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Investigation Of Building Materials Containing Algae-Prone Properties: Perspectives For Sustainable Façade Design

Doctoral-Thesis-Booklet

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2 Introduction

The constructive and hygrothermal measures to prevent moisture on building material surfaces have not yet had the desired long-term effects. Airborne algae still conquer façades and develop biofilms (Fig.1-2). The complete isolation of a building envelope from its environment is impossible and toxic organic biocides are still used to compensate for the deficits of the construction and measures.

Figure 1: North gable near Wismar/Germany after 7 years of renovation (Photo: Author)

The current EU directives force the manufacturers of building materials to restrict the use of biocides and to defuse the existing formulations regarding their negative ecological impacts. Climate change and the role of the greenhouse gas carbon dioxide pose great challenges to mankind. The important contribution of algae to global oxygen production and carbon dioxide sequestration must be preserved - even on façades. The present work pursues the approach of identifying further essential colonisation factors for algae on building component surfaces, which may be available as a control element of functional façades.

Figure 2: North gable near Wismar/Germany with pronounced infestation (Photo: author)

The principal aim of this study is to investigate the influence of magnesium-containing fillers on the early biofilm formation of algae on façade coatings. The biomass is quantified using a mobile in-situ fluorescence spectrometer, which was originally developed for water monitoring and is being tested for its applicability as part of the study. Within 730-days of outdoor weathering and supporting laboratory tests a dew-activated non-toxic functional filler has been investigated as possible defence strategy against algal infestation.

3 Aim of the work and research questions

Magnesium is not only part of the most important macronutrients for phototrophic organisms but also of outstanding importance as the central atom in the light pigment chlorophyll, as photosynthesis is impossible without this alkaline earth metal. It occurs in dissolved form in the world's oceans and inland waters and has been an integral system component of the algae and cyanobacteria that have evolved there for billions of years. The same biological principles apply to the colonization of building materials by airborne phototrophic microorganisms. It is therefore surprising why this key factor does not play a role in scientific publications regarding biofilms on building materials. Both modern and historical building materials are affected by the phenomenon of microbial colonization and both materials contain magnesium. During the theoretical studies and the present research work, the following specific research questions had to be answered in connection with the microbial colonisation of building material surfaces:

- Which advanced fluorescence measurement methods can be used to monitor algae biofilms on building component surfaces?
- What is the role of bioadsorption in the process of algae colonisation on building material surfaces?
- Which alternative sources of essential magnesium-based minerals result from the coating formulations?
- What are the long-term effects of magnesium-containing fillers on algae susceptibility of building materials?
- How to determine the area-related algae adsorption on building materials?
- What alternative biocide-free control strategies without toxic intervention to algae and environment can be developed?

The present work pursues the approach of identifying further essential colonisation factors for algae on building component surfaces, which are available as a control elements of functional façades.

4 State of the scientific and technological knowledge

4.1 Bioadsorption in the process of microbial growth

Looking for comparable environmental conditions for microalgae on façades, they can be found in the field of industrial algae production. The high and controllable content of fatty acids, proteins and carbohydrates makes green algae an important raw material in the production of biofuels and animal feedstock [10]. The main interest is the complex harvesting process, which can be simplified and optimized using calcium and magnesium compounds [11]. Algae cells are contained in wastewater as an organic component and lead to problems and higher costs in water treatment due to their dispersing properties [3]. Earlier studies have already shown a correlation between a high pH-value and magnesium compounds in the chemical flocculation of algae. This is driven by a complex bonding interaction of cationic metal-ions with the cell-wall-located functional groups where magnesium-compounds have shown high flocculation efficiency over a wide pH-range for *Chlorella spp.* [10][12]. In the study on the biosorption of uranium using the green algae *Chlorella vulgaris*, functional groups were determined on vital and dead cells by potentiometrically determined titration curves that confirmed carboxyl, phosphate, amino and hydroxyl groups [13]. This multifunctional bio-equipment enables the algae to buffer changes in pH and interact with several metal cations, which are widely contained in mineral based building material surfaces. The cell wall structure of algae is more complex than that of fungi and bacteria, so the evolutionary origin of the various algae species must be considered [14]. This is where the importance of a differentiating measurement system becomes particularly clear. On the metal side, the affinity towards biofilms is affected by ionic radius and electronegativity and magnesium plays a special role here [15].

When flocculating algae suspensions, the same chemical additives are used that are also found as fillers in façade paints. At this point, the research question arises regarding the expected adsorption effects of algae on building material surfaces.

4.2 Algae cell wall interaction with metals

The morphological structure of the various microalgae such as green algae, cyanobacteria and diatoms will not be discussed in detail here. However, the focus is on the presence of functional groups on the outer surface of these photosynthetically active microorganisms. These functional groups represent reactive points of contact for interaction among each other and other surface components, as they have real charges under certain conditions (Fig. 3). The general term of such interactions on the cell surface based on physical adsorption, ion exchange, chelation and complexation with functional groups is bioadsorption. These reactions can take place with living and dead biomass and depends on the pH value, temperature, cation concentrations of the metal and biomass in aqueous solutions [16].

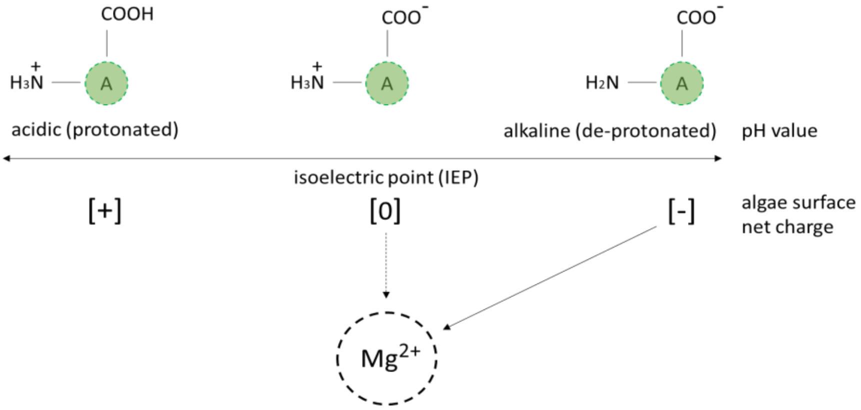

Figure 3: pH-depending charge-configuration of algal (A) functional groups

Chlorella vulgaris is a well-researched algae and consists of polysaccharides and proteins which provide several binding sites for the metals [12]. Representative of the two different charges of these groups, the amino and carboxyl function is shown in Fig. 3. The functional groups, such as carboxyl, hydroxyl, phosphoryl provide a negative, and to amino groups a positive charge on the cell surface [3]. The simultaneous presence of different functional groups leads to a resulting total charge under certain pH values. The isoelectric point (IEP) is the pH value at which the total charge is zero. At pH values above the IEP, negative charge excesses result and enable interaction with oppositely charged cations.

