

Investigation of microbiologically influenced corrosion

1. Characterization of natural outdoor conditions in Lithuania

**Rimantas Ramanauskas,
Eimutis Juzeliūnas,
Algimantas Narkevičius
and Dalia Buėinskienė**

*Department of Materials
Research and Corrosion,
Institute of Chemistry,
A. Goštauto 9,
LT-01108 Vilnius, Lithuania*

**Albinas Lugauskas,
Dalia Pečiulytė
and Loreta Levinskaitė**

*Institute of Botany,
Paliūjū ežerø 49,
LT-2021 Vilnius, Lithuania*

**Vidmantas Ulevičius
and Dalia Jasinevičienė**

*Institute of Physics,
Savanoriø 231,
LT-2053 Vilnius, Lithuania*

Atmospheric corrosion studies of Al, Cu, Zn and steel samples were carried out in the different regions (marine, rural, urban) of Lithuania with the aim to evaluate the corrosivity of atmosphere and to estimate the role of aerochemical parameters and microbiological ambience on the metal corrosion behaviour. The monitoring of wet and dry deposition rates of pollutants (air born Cl⁻, sulphur and nitrogen gaseous compounds and aerosols), time of wetness, identification of bacteria and fungal species on the metal surface and in precipitations collected from the samples were carried out. It has been determined that the corrosivity of Lithuanian atmosphere according to ISO classification corresponds to the "low" category. The wet and dry pollutant (Cl⁻ and sulphur compounds) deposition rates, as well as wetness duration influenced the corrosion rate of metals exposed to natural environment. Several fungal species able to survive or adapt to the metal substrata were detected on all the metals studied. It was established that bacteria might exert an accelerating influence on the corrosion process of Cu and Zn, while for Al and steel, on the contrary, bacteria caused corrosion inhibition.

Key words: atmospheric corrosion, atmospheric pollutant, microbiological corrosion

INTRODUCTION

A large number of atmospheric corrosion test programs have been implemented over the decades with the general aim to identify and quantify the most important environmental parameters involved in the atmospheric corrosion process [1–6]. The electrochemical nature of atmospheric corrosion requires the presence of electrolyte on the metal surface. The corrosion rate of a metal depends also on the characteristics of the electrolytic film formed, *i.e.* on the concentration of pollutants, thickness of the film, temperature. Numerous studies have provided evidence that corrosion rates under outdoor exposure conditions are strongly influenced by SO₂ and

Cl⁻ as well as by humidity and temperature of atmosphere [1, 6, 7–11]. Nevertheless, the general goal of atmospheric corrosion studies to predict the performance of a given metal in a given environment is far from being attained [12]. The reason lies in the difficulties to involve into models the numerous factors that may influence corrosion rates, such as uncontrolled pollutants, the nature and structure of the corrosion products formed, the diversity of microbiological influence, etc.

Metal corrosion is modified by various environmental factors, however, the role of microorganisms has been not sufficiently studied. Fungi function on metals in extreme conditions: in the presence of a minimal source of organic matter, shortage of water and sometimes high temperature. Fungal survival in such environment is determined by their metabo-

*Corresponding author. E-mail: ramanr@ktl.mii.lt

Table 1. Classification of Lithuanian atmosphere corrosivity in different regions (test sites) according to ISO 9223

Test site	Metals			
	Al	Cu	Zn	LCS
Urban 1	Low	Very low	Low	Low
Urban 2	Low	Very low	Low	Low
Rural 1	Low	Very low	Low	Low
Rural 2	Low	Very low	Low	Low
Marine	Medium	Low	Low	Low

lism peculiarities, their ability to transform and adapt their enzymatic systems to specific assimilation process [13–17]. There are no reliable data that fungi use metals as a substratum. It is known that many microorganisms produce various chemical compounds such as CO₂, H₂S, NH₃, organic and inorganic acids, which cause deterioration of metals. Therefore, fungi and their associations may participate in the metal corrosion process [18–20].

No systematic studies on the corrosivity of Lithuanian atmosphere were carried out up to date, therefore, the main goal of the present study was to evaluate this parameter in different regions (urban, rural and marine), evaluating also the influence of the main atmospheric pollutants (sulphur dioxide, chloride ions and air-born nitrogen compounds) on metal outdoor corrosion performance. The attention was focused on identifying strains of the microorganisms capable of colonizing metal surfaces during outdoor exposure.

EXPERIMENTAL

Atmospheric corrosion studies were carried out in the following five test sites on the territory of Lithuania: marine (Baltic Sea shore: Preila), rural 1 (Molėtai) and rural 2 (Utena), urban 1 (Vilnius: suburb) and urban 2 (Vilnius: centre) (Table 1). Atmospheric field tests and corrosion evaluation were performed according to the ISO standards 9223, 9224, 9225, 9226 [21–24].

Corrosion tests were started in June 2002 by exposing specimens (10 × 15 cm) of four metals: Al (Al > 99.5%), Cu (Cu > 99.5%), Zn (Zn > 98.5%), low carbon steel (LCS) (C 0.5–0.12%, Cu 0.03–0.10%, P < 0.07%). The samples were exposed at an angle of 45° to the horizon facing south. According to the test program, three samples were withdrawn from all test sites after every measuring period. The corrosion rates (mass loss) were determined gravimetrically. The corrosion products were removed according to ISO 9226 [24] using the following solutions: 500 ml/l HCl (d = 1.19 g/ml), 3.5 g/l hexamethylene tetramine for LCS 200 g/l CrO₃ for Zn; 54 ml/l H₂SO₄ (d = 1.84 g/ml) for Cu; 50 ml/l H₃PO₄ (d = 1.69 g/ml) 20 g/l CrO₃ for Al.

The time of wetness (TOW), *i.e.* the period in which an electrolyte film is present on the metal surface, was determined with the aid of a humidity tester consisting of thin dielectrically separated electrodes of all the metals studied, with monitoring the current or electromotive force when the thickness of the aqueous layer was sufficient to accelerate atmospheric corrosion.

