

## State of the Art and Biodeterioration

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Romania is famous for its historical monuments from the hypogeum till to painted churches. Minister for Culture is involved in protection of Romanian Cultural Heritage.

**Hypogeum and Roman pavement** dating back to the IV century (AC) were discovered by chance, during work to built dwellings. They are located the area named Tomis, a city near to Black Sea.

Some of them were restorated but because of humidity and improper conditions to conservation they are suffering from considerable degradation. Because their artistic value are included in Romanian Cultural Heritage. Poor microbiological studies revealed that microorganisms, humidity and salts are the main causes of deterioration.

**Painted churches** there are in all parts of Romania being specific for the time and techniques of painting (al secco or al fresco) or preparing supports for painting (intonaco and arriccio layers).

Mural paintings could be on the different supports:

- bricks - Casa cu Cerb (Sighisoara city), Sf.Nicolae Domnesc Church (Curtea de Arges);
- wood-Brezoi Church;
- stone - Corbii de Piatra Church

**Frescoes fragments provided by demolition of churches (Vacarasti) or from the churches in a high degree of deterioration (Ocnele Mari)** are also considered belong to the Romanian Cultural Heritage.

*Casa cu Cerb (House with a deer)* located in Sighisoara city dating back to the XIV century contents three dwellings including three rooms with mural painting. Just now in the room nr.2.7 and in the room nr 3.7 there is only a part of it representing flowers. Room nr.3.8 contents much more from the initial painting mural. Although the building was suffered because of the changes and a poor state of conservation, loss of cohesion of support and paint layer we can read just a part of it because most of the painting there is under whitewashing. On the walls there are paintings representing medallions with portraits and names, inscriptions with gothic characters, plants, flowers and baskets with flowers. On the vault there are a men portrait wearing Italian armour and inscription SFORTIA, portrait of an emperor and inscription MAXIMILIANUS and portrait of a knight.

Mural painting dating back to XVII reflecting a glorious past with portraits (Tamerlan, Sforza, Maximilian, Mathias, Ferdinand II) and historical paintings could be a small part of Europe and Transylvania history. Discovering of the whole painting may us to translate inscriptions and to understand Transylvanian art history.

Status of conservation is based on:

- examination was done visually using cold light, both direct and raking and with the aid of stereoscopic enlargement lenses;
- microbiological analyses

Visually examination revealed the following type of alteration:

- cracks in the plaster and bricks;
- lack of plaster cohesion;
- lack of plaster adhesion at various levels;
- powdering paint layers;
- detachment of the paint layer=flaking
- loss of paint layer;
- chromatic alterations;
- natural deposits:dust,insects broods;
- efflorescences;
- black shadows of flowers on the white washing looks like fungal colonies;

colored pitches on pieces of paper used as emergency method to fix pictorial layer but unprotected by any biocide.

Samples for microbiological analyses have been given using indestructible methods: scraping from powdery plasters or bricks, shadow and wiping with a sterile swab from mural painting and whitewashing area.

All samples analyzed content a small number of heterotrophic bacterial units forming colonies (UFC): $2,1 \times 10^2$ /m but a lot of fungi:  $8,4 \times 10^8$ UFC/m. Much more fungal UFC were found on the paper used for secure pictorial layer and in area where from whitewashing grow up shadows of flowers. As we mentioned above mural painting was covered in time by many whitewashings. The last one had a brown draw like flowers. Organic pigments and bone clay used to the last whitewashing, 70% RH, 6,0 pH and 20-28 C0 offered good conditions for fungi like *Cladosporium* sp and *Ulocladium* sp to grow. Significant is a shadow taken off by somebody who passed in that area which shows direction of moving reflected by new fungal colonies developed.

On the vault we also found on the paper bands *Cladosporium* sp, *Ulocladium* sp but mostly *Chaetomium* sp., *Fusarium* sp., *Trichoderma* sp. and *Penicillium* sp.

To establish an emergency treatment, sensitivity of microorganisms from studied samples was tested against Desogen by adding 1-3 % (v/v) in serial dilutions. The best concentration 3% (v/v) was applied with a brush (to prevent spreading of the spores).

Nowadays, the room nr.3.8 is closed, but has got a plan for emergency treatment and for general treatment.