4.3 Magnesium-containing fillers

In normative terms, the following applies to a filler in accordance with DIN 55943 and ISO 3262 Part 1: "*A substance consisting of particles that is practically insoluble in the application medium. Practically insoluble substance which is used to increase the volume to achieve or improve technical properties and/or to influence optical properties*" [17]. The required practical insolubility in a paint formulation leads to so-called dispersion paints. Fillers are predominantly of mineral origin and are present in the form of carbonates, silicates, sulphates, sulphides, oxides and possibly mixtures of these [18]. At 42%, fillers make up the largest proportion in paint and varnish formulations and are dominated in Europe by carbonates with a share of over 85% [18]. Magnesium is involved in the formation of dolomite, talc, montmorillonite, and bentonite, among others. Talc is a widely used filler, which is characterized by a high oil number, low shrinkage, low cracking tendency and a favourable critical pigment volume concentration in paint formulations [18]. The magnesium content of talc Mg3[Si4O10(OH)2] is 19.2%. With a normal surface application of 150-180 ml/m² of a façade wet paint according to the average manufacturer's application volume, the presence of talcum results at magnesium values of 2.7 g/m². The average magnesium content in particulate matter fine dust (PM10) is on average 0.053 µg/m³ of air. To deliver the same amount of magnesium by airborne PM10, 50.9 million cubic meters of air would be required and must be completely washed out by rain and transferred to 1 m² of the vertical façade surface. This comparison clearly reveals the great potential of mineral nutrients hidden in the coating formulations themselves.

4.4 Biocide-free algal growth defence strategy

In the present work, powdered zinc molybdate from Carl Roth, Germany with a purity of 99.0% was used. The practically water-insoluble, white powder with the molecular formula $ZnMoO_4$ (CAS No. 13767-32-3) has a molar mass of 225.3 g/mol. With the density of 4.3 g/cm^3 and a melting point >700°C [100], the pure white zinc molybdate meets the basic requirements of fillers [19]. Molybdenum compounds have been mentioned as a corrosion inhibitor more than 50 years ago [20] and is also known for its flame-retardant properties [21]. In addition, molybdenum compounds are described in various publications as additives having antimicrobial properties [22-29]. From a chemical point of view, compositions of the transition metal are attributed proton-releasing properties in combination with water or humidity to reduce the pH value to such an extent that pathogenic germs can be combated [8][9]. The release of protons in combination with water prompted the author of this work to investigate whether the active principle can be transferred to the control of early algae biofilm formation in the context of outdoor weathering of façade coatings (Thesis 4). Research assumes that it is not possible to achieve permanent pH values on external surfaces that are suitable for preventing biofilm development by microorganisms [30]. This application should clarify whether the zincmolybdate filler can overcome the buffering effects of the weathered surface and the algal reduction effect occurs.

4.5 Spectroscopic evaluation via BenthoTorch®

The bbe-Moldaenke BenthoTorch® (BTo) utilizes chlorophyll fluorescence in living organisms to measure the types of algae and total algal mass present in underwater and benthic environments. It can distinguish between three groups of algae - cyanobacteria, green algae, and diatoms by analysing the unique fluorescence patterns of their photosynthetic pigments (Fig.4). Cyanobacteria contain phycocyanin, diatoms contain fucoxanthin, and green algae have a specific combination of chlorophyll-a and -b. Chlorophyll-a, which is found in all photosynthetic organisms [31], is commonly used as an indicator for algal biomass.

The BTo provides data on total algal biomass as chlorophyll-a concentration per unit area and community composition as chlorophyll [µg/cm²] or cells/mm². That delivers a potentially more practical alternative to current complex and time-consuming methods, e.g. Pulse Amplitude Modulation Fluorometry (PAM) for characterizing supramural algal communities. A comparison between extractive laboratory methods and the BenthoTorch® showed strong correlations if the chlorophyll-a content was below 4 µg/cm² [2]. All measured values of the outdoor weathering were clearly below this limit in the linear measuring range.

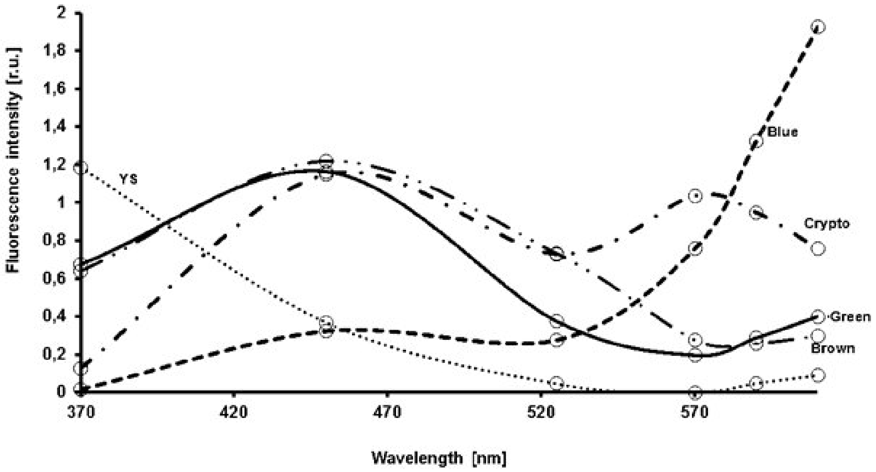

Figure 4: Algae-specific fluorescence response signals after excitation [32]

A special feature of the BTo is the use of three different excitation wavelengths. These address the species-specific photopigments and allow conclusions to be drawn about the composition of the biomass. With the PAM method, only a sum signal is obtained, as only one wavelength is used for excitation. It is of scientific interest to be able to differentiate between algae and cyanobacteria, as these have different effects on the colonization and corrosion processes of building materials. The development of bio-receptive component surfaces can be much more targeted with this extended information about possible symbiotic microorganisms.

