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Study of the deterioration of zinc and copper in different environments of Lithuania

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Investigation of zinc and copper deterioration after 10-year exposure in different environmental sites (rural, marine, industrial) of Lithuania has been completed. Different survival of mycobial communities on corroded zinc and copper at the end of ten-year experiment has been identified. Morphological and structural changes of the surface were evaluated using optical, scanning electron, X-ray diffraction microscopy and wavelength dispersive X-ray fluorescence spectroscopy. The atmospheric corrosion level was determined using the weight loss method. The lowest destruction level of copper samples exposed to industrial environment has been established. Zinc samples indicated the crystalline phases of the zinc base, $Zn_4CO_3(OH)_6 \cdot H_2O$, $ZnSO_4 \cdot 3Zn(OH)_2$ and $Zn_5(OH)_8Cl_2 \cdot H_2O$. The presence of ZnO and $Zn_5(CO_3)_2(OH)_6$ in some sites was detected. Copper samples contained Cu_2O and the crystalline copper phases. In some sites $(Cu, Zn)_2Cl(OH)_3$, $Cu_2Cl(OH)_3$, $Cu_4(SO_4)_2(OH)_6$ and traces of disordered $Na(Si_3Al)O_8$ were detected.

Key words: zinc, copper, deterioration, microanalysis, mycobiota

INTRODUCTION

Atmospheric corrosion of metals is affected by various environmental factors. The influence of temperature fluctuation and exposure to UV light, acidic rains, ozone, wind, the presence of typical pollutants (SO_2, Cl^-, NO_2, CO_2, etc.) in the atmosphere and microbial metabolism of the surface led to changes of its chemical and physical characteristics [1–7].

Nowadays, the role of microorganisms has been sufficiently studied. Metals and their compounds can interact with mycobiota in various ways depending on the metal, organism species and environment, while mycobiota metabolitic activity can also influence speciation and mobility [8–11].

As microbial survival depending on the environment is determined by their metabolism peculiarities under concrete conditions and their ability to transform and adapt their enzymatic systems to specific assimilation processes, these processes can change the type and concentration of ions, pH values, oxidation-reduction potential of the classical electrical interface [12–15]. Moreover, the elemental composition of the substratum (e. g. carbon, phosphorous, sulphur, metal content) may govern the initial establishment, growth and survival of mycobial communities [16–19]. The investigation of fungal survival is especially important when these fungi are potential candidates to produce mycotoxins. We have previously detected the total number of 172 fungal toxins (161 species) from 74 genera after the one-year exposure of metals to different types of environments [2, 20]. It has been shown that some species or specific composition of mycobiota may participate in the metal atmospheric corrosion process. It should be pointed that fungi differ in their interaction with metals depending upon the immediate environment and metabolic characteristics of the organism. Because oxide surfaces as the environmental interface play an important role in several chemical and biological processes, much attention has been devoted to the characterization of destruction products formed on the zinc and copper surface [1, 3, 4, 6, 7, 21, 22].

Since zinc and copper play an important role in technical applications, multiple studies have been completed to explain, predict and mitigate the problems of their corrosion. These investigations determine the deterioration of zinc and copper exposed in different environmental sites in Lithuania over a 10-year period. Also the present research provides information about the survival of mycobial communities and their response to the deterioration level of metals.

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EXPERIMENTAL

Atmospheric corrosion studies of zinc and copper were carried out in the following three sites on the territory of Lithuania: Molėtai–Kulionys (rural, R), Neringa–Preila – the Baltic Sea shore (marine, M), Vilnius–Visoriai (industrial, I) in different periods up to 10 years (May 2002 – November 2012). The aggressiveness of the tested sites was estimated from the pollution levels and weather factors according to ISO standards 9223, 9224, 9225, 9226 [2, 23]. The corrosivity of the Lithuanian atmosphere corresponds to the "low" category. Specimens exposed to the standard room condition (HN 69:2003) were used as the reference (control, C). The study was performed on zinc (99.5 Zn wt-%) and copper (99.5 Cu wt-%) metal plates 100 × 150 × 3 mm in size. All experiments were repeated three times.