Microorganisms were isolated from the metal plates in atmospheric corrosion test sites in two ways: 1) by direct isolation from the surface of plates using a sterile metal loop; 2) by isolation from precipitations collected from the metal samples. The latter case included the use of suspensions prepared from rainwater and then inoculated on two different media: a solid malt supplemented with antibiotics to suppress the growth of bacteria, which was used for isolation of microscopic fungi, and a solid meat peptone medium which was used for isolation of bacteria.

Microorganisms were grown at a temperature of 26 ± 2 °C. Their colonies were counted in the following way: bacteria after 2–3 days and fungi after 3, 5 and 7 days. Pure cultures were obtained from grown microorganisms and were identified according to their physiological, cultural and morphological peculiarities. Fungal species were identified as indicated by various manuals [25, 26]. The percentage of the distribution frequency and the population density were calculated according to the formula:

$$F = \frac{B}{C} \cdot 100\% , \quad (1)$$

where *F* is the distribution frequency, %, *B* is the number of samples in which a particular species was found; *C* – the total number of samples tested.

Precipitation sampling was performed on a monthly basis. The precipitation samples were analysed for the following cations and anions: sulfate (SO₄²⁻), nitrate (NO₃⁻), chloride (Cl⁻), ammonium (NH₄⁺), as well as for pH and conductivity. Air samples were collected within a one-week period using filter-packs. Ambient filter extracts were analysed for sulfate (SO₄²⁻), nitrate (NO₃⁻), chloride (Cl⁻), ammonium (NH₄⁺), sulphur dioxide (SO₂). SO₄²⁻, NO₃⁻ and Cl⁻ were analyzed using a Dionex Model 2010i ion chromatograph with conductivity detection. The pH was measured with an Orion combination electrode and a pH meter. NH₄⁺ was analysed spectrophotometrically with a continuous flow system by the indophenol method. Data quality was assured according to the EMEP manual for sampling and chemical analysis [27].

RESULTS AND DISCUSSION

Metal corrosion data

The corrosivity of the exposure location site is deduced from the corrosion rates (*K*) calculated from

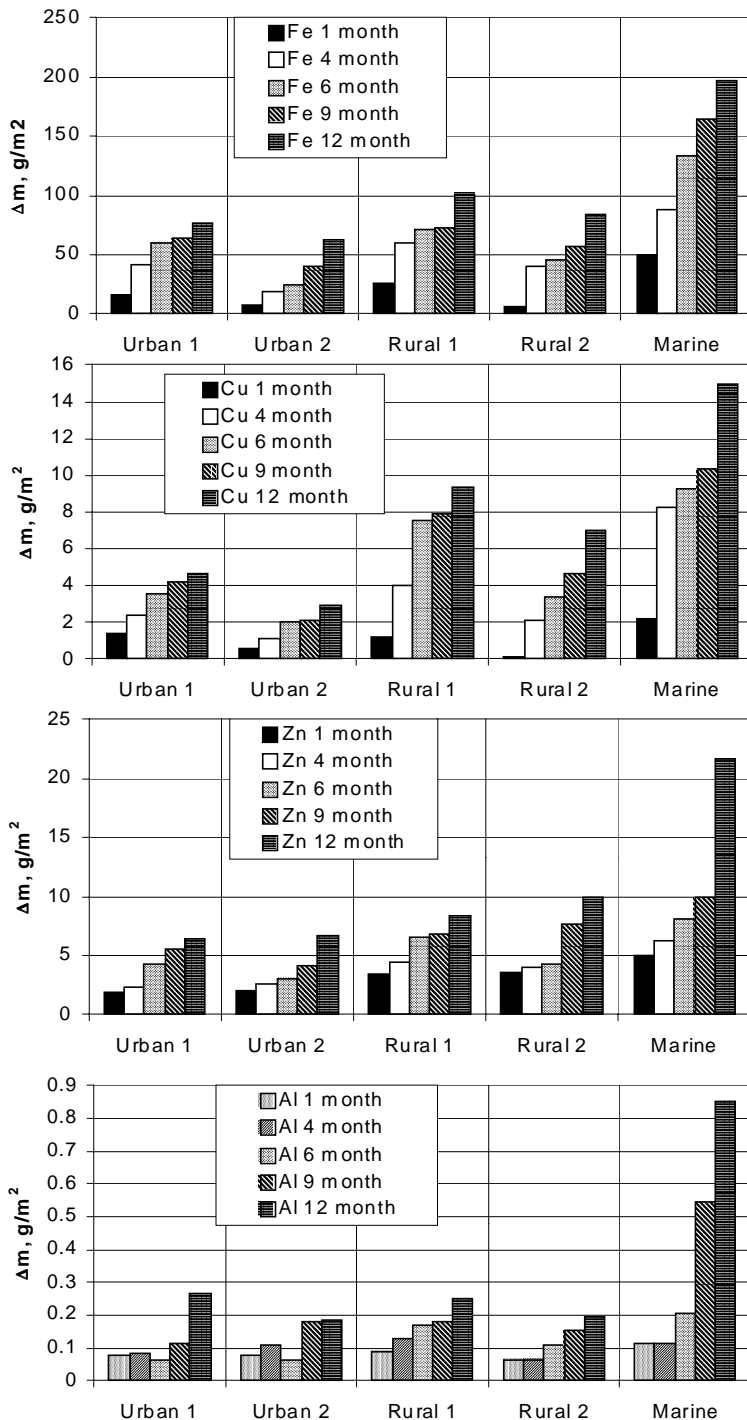


Fig. 1. Mass losses (Δm) of Al, Cu, Zn and LCS samples under different test site conditions

the loss of mass per unit area (Δm) of standard specimens following the descaling of corrosion products from the specimens after a one-year exposure. The mass loss measurements, which provide the most reliable indicator concerning the corrosion behaviour of metals, are summarized in Fig. 1.

