CHANGES IN DEVELOPMENT OF PROTECTIVE PATINA ON WEATHERING STEEL

[1]Kateřina KREISLOVÁ, [1]Markéta VLACHOVÁ, [1]Anna PÍŠKOVÁ, [1]Pavlína FIALOVÁ, [2]Petr POKORNÝ, [3]Vít KŘIVÝ, [3]Miroslav VACEK

[1]SVÚOM Ltd., Prague, Czech Republic, EU, kreislova@svuom.cz

[2]ČVUT in Prague - Klokner Institute, Prague, Czech Republic, EU, petr.pokorny@cvut.cz

[3]VŠB-TU in Ostrava, Ostrava, Czech Republic, EU, krivy@vsb.cz

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Abstract

Weathering steel structures are protected by patina layer. The development of the protective patina layer depends on exposure conditions. The specific parameters of this protective patina were characterized during long-term exposure of standard samples exposed at atmospheric test sites and bridge structures together with evaluation of corrosion mass loss. The new method for evaluation of protective ability of patina is verified.

Keywords: Weathering steel, patina properties, applications, testing methods

1. INTRODUCTION

The low alloy steels with improved resistance against atmospheric corrosion, called weathering steel, are one of the atmospheric corrosion resistant materials which are chemically formulated to develop a protective oxide layer called patina, that creates on the material surface. The proportion of all the specific alloying elements such as copper, chromium, silicon, nickel is in total only a few per cent (2 wt%). The main influences on the formation of the protective oxide layer are the local environment and the structural detailing of the construction to ensure the required alternate wetting and drying conditions. Corrosion of weathering steels in outdoor conditions has been monitored since their development in the 1930s and in the CR since their pioneering applications in construction works 1970ties [1-5]. Changing environmental conditions such as decreasing SO_2 pollution and changing ambient air temperature and relative humidity affect the conditions of formation and development of the protective layer of corrosion products of weathering steels as well as corrosion rate of these steels itself.

Reliable and effective use of the weathering steel in the implementation of various types of outdoor steels constructions is conditional to number of specific conditions and requirements. The first weathering steel bridges had been built in the CR in the 70ties. Since this period, the patina development, corrosion behaviour, defects and other parameters important for the service life of the bridge have been investigated [6,7]. The paper gives survey of evaluation weathering steel corrosion behaviour in the CR in respect to prediction of their service life. The results of evaluation standard samples exposure at atmospheric test sites and on real bridges gives large database of corrosion rates and patina properties which may improve the prediction of service life of existing and new built weathering steel bridges. Due to low demands on maintenance, a number of weathering steel bridges is increasing.

Focusing on the environments where a source of chlorides is de-icing salts, the long-term corrosion rates for weathering steels predicted following ISO 9224 on corrosion attack for metals exposed to outdoor atmospheres are compared with recent measurements taken in the Czech Republic [8]. New aim of study is the application of Electrochemical Impedance Spectroscopy (EIS) which is a very useful technique for providing information about the corrosion process as well as the protective behaviour of the patina [9,10].

2. EXPERIMENTAL

2.1 Material

Weathering steel is a family of low carbon alloy steels that consists of a variety of grades, some grades are proprietary, such as COR-TEN A. The ATMOFIX weathering steels were produced in the CR. All of these proprietary grades are similar to the ASTM classifications A 242 and A 588 and EN 10025-5 (**Table 1**).

Table 1 Chemical composition of weathering steel (wt%)

Steel type	C	Si	Mn	P	S	Cu	Ni	Cr	Al	Fe
CORTEN A	0.09	0.30	0.35	0.081	0.005	0.28	0.27	0.48	0.037	rest
ATMOFIX 52A	0.12	0.25-0.75	0.30-1.00	0.055	0.040	0.30-0.55	0.30-0.60	0.50-1.25	0.120	rest

The flat samples of size 100 x 150 mm were prepared with blasted surface. Samples exposed directly on bridge structure had back side protected by tape.

2.2 Exposure conditions

The samples were exposed at the atmospheric test sites at the Czech Republic with the different environmental conditions (Prague - urban, Kopisty - industrial, Kasperske Hory - rural) on the rack according to EN ISO 8565. During the exposure the environmental parameters characteristic for atmospheric corrosion were measured.

The samples exposed on bridges structures were installed directly on the surface of steel structure at the typical vertical and horizontal position (outside and inside beam webs, upper and lower surfaces of bottom flange, lower surface of upper flange, etc.) - **Figure 1**. The bridges are built in Ostrava city, industrial environment, on highway junction.

