IRON ALLOYS OUTDOOR CORROSION AND LABORATORY SIMULATION - COMPARISON

MAJTÁS Dušan[1,2], MÁCOVÁ Petra[1], KREISLOVÁ Kateřina[1], PŘÍHODA Jiří[2]

[1]*ITAM CAS v.v.i.- Institute of Theoretical and Applied Mechanics, Czech Academy of Science, Center of Excellence Telč, Czech Republic, EU*
[2]*Masaryk University, Brno, Czech Republic, EU*

Abstract

Simulation of iron alloy corrosion is widespread used to predict corrosion resistance. The simulation using corrosion chambers or climatic chambers provides reasonable information on corrosion resistance, the corrosion rate however must be compared to real exposition as the corrosion in simulated environment is accelerated compared to real situation. However the composition of corrosion products and its structure is different question. The corrosion products composition is dependent on corrosion process. The phases present are most likely the same; most voluminous hydrated oxides and oxy-hydroxides on the outside where the less voluminous oxides are present in the lower layers. However this macroscopic phase structure may not fully describe the layered structure of corrosion products, thickness of corrosion products or mechanical properties. In the vicinity of crack in corrosion products the structure is more likely to be similar to the structure near the surface.

Keywords: Corrosion, wrought iron, accelerated ageing, corrosion simulation

1. INTRODUCTION

The steel is widespread used construction material, which lifetime is strongly dependent on the corrosion resistance in the environment. Suitable way to determine material performance against the corrosion is to simulate corrosion in laboratory. Corrosion tests provide information about the material resistance in the specific, but the corrosion under such conditions is accelerated. The corrosion during real exposure and simulated exposure is not identical. The accelerated ageing favors short term processes. Long term processes still do occur but whether or not these results are significant is a matter of question.

Aim of the work was to find if the simulation - artificial ageing produce similar or identical corrosion products with similar or identical layered structure on microscale of these corrosion products.

2. CORROSION PREDICTION

Using corrosion tests to predict the capability of material to withstand the environment is used and standardized. Accelerated ageing is sometimes used to predict corrosion behavior in real situation. According to the works [1 - 3] on the long exposure the corrosion tends to produce layered structure where more voluminous corrosion products are on the outer edge and less voluminous are bellow to the metal surface. Generalizing from these papers and work [4] we may assume that results from long term exposure will be similar. On the contrary accelerated ageing does not duplicate environment absolutely, but rather use more aggressive conditions to speed up the corrosion.

2.1. Corrosion tests

Various testing procedures have been used to determine the corrosion resistance. These testing methods include wet/dry cycling, spraying with salt solution, or accompanying corrosive atmosphere. Methods for such

test are described in various standards [5 - 8]. In some cases tests including more than one type of corrosion simulation, for example combining salt spraying with artificial atmosphere such as [9], are making the simulation closer to the real corrosion situations.

Results are obtained in reasonable short period, in weeks compared to several decades in case of real exposure of objects during lifetime. This gives us advantage to predict performance against corrosion prior to its exposition depending on the information on environment. But do the conditions during the simulated exposition - accelerated corrosion match the reality?

2.2. Real situation

In case of real situation however there are constant conditions and there are conditions variable in time. Temperature, humidity, and atmosphere composition would not be constant but most likely will be changing in time. The changes may be cyclic given period of time such as change of temperature and humidity during day-night cycle or during the season change; or incidental such as the change of temperature and humidity due to weather front. Other possibilities are changes purely incidental which may not repeat.

As indicated in papers [1, 2, 9] long term exposure tends be controlled by environment rather the material composition. Additional factor is, that the corrosion products formed on the surface act as a corrosion protection [10, 11], especially for relatively stable oxides and oxy-hydroxides such as magnetite or goethite.

