Monitoring of the atmospheric corrosivity by resistive sensors

Kreislova K., Vlachova M.
SVUOM, Prague, Czech Republic
E-mail: kreislova@svuom.cz

Atmospheric corrosivity is classified according to EN ISO 9223 Corrosion of metals and alloys – Corrosivity of atmospheres – Classification, determination and estimation. For the determination and estimation of the corrosivity category, standardized approaches are used. Monitoring of corrosivity with the application of various sensors is an actual trend. The paper gives results of verification of some types of sensors for this monitoring with standardized flat samples at atmospheric test sites in the Czech Republic. The trend of decreasing atmospheric corrosivity is evident in the last decade. Monitoring of the corrosion rate and mapping of the corrosivity become a very important step in preventing failures in long-term atmospheric exposition. This type of monitoring was used on bridge construction to estimate the seasonal effect of de-icing salts deposition, too.

INTRODUCTION

Quantitative evaluation of the corrosivity of atmospheric environments is an extremely important issue for life estimation and maintenance control of structures [1–3]. Temperature, humidity, rainfall, airborne salt particles, corrosive gases, etc. may be mentioned as factors in the atmospheric environment which influence the corrosion of metals. The category of atmospheric corrosivity is crucial information for the choice of materials/protective coatings for structures. As long durability is suspected for these structures the monitoring of atmospheric corrosivity is important. Metallic materials react practically immediately onto changes of atmospheric corrosivity as well as increasing or decreasing.

An alternative approach is to use some type of sensors. Similarly, to the metal coupons, various types of sensors are used which provides continuous measurement of the corrosion rate of specific metal [4]. As the study of using the electrochemical methods for determination of atmospheric corrosivity and long-term corrosion had been performed since 70ties of the last century, these techniques are still limited for special application. A key question in the use of the electrochemical technique is a relation between the measured electric parameter (resistance) and corrosion rate, respectively mass loss of metallic coupons/standard specimens. In last time there is an effort to implement some type of sensors into technical standard as a common procedure for atmospheric corrosivity determination and monitoring. The new standard ISO 22858 *Corrosion of metals and alloys – Electrochemical measurements – Test method for monitoring atmospheric corrosion* for this measurement was published in 2020. This document specifies a test method for atmospheric corrosion measurements, using two-electrode electrochemical sensors. It is applicable to measurements of the corrosion rate of uncoupled metal surfaces (i.e. “free” corrosion rate), galvanic corrosion rate, the conductance of thin film solutions and barrier properties of organic coatings. It specifies electrochemical sensors that are used with or without organic coatings. The sensors are applicable to corrosion measurements made in laboratory test chambers, outdoor exposure sites and service environments. But there is missing verification of these measurements with standard EN ISO 9223 procedures.

There are available a lot of commercial devices for such purposes. A comparison of corrosion rates determined by weight loss and electrochemical techniques under thin layers of electrolytes indicates that the electrochemical data underestimate the true corrosion rates [7]. Electrochemical measurements carried out under identical conditions show the continuous increase of corrosion rates during the drying period.

In this paper, the comparison of corrosion loss of standard specimens and some types of sensors in the Czech Republic is given because published data are usually from atmospheres with very high corrosivity. Nowadays the atmospheric corrosivity in the Czech Republic is relatively low and the response of sensors is following these changes.