For corrosion tests the specimens were exposed on south-oriented metallic stands and situated at an angle of 45° to the horizon facing south. To determine the total metal mass loss (Δm) due to corrosion, the products formed during the process were removed by using the methods and the procedure described in the ISO 8407:2009 standards. For microbiological tests fungi were isolated from the metal plates by direct isolation from the surface using a sterile metal needle. Malt extract agar was used for cultivation of fungi [2]. Plates of the known area were suspended in saline (85% NaCl) and were shaken for 3 min. 0.1 ml of suspension was set into a Petri dish on malt agar enriched with 0.5 g l^{-1} of chloramphenicol. Samples were incubated for 5–7 days at 26 ± 2 °C. The variety of species was studied using the factor extraction turn for the maximal dispersion run, minimum Eigen value 1. The heterogeneity or interaction G test was used [18, 24].

Morphological changes in the surfaces of metals were evaluated by using a scanning electron microscope EVO 50 EP (Carl Zeiss SMTAG, Germany). Chemical analysis was performed using the wavelength dispersive X-ray fluorescence spectroscopy (WDXRF) method. A spectrometer Axios MAX (PANalytical, Netherlands) was used. X-ray diffraction (XRD) patterns were recorded using a D8 diffractometer (Bruker AXS, Germany, 2003) with Cu K_α radiation using a Ni/graphite monochromator. A step-scan mode was used in the 2-theta range from 5° to 70° with a step length of 0.02° and a counting time of 5 s per step. Qualitative analysis was performed with EVA (Bruker AXS).

RESULTS AND DISCUSSION

Earlier tests have shown that during the exposure at different sites of Lithuania on zinc plates 79 species from 43 genera dominated, while on copper plates 50 species from 26 genera dominated. Fungi from genera *Aspergillus, Penicillium, Scopulariopsis, Paecilomyces, Trichoderma, Fusarium, Rhizomucor, Rhizopus, Mucor, Alternaria, Aureobasidium, Phoma, Cladosporium, Oidiodendron* were most abundant on both zinc and copper. *Penicillium* genus was most greatly represented. Changes in the mycobiotical morphology of fungi and an increased number of sterile mycelium (*Mycelia sterilia*) were observed on both zinc and copper [2, 20]. A variety of mycobiota detected after 10 years of exposure (Table 1) was compared with the variety of the mycobiota diversity determined earlier.

Table 1. **Detected fungi species on the surface of zinc and copper plates after 10 years of exposure to rural (R), marine (M) and industrial (I) environments, new deposited (X) and survived (Y) fungi**

Fungal species	**Zn**			**Cu**		
	Environments					
	(R)	**(M)**	**(I)**	**(R)**	**(M)**	**(I)**
Acremonium kiliense				X		
Actinomyces sp.					X	
Alternaria alternata	Y	Y				Y
Alternaria tenuissima	Y					
Aspergillus clavatus				Y		
Aureobasidium pullulans			Y			Y
Chrysosporium merdarium	Y					Y
Candida albicans					Y	
Candida gobrata			X			
Cladosporium cladosporioides		Y				Y
Cladosporium herbarum	Y		Y			Y
Cladosporium sphaerospermum		Y			Y	
Curvularia lunata		X				
Fusarium oxysporum	X					
Fusarium solqni	X					
Paecilomyces parvus	Y	Y		Y		
Penicillium commune			X			
Penicillium puberulum	X					
Rhodotorula rubra						Y
Sclerotinia sclerotiorum		X				
Scopulariopsis brumptii	X					
Sporotrichum olivaceus	X					
Stachybotrys chartarum			X			
Trichoderma polyspora		X				
Mycelia sterilia	Y	Y	Y	Y	Y	Y

The viability results for fungi after 10 years of exposure on zinc revealed that *A. alternata, C. herbarum* and *P. parvus* survived under different types of environments. In some environments *Ch. merdarium* (M) and yeast-like fungus *A. pullulans* (I) were repeatedly detected. New fungi mostly in the (R) environment were obtained which soiled lots of organic pollution.