The highest Δm values and consequently the highest corrosion rates under natural exposure conditions were determined in the marine test site. They appeared to be at least twice as high as those in

urban and rural test sites. The Δm values of steel after one year of exposure to the marine conditions reached nearly $200 g/m^2$, while those for Cu, Zn and Al samples were $15 g/m^2$, $22 g/m^2$ and $0.9 g/m^2$, respectively. The lowest metal corrosion rates were determined in the urban (2) test site where Δm values were 3 to 5 times lower than in the marine test site. The following minimal Δm values were determined: Zn $6.4 g/m^2$, Cu $2.9 g/m^2$, Al $0.18 g/m^2$, LCS $62.4 g/m^2$. The atmospheric corrosion aggressiveness of the test sites increased in the following sequence: urban 2 < urban 1 < rural 1 \cong rural 2 < marine.

The corrosivity of Lithuanian atmosphere according to the ISO classification based on the corrosion behaviour of almost all investigated metals (data are listed in Table 1), corresponds to the "low" category. The exceptions were Al in the marine test site, whose K values corresponded to the "medium" corrosivity category, and Cu samples which fitted the "very low" corrosivity category.

Atmospheric pollution evaluation

Atmospheric corrosivity is usually characterized by a combination of three parameters: time of wetness (TOW) and the concentrations of SO_2 and Cl⁻ in the air [12]. However, numerous investigations based on both laboratory and field exposures have proved at least some gaseous constituents to be of significant importance in metal corrosion processes [12]: NO_2 , NH_3 , O_3 , H_2O_2 , H_2S , Cl_2 , HCHO. The presence of these substances may be the result of either natural or anthropogenic processes. The incorporation of atmospheric species into the aqueous layer on a metal surface may occur through either dry or wet deposition. In dry deposition, there is no involvement of any precipitation,

whereas wet deposition requires rain, dew, fog or snow for atmospheric pollutants to deposit.

The wet and dry air-borne pollutant concentration was monitored in the different test sites. The concentration of SO_4^{2-} , NO_3^- , NH_4^+ and Cl⁻ was determined in the rainfall collected in the different test sites. The results, together with the amount of precipitations, are listed in Table 2.

The pollutant concentration in the rainfall varied in a wide range (Table 2). The concentration

Table 2. The amount of precipitation and pollutant concentration in the rainfall at different test sites

Pollutant / rainfall	Value	Test site location		
		Urban 2	Rural 2	Marine
Rainfall mm/month	Minimum	0.8	10	1.5
	Maximum	55	126	136
	Average	28	58	43
SO ₄ ²⁻ mg S/l	Minimum	0.25	0.26	0.43
	Maximum	4.24	0.85	1.34
	Average	1.03	0.57	0.79
NO ₃ ⁻ mg N/l	Minimum	0.15	0.15	0.20
	Maximum	4.11	0.66	1.47
	Average	0.80	0.40	0.58
NH ₄ ⁺ mg N/l	Minimum	0.07	0.02	0.18
	Maximum	3.73	0.57	1.05
	Average	0.80	0.36	0.52
Cl ⁻ mg/l	Minimum	0.22	0.18	0.58
	Maximum	7.75	0.89	9.0
	Average	1.59	0.44	2.41

of pollutants in a wet deposition was strongly related to precipitation intensity. An increase in rainfall reduces the pollutant concentration and *vice versa*. The highest monthly average intensity of rainfall was registered in the rural (58 mm/month) and the lowest in the urban (28 mm/month) test sites. The largest difference between the minimal and maximal monthly concentrations of sulphur and nitrogen compounds was observed in the precipitations of the urban test site, while for Cl⁻ ions the largest difference was observed in the rainfall of the marine test site. The monthly average concentration of Cl⁻ pollutant in the rainfall was highest in the marine test site (2.41 mg/l), while the minimal concentration (0.44 mg/l) was registered in the rural one. The highest concentration of sulphur and nitrogen compounds was registered in the precipitates of the urban site and the minimal one in the rural test sites. The high concentration of pollutants in the urban test site is related to a small amount of precipitations.

The main proportion of the dry air-born sulphur compound consisted of gaseous SO₂, whose amount was 6 to 7 times higher in respect to SO₄²⁻ aerosol. The ratio between the dry and aerosol proportions of the sulphur pollutant varied depending on the season. The mentioned ratio was 1.5 in summer months and ~13 in the winter-spring season. The deposition rates of dry air-born pollutants are listed in Table 3. The largest difference between the maximum and minimum deposition values of air-born contaminants (SO₂, NO₂ and Cl⁻) was registered under the marine test site conditions. The monthly average deposition rate of Cl⁻ in the air on the seashore was 99.0 mg/m², which was approximately

Table 3. Deposition rates of dry atmospheric pollutants in the air of different test sites

Pollutant / rainfall	Value	Test site location		
		Urban 2	Rural 2	Marine
SO ₄ ²⁻ S, mg/m ²	Minimum	10.0	24.4	14.5
	Maximum	45.0	58.9	86.1
	Average	27.4	39.2	42.0
NO ₃ ⁻ N, mg/m ²	Minimum	14.1	17.7	7.3
	Maximum	49.5	51.6	89.3
	Average	26.1	36.8	38.6
Cl ⁻ mg/ m ²	Minimum	7.6	2.1	5.4
	Maximum	48.9	50.1	504.3
	Average	19.5	19.9	99.0

fivefold higher than that under urban and rural conditions, where this parameter was close to 20.0 mg/m². The monthly average flow of sulphur and nitrogen compounds was higher in the rural (39.2 mg/m² and 36.8 mg/m², respectively) than in the urban (1) test site (27.4 mg/m² and 26.1 mg/m², respectively). The monthly average dry deposition rates of pollutants were evidently higher in the marine while the minimum deposition was typical of the urban test site.

