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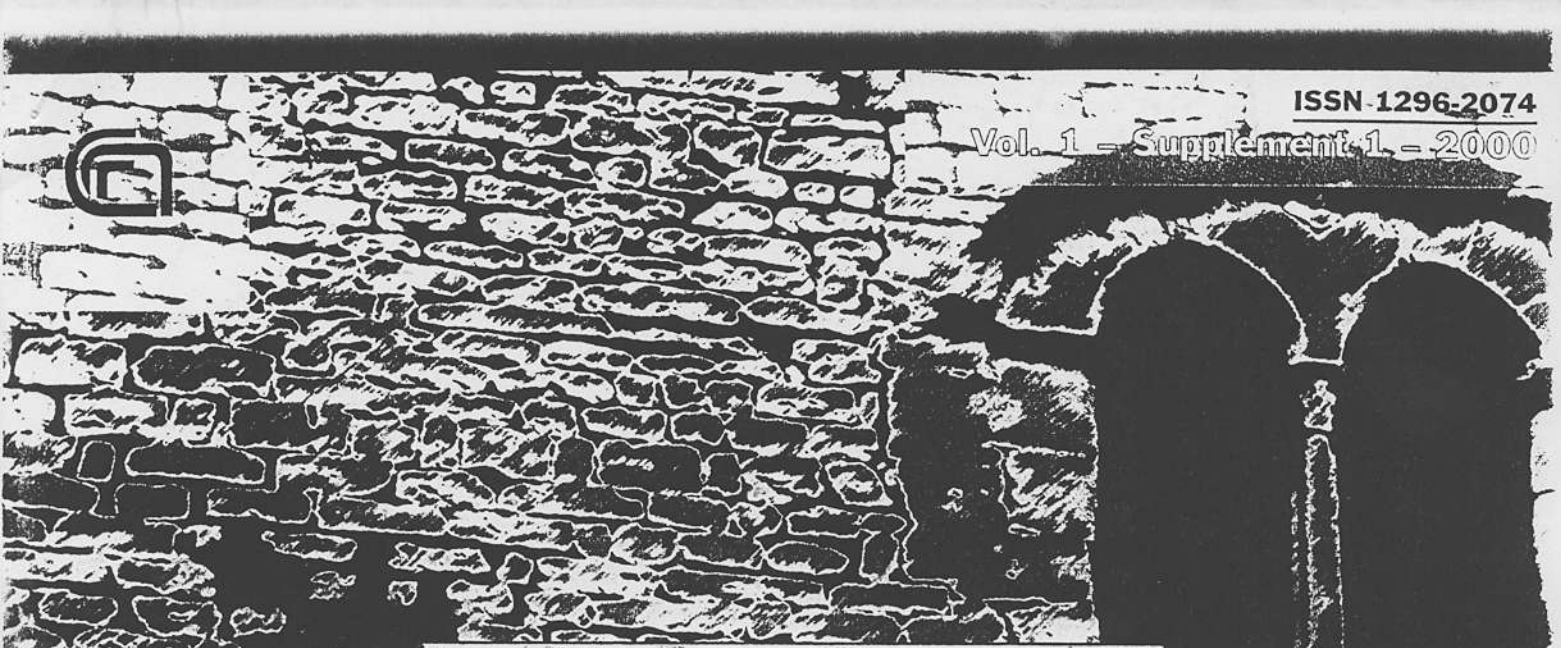

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Biogenic surface layers on historical window glass and the effect of excimer laser cleaning

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Abstract – The ablation of biofilms by excimer laser radiation was systematically examined in a series of model studies during which the biofilms originating from different historical panels were simulated on model glasses. The composition of these model glasses was modelled on that of the original historical glasses. Our studies have shown that glass composition, climatic conditions and biofilm formation are factors which interact synergetically. It could be observed that various biofilms grow differently on the same type of model glass and that the same type of biofilm shows a different development on various model glasses. The decisive factors for the effectiveness of biofilm ablation by laser irradiation is the formation of the biofilm on the one hand and its corrosive potential on account of its ability to accumulate moisture and to produce glass-damaging metabolites on the other. Glasses of low chemical stability promote the growth of dense biofilms and can be cleaned only with a high energy density, whereas glasses of high chemical stability merely allow for a slow growth of a biofilm spreading two-dimensionally on the glass surface which can be gently removed using low energy density. © 2000 Éditions scientifiques et médicales Elsevier SAS

Keywords: historical glass / biofilm / biocorrosion / laser cleaning / excimer-laser

1. Introduction

1.1. The Problem – microbial attack on glass

Conservation and restoration of historical stained glass windows is becoming ever more complex due to a huge variety of damaging factors. There are the well-known encrustations (weathering crusts, gel layers, darkening effects) on the exterior side of panels and there are new kinds of damage to be found especially on the painted, interior side of panels. In a surprisingly large number of cases this damage can be correlated to the growth of micro-organisms and the presence of biogenic layers which are frequently referred to as dirt or occasionally called patina. Medieval glass underneath the biogenic layer is often highly deteriorated. A vast contamination of micro-organisms leads to a heavy loss of glass material on the interior side which might even be more severe than the weathered exterior side of the panels [1, 2].