Figure 5: Application of BenthoTorch at building facade in Wismar/Germany [53]

4.6 Influencing of thermal properties

Hygrothermal approaches focus on building physics to avoid condensation and long-lasting water films [33]. Constructive measures have been known for centuries and are the easiest to implement to keep rain away from the building structure (i.e. roof overhangs). The selection and design of the building material surfaces influences porosity and roughness, which are essential factors that, together with moisture, lead to increased colonization of microorganisms [34]. More sophisticated approaches of the last four decades ended up in hydrophobic additives (lotus effect) [35], infrared absorbing pigments with lower emissivity [36], phase-change-materials (PCM) in plasters [37]. The chemical approaches focus on encapsulated biocides with long-lasting effect [38] and photocatalytic pigments (Anatase TiO2) tried to generate a selective destruction of microorganisms via free radicals [39]. The isolated investigation of individual strategies, partly in the laboratory and partly in the field, led to euphoric product launches. Unfortunately, the deficits only became apparent in real-life applications, while algae growth being delayed at best with PCM or even increased at worst with hydrophobic additives, that promotes the availability of dew on surfaces [40]. All these insufficient technologies in long-term ultimately led to the use of biocides and leaching of toxic substances into the environment still happens.

5 Applied analytical methods

5.1 Light reflectance value and sample brightness

The thermal load of façade coatings due to solar radiation poses a considerable risk. According to DIN 55699:2017 [41], when using dark colours on external thermal insulation composite systems (ETICS), their TSR value (Total Solar Reflectance) must be considered [42]. The previous brightness value (HBW, Hellbezugswert) and the TSR value (Total Solar Reflectance) set minimum requirements for the reflectance behaviour of final coatings to avoid thermal stress. The light-protective pigments of microorganisms (carotenoids, melanin and scytonemine) are extremely UV-light-stable [43][44] and remain on the facades even after the organisms have died. The reflection behaviour decreases and the thermal load due to long-wave irradiation increases. The evaluation according to brightness reference value is carried out by means of grey scale colour fans in which the brightness values (L* values Cielab colour space) are mapped with the brightness reference values Y* [45].

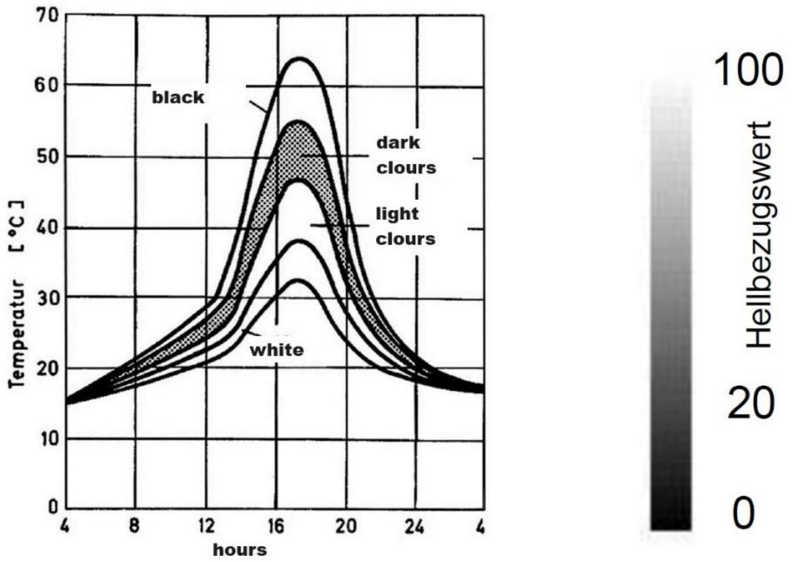

Figure 6: Surface temperature with different colour tones [41]

The lightness value expresses the brightness of a colour tone for the human eye in comparison to pure white (HBW100) or deep black (HBW0). The brightness reference values, and the brightness values are functionally related to each other. The reflectance measurement of the BenthoTorch® is performed in the near-infrared range at 700nm. The colour fan was measured in triplicate with the BenthoTorch® to determine a correlation (Fig.7).

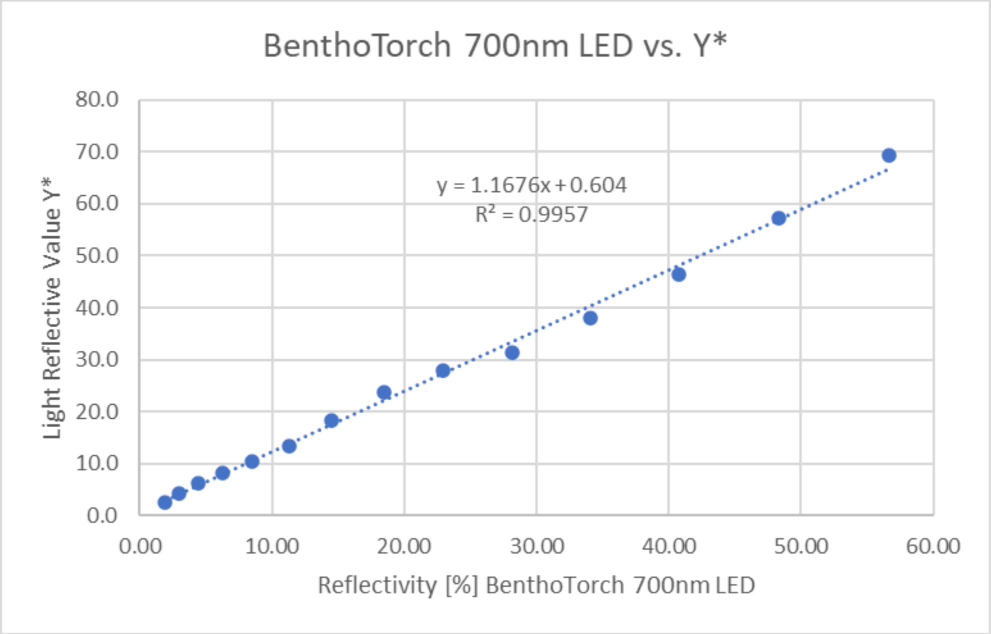

Figure 7: Relation of measured reflectivity at 700 nm vs. light reflectance value Y* [53]

5.2 Algae incubation test with different building materials

Standard EN 15458:2014 describes a laboratory method for testing coatings containing preservatives against algae [46]. An own modified incubation test of various building materials was carried out based on this standard. The process of initial contact of the microorganisms with the building material surfaces was investigated. Brick, marble, concrete, and sand-limestone as typical masonry building materials were first thermally disinfected (1h/120°C) and subjected to a 35-days wet incubation test at 23°C/75% RH to determine their tendency to colonize algal biofilms.

