CASE STUDY – BASEMENT OF THE NATIONAL MUSEUM OF COTROCENI

LUCREȚIA MIU[1], IOANA LIDIA ILEA[2], RODICA ROXANA CONSTANTINESCU[1], MADALINA IGNAT[1], NICOLAE CATRINA[3], MARCEL IONESCU[4], DOINA CREANGĂ[5], EMANUEL VĂCĂLIE[1]

[1]*The National Research & Development Institute for Textiles and Leather - Leather and Footwear Research Institute Division, Bucharest, Romania, rodica.roxana@yahoo.com*

[2]*Cotroceni National Museum, 1 Geniului Blvd., Bucharest, Romania, ioana.ilea@muzeulcotroceni.ro*

[3]*SC RESTAURO CONCEPT S.R.L., Romania*

[4]*SC EUROPLASTIC S.R.L., Romania*

[5]*Bucovina National Museum, Romania*

The work presents a series of aspects related to the degree of biodeterioration of some heritage objects made of inorganic substrates (brick), and the identification of fungi and bacteria with a damaging action on historical materials. Inorganic substrates represented by dust particles from walls and bricks were studied. Fired clay bricks can be severely affected by various macroscopic forms of degradation, as a consequence of chemical, physical-mechanical and biological degradation processes as a result of exposure to aggressive environmental agents. The samples studied (they were collected in compliance with conservation-restoration norms) are part of the "Small Cellar" of the Cotroceni Palace, one of the few spaces where the walls of the old foundation built by Șerban Cantacuzino between 1679-1681, are still preserved. By monitoring the microclimate parameters of the "small cellar" space, it was concluded that there is a greater variation of the relative humidity from 40% to 63%, but also of the temperature from 16℃ to 22℃, fluctuations due to the change of seasons. The samples taken, developed on the culture medium and isolated were analyzed from the point of view of microbiota, and the identified fungi mainly belong to the genera *Mucor* sp., *Alternaria* sp., *Rhizopus* sp., *Fusarium* sp. and *Penicillium* sp. Three different treatments, Clic, Q and Top Crete, were tested and applied on the wall by brushing. After 7 days, samples were collected and tested regarding microbial loading and the results are a proof of the treatment efficiency. The samples were further monitored from a microbiological point of view, but also from the point of view of the appearance given to the bricks after treatment (color change, brick texture, organoleptic properties, etc.).

Keywords: brick, biodeterioration, fungi and bacteria

INTRODUCTION

Heritage goods of an inorganic nature (stone, brick, marble, concrete, etc.) are subject to attack by autotrophic microorganisms (chemosynthesizing and even photosynthesizing). Humidity is a particularly important factor in the biodegradation process, on the one hand, and in the conservation of heritage assets, on the other hand (Johansson *et al.*, 2020). When we talk about humidity, we refer to the relative humidity of the air, but also to the humidity of the substrate; the latter depends a lot on the hygroscopicity of the materials, which is why water content varies. Relative humidity is always associated with temperature (Balksten *et al.*, 2021), these physical factors are particularly important in understanding biodegradation processes.

Bacteria and fungi spread in nature through spores; they resist the action of extreme environmental factors thanks to special resistance structures; under certain conditions they can enter a state of anabiosis (having minimized metabolic processes). Bacteria and fungi spores are transported by air currents along with various impurities of an inorganic or organic nature (dead particulate organic substances).

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Determination of mycobiota diversity: in order to determine mycobiota diversity, the samples taken and isolated were analyzed macroscopically and microscopically to identify specific characteristics. The presence of fungi on inorganic substrates is determined by microclimate conditions.

