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ScienceDirect
Journal of the European Ceramic Society 27 (2007) 1763–1766
www.elsevier.com/locate/jeurceramsoc

Influence of lichen biocorrosion on the quality of ceramic roofing tiles

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Available online 14 June 2006

Abstract

The lichens actions on the quality of ceramic roofing tiles were investigated in view of textural and microstructure changes. The ceramic roofing tiles, aged 20–30 years, as well as the model systems formed with the additives: Cu-slag powder (10 wt.%) and glass material (5 wt.%), presented the subject of the investigation. The interactions between lichens and ceramic body have been identified as the physico-chemical processes based on the oxalic acid actions excreted by lichens. These caused the ceramic matrix deterioration and consequently their ageing. The thalli of the lichen (*Verrucaria nigrescens*) were examined by scanning electron microscopy and FTIR analyses. The Cu-slag changed the quality of the surface tiles having a positive effect on the tiles response to the oxalic acid action. The textural alternations and the formation of the destructive crystal phase, whewellite, have been slowed down in comparison with the referent ceramic system.

Keywords: Calcination; Surfaces; Corrosion; Clays; Lichen

1. Introduction

Ceramic roofing tiles are systems with a relatively high amount of porosity (water absorption value up to 13 wt.%), therefore, they could be the subject of the physical and biochemical degradation known as ageing. Their exposures to oxygenated solutions initiate chemical and physical reactions whose results are mineral dissolution and crystallization of new phases. Only a few studies have attempted to identify the complex interactions among moisture, lithobiontic (rock-dwelling) organisms and ceramic roofing tiles weathering.[1] These transformations include enzymatic oxidations and reductions as well as the formation of chelates and complexes with proteins, amino acids, organic acids, etc.[2] It was demonstrated that microorganisms transform the crystalline forms as biotite and mica to vermiculite and certain rocks to an amorphous state.[2]

This paper examines the links among epilithic lichens (*Verrucaria nigrescens*), ceramic surface texture and weathering processes. The laboratory experiments were conducted in order to investigate the combined effect of the degree of air pollution (Fe, Cu, Zn and Ni presence), tile surface characteristics and oxalic acid actions on the model ceramic tiles degradation. The glass material (5 wt.%) and Cu-slag powder (10 wt.%), as the additives which could change the quality of the surface tiles and pores distribution, have been used. Only Cu-slag powder made adequate changes of tiles pores distribution which has a positive response to the oxalic acid actions.

2. Experimental

2.1. Real systems

Pressed ceramic roofing tiles of various time of exploitation (20–30 years) as well as the lichens sampled from the surface of the tiles presented the subject of the investigation.

2.2. Model systems

Three types of ceramic systems—RR: referent ceramic system (raw material based on ilite–kaolinite minerals and carbonates); RG: ceramic system based on glass additive (5 wt.%); RS: ceramic system based on Cu-slag (10 wt.%) were prepared on the laboratory scale by the extruded procedure of shaping (12 cm × 8 cm × 0.8 cm). They were stored for 48 h at room temperature and then dried at 110 °C to a constant weight. The obtained samples were fired in a laboratory kiln ($i = 2$ h, $T = 960$ °C) then treated with the defined concentration of oxalic acid (0.01 and 0.1 wt.%) for 28 and 50 days. The aim of this investigation was to simulate the deterioration effect of ceramic

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doi:10.1016/j.jeurceramsoc.2006.05.001

tiles in real conditions (the oxalic acid is one of the fundamental "lichen acids")—accelerated laboratory aging experiments.

The samples characterization was performed by the following methods: phase composition, XRD analyses, Philips PW 1050 Cu Kα; FTIR analyses, spectrophotometer Nexus 670 FT-IR; SEM and EDS investigation, JEOL JSM-6460LV; chemical composition, AAS spectrometer, Pye Unicam SP 191; low temperature dilatation, DuPont Instruments 943; Hg-porosimetry, Porosimeter Carlo Erba 2000.

