# České vysoké učení technické v Praze, Fakulta stavební

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# BIODETERIORACE STAVEBNÍCH A TECHNICKÝCH MATERIÁLU A KONSTRUKCÍ

# THE BIODETERIORATION OF BUILDING AND TECHNICAL MATERIALS AND CONSTRUCTIONS

#### **Summary**

**Part A.** describes in brief the level of knowledge as achieved in the line of biocorrosion of buildings. This line studies all undesirable changes of the building products due to the organisms which are denominated as the biodeteriogenes, now, in relation to the material sort. Within the biodeterioration framevork, there are studied not only the ways in which the building product get colonized by the microorganisms and the mechnism of their degradation, but also their preservation and increase of their service life and reliability. The biocorrosion in general means every change of properties in the technical and building products which is conditional on vital activities of organisms, it being understood that the biocorrosion can be caused by microbes, insects, rodents, birds or also by men. There is concerned then a specialized scientific line which is called the hylobiology in broarder context. It concludes as the individuals pertaining to different organism groups in systematic sequence, as also the individuals with different organization levels. However, the common relation to the technical and building materials representing their prevailng living envirinments is the unifying factor.

Part B. sumarizes the author's contributions to the development of knowledge items in the line of synergic degradation activities of the nitrifying and chemoorganotrophic bacteria om facades of the building objects. The attention, however, was aimed at the formation of biological crusts on the facade of St. Vitus Cathedral in Prague with cooperation on the atmospheric contamination, and at the formation of biological crusts and salinity increase on the archs of Charles Bridge as wetted with the rain water owing to the roadway nonfunctional hydoinsulation. An integral part of these studies was also the distinction and identification of the nitrifying bacteria in extensive degradations of the asbestos-cement roof coverings of the stable buildings with single-clading roofs. These works resulted in the methodical proposal and realization of biological liquidation of nitrogen salts in the moist masonry by means of the denitrifying bacteria. In the line of biocorrosion of plastics, the author aimed at studying the dagradation of organosilicone compounds, especially at developing the knowledge of mechanism of electric surface resistance of plastics as of the indicator of the plastics degradation by micromycetes. The main sphere of the works involved the studies of mutual microbial interactions on the aged and non-aged plastics as in natural, as also in semi-natural and laboratiry conditions. These studies resulted practically in the proposal of method of combined thermal liquidation of polyolefins in the soil being enriched with mineral oils with the resulting biodegradation by soil microflora, as well as in the discovery of the degradation mechnism of polyolefins in the human organism caused by the enzymic hydroxylation system consisting of cytochrom P 450, NADPH cytochrome reductase and alkohol dehydrogenase. The system is located on the bacterial membrane and in the microsomal fraction of liver cells and is induced with polyethylene, parafin, barbiturates, acrylates and silicone rubber present

**Part C. concluding remark:** Approximately 2% of all products in the world are degraded by biocorrosion yearly. The lectures in the line of biocorrosion of the building and technical materials enable to reduce the losses to minimum during the project preparation already.

### Souhrn

Část A. stručně popisuje dosaženou úroveň poznatků v oboru biodeteriorace staveb. Tento obor studuje všechny nežádoucí změny stavebních výrobků působené organismy, pro které se nyní ve vztahu k materiálu použivá označení biodeteriogeny. V rámci biodeteriorace se studují nejen způsoby osídlení stavebních výrobků mikroorganizmy a mechanismy jejich znehodnocení, ale rovněž jejich ochrana, zvýšení životnosti a spolehlivosti. Biokorozí obecně je míněna každá změna vlastností technických a stavebních výrobků podmíněná životní činností organismů, přičemž biokorozi může způsobit mikrob, hmyz, hlodavec, pták nebo i člověk. Jde tedy o specializovaný vědní obor označovaný v širších souvislostech jako hylobiologie, který zahrnuje jak jedince systematicky náležející k různým skupinám organismů, tak jedince s různým stupněm organizovanosti. Jednotícím prvkem je však společný vztah k technickým a stavebním materiálům jako k převládajícímu životnimu prostředí.

Část B. sumarizuje příspěvky autora k rozvoji poznání v oblasti synergického degradačního působení nitrifikačních a chemoorganotrofních bakterií na fasádu stavebních objektů. Pozornost byla zaměřena na vznik biologických krust na fasádě chrámu sv. Víta v Praze za spolupůsobení atmosférického znečištění a tvorbu biologických krust a zvyšování salinity na obloucích Karlova mostu smáčených dešťovou vodou vinou nefunkční hydroizolace vozovky. Nedílnou součástí těchto studií bylo i rozpoznání a identifikace nitrifikačních bakterií při rozsáhlých degradacích osinkocementové střešní krytiny stájových objektů s jednoplášťovou střechou. Vyústěním těchto prací byl metodický návrh a realizace biologické likvidace solí dusíku ve vlhkém zdivu pomocí denitrifikačních bakterií.

V oblasti biokoroze plastů se autor zaměřil na studium degradace organosilikonových sloučenin a zejména na rozvoj poznání mechanizmu povrchového elektrického odporu plastů jako indikátoru znehodnocení plastů mikromycetami. Hlavní oblastí prací bylo studium vzájemné mikrobní interakce na sestárlých a nesestárlých plastech a to jak v přírodních tak polopřírodních a laboratorních podmínkách. Praktickým vyústěním těchto studií byl návrh metodiky kombinované tepelné likvidace polyolefinů v půdě obohacené minerálními oleji s následnou biodegradací půdní mikroflorou a objev mechanizmu degradace polyolefinů v lidském organizmu působený enzymovým hydroxylačním systémem tvořeným cytochromem P 450, NADPH cytochromreduktázou a alkohol dehydrogenázou. Systém je umístěn na membráně bakterií a v mikrosomální frakci jaterních buněk a je indukován za přítomnosti polyethylenu, parafinu, barbiturátů, akrylátů a silikonové pryže.

Část C. Ročně podléhá biokorozi ve světě cca 2% veškerých výrobků. Přednášky z oboru biokoroze stavebních a technických materiálů umožňují minimalizovat ztráty již během projektové přípravy.

Klíčová slova

Biodeteriorace, biocidy, bioreceptivita, biologická krusta, ekologie, enzymy, hydroizolační folie, kontrola biokoroze, likvidace plastů, mikrobní interakce, modelace, osinkocement, organosilikonové sloučeniny, plasty, salinita, stavební a dekorační kámen,

### Key words

Asbestos cement, biodeterioration, biocides, biocorrosion control, bioreceptivity, biological crust, building and decorative stones, ecology, enzymes, hydroisulating foils, liquidation of plastics, microbial interaction, modelling, organosilicone compounds, plastics, salinity

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### A. State of the art

### 1. Introduction

The subject of biodeterioration of the buildings is dealing with all undesirable changes of the construction products due to the organisms which are denominated as the biodeteriogenes, now, with regard to the materials used. Within the framework of biodeterioration, not only the ways in which microorganisms are colonizing the construction products and the mechanisms of degradation of the building materials are being studied, but also the necessary preventatives, improvement of service life and reliability (1, 2).

The atmospheric biodeterioration of the buildings is caused by the ecosystem in which bacteria and micromycetes are dominant. It is observed in the cryptoclimate of the constructions built by the man (laundries, tanneries, silos, cooling towers, some agricultural and industrial plants and mines). The biodeterioration is habitual where water vapour is condensing, especially the thermally weakened masonry (public and residential constructions, historical buildings) (3), where soil moisture is elevated into the masonry capillaries, or where the masonry is sprinkled with the rain water (damaged eaves and rain-water downpipes).