EXPERIMENTAL

Metal coupons

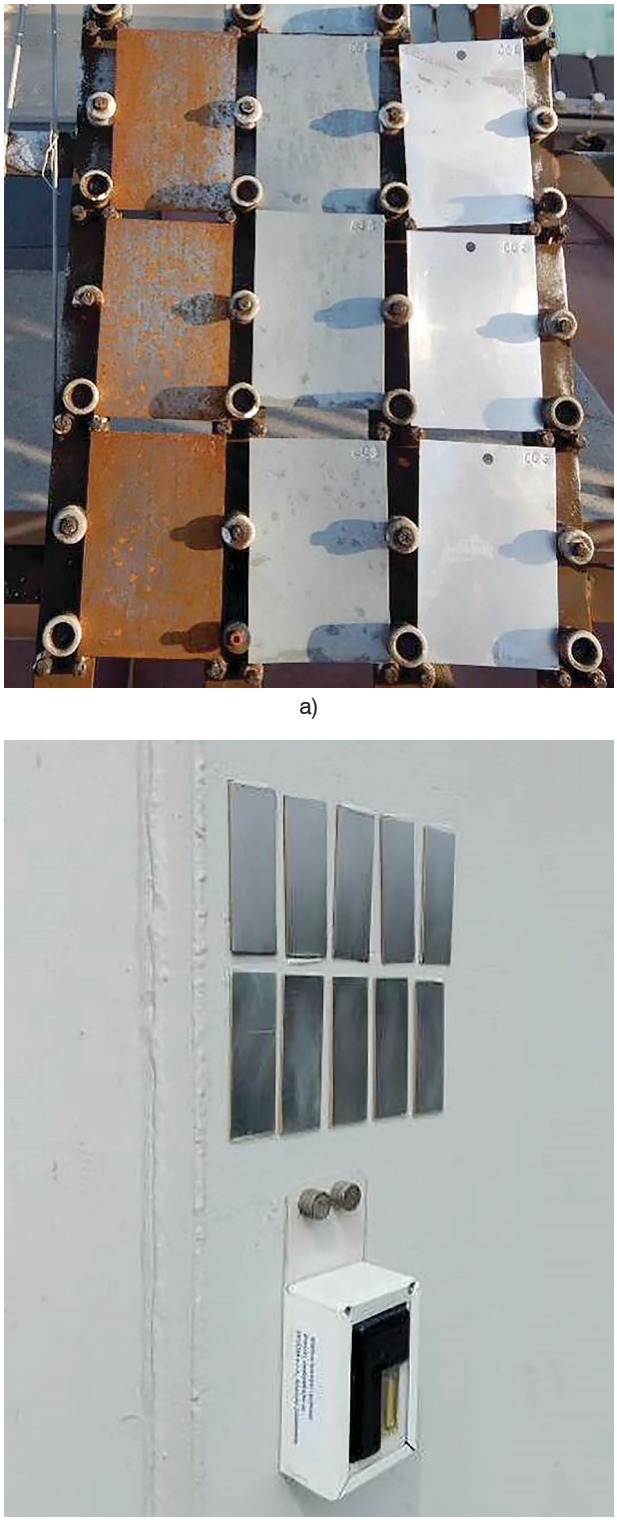
Metal coupons are frequently used for atmospheric corrosivity estimation due to their quick response to the environment and their sensitivity. The standard method of determination of atmospheric corrosivity is based on the exposure of standard specimens and their weight loss. This procedure is specified by EN ISO 9223 *Corrosion of metals and alloys – Corrosivity of atmospheres – Classification, determination and estimation* and is now widely used around the world. Coupons are exposed to the environment for a period from 1 year and thereafter they are analysed for the amount and type of corrosion products and corrosion mass loss. The main disadvantage of this method is that the relative long-term exposure (1 year) and the study of the specific seasonal effect is not accurate. In the case of corrosion rate study, each specimen can be used for only one time period corrosion rate determination, so that a considerable number of specimens is needed to determinate long-term corrosion rate.

In all exposures, the standardised coupons with dimensions 100 × 150 mm of carbon steel CR4 and zinc 99,9 were used. On the atmospheric test sites, the coupons were fixed on racks in standardised position and on bridge microclimate on a pillar in the vertical position – Figure 1.

Resistivity sensors

The oldest type of sensors is electrical resistance probes [8–10]. The resistivity sensor measurement method is based on the increasing electrical resistance of metallic materials as it is corroded. The electronic unit measures the change of electrical resistance with time in a metal thread placed on an insulating substrate. As the corrosion reduces the cross section of the thread the electrical resistance increases. Loss in thickness is estimated from the change in the electrical resistance of a sample of exposed metal as corrosion proceeds. Because this resistance can be measured continuously, the time dependence of the corrosion process can be followed. Corrosion rates of the metals were calculated from the change of the resistance of the carrying layer.

The resistivity sensors Fe and Zn [11] were exposed at the same localities as standard coupons – on the racks at the atmospheric test sites and in bridge microclimate. The Fe resistivity sensor stopped to measure on 3.3.2019 due to low battery capacity at atmospheric test site Prague. As the measuring area was significantly corroded and the producer recommends using one sensor for 1 year only, the measuring sensor was replaced by a new one. The measuring started from 1.5.2019 again. The Zn resistivity sensor was stopped to measure during June 2019.



a)

b)

Fig. 1. Exposure of metallic coupons

The exposure program was performed at field test site Prague – urban atmosphere with relatively low air pollution, in period 2016/21. The exposure program of standard metallic coupons on the bridge pillar was performed in the period 2018/20.