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The role of the micro-organisms in corrosion processes is still under debate. The contrary positions are best described by the following postulates: "The organism always wins" (K.C. Marshall, 1991) [3] and "Micro-organisms do not attack clean glass" (R. Newton, 1989) [4]. According to the most recent findings in Germany approximately 5–10 % of historical stained glass windows in need of conservation show microbial deterioration.

A very controversial discussion focuses on the appropriate conservation measures for the removal of microbial layers. From a scientific point of view it seems clearly advisable to remove those layers because they enhance the glass corrosion by accumulating humidity and pollutants and represent a permanent damage potential which may always be activated by slight pH changes.

1.2. Mitigation measures – cleaning of the surface

The cleaning of contaminated surfaces will achieve an important part of conservation measures in the future. Cleaning is necessary to prevent or to slow down corrosion activities, to regain transparency and to avoid health risks. However, stained glass conservators have encountered severe problems in removing biocorrosion phenomena such as dense surface layers of biomineralisations and microbially induced crusts. To this day, chemical and mechanical cleaning methods are preferred to remove these deposits. The removal of damaging microbes still requires the application of highly toxic chemical compounds (e.g. ethylene oxide) or the expensive, sometimes dangerous mechanical removal [5, 6], a process which constitutes a potential health hazard. The use of chemicals shows only limited success since carbonic nutrients remain on the glass surface and enable the renewed growth of micro-organisms. The disadvantages of such methods include risks such as the damaging of the protective gel layer, ranging from scratching of the surface to complete removal down to the core glass, which again can enhance corrosion reactions.

An innovative approach can be provided by excimer laser technology, which allows for a defined ablation of biofilms. The excimer laser used for the treatment operates in the UV region, which may be an advantage for two reasons: a) the micro-biocide properties of the irradiation enhances the cleaning result; b) the cold ablation process avoids the heating up of the substrate – a necessary prerequisite for the application of the method to the cleaning of medieval stained glass [7–12].

For these reasons the introduction of a gentle cleaning method would provide a number of important conservative and ecological advantages: core glass and gel layer remain intact, carbonic components can be removed residueless and the application of hazardous chemicals is unnecessary.

2. Biocorrosion of glass

2.1. Prerequisites and findings for biogenic contamination

The formation of biogenic layers on the glass surface depends on a number of parameters. Main influencing parameters are:

- environmental factors (relative humidity, temperature, temperature changes and the time of wetness on the glass surface);
- anthropogenic factors (concentration and type of carbonic nutrients);
- glass properties (water activity and Zeta potential of glass surface);
- corrosion behaviour (chemical durability of the glass which governs the pH value at the phase boundaries);
- glass properties and corrosion behaviour (mobilisation of biologically essential minerals and metal ions from the glass).

Resultant upon a great number of examinations of microbially attacked historical glasses the following common features could be observed:

- there is a correlation between wide-spread microbial contamination and a missing protective glazing of stained glass windows;
- the indoor climate exhibited long periods of high relative humidity (65–95 %RH) and moderate physiological temperatures;
- previous restoration measures with natural or synthetic polymers are documented (use of cold painting, oil and protein containing layers, oil putty, resins);
- micro-flora of contaminated glasses consists mainly of acid producing fungi, the micro-flora of chemical stable glasses consists mostly of bacteria;
- corrosion crusts with biogenic participation are mainly based on hyphomycetes containing biologically produced minerals [1, 13–15].

2.2. Influence of glass composition on the micro-flora

The formation of a highly corrosive micro-flora depends mainly on abiotic factors; namely, the overall climatic conditions and the availability of nutrients. If the environmental conditions are biologically appropriate one can detect differences in the biofilms growing on stable or less stable glasses concerning structure and size of the layers. Non-durable glasses have three-dimensionally structured biofilms of approximately 80–200 μm thick, whereas more stable glasses have thin, more two-dimensionally structured layers with a thickness not more than 5–10 μm.

A decreasing chemical stability of the glasses correlates with an increase in the damage probability by an increasing probability of biogenic contamination: The less durable a glass is, the higher the concentration of micro-organisms within the micro-flora. Another general trend is that the microbial contamination depends on the pH value of the glass surface and on the availability of water on the surface. The proportion of bacteria increases significantly with increasing concentration of alkali ions in the glass, thus with decreasing chemical durability of the glass.

The amount of adsorbed water depends on the type of glass and on the relative humidity of its environment. The water amount increases in the order of borosilicate glass, lead silicate glass, soda lime glass [16]. The water activity a_w on the surface increases in parallel to the formation of the gel layer and the incorporation of water molecules. This higher supply of water makes the glass more attractive for microbes and at the same time the corrosive damage potential of the hydrolytic attack increases.