Fig. 1 The fungi on the mineral thermal insulation of the roof of an agricultural building



Fig. 2 The fungi taken from the housing object atmosphere

In the biocorrosion process, the biodeteriogene works actively and the technical material, which may but need not be a substrate, works passively. The system of biodeteriogene-> material is open, because a lifeless material is incapable of preventing attacks by immune reaction. The resistance of the attacked materials can be increased only by a further intervention either sequentially (repressively) or preventively (by means of biocides), by which the effects of aggressive organismsare diminished. The simple form of interaction sets in upon a simple settling of a colony of microorganisms in the construction products already.

A number of complicated material, atmospheric and microbial interactions come into consideration in the complicated buildings (Charles Bridge, St. Vitus Cathedral). Therefore, upon the biocorrosion occurrence and during the biocorrosion process there are taken not only the conditions of external environment (the macroclimate) into account, but also the conditions which are prevailing at the contact of material->biodeteriogene immediately. Whereas the macroclimate affects the existence of biodeteriogenes in the environment

concerned, the microclimate (the actual temperature and humidity above all) can affect the material infestation by a specific biodeteriogene kind directly (see the ecological aspects of biodeterioration here-under).

The soil biodeterioration of the buildings is mostly caused by the ecosystems in which bacteria and actinomycetes are dominating. It always sets in when the construction products (the hydroinsulating foils of PVC-P, hydroinsulating layers of SBS modified rubbers as well as metal pipes) get in contact with the soil. The occurrence of electrochemical microcells stimulated by the vital activity of microbes (Desulfovibrio desulfuricans, and others) is typical. Thus, it is possible to speak of a combination of the biological and abiotic (electrochemical) corrosions in this case (4).

### 1.1 The symptomatology and diagnosis of the biodeterioration of buildings

In general, the biodeterioration of building materials by microorganisms can be classified as **The mechanical deterioration** 

- a) Irreversible (for example the destruction of woodwork constructions by wood-destroying fungi, the biodegradation of the building stone).
- b) Reversible, found in the constructions here and there (for example the temporary decrease of passage in the water mains due to iron bacteria). It is typical for the biodeterioration of insulants where processes of the degradation and revitalization of superficial electric properties take place during attacks.

### The chemical deterioration

- a) Assimilating (the destroyed material, for example timber, is the main source of nutrients and energy).
- b) Dissimilating (the biodeterioration is the principal degradation factor, but the destroyed material is not the main source of nutrients), for example the building stone degradation by the metabolites of the bacteria which are growing on the traces of hydrocarbons arising from the furnaces and of hydrocarbons produced by the automobile traffic (5, 6, 7).

## 1.2 The ecological aspects of biodeterioration of the buildings

Three stages are distinguished in the biodeteriogenesis like in the medicine to a certain extent: **The infection, adhesion** - the stage in which a constant contact between the biodeteriogene and material sets in. In anorganic substrates an adhesion of the microbial cells on the specific minerals proceeds, the decisive part being played by the pH value and the ionic force of the water film on the substrate.

**The incubation** - the phase from the infection up to the period in which the biodeterioration symptoms become evident, and/or represent a degradation which is significant from the technical viewpoint.

**The manifestation** - the phase in which the biodeterioration symptoms are evident and represent a degradation which is significant from the technical viewpoint.

The mentioned break-up of the biodeteriogenesis stage is useful in practice, above all in the biodeterioration of the timber-work components of the buildings (roof trusses, ceilings). To prevent possible destructions, it is necessary to identify the starting biodeterioration in time. To this purpose there are performed investigations of the occurrence of biodeteriogenes in the biotope in question and fixed the diagnosis according to the environmental conditions (favourable or unfavourable for the biodeteriogenesis process) still prior to the manifestation of the function defects. (8, 9)

The sources of the occurrence of biodeteriogenes in a specific environment are mostly the soil and the materials themselves. The infection results either from the source being identical with the attacked material (the homologous source, for example cellulolytic moulds and wooddestroying fungi from the attacked timber on the plasterboards), or the biodeteriogene does not result from natural sources being identical with the degraded material (the heterologous source). The growth of microbes on the plastic construction materials, of which several have the chemical structures which are unknown in the nature, is typical for this group (2).

# 2. The mechanism of biocorrosion of the anorganic substrates (building and decorative stones)

First of all, there is concerned the so called **bioreceptivity** (11), i.e. the properties of the building materials which supply the biodeteriogenes with nutrients (the surface contamination, deposits) and the corresponding living environment. The building stone biocorrosion is a synergic process which mostly takes place at the same time with the building stone deterioration by moisture effects. The stone is colonized by a number of microbes producing the mineral and organic acids which dissolve calcium silicates and aluminates at the simultaneous formation of water-soluble salts or water-soluble complexes.

The degradation proceeds in a not yet clear way even deep in the masonry. Bizzare not yet identified organisms participate in this degradation process by cooperating in the gradual moistening and ageing of the masonry. As several degradation processes are always acting simultaneously in the building material corrosion, it is often very difficult not only to fix a correct diagnosis of the whole process, but also (above all), to find as the biological as also the dominant factors of the degradation (12).



Fig. 3 The bacteria on masonry of Old Palace, Prague Castle

The microbial degradation of the building stone is affected by its own mineralogical composition (the portions of carbonates, mica, clayey minerals, etc.), petrophysical parameters (the size of internal surface, porosity), architectonic properties of objects, object orientation to points of compass, local climatic conditions and used preservatives.

**Manifestations of biodegradation processes** are often very similar to the completely physical degradation. The surface of building materials gets coarse, pulverization, efflorescences, fine cracks, scaling-off of surface layers, coloured stains and patinas and/or deposits of anorganic materials are observed. As several degradation processes take place in the building material corrosion always at the same time, it is often very difficult not only to fix a correct diagnosis of the whole process, but, above all, also to find out as the biological as also the dominating factor of the degradation process (12).

### **2.1.** The biogeophysical deterioration of anorganic materials

The atmosphere of our time contains increased concentrations of sulphur oxides, nitrogen oxides, carbon dioxide, carbon monoxide, ammonia gas and a number of other, above all organic compounds which are infiltrating the masonry together with the rain water. When the bricks contain moisture of approx. 5% by weight, various kinds of bacteria grow in the surface layer at first and in the masonry deeper parts later. These bacteria are vegetating on the traces of impurities and of dust which was entrained by the wind onto the masonry. At the

same time the biofilm and biological crust are formed on the masonry. The microbes produce a number of specific metabolites in it, above all the anorganic and organic acids and aminoacids. These produce, together with mineral substances in the masonry, the salts which accelerate the moisture migration (13).

In the evaporation zone, the sulphur oxide s as well as ammonia get transformed into the sulphuric and nitric acids by the chemolitotrophic nitrifying and sulphur bacteria, with the accompanying bacteria cooperation, according to following equations: (7)

Sulphur bacteria:  $H_2S + 2 O_2$ -----> $SO_4 + 2 H^+$ 5  $H_2S + 8 NO_3$ ----->5  $SO_4 + 4 N_2 + 4 H_2O$ Nitrifying bacteria: 2  $NH_4 + 3 O_2$ ---->2  $NO_2 + 2 H_2O + 4 H^+$ 

$$NO_2 + O_2 - 2 NO_3$$

The originated acids react with the calcareous components of the binder above all, for example:

 $Ca(OH)_2 + HNO_3$  (nitrifying bacteria)  $Ca(NO_3)_2 + 2 H_2O$  $CaCO_3 + H_2SO_4$  (sulphur bacteria)  $CaSO_4 + H_2O + CO_2$ 

The originated CaSO<sub>4</sub>.2 H<sub>2</sub>O shows higher stability, greater weight by volume and thermal expansivity compared with the original CaCO<sub>3</sub> is subject to easy extraction by the water .This fact also weakens the stone binder component. The stone corrosion is also assisted by secondary minerals produced with the cooperation of microorganisms, especially of mixed K and Na saltpetres (alums), and plaster stone  $Ca(SO_4)_2 \cdot 2 H_2O$ . When compared with the former findings, the growth of sulphur bacteria on the building stone is poor, even negligible (14). The recent findings of the massive populations of sulphur bacteria on the external face of sandstones in Charles Bridge and findings of sulphur bacteria on the concrete centerings of surface-water sewers represent the only exception.