3. Results and discussion

3.1. Real systems

Within the investigation of the real systems, the content of the defined metals (Fe, Cu, Ni, Zn) in the air dust and in the lichen samples was determined. The air dust and lichen samples were taken from the two zones (I: centre of the town of Kanjiza and II: near the river Tisa). The sampling was done in: autumn (a) and winter (w). Based on the obtained AAS spectrometer results for the two periods, the only difference was observed between the samples of the air dust. The following metal content ranges could be established—autumn period: Fe > Ni > Zn > Cu, whereas for the winter period it was: Fe > Cu > Ni > Zn, Fig. 1. The concentration of the investigated metals in the lichen samples was 5–10 times higher in the samples taken from the centre of the town than in the ones sampled from the river side, Fig. 2. Comparing the quantitative content of the metals in the air dust and in the lichen samples, for the two localities and two sampling periods, only in the winter period (zone I) the significance difference could be noticed: air dust Fe > Cu > Ni > Zn; lichens Fe > Zn > Cu > Ni. It is evident that the content of Fe is the highest among the investigated metals in the two cases. The Cu, Ni and Zn concentrations were changeable due to the locality environmental characteristics. It could be concluded, based on the order of the metal decreasing concentration, that Cu and Ni present the smallest amount accepted by the lichens as apparent toxicants. The very high toxicity of copper depends on the free Cu^{2+} ions in the solutions which could reduce the growth of the lichen photobiont and alter the pigment content.[3,4] This fact was one of the reasons for the application of copper (Cu-slag) as the raw mixture additive with the aim to protect ceramic tiles from lichen growth. The FTIR analyses of the lichens sampled from the surface of the ceramic tiles identified the presence of tetraethyl pyrophosphite $(C_2H_5O)_2POP(OC_2H_5)_2$, calcite, whewellite ($CaC_2O_4\cdot H_2O$) and water. The SEM investigation of the cross section of the system lichen/ceramic tile pointed out a damaged structure formed from the CaO agglomerates,

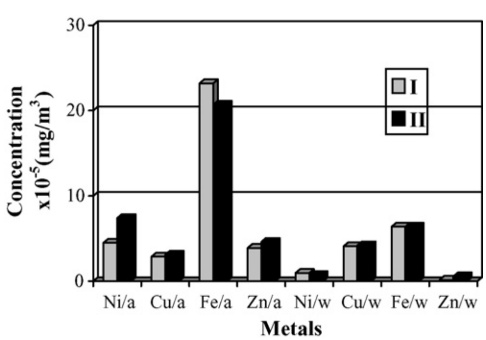


Fig. 1. The metals content in the air dust samples (two temporal periods—a: autumn, w: winter; locations I and II).

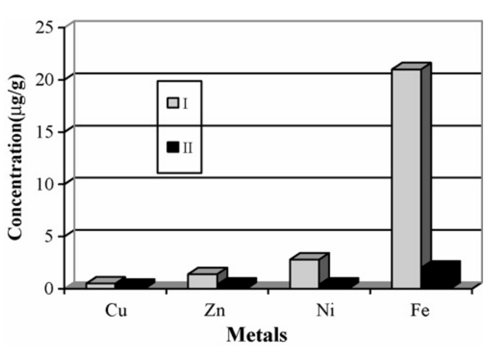
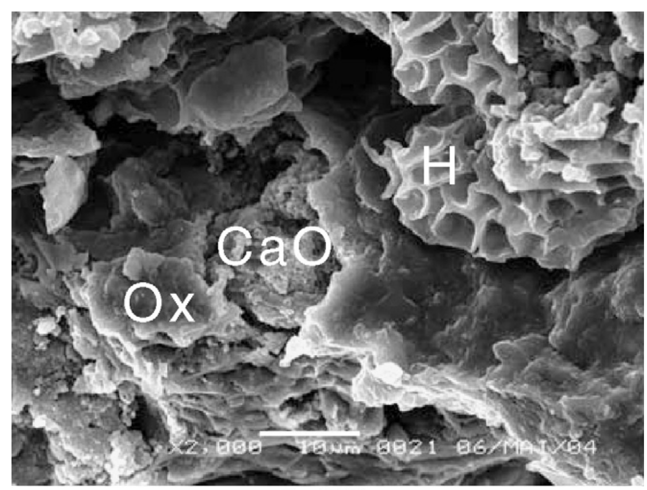
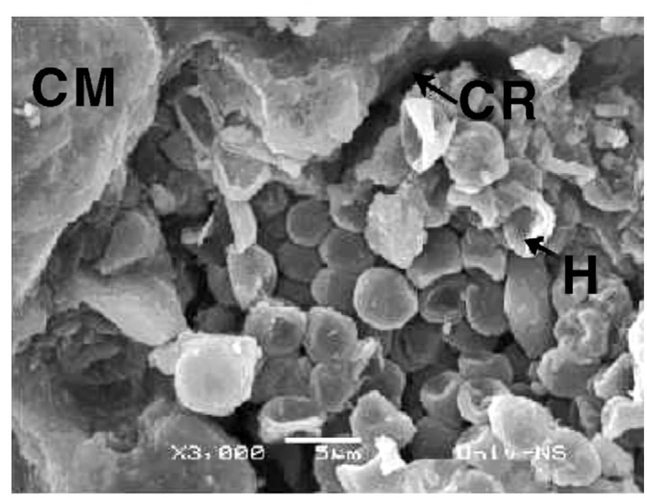