Figure 8: Material samples (from left to right: brick, concrete, marble fine, marble grey, marble coarse, lime-sandstone)

A day-night-cycle of 16h/8h was applied by using a cultivation-lamp. The algae cultures for inoculation were collected over a period of 14 days at the outdoor weathering site, cultivated and microscopically examined. The building material samples (Fig.8), 50x50x5 mm in triplicate, were both the substrate and the sole source of nutrients after inoculation. After 0, 7, 14, 21, 28 and 35 days at 23°C and a relative humidity of 75%, the total cell count, and chlorophyll-a content were analysed using a BenthoTorch® fluorescence spectrometer. The humidity in the climate chamber was adjusted using a saturated sodium chloride solution (Fig. 9). After every 7 days, the samples were measured using the BenthoTorch fluorescence spectrometer and the chlorophyll-a content and total cell count were determined.

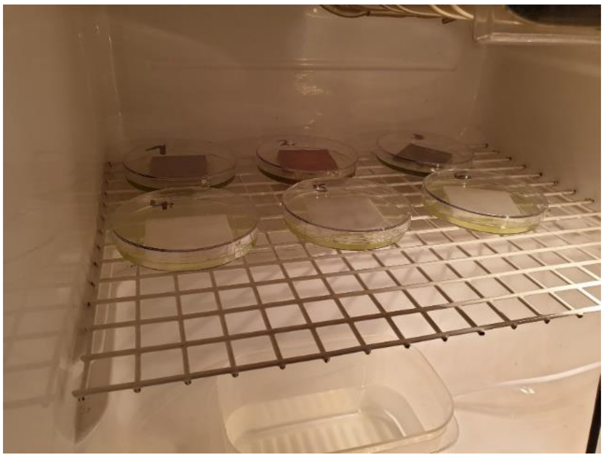

Figure 9: Incubation chamber with cultivation lamp and samples

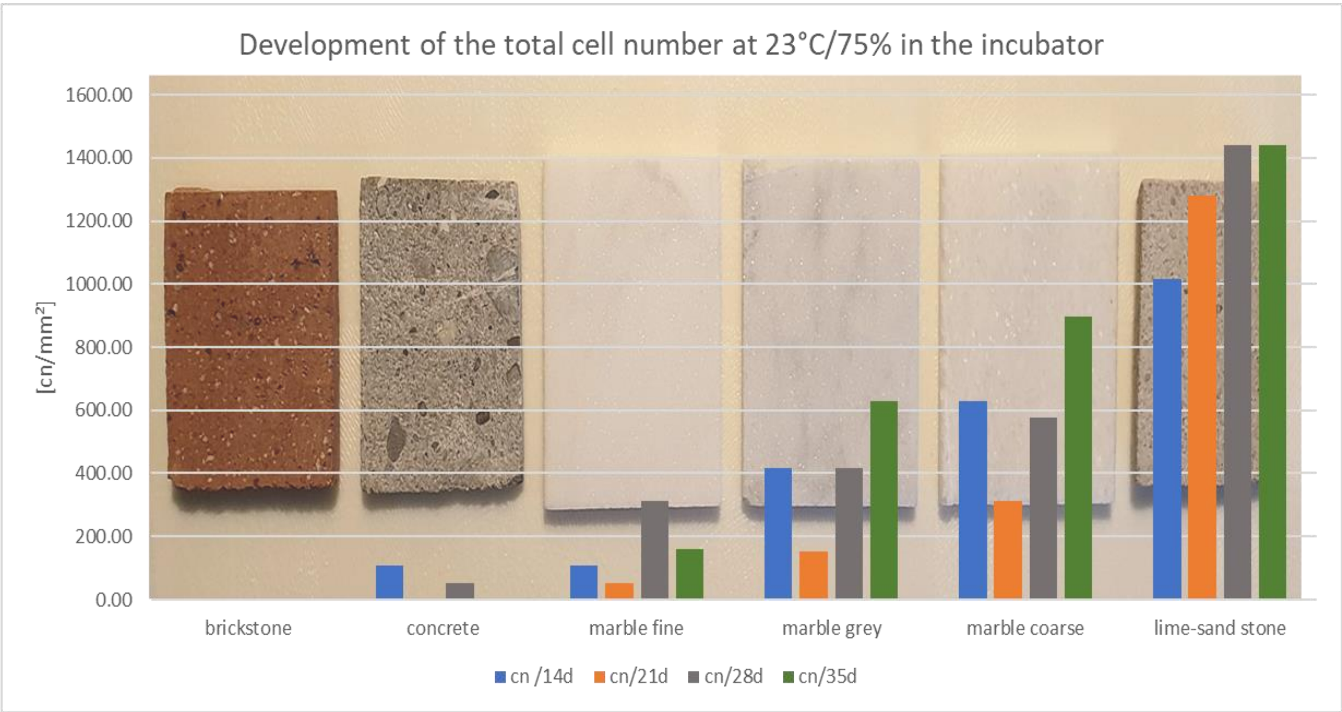

Figure 10: Total cell-numbers all species (cells/mm²) trend while incubation test

The elemental composition of the material samples was analysed in triplicate by Scanning Electron Microscopy, FEI Quanta 250 with Noran System 7 EDX detector in the laboratory of the Faculty of Civil Engineering at the University of Wismar and cross-checked by ICP-AES elemental analysis with $R^2=0.97$ for calcium.

5.3 Area-specific algae adsorption test

For realizing the area-specific adsorption rate (algae cells/cm²), the prior thermal disinfected (1h/120°C) building material samples (50x50x5mm) were subjected in triplicate to a newly developed algae suspension test. The algae culture from incubation test was diluted with tap water using a 1l-pot of black opaque polypropylene equipped with magnetic stirrer, pH-electrode, and BenthoTorch® fluorescence spectrometer (Fig.11). Before each measurement the cell number per volume of the suspension was set according to Tab. 3 by dropwise adding the algal culture. The temperature of the suspension was 10±1°C in each run. A few drops of 5% aqueous ammonia solution were used to adjust the pH-value.