Further groups of bacteria affect the buildings, too:

The ammonization bacteria (urobacteria) decompose urea and cause the formation of ammonia. They are counted among common soil bacteria. They are the predecessors of nitrifying bacteria too which they yield ammonia for their metabolic process according to following equations:

 $NH_2CONH_2$  (diamide of carbonic acid) +  $H_2O$ ---->( $NH_4$ )<sub>2</sub>  $CO_3$ ( $NH_4$ )<sub>2</sub>  $CO_3 = 2 NH_3 + CO_2 + H_2O$ 

When growing without oxygen present, the denitrifying bacteria utilize nitrate as the electron acceptor. In general, the main mechanism of nitrogen liberation is the following reaction:  $2 \text{ NO}_3 + 10 \text{H}$ ----->N<sub>2</sub> + 4 H<sub>2</sub>O + 2 OH

The desulphurizing bacteria are counted among the strictly anaerobic, facultatively autotrophic microorganisms. They occur as the accompaniment of sulphur, nitrifying and denitrifying bacteria. From the biodeterioration aspect, their role consists in supplying the sulphides for further oxidation by sulphur bacteria.

The main oxidizing (dehydrogenating) reaction

 $4 H_2 + SO_4 + 2H$ -----> $H_2S + 4 H_2O$ 

They obtain H<sub>2</sub> by reduction of the organic acids, ethanol and glycerol into acetate.

2.2. The biogeochemical degradation of building materials. Great numbers of

**chemoorganotrophic bacteria** are found on the decorative and building stones almost at any time. These bacteria realize the same mineralization processes here as in the soil and, by producing the organic acids, are capable to interact with silicates and alumosilicates of the building stone as much as 10-times more intensively than other soil bacteria. (15) The silicate microorganisms form an artificially constructed group which contains a number of different genera. Their single common feature is the increased production of organic acids which results in the acidolysis of anorganic substrates. This fact was ignored for a very long time. However, the contemporaneous items of knowledge have proved that the building stone surface has a sufficient amount of organic materials (dust, dirt, hydrocarbons) that are suitable for the ample development of microbes on the stone surface as well as inside the stone. The chemoorganotrophic bacteria influence the stone weathering process in two ways:

a) By the excretion of organic acids which results in the consequent extraction of the stone binder and in the loosening of the mineral structure. The leadung part in this processes is played by clay minerals activity which are affecting the bacteria metabolic function by their surface, osmotic properties and sorption activity.

b) By the excretion of extracellular polymer substances (EPS) which results in a change of the stone porosity and permeability. The excretion sets in at the assimilation of aliphatic and aromatic hydrocarbons (hydrocarbon residues) and fatty acids. The production of glycolipids and phospholipids, emulsifiers and surfactants (16) can be proved in 75% of bacterial population. They cause decrease of the water surface tension, stabilize the organic compounds emulsion in water solution and are related directly to the level of the water capillary transfer by the stone. (17)

Fungi (micromycetes) also contribute to the pulverization of the building stone, above all by dissolution, recrystallization and redeposition of calcite. They influence the stone demineralization and Al, Mg, Si, Fe and Mn extraction by producing the organic acids which are functioning as the chelatization agents. As for organic acids, there are found on the building materials oxalic acid, puruvic acid and lactic acid above all, whose chelatization effect is considerable. As for aminoacids, there were trapped phenylalanine massively and aspargine, serine, alanine, arginine, glycine, histidine, tyrosine and glutamic acid in smaller amounts (3).



Fig. 4 Aspergillus flavus, the biodeteriogen and pathogen, producer of a number of organic acids



Fig. 5 The micromycetes on hardened moulding material with wood-flour filling

In the ion exchange that proceeds during the building stone hydration, protons of organic acids and aminoacids can be replaced with alkalis of minerals. This results in a destruction of internal and external structures of the rock-forming minerals and is denominated as the chemical opening of minerals. The formation of acids proceeds on a number of metabolic pathways and cannot be described by a simple equation. For example in plastics and paints a methyl ketone pathway is possible with the simultaneous formation of internal ketone. Further building materials, such as bituminous insulations, coatings and painter's whitewash components, various types of PVAC dispersions, wallpapers, etc. are transformed by fungi most often according to the following considerably simplified scheme:

Oxidation reaction:	Reduction reaction:
-CH <sub>3</sub> >CH <sub>2</sub> OH	-CH=CH>CH <sub>2</sub> -CH <sub>2</sub>
-CH <sub>2</sub> -CH <sub>2</sub> >CH=CH <sub>2</sub>	
Hydrolysis:	Esterification reaction:
$RCOOR + H_2O>ROH + RCOOH$	$RCOOH + ROH> RCOOR + H_2O$

According to several studies (17), micromycetes contribute to the stone weathering more than the nitrifying bacteria. It is known that a number of micromycetes are intensively attacking the minerals genthite and nathrolite with the simultaneous Mg and Al solubilization. Micromycetes are invading into the building stone, are softening calcite and dolomite grains and are penetrating by hyphas along the weathered minerals where, in the interaction with parasiting mites, they are generating specific biodeteriogenic substances. In this respect the concrete biocorrosion, in which the strong destruction due to fungus Fusarium sp. was detected, deserves an extraordinary consideration. The micromycete liberated Ca<sup>2+</sup> from concrete and the material mass loss was observed at the same time.

### 3. The biodegradation of building plastics

Although plastics and coatings do not play such a significant part as anorganic materials do in the building industry, their use is not negligible at all. Plastics find their application especially as all-surface floorings, heat-insulating fillers, constructional materials, hydroinsulating materials against moisture and water capillary action, as well as against radon escape. A number of plastics are also used as decorative materials. As plastics in the constructions are often applied in the foundation parts of the buildings and mostly are in permanent contact with the soil moisture and/or with the soil itself (the insulation of river beds), ideal conditions arise for biodegradation starting.

The materials of hydroinsulating foils, designed to be used in the roof claddings and insulations of building foundations, whose application - with the exception of softened PVC started at the beginning of the seventies only, were studied substantially less with respect to possible biocorrosion. The idea was prevailing that the hydroinsulating plastic foils being exposed to the direct weather effects cannot be attacked by microorganisms much seriously in the climatic conditions of Central Europe. In addition, these materials are highly stabilized, resistant to UV radiation, almost moisture-resistant, stable within temperatures of -30 to  $+130^{\circ}$  C and relatively resisting to the growth of fungi (18). However, it has become evident in the course of time that the soil bacteria above all are capable, under favourable conditions of moisture and temperature, to attack (transform) external layers even of highly resistant plastics. The plastics become then better susceptible to photooxidation and, subsequently, also to deeper biodegradation which can result in a decrease of the material tensile and bending strengths (the hardening and embrittlement of plastics) (19).



Fig. 6 The biodegradation of hydroindulating foils in the soil, SBS modified hydroinsulating asphalt belt



Fig. 7 The biodegradation of hydroindulating foils in the soil, softened PVC

However, the problem of biodegradation of building plastics is far more extensive. Regular natural organic compounds contain OH and CO groups. Therefore the energetic metabolism is bound with oxidation reactions (transfer of H2 --> NAD, NADP) which supply energy for the biosynthetic or phosphorylation reactions. The building plastics and further biochemically inert compounds (alkanes, cycloparaffins) do not contain  $O_2$  and, therefore, represent no suitable subject for dehydrogenation reactions which are characteristic of the biological oxidations. Instead, reaction sequences are initiated which utilize singlet oxygen for the oxidation of plastics. It is taken for granted that monooxygenases can react with some plastics as is the case by analogy in monooxygenases contained in the eukaryotic hepatocytes. The so-called "stress factor" has been identified lately which enables microorganisms to get quickly adapted to new nutrition conditions. This, too, can be the way in which the microbes can become adapted to plastic substrates.