2.3. Glass composition and biocorrosive attack

The microbial attack on glass is partly of a biochemical nature. It is based on hydrolysis and ion exchange reactions. Biophysically induced crystal precipitation on the surface and within the gel layer amplifies the corrosive action. The majority of the damage is brought about by the impact of acidic solutions. Key roles in the generation of leached corrosion crusts will have to be assigned to carbonic acid (H_2CO_3) formed by CO_2 and H_2O – resulting from the degradation of organic compounds – and to biologically produced organic acids.

Direct effects on the glass resulting from biogenic attack include etching, pitting, formation of gel layers, discoloration, glass degradation and an extreme soiling of the original glass surface. Bioindicative factors are atypical enrichments of biologically important elements (potassium, sulphur, phosphor, calcium, manganese) and the precipitation of biominerals. The presence of whewellite, weddellite (calcium oxalate), calcite and aragonite (calcium carbonate) is usually direct evidence for biogenic activity [14, 17].

3. Laser cleaning experiments

To test the removal of biogenic layers by excimer lasers, sensitive model glasses were contaminated with biofilms, incubated, and then treated with the laser. The chemical composition of the glass samples was chosen so as to be comparable to historical originals [18] (*table I*). However, the dimension of the samples and the standardised test procedures allow an early registration of corrosive influences [19, 20].

Table I. Composition and thresholds of the model glasses [18].

Model glass	M1.0	M1	M6	M5
Composition	SiO_2: 54.2 % K_2O: 28.8 % CaO: 17.0 %	SiO_2: 48.0 % K_2O: 25.5 % CaO: 15.0 % Na_2O: 3.0 % MgO: 3.0 % Al_2O_3:1.5 % Pb_2O_3: 4.0 %	SiO_2: 48.0 % K_2O: 25.5 % CaO: 15.0 % Na_2O: 3.0 % MgO: 3.0 % Al_2O_3: 1.5 % Pb_2O_3: 4.0 % MnO: 1.0 %	SiO_2: 48.0 % K_2O: 24.5 % CaO: 14.0 % Na_2O: 3.0 % MgO: 3.0 % Al_2O_3: 1.5 % Pb_2O_3: 4.0 % MnO: 1.0 % Fe_3O_2: 1.0 %
Core glass: threshold for the ablation (J/cm²)	2.0	2.5	2.0	0.5
Gel layer: threshold for the ablation (J/cm²)	1.5	1.5	1.5	0.5

3.1. Preliminary examinations – moulds as test organisms

The laser cleaning examinations were carried out by a KrF-excimer laser (Lambda Physik EMG 201) at a wave length of $\mu = 248$ nm with various energy densities and pulse rates. It was observed that no damage or removal of the glass substance occurs below an energy density of 1.5 J/cm^2 and 200 pulses. Higher energy densities or pulse rates lead to a photochemically or thermally induced alteration of the glass matrix.

For the preliminary examinations typical representatives of glass-populating fungi were selected which were isolated from contaminated objects (optical glass from Brazil; glass sensors of the Fraunhofer Institute for Silicate Research, Würzburg). They were identified as *Aspergillus niger* (van Tieghem) and *Penicillium aurantiogriseum* (Dierckx). Potassium lime silicate glasses served as substrate (*table I*). The glass surface was treated with a 3 % glucose solution, incubated, and kept at 95 % RH for 40 days. After that, the biofilm and the corrosion layer were characterised and subjected to laser treatment.

It was shown that an energy density of 0.5 J cm^2 and 200–300 pulses were sufficient to remove the fungus tissue of *A. niger* completely. *P. chrysogenum* could only be removed partially at the same energy density. The cause of this difference is the divergent amount of biogenically synthesised extracellular polymeric substances which leads, in the case of *P. aurantiogriseum*, to biofilm growing strongly attached to the substrate.

In both cases biominerals (calcite, kalicinite, whewellite) remained on the glass; their removal required energy densities of more than 2–2.5 J/cm^2 corresponding to the energy density required for ablation of inorganic corrosion crusts. This is already the energy threshold for the ablation of core glass material which will damage the glass (*table I*) [7].

3.2. Main study – the interaction between biofilms and glass samples

The main investigations were part of the interdisciplinary research project 'Laser Cleaning of Stained Glass Windows'. The model glasses for the examination of biofilm simulation and laser cleaning were prepared at the Fraunhofer Institut für Silicatforschung (ISC), Würzburg. The microbiological part of the project is concerned with the examination of biofilms on historical glass windows, the simulation of those layers and the cleaning effect of their treatment by excimer lasers. The task of the laser cleaning of model glasses was carried out by the Laserzentrum FH-Münster (LFM), Fachbereich Physikalische Technik, Steinfurt.

3.2.1. Simulation of tight growing biofilms (two-dimensionally spreading biofilms)

Modern glass of the late 19th and early 20th century corrodes only slightly, owing to the high chemical durability of the soda lime glass used. The gel layers have a thickness of below 5 µm, the glass surface is largely intact and only occasionally cracked. The leaching rates of minerals, such as calcium or potassium and of tracer elements are low. This causes the resulting biofilms to measure at most 10 µm in thickness; they consist of only a few cellular sheets, and spread mainly two-dimensionally. Fungus textures with a three-dimensional structure can only rarely be found. The distinguishing mark of biofilms on these types of glass is therefore a two-dimensional spread without an embedment of significant amounts of biominerals (two-dimensional biofilm).