The same type of sensor was installed on highway D11 bridge pillar of supporting steel structure above bridge deck in the middle of the highway and exposed to all pollution from highway transport including deposition of de-icing salts in the winter season. Together with corrosion rate measurement, the chloride deposition was measured.

RESULTS

The early average environmental parameters measured on atmospheric test site Prague are given in Table 1. Data were measured directly on the test site by the meteorological station. The increasing trend in air temperature and decreasing trend of SO_2 are evident. This test site is not affected by chloride deposition. Long-term measurement gives average chloride deposition rate as background level S_0 according to EN ISO 9223 – 2,5 mg m^{-2} d^{-1}.

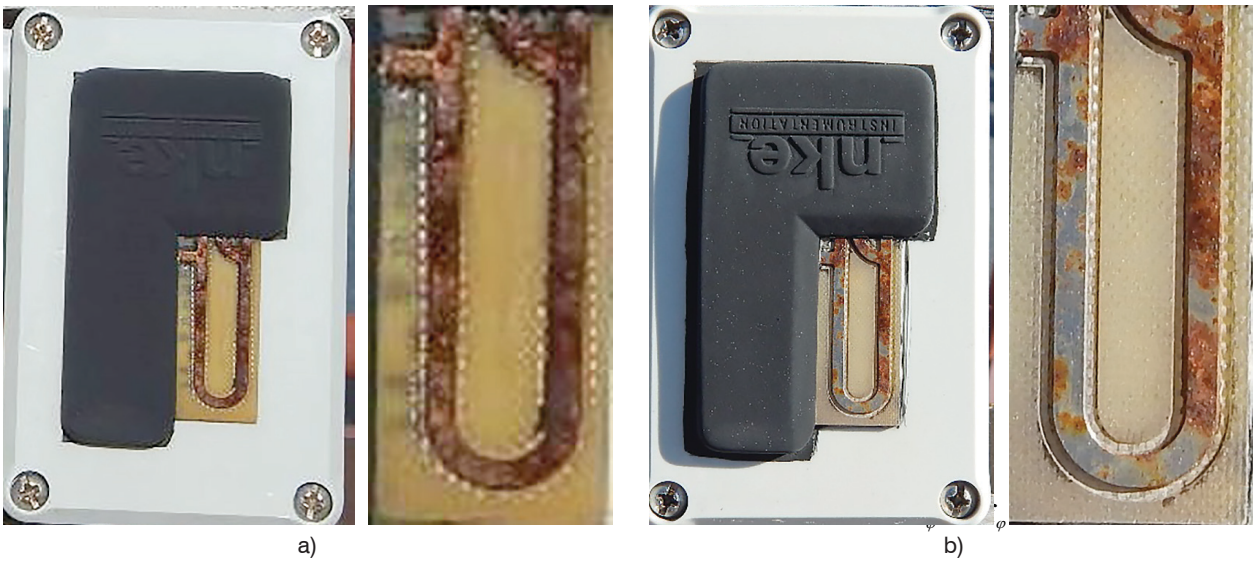
In Figure 2 the appearance of exposed Fe resistivity sensors after 1 year exposure is showing the change of corrosivity. In Figure 3 there are the graphs of corrosion rate from these sensors after 1 year´s exposures in periods 2016/17 and 2019/20 (new sensor). Figure 3 is a screenshot for software of Fe resistivity sensor showing also corrosivity classification. In the same periods, the standard flat carbon steel (CS) coupons were exposed on the test site – Figure 4. Measured yearly corrosion losses/rates are given in Table 2.

Tab. 1. Environmental parameters during 5 years´ exposure at Prague test site – average yearly data

Exposure period	T (°C)	RH (%)	SO_2 (µg m^{-3})	NO_x (µg m^{-3})	Precipitation (mm)	Days with snow
2016/17	9.9	73	6.2	21.0	563	46
2017/18	10.5	70	6.0	18.3	552	23
2018/19	11.6	66	3.9	30.4	355	21
2019/20	11.5	68	3.2	25.1	486	2
2020/21	10.3	71	2.7	22.4	578	36
average	10.8	70	4.4	23.4	507	26

Tab. 2. Corrosion losses/rates from atmospheric test site Prague

Exposure period	Fe resistivity sensor (µm a^{-1})	Corrosivity category	Standard CS coupons (µm a^{-1})	Corrosivity category
2016/17	6.67	C2	7.00	C2
2019/20	1.21	C1	0.54	C1