Therefore, to determine the biosusceptibility (bioreceptivity) of polymers, it is essential to know the structure and distribution of the polymer crystallization and amorphous parts as well as the size of the polymer basic units and its above molecular structure. As shown in the recent study (21), not only plastics based on polyolefins are attacked by microorganisms, but also as resistant materials as the phenolic composites filled with glass fibres which are used to reinforce the timber works attacked by wood-destroying fungi. The attack by wood-destroying fungi resulted in a considerable decrease of the shearing strength of phenolic composites.

A significant factor in the biodeterioration of plastics is evidently the relative molecular weight (the high-pressure PE is attacked up to molecular weight of 13 800, the higher n-paraffins only up to molecular weight of 451 ( $C_{32}$ ). As for the other plastics (PS, PP, PIB), their degradation is hindered by the presence of phenyl and methyl groups and/or by the side chains branching. As for the PVC, atom Cl provides shielding. However, in all studied polymers, oligomeric particles of polymers only are always assimilated, but the polymer matrix proper is not attacked.



Fig. 8 The surface of PE foil with addition of the potato starch and prodegradation agent after 30 days exposure in the compost soil



Fig. 9 The soil bacteria in dot after the decomposed potato starch

### 4. The biocorrosion control

It is possible to hinder biodeterioration and to prevent losses on the building materials by the constructional adaptation (the thermal technical measures) or by using the naturally resistant materials (which is mostly inapplicable in the building industry; the anorganic materials are resistant to biodeterioration inherently and, despite this fact, metabolites of the microbes are decomposed; this is possible in the wood-based products by choosing stable wood species; applied in hydroinsulating plastic foils) (20). Perspectively, there can be taken into account for example also the increase of the efficiency of biological prevention against wood-destroying insects. The introduction of Cleridae against the wood-worms and of Braconidae against the longicorn beetles.

Another possibility is either to increase the resistance of materials (especially of plastic foils) by choosing suitable fillers and softeners, or to change physical and/or chemical properties of the plastics so that they become inacceptable to biodeteriogenes (for example the chemical modifications of the plastic basic polymer unit, and others). The most common prevention used till now is the treatment of the building materials with specific chemical compounds and biocides (fungicides, bactericides). This can be done either by sprays, impregnation or additives introduced into the material (21).

The biocide efficiency depends on the quantity of liquidated microbes (during the interaction, the biocide reacts with the cell surface, gets inactivated and its concentration decreases), on temperature dur ing the application and on the pH value (the compounds, such as phenol, benzoic and sorbic acids, are efficient only in the nonionized form). When pH increases, the number of negatively charged spots on the cell surfaces increases, too. Some biocides, such as for example Quaties, are bound to these spots better. Also the interfering compounds make a great difference dur ing the application of biocides. There are concerned for example the residues of milk, foodstuffs, blood, soil, detergents as well as metal ions  $(Mn^{2+}, Zn^{2+})$  (22).



Fig. 10 The determination of fungicide activity on the broth by Czapek-Dox. Test organisms: Aspergillus flavus, antimycoticum nystatin

The biodeterioration preventive control represents at present a widely elaborated, though not yet finished branch with the strikingly practical basis. There have been tipped a number of various compounds, but their toxicity for the man, formation of resistant forms, question of stability during treatment, durability in materials, compatibility with materials, inertness to additives used in treatment, resistance to atmospheric effects and hygienical unobjectionability are known quite cursorily only.

# **B.** Authors contribution to the development on the line of biodeterioration of building and technical product and instalation

1. The typical simple interaction between the building material and microorganisms is the degradation of the asbestoscement roof covering in the agricultural objects with the single-cladding roofs and non-ventilated roof cavities. The significant destruction was observed on cowsheds, partly on stables, sheepsheds and poultry houses, but never on hogsheds. However, it was revealed on the auxiliary constructions neighbouring with the hogsheds.



Fig. 11 The cow-shed K174 after reconstruction



Fig. 12 The desintegrated asbestos-cement roof covering

The increased content of nitrates and nitrites was found out in extracts from the decayed roof covering; the calcium quantity decreased. The roof covering moisture content was higher significantly compared with the covering non-attacked parts. The protective coating with  $Ag_2CO_3$  suspension stopped the degradation process for the period of 10 years. Bacteria Nitrosomonas and Nitrobacter spp. were isolated from the degraded roof covering. They were accompanied by numerous organotrophic microflora which stimulated the activity of the nitrifying bacteria.

The entire process was modelled in mineral media and in climatic chamber Brabender KS 500/90 (FRG). It was obvious from the results that the covering destruction consists in the fact that the asbestos cement is attacked by nitrous or nitric acids (metabolites of nitrifying bacteria) and/or by ammonium salts of these acids. The water vapours which are transferred from the horse stable object through the roof insulation precipitate on the lower face of the asbestos-cement roof covering and wash soluble  $Ca(NO_2)_2$  and  $Ca(NO_3)_2$  out of the covering. This causes the porosity increase and reduction of the asbestos-cement strength. The water vapour which penetrates into capillaries and pores of the weakened covering generates pressures that destroy the covering during the vapour phase changing into the ice.

Condensate	Type of agricultural object		
component	cowshed K174	hogshed K174	
NO <sub>2</sub>	$0,17 \pm 0,12$	traces	
NO <sub>3</sub>	0,53 ± 0,04	$0,04 \pm 0,01$	
NH <sub>4</sub>	$0,25 \pm 0,02$	$0,79 \pm 0,25$	
condensate pH	6,7	7,-	

Tab. No.1. The chemical composition of condensate (mg.ml<sup>-1</sup> on the internal face of asbestoscement roof covering (the winter season)

Considerable amount of ammonia produced during the hog-breeding functions as a sterilizer, hinders the growth of nitrifying bacteria on the hogshed roof covering. On the contrary, the ammonia amount in the cowshed atmosphere is just suitable for the intensive growth of nitrifying bacteria.

Climatic effects together with microbial attacks had significant consequences also on indoor plasters of the cowshed objects. The winter season, above all, is favourable for the development of microbes, as the relative humidity increases above 80% upon the stable object closing for a longer period of time. The permanent condensation on the masonry that is underdimensioned to temperature and the vehement growth of moisture occur. Micromycetes and bacteria entrained to the stable with the litter above all propagate quickly on the masonry internal surfaces. The condensate taken from the surfaces of metal part s of the installations fixed on the peripheral jacket internal face contained NH<sub>4</sub>NO<sub>3</sub>, NH<sub>4</sub>NO<sub>2</sub> and H<sub>2</sub>S traces above all. The growth of micromycetes set in and the quick degradation of internal plasters was observed.

The microclimate and, consequently, also "biological parameters" of the objects were changed very intensely after the reconstruction of the cowshed objects K 174. The reconstruction consisted in producing a simple ventilation system, in reducing the number of windows (the reduction of thermally weakened surfaces) and in installing the lower-ceiling vapour-tight barrier of PE foil as well as in increasing the thermal insulation of the single-

### cladding roof.

The effect of nitrifying bacteria was proved also on the **facades of Prague Castle objects**. The plaster plate corrosion was observed in places in which the carbamide was used for some time. At the same time, nitrifying bacteria were detected in plasters in such an amount that was dependent on the concentration distribution of ammonium salts. It was obvious that the ammonization flora which was present in the objects foundations transformed the spread carbamide into ammonium salts which were transformed into nitrites and nitrates by nitrifying bacteria after the transfer of soil moisture over the ground level into the masonry. As the concentrations of nitrates in the plaster exceeded 1%, the nitrogen salts represented a significant degradation factor in the facade.