As an example of these kinds of biolayer, one might consider the microbial contamination of the stained glass windows at the church of Bad Driburg, built in 1970 (*figure 1*). In order to simulate that particular type of biofilm, a suspension of original biogenic matter was applied to fire-polished and non-corroded glass samples. After an incubation period of 83 days (95 % RH, 26 °C), the biofilm was characterised and subsequently removed by excimer laser treatment at various energy densities.

3.2.2. Simulation of compact biofilms (three-dimensionally spreading biofilms)

Contrary to modern soda lime glass, the chemical durability of medieval potassium lime silicate glass is relatively low. Because of the supply of hydrolytically mobilisable cations (potassium, calcium) and transition metals (iron, manganese) and the presence of aquaeous gel layers of 20–30 µm thick, far better conditions for microbial growth exist. Organic coatings have led in the past to the development of a compact, biogenically structured layer. Hence, the preferred direction of the microbial growth is not merely the x, y-plane parallel to the glass surface, but also the third dimension in the direction of the z-axis (three-dimensional biofilm).

As an example of such a biofilm, the surface layers of the medieval glazing of the Altenberg cathedral (built 1381–1392) were removed (*figure 1*). For the simulation of the three-dimensional

Figure 1. Three-dimensional biofilm on the historical panel of the cathedral of Altenberg on the left: two-dimensional-biofilm on the historical panel of the church of Bad Driburg on the right.

structure, the biofilm was applied to pre-corroded glass samples which had been treated with a 3 % glucose solution. The gel layer of the glass samples measured approximately 25 µm. After an incubation period of 96 days (95 % RH, 26 °C) the biofilm was characterised and subsequently ablated by excimer laser at various energy densities (*table II*).

3.3. Influence of the biofilm structure on the effectiveness of laser cleaning

3.3.1. Lasercleaning of two-dimensional biofilms

Two-dimensional spreading biofilms, for example the biofilm of Bad Driburg (*figure 1*), can be easily removed from the glass surface with a relatively low energy density. For the biofilm ablation of chemically stable glass (M6) a smaller energy density is more necessary than for chemically less stable glass (M1.0). The reason for this is the higher corrosion sensitivity of the M1.0 glass which allows a stronger adhesion of biofilms to the corroded glass surface.

In the case of chemically stable glass the laser cleaning could be performed with an energy density of less than 0.8 J/cm^2; in the case of the chemically unstable glass it was necessary to work with an energy density of more than 1.0 J/cm^2 (100 pulses, frequency: 10 Hz) (*figure 2*).

3.3.2. Laser cleaning of three-dimensional biofilms

Three-dimensional spreading biofilms cause particularly fundamental damage to the chemically unstable glass. In the course of the microbially induced corrosion a thick gel layer is formed which can easily be settled by micro-organisms. The consequence is a strong adhesion of the biofilm to the gel layer. The interaction of metabolites, especially organic acids, to the bulk glass cause a biocorrosive attack to the glass and the deposition of a precipitation layer which is often enclosed into the biofilm. The inhomogeneous biomat has a spongy effect accumulating moisture, metabolites, and biominerals (*figure 3*).

The biocorroded glass surface is more sensitive and the biominerals increase the threshold of the biolayer, so that the ablation of the organic matter without impairment of the corrosion layer becomes more difficult.

Dense microbial layers (> 200 µm) could not be satisfactorily removed despite a high energy density. The laser treatment (2.9 J/cm^2) damaged the glass surface deeply (*figure 4*).

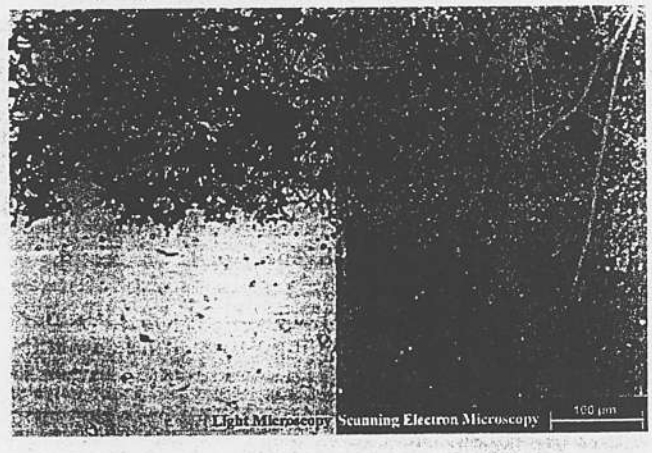

Figure 2. The laser cleaning of two-dimensional biofilms is successful with an energy density of 1.0 J/cm^2.

Table II. Derivation of the biofilms and the microbial community.