TOW evaluation

The aqueous phase on the metal surface acts as a solvent for gaseous constituents of the atmosphere. The properties of aqueous films thicker than three monolayers approach those of bulk water [12]. The relative humidity in this case is close to the critical relative humidity, above which atmospheric corrosion rates increase substantially and below which atmospheric corrosion is insignificant. The critical relative humidity for different metals in the presence of pollutants has been reported to be between 50 and 90% [12, 28]. However, this definition should not be taken too literally, since the actual time when the surface is wet enough for rapid corrosion depends on many other parameters, such as the type, mass, orientation of metal, hygroscopic properties of both corrosion products and surface contaminants, the type and level of pollutants, wind velocity, presence of biofilm and solar flux [12]. Therefore, a more convenient way to determine TOW is direct application of humidity detectors but not calculation of the time when relative humidity exceeds a certain value. The results of TOW measurements for various metals applying humidity testers under the different test site conditions are presented in Fig. 2.

It is evident that under the same conditions the TOW values for various metals were different. The highest TOW values were typical of Al (up to 20% of exposure time) in all test sites, while those mi-

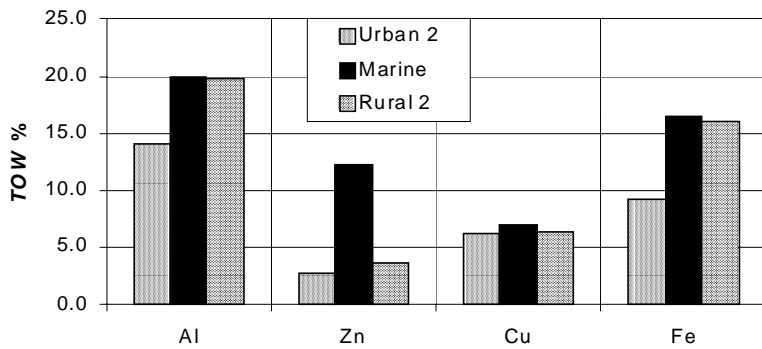


Fig. 2. TOW of various metals under different test site conditions during June 2002 – June 2004

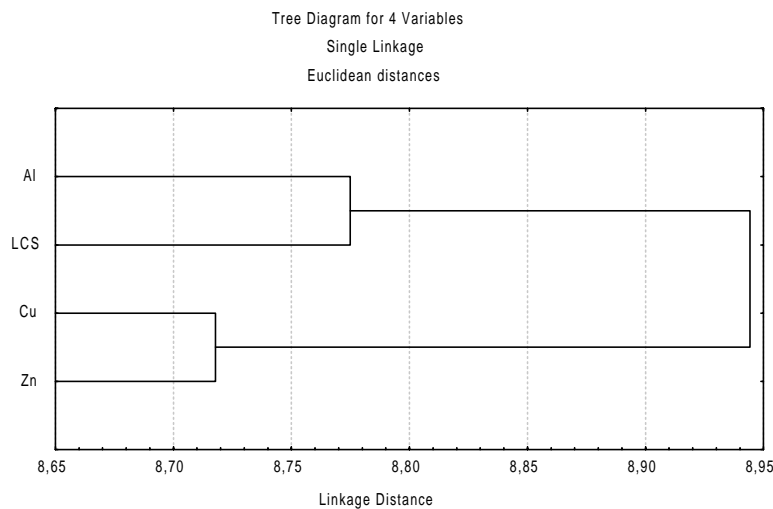


Fig. 3. Cluster analysis of fungal species on different metal plates

nimal were determined for Zn samples (up to 2.5–3% of exposure time), except the seashore site where Cu had the shortest moisturizing period. On comparing the test sites, it became evident that the lowest TOW was characteristic of the urban sites, while the highest ones were observed under marine conditions.

Microbiological studies

The total number of 172 fungal taxa (161 species) from 74 genera were isolated and identified during one-year exposure in all test sites. The number of the fungal species found depended on the metal nature. The greatest variety of fungal species was detected on LCS (93 species from 45 genera). The number of those detected on Cu plates was approximately twice lower (50 species from 26 genera). The number of species found on Al and Zn plates appeared to be very similar: 84 species from 41 genera and 79 species from 43 genera, respectively. The genus *Penicillium* was most representative among the fungi (26 different species).

Approximately 75% of all identified species were detected at least three times. The detection frequency of the other species is presented in Table 4. The species *Alternaria alternata*, *Aspergillus niger*, *Au-*

reobasidium pullulans, *Cladosporium cladosporioides*, *C. herbarum* and *Paecilomyces parvus* were most frequently isolated from all exposed metals. Their general (on all metals) detection frequency ranged from 16% to 27%. Furthermore, the above-mentioned fungi *Alternaria alternata*, *Aspergillus niger* and *Paecilomyces parvus*, as well as some species from the genus *Cladosporium*, were detected rather frequently as compared to other fungal species on all kinds of metals. Their detection frequency ranged from 10% to 38% depending on the metal. The fungus *Aureobasidium pullulans*, which was relatively frequent on Al, LCS and Zn corroded plates (detection frequency 10–36%), was detected only in specific cases on Cu plates (detection frequency reached only 4%). Several fungus species were found more frequently (detection frequency reached 10% and more) on certain metals: *Fusarium solani* and *Rhizopus stolonifer* – on Al, *Exophiala jeanselmei*, *Fusarium oxysporum* and *Rhizopus stolonifer* – on LCS and *Oidiodendron echinulatum* – on Zn surface. It may be supposed that these species adapt better to the test substrata under the exposition conditions.

This fact coincides with the results of another investigation which indicated that *Aureobasidium*, *Cladosporium*, *Paecilomyces*, *Oidiodendron*, as well as *Geomyces* and *Torula* genus fungi were tolerant to high concentrations of heavy metals [30].