***Sf.Nicolae Domnesc (Saint Nicholas) Church*** is located in Curtea de Arges city aging from XIV century was the first residence of the Romanian Country. It is the first and the biggest ecclesiastic monument from this part of the Romanian Country (the South part of Romania). Mural painting is a valuable example of the beginning of Romanian medieval art and an example of expansion of Byzantine art at the North of Danube. Painting techniques is al fresco. Some repair works has been done in XVIII-XIX century but the consequences of very bad earth quick from 1977 went to start a new program of restoration and conservation.

*The state of preservation of the monument.* External walls are damp after heavy rains and contain efflorescences as a result of salt precipitation and crystallization. On the East wall above the window is easy to see two kind of green spots. Chemical and microbiological analyses suggest that blue-green spots are due to  $\text{CuSO}_4$  flow to the roof and light or black

green are due to *Cyanobacteria*. Also it were found lichens colonies (*Xanthoria parietina*)

Internal walls had different steps of explosion of fungal growth. The first one was after wooden scaffolding has been assembled because the wood was dump and had not treated with a biocide. Next one was after dust brushing and securing loose fragments, cracks and pictorial layer with small steps of fine paper adhering to the wall with CMC (carboxymethylcellulose) when the water was infiltrated into the wall. Rising of RH up to 85% went to dump into the scaffolding and a new cycle of fungal growth. Because of visitors and air currents very easy fungal spores fly and settle down to other uncontaminated surface. It was proposed to close the monument for visitors and to fumigate and to treat the scaffolding with a biocide against fungi. The other one proposal was to remove the wooden scaffolding and to put another one made by metal.

The vault is damp especially after rainfall because of the infiltration and of the scaffolding which is a barrier for evaporation. On the vault we found salt efflorescence, halophylic bacteria, halotolerant bacteria and fungi. The organic compounds provided by before restoration (CMC, ligants, fixatives).

In the nave on the scene Coming into Jerusalem we found cracks, and peeling of the pictorial layer. Also it is easy to see colored or discolored spots. From mycological point of view in that samples there are: *Penicillium sp.*, *Paecilomyces sp.*, *Sporotrichum sp.*, *Spicaria sp.*, *Aspergillus sp.* The emergency treatment based on sensitivity of fungi to Desogen 5% was applied. Against halophylic bacteria is need to clean the wall and to prevent salt crystallization.

**The Virgin Mary's Asleep Church** was built in XVI century and was painted in XVIII century (in Ocnele Mari district of Rimnicul Vilcea). Now it is a ruin without any roof with most of the mural painting exposed to rainfalls, snow, and wind and polluted atmosphere. In addition soil contents a high concentration of salts because of salts deposits. Some months ago took placed falls of ground not far away from the church. There is a very simple architecture with altar, nave, two absides, ante nave and porch. There is a vault up to the nave and a tour with a bell up to the porch.

*State of the preservation* of the whole church is very bad. On the socle all around the walls it can see salt efflorescences different high levels of salts moving, *Cyanobacteria*, lichens belonged to the species *Xanthoria parietina* and *Diploicia canescens*. The thalli of lichens colored the socle in yellow, grey or black according to their age and metabolic activity. Lichens can withstand desiccation and water reabsorption. Holding the water, during winter time they help physical weathering by frost action. Also they take off particles from the plaster by adhering and penetration fungal partner. Lichen colonies remove minerals from the plaster causing damages. In altar area it can see erosions in cement which contents chemolithotrophic bacteria (mostly *Thiobacillus sp.*). In the salt efflorescences we also found extremhalophylic bacteria (grown into the nutritive media containing 23g% salts).

In the large cracks grow up creepers and vines with a strain having about 10 cm diameter. They are involved in maintaining damp and dust in the wall and in enlarging of the crack. Their neglected growth provides harbourage for birds and insects which can damage themselves. Their strains are ways for enter of rodents into upper storey windows or roof spaces. Unchecked growth of creepers allowed covering part of roof and impairing drainage, penetrating soft roofing materials and put strains and leaves on it. In these conditions, fungal decay of wooden roof and other area form the church are accelerated.

Vault is built by bricks and between them there is mortar. Cohesion of the mortar and bricks is lost so lichens, mosses and grass are grown. Mosses have an important role in trapping debris and making up soil but once detached by heavy rain moss clumps block drains and gutters. We measured in some area 1-3cm of fertile layer of soil. In other area fertile layer is more thickly and supports the growth of *Salix sp.*, *Sambucus sp.* and *Populus sp.* Their roots take off minerals from the bricks and mortar and go down into cracks enlarged them. Also all plants maintain humidity in substrate which is very important for microbial

growth both on external and internal walls. Once this stage has been reached, removal of higher plants and restoration of the structure may involve complete reconstruction of vault.