3. SAMPLE PREPARATION

Artificially prepared samples were obtained by two ways: exposure to artificial atmosphere simulating industrial pollutants of sulfur dioxide and nitrogen dioxide as dominant atmosphere pollutants during the twentieth century, with high relative humidity in the chamber, but without the simulation of rain to prevent the corrosive film removal from the surface. It was assumed this would simulate exposure of roof structure - crossbeam, except the corrosion speed due to the higher values of pollutant concentrations, temperature and relative humidity. The samples at the atmospheric test site were exposed to climatic conditions that are comparable to the conditions of long term exposure, but with the periodical cleanup of the corrosive film on the surface due to rain. Composition of riveted crossbeam from the roof structure is in the **Table 1**.

Table 1 Chemical composition of material (wt. %)

Element	C	Mn	P	S	Cu	Ni	Mo	V	N
Roof structure	0.044	0.32	0.038	0.084	<0.01	<0.013	<0.005	<0.004	0.002

3.1. Test conditions

Corrosive atmosphere with gaseous pollutants was simulated in the corrosion chamber with artificial atmosphere under controlled conditions. These conditions were as follows: temperature 25 °C, relative humidity 75 %, concentration of SO_2 0.3 ml / min, concentration of NO_2 0.75 ml / min. Two sets of samples were used with exposition times 7 days and 14 days.

Additional samples exposed to outdoor atmosphere under the monitored climatic conditions had been controlled by obtaining data from Czech Meteorological Institute collected in the nearby station Kostelni Myslova, citizen weather station at Pocatky and finally by weather station at the test site (Telc). Corrosivity was estimated using corrosion maps [12, 13], both for test site and the real corrosion problem, using data from given geographical location.

3.2. Real exposure situation

Samples from long term exposure were obtained during the restoration of Prague main railway station. Sample was taken from crossbeam of platform roofing. The material from which the sample was taken was not directly exposed to rainfall. The exposure time was approx. 110 years - the platform roofing has been built between years 1901 and 1909.

The crossbeam was initially coated by paint, but the maintenance was insufficient, the only reparation that was file on record was during the 1980s and according to the crossbeam surface, at least this particular crossbeam was not affected by this restoration. Drainage was not maintained properly and water leaked through the roof.

4. ANALYSIS

Analysis of the corrosion products was based on the previous work [14]. For the analysis X-ray Diffraction (XRD) and Raman spectroscopy has been used, in the cooperation with the optical 3D microscopy. Although the 3D surface reconstruction has its limitations, it is useful method for viewing the surface morphology prior to cross sectioning and thus without destroying the sample.

4.1. Instrumentation

Corrosion products were analyzed using optical microscope on sample surface and cross section by HIROX KH-7700 3D microscope. Phase composition was analyzed by XRD and Raman spectroscopy.

Phase composition of the bulk was analyzed on Bruker D8 Advance XRD, at: generator settings 40 mA and 40 kV, tube position line focus, axial soller 250°, slits 0.6 mm, angular range (2Ө) 5 - 90º, step size 0.01º, counting time / step 0.01 s, anode material Cu.

Phase analysis was done using DXR Raman microscope (Thermo Scientific). Raman spectra were collected using 532 nm laser, 20 x lens (N.A 0.40) and high resolution grating (1800 lines mm^{-1}, spectral resolution 2 cm^{-1}) in the spectral range 1800 - 50 cm^{-1}. The laser power on the sample was set on the lowest possible value (0.1 mW), to avoid sample transformation or destruction.

4.2. Surface analysis

Surface of corrosion product layers formed on top of roof crossbeam and samples from atmospheric corrosion test site showed height difference - caused by localized corrosion (shown in **Figure 1**). The whole surface is covered by corrosion products. On the samples from corrosion chamber the reconstruction did not work properly due to the relative flatness of the surface. The height difference in the corrosion products formed was below the method detection.
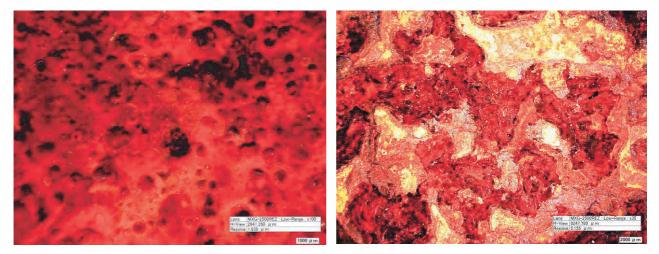