The microflora distribution in the objects masonry with respect to the depth was also remarkable. In the area of Hradčany, nitrifying bacteria together with the accompanying microflora were found close under the plaster surfaces in the places in which the maximum concentrations of nitrates and ammonium salts were also found. The secondary maxima of the occurrence of bacteria and ions of NH<sub>4</sub> and NO<sub>3</sub> at the depth of 2 cm and 5 cm were corresponding to the transition zones between older plasters of the objects. Sulphur bacteria were found at a greater depth (above 5 cm). Actinomycetes and the accompanying microflora had their maximum (<  $1.10^6$  germs/g of masonry) only at the depth from 8 to 20 cm of the masonry at the masonry moisture content of 2 - 5% by weight. The whole process was blocked successfully prior to the application proper of the plasters by spraying the masonry with the water solution of the nickelous and cobaltous fluorosilicates.



Fig 13 Prague Castle, Old Palace





# 2. The biochemical interactions of microbial metabolites with rock-forming minerals of structural components of buildings

# 2.1. The formation of biological crusts under the cooperation of atmospheric contamination

Out of the bacteria isolated from the sandstone masonry of St. Vitus Cathedral there were selected the genera that decomposed fuel oils (modelling the stone atmospheric contamination) and that degraded sandstones at the same time.



Fig. 15 St Vitus Cathedral, black crusts in the places sprinkled with the rain water



Fig. 16 Micromycete Cladosporium sp. on the surface of sandstone of St. Vitus Cathedral

Tab. No. 2. The degradation activity of the bacteria isolated from sandstones of St. Vitus Cathedral

Bacteria	Degradation of	
genera	minerál oil	sandstone
Comamonas acidovorans	+++	+++
Pseudomonas vesicularis	+++	++
Pseudomonas pseudoalcaligenes	++	+++
Pseudomonas paucimobilis	++	+++
Bacillus mycoides	0	+
Micrococcus sp.	0	+

Note:

mineral oil degradation: 0 - none, + - poor, ++ - strong, +++ - very strong sandstone degradation: + - poor, ++ - surface degraded here and there, +++ - surface degraded completely

It became evident that micrococci that were inactive in degradation rather reduced the amounts of Fe<sup>2+</sup> and Mn<sup>2+</sup> (both metals were evidently built in the cellular mass). On the contrary, bacteria Comamonas acidovorans raised the amounts of Mn<sup>2+</sup> 25 times, Pseudomonas alcaligenes 20-times and Pseudomonas paucimobilis 17-times. The concentration of Fe<sup>2+</sup> on the sandstone increased less substantially. In Comamonas acidovorans 1.5-times, in other microbes the amounts remained unchanged or even decreased.

Analogous experiments were realized on the building sandstone surfaces on the western front of St. Vitus Cathedral. Ferrous, ferric and manganous salts were applied here in order to accelerate the blackening process on the sandstone surface, in the natural abiotic way on the one hand and with the specific microflora present on the other. Certain changes on the masonry were observed after 6 months of exposure already. The stone darkening was perceptible on the surface treated with FeCl<sub>2</sub> quite clearly. The surface treated with MnCl<sub>2</sub> remained unchanged. The stone surfaces that were bacterized additionally (surfaces with added microflora cultivated from the surfaces of St. Vitus Cathedral in the laboratory) were more susceptible to pulverization and degradation and darkening of the surface became more apparent. The content of SO<sub>4</sub> increased from 9,5 mg.g<sup>-1</sup> sandstone as high as 40 mg.g<sup>-1</sup> sandstone on the darkened surfaces.



on the surface of sandstone of St Vitus Cathedral

The mentioned observations offend the generally accepted idea about the formation of gypsum crusts, according to which gypsum gets washed away from the stone together with impurities thanks to certain gypsum dissolubility in the places being exposed to the precipitation water. On the contrary, in the places that are shielded against the rain water, gypsum crusts accumulate either as a discontinuous layer or as a strongly bonded incrustation. The noticed discordance can be explained only so that the major part of crusts on St. Vitus Cathedral are the biological ones which, on the contrary, necessitate water for their formation. This biological hypothesis agrees with the phenomena observed on the stones of St. vitus Cathedral, when the sandstone surfaces exposed to the rain water effects show highly developed black gypsum crusts, whereas the places shielded against the rain water are light-coloured constantly. However, if some places on the Cathedral surface are subject to frequent running-down of the rain water, then, on the contrary, the stone colour in these places is light and the calcite surface is perceptible instead of the sulphatic crusts. The acid rains themselves also forward the formation of sulphates.

# **2.2.** The formation of biological crusts during nutrients transport by the rain water through the archs of Charles Bridge in Prague

Orientative analyses performed on bridges at Roudnice, Litovel and Charles Bridge in Prague ha ve proved that the maximum concentrations of water-soluble salts exist just in the construction body of Charles Bridge. The ever accelerating tendency to the growth of salt concentrations on the sandstone surfaces is well perceptible in the salinity increase in arch IV within last 3 years. The increase of sulphates and nitrates is particularly considerable.

Locality in	pН	Concentrations of ions of salts and urea (mg.g <sup>-1</sup> sandstone)					
arch/ year	level	Cl	$SO_4$	NO <sub>3</sub>	NO <sub>2</sub>	$\rm NH_4$	Močov.
Foot, y. 2000	7,-	0,55	12,84	11,-	NT	0,-	0,22
Centre, y. 2000	7,-	0,94	5,94	15,85	NT	0,021	0,44
Foot, y. 2003	5,-	2,54	44,-	44,-	0,-	0,06	0,14
Centre, y.2003	7,-	2,42	80,-	84,-	0,12	0,16	0,56

Tab. No. 3. The salinity development in the centre and foot of Charles Bridge arch VI. in 2000 to 2003 years

The weighty occurrence of organotrophic microbes is conditional, above all, on the high moisture in Charles Bridge construction body (16 to 32% by weight here and there) which is due to the rain water seepage through the degraded hydroinsulation as well as on the amount of get-at-able nutrients which are transported to the bridge surface by the rainfalls and wind. The microorganisms were growing, in dependence on the oxygen access, mostly to the depth of 2 - 5 cm, while their amounts mostly decreased at the depth of 10 cm considerably. In several locations a great number of germs were found even at the depth of 10 cm.

The drill holes made in Charles Bridge piers brought interesting results. The aerobic and micro-aerophilic strains were prevailing on the surface and even to the depth of approx. 1 m. The same microflora was found even at the depth of approx. 3 - 4.5 m in all drill holes which hit these areas a matter of fact (the ambient parts of drill holes shove and below this level were always sterile). The found microbial recesses were in no relation to the material composition of the piers (concrete, expanded-clay concrete, reinforced concrete, sandstone, arenaceous marl, mortar). The occurrence of the aerobic flora did not correlate with the moisture progression as well. A real explanation of this phenomenon has been missing till now (cracks in the pores?).



Fig. 18 The black crusts on arch 14 of Charles Bridge in Prague



Fig. 19 The microaerophilic flora in piers of Charles bridge

The high concentrations of nitrates and the increase of total number of the microflora from average value of approx.  $10^4$  to  $10^6$  up to  $10^7$  were affected by the application of carbamide on the bridge roadway surface in winter. Namely, carbamide, as the basic waste product of all higher organisms, is decomposed quickly by urobacteria and ammonizing bacteria at the origination of ammonia which is transformed into the nitrites and nitrates by nitrifying bacteria.

The increasing concentration of nitrogen salts is related further to the increasing concentration of nitrogen oxides in the atmosphere (the automobile traffic) and to effects of the acid rains which also contain nitrates and infiltrate into Charles Bridge through the degraded hydroinsulation. The residues of synthetic fertilizers which also contain nitrates and which appear in the atmosphere during agricultural seasonal works infiltrate into the bridge construction body together with the rain water.