Vault has a wooden resistance structure which there is in a high degree of deterioration. Some fragments of it lie down on the pavement full of *Coniophora sp.* and *Phomes sp.* or hole of wooden insects. Other fragments soft, whiteness or brown are attacked by white rot fungi or brown rot fungi.

House of the staircase which climbs from the antenave to the vault, made by stone is in a medium state of conservation. Its walls made by bricks and covered by plaster are not in a good state of conservation. Plaster is lost, mortar and bricks are powdery and covered by Cyanobacteria and salt efflorescences.

In the porch there are areas where vegetal material from the intonaco is not covered by any layer so that fungi producing cellulose like: *Trichoderma viride*, *Chaetomium sp.*, *Verticillium sp.*, *Acremonium sp.*, *Mucor sp.*, *Rhizopus sp.*, *Ulocladium sp.*, *Fusarium sp.*, *Aspergillus sp.*, *Penicillium sp.* grow. Some of them can produce in the same time organic acids acting as chelating agents.

On the East wall of the porch there is Scene on The Last Judgement: The haven to the left and The hell to the right. Intonaco is powdery and color is lost more than 90%. Also mortar and bricks lost their cohesion. Alga, mosses and lichens grow on the plaster and grass on powdery mortar between bricks. There is also a large fracture full of vegetal debris, dust and covered by cobweb. Only red pigment moves down from the original place.

On the South wall of the porch all pictorial layer is covered by salt efflorescences (1-2mm). It was also found halophilic bacteria and *Alternaria sp.*

In the antenave, there are areas of walls covered by *Cyanobacteria*. It was also noticed very good growth of *Cyanobacteria* on some pigments of the mural painting so that part of the saints' clothes are green not red or blue. In other areas frequently there are streaks of growth following ways of dampness and water run-off. They form slippery biofilms keeping dampness and reaching with organic matters the wall. On the base of the wall there are salt efflorescences containing halophilic bacteria. In some areas it can see three repaintings in time.

In the nave all arches are deteriorated full of alga and salt efflorescences.

Both in the altar and in the nave it can see powdery plaster, detachment of the pictorial layer, powdery pictorial layer and cracks.

Iconostasis is made by stone not by wood (like is common) and it is full of alga and *Cyanobacteria*.

The detachment of wall paintings remains a controversial method of conservation. According to Mora (1984) a mural painting is an integral part of the architecture it completes. Therefore, any separation of the painting from its original support constitutes a radical and irreversible alteration of both, and it is consequently an extreme measure, which would only be restored to if an examination of the situation as a whole established without any doubt that primary causes of alteration could not be eliminated in situ. In case of The Virgin Mary's Asleep Church, the primary causes of alteration can not eliminate in situ because resistance of structure is badly damaged, mural paintings is up to the sky, soil contents a huge amount of salts and relative and capillarity humidity is high so that the only way to save it is to detach it. The work is in progress and detachment will be done in the next spring keeping in mind all rules for a professional work. This church could be a real laboratory for students' practice.

The Virgin Mary's Asleep Church has very valuable mural paintings and it is included in Romanian Cultural Heritage but unfortunately it can not be restored in situ. In the same situation could be much more churches in Romania or in any other country so that work to find them are an emergency.

**Brezoi Church** is a country church built in XVIII century. The place of the church is in the yard of the cemetery but nearest it there is a new big church. Mural painting applied on the plaster has resistance structure made by hard wood.

To include this monument in the Romanian Plan of the Restoration has been done a special research to establish degree of deterioration and the emergency treatment.

The research had been done by architects, conservators, biologists, geologists and building engineers.

Biological research based on establishing the main causes which go to biodeterioration, analyses of morphological aspects of the deteriorated surfaces, pointing areas biodeteriorated and microbiological analyses.

The main surfaces studied were: wood from external walls, pieces of wood from the resistance structure, mural painting from the antenave, mural painting from the altar and the porch.