Meanwhile, the growth of mycobiota colonies in different environments on copper was uneven and sparse. This was assumed related to destructed copper action as fungal growth poison. The following species were repeatedly revealed at certain test sites: *A. alternata* (I), yeast-like fungus *A. pullulans* (I), *A. clavatus* (R), *C. albicans* (M), *Ch. merdarium* (I), *C. cladosporioides* (I), *C. herbarum* (I), *C. sphaerospermum* (M), *P. parvus* (R), yeast-like fungus *Rh. rubra* (I). It should be noted that under the (I) conditions yeast-like fungi *A. pullulans* and *Rh. rubra* were abundant.

In all variants of the experiment *Mycelia sterilia* was detected.

The data of SEM morphological studies are given below (Fig. 1). SEM imaging has shown that there was no mycobial growth detected on plates C. On zinc exposed to the (R) environment tangles of stretching mycobiota mycelium and a hoard of mineral substances around them were seen (Fig. 1, Zn). On the surface exposed to the (M) environment threads of mycobiota mycelium interspersed into deposits were observed. On zinc exposed to the (I) environment *Mycelia sterilia* as well as *Aureobosidium* and *Candida* colonies were identified. In the (R) environment a rich biolayer and separate fragments of biota could be seen.

Meanwhile a lot of mineralization products on copper exposed in (M) and (I) environments could be observed (Fig. 1, Cu). It has been reported in many studies that the accumulation of metal by fungal cultures is specific. Some fungi can also precipitate metals in amorphous and crystalline forms, such as secondary mycogenic minerals [10, 18, 25].

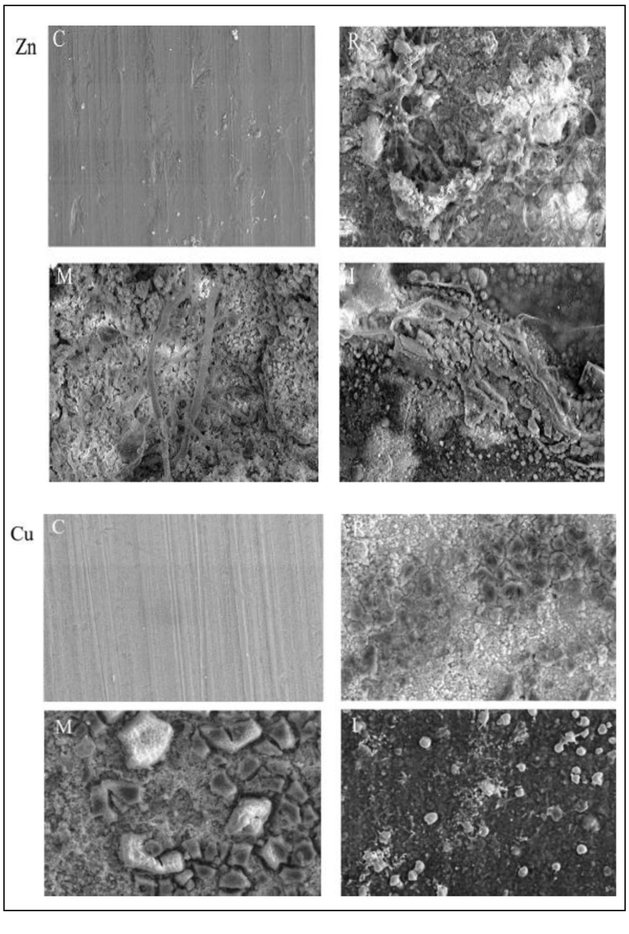

Fig. 1. SEM images on the surface of zinc (Zn) and copper (Cu) after 10 years of exposure to rural (R), marine (M) and industrial (I) environments. Reference sample (C)