Fig. 2. The metals content in the lichen samples; period of sampling-winter, locations: town center (I) and the river side (II).



3a, x2000



3b, x3000

Fig. 3. (a) SEM micrograph of the cross section of ceramic roofing tile, 2000× (H: hyphae, CaO: calcium-oxide, Ox: oxalate). (b) SEM micrograph of the hyphen penetration into the tile body, 3000× (H: hyphae, CM: ceramic matrix, CR: crack).

Table 1
Chemical composition (wt.%) of the applied additives

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	BaO	B_2O_3	PbO	Na_2O	K_2O
Glass additive	50	6.10	–	2.50	–	0.8	9.3	25	4.8	1.3
Cu-slag	37.1	10.8	0.8	41.8	7.7	–	–	–	0.8	0.7

Table 2
Phase composition of the ceramic model systems

	Phase						
	Quartz	Plagioclase	Hematite	Diopside	Wollastonite	Anorthite	Amorphous phase
RR-referent	33	38	10	4.0	–	–	10–15.0
RG-system	26	44	9.0	4.0	–	–	15–20.0
RS-system	27	28	12.0		7.0	8.0	15–18

calcium oxalate deposits and lichen hyphae penetration of the ceramic tile substrate, Fig. 3. Calcium oxalate usually crystallizes as a monohydrate (whewellite), as is the case in our system, but may also exist in the dehydrated form known as weddelite.[1] The salts excretion on the tile surface causes the tiles to crack, Fig. 3b, the fact which, together with the colour changes of the tile surface, presents serious deterioration phenomenon.

3.2. Model ceramic system RG

The applied glass as the additive, Table 1, activated the thermal decomposition of calcite and dolomite minerals enabling the entrance of a significant amount of CaO and MgO components into the alumno-silicate phase, Table 2. As for the water absorption values no important changes were identified: the referent had 9.88 wt.%, while the modified 8.43 wt.%.[5] Regarding the pores distribution, the main changes were identified in the pores with size radius less than 0.032 μm, which were closed, and in the interval pore with radius above 0.5 μm, the percentage of these pores were increased, Fig. 4.

3.3. Model ceramic system RS

The addition of Cu-slag, Table 1, increased the content of glass phase, Table 2, minimizing surface textural faults (surface cracks). Namely, the pore size radius was changed within the intervals: 0.25–0.50 and 2–4 μm, Fig. 4. As for the changes of the character and content of the crystal phases, the presence of wollastonite and anorthite was noticed, Table 2.

As the radius of lichen hyphae was about of 1.50–5.0 μm,[6] it was obvious that the pores of the diameter less than 3 μm, the case of the RS model system, were not accessible for their penetration. This kind of pores could be function only for lichens colonization. This fact presented the basic reason for approv-

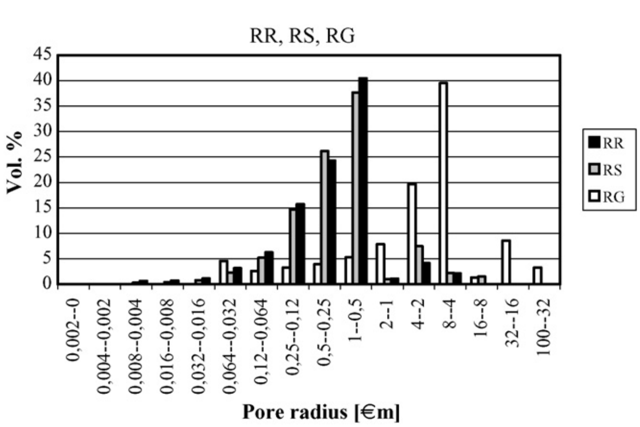


Fig. 4. Pores size distribution of the ceramic model systems.