Cluster analysis of fungal species isolated from various metals exposed to different test sites showed that the species composition was more similar between those found on Zn or Cu and between Al and LCS (Fig. 3).

Although the corrosion test sites varied in climate conditions, the following fungal species were detected in all of them: *Alternaria alternata*, *Aspergillus niger*, *Aureobasidium pullulans*, *Cladosporium cladosporioides*, *C. herbarum* and *Paecilomyces parvus*, *Aureobasidium microstrictum*, *Cladosporium tenuissimum*, *Cylindrocarpon destructans*, *Exophiala jeanselmei*, *Fusarium moniliforme*, *F. solani*, *Mortierella hyalina* and *Scytalidium lignicola*. Further perennial investigations are required for regularity estimation, because the fungal development and survival strongly depend on season alternation.

The surface of metals due to formation of a corrosion product film undergoes permanent changes in the superficial chemical compositions and morphology. However, frequently found fungal species (*Alternaria alternata*, *Aspergillus niger*, *Aureobasidium*

Table 4. Fungal species detection frequency (%) on metal plates during 12 months of exposition in five different sites

Fungal species	Detection frequency on metal plates, %				
	Total	Al	Cu	LCS	Zn
<i>Alternaria alternata</i> (Fr.) Keissl.	25.5	34.0	14.0	26.0	28.0
<i>Alternaria solani</i> Sorauer	2.5	4.0	2.0	4.0	0.0
<i>Alternaria tenuissima</i> (Kunze ex Pers.) Wiltshire	3.0	2.0	2.0	2.0	6.0
<i>Arthrinium phaeospermum</i> (Corda) M. B. Ellis	4.5	8.0	4.0	2.0	4.0
<i>Aspergillus flavus</i> Link	2.0	0.0	2.0	0.0	6.0
<i>Aspergillus fumigatus</i> Fresen.	2.5	4.0	2.0	4.0	0.0
<i>Aspergillus niger</i> Tiegh.	27.5	20.0	38.0	24.0	28.0
<i>Aspergillus penicilloides</i> Speg.	3.0	6.0	0.0	4.0	2.0
<i>Aspergillus terreus</i> Thom	2.0	2.0	2.0	2.0	2.0
<i>Aureobasidium microstrictum</i> (Bubak) W. B. Cooke	6.5	8.0	4.0	6.0	8.0
<i>Aureobasidium pullulans</i> (de bary) G. Arnaud	16.5	16.0	4.0	36.0	10.0
<i>Botrytis cinerea</i> Pers. et Fr.	3.0	4.0	0.0	8.0	0.0
<i>Chrysosporium merdarium</i> (Link ex Grev.) J. W. Carmich.	2.5	2.0	0.0	4.0	4.0
<i>Cylindrocarpon destructans</i> (Zinssm.) Scholten	4.0	8.0	2.0	10.0	0.0
<i>Cladosporium cladosporioides</i> (Fresen.) G. A. de Vries	26.0	28.0	20.0	28.0	28.0
<i>Cladosporium herbarum</i> (Pers.) Link ex Gray	16.0	22.0	14.0	16.0	12.0
<i>Cladosporium sphaerospermum</i> Penz.	4.0	6.0	2.0	2.0	6.0

Table 5. Values of constants A , A_{TOW} and b in equation (2) for various metals exposed to different test sites

Metal	Constants	Test site				
		Urban 1	Urban 2	Rural 1	Rural 2	Marine
Al	A	0.065	0.077	0.38	0.44	0.077
	A_{TOW}	0.141	0.170	0.129	0.087	0.330
	b	0.36	0.36	0.38	0.44	0.78
Cu	A	1.31	0.55	1.31	1.01	2.40
	A_{TOW}	4.94	2.88	8.52	4.84	14.28
	b	0.51	0.65	0.84	0.70	0.73
Zn	A	1.66	1.74	3.25	2.97	4.13
	A_{TOW}	8.26	6.62	10.30	10.52	11.35
	b	0.51	0.42	0.35	0.38	0.49
LCS	A	17.23	6.36	27.27	6.21	47.35
	A_{TOW}	93.65	62.52	54.66	27.4	134.28
	b	0.62	0.84	0.51	1.08	0.56

pullulans, *Cladosporium cladosporioides*, *C. herbarum*, and *Paecilomyces parvus*) were isolated in each soiling. Some species, such as *Aspergillus fischeri* (Wehmer, Malloch et Cain), *Fusarium graminearum* (Schwabe), *Rhizopus oligosporus* (Saito), *Trichosporiella hyalina* (Kamyschko ex W. Gams et Domsch) and others were detected only at the initial periods of metal sample exposure (after 1 and/or 4 months). Fungal species such as *Acremonium strictum* (W. Gams), *Chaetomium globosum* (Kunze), *Costantinella terrestris* (Link ex Fr.) S. Hughes, *Mucor mucedo* (Fresen.), *M. piriformis* (A. Fisch.), many representatives of the genus *Penicillium* and others were detected on the metal surfaces only on longer exposures, possibly because of the chemical and/or struc-

tural changes in the metal surface. The atmospheric conditions (air temperature, precipitations, pollutant concentration) also should be taken into consideration.

Statistical analysis of corrosion data

The statistical analysis of the metal atmospheric corrosion test results is frequently made using the exponential function [31–36]:

$$K = A t^b, \quad (2)$$

where K is the specimen corrosion rate (mass losses in g m^{-2}) over the period t (time in years), A is the corrosion rate during the first year, and b

stands for exposure site dependent constants, which for a given set of experimental data are functions of the nature of metal, the meteorological and aerodynamic parameters of the atmosphere and the properties of corrosion products. The constant A is related to atmospheric parameters, whereas the exponent b characterizes the passivity (protective) properties of the corrosion product film. Metal corrosion occurs only in the presence of an electrolyte layer on the surface, therefore it is reasonable in equation (2) to use TOW instead of the time of exposure t [31, 35]. In that case, the constant A_{TOW} means the corrosion loss during one year of wetness.