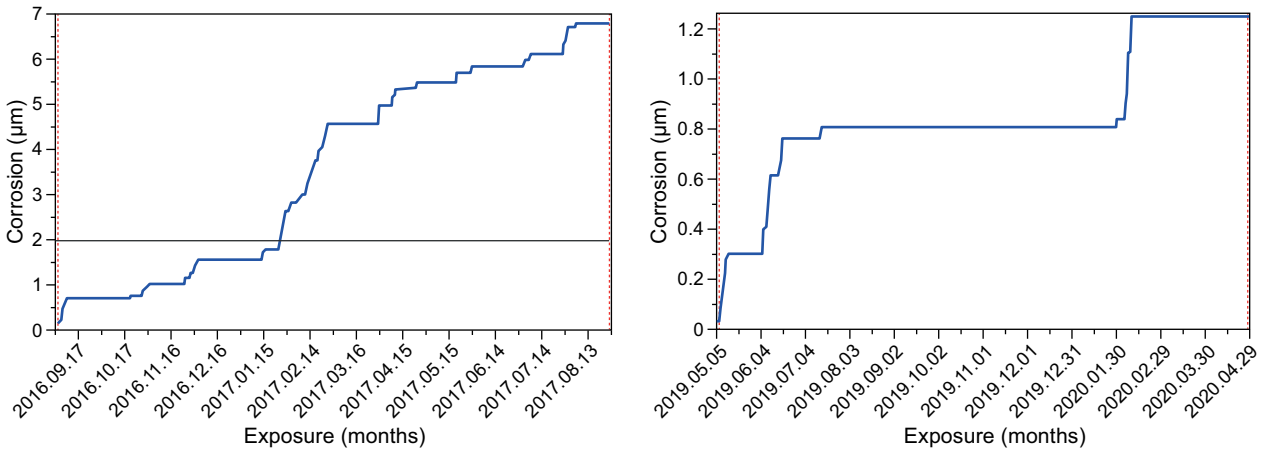


a) b)

Fig. 2. Fe resistivity sensor after 1 year of exposure at Prague test site in 2017 and 2019

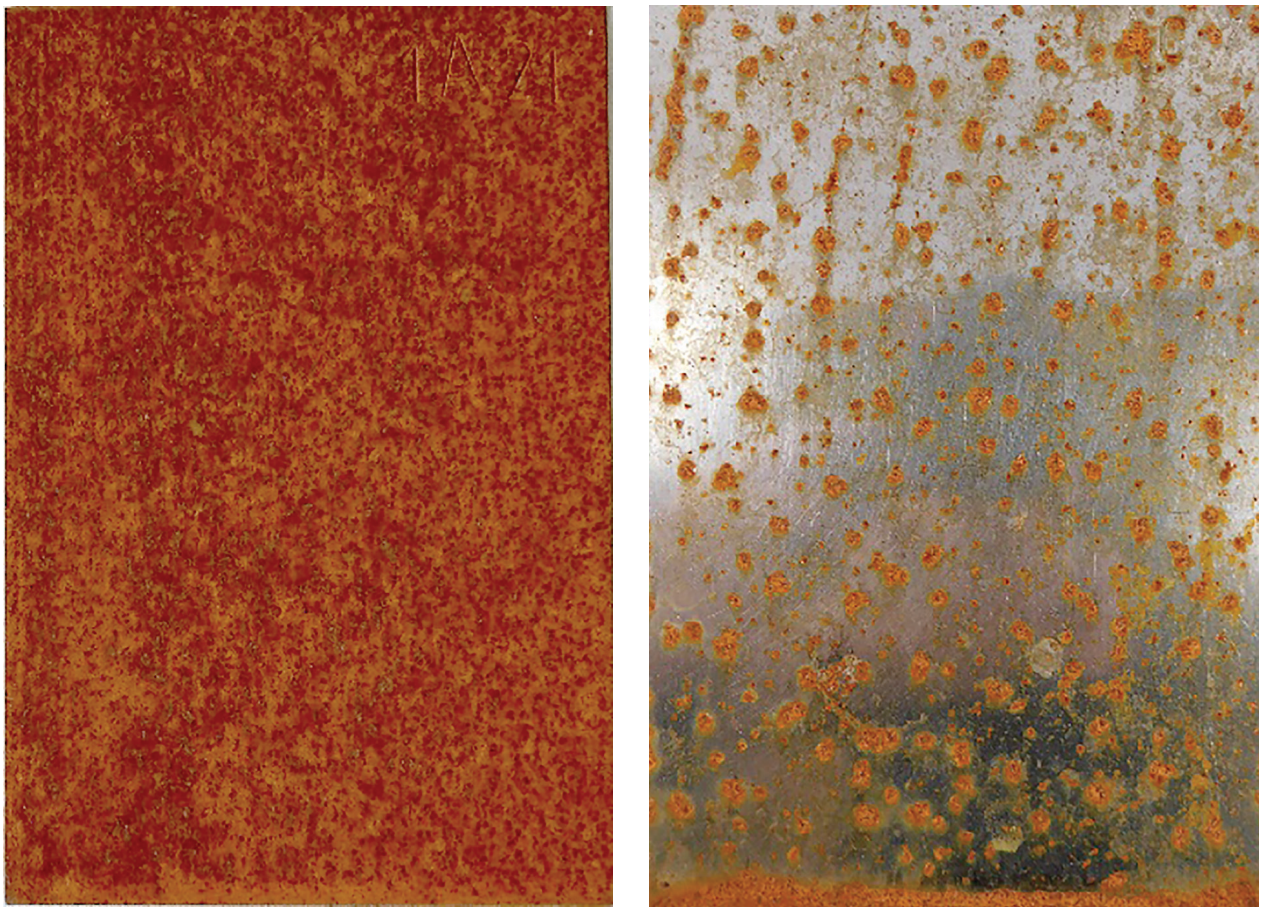
Tab. 3. Parameters from bridge microclimate exposure