Quantification of elemental components was determined in accordance with the WDXRF spectroscopy results (Table 2). The distribution of elements occurring on the surface after 10 years of exposure in the logarithmic scale is shown in Fig. 2. The WDXRF data showed that the surface elemental components both exposed to the natural environment and a sample (C) markedly differed from those of bare metals. An increased quantity of calcium 0.535 wt-% in copper plates in the (I) environment (Table 2) suggests that here surface biomineralization takes place. It should be noted that the samples after exposure became siliceous. The elemental analysis has shown that silicon was present in both samples (C) in minor quantities in comparison with all exposed samples (0.029 wt.% silicon on zinc and 0.011 wt.% silicon on copper). In the samples exposed near the Baltic shore the greatest quantities of chlorine that promote corrosion were typically found. A markedly increased oxygen quantity as compared to that in samples (C) evidences a strong oxidation and deterioration of zinc and copper surfaces (Fig. 2).

It should come as a norm that copper (standard potential E° = +0.34 V) corrosion rates are markedly lower than those obtained for zinc (E° = –0.76 V) (Fig. 3). In the (M) environment the highest zinc and copper Δm due to corrosion was determined [1, 4, 7, 21]. However, despite the modest oxygen mass gain (26.4 wt-%) in the (I) environment (Table 2) the lowest destruction level of copper in the (I) environment compared with (R) and (M) sites was established (Fig. 3b). Δm measurements have shown that copper destruction, in contrast to that of zinc, at the last exposure period between 5 and 10 years decreases (Fig. 3) and that the destruction courses in different experiments were diverse.

The results from the XRD microscopy analysis established the compositional differences of the atmospheric corrosion products formed in different environments on zinc and copper (Fig. 4). In the XRD images of the zinc plates exposed to all environments zinc basis lines were seen (PDF 4-831). The lowest intensity of zinc basis lines in the (M) environment suggests the greatest surface changes (Fig. 4a). Zinc exposed to the (R) environment had the most intensive zinc lines. The zincite zone (PDF 36-1451) initially formed under the influence of the atmospheric oxygen was detected only on zinc under the (M) and (I) environments. In all the studied environments on the surface zinc carbonate hydroxide hydrate $Zn_4CO_3(OH)_6 \cdot H_2O$ (PDF 11-287) was detected (mainly on the plates exposed to the (M) environment), as well as a minor quantity of hydroxysulfate $ZnSO_4 \cdot 3Zn(OH)_2$ (PDF 36-1451) and simonkolleite $Zn_5(OH)_8Cl_2 \cdot H_2O$ (PDF 7-155) [7, 26, 27]. The surface exposed to (R) and (I) environments is generally composed of the mineral compound hydrozincite $Zn_5(CO_3)_2(OH)_6$

Table 2. **The quantity of microelements on zinc and copper surface after 10 years exposure to rural (R), marine (M) and industrial (I) environments,wt-%**

Elements	**Metal matrix**		**(C) reference**		**Environments**					
					(R)		**(M)**		**(I)**	
	Zn	**Cu**	**Zn**	**Cu**	**Zn**	**Cu**	**Zn**	**Cu**	**Zn**	**Cu**
O			3.260	0.585	28.012	25.850	33.200	24.300	29.020	26.400
Na			0.080	0.042	0.102	0.329	0.682	2.470	0.123	0.234
Mg	0.072		0.115	0.021	0.137	0.024	0.268	0.287	0.144	0.099
Al	0.180	0.111	0.014	0.005	0.533	0.047	0.890	0.067	0.725	0.071
Si	0.218	0.172	0.029	0.011	0.447	0.134	1.560	1.170	0.784	0.616
P			0.004	0.027	0.673	0.028	0.281	0.129	0.457	0.056
S			0.041	0.015	0.201	2.730	0.164	0.209	0.283	2.780
Cl			0.057	0.016	0.260	0.757	0.608	3.770	0.378	1.070
K			0.006	0.003	0.040	0.051	0.110	0.061	0.074	0.088
Ca			0.009	0.004	0.022	0.043	0.079	0.051	0.032	0.535
Fe	0.013	0.021	0.013	0.014	0.075	0.027	0.271	0.033	0.190	0.053
Ni			0.019	0.011	0.017	0.014	0.015	0.012	0.016	0.013
Cu	0.014	99.54	0.011	99.200	0.017	69.900	0.024	67.400	0.021	67.900
Zn	99.50	0.092	96.250	0.044	69.360	0.046	61.700	0.045	67.600	0.082
Pb					0.107		0.145		0.160	
Sn		0.055	0.090	0.018		0.021		0.019		0.018