Figure 11: Experimental setup for algae suspension test

Table 1: start conditions of algae suspensions measured at 10°C

sample	pH1	pH2	Cells/ml
brick	7.0	10.8	20,000
sand-limestone	7.0	10.8	20,000
Marble coarse	7.0	10.8	20,000

After thermal disinfection, the samples were first cooled to room temperature and then saturated in water of 10°C (expected mean temp. of outdoor exposure). Water saturation cools down to 10°C and compensates for capillary suction effects due to the different porosity and roughness of the specimens, which influence adsorption of material samples [47]. The adsorption of the algae cells should therefore be almost completely determined by the chemical substrate surface. Algae suspension is stirred gently, and the cell count is read on the display. Once a stable cell count has been established, the respective test specimen is completely immersed in the algae suspension. The cell counts were read and recorded at 2-minute intervals until there is no more change.

The BenthoTorch® display shows the cell number in the unit cell number/mm². Calibration is performed using a calibration disk (Fig.12), which is included in the scope of delivery. This measures 100µl of the algae suspension on a sample area of 1.0 cm² and achieves a very low layer thickness. This allows the area-related cell-count to be converted to a volume-related cell count. In the suspension test, however, the cell-count per material area is to be determined, so the measured values can be taken over and interpreted directly. The difference between starting cell number and end value will give the amount of adsorbed algal cells.

Figure 12: Calibration disk with 100µl algae suspension for cross-check

For the algae suspension test, three building materials were selected from the incubation test, which showed clear differences in colonization behaviour. Brick without colonization, sand-limestone with the strongest colonization and marble coarse with medium algal colonization. This allows a greater differentiation of the

Figure 13: ETICS with algae infestation starting around marble grains

samples and the expected results in the following suspension test. Marble was selected because it is used as a coarse grain for structuring in plaster preparations. Our own observations have shown that algae colonization starts around the marble grains (Fig. 13).

5.4 Free-weathering test of coating recipes

The present investigation was carried out in the geographical area of the air quality reports. In the search for alternative sources of nutrients within the final coatings - the focus is on fillers. Mineral fillers fulfil numbers of important technological functions and reduce manufacturing costs. Looking through various recipes of façade paints, regularly magnesium-containing fillers like dolomite and talc will be found [4]. Calcium carbonate is the most important filler and, depending on its geological origin and quality, contains significant amounts of magnesium-based accessory minerals [48]. The chemical composition of the fillers ideally meets the requirements of phototrophic microorganisms as they are obtained from natural mining resources that are the result of primeval marine organism activities. This common past of algae and fillers will meet again on modern façades today and prompts the author to investigate further, because there is no photosynthesis without the magnesium core-ion of chlorophyll-a.

5.4.1 Test location and conditions

The aim of the weathering test was to compare the algal susceptibility of acrylic-dispersion paints containing different types and amounts of magnesium-containing fillers. The outdoor exposure lasted from December 2019 until December 2021 and included 7 painted panels. The panels were mounted vertically on the north gable of a brick house at an angle of 5 degrees. The test site is situated in a rural area with dense vegetation and agricultural use (Fig. 14). The direct distance to the Baltic Sea is 4.5 km in a North-Western direction. The A24 motorway runs 2 km southern of the site.

Figure 14: Weathering location rural area near Wismar, Germany (Google Earth for Chrome, Goldebee 53°89’44’’N 11°60’08’’E, © GeoBasis-DE/BKG 2009, URL: http://google.com/earth.

Air temperature ranged from -11.5 °C to 36.6 °C with a mean of 10.6 °C and relative humidity ranged from 36.9% to 100% with a mean of 81.3% (Fig.16). Data collection was proceeded using Datalogger UNI-T UT330C for humidity, temperature, and air pressure with an interval of 30 minutes (36,372 data sets). The dew-point was calculated via intern algorithm of the datalogger (Fig.15).

Figure 15: Position of data recorder at the test panel

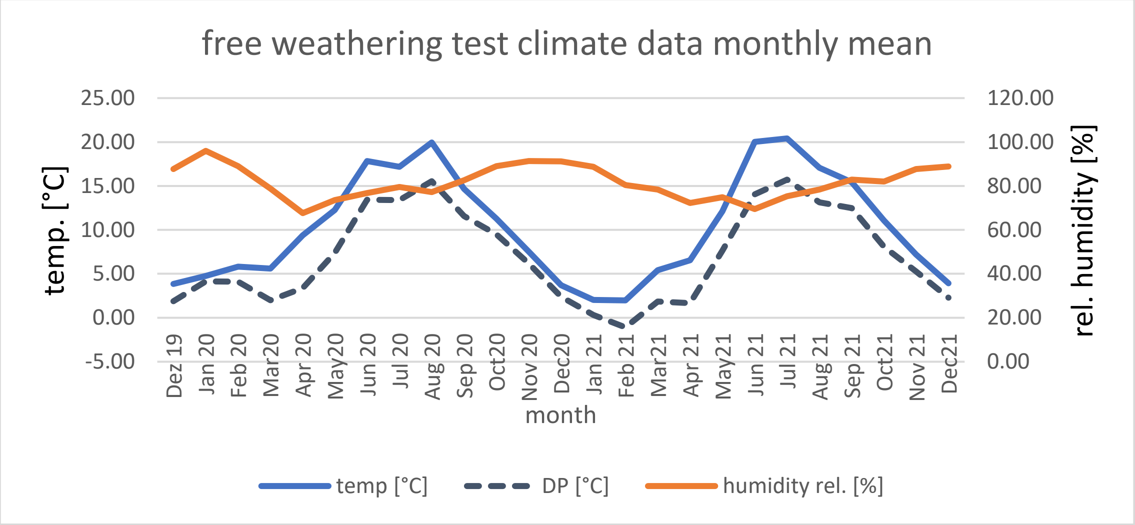

Figure 16: Averaged climate data collected by data logger (n=36,372)

gable of the building at an angle of 5° using wall hooks and plastic clips to make them windproof. The panels have no direct contact with the building, and heat flow through the double-skin brick wall with air layer is not possible. The low angle was intended to reduce the influence of rain events and to ensure humidification mainly via condensation water. The main wind direction in the test area was west. The weather data were recorded via data logger for air temperature, relative humidity, air pressure and dew point temperature in a 30-minute-interval. This configuration resulted in a comparable specific heat capacity of the surfaces to avoid different condensation loads [30]. The coatings were applied on expanded-polystyrene-based, lightweight Ultrament® building boards (Ultrament GmbH & Co. KG, Bottrop/Germany) with dimensions of 20 x 600 x 600 mm each. The concrete-slurry-coated surface, reinforced by a 10 x 6 mm plastic mesh, delivered a well-defined structure for every sample surface (Fig. 17) to avoid structural effects on the biofilm distribution between samples.