The main types of deterioration of the wood are the following:

- brown color, cross and longitudinal cracks;
- discolored area and powdery aspect;
- black spots according to the fungal colonies;
- holes of wooden insects;
- fruit bodies provided by Basidiomycetes;
- fungal vegetative structures: mycelia.

The main types of deterioration of the mural painting are the following:

- black spots;
- discolored area without any pictorial layer under them;
- addition structures: brown and thick mycelia;
- addition structure: very thin mycelia;
- mycelial threads;
- gaps as a result of loosing pictorial layer because of humidity, salt efflorescens or biodeteriogens;
- detachment of the pictorial layer.

The main causes which sustain development of biodeteriogens are:

- a poor roof with a lot of gaps;
- absence of some areas of the walls;
- absence of windows;
- absence of pavement and a solid resistance structure;
- humidity (relative and capillarity);
- careless for cleaning and protecting the monument.

The main biodeteriogens are: plants, insects, microorganisms and occasional birds and bats. Also it has to notice graves very closed to the church (about 30cm).

Wooden resistance structure and wooden roof there are in a high degree of deterioration because of the physical, chemical and biological factors. The structure of the wood is completely destroyed so it is impossible to recover or to restore some parts of it.

Wood is very brown, divided in squares, very soft even powdery, with winding circular tunnels, circular emergence holes, tunnels with oval section, deep and crater-shaped holes.

Insects pass through four stages of development of the metamorphosis: egg, larva, pupa and adult. The larvae emerge from eggs, bore their ways through wood, grind and eat it with their mouth. As a result, in the wood appear tunnels or frass galleries. Pieces of chewed wood and excrements are combined and make up bore dust. According to the shape and color in the wood there are *Lyctus brunneus* and *Hylotrupes bajulus*. Because of the high relative humidity and moisture content of the wood, insects grow in very good conditions. In addition, because fungi had very good conditions too, insects contribute to the spread of fungal spores. Temperature also has an important role in development of the larvae as well as influencing the behavior of the adult insects when they swarm, mates or lay eggs. During hot summer some of them die but during mild autumn cycle is started again.

Also it is noticed bees, wasps, earwigs, slugs and snails. They are coming seasonal and may be influenced by freak weather conditions.

Rodents are very destructive vertebrates. Buildings and materials are physically damaged owing to constant gnawing and their hair, urine and faeces spoil all kind of substrate. The possible points of entry are: gaps, holes, windows which are lost or are not protected with a fine mesh and certainly the door.

Pigeons both roost and nest on the church. Nests may block roof gutters and drains and harbor invertebrates which damage mural painting.

Wooden structure of the church was attacked by *Phelinus cryptarum*, *Poria xantha*, *Schizophyllum commune* and *Merulius lacrymans*. Because the external walls are made by rods which are almost entirely damaged they can not be recovered or restored. Also, because of high degree of damage wooden resistance structure and a high level of aquifer, graves very close to the church, the only one solution is to move it in another place so that detach mural painting is a priority.

Mural painting from the antenave is badly damaged. On the South wall there are areas covered by brown, thick, fungal mycelia. Under detached pictorial layer it were found pupa as one of the stages of metamorphosis of insects.

On the mural paintings in the altar there are efflorescences, brown and thick mycelia as an old fungal attack. But it was found new attack looks like very thin, white and branched mycelia.

Number of bacterial UFC was low ( $1,0 \times 10^2$  -  $1,1 \times 10^3$ ) but those fungal UFC was higher ( $1,5 \times 10^3$  -  $1,8 \times 10^5$ ). Fungi belong to the following genera: *Alternaria*, *Ulocladium*, *Penicillium*, *Fusarium*, *Wallemia*, *Mucor*, *Trichoderma*.

Fungi stain mural painting with dark spots. The following genera: *Cladosporium*, *Stachybotrys* and *Alternaria* produce melanins inside mycelium and it is very difficult to remove. The mycelium penetrates deeply inside the plaster of wall paintings (about 10 mm deep or more), causing loss of cohesion and detachment of paint layer. Fungi produce organic acids (citric, oxalic, gluconic, glucuronic, lactic, fumaric) which latter form chelation complexes with metal cations from the substrate. Also they can dissolve lime ground and accelerate peeling of the paint layer. Mycological attack of pictorial layer depends on nature pigments, organic binders and organic fixatives.