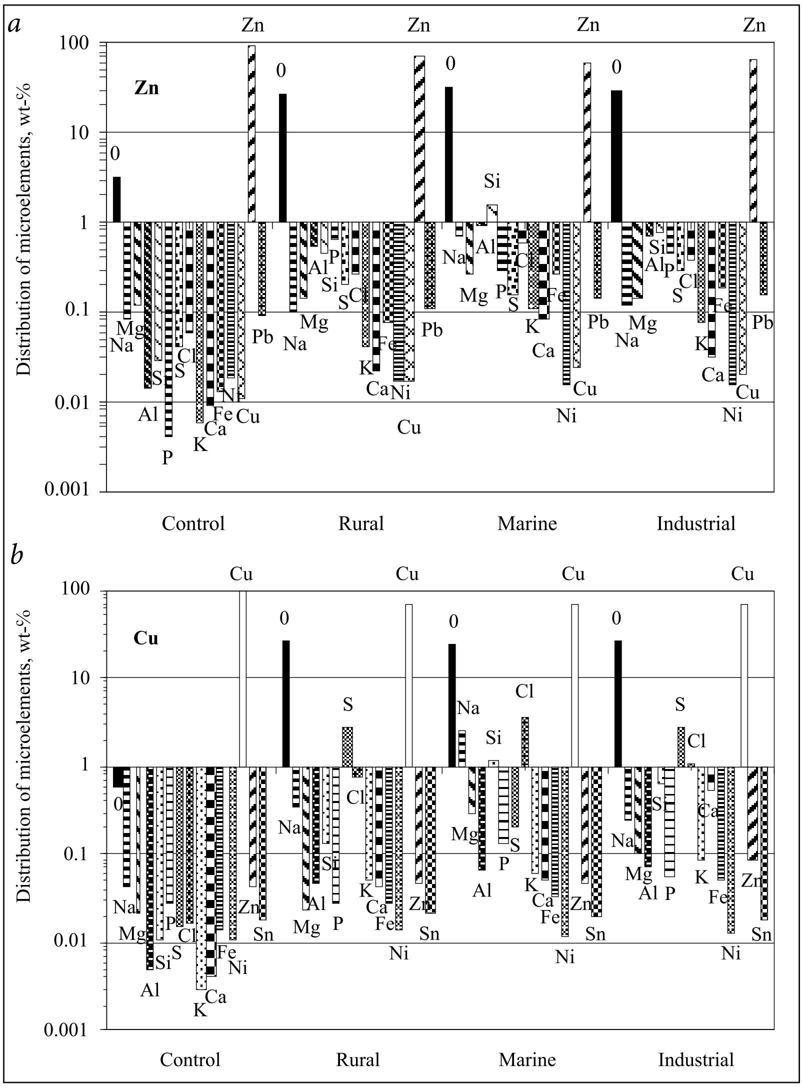

Fig. 2. Distribution of microelements after 10 years of exposure to rural (R), marine (M) and industrial (I) environments: (*a*) zinc; (*b*) copper, wt-%