The increased content of nitrogen salts in Charles Bridge construction body is evidenced even by the results of chemical analyses of the water flowing through arch VI. During analyses of the water which was flowing through the drain pipe following values were obtained: pH 7, Cl 120, SO<sub>4</sub> 285, NO<sub>3</sub> 1100, NO<sub>2</sub> 0.14, NH<sub>3</sub> 0.73, urea 0.3 mg/l000 ml water. The quoted values characterize at the best the considerable intensity of chemical and biological processes that are taking place in the bridge.

The increase of sulphates on the surface of Charles Bridge sandstones during a single year is caused by ever still high concentrations of sulphur oxides in the atmosphere (due to burning sulphurous coal sorts) which get adsorbed on the sandstone surface and are transformed into sulphates in the abiotic way or with the biological stimulation. The transformation of sulphur oxides is related to the activity of chemoorganotrophic bacteria which produce organic acids and aminoacids in Charles Bridge building stone. These acids then liberate iron and manganese from the clayey minerals by means of the chelatization process. Ions of both elements function as catalyzers in the abiotic transformation of sulphur oxides (sulphur dioxide via sulphur oxide) into sulphates.

Compared to other years, quite extraordinary values were ascertained in the numbers of sulphur bacteria. Whereas their concentration was negligible in the last years (1 - 5 cells.g<sup>-1</sup> sandstone), we found the continuous growth of sulphur bacteria on arch III. In the arch central part it reached thevalue of  $5.10^5$  cells per 1 g sandstone and correlated well with the concentration of sulphates in these localities.

 $H_2S + 2O_2$  (Thiobacillus thioparus)----->  $SO_4 + 2H^+$ 5  $H_2S + 8 NO_3$  (Thiobacillus denitrificans)----> 5  $SO_4 + 4 N_2 + 4 H_2O$ 

It is evident that also microflora metabolites participate in the formation of a number of secondary minerals. There is concerned, above all, the well known and frequent mineral goethite (FeOOH) which originates with cooperation of lichens and synergic bacterial flora. Further, nitrokalite (KNO<sub>3</sub>) and nitronatrite (NaNO<sub>3</sub>) which originates, among others, by the effect of nitrifying bacteria. Also ginite  $(Fe^{2+}Fe^{3+}_4(PO_4)_4(OH)_2H_2O)$ , darapskite (Na<sub>3</sub>(SO<sub>4</sub>)(NO<sub>3</sub>)H<sub>2</sub>O) and some minerals (for example pickeringite MgAl<sub>2</sub> (SO<sub>4</sub>)<sub>4</sub> 22 H<sub>2</sub>O), whose molecule contains SO<sub>4</sub> group (the synergic effect of chemoorganotrophic bacteria at SO<sub>2</sub> transformation into SO<sub>4</sub> on the wet stone) can also be of the biological origin. Ions of NO<sub>3</sub> in wet deposits of Charles Bridge open and dissolve the sandstone surface under the origination of K and Na saltpetres and, thus, enable other liquid and gaseous harmful substances to penetrate into deeper layers of the stone. However, the same process takes place also on the wrong side of Charles Bridge stone lining. Here, the NO<sub>3</sub> appropriation is regulated by the rain water seepage through the roadway degraded hydroinsulation.

Owing to high concentrations of salts in the sandstone and origination of secondary minerals (all studied samples of building stones from Charles Bridge construction differ from the original ones by carbonate-sulphate cement, i.e. calcite, gypsum + sulphates of alkali metals), there is no reason for the argument that the hydration and crystallization pressures (2 to 50 MPa) take part in the formation of microcracks in the stone which then grow in size and, thus, increase the surface of reaction areas of the building material. In this way (together with the occurrence of static failures), the extensive system of cracks is formed which represents already a menace to the stability of the stone surface layers.



#### 2.3. The interactions of chemoorganotrophic bacteria and salted masonry

The analyses performed on the MPA with the addition of 5% NaCl have evidenced that great numbers of microorganisms ( $10^5$  to  $10^6$  .g<sup>-1</sup> plaster) are vegetating in the zone of moist and salted masonry and on the salted classic and maintenance plasters with higher pH (pH 8.5 to 9.5). As it is known from the masonry microflora researches that the common cultivation methods can entrap a small part of microbial population only (max. 1 to 10%), it is necessary to take account of the occurrence of  $10^7$  to  $10^8$  cells of bacteria and yeast per 1 g plaster as the minimum in the moist masonry zone.

Orientation analyses have revealed, compared to non-salted surface, increased amounts of organic acids (formic acid, acetic acid, butyric acid, succinic acid, malic acid, citric acid, oxalic acid) and a whole spectrum of aminoacids. On the outside the attacked plasters presented the small netting of cracks, pulverization and/or falling-off of surface layers, of course only provided that the surface of plasters was not degraded fully by efflorescences of corrosive experimental salts.

Tab. No.X The water content, total number of bacteria  $(x10^5)$  and salting extent in maintenance plasters applied on brickwork columns after three years' effect of following salt solutions: NaCl 3.5 %, NaNO<sub>3</sub> 1,5%, Na<sub>2</sub>SO<sub>4</sub> 0.5 %.

Type of	Heigh of sample taking	Water content	Number of bacteria	Content	of salts (mg.g <sup>-1</sup>	plaster)
plaster	(cm)	(%)	$(10^5)$	Cl-	NO3	SO4
lime plaster	0	8,5	1,8	4,1	3,4	5,8
-	20	9,-	1,8	60,6	16,2	101,6
	40	8,5	0	135,3	31,5	94,1
	60	8,5	0	22,3	14,6	57,1
maintenance	0	9,-	1,5	0,9	0,4	2,9
plaster	20	9,-	2,8	95,4	7,5	80,-
	40	8,5	0,2	0,6	0,3	2,5
	60	8.5	0	0.6	0.1	1.9

It was observed at the same time that owing to considerable concentrations of salts which accumulated in the evaporation zone a number of isolated microorganisms were capable of living immediately without any adaptation in MPA with the addition of 5 to 10 % NaCl. It was possible to make some strains accustomed even to the concentration of 20 % NaCl by the gradual transferring. Such organisms can be ranked among the medium halophiles-extremophiles by full right.

In case of high moistures of the masonry and salts, nor a good-quality maintenance plaster has unlimited service life either. The plaster pores get filled with the salts, the plaster loses its efficiency gradually before it gets deteriorated. The obtained results evidence that this proceeds with the synergic cooperation of halophilic or even extremely halophilic microflora. The destruction phenomenon of this type is a new, not yet fully researched degradation factor in the moist masonry plasters.

### 3. The removal of nitrates from the masonry in biological way

The population of microbes which are capable of transformation and denitrification of nitrogen compounds is relatively large. With the exception of micromycetes and actinomycetes which are not apt for this purpose, there is a large group of microbes (Pseudomonas, Achromobacter, Bacillus, Micrococcus, Mycoplana, Serratia, Vibrio, and others). Active genera are not found in the soil only, but also on the moist masonry. The main mechanism of nitrogen liberation and N<sub>2</sub>O formation is the microbial denitrification,. insummary:

 $2NO_3 + 10 \text{ H} -----> N_2 + 4 \text{ H}_2\text{O} + 2 \text{ OH}$ 

The mentioned hypotheses were verified on the masonry of four stable objects at Ctěnice Castle which are situated at approx. 15 km from Prague centre. Such places were looked for, in which the object "self-healing" cure occurred, to put it metaphorically. These places were found in all studied objects. Although it must be admitted that the anomalies in the total number of chemoorganotrophic flora were influenced by the moisture fluctuation partly, it is obvious that the fluctuation of the total number of microbes is reflected then also in the denitrification activity of the whole microbial community. An indiderect dependence between the number of chemoorganotrophic flora and the amount of NO<sub>3</sub> (mg.g<sup>-1</sup>) was evident on most of the masonry well.