Micro-fungi act mechanically, biochemically and chemically. Filamentous hyphae spread over pictorial layer masking design and color. Also hyphae and fruiting bodies grow inside the painting support causing fissuring, friability and loss of the paint layer. Exoenzyme activities producing badly damages by decomposition of some components of paint layer or of the support material.

*Merulius lacrymans* coming from the wooden roof or from the wooden walls pass through mural paintings to the other wooden substrate, developing a thick hyphae network. Producing thick conducting strands of hyphae (rhizomorphs) behind its growing front the fungus can translocate water and nutrients from the drier surfaces. Also they adhere to the pictorial layer and take off some pigments leaving a shadow on it according to hyphae or rhizomorphs.

For monitoring microbial attack line drawing of it made to scale and the data produced from the in situ was then transferred to these.

In the end of the scientific work it was planned an emergency treatment on the most endangered areas of the mural painting. The main target was to stabilize the pictorial layer using a reversible minimal intervention but the painting to be secure because conservation treatment was not carried out in the following season. According with the conservators' proposal treatment consisted of securing loose fragments and cracks with small fine-grained Japanese paper using Desogen as a biocide. In case where fragments were almost completely detached from the wooden support they were sustain with wooden logs treated with a biocide.

**Corbii de piatra Church (Rock ravens)** is located in Arges district and it was built in the stone in XIV century. The church is closed always except on 29 of June when are celebrated Petre and Pavel Saints. Relative humidity is more then 80%, depending on the season. On the wall of the altar water flows all the time.

Deposits of dust, smoke, organic matters or rest of candles together of liquid or gas water go to a good growth of microorganisms.

Pictorial layer is powdery, detached like scales or is lost because of humidity and microbial activity. Black spots or discolored areas are signs of fungal and bacterial growth.

To each corner there are cobwebs, spiders and other insects. Some of them put their eggs under pictorial layer pushing it outside.

Plaster is powdery and very dump and salt efflorescens there are on all walls. Pavement and some walls according to the light way are covered by *Cyanobacteria* and alga making biofilm. They are slippery and green in active areas or slippery and black in those inactive. Green layer make impossible to read iconography which in partial damaged. Mosses are grown as a sign of very thin layer of fertile soil.

Being a very valuable monument it has to study it from geological, physical, biological and chemical point of view before deciding on and undertaking a conservation treatment.

**Frescoes fragments detached from Vacaresti Church** which was demolished in 1985 there were in Laboratory of The Art University to be restored. The church was built in XVIII century. Although some of the church was restored in 1985 it communist party decided to demolish it. Specialists and students from Art Academy in a very short time detached 120m<sup>2</sup> from the inner mural painting. Technique to detach was stacco + intonaco without or with fixative (Paraloid B-72). Some of them are restored and there are in museum.

Biodeterioration of Cultural Heritage is a result of interactions between living organisms, specific substrate and environment. The decay of the substrate is very closed links to external factors from indoors or outdoors. Appears that biodeterioration is a result of biological growth and physical and chemical effect of it. Detecting of biodeteriogens could be very easy or very hard. So it is easy to see a plant, an insect, an animal or a mushroom but very hard even impossible to see bacteria. Also it is incredible to suppose that in salt efflorescens can find microorganisms. Modern methods can be used to detect microorganisms when they are just a few and to save some of objects from Cultural Heritage.

Identification of the causes of deterioration is imperative before restoration process is adopted. Materials and techniques are improved but they have to be applied after identification of the disease and its pathogens. As little as microorganisms are they can go to completely damaged of objects from Cultural Heritage which could be sometimes a proof of history.

Like in every ecosystem chemical composition of art object selects microorganisms and environment allow them to grow. On a common substrate like can grow a lot of microorganisms in steps, depending on the chemical content, metabolites, pH, water availability, temperature. A will select very special substrate containing salts only bacteria and some fungi highly adapted. Any other spores or vegetative structure will only survive or will die because of osmotic pressure.

A new substrate will be colonized by a special type of microorganisms which in a good environment will have an equilibrated growth. After secondary growth fellow stress conditions and cell lysis. Depending of intermediate metabolic produces and chemical composition of the substrate other microbial community will settle. Metabolic events in microbial cells go to superficial and esthetical damages, fissure, cracks, detached pictorial layer, deep acid attack, deep enzymic reactions and release nucleic acids as a target to detect exactly microorganisms.

Our professional job is to prevent microbial growth, to detect it in time and to save our Cultural Heritage as a proof of our existence.