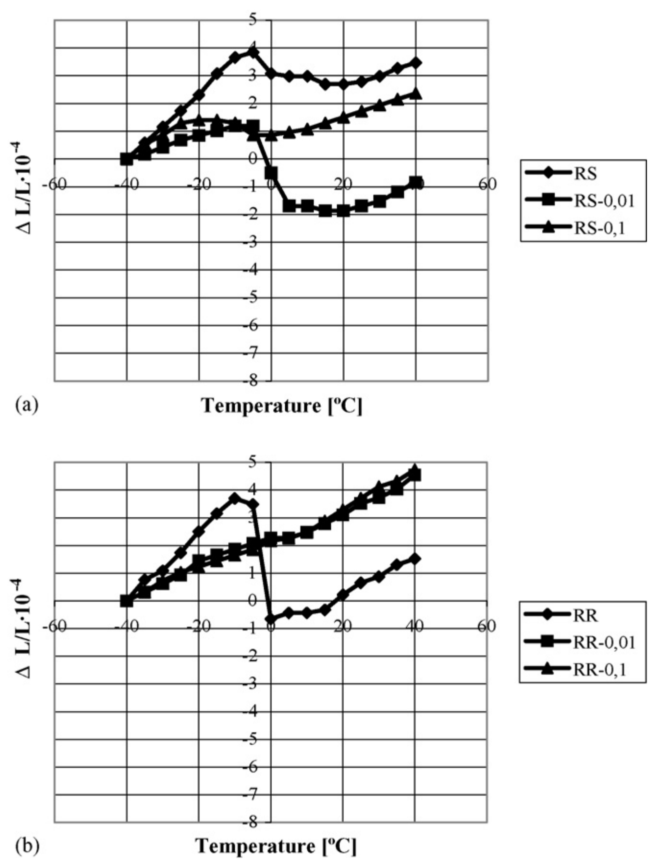


Fig. 5. Low temperature dilatation values of RS (a) and RR ceramic model (b) before and after oxalic acid actions (0.01 and 0.1 wt.%)—all samples were 24 h water saturated.[7]

ing the Cu-slag as the adequate additive. If the lichen hyphae has already entered the RS ceramic body the acid solution execrated by the lichen (mostly consisted by the oxalic acid) in the water presence makes free the Cu ions from the tile surface which in the range of 10^{-10} to 10^{-9} mol/l have toxic effects.[3] Regarding the behaviour of RR and RS samples in the water saturated and freezing conditions of exploitation (−40 up to +40 °C), Fig. 5, the system RS, Fig. 5a, did not even show the brusque linear dilatation changes noticed in the case of the referent RR sample, Fig. 5b. Our previous papers[7] showed that the glass and crystal phase contents in the tile ceramic structure are the dominant parameters which define the linear dilatation value of the samples in the freezing conditions of exploitation. Evidently the phase composition, Table 2, changes of the modified ceramic system RS, besides its biocorrosion resistance, showed a lower freezing dilatation value than the referent one. The Ca-oxalate forms, after the action of low oxalic acid concentrations: 0.01 and 0.1 wt.%, encircling the wall pores decreased the total linear dilatation values of the systems RS-0.01 and RS-0.1.

4. Conclusion

The investigation in the field of the real systems, ceramic roofing tiles, explained the lichen (the species *Verrucaria nigrescens*) actions considering the deterioration phenomenon, while the design of the model ceramic systems enabled the approach to a frost and lichen resistant product. The oxalic acid and frost actions on the ceramic models are manifested by the pore size variations and the Ca-oxalate crust formation (mineral-whewellite) on the pores wall. Their mutual effect, in the case of the ceramic system designed with Cu-slag as the additive, had less effects on the total tile dilatation value during the thawing within the temperature interval (−40 up to +40 °C) and consequently to the relaxed tension of the tile structure. This presented the prime factor for approving the Cu-slag as the additive for designing a ceramic system resistant to the biocorrosion actions of the lichen identified as *Verrucaria nigrescens*.

Acknowledgement

The authors gratefully acknowledge the financial support of this work to the Serbian Ministry of Science and Environment (Contract No. TR.6735B).

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