The values of constants A , A_{TOW} and b were calculated by best fit regression analysis for each spe-

Table 6. Values of constants c_1 , c_2 , c_3 in equation (3) for various metals exposed in different test sites, taking into account dry pollutant deposition rates

Metal	Coefficient			Regression coefficient
	c_1	c_2	c_3	
Al	1.5	1.62	-0.97	0.91
Cu	1.98	-1.94	2.34	0.92
Zn	3.85	-3.67	3.89	0.83
LCS	1.6	1.68	-1.73	0.87

Table 7. Values of constants c_1 , c_2 , c_3 in equation (3) for various metals exposed to different test sites, taking into account wet pollutant concentrations

Metal	Coefficient			Regression coefficient
	c_1	c_2	c_3	
Al	0.18	-0.25	0.14	0.91
Cu	4.1	-3.5	3.78	0.89
Zn	10.2	-4.41	2.55	0.90
LCS	1.23	-0.87	3.2	0.87

cimen exposure site, and the data obtained are listed in Table 5. The regression coefficients were not lower than 0.9 and 0.85 for all determined A_{TOW} and A constants, respectively. As might be expected, the determined A_{TOW} values were significantly higher than those of A . Moreover, the highest values of both constants were obtained under marine conditions. The following sequence of A_{TOW} values in all test sites was determined: (Al) $A_{TOW} <$ (Cu) $A_{TOW} <$ (Zn) $A_{TOW} <$ (LCS) A_{TOW} with one exception, (Zn) $A_{TOW} <$ (Cu) A_{TOW} in the marine test site. It is also evident that the values of constants A and A_{TOW} strongly depend on the test site location. The following sequence is valid: A_{TOW} (urban) $<$ A_{TOW} (rural) $<$ A_{TOW} (marine).

The highest values of exponent b were also determined for the steel samples. It is well known that atmospheric corrosion products of steel do not exhibit a good protective capacity. In general, the highest values of b for the majority of metals were determined for samples exposed to the marine test site conditions [35].

The constant A_{TOW} was determined in order to apply it for evaluation of pollutant influence on the corrosion rates of metals. It is known that SO_2 and Cl^- are the main corrosion promoting factors [35, 37] and that the constant A_{TOW} could be approximated as a linear function of SO_2 and Cl^- deposition rate:

$$A_{TOW} = c_1 + c_2 [SO_2] + c_3 [Cl^-]. \quad (3)$$

The values of constants c_1 , c_2 , c_3 in equation (3) were determined taking into account dry and wet

deposition rates of pollutants. The results are listed in Tables 6 and 7. A detailed evaluation of atmospheric parameter influence on metal corrosion requires data on more than one year of exposure. Nevertheless, several preliminary conclusions may be drawn from one-year exposure data.

Taking into account the dry deposition of a pollutant, the values of the calculated constants c_2 and c_3 (Table 6) imply that sulphur compounds (coefficients at c_2 are positive) accelerate Al and steel while Cl^- ions (coefficients at c_3 are positive) Cu and Zn corrosion. In the case of application of wet pollutant deposition, Cl^- ions accelerated the corrosion of all metals studied. The regression coefficients in determining the parameters of equation 3 were higher than 0.8.

An attempt was made to evaluate the influence of nitrogen compounds, assuming, that A_{TOW} may be approximated as a linear function of SO_2 and Cl^- and NO_2 deposition rates:

$$A_{TOW} = c_1 + c_2 [SO_2] + c_3 [Cl^-] + c_4 [NO_2]. \quad (4)$$

A statistical analysis of the corrosion and the pollutant data was performed, however, the relatively low regression coefficients (< 0.60), did not allow reasonable conclusions regarding the influence of nitrogen compounds on atmospheric corrosion. It seemed that there were no corrosion data enough for analysing the influence of more than two factors. Therefore, the obtained results are not presented and the analysis will be repeated after more data on atmospheric corrosion are obtained.

Atmospheric corrosion and microbiological environment relationship

The highest variety of fungal species was detected on steel plates, which exhibited also the highest corrosion rates, confirming that steel corrosion products are not toxic for many fungal species [30]. Besides, fungal mechanical entrenchment (consolidation) is easier on a more corroded surface. The lowest number of fungal species was detected on Cu plates, indicating fungicidal properties of copper corrosion products.

A great dependence of fungal species variety on metal nature was observed in our study. In this sense, species variety on Al and LCS plates is more comparable without regard to different corrosion degrees. Nevertheless, some fungal species (*Alternaria alternata*, *Aspergillus niger*, *Aureobasidium pullulans*, *Cladosporium cladosporioides*, *C. herbarum* and *Paecilomyces parvus*) were detected on all study metals exposed to different environmental conditions of test sites and different corrosion degrees. These species could be supposed to be able to survive on or adapt to such substrata.