SHORT DESCRIPTION OF THE SPACE

The space where the tests were carried out is part of the Cotroceni Ensemble, a historical monument of category A, (according to LMI List – Cotroceni Palace – Presidential Administration LMI Code: B-II-a-A-19152), being known as the "Small Cellar", actually one of the few spaces where the walls of the old foundation of Șerban Cantacuzino are still preserved, built between 1679-1681 under the careful supervision of the ruler and entrusted for execution to his brother, Mihai Cantacuzino. This included the Orthodox rite church, the princely houses, the abbot's houses, the monks' cells and other annexes surrounded by an enclosure whose walls gave the whole the appearance of a real fortress. As a result of some calamities such as: fires and earthquakes, damages caused by the establishment of armies in the immediate vicinity or the transformations that occurred according to the taste of the rulers who lived in Cotroceni, the monumental complex has undergone radical changes and a major expansion over time. The descriptions from the chronicles made by foreign travelers, the information from the documents of the Cotroceni monastery and above all, the discoveries of a more recent date caused by the extensive restoration works carried out after the earthquake of 1977, allowed the recomposition of the major data of the Cotroceni architectural ensemble. The area that now houses the Cotroceni National Museum includes two groups of medieval spaces, located on the ground floor and basement, which have maintained their original constructive integrity: the kitchen, the dining room, the cells, the cellars of the princely houses and this cellar which probably belonged to the abbey (Ciho *et al*., 1993). The "small" cellar is located on the north side towards the large kitchen and has an area of 92 m^2. It consists of bays covered with semi-cylindrical vaults with three transverse arches. The walls facing the inner court have four niches above which are as many windows finished in broken arches, unlike those on the opposite side, which end in arches. The entrance to the cellar is through a smaller room, located at a higher level and whose ceiling is semi-cylindrical with broken arches (Ipate *et al*., 2011).

Currently, the "small cellar" houses elements from the lapidary of the Cotroceni National Museum, and it is also here that they want to lay the foundations of a documentation center for decorative arts. Being a space located below ground level and probably due to the concurrence of several factors such as: the age of the preserved elements of the old load-bearing masonry building made of brick with mortar and the fluctuations of humidity and temperature between seasons, degradations have appeared, somewhat specific to these types of rooms. The main types of damage noticed by visual examination (Balksten *et al*., 2021) consist of multiple areas and surfaces with chromatic changes consisting of white and gray spots, efflorescence, exfoliation of the layer covering the brick, degradation of this layer and of the brick itself to pulverization, probably due to the capillarity phenomenon, to atmospheric humidity or even to a potential biological attack; degradations of a physical nature: spalling, separation of layers from the surface, erosion and some mechanical damage at the plinth level.

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Pre-industrial fired clay bricks were manufactured using a manual technology, involving variable firing temperatures and therefore a great heterogeneity of the final material (Franzoni *et al*., 2013). In particular, ancient fired clay bricks are characterized by variable open porosity, ranging from a few percent (for over-fired pieces) to about 45–50 %. Such high porosity makes bricks vulnerable to the same physical-mechanical degradation processes that affect natural stone, such as freeze-thaw cycles, crystallization of soluble salts (efflorescence and sub-efflorescence) and biological growth, mainly due to the presence of moisture in pores and salts.

Although there is a permanent interest for constant monitoring of microclimate parameters and two DH9 dehumidifiers are used, fluctuations in temperature and relative humidity between seasons are noted. Following the recordings made with a TROTEC BC05 thermohygrometer, we observe for the month of February this year an average temperature of 21.3°C and relative humidity of 40.1%, in April an average temperature of 16°C and RH of 50.6%, and in July an average temperature of 22.4°C and an average RH of 63.4%.

EXPERIMENTAL PART

Materials and Methods

1. Preliminary findings regarding the affected areas for sampling (Figure 1):
   - Whitish dust
   - Spots of different colors
   - Brown-black dots of various small sizes, very dense
   - Cracks with material separation


a

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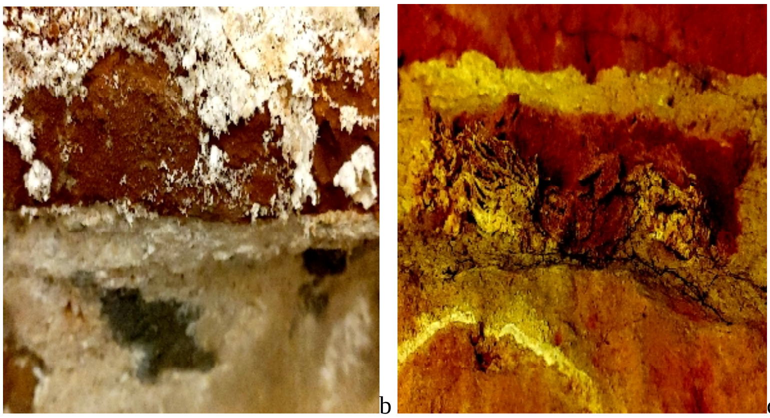

b c

Figure 1. The small cellar - The Cotroceni Ensemble (a), deterioration details (b, c)