Total amount of bacteria in 1 g	$NO_3 (mg.g^{-1})$	Masonry moisture
masonry		(U%)
$10^{2}$	178	9,1
$10^{3}$	206	12,4
$10^{4}$	149	9,7
10 <sup>5</sup>	7,5	11,5
10 <sup>6</sup>	23,5	9,4

Tab. No.5. The microbial settlement effect on the total amount of nitrates on the masonry of Ctěnice

Note: the masonry of objects was built of sandstone and was patched with bricks here and there the amount of  $NO_3$  is quoted in mg per 1 g sandstone, U % - the masonry moisture in % by weight

It is evident from microbiological analyses of the stable building masonry that nitrification and denitrification activities are not related closely and that they are not conditional on each other. It is due to the fact that the masonry contains a considerable amount of freely accessible nitrate and, too, that denitrification processes in the majority of chemoorganotrophic microorganisms are not essential for keeping them alive.

Orientation laboratory experiments with crushed sandstone containing nitrates in concentration of 150 mg.g<sup>-1</sup>, suspended in a medium which was modified for denitrifying bacteria and inoculated with isolated strains, proved that denitrifying bacteria reduced the nitrate concentration to 18 mg.g<sup>-1</sup> sandstone within 14 days. Analogous results were also obtained in the real conditions of Prague Castle. In the masonry of Old Burgrave's House which is saturated with nitrates (120 mg.g<sup>-1</sup>) the content of nitrates was reduced by more than a half successfully within four weeks.

Analogous and still more complicated relations between microorganisms and substrate were found in plastics.

## 4. Biodegradation of building plastics

### 4.1. The ageing of plastics in combination with the microbial deterioration

UV radiation, oxygen, increased temperature and water. The course of the plastics changing caused by the weather degradation factors can be characterized as the rupture of polymeric chain, change of chain chemical structure, change of side groups, cross-linking, cyclization and further polymerization as well as change of polymer crystallinity degree.

It was found out that the thermooxidative ageing of plastics based on polyolefins has, from the biodeterioration viewpoint, the character of two processes linking to each other continually which cause considerable resistance variability in the course of time. In the first phase a free radical chain reaction and formation of spatial structures (crosslinking/screening) of the plastic occur, which results in the decrease of the moisture transport into plastics and decrease of the moisture level (the actual water amount in the material). This is also reflected in reduced attacks of microorganisms on plastics (thermoplastics PE and PP). During the further phase of ageing the plastic thermo- or photooxidation destruction proper is observed which affects the biocorrosive activity of microbes specifically according to reaction waste products. (In PVC the volatilization of softeners results in a decrease of biosusceptibility, in PMMA and PA the origination of the degradation assimilatable waste products results in an increase of biosusceptibility.

4.2. The liquidation of plastic wastes. There was found out the method of combined thermal degradation of polyolefins in the soil enriched with (aged) mineral oils with subsequent biodegradation by the soil microflora. It was stated that the preliminary degradation of polyolefins by mineral oils at an increased temperature (50 - 60°C) in the compost filling for the period of several weeks or by steaming of the combined carrier substrate by live steam for the period of several hours caused a deep oxidation of plastics (considerable expansion of olefinic, carbonyl and partly also vinyl groups in polyolefins). In this way, the polymer becomes susceptible to the soil microflora fully, especially to the strains which were adapted to mineral oils and polyolefins. These strains decomposed even the oil residua including aromatic portions during the substrate ageing at the same time. It was evidenced that the wastes from polyolefins disintegrate and are biosusceptible fully also provided that the carrier substrate is not saturated with oil (e.g. compost, crushed solid household garbage, light ashes, blow sands, gangue), but the plastic wastes are covered with the oil film and the carrier substrate and heated close before the homogenization process. The found out results were supplemented by vegetation tests of water extracts from the composts which were obtained by the combined biodegradation of plastics.



Fig. 23 The disintegration of thermall predegraded PE foil after 18 days maturing in compost stowage with traces of the mineral oils



Fig. 24 The cracks in PE foil the was thermally predegraded in topsoil substrate enriched with trace amounts of the mineral oils and inoculated with the bacteria strains adapted to polyolefins

The tests indicated that the standard application concentrations do not affect the seed germination negatively. On the contrary, a slight stimulation of the germination process was noted. The technology of the plastics liquidation is suitable especially for thermal and nuclear power plants which dispose of sufficient surplus of superheated water vapour.

**4.3.** The biodegradation of polyolefins in the human organism and its modelling in microbial cultures Polyolefins PE, PP and silicone rubber are not stable in the human organism After implantations, the strong oxidation of polymers, the formation of ester, ketone

and carboxyl groups, and the decrease of mechanical properties (tensile as well as bending strengths) were observed for the period of several months or even years. For modelling the observed oxidation, the bacterial homogenates of microbes which were transferred for a long time with present PE (Pseudomonas putida, Pseudomonas fluorescens, Bacillus pumilus, Bacillus brevis) and hepatocytes of eukaryotes were used. These were chosen owing to the fact that a number of biochemical processes take place in them, inclusive of transformation reactions of the matters which are foreign for human and animal organisms.



Fig. 25 The PE insulation of the pacemaker electrode in the place of pitting. Implantation time 1740 days, Electronic raster microscope magnification 1000 times



Fig. 26 The PE macroscopic crack in PE insulation of the pacemaker electrode. Implantation time 1095 days

During exposures in cellular homogenates, changes in the range of 1720 cm<sup>-1</sup> were observed on infrared spectra of PE Bralen 7-25 after two hours of exposure already. During the period of 8 - 24 hours, there was observed the confluent growth of the absorption band of OH group (3380 cm<sup>-1</sup>) and of C-O bond of aliphatic alcohols in the range of 1020 cm<sup>-1</sup>,which disappeared again later at the simulatenous growth of the absorption band of CO group (1720 cm<sup>-1</sup>) and formation of ester (1740 cm<sup>-1</sup>). Stil later, there were observed the absorption band of double bond (1640 cm<sup>-1</sup>) and further degradation in the range of 1050 - 1200 cm<sup>-1</sup> The oxidation of silicone rubber Lukopren G 1000 proceeded in the range of 1720 cm<sup>-1</sup> (the formation of carbonyl) and in the range of 1650 cm (probably the group CH<sub>2</sub> = CH(CH<sub>3</sub>)<sub>2</sub> Si(CH<sub>3</sub>)<sub>3</sub>). The degradation intensity was dependent on the relative molecular weight of polymer, for example: CO index for PE NA 7-25 =1.8 to 2.2; for PE SA 200-22 = 2.4 to 2.8.

The inhibition of PE oxidation process was possible either by bubbling the microsomal fraction with technical  $N_2$  for all the time of oxidation process or with CO for 3 - 15 minutes. The activity of dehydrogenases which take part in the formation of double bond in polymer was not stopped by the CO effect. Nor the alcohol dehydrogenase which transforms OH groups in the polymeric chain into ketone was blocked either. It was possible to block the carbonyl formation by adding the inhibitors of dehydrogenases CuSO<sub>4</sub> (10<sup>-3</sup>M) or NaN<sub>2</sub> (10<sup>-3</sup> M). Upon the application of the inhibitors of cytochrome P 450 (vaccine Corynobacterium parvum, pyridine residue and endotoxin E. coli), the adequate depression of the concentration of cytochrome P 450 was found in the experimental mice. This was also evidenced by the reduced content of carbonyl groups.