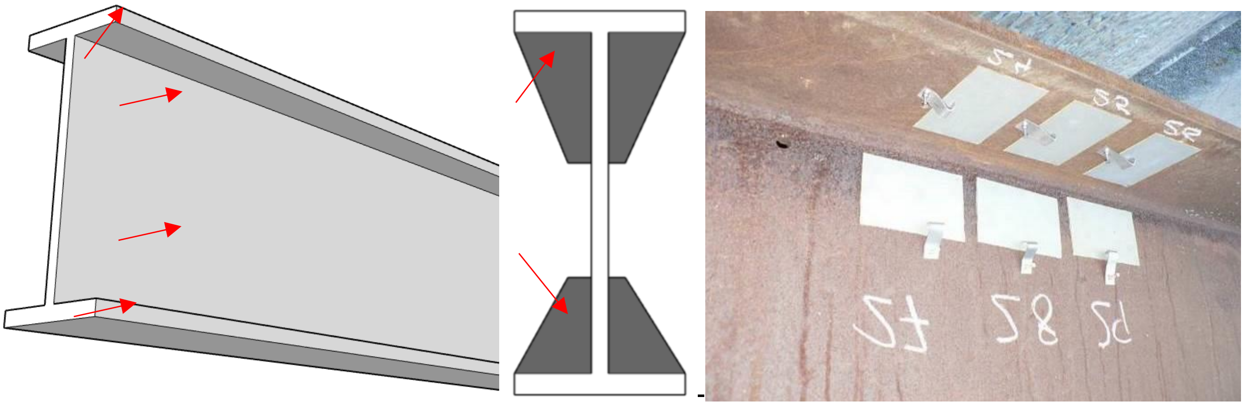

Figure 1 Example of the samples´ installation on the bridge steel structure

Chloride deposition was measured by wet candle method according to EN ISO 9225 directly on exposure sites.

2.3 Method of evaluation

Exposed samples were evaluated visually and characteristics of patina were measured (colour, glass, thickness, adhesion, etc.). The chemical composition of patina was analysed by several methods (XRD, EDS, AAS) and specific parameters of protective ability index (PAI) was calculated according to equations (1) - (3):

$$PAI\ (\alpha) = \frac{\alpha}{\gamma^*} \qquad (1)$$

and

$$PAI\ (\beta) = \frac{(\beta + s)}{\gamma^*} \tag{2}$$

where:

α - the content of goethite in the corrosion product layer (wt%),

$$\gamma^* = \beta + \gamma + s \tag{3}$$

β - the content of akageneite in the corrosion product layer (wt%),

γ - the content of lepidocrocite in the corrosion product layer (wt%),

s - the content of magnetite in the corrosion product layer (wt%).

The correlation between the phase composition of the patina on the surface of weathering steels and its stability, which directly affects the corrosion rate, is specified as the α/γ ratio and indicates the reactivity ($\alpha/\gamma < 1$) or stability ($\alpha/\gamma > 1$) of the protective layer [11]:

- the corrosion rate of the steel is less than 0.01 $mm.a^{-1}$,
- while if PAI(α) < 1, then the corrosion rate can be varied and depends on PAI(β):
  - if PAI(β) ≤ 0.5, then the corrosion rate is less than 0.01 $mm.a^{-1}$,
  - if PAI(β) ≥ 0.5, then the corrosion rate exceeds 0.01 $mm.\ a^{-1}$.

Corrosion mass losses were determined by interval pickling according to EN ISO 8407.

Electrochemical Impedance Spectroscopy (EIS) have shown the protective ability of the patina layer. In this study, the electrochemical cell consists of a stainless steel mesh as counter electrode, a Ag/AgCl electrode as a reference and the exposure electrolyte was a saturated sodium sulfate solution - **Figure 2a.** To obtain information about the measured systems it is useful to fit the results to a simplified equivalent circuit - **Figure 2b**. EIS analysis have been performed with a Gamry Reference 600 potentiostat, the sequence applied was 1800 seconds of Open Circuit Potential (OCP) and EIS from 100 kHz to 10 mHz with an amplitude of 10 mV. The fit of the results was made with Zview software.