Exposure period	T (°C)	RH (%)	SO_2 (µm m^{-3})	Cl^- deposition (mg m^{-2} d^{-1})	Fe resisitivity sensor (µm a^{-1})	Corrosivity category	Standard CS coupons (µm a^{-1})	Corrosivity category
2018/19	10.0	76	7.5	240	36	C3	27	C3
2019/20					25	C3	18	C3



a) b)

Fig. 3. Fe resistivity sensors output after 1 year from atmospheric test site Prague



a) b)

Fig. 4. Standard CS coupons after 1 year of exposure at Prague test site in 2017 and 2020

In Table 3 the environmental parameters for bridge microclimate locality are summarised. The chloride deposition in this locality was measured by dry plate method $S_{d,p}$ and average yearly value was expressed as $S_{d,c}$ multiplied by 2,4 coefficient according to EN ISO 9225.

In Figure 5 there are the graphs of corrosion rate from these sensors after 1 year´s exposures in periods 2018/19 and 2019/20. Unlike the corrosion rate from the atmospheric test site, the effect of the winter season on corrosion rate is evident. The increase of corrosion rate is caused by de-icing salt application [12].

DISCUSSION

The yearly corrosion losses of carbon steel determined by standard coupons in all exposures show a very good correlation to values obtained by resistive sensors. There are derived few dose-response functions from different exposure programmes based on different international environmental parameters [3, 13]. In Table 4 the results of the corrosion losses determined or estimated by different measurements (standard coupons, resistive sensors) and different dose-response equations are compared for an atmospheric test site. The EN ISO 9223 dose-response equation was used because only limited environmental parameters were measured in bridge microclimate. This dose-response function had a better fit than the others. The estimated (calculated) values are significantly higher than determined (measured) values of corrosion loss of carbon steel for atmospheric test site exposures.

The resistivity sensors are very sensitive to actual corrosion load. They showed the seasonal changes of it for all exposures. But the nowadays corrosion load is

