing the cells and the presence of the so called „resistive paths" in the coating, enabling access of water to the metal surface and development of electrode processes on the metal-coating phase interface. A relatively high value of the logarithm of the impedance modulus (approx. 8.7 Ωcm^2) indicates maintaining of high protective properties in these regions.

Analysis of the curves presented in Fig. 2 concerning coatings on horizontal surfaces (0.5 h after immersing the cell) indicates a maintained barrier character of the evaluated coating system in the case of coatings on the bridge in Fordon (2 years of exploitation). In this case the logarithm of the impedance modulus at 1 Hz was equal to approx. 10 Ωcm^2 . Measurements performed 24 h after immersing the cells point to penetration of water inside the coatings, this being indicated by a small change of the angle of inclination of the curve, showing presence of the resistive component and a decrease of the curve indicating a change of the dielectric constant of the external part of the coating.

Results of calculations of electric parameters obtained through correlation analysis of the equivalent electric circuit confirm conclusions from the graphical analysis of impedance spectra. Coatings inside the bridge in Fordon are characterised by a lower resistance, higher capacitance and lower coefficient „n" in comparison with coatings on external surfaces. 24 h after immersing the cells electric parameters of coatings change (the resistance decreased, the capacitance increased and the coefficient „n" decreased), indicating penetration of water inside the coatings. However, the obtained parameters generally point to maintaining of good protective properties of coatings in both locations.

4. Summary

Investigations have shown that the epoxy-polyurethane coating system on the steel structure of two bridges after a 2 and 3 year exploitation period is still characterised by high protective properties in regions of lower moisture presence.

The tested coatings, in spite of high initial barrier properties, show susceptibility to penetration by water. Lower barrier properties in shaded places point to this and on horizontal surfaces under the platform plate, which are frequently moist, as well as a distinct decrease of barrier properties during 24 h of coating exposure under affixed measurement cells.

Results of „on site" measurements of the coatings were similar to those obtained in laboratory conditions.

5. Conclusions

5.1 A possibility has been stated of obtaining repeatable results in the case of impedance investigations of paint coating systems on large bridges. Obtained results correlate well with results obtained for a/m coatings and linings in laboratory conditions.

5.2. Performed measurements allow determination of regions of an especially high corrosion hazard on large structures and comparison of protective properties of different paint systems in real exploitation conditions.

5.3. Systematic impedance evaluation of coatings and linings can allow monitoring of their properties and prognosis of their durability in natural conditions.

5.4. Impedance investigations also can become the criterion in quality control of execution of anticorrosion works with the use of paint coatings, allowing significantly earlier determination of their quality in relation to visual symptoms of damage to protective systems.

References

1. A. Mansfeld, Corrosion, 29, 1973, 397.
2. C. Gabrielli, Identification of Electrochemical Process by Frequency Response Analysis, Solartron Instrumentation Group, 1980.
3. I. Epelboin, M. Keddam, H. Takenouti, Journal of Applied Electrochemistry, 2, 1972, 71.
4. W. J. Lorenz, F. Mansfeld, Corrosion Science, 21, 1981, s. 647.
5. D.D. Macdonald, Journal of the Electrochemical Society, 125, 1978, 2062.
6. M. W. Kending, E. M. Meyer, G. Lindberg, F. Mansfeld, Corrosion Science, 23, 1983, 1007.
7. J. O. Bockris, A. K. N. Reddy, Modern Electrochemistry, Plenum Press, New York, 1970.
8. F. Mansfeld, Evaluation of Corrosion protection Methods with Electrochemical Impedance Spectroscopy, Corrosion'87, paper 481, San francisco, March 1987.
9. R. D. Armstrong, M. F. Bell. A. A. Metcalfe, The AC Impedance of Complex Electrochemical Reactions, Electrochemistry, 6, 1976, 98.
10. ASTM Designation: G 106-89 (Reapproved 1994). Standard Practise for Verification of Algoritm and Equipment for Electrochemical Impedance Measurements.
11. Mansfeld F., Kendig M.W., Tsai S.: Corrosion 38, 1982, 478.
12. Jùtner i in.: Werkstoffe und Korrosion 36, 1985, 120.
13. Walter G.W.: Corr. Sci. 26, No 9, 1986, 681.
14. Titz J. i in.: Corrosion 46, No 3, 1990, 221.
15. Kendig M.W.: Corrosion 46, No 1, 1990, 22.
16. Bordziłowski J., Miszczyk A.: Ochrona p. Korozją 36, nr 2, 1993, 34.
17. Mansfeld F., Kendig M.W.: Corrosion 41, 1985, 490.
18. Feliu S., Galvan J.C., Morcillo M.: Prog. in Org. Coat. 17, 1989, 143.
19. Miszczyk A., Bordziłowski J.: Farbe und Lack 95, No 8, 1989, 564.
20. Miszczyk A., Bordziłowski J.: Farbe und Lack 96, No 11, 1990, 860.
21. Hack H.P., Scully J.R.: J. Elektrochem. Soc. 138, No 1, 1991.
22. Kendig M., Scully J.: Corrosion 46, No 1,1990, 22.
23. Murray J.N., Hack H.P.: Corrosion 48, No 8, 1992, 671.
24. Bordziłowski J., Miszczyk A.: Corrosion-mechanical investigation of organic coatings, Proceedings of XX Conference "Science and Practical Against Corrosion", Kule, 27-29.10.1993, p. 89.
25. Bordziłowski J., Miszczyk A., Klenowicz Z.: Evaluation of thick organic coatings used for tank conservation, Proceedings of the Colloquium "Technical Inspection and Storage Tanks Repairs" Gdańsk, 14-16. 04. 1994, p.185.

26. Bordziłowski J, Darowicki K., Krakowiak S., Królikowska A., Impedance measurements "on site", Proceedings of VII Polish Symposium, ”The New Achievements i Corrosion Investigations” Poraj 15-17. 11.2000, p. 317.
27. Krakowiak S., Darowicki K., Bordziłowski J., EIS Investigations for evaluations of rubber linings "on site" Proceedings of VII Polish Symposium, ”The New Achievements i Corrosion Investigations ” Poraj 15-17. 11.2000, p. 348.