Biolayer	Altenberg	Brakel	Stockkämpen	Bad Driburg
Century	13th	19th	19th	20th
Original glass surface	corroded	organic layer (cold setting)	layer of lead silicate glass	uncorroded
Majority of micro-organisms on original panels	fungi	fungi	bacteria, (fungal spores)	fungi
Majority of micro-organisms on model glasses	fungi	fungi	fungi, bacteria	fungi

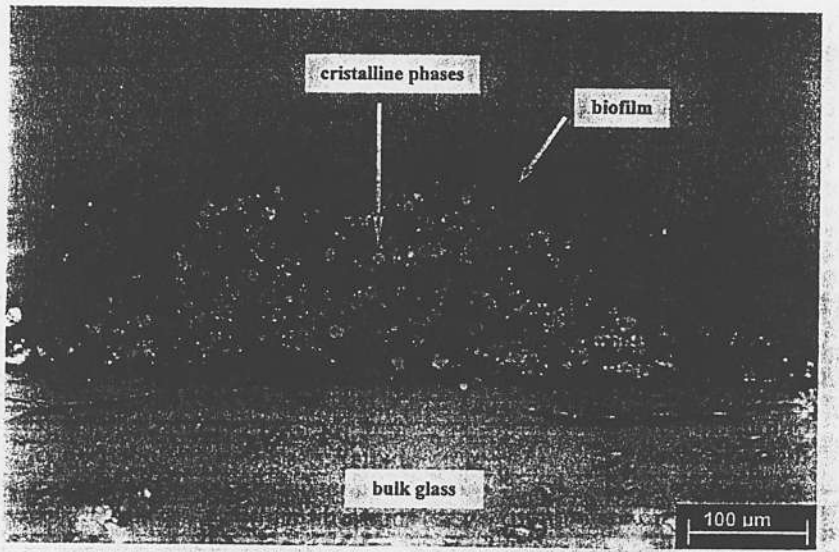

Figure 3. Three-dimensional biofilm in the thin section: particles of the corroded glass, biominerals and other biogenic material are enclosed in the mycel of filamentous fungi (*Cladosporium* sp.). The three-dimensional biofilm functions as a sponge on the glass surface enhancing the hydrolytical and acidic attack of the bulk glass.

As a rule, in the case of chemical stable glass (M6) three-dimensional biofilms of a thickness up to 100 µm can be satisfactorily ablated with an energy density higher than 1.3 J/cm². In the case of chemically unstable glass (M1.0) significantly higher energy densities (approximately 2.0 J/cm²) have to be applied (*figure 5*).

3.4. Influence of varying biofilms and model glass compositions on the effectiveness of laser cleaning

The development of biofilms on model glass depends both on the glass composition (*table I*) and the kind of biofilm (*table II*).

3.4.1. Characterisation and simulation of biofilms

The biofilms were taken from the original historical panels and simulated on model glasses, afterwards the original and simulated biofilm were compared (*table II*).

The structure of biofilms was examined microscopically [(light microscopy (LM), scanning electron microscopy (SEM), confocal laser scanning microscopy (CLSM)] (*figures 3* and *6*). Using molecular biological methods [polymerase chain reaction (PCR), denaturing gradient gel electrophoresis (DGGE)] the bacterial community of the biofilm was analysed (*figure 7*).

In addition to the biofilms of the historical panels of Altenberg and Bad Driburg two further biofilms were applied for simulation purposes: the microbial community on the panels of the church of Brakel and of the church in Stockkämpen, both dating to 19th century (*table II*).

The biovolume varied from 5×10^4 to 1×10^6 µm³/cm² and the lowest volume was determined for the bacterial biofilm on the Stockkämpen panels.

Molecular biological analyses established that the original surface of the panel from Stockkämpen shows a wide variety of bacteria species. Among them, the genus *Nitrospira*, which belongs to the ammonium-oxidizing, nitrifying bacteria could be identified. The result of the oxidation of ammonium is nitric acid. This inorganic acid has the potential to deteriorate materials such as stone and glass.

Furthermore, *Actinomycetes* could be found which form mycels similar to the filamentous fungi and produce metabolites that could be responsible for the deterioration of glass [21].

Methods of molecular biology for the characterisation of biofilms are of supreme importance