Because of the contribution of different parameters to atmospheric corrosion it is difficult to determine the influence of any single factor in the field

Table 8. The amount of bacteria and fungal species (kfv/ml) in precipitations from metal samples exposed (1 year) to the different test sites

Test site	Metal	Number of bacteria (kfv/ml)	Number of fungi (kfv/ml)
Rural 1	Al	$(516.78 \pm 114.52) 10^3$	8.3 ± 1.5
	Cu	$(0.26 \pm 0.14) 10^3$	440.2 ± 188.3
	Fe	$(61.85 \pm 12.74) 10^3$	13.3 ± 5.7
	Zn	$(1024.55 \pm 279.88) 10^3$	$(25.7 \pm 14.8) 10^3$
Marine	Al	$(899.52 \pm 254.71) 10^3$	51.3 ± 6.1
	Cu	$(18.89 \pm 124.83) 10^3$	1378.0 ± 574.0
	Fe	$(61.24 \pm 24.51) 10^3$	8.3 ± 1.5
	Zn	$(193.24 \pm 54.71) 10^3$	690.2 ± 14.5
Urban 1	Al	$(75.84 \pm 28.76) 10^3$	21.7 ± 1.7
	Cu	$(0.68 \pm 0.13) 10^3$	1.5 ± 3.8
	Fe	$(190.34 \pm 62.11) 10^3$	13.3 ± 5.7
	Zn	$(387.5 \pm 142.8) 10^3$	$(324.5 \pm 33.3) 10^3$
Urban 2	Al	$(9.96 \pm 2.04) 10^3$	560.0 ± 62.0
	Cu	$(0.042 \pm 0.00) 10^3$	2.4 ± 0.8
	Fe	$(1180.00 \pm 276.20) 10^3$	333.3 ± 152.7
	Zn	$(0.86 \pm 0.30) 10^3$	19.4 ± 5.8

Table 9. Values of constants c_1 , c_2 , c_3 , c_4 in equation (5) for various metals exposed to different test sites, taking into account MIC_1 , the number of bacteria in the precipitation collected from the exposed samples

Metal	Coefficient				Regression coefficient
	c_1	c_2	c_3	c_4	
Al	0.53	-0.55	0.61	-0.69	0.89
Cu	0.50	-0.41	-0.22	0.55	0.91
Zn	-0.66	0.86	-0.16	1.8	0.90
LCS	-2.07	2.10	-1.85	-1.14	0.87

Table 10. Values of constants c_1 , c_2 , c_3 , c_4 in equation (5) for various metals exposed to different test sites, taking into account MIC_2 , the number of fungi in the precipitation collected from the exposed samples

Metal	Coefficient				Regression coefficient
	c_1	c_2	c_3	c_4	
Al	0.52	-0.49	0.72	-0.44	0.81
Cu	0.55	-0.3	0.38	0.28	0.87
Zn	2.61	1.16	1.22	-0.39	0.90
LCS	-1.1	2.10	-1.85	-2.78	0.91

tests. Nevertheless, an attempt has been made to evaluate the effect of pollutants and microorganisms on the corrosion rates of metals exposed to natural conditions. In order to quantify the fungal and bacterial species that might actively participate in corrosion processes, analysis of precipitates collected

from the surface of exposed metals was performed. The results are listed in Table 8; they were analysed together with metal corrosion data. An assumption has been done that the constant A_{TOW} may be approximated as a linear function of SO_2 and Cl^- deposition rates and the number of microorganisms (bacteria or fungi):

$$A_{TOW} = c_1 + c_2 [SO_2] + c_3 [Cl^-] + c_4 [MICx], \quad (5)$$

where MIC_1 is the number of bacteria and MIC_2 is the number of fungi in precipitation collected from the exposed samples. A statistical analysis on the basis of equation

5 has been done and the obtained coefficients are listed in Tables 9 and 10.

The results imply a different effect of microbiological species on the corrosion behaviour of metals. The positive coefficient c_4 for Cu and Zn samples (Table 9) indicates that bacteria may exhibit an accelerating effect on corrosion rates. By contrast, the coefficient for Al and steel is negative due to inhibition effect. Some similar effects for Al (inhibition) and Zn (acceleration) were observed in laboratory tests with different fungi, using electrochemical impedance spectroscopy [38]. The corrosion inhibition effect for Al can be stated also on the basis of fungal effect analysis on corrosion rates (c_4 in equation 5 is negative) (Table 10).

CONCLUSIONS

The corrosivity of Lithuanian atmosphere according to ISO classification corresponds to the "low" category.

Wet and dry pollutant (Cl^- and sulphur compound) deposition rates as well as the time of wetness determined the corrosion rates of metals exposed to natural conditions. The deposition rates of Cl^- (wet and dry) and sulphur / nitrogen (dry) were the highest under marine conditions, while wet sulphur / nitrogen compound deposition was most intensive under urban conditions. Al showed the highest values of time of wetness among all metals, while Zn and Cu samples possessed the lowest ones.

Several species (*Alternaria alternata*, *Aspergillus niger*, *Aureobasidium pullulans*, *Bacillus mycoides*, *Cladosporium cladosporioides*, *C. herbarum*, *Paecilomyces parvus* and *Penicillium frequentans*) were detected

ted on all metals exposed to different atmospheric conditions and on samples with a different level of corrosion damage. These species may be supposed to be able to survive on or adapt to the metal substrate.

Statistical analysis of metal corrosion, time of wetness and pollutant concentration data has shown that dry deposited sulphur compounds accelerate Al and steel while Cl⁻ ions enhance Cu and Zn corrosion rates. Taking into account wet pollutant deposition, it was established that Cl⁻ ions accelerated the corrosion processes of all study metals. The results of statistical analysis indicated that microorganisms may have an accelerating influence on the corrosion processes of Cu and Zn, while corrosion inhibition was characteristic of Al and steel.

ACKNOWLEDGEMENTS

This study was carried out as part of a complex research program supported by the Lithuanian Science and Studies Foundation.