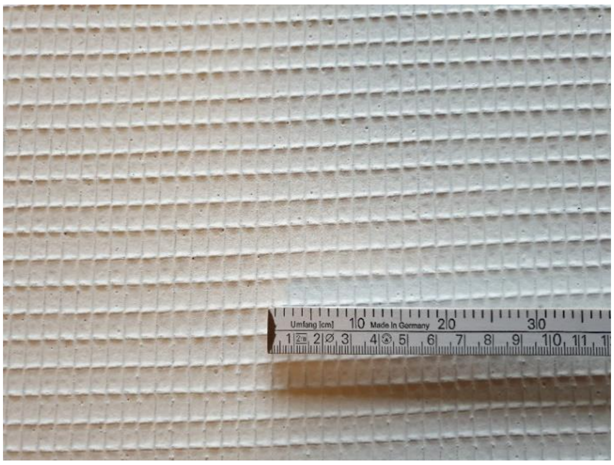

Figure 17: Ultrament® construction board with surface texture, coated

Table 2: Composition of coating recipes of free weathering test

Components [g]	PK00	PK01	PK02	PK03	PK04	PK05	PK06
Titanium dioxide	7.5	7.5	7.5	7.5	7.5	7.5	7.5
Calcium carbonate	112.5	112.5	112.5	112.5	112.5	112.5	112.5
Quartz powder	4.5	4.5	4.5	4.5	4.5	4.5	4.5
Dolomite	-	21.0	45.0	77.0	76.0	75.0	-
Talcum	-	-	-	-	26.0	-	-
Mg-Hydroxycarbonate	-	-	-	-	-	70.0	-
Zinc molybdate	-	-	-	-	-	0	9.4
Pure Acrylic Disp. 50%	105.0	125.0	140.0	170.0	190.0	250.0	110.0
Water	60.0	70.0	80.0	95.0	110.0	125.0	65.0
Total [g]	289.5	340.5	389.5	466.5	526.5	644.5	308.8
Pigment vol. conc. [%]	50.0	50.0	50.0	50.0	50.0	50.0	50.0
Non volatiles [g]	177.0	208.0	240.0	287.0	322.0	395.0	189.0
Solid content [%]	61.0	61.0	61.0	61.0	61.0	61.0	61.0

5.4.2 Detection of algal biomass

The algal biomass was quantified using the BenthoTorch® fluorometer (from German company bbe moldaenke GmbH, 24,222 Schwentinental, referred to as BTo for short in the following. While sampling was not necessary the destruction of microorganisms and components could be avoided. The panels were humidified in a controlled manner by using a water spray bottle 15 min before measurement. Using a 13-dot template, each test panel was measured 13 times between December 2019 and December 2021 (n =169). The single mode measuring process took 20 s (including 10 s diode initialization) and covered an area of 13 x 1 cm² (Fig.18). Previous dark adaptation was omitted and limited to the initialization phase of the diodes before the measurement process started. The sponge attachment of the measuring optics was changed each time the test specimen was changed to avoid contamination between the samples. Due to the surface texture of the carrier plates, contact with the back of the measuring template was negligible. In addition, the back of the template was cleaned with a damp paper towel before each change

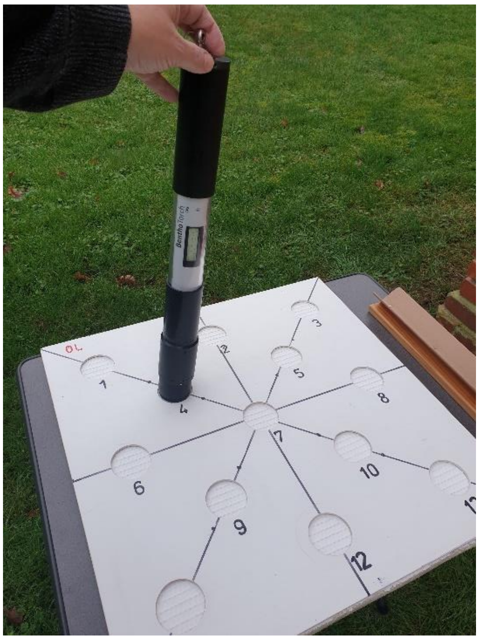

Figure 18: 13-dot template for fluorescence measurement

5.4.3 Development of algal biomass via BenthoTorch®

During weathering, the coatings showed a strong fluctuating stock of algal biomass. The first signals of green algae were detected after 44 (PK04) and 89 days (PK03) but disappeared again in the further course and were below the visual threshold. Above exposure time of 327 days permanent signals of green algae appeared (PK03, PK04, PK05). Sample PK05 was continuously and visibly colonized from day 327. Fig. 20 depicts the mean value of the total cell numbers of all algae species after 730 days of each sample. The corresponding chlorophyll-a contents were between 0.01 and 0.60 mg cm². The mean value of fluorescence detected algal biomass was composed of 92.3% green algae, 6.3% cyanobacteria, and 1.4% diatoms.