The stimulation of PE oxidation process was possible by applying phenobarbital to the experimental mice. The following values were measured for PE Liten BB 29 and microsomal fraction of mouse liver: The concentration of cytochrome P 450 increased from 0.46

(reference samples) to 1.26 n mol.mg<sup>-1</sup> protein (phenobarbital). CO index at 1720 cm<sup>-1</sup> increased from 1.56 (reference samples) to 2.69 n mol.mg<sup>-1</sup> protein (phenobarbital).

The original results evidenced that the bioredemption (biodegradation) of plastics is caused by the enzymic hydroxylation system consisting of cytochrome P 450, NADPH cytochrome reductase and alcohol dehydrogenase. The system is located on the bacterial membrane and in the microsomal fraction of liver cells and, in our experiments, was induced with PE, paraffin, barbiturates, acrylate and silicone rubber present.

### C. Concluding remark:

The line of biokorozion of the technical and building materials does not include theoretical disciplines only, but is of great importance in practice, too. Whereas 2% of all products get degraded by biocorrosion in the world yearly according to (9), the yearly loss in Poland represented more than 9 bilion zloties in recent years (in. 2000). The main breakdowns due to biocorrosion were observed especially in the folowing industrial branches all over the world (the term "breakdown" means, in this case, large laterial losses which werw often related even with the life-danger to employees or people)

Building industry, roof structures, peripheral mantles, thermal insulation, floors, floor coverings, hydoinsulating foils, (extensive mycotoxicoses in housing and civils constructions), mining (underground transport machinery, belt conveyrs, motor windings, cables), agricultural and food-stuff industries (horse stable accessories, mils, sugar factories, meat-processing plants), textile industry (textile fibres of all sorts), chemical, petrochemical and farmaceutical industries (decomposition of fuels and oils, corrosion of fuel tanks, corrosion od dispersed dyes), metallurgical industry (emulsion liquids, hydraulic oils), machine industry (heat distribution systems, air-technical plants, heat exchangers, cooling towers, transporters and conveyers), electrical industry (transformers, transport oils, aircraft fuels), libraries and museums (library and museum collections).

It is evident from what was mentioned here-above that the incorporation of lectures dealing with the problem of biocorrosion of the technical and building materials is a matter of principle for the improvement of the project preparation above all, as it will enable to reduce the losses to minimum during designing the buildings and equipment already. The aforementioned corrosion of the asbestos-cement roof covering on the cowesheds stable buildings can be regarded as a typical example already.

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### **CURICULUM VITAE**

Doc. Ing. Richard Wasserbauer, DrSc.

### **EDUCATIONS**

- Msc. (Ing.) 1959, University of Agriculture in Prague, subject: the soil microbiology
- PhD. (CSc) 1978, Czech Techical University Electrical Engineering, Prague, subject the electrical technology, specialization: the microbial corrosion
- DSc. (Biol. Sci) 1992, Institute of Microbiology of Czechoslovak Academy of Sciences in Prague, subject: the technical works biocorrosion
- Assoc. Prof. (Doc.) 1997, Czech Technical University Faculty of Civil Engineering, Prague, subject: the building materials

Authorized expert 1992, specialst in biocorrosion of building and technical materials

### **PROFESIONAL POSITIONS**

- 1961 1978 Independent engineer, from 1967 head of microbiological laboratory at the Electrotechnical Testing Institute in Prague-Troja (EZU)
- 1978 1984 Scientific worker II/IA/2b, head of microbiological laboratory at the EZU
- 1984 1987 Independent scientific worker II/I/A3, head of the microbiological laboratory at the EZU
- 1987 1993 Chief scientific worker I, head of the biocorrosion laboratory at the EZU
- 1993 Chief technical worker in laboratory OL 124, Dept of the Building structures, Czech Technical University – Faculty of Civil Engineering, Prague

### **TECHNICAL INTERESTS**

The biodegradation of building material and constructions: microbial diagnosing of buildings; biodegradation of building stones, bituminous hydroinsulating foils, silicone infusion, building plastics, biodegradation of electrotechnical products, polymer implants; liquidation of plastics wastes preservation of living environment and prediction of microbial corrosion in storage spaces of atomic power plants waste products.

### **TEACHING ACTIVITIES**

The biodegradation of building and technical materials, unobjectionability of buildings from hygienical viewpoint, biodegradation in building-technical and historical research works.

#### MEMBERSHIP IN INTERNATIONAL ASSOCIATIONS

Expert in the biocorrosion line IEC TC 50 "Environmental Testing" Wg8 "Mould Growth". Expert in the biocorrosion line ISO TC 61 Plastics "Biological Attack". Specialist of the COMECON in the National Comittee of the Czechoslovak Federal Republic for Fungal Tests.

#### MEMBERSHIP IN NATIONAL ASSOCIATIONS

Chairman of the Subcommission for Biodeterioration of the Czechoslovak Society of Microbiology at the Czechoslovak Academy of Sciences, member of the Commission of the Presidium of the Czechoslovak Academy of Sciences for Tropic-Proofing Technique, member of the Commission of the Presidium of the Czechoslovak Academy of Sciences for Technical Sciences, member of the Expert Section of the Czechoslovak Scientific and Technical Society for Material Corrosion and Protection, member of the Society for Industrial Chemistry, the Expert Group for Secondary Raw Materials and the Expert Group for member of Technical Commision of ČIA Prague for Microbiological Analysis.

### AWARDS

- 1975, Diploma appreciation of merits for development of the line of metal preservation against corrosion, the State Research Institute for Material Protection, Prague
- 1976, Diploma appreciation of merits for development of the institute and testing lines, the Testing Institute in Prague-Troja
- 1986, Diploma appreciation of honour for the development of the testing line in electrical engineering Electrotechnical Testing Institute in Prague-Troja
- 2000, Diploma appreciation of honour for publication "Biological Degradation of Buildings", The Eleventh Building Trade Fair "FOR ARCH"
- 2002, Prestige prize "International Scientist of 2002, IBC Cambridge, England

### VISITING POSITIONS

- 1961 1965 the State Research Institute for Material Protection, laboratory of biocorrosion of technical products
- 1963 Short term visit at the Microbiological Laboratory of University Greifswald GDR
- 1965 Short term visit at the Commonwealth Mycological Institute, Kew Surrey, United Kingdom
- 1972 Short term visit at the Microbiological Laboratory GIG, Katowice, Poland

### PUBLICATIONS

Within last 20 years over 170 publications in technical journals and proceedings of conferences.

### **PROFESSIONAL EXPERIENCE**

The discovery of the biodeterioration mechanism in asbestocement roof covering of horse stable building object not only enabled the proposal and realization of roof reconstructions at a number of stable building object in the Czechslovak Federal Republic, but also initiated the start of analogical analyses of microbial colonies and the depth bacteriological research of facades of historical buildings In this way it contributed to the improvement of qualities of maintenance works, among others also at Prague Castle (the bactericide preservation of the facade at Prague Castle against nitrifying bacteria).

As for further works, the following are concerned above all: Technical cooperations in the line of biological clasification for the roofs and floors in various environments of the housing and civil constructions with the Research Institute of Building Overground, Zlín and Technoplast, Chropyně, in the line of controlled biodegradation of plastics and of treatment of the textile industry waste water PVAC dispersions for the Textile Research Institute, Liberec.

For the Skoda Works, Pilsen, diagnostic methods were elaborated for determination of the biodeterioration of transformer oils and, consequently, also of the service life and durability of very high voltage transformers working in the humid tropical regions.

The discovery of the part of enzymic hydroxylation system in the biodegradation of implanted polyethylene and silicone rubber, as well as the discovery of the mechanism of silicone oil degradation were essential for prognosing the service lives of plastics and technical products and for elaborating the relevant state standards.

On the basis of formerly elaborated testing and diagnosing processes, there are realized microbiological tests in the form of secondary economic activities in laboratory OL 124 KPS for all principal spheres of national economy (building, timber, machine and electrical industries).