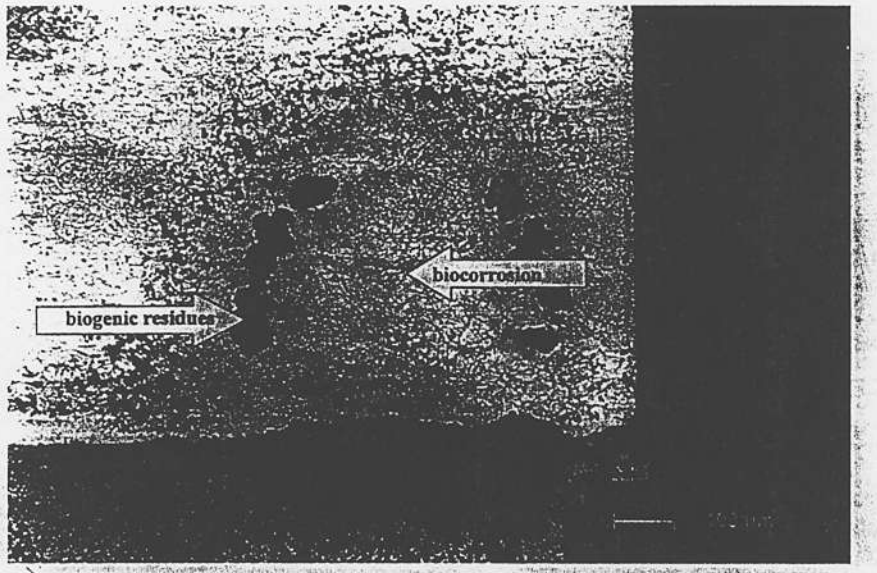

Figure 4. The biocorroded surface of the model glass is more sensitive to the laser irradiation as the atmospheric corroded surface. The three-dimensional biofilm could not be totally ablated despite an energy density of 2.9 J/cm^2.

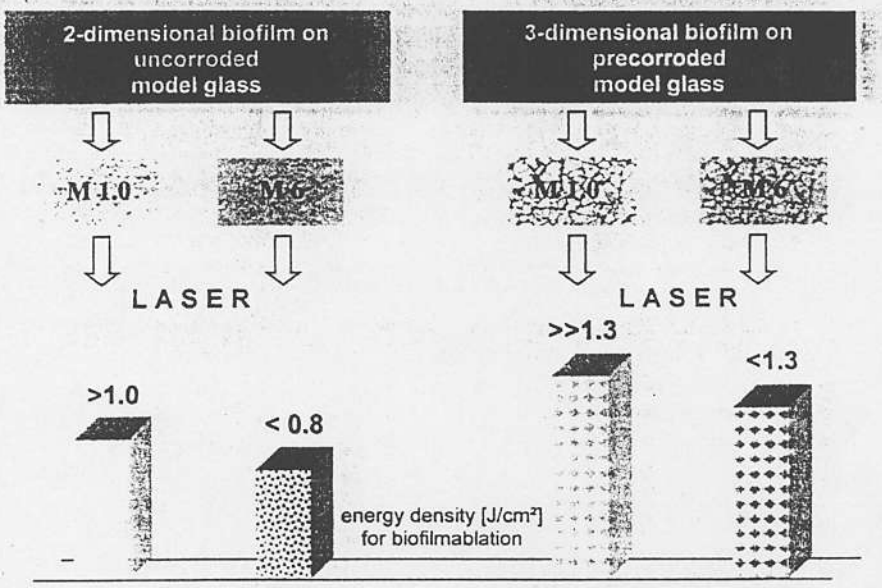

Figure 5. Results of the laser cleaning studies concerning the ablation of two-dimensional and three-dimensional biofilms on model glasses.

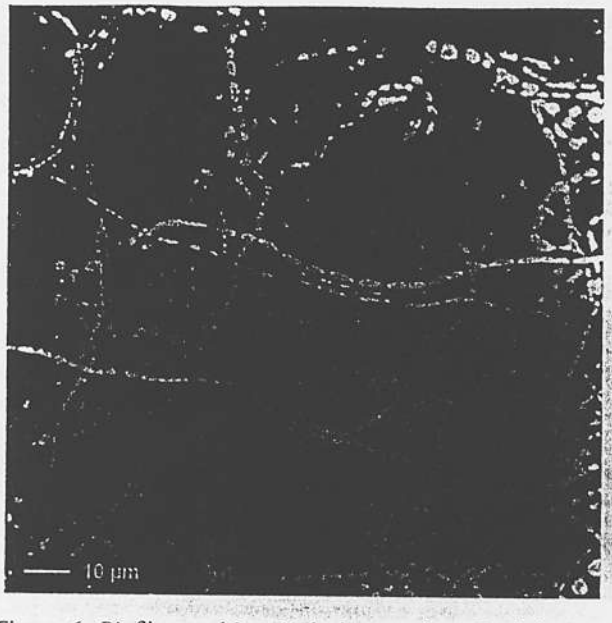

Figure 6. Biofilm on historical glass surface (Brakel); nucleic acid staining (Syto17). CLSM image: projection of z-series (16 xy-sections, 3 µm); excitation at 543 nm (TU Munich).

Figure 7. Ethidium-bromide-stained DGGE separation pattern of DNA fragments. The samples were taken from an original biofilm of a glass panel of the church of Stockkämpen (lanes 2–4) and the artificial biofilm (lanes 5 and 6). Lane 1 represents a reference marker of known bacteria (Vienna University).

because traditional cultivation strategies can detect only a part of the microbial community. The PCR method, together with the DGGE method, made it possible to compare the original biofilm with the simulated biofilm on the model glass.

The obtained DGGE band pattern reflects the bacterial diversity in the sample. As one DGGE band originates from one taxon, a complex pattern would indicate a high diversity in the original sample, whilst a low number of bands in the pattern would suggest a bacterial community with a low bacterial diversity. The comparison of DGGE patterns from different samples provides information about similarities and differences in their community structure. The application of this approach revealed that the sample material taken from historical glass panels was associated with complex microbial communities (*figure 7*, lanes 2–4). The identification of individual members demonstrated the presence of bacteria that had not previously been found on glass objects.