Figure 19: Biofilm visual impression of weathered samples after 730 days

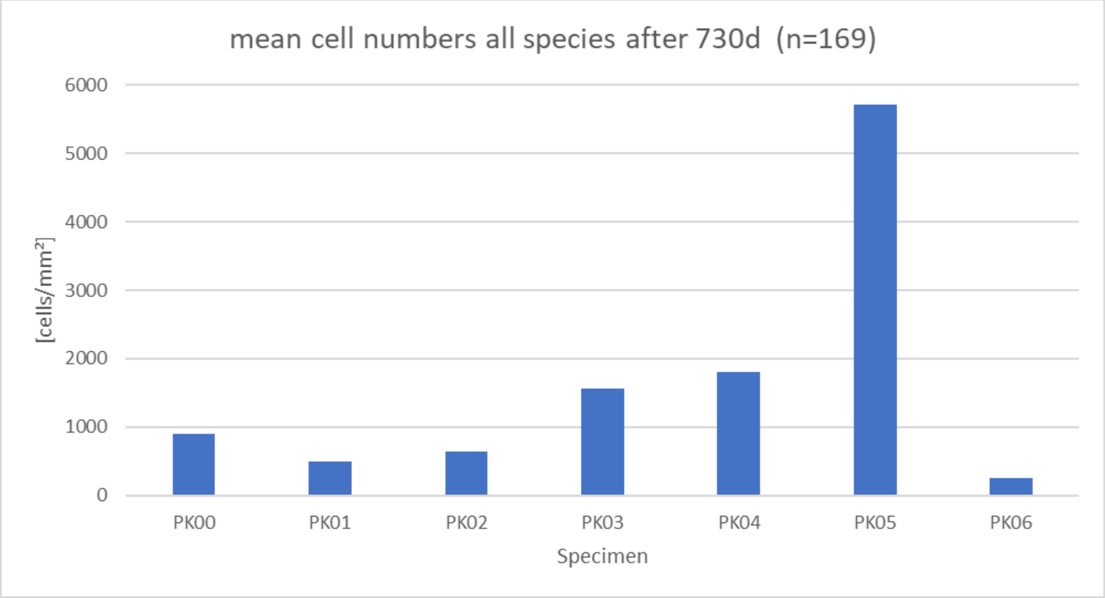

Figure 20: Biofilm total cell number after 730-day weathering [54]

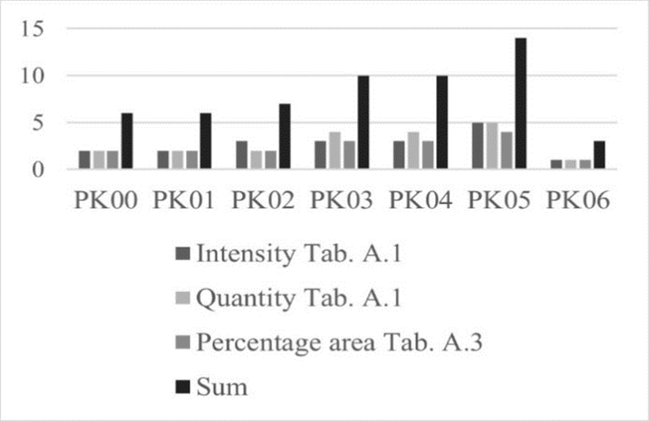

Figure 21: Evaluation based on criteria of annex A EN ISO 4628-1 [54]

Table 3: Data sets for correlation of results between all methods [54]

Sample	ImageJ area [%]	BTo [cells/mm²]	EN16492 sum	Mg [%]
PK00	7.52	906	6	0.76
PK01	13.75	497	6	1.96
PK02	16.26	648	7	3.00
PK03	23.98	1563	10	3.96
PK04	22.19	1806	10	5.00
PK05	38.46	5712	14	7.35
PK06	4.95	261	3	0.71

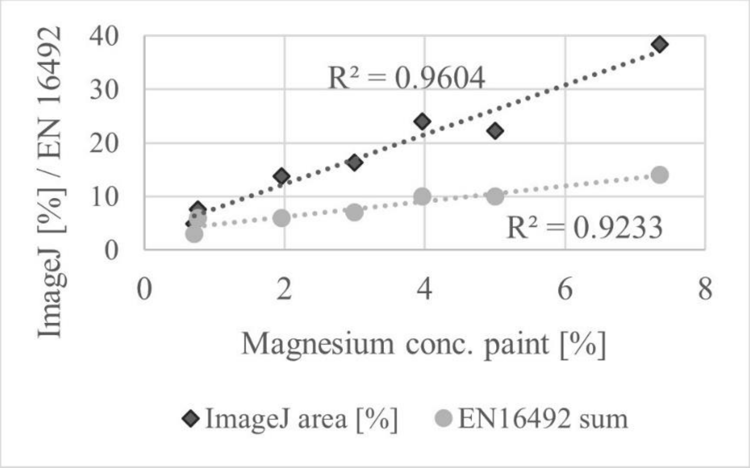

Figure 22: Correlation of algal growth vs. Mg-content coating sample [54]

6 Results and Discussion

730 days of outdoor exposure revealed a significant difference in the algal susceptibility between the identical constructed samples with different coating recipes. The fluorescence-measured sum of algal biomass [cells/mm²] via BenthoTorch® is positive related ($R^2 = 0.97$) to the magnesium content of applied paint coatings. The cross-check according to the visual evaluation via Standard DIN EN 16492:2014 ($R^2 = 0.92$) and the digital image area analysis ($R^2 = 0.96$) ensured the results. The coefficients of determination between results of evaluation methods (Table 2) were BTo [cells/mm²] vs. DIN EN 16492 sum ($R^2 = 0.95$) and BTo [cells/mm²] vs. ImageJ area [%] ($R^2 = 0.97$). After comparing the test methods, the correlation of the determined algal biomass to the magnesium content of the coatings was performed. Fig. 22 reveals the strong relationship between algal biomass and magnesium content of painted samples (Table 2).

The very first infestation was detected on samples PK03-PK05 after only 9 months but did not persist. The test specimens PK00-PK02 only showed the first fluorescence signals of chlorophyll-a after 24 months and were still below the visual limit. After a start-up period of 12 months, permanent algal growth was observed on the sample with the highest Mg-based filler content (PK05), while the samples with a low filler content were significantly less colonized only after two years. The composition of the biofilm at all samples was identically dominated by green algae (92%) and cyanobacteria (6%), while diatoms (1%) played a subordinate role. The surface pH value of the reference (PK00) and the samples (PK01-PK05) were at a comparable level. The comparison with the magnesium-free reference sample PK00 proved to be difficult in retrospect, as the calcium carbonate used in the formulation contained accessory mineral traces of magnesium compounds. The differences in Mg-concentration and the statistical significance between the test specimens (PK01-PK04) and reference (PK00) were therefore weakened but sufficient.