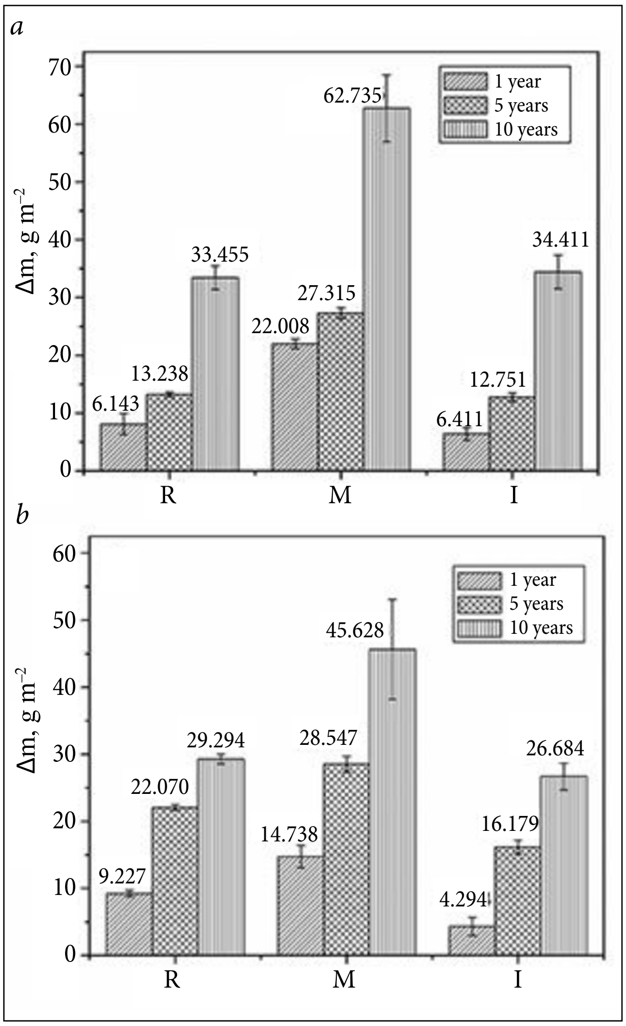

Fig. 3. Total mass loss of metals (Δm) after 1, 5 and 10 years of exposure to rural (R), marine (M) and industrial (I) environments: (*a*) zinc; (*b*) copper, g m^{-2}

(PDF 19-1458) [21, 28]. It has been noted that the mentioned biomineralization product gives an anti-fouling film on the zinc surface [21]. The silicon compounds were not detected by the XRD analysis and this was assumed that silicon compounds existed on the surface in a non-crystalline alumino-silicates form.

In the XRD patterns on copper the formation of crystalline copper and cuprite Cu_2O (PDF 5-667) in all the samples has been observed (Fig. 4b). In the chloride-rich (M) environment compounds possessing a chlorine Cu-Zn solid solution $(Cu,Zn)_2Cl(OH)_3$ (PDF 50-1558), geomaterial atacamite $Cu_2Cl(OH)_3$ (PDF 50-1559) and considerable quantities of mineral brochantite $Cu_4(SO_4)_2(OH)_6$ (PDF 43-458) were formed [1, 4, 29, 30]. In the (I) environment traces of disordered albite $Na(Si_3Al)O_8$ (PDF 10-393) were observed. It should be noted that due to $Na(Si_3Al)O_8$ the formation of inorganic polymer gels occurred [31]. It may be supposed that the nanostructural development of minerals and geopolymers in the (I) environment hindered environmental aggressiveness to the metal surface.