The comparison of the original biofilms with the band pattern of the artificial biofilm of the model glass revealed that the latter was less complex. However, some of the main species in the original biofilms (lanes 2–4) were also represented in the biofilm on the model glass (lane 6).

3.4.2. The interaction between biofilm and glass

In a further study the effect of both different biofilms on one model glass type and one biofilm on different glass types was investigated. The objective of this cross-over test was to determine the influence of the biofilm parameters and glass composition on the laser cleaning.

Figure 8 demonstrates the interaction of microbial growth and glass composition. Topic A shows the different development of two different biofilms growing on the same glass over a period of 230 days. Topic B demonstrates the development of one biofilm that was applied to different glass types: the same biofilm from the historical panel from Brakel generates a quite different formation on the model glasses M5 and MI. The exposure time was also 230 days.

As seen in *figure 9*, in the first column for 0.5 J/cm^2, the M6 model glass is insufficiently cleaned of the Stockkämpen and Altenberg biofilms, microbial residues remain on the glass. The evaluation is quite similar. The same effect can be observed on the model glass MI covered with the Brakel biofilm. Only the model glass M5 shows an effective laser cleaning with an energy density of 0.5 J/cm^2.

However, in the column for 1.0 J/cm^2, both biofilms on model glass M6 can be successfully ablated. An excellent cleaning effect is achieved for model glass MI covered with the Brakel biofilm. In contrast, an energy density of 1.0 J/cm^2 is enough to damage the model glass M5. The surface of the glass is severely damaged and an extended crack pattern can be established. This feature can be led back to a sensitivity of this model glass to laser irradiation. Lastly, an energy density of 1.5 J/cm^2 causes an

increasing gel layer on glass M5, whereas glass MI can be cleaned with a very good success without damaging the glass surface. The ablation of the Altenberg biofilm gives a better result than the ablation of the Stockkämpen biofilm dominated by bacteria.

It can be established that the ablation of the biofilm depends significantly on the glass composition. Furthermore, it is clear that differences in the microbial community can be responsible for the effectiveness of the laser cleaning.

3.4.3. Schematic representation of the synergetic effect

The interaction of glass and biofilm influences the formation of corrosion layers (*figure 10*). Glass of high sensitivity will be easily corroded by weathering. In the following, the growth of micro-organisms and the abiotic-induced crust formation is a result of the formatted corrosion layer. A three-dimensional biofilm will be formed on a highly sensitive glass surface and in contrast a two-dimensional one on a glass of low sensitivity. The improved adhesion of the micro-organisms and the subsequent leaching of minerals out of the glass strengthen the corrosion process and the biocorrosive attack is speeded up. Eventually, glass of high sensitivity biocorrodes heavily and high energy densities are necessary for a satisfactory ablation of the biogenic layer whilst glass of a low sensitivity can easily be cleaned using low energy levels. In conclusion, the weaker the glass, the easier is the microbial deterioration, and the more complicated the cleaning.

4. Conclusions

It can be stated that the effectiveness of biofilm ablation by excimer laser cleaning depends crucially on the nature of the formation of biofilms. Decisive factors are the biovolume and the spatial distribution as well as the composition and the surface properties of the glass: the corroded surface of sensitive glasses enables an increased adhesion of the

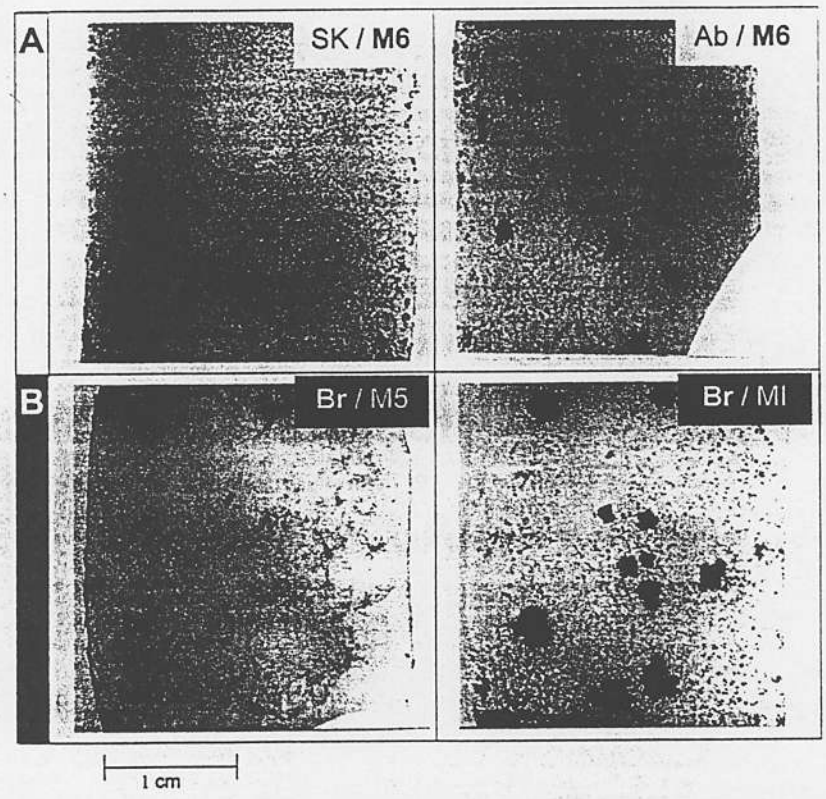

Figure 8. Macroscopic observation of the development of A) two different biofilms, Stockkämpen (Sk) and Altenberg (Ab), on one model glass type (M6); B) one biofilm type, Brakel (Br), on two different model glass types (M5, MI).