Figure 1 Comparison of the corrosion products surface: 1a atmospheric test site, 1b roof crossbeam
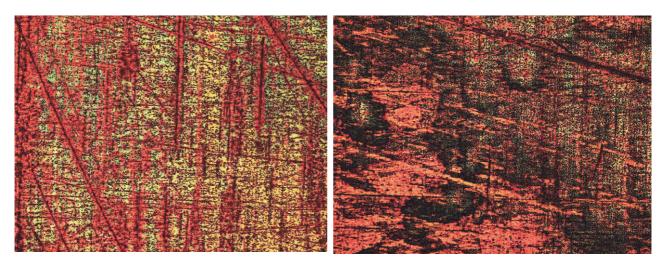
Figure 2 Comparison of the corrosion products surface: 2a 14 days exposure, 2b 28 days exposure

The surface of crossbeam and the coupons from atmospheric test site may be considered comparable. Corrosion in artificial atmosphere is visually different. The difference in the results of 14 days and 28 days exposure has been observed (shown in **Figure 2**). This difference suggests the longer exposure time will lead to surface fully covered by corrosion products.
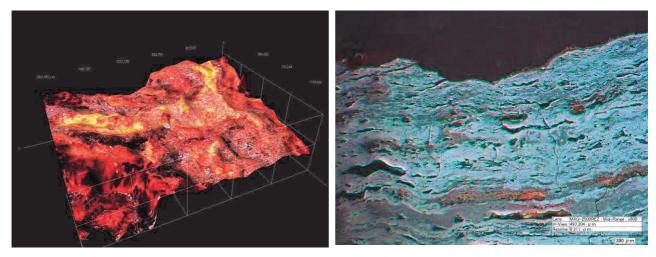

Figure 3 Crossbeam corrosion products: 3a surface reconstruction, 3b cross section

Different situation is the cross sectioning. Corrosion products formed on samples prepared by artificial ageing were not sufficiently voluminous to provide cross section. Only suitable samples for cross sectioning were taken from the long term exposure, crossbeam samples (**Figure 3**).

Thin metal coupons in combination with short term exposure do not provide usable results for cross sectioning. The effect of the longer exposure to accelerated ageing on the possible comparability of corrosion products should be further tested.

4.3. Phase composition

The phase analysis consisted of two steps. First phase composition of the bulk using XRD and then analyzing of the corrosion products using Raman microscopy. Methodology for this investigation was based on previous research [14].

Phase analysis of bulk was done by powder XRD, using powdered corrosion products taken from the sample. Due to previously mentioned insufficient thickness of the corrosion products formed on the samples from chamber and the atmospheric station the Raman microscopy was made only on the samples from the roof crossbeam. The phase composition obtained by both methods is shown in the **Table 2**.

Table 2 Phase composition of corrosion products

Sample description	Phase composition	
	XRD	Raman spectroscopy
Atmospheric test site	goethite, lepidocrocite	-
Artificial atmosphere s SO₂ a NO₂	goethite, lepidocrocite	-
Real corrosion exposure	hematite, maghemite, goethite, lepidocrocite, wüstite	hematite, maghemite, goethite, lepidocrocite

Presence of wustite in the corrosion product from the crossbeam of roof structure is due to the manufacturing process and is not connected to the corrosion mechanism. In all three cases the goethite and lepidocrocite has been found. Hematite and maghemite were not found on XRD spectra obtained from atmospheric test site and artificial atmosphere samples

It is questionable whether the absence of magmehite and hematite in the artificial samples is due to different corrosion process or there is a small amount of these phases was present but was below detection. As noted in the previous chapter, thickness of corrosion products on the surface of samples prepared by accelerated ageing was insufficient to prepare cross sections for Raman microscopy. It is possible to estimate corrosion resistance, but not analyze corrosion layers formed. The short term corrosion environment simulation does not provide comparable results.