Received 10 December 2004

Accepted 7 February 2005

References

- J. M. Costa and M. Vilarrasa, *British Corr. J.*, **28**, 177 (1993).
- J. R. Vilche, F. E. Varela, G. Acuna, E. N. Codaro, B. M. Rosales, A. Fernandez and G. Moriena, *Corros. Sci.*, **37**, 941 (1995).
- I. Odnevall Wallinder and C. Leygraf, *ibid.*, **43**, 2379 (2001).
- J. J. Santana Rodriguez, F. J. Santana Hernandez and J. J. Gonzalez, *ibid.*, **45**, 799 (2003).
- I. T. E. Fonseca, R. Picciocchi, M. H. Mendonca and A. C. Ramos, *ibid.*, **46**, 547 (2004).
- D. Bengtson Blucher, J.-E. Svensson and L. G. Johanson, *J. Electrochem. Soc.*, **150**, B93 (2003).
- T. E. Graedel, *ibid.*, **136**, 193C (1989).
- J. Tidblad and C. Leygraf, *ibid.*, **142**, 749 (1995).
- R. Lindstrom, J. E. Svensson and L. G. Joansson, *ibid.*, **1496**, B57 (2002).
- S. Oesch and M. Faller, *Corros. Sci.*, **39**, 1505 (1997).
- Z. Y. Chen, S. Zakipour, D. Person and C. Leygraf, *Corrosion*, **60**, 479 (2004).
- Corrosion Mechanism in Theory and Practice, ed. P. Marcus, J. Oudar, Marcel Dekker, 1995, p. 422.
- A. V. Ostapljuk, *Mycology and Phytopathology*, **4(2)**, 192 (1970).
- Mikrobiologiniai medžiagų pažeidimai, A. Lugauskas (sudarė), Vilnius: UAV „Valstiečių laikraštis“, 1997, p. 670.
- J. D. A. Miller, *British Corrosion Journal*, **15(2)**, 92 (1980).
- B. J. Little, R. Staehle and R. Davis, *Biodeterioration and Biodegradation*, **47**, 71 (2001).
- A. Nagiub and F. Mansfeld, *Electrochimica Acta*, **47(13)**, 2319 (2002).
- Z. A. Turkova, *Mycology and Phytopathology*, **12(2)**, 124 (1987).
- E. Z. Kovalj and L. P. Sidorenko, *Mycodestructors of industrial materials*, Kiev: Naykova Dymka, 1989, p. 192.
- W. Sand, *International Biodeterioration and Biodegradation*, **40(2-4)**, 183 (1997).
- ISO 9223: Corrosion of metals and alloys—Corrosivity of atmospheres—Classification, 13 p. 1992.
- ISO 9224: Corrosion of metals and alloys—Corrosivity of atmospheres—Guiding values for the corrosivity categories. 3 p., 1992.
- ISO 9225: Corrosion of metals and alloys—Corrosivity of atmospheres—Measurement of pollution, 10 p., 1992.
- ISO 9226: Corrosion of metals and alloys—Corrosivity of atmospheres—Determination of corrosion rate of standard specimens for the evaluation of corrosivity, 4 p., 1992.
- M. B. Ellis, *More Dematiaceous Hyphomycetes*. Kew: Common. Mycol. Inst., 1976, p. 567.
- K. H. Domsch, W. Gams and T. H. Anderson, *Compendium of Soil Fungi*, London: Academic Press, 1980, p. 859.
- EMEP Manual for Sampling and Chemical Analysis, EMEP/CCC-Report 1/95. Norwegian Institute for Air Research 1995.
- P. J. Sereda, *ASTM Bull.*, **53**, 228 (1958).
- F. Mansfeld and J. V. Kenkel, *Corros. Sci.*, **16**, 111 (1976).
- G. M. Gadd, *New Phytologist*, **124**, 25 (1993).
- M. Benarie and F. L. Lipfert, *Atmospheric Environment* **20**, 1947 (1986).
- P. V. Strelakov and Yu. M. Panchenko, *Prot. of Metals* **30**, 448 (1994).
- E. Julve and L. L. Gustems, *Corros. Sci.* **35**, 1273 (1993).
- I. S. Cole, R. Holgate, P. Kao and W. Ganther, *ibid.*, **37**, 455 (1995).
- R. Ramanauskas, L. Muleshkova, L. Maldonado and P. Dobrovolskis, *ibid.*, **40**, 401 (1998).
- W. Hou and C. Liang, *Corrosion*, **60**, 313, (2004).
- R. Ramanauskas, J. Pérez, L. Muléshkova and F. Corvo, *Pinturas y Acabados*, **209**, 35 (1994).
- E. Juzeliūnas, R. Ramanauskas, A. Lugauskas, M. Samulevičienė, K. Leinartas, E. Ivaškevičė and D. Bridpivienė (to be published).

Rimantas Ramanauskas, Eimutis Juzeliūnas, Algis Narkevičius, Dalia Buėinskienė, Albinas Lugauskas, Dalia Pečiulytė, Loreta Levinskaitė, Vidmantas Ulevičius, Dalia Jasinevičienė

MIKROBINĖS KOROZIJOS TYRIMAI 1. ATMOSFERINĖ KOROZIJA LIETUVOS SĄLYGOMIS

Santrauka

Siekiant įvertinti Lietuvos atmosferos agresyvumą bei nustatyti aerocheminių parametrų ir mikrobiologinės aplinkos įtaką metalų korozijai, buvo vykdomi Al, Cu, Zn ir plieno

atmosferinės korozijos tyrimai pajūrio, kaimo ir miesto sąlygomis. Stebėti ir analizuoti sausi ir drėgni atmosferos teršalai (chloridai, sieros ir azoto dujiniai junginiai ir aerozoliai), drėkinimo laikas, apibūdintos bakterijos ir grybai tiek ant metalo paviršių, tiek lietaus vandenyje, nuplautame nuo eksponuojamų pavyzdžių. Nustatyta, kad Lietuvos atmosferos agresyvumas pagal tarptautinę klasifikaciją atitinka „pe-

mo agresyvumo“ lygį, o metalo atmosferinės korozijos greitą sąlygoja chloridų ir sieros junginių koncentracijos ore ir krituliuose. Buvo aptikta keletas grybų ir bakterijų, kurie išlikdavo gyvybingi ir sugebėdavo prisitaikyti prie koroduojančio metalo. Nustatyta, kad bakterijos gali turėti akcelerojantį korozijos poveiką Cu ir Zn, tuo tarpu Al ir plienui, priešingai, galimas inhibicinis poveikis.