2. Working methods for determining the microbial load

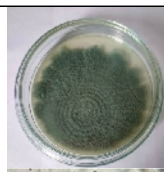
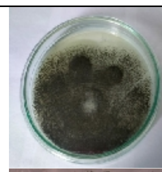
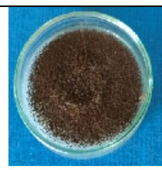
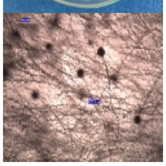
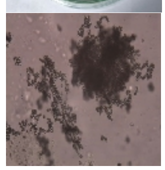
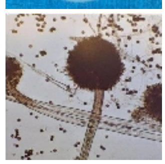
Sampling method: the fingerprint method, used especially for collecting samples from heritage objects of high value. Another method used is that of sampling from different media. The samples obtained from the museum objects are small in size and were taken in compliance with the norms and principles of conservation (Franzoni *et al*., 2013; Vučetić *et al*., 2014).

The culture medium used was Sabouraud dextrose agar, and the plates were incubated for 5-7 days at temperatures of 20-25°C. In order to determine the diversity of the mycobiota, the samples taken and isolated were analyzed macroscopically and microscopically to identify specific characters.

RESULTS AND DISCUSSIONS

In the case of all types of substrates, a considerable fungal load was found, expressed in the number of colonies developed on the culture medium after sampling (Table 1).

Table 1. Microbiological characterisation

Macroscopic images				
Microscopic images Steromicroscop Leica, x50				
Description	*Mucor* sp. *Alternaria* sp.	*Aspergillus fumigatus*	*Penicillium* sp. *Aspergillus niger*	*Aspergillus niger*

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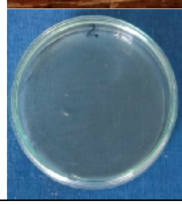
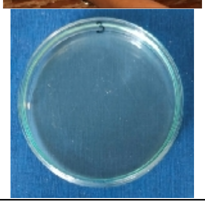
The presence of fungi on inorganic supports is determined by the microclimate conditions. The identified fungi mainly belong to the genera *Mucor* sp., *Alternaria* sp., *Rhizopus* sp., *Fusarium* sp., *Penicillium* sp. Among the frequently encountered genera, *Alternaria* stands out, which is considered a cosmopolitan genus. The species of the genera *Fusarium* and *Penicillium* can develop in the presence of a water content of 6-10% of the substrate up to the relative humidity of 62-65%. The presence of fungi increases the retention capacity of dust particles, associating with the substrate and providing new nutrient resources for fungi.

Three different treatments were tested and applied on the wall by brushing (Table 2).

Table 2. Characterisation in terms of treatments applied

No.	Treatments		
	CLIC Sodium dichloroisocyanurate	Q Solution based on ammonium salts	Top Crete A+B Composition based on polyurethanes
1. Images of treatment application on the brick			
2. Images of Petri plates after 5-7 days from treatment application			

After 7 days, samples were collected and tested regarding microbial loading and the results are a prove of the treatment efficiency. Petri plates images shows no growth of microorganisms.

CONCLUSION

Application of the methodologies proposed in our study for the evaluation of cultural heritage concrete wall is a useful tool for obtaining analytical results that reflect the composition of the entire object.

The results show the isolation and identification of microorganisms involved in the biodeterioration of the concrete wall.

The treatments were monitored at 7 days, 21 days and 1 month and will be under observation for 6 months, 1 year, 2 years, etc., to check the biological effectiveness and the changes that may occur on the treated bricks. Depending on the results obtained, the optimal treatments will be selected or their optimization will be carried out.

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