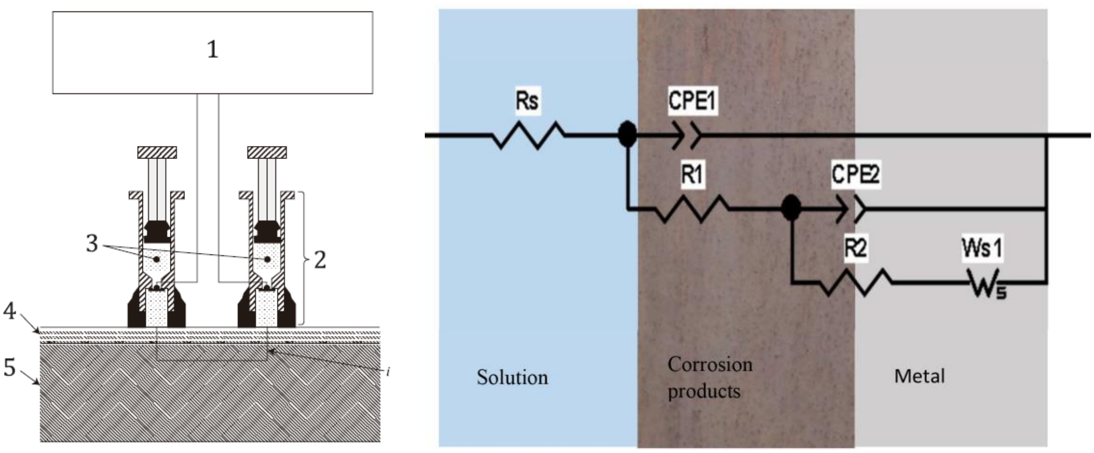

Figure 2 Example of measuring cell (ISO 22410) and equivalent circuit proposed and its representation in the corrosion layer

3. RESULTS

The average yearly environmental parameters significant for atmospheric corrosion are summarized in **Table 2** for exposure periods, i.e. for period 2008-2022 for atmospheric test sites and for 2013-2022 for bridge structures. These parameters are measured directly on atmospheric test sites in monthly intervals. Chloride deposition measurement by wet candle method started at 2016 at atmospheric test sites. Environmental data for bridge structures were used from meteorological service, only the chloride deposition was measured directly on bridge structures in Ostrava since 2018 [12].

Table 2 Average yearly environmental parameters for exposure periods

site	temperature (°C)	relative humidity (%)	amount of precipitation (mm)	pH of precipitation	SO_2 (μg.m^{-3})	Cl^- (mg.m^{-2}d^{-1})
Prague	10.3	72	549.6	6.3	5.6	2.47
Kopisty	9.7	76	496.8	5.8	12.6	2.24
Kašperské Hory	7.6	77	764.4	5.5	6.9	-
Ostrava	9.1	74	699.0	-	5.1	3.76

Weathering steel samples´ corrosion losses are given in **Table 3** and in **Figure 3** for all exposure periods. The range of corrosion losses specified for atmospheres with corrosivity category C2 according to EN ISO 9224 is indicated, too. The long-term corrosion losses from atmospheric test sites with various environmental conditions and from the bridges at industrial environmental conditions belong into corrosivity category C2.

Table 3 Corrosion losses of weathering steel samples

Exposure site	corrosion loss (μm)					
	1 year	3 years	4 years	8 years	9 years	14 years
atmospheric test site Prague	10.6	-	17.6	22.1	-	23.9
atmospheric test site Kopisty	21.4	-	35.1	54.5	-	56.6
atmospheric test site Kasperske Hory	8.7	-	15.4	20.5	-	19.8
bridges Ostrava, vertical positions	5.8	10.4	-	-	20.9	-
bridges Ostrava, horizontal positions	12.9	23.0	-	-	39.4	-

The results of evaluation of patina layers from the exposed samples are given in **Table 4**. The presented data contain also evaluation of samples after short exposure (1 year as basic parameters) and evaluation of samples exposed in such condition when the protective patina was negatively affected by leakage from failed drainage system of bridges (PAI(β) was 0.85).

The specific resistance measured by EIS technique shows increasing values with the protective ability of patina layer. The highest value shows the patina from sample exposed for 14 years in industrial atmosphere when the higher SO_2 pollution level had positive effect on its development. The sample exposed for 14 years at urban test site without the effect is not fully protective yet.

The samples from bridges were especially selected from these localities affected by leakage of de-icing salts from bridge deck onto steel surfaces. The chloride content shows this effect, and the corrosion losses were ca 55 μm, i.e. about 30 - 40% higher than on the other bridge surfaces. Non-protective character of rust layer is evident from PAI values and also from specific resistance values. In **Figure 4** there is the first relation between the corrosion loss of weathering steel samples and their corrosion product layers´ specific resistance. The result from sample negatively affected by leakage is evident as outlaying point. The study continues to create large database.