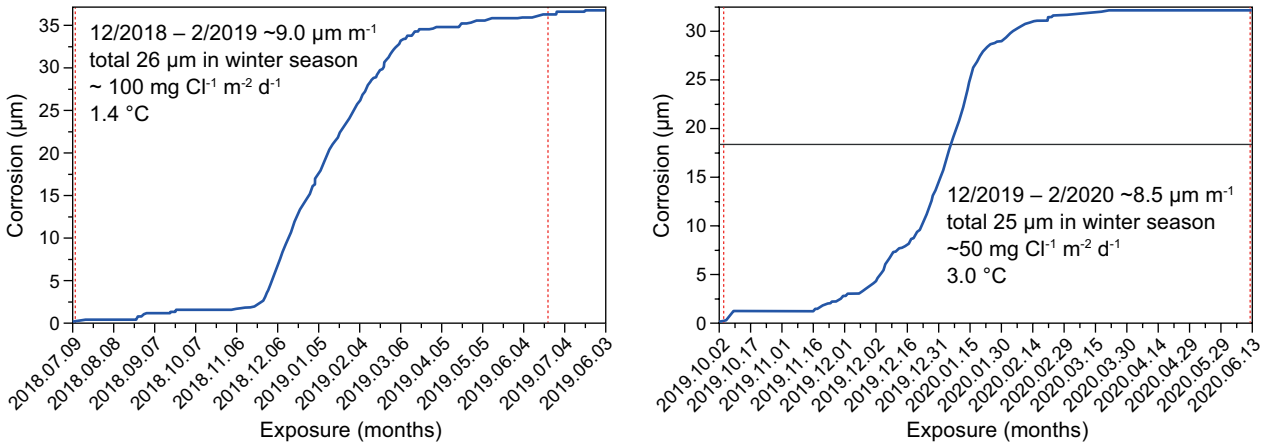


Fig. 5. Fe resistivity sensors output after 1 year´s from bridge microclimate

Tab. 4. Comparison of measured and estimated corrosion losses of carbon steel

Locality	Exposure period	Method	Corrosion loss (µm a^{-1})	Corrosivity category
atmospheric test site	2016/17	standard CS coupons	7.7	C2
		Fe resistivity sensor	8.0	C2
		ISO 9223 D-R	17.8	C2
		Multi-Assess D-R	15.0	C2
		UN ECE ICP D-R	22.4	C2
	2019/20	standard CS coupons	0.54	C1
		Fe resistivity sensor	1.21	C1
		ISO 9223 D-R	8.0	C2
		Multi-Assess D-R	12.2	C2
		UN ECE ICP D-R	20.7	C2
bridge pillar	2018/20	standard CS coupons	27.0	C3
		Fe resistivity sensor	36.0	C3
		ISO 9223 D-R	26.0	C3

very low to cause the response of sensors in background atmospheric environments except a few days in years with high humidity due to heavy and long-term rains (Fig. 3b). The results illustrate that SO_2 air pollution bellow 3 μm m^{-3} is too low to significantly affect atmospheric corrosion rate.

CONCLUSIONS

The results of long-term and repeated exposure of resistive sensors show:

- resistive sensors are suitable for monitoring of atmospheric corrosivity,
- resistive sensors are sensitive to actual climatic parameters and pollution levels,
- the Fe resistivity sensors are not probably sufficiently sensitive for atmospheric environments with low corrosivity category C1,
- measured values of corrosion rate and determination of corrosivity category by different methods are in very good correlation.

Acknowledgement

This paper was prepared with the support of research project MPO IP DKRVO.

REFERENCES

1. Halama M. et al., Prediction of Atmospheric Corrosion of Carbon Steel Using Artificial Neural Network Model in Local Geographical Regions, *Corrosion* **2011**, 67, 1-6.
2. Kreislova K. et al., Actual maps of atmospheric corrosivity for the Czech Republic, Proceedings of EUROCORR 2015, **2015**.
3. Kreislová K., Comparison of methods for estimation of atmospheric corrosivity, Proceedings of EUROCORR 2017, **2017**.
4. Fuse N. et al., Field test validation of corrosivity environment analysis based on sensor monitoring in transmission towers, Proceedings of EUROCORR 2019, **2019**.
5. Tatsuoka T. et al., Height Directional Distribution of Corrosion Rate, Deposited Sea Salt and Time of Wetness on Transmission Towers, Proceedings of EUROCORR 2019, **2019**.
6. Kasai N. et al., Correlation between corrosion rate and AE signal in an acidic environment for mild steel, Corrosion Science **2009**, 51, 1679-1684.
7. Mansfeld F., Evaluation of electrochemical techniques for monitoring of atmospheric corrosion phenomena, *ASTM Symposium Progress in Electrochemical Corrosion Testing*, **1979.**
8. Jirovsky I. et al., *Werkstoffe und Korrosion* **1976**, 27.
9. KcKenzie M., Vassie P.R., Use of weight loss coupons and electrical resistance probes in atmospheric corrosion tests, *Br. Corros. J.* **1985**, 20, 117-124.
10. Li S. et al., Application of steel thin film electrical resistance sensor for in situ corrosion monitoring, *Sensors and Actuators B: Chemical* **2007**, 120(2), 368-377.
11. T. Prosek et al., Real-time monitoring of indoor air corrosivity in cultural heritage institutions with metallic electrical resistance sensors, *Studies in Conservation* **2013**, 58, 117-128.
12. V. Krivy et al., Experimental measurement of chlorides deposition and their influence on the development of corrosion products on weathering steel bridges, *Metals* **2017**, 7, 336;
13. Kreislova K. et al., Modely atmosférické koroze, *Koroze a ochrana materiálů* **2017**, 61, 59-66.