4   CONCLUSION

- Difference between corrosion products formed in real exposure conditions and simulated artificial atmosphere is obvious. The surface from atmospheric test site and real corrosion is visually comparable
- Accelerated ageing in corrosive atmosphere at given conditions is not sufficient in forming corrosion on the surface that is visually comparable to the rest of the samples. It is not possible to simulate results of long term corrosion using short term exposure in the corrosion chamber.
- It is assumed, that the comparable layered structure will be obtained at longer exposure times. However it is necessary to further verify this statement.
- The phase analysis of the bulk for accelerated ageing and real exposure may produce results comparable to some point but not identical. Results obtained may be used as preliminary estimation not suitable simulation.

ACKNOWLEDGEMENTS

REFERENCES

[1]   MONNIER, J., NEFF, D., RÉGUER, S., DILLMANN, P., BELLOT-GURLET, L., LEROY, E., FOY, E., LEGRAND, L., GUILLOT, I. A corrosion study of the ferrous medieval reinforcement of the Amiens cathedral. Phase characterisation and localisation by various microprobes techniques. *Corrosion Science*, 2010, vol. 52, no. 3, pp. 695-710.

[2] HOERLÉ, S., MAZAUDIER, F., DILLMANN, P., SANTARINI, G. Advances in understanding atmospheric corrosion of iron. II. Mechanistic modelling of wet-dry cycles. *Corrosion Science*, 2004, vol. 46, pp. 1431-1465.

[3] MONNIER, J., BURGER, E., BERGER, P., NEFF, D., GUILLOT, I., DILLMANN, P. Localisation of oxygen reduction sites in the case of iron long term atmospheric corrosion. *Corrosion Science,* 2011, vol. 53, pp. 2468-2473.

[4] VEGA, E., DILLMANN, P., FLUZIN, P. A study on species transport in the corrosion products of ferrous archaeological analogues - a contribution to the modelling of iron long term corrosion behavior, *proceedings of EUROCORRR2004*, 12 - 16 September 2004, Nice, France.

[5] ISO 9227:2012, Corrosion tests in artificial atmospheres - Salt spray tests.

[6] ISO 10062:2006, Corrosion tests in artificial atmosphere at very low concentrations of polluting gas(es).

[7] ISO 11130:2010, Corrosion of metals and alloys - Alternate immersion test in salt solution.

[8] ISO 16151:2005, Corrosion of metals and alloys - Accelerated cyclic tests with exposure to acidified salt spray, "dry" and "wet" conditions.

[9] ISO 16701:2003, Corrosion of metals and alloys - Corrosion in artificial atmosphere - Accelerated corrosion test involving exposure under controlled conditions of humidity cycling and intermittent spraying of a salt solution.

[10] TAMURA, H. The role of rusts in corrosion and corrosion protection of iron and steel. *Corrosion Science,* 2008, vol. 50, pp. 1872-1883.

[11] YAMASHITA, M., MIYUKI, H., MATSUDA, Y., NAGANO, H., MISAWA, T. The long term growth of the protective rust layer formed on weathering steel by atmospheric corrosion during a quarter of a century. *Corrosion Science*, 1994, vol. 36, no. 2, pp 283-299.

[12] KREISLOVA, K., KNOTKOVA, D., SKOREPOVA, I. Korozní mapa ČR pro uhlíkovou ocel: speciální korozní mapa. Praha: SVÚOM, 2008.

[13] KREISLOVÁ, K., GEIPLOVÁ, H., SKOŘEPA, I., SKOŘEPOVÁ, J., MAJTÁS, D. Actual maps of atmospheric corrosivity for the Czech Republic, *proceedings of EUROCORR2015*, 6 - 10 September 2015, Graz, Austria.

[14] MAJTÁS, D., MÁCOVÁ, P., KREISLOVÁ, K. Cross-section analysis and mapping using Raman spectroscopy. In *METAL 2016. 25th International Conference on Metallurgy and Materials.* Ostrava: Tanger, 2016, pp. 531-536.