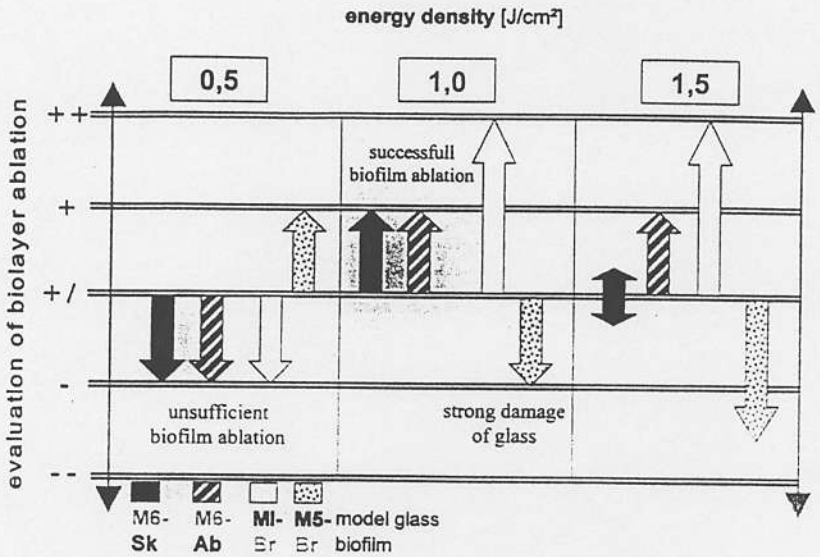

Figure 9. Cross-over test: one biofilm on different types of model glass and different biofilms on one model glass: Sk: Stockkämpen biofilm on M6, Ab: Altenberg biofilm on M6, Br: Brakel biofilm on MI and M5. The plus and minus signs correspond to the evaluation of the biofilm ablation. At the top, the double plus label reflects a very good cleaning result: at the bottom the double minus label shows a bad cleaning result, because the biofilm ablation is not satisfactory or the corroded glass surface is damaged; in the middle we observed neither a laser cleaning effect nor damage on the glass surface.

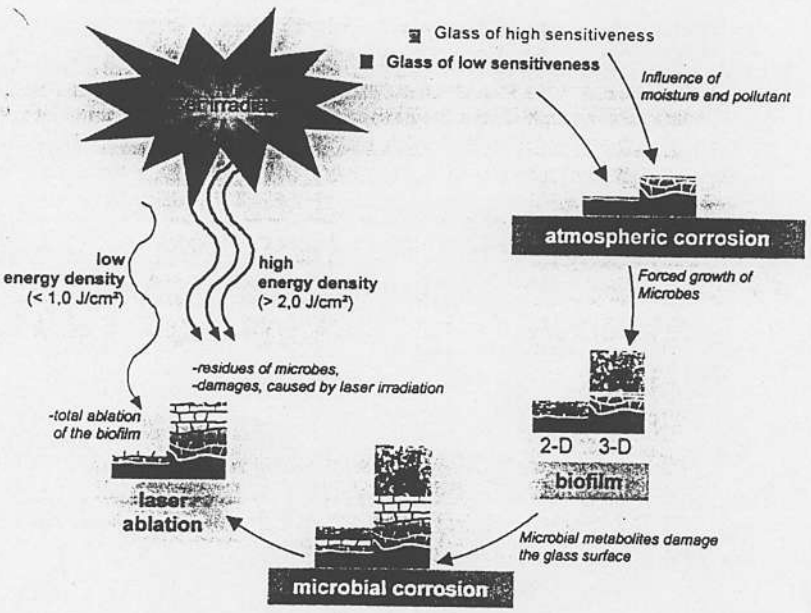

Figure 10. Interaction of glass and biofilm and the synergetic effect of glass composition, abiotic corrosion, biogenic corrosion and growth of biofilm, factors which influence the effectiveness of the laser cleaning.

micro-organisms and the production of metabolites penetrating into the gel layer and the bulk glass. This process encourages the development of the microbial layer. As a result, several negative factors are responsible for the difficulties concerning the cleaning processes of such glass.

In contrast, the non-corroded surface of stable glass will be settled by a thin biogenic layer. Therefore, the biocorrosion is slowed down and the two-dimensional, less adhesive, biofilm can be easily ablated by the laser.

A further important subject is the sensitivity of the glass with regard to laser irradiation. However, this fact does not influence the formation of the biofilm so the limiting factor of the laser cleaning process is the glass by itself.

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