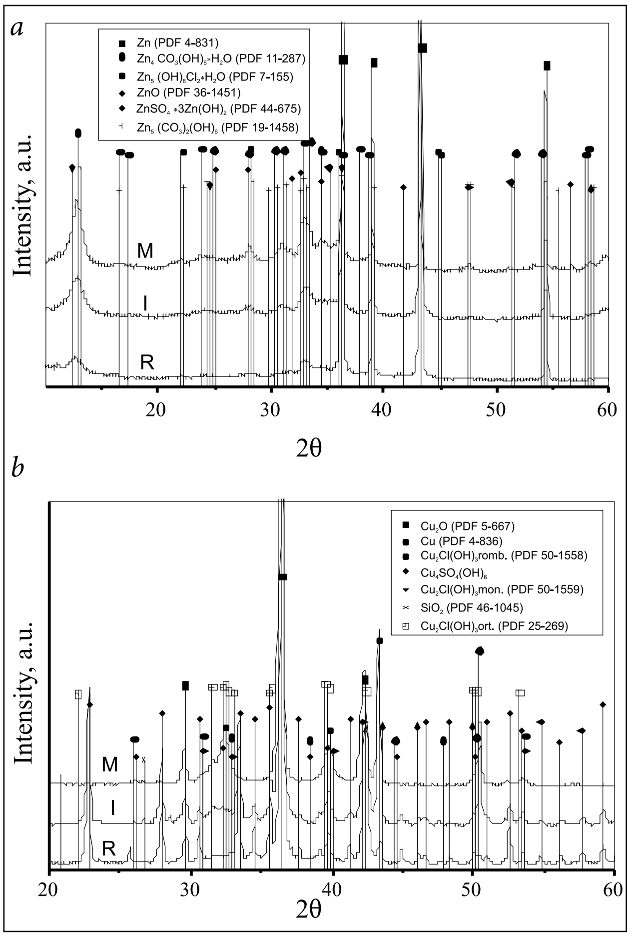

Fig. 4. XRD pattern after 10 years of exposure to rural (R), marine (M) and industrial (I) environments: (*a*) zinc; (*b*) copper

CONCLUSIONS

Different survival of mycobial communities and its impact on the structural properties of zinc and copper after 10-year exposure in the Baltic region (R), (M) and (I) environments has been determined. At the end of the 10-year experiment *A. alternata, C. herbarum, P. parvus* mostly survived on zinc. The composition of mycobiota colonies species on copper in different environments was sparse and uneven. In the (I) environment yeast-like fungi *A. pullulans* and *Rh. rubra* abundantly survived on the copper surface. All zinc samples indicated the crystalline phases of the zinc base, $Zn_4CO_3(OH)_6 \cdot H_2O$, $ZnSO_4 \cdot 3Zn(OH)_2$, and $Zn_5(OH)_8Cl_2 \cdot H_2O$. The presence of ZnO and $Zn_5(CO_3)_2(OH)_6$ was detected only under some conditions. All copper samples contained Cu_2O and crystalline copper phases. In some sites $(Cu,Zn)_2Cl(OH)_3$, $Cu_2Cl(OH)_3$, $Cu_4(SO_4)_2(OH)_6$ and traces of disordered $Na(Si_3Al)O_8$ were detected. It should be noted that the lowest destruction level of copper samples, which were exposed to the (I) environment, has been established.

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CINKO IR VARIO KOROZINIO PAŽEIDIMO TYRIMAS SKIRTINGUOSE LIETUVOS REGIONUOSE

Santrauka

Cinko ir vario bandinių koroziniai pažeidimai įvertinti po 10 metų įvairių Lietuvos aplinkos sąlygų (agrarinių, jūrinių, pramoninių) poveikio. Nustatyta, kad mikobiotų, esančių cinko ir vario paviršiuose, įvairovė priklausė nuo aplinkos. Morfologiniai ir struktūriniai paviršiaus pokyčių tyrimai atlikti naudojant optinį ir skenuojantį elektroninį mikroskopą, cheminė analizė – rentgeno fluorescencinės spektroskopijos su bangų dispersija bei rentgeno difraktometrijos metodais. Atmosferinės korozijos laipsnis buvo įvertintas masės netekties metodu. Mažiausiai pažeisti vario bandiniai buvo pramoninėje aplinkoje. Eksponuotuose cinko bandiniuose rasti cinkas bei kristalinės $Zn_4CO_3(OH)_6 \cdot H_2O$, $ZnSO_4 \cdot 3Zn(OH)_2$, $Zn_5(OH)_8Cl_2 \cdot H_2O$, ZnO ir $Zn_5(CO_3)_2(OH)_6$ junginių fazės. Vario bandiniuose nustatyti varis bei Cu_2O, $(Cu, Zn)_2Cl(OH)_3$, $Cu_2Cl(OH)_3$, $Cu_4(SO_4)_2(OH)_6$ ir $Na(Si_3Al)O_8$ junginiai.