The water-activated defence-strategy with zinc molybdate (PK06) was significantly able to limit the biomass within the experimental conditions and algal species involved. This sample showed the lowest cell counts during the weathering period of two years and no measurable change in surface reflectivity. Surprisingly, the expected lower pH level due to zinc molybdate was only achieved after the start-up period of 12 months and remained stable until the 19th month. The measurement was then terminated due to a defective electrode. Current research results confirm the pH-depending bioadsorption of algae, which is determined by the chemical composition of the building material surface. The brick stone showed no measurable algal colonization after 35d-incubation and had an adsorption rate of 0% in the suspension test at pH 10.8/10°C. The sand-limestone showed the strongest algal growth after incubation as well as the highest adsorption rate of 32,2% in the suspension test. The marble specimen shows the second strongest algal growth after incubation and an adsorption of 17,6%. The strong differences in algal growth could not be explained by the physical parameters of water uptake as they were compensated by water saturation.

Transferring the principle of algae harvesting (tested inoculum) to the tested building material surfaces, the initial settlement of algae can be explained by the presence of necessary mineral components, as well as the alkaline pH-value. Bioadsorption of algae is driven by Ca- and Mg-compounds that interact with the cell wall-located carboxylic groups of algae. All EDX-tested wall materials contained Ca and Mg-compounds. The high firing temperature (>1000°C) of brick lead to very low surface-availability of Ca and Mg due to sintering effects and no detectable algal colonization in both laboratory tests. The production process of sand-limestone (hot steam at 200°C) maintains the chemical structure of the components and their surface availability. Algal growth occurs if enough cells are enriched on the component surface. Both play an important role in bioadsorption of algae and are essential nutrients for further growth. Understanding the adsorption process provides important information for the development of biocide-free defence systems and sustainable designed façades.

Construction planner and designer are calculating with a wide variety of load cases. In terms of future façade-projects the assessment of final coatings can be improved based on these results. The simultaneous combination of environmentally hazardous biocides with algae-prone magnesium-based fillers in façade paints is not advisable. Especially since the organic biocides have only a temporary effect and the algae-prone fillers reach the surface during the aging process to develop the effects revealed in this research work. Understanding these interactions provides important information and methods on the reduction of organic biocides in product development. These research results contribute to more sustainable designed true green façades without killing future algal populations and may support the development of bio-receptive building materials.

7 Conclusion to the Theses

Thesis 1 - Applicability of a benthic detection device for the determination of algal biomass on building material surfaces

Using the mobile BenthoTorch® fluorescence spectrometer, I have quantified phototrophic microorganisms on building material surfaces and differentiated between green algae, cyanobacteria, and diatoms without the need for complex microbiological methods and expertise. I have thus also proven that water films on building materials can be regarded as temporary aquatic habitats, as favoured by benthic biofilms. I have proven through laboratory and field tests that the BenthoTorch® is suitable as a sensor for the non-destructive area-related determination of cell counts and chlorophyll concentrations on moist building material surfaces. I was the first to develop a new algae suspension test using the BenthoTorch® sensor to determine the pH-depending bioadsorption of algae cells on building material surfaces in real time. I have extended the 700 nm LED included in the spectrometer for background compensation to determine the light reference value, which allows the assessment of surface greying independent of biofilm vegetation in one step of the measurement. The results obtained were directly interpretable and I demonstrated that the mobile fluorescence spectrometer is suitable for the measurement requirements. Based on these results, I recommend the assessment of surface disfigurements caused by algae and fungi in accordance with DIN EN 16492:2014 by using BenthoTorch®.

Related publications: [53, 54, 57]

Thesis 2 - Bioadsorption as the initial step in the process of algal colonisation of building materials

To determine the adsorption behaviour of algae cells on building material surfaces, I was the first to develop a real-time suspension test that determines the area-related cell count. Due to the special experimental set-up, I was able to separate the physical deposition from the pure chemical interaction of the functional groups of the algal cells. Using a natural algae culture, I proved that cell adsorption on building materials is dependent on the pH value and can be influenced by targeted manipulation. I have revealed that the measured values of the BenthoTorch® sensor can be used directly in the measurement set-up for the volume- and area-related conversion. After cross-check with 35 days of incubation test, I confirmed that the building materials without measurable cell adsorption in the suspension test also showed no measurable colonisation, while the samples with maximum colonisation also had the highest adsorption rates.

Related publications: [55]

Thesis 3 - Magnesium-containing fillers increase the formation of algal biofilms on façade coatings

After two years of outdoor exposure, I revealed a significant difference in the algal susceptibility between identically constructed and mounted samples. Using the BenthoTorch® fluorescence spectrometer, I proved a positive related (R^2=0,97) sum of algal biomass to the magnesium content of the applied coating. Comparing the standard DIN EN 16492:2014 (R^2=0.92), the digital image analysis (R^2=0.96), and statistical HSD analysis, I ensured the results. Based on the experimental set-up, I secured condensation water as the only source of moisture and confirmed that these quantities are sufficient for algae colonisation and can't be avoided. Based on data analysis of air quality annual reports and coating recipes, I conclude that magnesium-containing fillers are a more important source of essential nutrients for phototrophic microorganisms than airborne dust. From the presence of lichens only on PK06, I conclude that in addition to the triggered accumulation of algae cells due to the highest content of Mg-based fillers, vegetative reproduction has also taken place. In the outdoor weathering experiment, I demonstrated that Mg-based fillers act as harvesting aids in the short term and as a source of nutrients in the long term. I have demonstrated that the change in the light reflectance value of the test specimens is suitable as a sum parameter for the evaluation of increasing biogenic and non-biogenic pollution.

Related publications: [52, 54, 58]

Thesis 4 - Efficacy of an algae defence strategy by water-activated functional filler

After 730 days of outdoor weathering and statistical HSD analysis, I proved the effectiveness of a dew water-activated functional filler against airborne algal biofilm formation. Equipping an acrylate-based emulsion paint with zinc molybdate, I demonstrated a 73% reduction of algal biofilm compared to the identical reference without functional filler. Using a surface electrode, I proved that the functional filler significantly lowered the pH level by 1.2 units on the logarithmic pH scale. I proved the absence of visible biofilm accumulation by fluorescence detection and non-biogenic disfigurements by 700nm-light-reflectance measurements using the BenthoTorch® spectrometer. Since condensation water was the only source of water, I proved the activation of the functional filler in this way. Instead of elaborately avoiding the dew water, I recommend this non-toxic control strategy without killing future algal populations as contribution to the design of sustainable façades.

Related publications: [54,56]

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