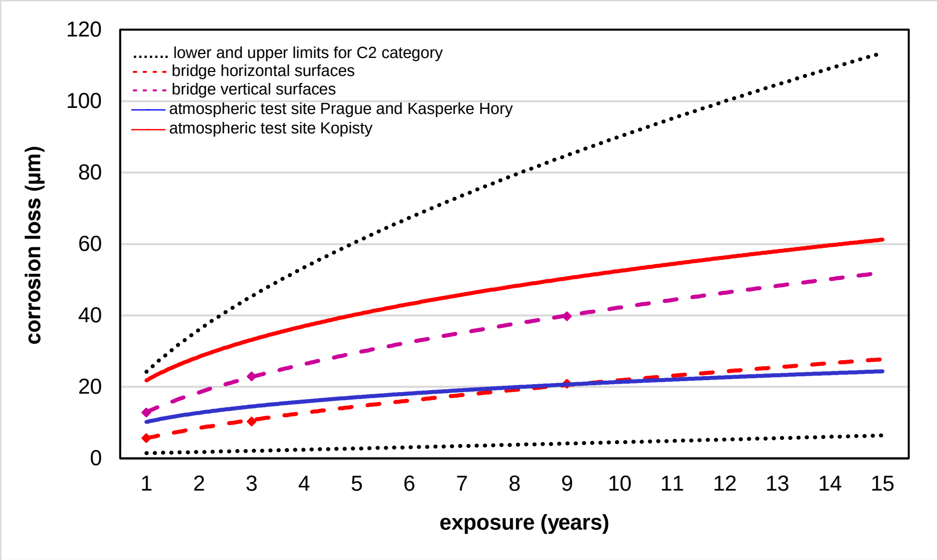

Figure 3 Time development of corrosion loss of weathering steel

Table 4 Evaluation of patina on weathering steel samples

sample	exposure (years)	thickness of patina layer (µm)	Cl^- content in rust (wt%)	PAI(α)	PAI(β)	specific resistance (Ω·cm^2)
test site Prague	1	31	0.05	0.05	-	40
test site Prague	14	84	0.08	0.80	-	1100
test site Kopisty	14	120	0.04	1.43	0.14	2000
bridge with leakage	9	179	2.32	0.15	0.85	300
bridge with leakage	9	513	0.80	0.15	0.85	700

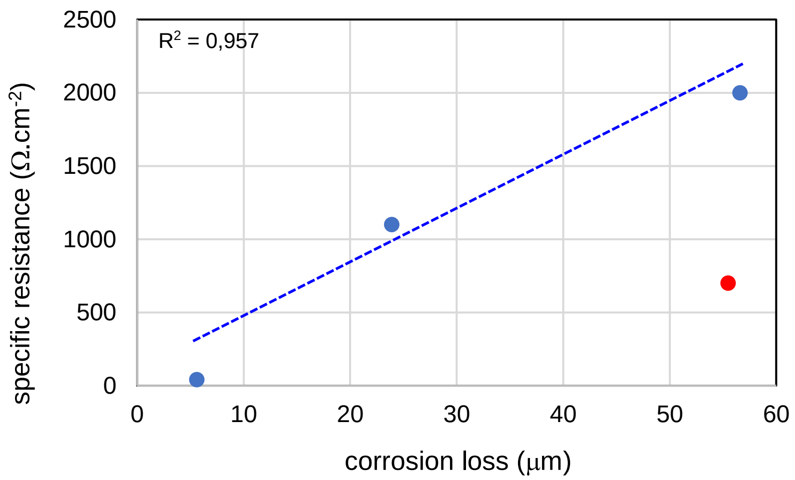

Figure 4 The relation between corrosion loss of weathering steel and specific resistance

4. CONCLUSION

Weathering steel is a construction material suitable for outdoor application with long-term durability and minimum maintenance. The evaluation of weathering steel corrosion behaviour in the CR shows their low corrosion rate and prospect for planned service life. The development of a protective patina layer with complex composition, effectively reducing the corrosion rate usually takes 5 - 10 years depending on the corrosivity of atmosphere in the locality. The non-destructive methods/techniques for estimation of the progress in patina layers and prediction of corrosion rate resp. corrosion loss would be very useful for anybody who takes care about such structure. In this project the various methods are verified. The first results show the prolonging the period to stabilize the protective patina but the reduction of corrosion rate in general in the Czech Republic atmospheres. For the bridges with the bridge deck above the steel structure the effect of chloride deposition is significant only if these bridges cross the highway, which is not the conditions of bridges when the samples were exposed.

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